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# PROCESS ENGINEERING DESIGN FOR MANUFACTURE OF GUANIDINE NITRATE

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# PROCESS ENGINEERING DESIGN FOR MANUFACTURE OF GUANIDINE NITRATE

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Volume I of Volumes I and II

(Unclassified - Department of the Army)

N. W. Steele
J. A. Doyle
M. C. Whipple

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13. ABSTRACT

The object of this program was to develop design data and produce 40,500 lb of guanidine nitrate (GN) via the catalytic reaction of ammonium nitrate (AN) and urea. Laboratory and pilot plant experiments confirmed the soundness of the process as described in the literature. Mathematical models and computer programs developed on the basis of laboratory kinetic and process variable data proved to be fully capable in predicting the behavior of packed bed tubular reactors. A semi-continuous pilot plant (nominal capacity of 50 lb GN/hr) was constructed on the basis of laboratory data. The plant, containing eight parallel 4-inch-dia. tubular reactors, employed production plant prototype equipment. About one ton of 96+% purity GN was produced using a single aqueous crystallization step for product recovery. This material was capable to being converted to nitroguanidine (NQ) comparable to NQ produced in the Cyanamid of Canada production facilities. Total production was not met because of catalyst poisoning, which was traced to phosphates and perhaps borates in commercial grade AN. When commercial additive-free AN and urea were used with Houdry CP-532 silica beads (only known suitable catalyst for packed beds) in a 4-inch-dia. reactor, the following results were obtained: 38 lb GN/lb catalyst minimum mileage, 83% urea conversion and 95% urea to GN yield. A minimum mileage of 65 gm GN/gm catalyst was demonstrated in a 1-in.-dia. reactor. These results surpassed the literature values. Sensitivity and hazards analyses show that no in-process material is capable of self-propagation. Preliminary economic studies indicate cost advantages over the British aqueous fusion process. Continuation of pilot plant operations to extend catalyst mileage data, particularly with recycle, and more detailed cost analysis are recommended.

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| Ammonium nitrate | | | | | | |
| Urea | | | | | | |
| Catalyst poisoning | | | | | | |
| Houdry silica beads | | | | | | |
| Reactors | | | | | | |
| Packed bed tubular reactors | | | | | | |

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The findings in this report are not to be construed as an official Department of the Army position.

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# I. SUMMARY

A contract (DAAA21-71-C-0193) was executed between Hercules Incorporated and the U. S. Government, Picatinny Arsenal, on October 23, 1970, for a process engineering design for the manufacture of guanidine nitrate (GN), an intermediate chemical for nitroguanidine (NQ). This program was designed for four phases, ranging from laboratory process confirmation/kinetic studies through pilot plant GN production and culminating in battery limits process design criteria, for a total period of performance of 23 months. The total program was not completed because of technical problems noted in the following summary discussion. It is believed that the major problems have been resolved, and consequently, a proposed follow-on program has been submitted to Picatinny Arsenal to complete (with the exception of the Phase IV design criteria) the original scope of work. This report (Volume I) presents in detail the work, accomplishments, conclusions and recommendations for the period of performance from October 23, 1970 through February 4, 1973. The additional work beyond the original contract expiration date of September 23, 1972, was covered by contract modifications. A second volume (Volume II) will be issued at a later date to report the work accomplished on this program after February 4, 1973.

The preparation of guanidine nitrate from the catalytic reaction of urea and ammonium nitrate was patented by L. G. Boatright and J. S. MacKay, American Cyanamid Company, on February 26, 1957 (Patent U.S. 2,783,276).[1] The basic chemistry of the reaction is as follows:

$$2NH_2CONH_2 + NH_4NO_3 \xrightarrow[\text{ca. } 190°C]{\text{Catalyst}} NH_2C(=NH)NH_2 \cdot HNO_3 + 2NH_3 + CO_2$$

Urea — Ammonium Nitrate — Guanidine Nitrate — Ammonia — Carbon Dioxide

Subsequent patents were issued to J. S. MacKay, Pittsburgh Coke and Chemical Company, for increased yields through the use of a columnar reactor, recycle, temperature variation, etc. (Patent U.S. 2,949,484, August 16, 1960)[2] and to E. Roberts and T. Martin, Minister of Aviation in Her Majesty's Government, London, England, for the eutectic crystallization of guanidine nitrate (Patent U.S. 3,043,878, July 10, 1962).[3]

## Laboratory Studies

Thirty-seven batch reaction experiments (1 lb level) were carried out during Phase I. The primary objectives of these runs were to verify earlier results of MacKay;[4] define reaction kinetics as a function of temperature, time and feed mole rates; establish data for construction of mathematical models; establish urea conversion and GN yield data; determine the effect of feed purity on conversion, yield and reaction rate; select a primary catalyst for the pilot plant, etc. Yield and concentration profiles from kinetic batch reaction runs employing the catalyst Grace 40 silica gel and reagent grades AN and urea were smooth, consistent and provided the needed kinetic parameters. Based on these data, and on yield data at different operation temperatures as a function of reaction time, it was concluded that the previous claims relating to the reaction step of the AN/U/catalyst-to-GN process were well founded; i.e., yields and reaction rates were comparable. It was found that mechanical agitation reduced the silica gel particle size, resulting in higher urea conversions (81% for 6-12 mesh catalyst vs 94% for 100/325 mesh catalyst).

At a constant AN/U ratio, an increase in the catalyst dosage results in significant increases in both GN yield and urea conversion. An AN/U silica gel molar ratio of 2/2/1.7 appeared optimum.

Evolution of gases during the reaction provided sufficient mixing for adequate heat and mass transfer. Subsequent experiments in a continuous upflow 2-in.-diameter reactor and the magnitude of the activation energy (33,000 cal/g-mole) determined from an Arrhenius plot of rate constants showed that the reaction was not mass transfer limited. Catalysts other than Grace 40 silica gel were evaluated. These included Mobil Sorbead R (silica gel), Mobil Durabead I (silica-alumina), Type 4A Molecular Sieves, Grace 59 silica gel, Cab-O-Sil (submicron pyrogenic silica), Houdry macroporous silica beads, Houdry mineral zeolite HZ-1 cracking catalyst, Houdry S-46 silica-alumina catalyst, Filtrol 13 filter clay and Grace 63 silica gel. Both Houdry macroporous silica beads (CP-532) and Grace 59 silica gel exhibited more activity than Grace 40 silica gel. Three catalysts were selected for further consideration in the program. Emphasis, however, was placed on Houdry CP-532 macroporous silica beads because of their outstanding physical strength characteristics. Yield and conversion data for the candidate catalysts, as well as the base reference Grace 40 silica gel, are tabulated below. The results are for a nominal reaction time of 60 minutes, 190°C and a 2/2/1.7 (AN/U/catalyst) molar ratio.

COMPARISON OF BEST PERFORMING CATALYSTS
(One-Liter Batch Reactor)

| Catalyst | Urea Conversion (%) [a] | GN Yield (%) [b] |
|---|---|---|
| Grace Grade 40 Silica Gel | 68 | 74 |
| Grace Grade 59 Silica Gel | 93 | 61 |
| Houdry CP-532 Silica Beads | 88 | 73 |
| Mobil Sorbead R Silica Gel | 67 | 59 |

(a) Moles urea reacted per moles urea fed.
(b) Moles GN per mole urea reacted x 2.

A careful assay of reaction off-gases from an argon-blanketed, one-liter batch reaction experiment showed no noncondensable degradation products from the reaction. Both reagent and various commercial grades of ammonium nitrate and urea were evaluated. There were no distinguishable differences in yield and conversion results. Batch reactor data showed that the water insolubles (ammelide) in the reaction mix increased with increasing reaction temperature and urea concentration in the feed. At reaction conditions of 1/1 AN/U molar feed ratio and 190°C, 2-3% ammelide was produced based on final dry GN product. A sharp buildup of biuret was noted during reaction but declined, indicating the biuret is a reactant and that its presence has little technical economic effect on the process. A detailed literature search confirmed this observation and supported the assumed reaction mechanism.

## Mathematical Modeling

Mathematical models describing the behavior of packed bed tubular reactors and a series of continuous stirred tanks were prepared. Digital computer programs implementing these models were written and used to study the effects of various operating parameters. As an example, the computer printout for a tubular reactor notes the molar flow rates, mole fractions, conversion, yield and temperatures as a function of axial distance plus product rate and composition for any set of initial conditions. The models have full predictive capabilities. They were utilized to size tubular reactors for both bench-scale studies and the pilot plant. Resulting experimental data confirmed their accuracy and value for future use. Calculations showed that cascaded stirred tank reactors were more attractive than tubular reactors from the standpoint of GN yield. However, stirred tank reactors were not selected for the pilot plant because of their unknown potential hazards and inherent design problems regarding catalyst confinement, fluid flow and heat transfer.

## Bench-Scale Reactor Studies

A 2-in.-diameter reactor was operated with both up-flow and down-flow conditions. This reactor was a prototype of the eight 4 in. diameter by 12 ft tall reactors employed in the pilot plant. Operation of this reactor demonstrated the feasibility of packed bed tubular reactors with the production of GN at predicted rates. Reactor effluents contained as much as 55 wt. % GN. The yield, conversion, product composition and temperature profile data agreed favorably with the predicted values. Parameters investigated included temperature, AN/U ratio, grades of reactants, feed rate, bed height and GN in feed. An overall material balance of 95.1% (AN - 99.7%, U - 91.9%) with yields of AN = 99.3%, U = 85.2% and a urea conversion of 47.8% was achieved for one run. The data were consistent with those obtained in the batch reactor experiments.

Results from batch reactor experiments, 2-in.-diameter reactor runs and pilot plant operations upheld the objectives that were originally foreseen for the process in the area of waste disposal and pollution control.

## Pilot Plant Design

Following completion of the laboratory and bench-scale reactor studies, a pilot plant was designed and constructed for producing guanidine nitrate at a nominal rate of 50 lb/hr via the catalytic ammonium nitrate/urea process. The reactor system consisted of eight 4 in. diameter by 12 ft tall jacketed reactors installed in parallel with common feed and gas-liquid separators. Steam for the reactors and other selected operations was supplied by captive, electrically operated, 400 psig boilers. Remaining pieces of pilot plant process equipment were also designed as prototypes of items to be employed in a production plant. This included equipment for the following unit operations: AN/U melting, reactor product water quenching, water-insolubles removal, GN crystallization, centrifugation for GN recovery and mother liquor evaporation for AN/U/GN recycle. The selected dryer was a production plant prototype; however, operating experience showed that it and other types of mechanically agitated, indirectly heated dryers

are unsatisfactory for drying water-wet GN. It appears that direct air heated dryers will be satisfactory. The pilot plant complex was designed and constructed as an almost totally contained system; i.e., reactor off-gas collection system, electric substation, vacuum system, chilled water system, etc. Rules and regulation regarding safety and ecology were adhered to. Procurement and installation of all process and auxiliary equipment, piping, instrumentation, electrical, etc., were completed in six months. The primary catalyst employed was Houdry CP-532 Macroporous Silica Beads. Other catalysts were evaluated and are noted below.

Pilot Plant Operation

Start-up of the pilot plant required longer than anticipated because of the following problems: plugged lines resulting from insufficient steam tracings, hot AN/U gassing in transfer and metering pumps, loss of high-pressure steam due to repeated failures of the electric boilers, vacuum leaks, etc. Eventually, the entire pilot plant was operated as an integrated unit to demonstrate the basic design concept. During the start-up period, the Houdry beads were severely thermal cycled, resulting in physical breakdown of the catalyst and loss of flow through the reactor tubes. Inoperability of the reactors was due, on at least one occasion, to buildup of ammelide.

Two separate compaigns were carried out in attempts to produce the contractual requirement of 40,500 lb of GN. Mechanically, the plant ran well during most of the time; however, only about one ton of GN was produced over approximately a 2-month period. This period had considerable down-time for repairs, catalyst changing, etc. The GN produced was 96+% pure. A representative sample of GN was converted to nitroguanidine at Cyanamid of Canada. The resulting NQ was similar, in all respects, to Cynamid's normal production material. Reaction melt was quenched with water and then subjected to a single crystallization for GN recovery. This method of GN recovery was based on the results of laboratory experiments where both the single aqueous crystallization and the dual eutectic-aqueous crystallization systems were investigated. The laboratory data showed no advantage to the dual recovery scheme. Water insolubles were satisfactorily removed from the hot aqueous quench solution with a high-speed solid bowl centrifuge. Recovery of GN crystals from the crystallizer slurry with a basket centrifuge presented no problems.

Catalyst Poisoning Resolution

During the above pilot plant production efforts, productivity decreased from about 3-4 lb GN/hr/tube to 1 lb GN/hr/tube within one week when using Houdry CP-532 silica beads. Single, 4-in.-diameter reactor experiments were performed using pilot plant feed ingredients and three different types of catalyst - Houdry beads, Mobil Sorbeads R, and Grace grade 59 silica gel. Operating conditions such as feed makeup, feed rate and temperature were carefully controlled. Initial productivities were consistent with predicted values; however, they decreased as a function of time. Catalyst half-life

times ranged from several hours to about five days. It was reasoned that the catalyst problem could arise from (1) impurities in the feed materials, (2) by-products from degradation of feed material, especially urea, or (3) heterocyclic products, such as ammelide, which are formed as co-products in the GN reaction. In a series of continuous down-flow runs in a 1-in.-diameter column containing Grace 59 silica gel catalyst, following a logic diagram, it was concluded that chemical crystal habit modifiers (diammonium phosphate, diammonium sulfate, and boric acid) were the most important culprits. It was concluded that phosphates definitely are poisons. Borates, another suspect, are probably not detrimental on a one-pass operation but might still be detrimental on recycle. Laboratory experiments were consistent with these results, indicating that phosphates and borates did tend to be removed from feeds. Commercial ammonium nitrate containing a crystal habit modifier produced a somewhat lower yield than reagent grade AN. A literature review generally reinforced the conclusion that impurities in the AN were the key problem.

Several attempts were made to demonstrate sustained GN productivity in a single, 4-in.-diameter reactor containing Grace 59 silica gel and with additive-free ammonium nitrate. The tests were inconclusive because of flow restriction caused by catalyst breakdown. This breakdown was attributed to the presence of water in the feed. Subsequent diagnostic tests in a 1-in.-diameter down-flow reactor and additive-free grades of AN and urea feed containing 1% water showed that Grace 59 silica gel softens and tends to powder under such conditions. It was concluded that Grace 59 silica gel is not suitable for packed bed reactors.

Houdry CP-532 silica beads were tested with additive-free AN and urea, containing 1% water, in a 1-in.-diameter down-flow reactor. Reactor operation was voluntarily terminated after 335 hours of continuous operation, resulting in a mileage of 65 gm GN/gm catalyst and no indications of catalyst activity decay. A single, 4-in.-diameter reactor containing Houdry beads and continuously fed with virgin additive-free melt (AN and U with ca 0.8% water) yielded a mileage of 38 lb GN/lb catalyst in 115 hr of operation. Activity decay and physical breakdown of the Houdry beads were not evident. Houdry beads are the only known satisfactory catalyst for a packed bed reactor. During this experiment, urea conversion to GN and ammonium carbamate was 83%. Guanidine nitrate yield (assuming full credit for the ammonium carbamate off-gas) was 95% based on urea reacted. Production rate at a 1/1 AN/U molar feed ratio and a reactor jacket temperature of 208°C averaged 9.0 lb GN/hr/reactor. These results were in almost complete agreement with values predicted from the mathematical model and represent a significant advancement in the technology for manufacturing GN via the U/AN route.

Process Hazards Analysis

Sensitivity testing showed that no material in the pilot plant would transit from burning to explosion. In other words, the system is not capable of acting as an explosive shock donor to process materials. The

reactor effluent and guanidine nitrate will propagate an explosive reaction if sufficiently boostered. Critical diameter for each material is less than one inch while other process materials will not sustain explosive reactions in 1-in.-diameter interconnecting lines. Testing in accordance with TB-700-2 showed that guanidine nitrate is a Class B material. However, based on these data and in-house data, the government has tentatively classified GN (less than 25% water content) as Class 7 for in-process and as an oxidizing agent for storage and shipping. An engineering analysis of pilot plant equipment for possible hazards and safety margins showed no hazards for normal operating conditions. If initiation were to occur, only a fire would result. A computer simulation of a logic model (Fault Tree) over an operating period of 800 hr resulted in a probability of initiation of $4.6 \times 10^{-3}$ or a corresponding probability of no initiation of 0.9953.

## Materials of Construction

Materials of construction were previously evaluated briefly by MacKay in his 1955 work.[4] Limited exposure of 5052 aluminum, 394 and 316 stainless steel in reactor feed and reactor effluent media verified his findings that 304 stainless steel would be the preferred material of construction for the reaction and workup stages. All materials showed very low corrosion rates in mils per year; the material having the highest rate, 1.54 mils per year, was the aluminum used in the reactor effluent.

## Preliminary Economic Studies

Preliminary economic studies were conducted for the AN/U process for manufacturing guanidine nitrate. The object of adding an economic dimension to the parameters involved was to show the effect of economics on engineering alternatives. Cost estimates were made on the basis of a chemical type plant, continuous operation with recycle and within battery limits. To indicate the engineering effect of parameter change, an industrial accounting system was used. Costs were also generated by a United States Government accounting system which does not include insurance, taxes, depreciation and profit. Since manpower, raw materials, etc., alone do not adequately indicate the changes in the process engineering system, the government accounting system was not used as the primary indicator of parameter incremental differences. A basic 40 million lb GN per year plant with packed bed reactors yielded a total mill cost of 10.12¢/lb GN with a 30% return transfer price of 17.2¢/lb GN. The cost advantage of production operation appears to level off at a plant capacity of 70 to 90 million lb per year at which the transfer price of GN drops approximately 15%. These values are based on zero by-product (ammonium carbamate off-gas) credit. Maximum credit value for AC is estimated at 3¢/lb AC. This would result in a reduction of about 1.8¢/lb GN in the mill cost. For each 1¢ decrease in urea price, the GN mill cost decreases 1.25¢ per pound. The optimum residence time for a packed bed reactor is one hour, which gives an 80% urea yield. Similarly, the optimum AN/U ratio in the reactor feed is very nearly one. A substantial cost incentive is seen for the single aqueous crystallization as compared to the combined eutectic-aqueous crystallization method for GN recovery. A comparison of packed beds vs stirred tank reactors, neglecting safety and potential design problems, showed a definite cost advantage for stirred tanks. In all

cases, a six-month catalyst life with Houdry macroporous silica beads was assumed. Even with a 2-month life, the catalyst portion of the costs would be only 0.45¢/lb GN, which can be tolerated.

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To summarize, this program has demonstrated the fundamental concept of manufacturing GN by the catalytic reaction of ammonium nitrate and urea. Operation of 1-in. and 4-in.-diameter reactors has yielded data surpassing any data reported in the literature pertaining to on-stream time, catalyst displacements (lb feed/lb catalyst) and catalyst productivity (lb GN/lb catalyst). Houdry beads, which have been found to be physically strong and insensitive to water, appear to be an excellent catalyst. However, further work is required to assure their continued availability and/or to determine a second source of a suitable catalyst. Certain materials in commercial grades of ammonium nitrate can poison the catalyst, but judicious selection of virgin AN will eliminate this problem. The process has only two by-products--ammonium carbamate (AC) off-gas and water insolubles (ammelide). The AC can be collected and used to produce process feed materials (AN and/or urea) or sold as nitrogen and carbon dioxide. The ammelide can possibly be used as a slow release fertilizer or hydrolyzed to $NH_3$ and $CO_2$. Preliminary and unreported cost calculations indicate that the AN/U process will require less investment and lower operating costs than the LAF process.

In view of the progress made during this program, additional work for the immediate future is justified. Consequently, a follow-on proposal has been submitted to the United States Government to accomplish the following:

(a) Modify the GN pilot plant to minimize operating problems.

(b) Operate the pilot plant to obtain additional process engineering data, demonstrate a catalyst mileage of about 200 lb GN/lb catalyst with recycle, and produce a sufficient quantity of GN for subsequent conversion to nitroguanidine.

(c) Conduct an economic study to permit a logical and timely decision between the BAF and AN/U processes. The studies would consist of alternate processes for reactor off-gas utilization and investment plus operating costs for a total nitroguanidine facility utilizing the AN/U reaction for GN.

(d) Place the pilot plant in a standby condition.

## II. CONCLUSIONS AND RECOMMENDATIONS

Although the complete work scope of the original contract has not been accomplished, the results obtained thus far have led to several firm and important conclusions. These are discussed below in some technical detail. The conclusions and recommendations are based on data obtained only through February 4, 1973.

1. The process for producing guanidine nitrate (GN) by the elevated temperature catalytic conversion of ammonium nitrate (AN) and urea (U) is fundamentally sound and operable from both theoretical and practical points of view. This conclusion is based on the operation of an integrated pilot plant employing prototype production plant equipment to produce about one ton of GN that can be converted to nitroguanidine (NQ) comparable to material produced in the Cyanamid of Canada production facilities.

2. The key question now is whether an economic catalyst mileage can be obtained in steady recycle operation. A corollary need is to show that the production of ammelide by-product stays at a low level (1-2%) so that problems with catalyst blockage, purification or disposal do not arise.

3. GN productivity, urea conversion, GN yield, and reactor temperature values predicted from laboratory data and a packed bed tubular reactor mathematical model were demonstrated in the pilot plant in which virgin (nonrecycle) AN and urea feed were used. The mathematical model can be used to accurately predict incremental reactor conditions and final results under a variety of operating parameters, e.g., feed rate and molar ratio, and reactor temperature, length and diameter. The pilot plant reactors, designed on the basis of the mathematical model, performed as predicted.

4. The AN/U process for manufacturing GN is chemically clean in that the by-product level is low and the unconverted reagents can be recycled with minimal rework. The major product, water-insoluble ammelide, is produced at a level of less than 2 wt. % (based on GN) and can be controlled by altering process conditions such as feed AN/U mole ratio and reactor temperature. This by-product can be removed, by centrifugation, from a hot aqueous stream before recovery of GN. A reactor GN yield of 95%, accompanied by an 83% urea conversion, was demonstrated in the pilot plant with virgin feed.

5. A packed bed tubular reactor operated in a continuous manner is a reasonable and sound approach for a GN production plant. In principle, this type of reactor can be scaled up for production requirements consistent with economics and safety. Since the operation of the tubular reactor has been demonstrated in essentially a production-sized module, alternate reactor designs such as stirred tanks do not warrant investigation at this time. This latter type of reactor design will present problems related to catalyst attrition, scale-up kinetics and heat transfer, equipment structural integrity, and safety. The chief justification would be as backup in case a cheap, structurally weak, low-mileage catalyst is the only available one.

6. Catalyst mileages of 68 gm GN/gm catalyst and 38 lb GN/lb catalyst (Houdry CP 532 Macroporous Silica Beads) have been demonstrated in continuously operated 1-in. and 4-in. diameter tubular reactors, respectively. These values are in excess of or equivalent to those obtained by McKay and other researchers in laboratory size equipment. These results were obtained with virgin feed material and the runs were terminated voluntarily, i.e., not as a result of catalyst deactivation. It is believed that mileages comparable to or greater than the above can be attained with recycle of unreacted AN and urea. Satisfactory operation of the pilot plant with recycle feed and a demonstrated longer catalyst mileage are required.

7. During the operation of the pilot plant, catalyst poisoning became a paramount problem. A series of experiments was performed in a down-flow, 1-in.-diameter column following a logical decision tree. It was concluded that the crystal habit modifier impurities in the commercial grade ammonium nitrate were the major contributor to catalyst poisoning. It was further shown that phosphates were the most important detrimental chemical. Borates, another suspect, are probably not detrimental on a single-pass operation but might be in a continuous recycle system. Ammonium nitrate and urea feed materials completely free of any additives are recommended for all future guanidine nitrate programs - development or production. (It should be noted that the standard military specification grades of AN are not suitable for this process because of the above noted crystal habit modifiers.)

8. The rate of poisoning is a function of the type of catalyst. This is presumably associated with particle geometry, pore volume and pore diameter. Three catalysts that were extensively evaluated showed the following decreasing rate of poisoning: (a) Mobil Sorbeads, (b) Houdry CP 532 silica beads, and (c) Grace grade 59 silica gel. Houdry beads are preferred because of physical integrity.

9. In addition to affecting yield, the presence of free water (about 1%) in the reactor feed results in physical degradation of Grace grade 59 silica gel and Mobil Sorbeads. Thermal cycling of a packed bed tubular reactor affects the physical characteristics of all catalysts to varying degrees. Mobil Sorbeads lose their original identity very easily while Grace 59 silica gel breaks down less rapidly. Houdry CP 532 silica beads showed evidence of attrition only during the initial period of pilot plant operations when the reactors were thermally cycled numerous times with occluded reaction melt. No evidence of Houdry bead attrition was evident when pilot plant reactors were operated under design conditions. It was concluded that Grace 59 silica gel and Mobil Sorbead catalysts are unsatisfactory for packed bed tubular reactors. Houdry CP 532 silica bead catalyst is the only known acceptable catalyst for this application. The Houdry catalyst is presently available only in experimental quantities, but presumably could be available at a reasonable price-volume relationship.

10. Both laboratory one-liter batch reaction experiments and continuous single-tube pilot plant reactor operations show that the ammonium carbamate reactor off-gas and guanidine nitrate are produced at a one-to-one molar ratio.

11. Observation of a 2-in.-diameter glass columnar reactor showed the presence of gas bubbles throughout the catalyst bed. Based on the visual observations, the eight parallel pilot plant reactors were designed with the assumption that liquid melt feed would distribute evenly among the reactors. It was subsequently concluded that other provisions must be made for flow distribution, e.g., individual flow controllers or properly designed back pressure feed orifices. Disengagement of reactor off-gases from the reaction melt is fairly complete with a short residence time. No entrainment of liquid was noted in the off-gas.

12. A density controller was incorporated into the pilot plant for the sole purpose of determining the proper ratio of recycle and virgin feed streams for a prescribed AN/U mole feed ratio to the reactors. It has been concluded that such a refined system is not required since the overall process is self-compensating. The reaction produces a low level of by-products and consequently, essentially all of the urea and ammonium nitrate that is converted goes to guanidine nitrate and ammonium carbamate (equal to GN produced). Therefore, it is necessary to add only fresh AN and urea to the system equivalent to the GN produced, i.e., 0.5 mole AN and 1 mole urea plus respective yield losses per mole of GN produced.

13. Reactor performance during operations can be monitored easily through elementary calculations of reactor productivity, conversions, and yields. These calculations are based only on feed rates plus feed and product analyses and employ the premise of total nitrate conservation. This method has been shown to compare favorably with the more conventional method of calculating these parameters based on a total material balance. This latter method can be done only over long time intervals and with complete process stream weights and analyses. The estimate method based on total nitrate conservation is recommended for future operations as the method of monitoring reactor performance.

14. The single aqueous crystallization method for recovering guanidine nitrate from the reaction mix of GN, AN and urea has been shown to be satisfactory. A reaction mix containing less than 50% GN and diluted with hot water can be crystallized easily (evaporative cooling in the pilot plant). The resultant crystals were totally retained in a polyethylene cloth-lined basket centrifuge and, with subsequent centrifugal water washing, yielded a product of 96 + % purity GN. The resulting mother liquor can be concentrated, for recycle to the reactors, to < 0.5% water in a two-stage, falling film, steam-heated, air-swept evaporator. Variations in the reactor product composition do not seem to affect the GN recovery operation appreciably.

15. Drying of water-wet GN did present a problem. It was concluded that indirectly heated, rotor-type dryers (e.g., Strong-Scott and Littleford) are not satisfactory for drying GN. This method of drying results in the formation of wet paste, and consequently, in adhesion of dry GN to the dryer internal surfaces following evaporation of the water. Limited test data indicate that a direct heated (e.g., hot air) dryer with minimum solids agitation will be satisfactory. Additional testing is required.

16. One-liter batch reaction experiments were valuable in determining reaction kinetics, catalyst selection, and subsequent development of the proven packed bed tubular reactor mathematical model. Problems encountered in the pilot plant with catalyst poisoning showed that single batch reactions with fresh catalyst were not totally satisfactory in predicting potential problem areas. Batch reactor experiments should continue to be used for scouting purposes, but any new major reactor process changes should be checked out prior to pilot plant operations in a 1-in.-diameter, down-flow continuous column. The use of such a column was very beneficial in resolving problems of catalyst poisoning, catalyst attrition, etc.

17. Sensitivity test data show that the AN/U pilot plant process for producing guanidine nitrate is inherently safe because (a) process materials are relatively insensitive to impact, friction, ESD and thermal stimuli, (b) no material in the pilot plant will transit from burning to detonation and hence, the system is not capable of acting as an explosive shock donor to process materials; and (c) equipment showed no potential explosive hazards under normal operating conditions. A computer simulation (800 hr of operation) of a logic model resulted in a probability of initiation of $4.6 \times 10^{-3}$ or a probability of no initiation of 0.9953.

Results obtained during the latter phases of this program, following the resolution of the catalyst poisoning problem, have instilled confidence in the future of the U/AN process for manufacturing guanidine nitrate. An analysis of the basic process - considering such items as raw material supplies, recycle streams and by-product formation - shows that this process has potential economic and operating advantages over the British Aqueous Fusion (BAF) process. Demonstration of a satisfactory catalyst mileage (estimated 300 lb GN/lb catalyst from an economic point of view) is anticipated. The supply of production quantities of a satisfactory catalyst can probably be obtained. The potential advantages (facility cost, operating costs, fewer operations, minimum by-product formation, etc.) of this process, when compared to the BAF process, justify additional work for the immediate future. It is believed that a decision as to whether or not to consider this process for a first generation, state-side production facility can be made in the third quarter of 1973. It is recommended that the following program be implemented:

1. Modify the GN pilot plant at Hercules/Kenvil consistent with past operating experience and experimental data generated during this program. Basically, the modifications would consist of streamlining process flows, unit operations and instrumentation to minimize process stream contamination, minimize process upsets resulting from down-time and assure improved distribution of feed to the reactors.

2. Operate the modified pilot plant to produce a target quantity of 40,000 lb of guanidine nitrate and also to obtain process variable data required for plant design. Commercial, reagent grade ammonium nitrate - free of all additives - would be used in conjunction with commercial grade Olin urea. The plant would be operated with recycle and continuously under a pre-selected set of conditions to yield a design production rate of 50 lb GN/hr, low ammelide by-product formation, and a demonstrated catalyst mileage of 200 lb GN/lb catalyst (minimum). Shipment of the dry GN would be under the direction of the Picatinny Arsenal Project Officer.

3. Conduct an economic study to permit a logical and timely decision between the BAF and AN/U processes as an intermediate in the manufacture of nitroguanidine (NQ). The study would consist of two specific tasks as follows:

   a. Perform an economic evaluation of alternative processes for utilizing off-gas $NH_3$ and $CO_2$ in the U/AN process for GN in combination with various raw material choices. A decision of the best utilization of the off-gas would be based on economics as well as by-product disposition.

   b. Determine the investment and operating costs for a total nitroguanidine facility utilizing the AN/U reaction for GN. The manufacturing costs would be developed in the same format as reported for the BAF process to NQ in the PDCM dated February 11, 1972 under Corps of Engineers Contract DACA45-71-C-0121. Investment costs for the total AN/U-to-NQ facility would be developed in the format reported for the BAF process in the P-15 estimate, dated April 28, 1973 for AMC Project 5742632 (COE Contract DACA45-73-C-0015). The comparative costs of NQ via the AN/U and BAF routes will permit a more realistic comparison of the two processes than if the GN-only battery limits costs via the AN/U process were estimated as noted in the original scope of work of this contract (Phase IV). The expanded cost estimates plus off-gas utilization studies would eliminate the need for the original Phase IV scope of work.

4. Place the pilot plant in a standby condition. This would involve complete cleaning of all equipment and tagging of all equipment with respect to condition, purchase order number, and vendor.

5. One of the items to be considered for a production facility is the availability of production supplies of an adequate catalyst. It is recommended that a firm commitment be made regarding the future supply of Houdry CP 532 macroporous silica beads and that studies be implemented to develop a catalyst equal to or better than Houdry Beads.

## III. TECHNICAL STATUS
## (As of February 4, 1973)

During the course of this development program, considerable progress has been made in advancing the technology of manufacturing guanidine nitrate (GN) by the catalyzed reaction of ammonium nitrate (AN) and urea (U) over a siliceous catalyst. Reactions have been carried out in both laboratory batch and continuous-flow packed bed tubular reactors. In the latter case, reactors with diameters of 1, 2, and 4 inches have been employed. The fundamental concept for producing guanidine nitrate from AN and urea is sound. The literature regarding this process has been surveyed, and the results obtained from the efforts of this program have surpassed previous results in terms of reactor on-stream time (hours), catalyst displacements (lb total feed per lb catalyst), catalyst productivity (lb GN produced per lb catalyst), reactor size (4 inch diameter x 12 ft), operation of a totally integrated process and demonstration of production plant prototype equipment. Utilization of a single, aqueous crystallization step for recovering GN from the reactor product resulted in satisfactorily pure product. Normal variations in reaction melt composition do not appear to affect the GN crystallization-recovery operation.

Reaction kinetic data generated from laboratory experiments were used to develop mathematical models and computer programs for both packed bed tubular and cascaded stirred tank reactors. Outputs from the programs indicated that the stirred tank reactor concept has urea conversion and yield advantages over tubular reactors. However, the packed bed tubular reactor concept was selected for further study and scale-up on the basis of safety, operational simplicity, direct scale-up and minimum design problems. Experimental results obtained from 1-inch, 2-inch and 4-inch diameter reactors confirmed that the models are capable of predicting reactor performance under a variety of conditions. Acceptable yields, conversions and GN productivities have been demonstrated on a pilot plant scale.

The performances of many catalysts were experimentally measured in laboratory batch reactions. Three catalysts were selected as prime candidates for packed bed reactors and subsequently characterized; namely, alumina-containing Mobil Sorbeads R, Grace grade 59 Silica Gel, and Houdry CP-532 Macroporous Silica Beads. As of this time, Houdry Silica Bead catalyst is an excellent choice for packed bed reactors by virtue of its mechanical strength, insensitiveness to low moisture levels in the feed melt, and a demonstrated mileage of 65 gm GN/gm catalyst. Grace 59 or similar material may be a contender, but further work by the supplier is required to produce a less friable material. Mobil Sorbeads are no longer in contention.

The literature had not reported any problems with catalyst poisoning from ammonium nitrate feed stock. Presumably all previous work had been done with reagent grade material. The fact that silica gel-type catalyst can be poisoned came to light when operating a packed bed tubular reactor in a

continuous mode. The poison (diammonium phosphate) was identified through selective experimentation and directed attention to the use of complete additive-free chemicals.

Preliminary cost calculations indicate that the U/AN process for producing guanidine nitrate is lower in investment and operating costs than the BAF process. In principle, the U/AN process would be simpler to operate. To place both processes on a comparable basis, more detailed cost analyses are required for a total GN-to-NQ facility via the U/AN approach. These costs could then be compared directly with BAF process costs generated under a separate contract. Complementing this effort would be a detailed cost analysis for the disposition of the reactor carbon dioxide and ammonia off-gases.

There are three technical areas of uncertainty which must be evaluated before the U/AN process can be considered acceptable:

(1) The stability of the process in a total recycle mode of operation must be determined. It must be established whether the recycle liquor (AN, GN and urea) stabilizes at a workable composition or whether impurities accumulate to affect either the GN crystallization or the reactor behaviors.

(2) A catalyst life reasonable for pilot plant operations must be demonstrated; e.g., 200 lb GN/lb catalyst. If a catalyst mileage of this magnitude can be obtained, then extrapolation to higher values should be reasonable. Future modifications to the process should yield even better mileage values. These modifications would consist of changes in process operating parameters, interstage reactor feeding of urea and improved catalyst properties. A catalyst mileage of about 300/1 is desirable on the basis of preliminary cost analysis and practical operations.

(3) The steady-state average ammelide production rate must be determined. It is assumed that the effective catalyst life is related to ammelide production; i.e., as ammelide builds up in the reactor, it either blocks the active sites, causing a decrease in activity, or the ammelide production increases in quantity and presents disposal problems. There are some indications that ammelide production may be related to the quantity of water in the reactor feed. The control of ammelide formation is important in the event that it cannot be used as a fertilizer and must be stockpiled. It has been reported in the literature(5) that ammelide will hydrolyze to $NH_3$ and $CO_2$ at 170°C.

The U/AN process for producing guanidine nitrate is at a crossroad with respect to being considered for production plant design. There is a high level of confidence among those involved in this program that the remaining major technical problems listed above can be resolved. Consequently, Hercules Incorporated has submitted a follow-on proposal with the primary goals of (1) modifying the pilot plant, consistent with post-operating experience, to yield an improved operation; (2) operating the pilot plant to demonstrate a catalyst mileage of about 200 lb GN/lb catalyst and produce sufficient product for conversion to NQ in Cyanamid of Canada production facilities; (3) preparing a semidetailed cost analysis for a total GN-to-NQ facility, including the optimum method for utilizing the reactor off-gases. Negotiations for this follow-on program are in process. In the interest of time, Hercules Incorporated has proceeded with the required pilot plant modifications with a scheduled start-up in May 1973.

# IV. INTRODUCTION

## A. OBJECTIVES AND PROGRAM DESCRIPTION

In response to Picatinny Arsenal Solicitation No. DAAA21-70-Q-0211, Hercules Incorporated proposed to undertake a process engineering design for the manufacture of guanidine nitrate (GN). Hercules Incorporated was subsequently awarded a 23-month contract effective October 1970. The principal objective of the proposed program was to achieve a safe, reliable and economical route to GN from urea (U) and ammonium nitrate (AN) using a catalyst reactor system. The approach used was based on the Boatright-Mackay-Roberts (BMR) process described later in this Introduction. The contracted program consisted of four phases as outlined below:

Phase I. Work planned for this phase consisted of the following: (1) laboratory batch studies of the U/AN/catalyst reactor system to provide basic information regarding catalyst(s) and chemical kinetics, crystallization, solids-liquid separation and drying; (2) operate a 2-inch-diameter reactor column to investigate variables such as top and bottom feed, feed rate, temperature, type of catalyst, etc.; (3) develop information on materials of construction; (4) determine the safety of the proposed process by using hazards analysis techniques to conduct a Fault-Tree analysis which assures an optimized balance between loss potential and loss probability; (5) investigate a study of a mathmatical model involving the reactor(s) to provide the basis for optimum reactor design; and (6) perform preliminary economic studies to assess the economic importance of various parameters as related to battery limits.

Phase II. This phase of the program was planned to culminate in a pilot plant design based on the experimental process and hazards analysis findings of Phase I. The effort required preparation of a flow sheet complete with heat and material balances, preliminary equipment layout, specification of equipment, and an engineering analysis of these equipment items from a hazards analysis standpoint.

Phase III. This phase of the program was to consist initially of procuring and installing equipment, specified in Phase II, in a building located at Hercules Incorporated, Kenvil, N. J. This equipment was required to be suitable for Class 7 explosives operation. The main objectives of operating the pilot plant were as follows: (1) verify the results of the bench-scale studies; (2) investigate the effects of process upsets on safety, yields, product quality, etc.,; (3) generate design data for production plant design; and (4) produce 40,000 lb of GN suitable for conversion to nitroguanidine.

Phase IV. This phase was designed to comprise a full-scale Process Design, within battery limits, of the urea/ammonium nitrate/catalyst system. The information furnished in the design criteria was to include economics, hazards analysis, energy and material flow sheets, equipment requirements with preliminary specifications. The information was to be of such quality that it could be used by an architect-engineer to design a commercial size operating plant.

Because of technical problems associated primarily with catalyst poisoning encountered while operating the pilot plant, only two of the above four-phases in this program have been completed. However, the catalyst problem has been resolved in an extension of Phase III, and the technology developed has shown excellent potential. The purpose of this report is to provide a comprehensive summary of the program to date. The results, accomplishments, problem areas, etc. are discussed in the sections devoted to descriptions of Phases I, II, III and III Extension.

## B. IMPORTANCE OF DEVELOPING NEW GUANIDINE NITRATE PROCESS

Nitroguanidine is an important component of triple-base cannon propellants. It is cool burning and high in nitrogen. These properties are of particular importance since they lead to formulations yielding a flashless exhaust. Guanidine nitrate, the intermediate from which nitroguanidine is manufactured, is converted to nitroguanidine by sulfuric acid dehydration or "nitration" of GN, a process that is very well understood from an engineering standpoint.

Presently, all nitroguanidine used by the U. S. military is manufactured in Canada by the Welland process. However, the technology on which this process is based has been surpassed by several new processes. The lack of a domestic source for nitroguanidine has been a continuing concern of the Army Munitions Command. Because of this concern, construction plans were prepared for building a facility at Pryor, Oklahoma, for production of guanidine nitrate based on a modified Welland process; later, these plans were changed and it was proposed to build the facility at the Sunflower Army Ammunition Plant.

About twenty chemical routes exist for the production of guanidine nitrate, but most of these are quite expensive and impractical for commercial consideration since they involve uncommon and expensive raw materials and require technically difficult processing conditions. Four of the possible routes, however, have shown sufficient economic promise either to have been studied extensively on pilot scale or to have been commercialized. A summary of these processes is given in Table 1.

## TABLE 1

## NITROGUANIDINE PROCESSES*- PRICR ART

| | 2,500 T/Mo. Welland ("Dicy") Process | 2,000 T/Mo. British (ICI) Aqueous Fusion Process (Modified Welland) | Waterbury (Ammonium Thiocyanate) Process | Roberts Fusion Process |
|---|---|---|---|---|
| NQ Yield, % | 72.5 | 80.5 | 99 | 65 |
| Raw Material Cost, ¢/lb NQ | 5.8-8.6 | 5.4-8.0 | 4.7-20.0 | 13-14 |
| Maintenance Cost, ¢/lb NQ | 16.4 | 15.4 | - | - |
| Elec. Power, KWH/ton NQ | 6,500 | 4,500 | 700 | - |
| Capital Invest., Millions $ | 21 | 20 | - | - |
| Advantages | 1)A proven process giving moderate yields of high-quality NQ.<br>2)Minimal explosion hazard. | 1)Economic advantage over "Dicy" process.<br>2)Readily attainable raw materials.<br>3)Now being operated in Great Britain (Bishopton, Scotland). | 1)Possibly lowest packaged NQ cost. | 1)Capital investment low.<br>2)No critical raw materials.<br>3)No waste disposal problems of any consequence.<br>4)A readily marketable by-product.<br>5)No high pressure or temperature.<br>6)No corrosion problems. Minimum hazard.<br>7)All stages of process can be carried out in one vessel. |
| Disadvantages | 1)High-pressure equipment required.<br>2)Waste disposal problems.<br>3)Dependent on electrical power.<br>4)Difficult to produce desired granulations.<br>5)"Dicy" manufactured only in Canada. | 1)Sludge filtration. Degree of corrosion. Reactor design and control. Accumulation of impurities. Production of high-purity $CaCN_2$. Hydrolysis losses.<br>2)Waste disposal problems.<br>3)Explosion hazard.<br>4)$CaSO_3$ disposal problem. | 1)Corrosion problems.<br>2)Very close control of frac. cryst. step needed.<br>3)Purging may be necessary.<br>4)Sep. of $NH_3$ and $H_2S$ not established<br>5)Requires cycling and oxidation of >6 lb per lb GN and depends on sulfur economics. | 1)The manufacturing cost of NQ is higher.<br>2)Dependent on the economics of the conversion of diethyl sulfate to EtOP.<br>3)Only one Et group of diethyl sulfate reacts. |

*Costs - 1968 basis.

The Welland process is currently the source of supply to United States nitroguanidine. The British Aqueous Fusion (BAF) process, which is a more efficient version of the Welland process, is currently used by the British to produce nitroguanidine. Both the Waterbury process and the Roberts fusion process have been studied extensively in pilot plants, but the need for and the feasibility of commercializing them have not materialized.

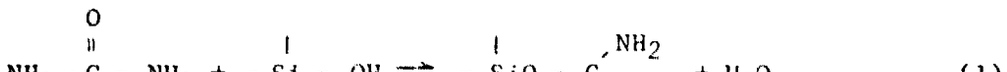
It can be seen from Table 1 that all four processes suffer from rather substantial disadvantages either because they are not economical or because they pose technical or waste disposal problems. For these reasons, there is currently great interest in a fifth process, which is based on the reaction of molten urea and molten ammonium nitrate on silica. This process has been referred to as the BMR (Boatright-MacKay-Roberts) process.

## C. BOATRIGHT-MACKAY-ROBERTS (BMR) PROCESS

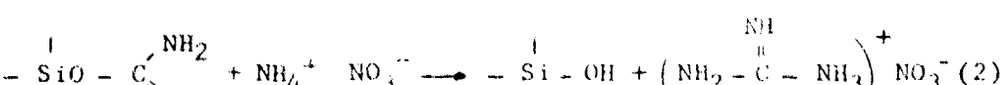
### 1. Chemistry of BMR Reaction

Although the Boatright-MacKay-Roberts process had not been studied at the pilot plant or full-scale plant level, laboratory experiments had shown that the process has great promise in economy, safety, technology and freedom from waste disposal problems. Historically, the BMR process resulted from the finding of Boatright and MacKay that guanidine nitrate (GN) is formed by passing a melt of urea and ammonium nitrate over silica gel, and from the contribution of Roberts who showed that GN can be crystallized directly from the reaction product.[1,2,3]

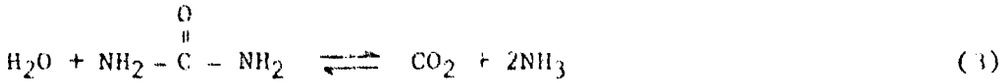
The chemistry of guanidine nitrate production from urea and ammonium nitrate is not well known. Experiments conducted to elucidate the chemistry have shown reactions of substituted ureas, other ammonium salts, and substituted ammonium salts as well as a small range of catalyst types. These experiments as well as other known routes to guanidine nitrate suggest the following reaction sequence:



(Enol form) (Silica gel) Adsorbed species (1)



(2)



(3)

The first step shows urea in the enol form. If a slightly acidic oxide is present, coupling of the urea of the hydroxide occurs with loss of water. The second step is reaction of the O-substituted urea with ammonium nitrate to form guanidine nitrate. The water formed in the first reaction will immediately hydrolyze a mole of urea, since this reaction (3) is just the reverse of the urea synthesis reaction.

The O-substituted urea is probably the adsorbed species when the proper catalyst is present. This mechanism suggests that other catalysts, particularly mildly acidic materials from the middle groups of the periodic table of the elements, may be effective catalysts for this class of reactions. Examples of such catalysts may include typical acid-absorbent clays, silica-alumina cracking catalyst, oxide gels of the zirconium or titanium groups and perhaps even crosslinked polymers which include available pentaerythritol groups. Homogeneous catalysts may also be found in the group of materials related to silicon tetraisopropoxide, since this type of material would also be expected to form the desired urea substitution product.

## 2. Description of BMR Process

The BMR process consists of continuously passing an equimolar mixture of urea and ammonium nitrate over silica gel, adding urea to the reactor effluent to give a composition close to the binary eutectic, and separating and recrystallizing GN while recycling mother liquors. The GN can be recovered from the reactor effluent using an alternate method of recrystallizing it directly from water, but this alternate method may sacrifice some economy.

If adequate yields can be obtained from the BMR process, it is quite apparent that the BMR process offers distinct advantages over the British Aqueous Fusion process, its closest competitor. The latter process uses the relatively expensive cyanamide as a starting material which itself requires large amounts of electrothermal energy for synthesis. Further, it requires large amounts of process water for product recovery and produces large amounts of impure calcium sulfate. Conversely, the BMR process requires inexpensive starting materials, does not require large amounts of water, and has virtually no disposal problem as will be elucidated in a later section.

A schematic of the BMR process is shown in Figure 1. Loss of urea is minimized by using an excess of ammonium nitrate (AN). An equimolar mixture of molten AN and urea is formed by melting these materials and mixing with returning mother liquor from a crude product crystallization. This feed is preheated and introduced to a group of packed reactors which operate in parallel. The reactors contain 18/30 mesh silica gel and are heated to about 190°C. The reactor effluent contains gaseous

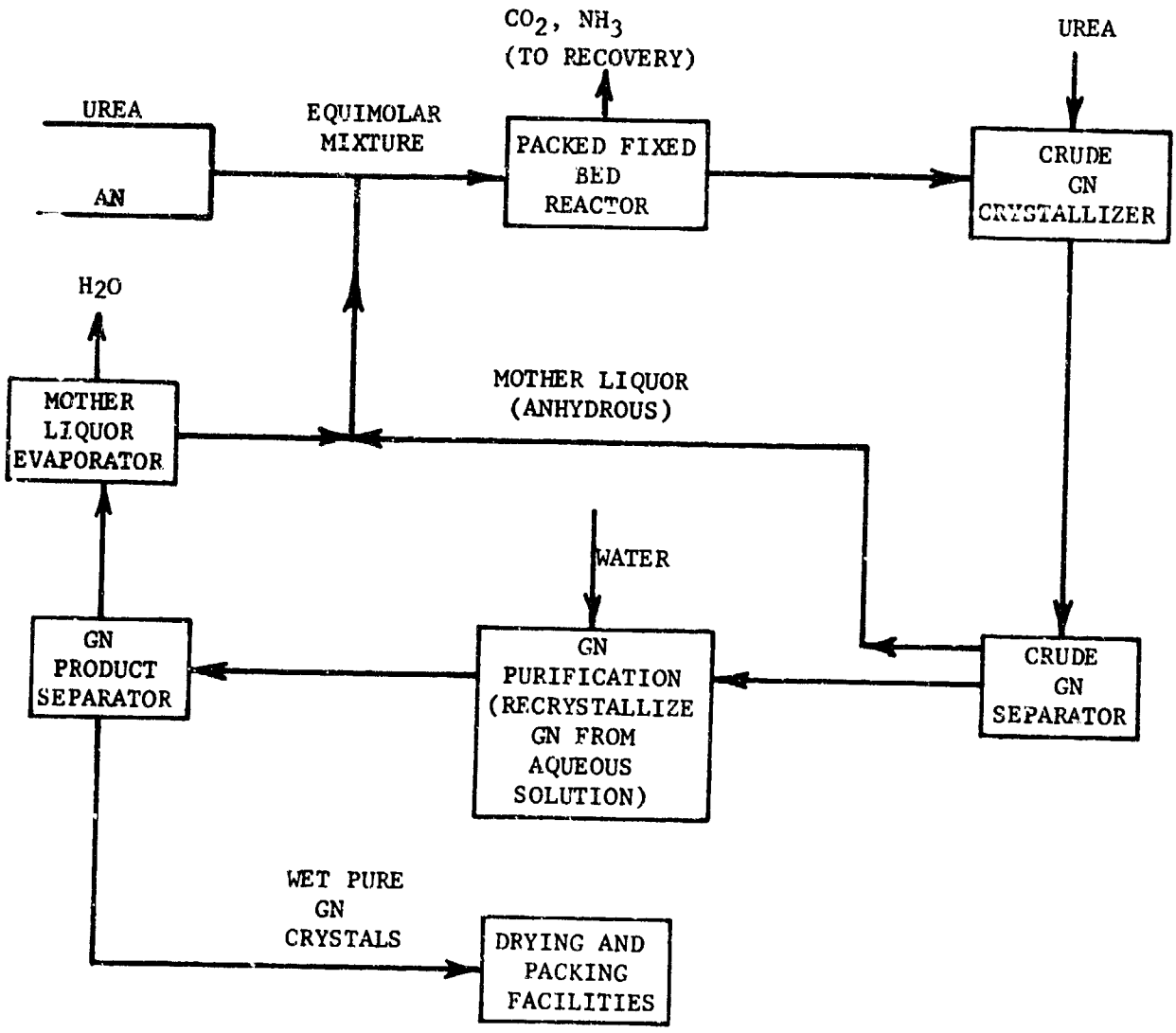



Figure 1. Urea-Ammonium Nitrate (BMR) Process Diagram (As originally proposed. See Figure 1-A for current process that employs aqueous quench in place of eutectic crystallization.)

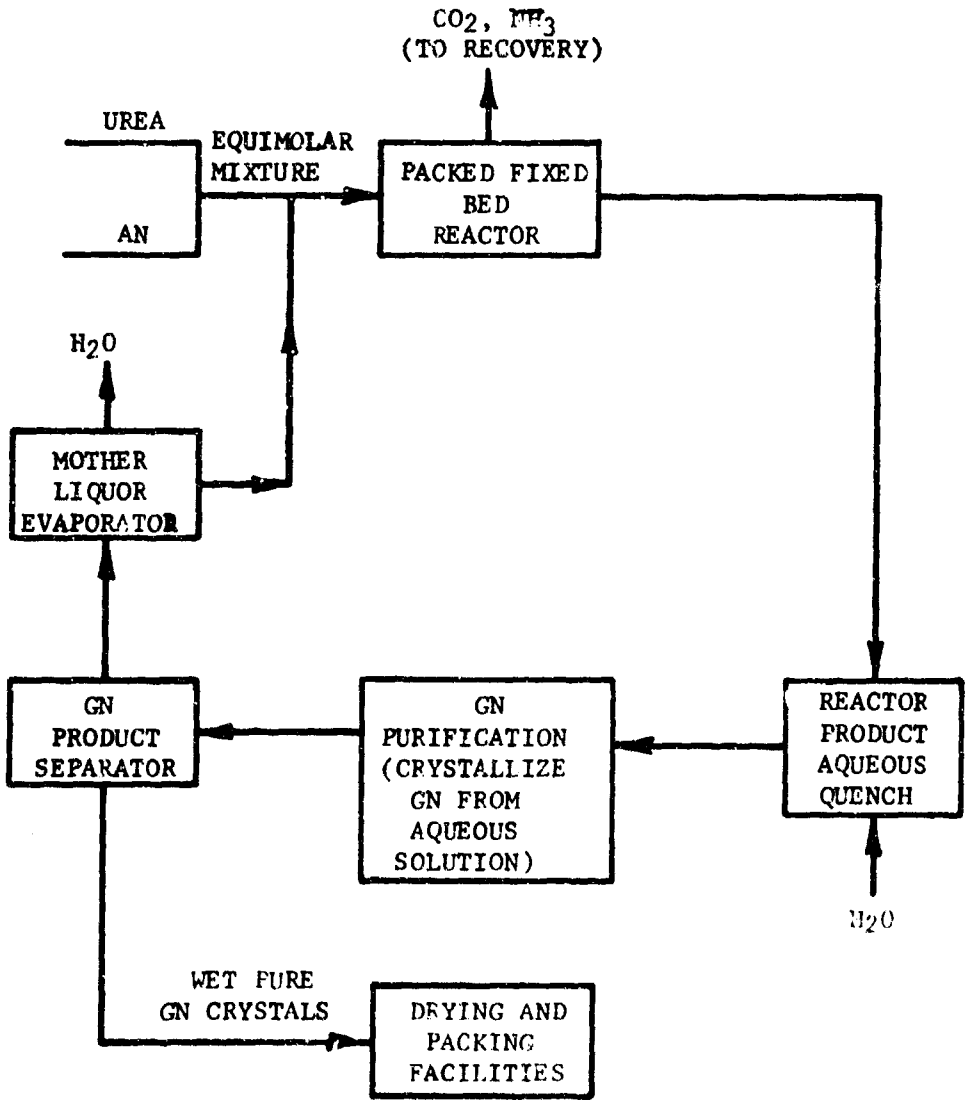



Figure 1A . Urea/Ammonium Nitrate Process Diagram (Process Employing Aqueous Quench)

ammonium carbamate (decomposed into $CO_2$, $NH_3$ and a small amount of $N_2$), liquid urea, AN and GN with small amounts of an insoluble by-product. The ammonia and carbon dioxide are reconverted to urea or made into ammonium nitrate. The liquid reaction product is mixed with fresh urea to roughly the binary eutectic composition, and is cooled to about 60°C. At this temperature, guanidine nitrate crystallizes from the melt and may be separated by filtration or centrifugation. The mother liquor is returned to feed and GN is purified by recrystallization from water and dried as product.

### 3. Advantages of BMR Process

From a cursory inspection, it is evident that the economics of this process are competitive and favorable when compared to other processes described in Table 1. Its advantages are based on use of a single reaction step and standard purification techniques and low costs of urea and ammonium nitrate.

In addition to the technical and economic advantages, there are substantial incidental process advantages. (1) The raw materials (urea and ammonium nitrate) present no toxicity hazard to plant workers and essentially no fire or explosion hazard. (2) Although some of the process mixtures are highly energetic, they seem to be insensitive to detonation stimulus. (3) In a time of particular awareness of the effect of chemical processes on natural environment, it is of interest to note that the BMR process in principle produces no disposal streams and therefore creates no pollution problem. Based on the data available from the patents, it is clear that the off-gases can be used to regenerate urea or, alternatively, to produce AN or a fertilizer solution. Similarly, the recrystallization liquor can be evaporated to give a stream of pure water and process feed which can be recycled to the reactor. Small purge streams are expected, but these should be easily combustible in a commercial facility.

### 4. Current Status of U/AN Process

It should be noted that the BMR process as described above was modified during the Phase I laboratory study to eliminate the eutectic crystallization and to add an aqueous quench. Thus, the molten reactor product is now added directly to water, the solution is centrifuged to remove water-insolubles, and the aqueous solution is evaporated and crystallized. (See Figure 1-A.) A flow sheet for guanidine nitrate production, using the aqueous workup, is shown as Figure 1-B. Material balance for a specific production case (Case 100) is illustrated in Figure 1-C. A photograph of the tubular reactors employed is included as Figure 1-D; and a photograph of the recovery system, including the guanidine nitrate crystallizer and basket centrifuge, is given as Figure 1-E.

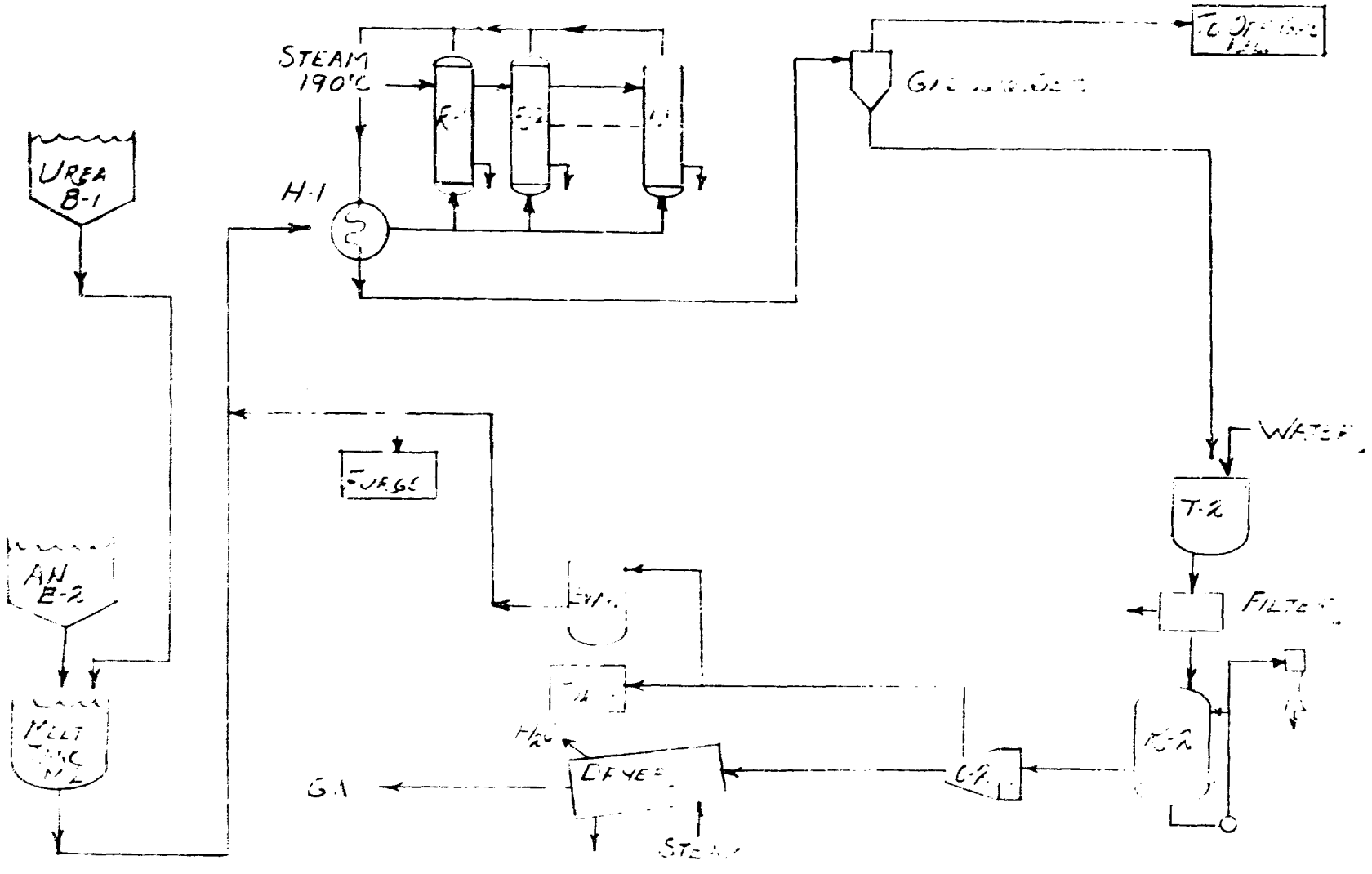
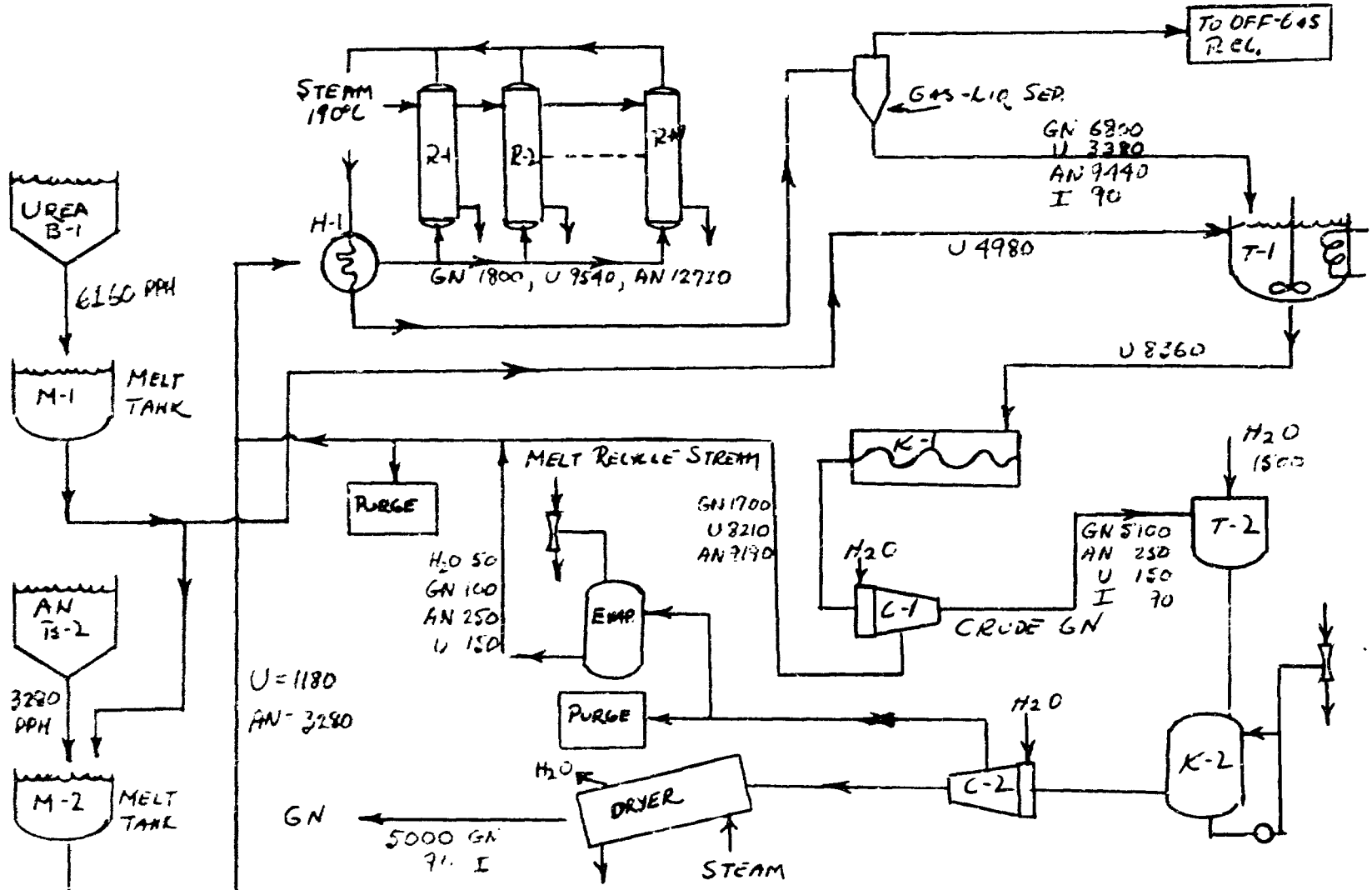



Figure 1-B. Flow Sheet for Guanidine Nitrate Production (Aqueous Workup)




Case 100

| | |
|---|---|
| Urea yield | 80% |
| Urea conversion | 64.5 |
| AN conversion | 32 |
| AN/U | 1.0 |
| Product | 98% |

$$U = \frac{6160}{5000} = 1.232 \text{ lb/lb GN}$$

$$AN = \frac{3280}{5000} = 0.656 \text{ lb/lb GN}$$

Figure 1-C. Material Balance for Case 100

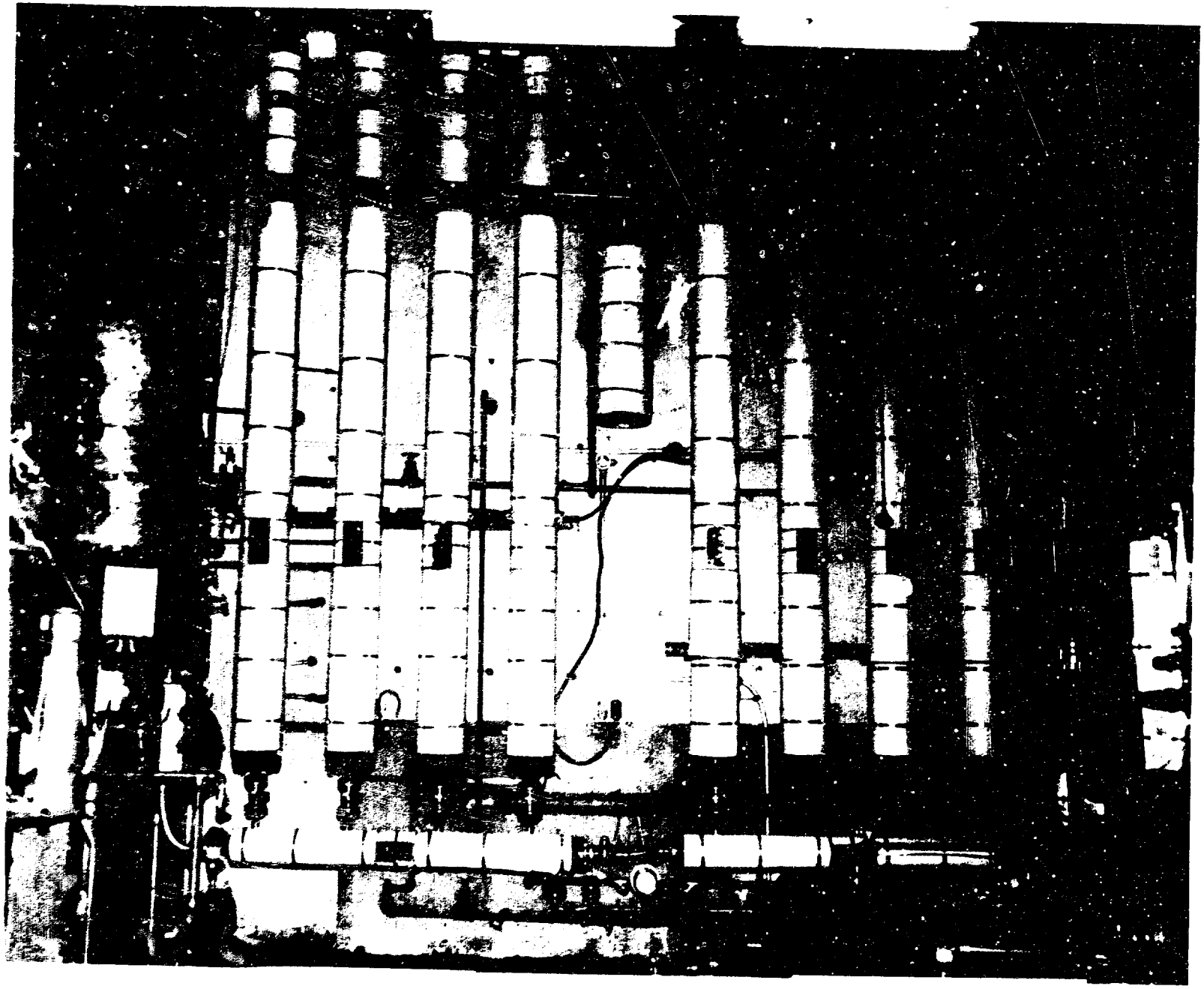


Figure 1-D. Guanidine Nitrate Catalytic Tubular Reactors

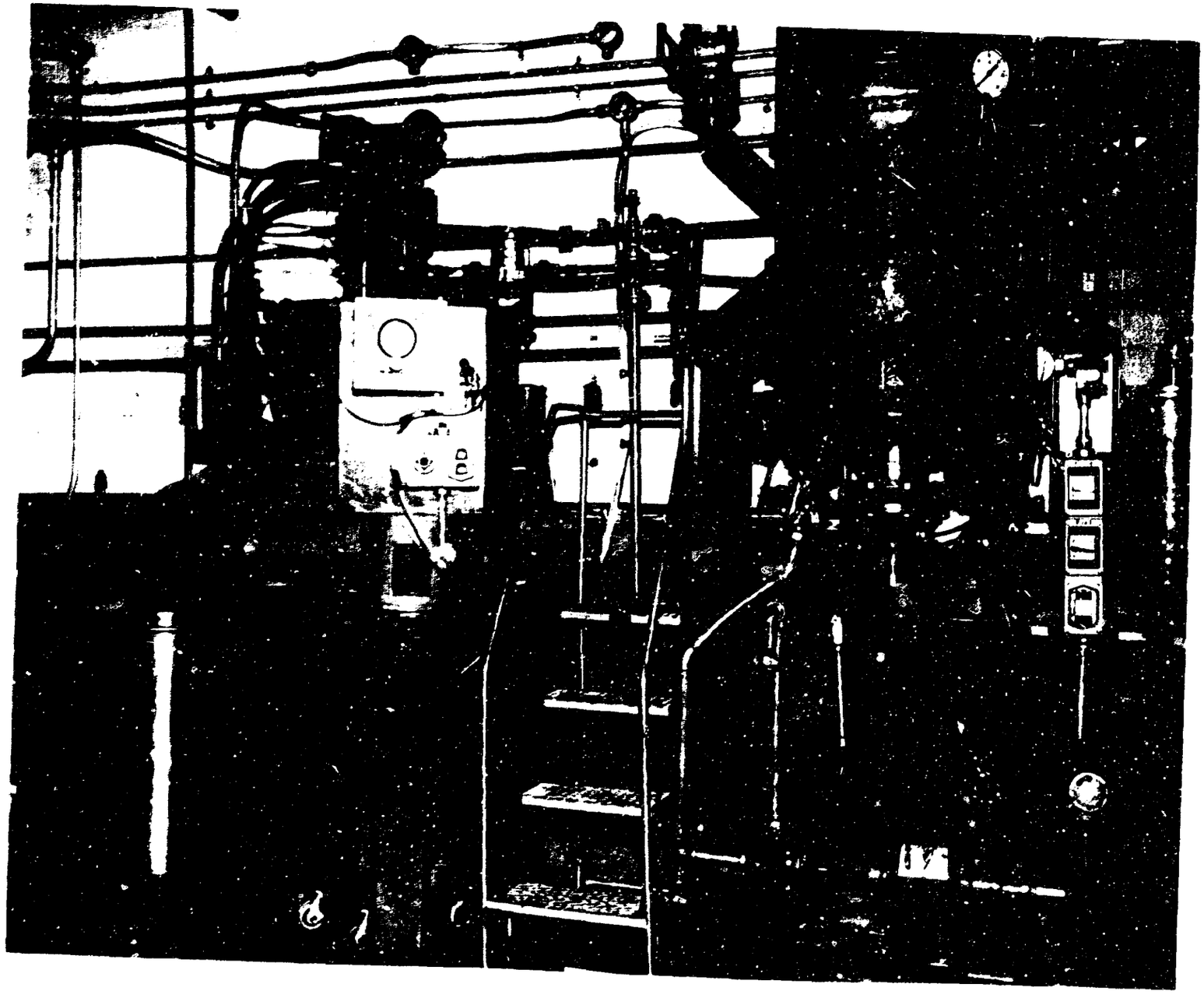


Figure 1-E Guanidine Nitrate Crystallizer and Basket Centrifuge

# V. DISCUSSION

## A. PHASE I - LABORATORY, ENGINEERING, ECONOMIC AND TECHNOLOGY STUDY

### 1. Summary

#### a. Part 1 - Laboratory Studies

The first part of Phase I was concerned with the one-liter batch reactor runs and other laboratory and analytical work conducted at the Hercules Research Center.

Forty-one batch reactor runs were conducted. This work confirmed the literature concerning the AN/U/silica gel reaction, provided kinetic data used in preparing the mathematical models, determined the effect of various process conditions on yield and conversion, and helped establish operating conditions for the bench reactor operated at Kenvil. Alternate catalysts were also screened at this time.

The data presented in the literature were verified. No unexpected departures from previous work were found.

The laboratory work can be summarized as follows:

(1) Final reaction runs using commercial feeds showed that, aside from requiring filtration to remove anti-caking additives, these materials perform in the same manner as analytical grade feeds.

(2) Isolation of insolubles in the reactor product showed that at the preferred reaction conditions, 2-3% ammelide is produced based on final dry GN product.

(3) Sharp buildup of biuret followed by gradual decline was traced by analysis in several batch runs; this improved the already good analytical closure. Since biuret is itself a reactant, its presence has little technical or economic effect on the process.

(4) Use of biuret and ammelide analyses made possible a carbon balance which showed that only 3-4% of the urea reacted is not accounted for. Urea accounted for on a carbon basis

consisted of urea, ammonium carbamate and guanidine nitrate (80-86 combined wt. %), and ammelide and biuret (9.5 - 16.6 combined wt. %). The remaining 3-4% results from losses, analytical errors and possible unknown by-products.

(5) Data were obtained on the recovery of guanidine nitrate by (a) melt crystallization followed by aqeous recrystallization vs (b) aqueous workup and crystallization.

(6) Drying runs demonstrated that the material dries easily.

(7) This work generally upheld the objectives that were originally foreseen for the process in the areas of waste disposal and pollution control.

A brief corrosion study showed that the best construction material for the main process equipment would be 304 stainless steel, confirming the findings of MacKay.

b. Part 2 - Mathematical Modeling

The laboratory data obtained in Fart 1 were used to build kinetic expressions which were incorporated into a mathematical model expressing both packed bed and stirred reactors.

It has been demonstrated that the models have full predictive capabilities as to the design and operating parameters on reactor performance. The sizes of both types of reactors were calculated for a pilot plant to produce GN at 50 lb per hr, affording a brief preview of the Phase II design work.

c. Part 3 - Bench-Scale Reactor Studies

The 2-inch-diameter packed bed reactor was operated for a total of 21 runs. Feasibility of the continuous packed bed reactor was demonstrated with production of GN at predicted rates. Reactor effluents contained as much as 55% GN, representing a high urea conversion. Composition data for the packed bed reactor products compare favorably with sample data from the packed bed mathematical model. This good agreement confirms the accuracy of the model which was based on laboratory batch reactor kinetic data. The parameters investigated in the bench-scale unit were temperature, AN/U ratio, grades of reactants, feed rate, bed height, GN in feed, reactor materials of construction, upflow and downflow.

Measured temperature profiles in the bench reactor compared qualitatively with those predicted by the mathematical model. The initial $\Delta T$ was slightly larger than predicted. The gas-liquid flow pattern assumed in developing the model was confirmed by visual observations of the glass bench reactor.

Yields and conversion data for the bench reactor runs were erratic and sometimes inconsistent. This was due to some relatively poor material balances as a result of (1) short operating times at equilibrium, (2) difficulties in measuring total feed input, (3) system holdup, (4) losses not accounted for and (5) analytical inaccuracies. One run designed for a material balance yielded an overall weight balance of 95.1% (AN - 99.7%, U - 91.9%) with yields of AN = 99.3%, U = 85.2% and urea conversion of 47.8%. These data are consistent with those obtained in the batch reactor experiments.

Continuous bench reactor data indicate that GN production rate is dependent on catalyst contact time and is not necessarily a function of flow rate at a given bed height. The system is not mass transfer-limited. The weight per cent insolubles in the product is a direct function of reaction temperature and urea concentration in the feed. There was no evidence of formation of gases other than ammonium carbamate.

d. Part 4 - Economic Evaluation

The economic evaluation disclosed that the most economical process utilizes stirred tank reactors and aqueous workup. This process has a projected mill cost of 9.3¢/lb GN* and a price of 14.6¢/lb GN for transfer to nitroguanidine conversion, reflecting a realistic burden. If the reactor is to be of the packed tubular type, the optimum residence time is two hours, which gives an 80% urea yield. Similarly, the optimum AN/U ratio in the reactor feed is very nearly 1 for both types of reactor. Finally, a catalyst life as short as two months will not materially affect mill cost.

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*Industrial accounting system (values were also calculated for a government accounting system).

## 2. Part 1 - Laboratory Studies

The urea/ammonium nitrate/silica gel reaction was studied in a one-liter batch reactor at the Hercules Research Center. The primary objectives of these studies were (1) to verify the urea-ammonium nitrate-silica gel reaction results found in the literature, (2) to investigate alternate catalysts, (3) to establish reaction rate data needed for preparation and evaluation of a mathematical model, and (4) to define operating conditions for the Kenvil bench reactor.

### a. Batch Reactor Equipment and Procedures

The laboratory studies were confined to a nominal 1-pound level. A one-liter glass reaction kettle fitted with a flanged lid containing several ground-glass ports was used as the reactor. The reactor temperature was controlled by using a heated silicone oil bath. The reaction gases generated passed through a series of three dry ice traps.

To measure gas volumes, noncondensable gases were passed through the traps and collected in a plastic bag over water (water displacement apparatus). Samples of the reaction mixture were taken by "drawing" some melt into a glass tube fitted with a fritted glass disc.

In a typical experiment, 6-12 mesh silica gel (W. R. Grace, grade 40) was dried in an oven at 200°C for about two hours. After tare weights had been obtained on the reaction equipment, urea and ammonium nitrate (AN) were charged, and the reactor was heated to 5-10°C above the desired reaction temperature. The hot, dry silica gel was then added, and the system was sealed. The ensuing endotherm lowered the reactor temperature to about the desired temperature. The bath was then used to maintain the reactor temperature at the proper level.

It was found that mechanical stirring or agitation reduced the particle size of the silica gel. Since the gases evolved during the reaction appeared to provide sufficient mixing for adequate heat transfer, the reactor was usually not stirred. In this way, particle size was not a variable during a particular run.

The reaction mixture was sampled as discussed above. Material balances and gas samples were weighed at the end of a run.

A crystalline sample of the mixture was dissolved in water and, if necessary, filtered to remove small particles of silica gel. The solution was analyzed for urea, AN, and GN using the following methods:

(1) Urea determined volumetrically by the urease method.

(2) AN determined volumetrically by the formal titration (reaction with formaldehyde).

(3) Total nitrate determined spectrophotometrically by measurement at 320 nm.

(4) GN calculated using the total nitrate value by subtracting the AN contribution from the total nitrate absorbance.

b. Reaction Kinetics

Fourteen batch reaction experiments were made in this series. The effects of the following were studied: (1) urea (U) to ammonium nitrate (AN) molar ratio, (2) reaction temperature, (3) silica gel dosage, (4) silica gel particle size, and (5) mechanical agitation.

A summary of the results of these verification kinetics runs (1 through 14) is presented in Table 2.

Table 2 lists the results for five isothermal batch experiments (Runs 7, 8, 9, 11, and 12) conducted with temperatures ranging from 170°C to 210°C. The purpose of these runs was to provide data for estimating the reaction orders with respect to urea and ammonium nitrate, the appropriate rate constants, and the temperature of the various rate constants. A preliminary investigation of the data indicated that an Arrhenius plot of the rate constants is linear and yields an activation energy of about 33,000 cal/gmole. These experiments were conducted without mechanical agitation since agitation caused serious particle size reduction and particle size has a strong effect on reaction rate of this system. The magnitude of the activation energy obtained from these runs indicates that mass transfer from the melt to the catalyst is not a limiting factor in these experiments and that the agitation provided by the evolution of gases was sufficient. The refined estimates for the rate constants through least squares fitting of the data and rate expressions are presented in a subsequent section.

Runs 3 and 4 in Table 2 illustrate the effect of particle size reduction, caused by agitation, on yields and conversion. At identical operating conditions, the conversion of urea was increased from 81.4% in Run 4 to 97.6% in Run 3 where agitation was used. Furthermore, in Run 6 where 100/325 mesh silica gel was used instead of the 6-12 mesh used in Run 4, the conversion of urea was increased to 93.9% (Run 6) from 81.4% (Run 4).

# TABLE 2

## GUANIDINE NITRATE REACTION STUDIES - INITIAL KINETIC STUDIES

| (1) Run No. | (2) Alk. Ni. SiO2 (Mole/l) | (3) Type | (4) Alk. Ni. (gm-moles) | (5) Charge Urea (gm-moles) | (6) Silica Gel (gm-moles) | (7) XCN Mix'd (gms) | (8) Urea - AC (gm-moles) | (9) (gms) | (10) Sample AM. NIT. (gms) | Wt% | (mole frac.) | (11) UREA Wt% | (mole frac.) | (12) GN Wt% | (mole frac.) | (13) $ Wt. % | (14) Material Balance Loss (gms) | % | (15) Yield (%) mGN x100 / mUrctd | (16) mAC x100 / mUrctd | (17) Conversion (%) mUrctd x100 / mUfed | (18) mANitd x100 / mANfed | (19) Yield2(%) mGN x100 / mUfed | (20) mAC / mGN | (21) Final Product Check (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.2[illegible] | 100 | 2.0 | 2.40 | 4.0 | 197.2 | 3.29 | 493.9 | 31.6 | - | 11.1 | 63 | 31.1 | - | 26.9 | - | 16.2 | - | 74.2 | 60.6 | 10.1 | - | - | - | - | - | -29.4 |
| 2 | 1.2[illegible] | 100 | 2.0 | 2.40 | 4.0 | 264 | 3.40 | 448. | 224 | 1.69 | 36.3 | 62 | 19.9 | .254 | 11.3 | .193 | 66.4 | .555 | 97.6 | 15.7 | 2.6 | 77.9 | 45.2 | 88.1 | 68.6 | 69.5 | 1.16 | + 3.0 |
| 3 | 1.2[illegible] | 100 | 3.0 | 2.40 | 3.0 | 354.1 | 2.57 | - | - | - | - | 74 | 57.8 | .876 | 1.5 | .023 | 39.2 | .301 | 98.5 | - | - | 63.1 | - | 97.6 | 30.6 | 61.6 | - | - |
| 4 | 1.2[illegible] | 100 | 4.0 | 2.40 | 3.0 | 440.4 | 2.59 | 393.9 | 74.9 | .56 | 58.1 | 71 | 55.2 | .706 | 10.7 | .117 | 32.9 | .237 | 98.8 | 40.5 | 7.0 | 69.0 | 49.3 | 81.4 | 28.1 | 56.2 | 1.14 | -2.6 |
| 5 | 1.2[illegible] | 100 | 4.0 | 2.40 | 4.0 | 353.8 | 2.56 | 586.4 | ve.7 | .80 | 24.8 | 53 | 66.8 | . 89 | 11.9 | .164 | 21.7 | .147 | .00.4 | 15.9 | 2.3 | 74.6 | 40.3 | 70.6 | 17.6 | 52.7 | 1.06 | + 2.8 |
| 6 | 1.2[illegible] | 100 | 3.0 | 2.40 | 3.0 | 353. | 2.55 | 401.4 | 99.0 | 1.27 | 21.0 | 62 | 50.5 | .591 | 3.69 | .058 | 45.7 | .351 | 99.89 | 24.2 | 4.2 | 79.3 | 45.1 | 93.9 | 37.2 | 74.5 | 1.14 | - .47 |
| | | | | | | | | | 2.4 | 65 | 47.8 | .563 | 3.67 | .056 | 49.2 | .379 | 100.77 | - | | 85.7 | - | 93.9 | 40.3 | 80.5 | | - |
| 7 | 1.2[illegible] | 100 | 3.0 | 2.40 | 3.0 | 353 | 2.57 | 443.1 | 61.5 | .794 | 16.9 | 61.5 | 59.6 | .585 | 27.4 | .359 | 8.74 | .056 | 95.7 | 14.3 | 2.5 | 39.8 | - | 44.1 | 8.77 | 17.5 | | - |
| | | | | | | | | | 18.9 | 120.2 | 57.8 | .590 | 22.5 | .306 | 15.4 | .103 | 95.7 | | | 53.3 | - | 55.8 | 14.9 | 29.6 | | - |
| | | | | | | | | | 38.0 | 181. | 55.1 | .593 | 16.9 | .240 | 23.8 | .168 | 55 6 | | | 64.4 | 38.6 | 68.5 | 22.1 | 44.1 | 1.20 | + 1.3 |
| 8 | 1.2[illegible] | 50 | 3.0 | 2.40 | 3.0 | 353 | 2.55 | 432. | 76.9 | .97 | 15.5 | 37.0 | 60.6 | .595 | 26.5 | .347 | 9.08 | .058 | 96.11 | 16.6 | 2.9 | 38.1 | - | 46.9 | 8.95 | 17.9 | | - |
| | | | | | | | | | 13.0 | 67.5 | 57.5 | .588 | 28.5 | .384 | 19.04 | .128 | 97.7 | | | 59.1 | - | 60.4 | 17.6 | 35.7 | | - |
| | | | | | | | | | 24.9 | 127.5 | 53.6 | .586 | 12.1 | .177 | 32.8 | .236 | 98.5 | | | 72.9 | 41.1 | 78.5 | 28.6 | 57.3 | 1.13 | + 2.4 |
| 9 | 1.2[illegible] | 150 | 3.0 | 2.40 | 3.0 | 353 | 2.55 | 421.5 | 97.2 | 1.26 | 17.2 | 15.8 | 61.7 | .601 | 28.0 | .354 | 5.60 | .036 | 95.3 | 7.2 | 1.3 | 28.2 | - | 42.5 | 5.62 | 11.2 | | - |
| | | | | | | | | | 13.1 | 31.0 | 61.2 | .611 | 22.5 | .301 | 13.4 | .088 | 96.9 | | | 44.2 | - | 57.0 | 12.6 | 25.2 | | - |
| | | | | | | | | | 16.1 | 60.3 | 54.3 | .594 | 14.1 | .206 | 28.0 | .231 | 98.4 | | | 68.2 | - | 74.1 | 25.3 | 50.5 | | - |
| | | | | | | | | | 20.4 | 121.5 | 50.9 | .602 | 4.13 | .065 | 43.0 | .333 | 98.03 | | | 76.6 | 44.8 | 93.0 | 35.7 | 71.3 | 1.17 | - 3.9 |
| 10 | 1.2[illegible] | 150 | 3.0 | 2.40 | 3.0 | 353 | 2.55 | 431.3 | 51.2 | .664 | 23.6 | 61.5 | 57.6 | .675 | 22.4 | .297 | 19.6 | .124 | 98.6 | 16.5 | 3.2 | 63.0 | - | 57.7 | 18.2 | 36.4 | | + 3.3 |
| | | | | | | | | | 8.2 | 63.5 | 55.8 | .571 | 22.4 | .301 | 18.3 | .123 | 96.5 | | | 62.3 | 37.9 | 55.0 | 17.7 | 35.4 | 1.20 | - |
| 11 | 1.2[illegible] | 200 | 3.0 | 2.40 | 3.0 | 353 | 2.55 | 3[illegible] | 102.1 | 1.33 | 40.8 | 26.[illegible] | 59.2 | .676 | 31.0 | .287 | 1.0 | .107 | 96.2 | 42.3 | 3.8 | 50.[illegible] | - | 59.8 | 15.1 | 30.1 | | - |
| | | | | | | | | | 11.9 | 30.5 | 56.8 | .623 | 14.9 | .159 | 26.2 | .188 | 95.9 | | | 60.5 | - | 76.8 | 23.2 | 46.5 | | - |
| | | | | | | | | | 10.4 | 62.7 | 52.2 | .[illegible] 2 | 2.32 | .046 | 46.8 | .354 | 101.92 | | | 77.7 | - | 95.3 | 37.0 | 74.1 | | - |
| | | | | | | | | | 37.4 | 123.0 | 50.7 | .617 | 0.34 | .0055 | 47.4 | .378 | 98.44 | | | 76.4 | 43.9 | 99.5 | 38.0 | 76.9 | 1.15 | + 2.71 |
| 12 | 1.2[illegible] | [illegible] | 3. | 2.40 | 3.0 | 100 | 3.0 | 153 | 2.55 | 361.4 | 91.1 | 1.17 | 13.0 | 14 4 | 59.5 | .635 | 15.8 | .225 | 20.0 | 140 | 95.4 | 36.6 | 6.4 | 50.9 | - | 71.0 | 18.1 | 36.1 | | - |
| | | | | | | | | | 31.2 | 29 5 | 55.6 | .[illegible]34 | 3.46 | .052 | 42.1 | .314 | 101.4 | | | 70.1 | - | 94.5 | 33.1 | 66.2 | | - |
| | | | | | | | | | 35.4 | 61 5 | 53.5 | .[illegible]38 | 0.29 | .0049 | 45.5 | 358 | 99.6 | | | 72.2 | - | 99.5 | 35 9 | 71.9 | | - |
| | | | | | | | | | 21.3 | 97.5 | 52.6 | .623 | 0.42 | .0066 | 47.8 | .370 | 101.0 | | | 75.0 | 39.3 | 99.3 | 37.3 | 74.5 | 1.05 | + 1 3 |
| 13 | 1.2[illegible] | 150 | 3.0 | 2.40 | 3.0 | 100 | 3.0 | 224 | 2.55 | 334.0 | 90.6 | 1.16 | 21.6 | 61.6 | 52.5 | .598 | 6.65 | .101 | 40.3 | .301 | 99.45 | 18.3 | 2.8 | 75.4 | 43.6 | 88.8 | 33.5 | 67.0 | 1.17 | + 2.3 |
| 14 | 1.2[illegible] | 150 | Nitrogen Sparge | 2.40 | 3.0 | 100 | 3.0 | 153 | 2.55 | 458.6 | 12.5 | .173 | 21.9 | 61.5 | 57.3 | .6335 | 8.63 | 127 | 33.0 | .239 | 98.93 | 50.0 | 8.7 | 66.2 | 26.3 | 85.4 | 29.4 | 54.8 | 0.82 | + 4.2 |

NOTES: 1. Catalyst - wt. % Grace, Type 60, 0.12 mesh unless noted, oven dried 2 hrs @ 200°C.

2. Urea and ammonium nitrate - reagent grade.

3. Molecular weight of silica gel assumed to be 60.

Notes For Tables 2, 3, and 5:

(1) Run number and the nominal ammonium nitrate/urea/silica gel ratio. Where appropriate, a description of the catalyst is also included.

(2) Temperature in °C.

(3) Agitation rate.

(4),(5),(6) The ammonium nitrate, urea, and silica gel used in the initial charge reported in grams and gram-moles.

(7) The weight in grams of the reactor contents at the end of the experiment.

(8) The amount of ammonium carbamate recovered in all of the dry ice traps at the end of an experiment, reported in grams and gram-moles.

(9) The sample weight in grams and the time in minutes at which the samples were taken.

(10), (11), (12) The ammonium nitrate, urea, and guanidine nitrate in the samples reported as weight per cent and mole fraction.

(13) The analytical closure or the weight per cent in the melt given in columns 10, 11, and 12.

(14) The weight loss during the experiment reported in total grams and per cent of the total weight of starting material.

(15) Yield (%) expressed as moles of guanidine nitrate per mole of urea reacted. This number incorporates the ratio of stoichiometric coefficients; i.e., two moles of urea yield one mole of guanidine nitrate in order that the yields may be compared with those given by Roberts and by MacKay.

(16) Yield (%) expressed as moles of ammonium carbamate per mole of urea reacted.

(17) Conversion of urea expressed as moles of urea reacted per mole of urea fed (%).

(18) Conversion of ammonium nitrate expressed as ammonium nitrate reacted per mole of ammonium nitrate fed (%).

(19) Yield$_2$ expressed as moles of guanidine nitrate per mole of urea fed. Equal to the product of the figures in columns 15 and 17.

(20) The molar ratio of ammonium carbamate to guanidine nitrate produced in the experiment.

(21) The final product check in percent. To conver the weight percent reported for the analytical ana ysis of the samples into useful information, the weight of the reactor contents at the different sampling times is required. This is available only at the final sampling time, i.e., at the completion of the experiment. The weight of the reactor contents at the other sampling times (for the kinetic experiments) must be estimated. The final product check is the discrepancy between the estimated weight evaluated at the final reaction time and the actual weight of the reactor contents measured at that time. It therefore provides a check on the assumptions used in estimating the reactor weights.

No results for off gas analyses are reported for each run in Tables 2, 3, and 5 since all of the $NH_3$ and $CO_2$ were condensed as ammonium carbamate (AC) in a series of dry ice traps. Although a positive analysis for the AC condensed in the traps was difficult, the ultraviolet spectrum of the AC in the traps was identical to the published spectra for AC. The amount of AC formed in each run is reported as the ratio of the moles of AC to urea reacted. Deviations from the theoretical ratio of 0.5 cannot be explained at this time. Gas samples were taken after the dry ice traps in runs 2, 3, 4, and 5. Mass spectroscopy showed that all of the samples were 99 mole % air. This air was in the system initially or entered during sampling.

Runs 4, 10, and 13 indicate the effect of catalyst dosage on yield and conversion. For the same ammonium nitrate/urea ratio, the yield of guanidine nitrate with respect to urea reacted increased from 63.3% to 69.0% to 75.4% as the catalyst charge was increased (AN/U/SG) from 2/2/1.0 to 2/2/1.7 to 2/2/2.5, respectively. The conversion of urea also increased respectively from 55.6% to 81.4% to 88.8%.

Figures 2 and 3 are plots of yield and conversion, respectively, vs reaction time at five isothermal temperature conditions (Runs 7, 8, 9, 10, and 12). The AN/U/catalyst (Grace 40) ratio was 2/2/1.7 for these tests. The curves obtained were smooth and consistent. From these plots it could definitely be concluded that the literature claims as to the reaction step of the BMR process were well founded. Although the catalyst mesh size and charge were slightly different than those used by Roberts and MacKay, the yields and rates obtained here were comparable for batch operations.

Figure 4 is also a plot of data obtained from Runs 7, 8, 9, 11, and 12. In the figure, the U/AN ratio in the product at various times is plotted for five isothermal temperature conditions.

The total weight of insolubles produced in an experimental run was generally less than 1%. The final product checks listed in Column 21 in Table 2 were good and, in general, less than 4% in magnitude. The percentage was both positive and negative when the discrepancy was calculated as (actual weight - estimated weight) actual weight.

c. Alternate Catalyst Screening

Because of the decrepitating characteristics of Grace grade 40 silica gel catalyst and the requirement for an alternate catalyst, a series of experimental batch runs were conducted employing ten different commercially available catalysts. Operational and analytical procedures were similar to those employed for Runs 1 through 14, and equimolar ratios of urea and AN were used. The catalyst dosages were comparable to those used for the above runs, with the exception of Runs 27, 28, and 29 when reduced catalyst levels were used to determine if lower catalyst levels would provide sufficiently high yields and conversions. No such advantage was found. The kinetic data from all these test runs (Runs 15 through 29) are presented in Table 3.

Of the alternate catalysts investigated, only three types were equivalent to and/or better than Grace Grade 40 silica gel. These were:

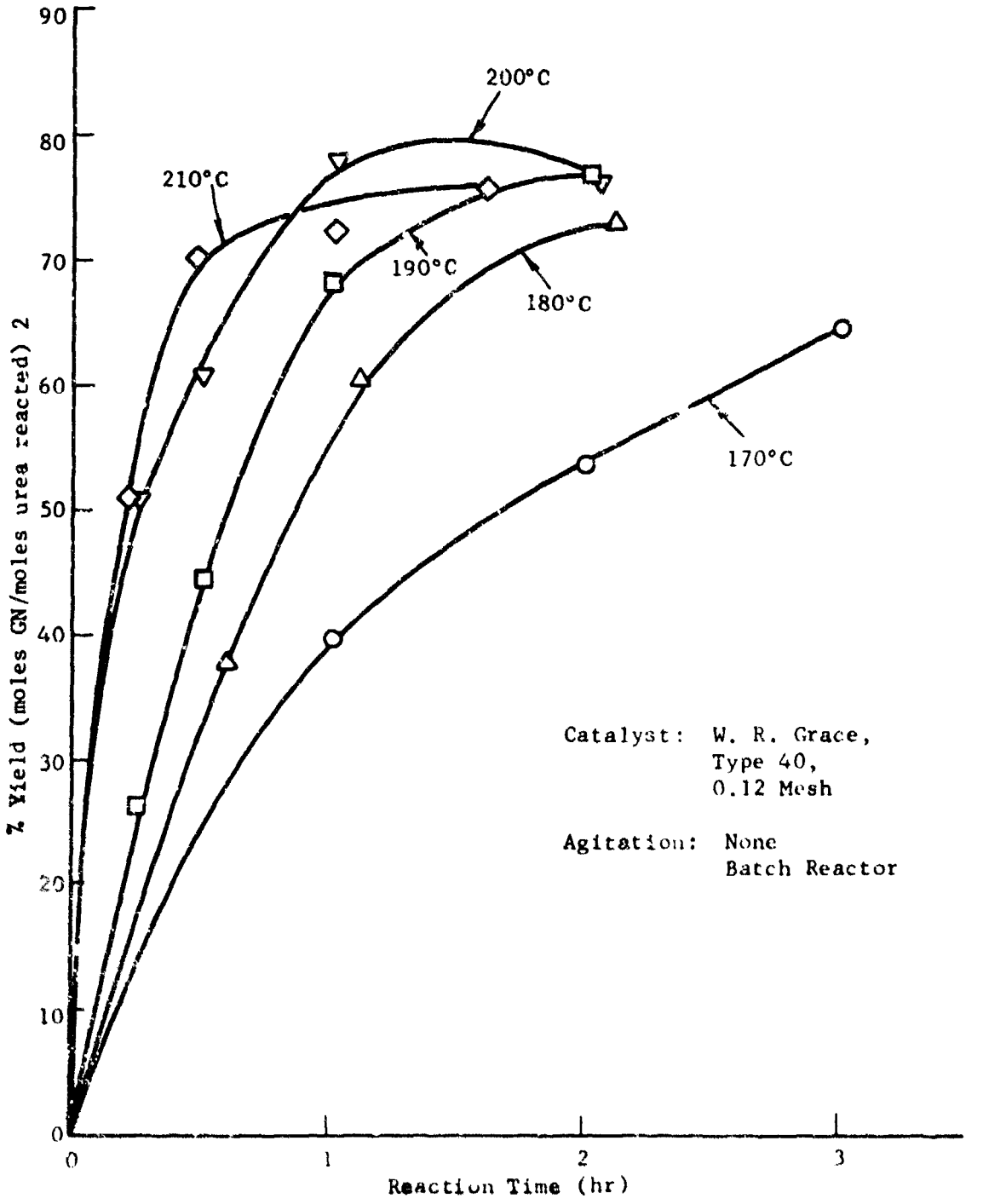



Figure 2. Yield vs. Reaction Time 2/2/1.7 (AN/U/SG)

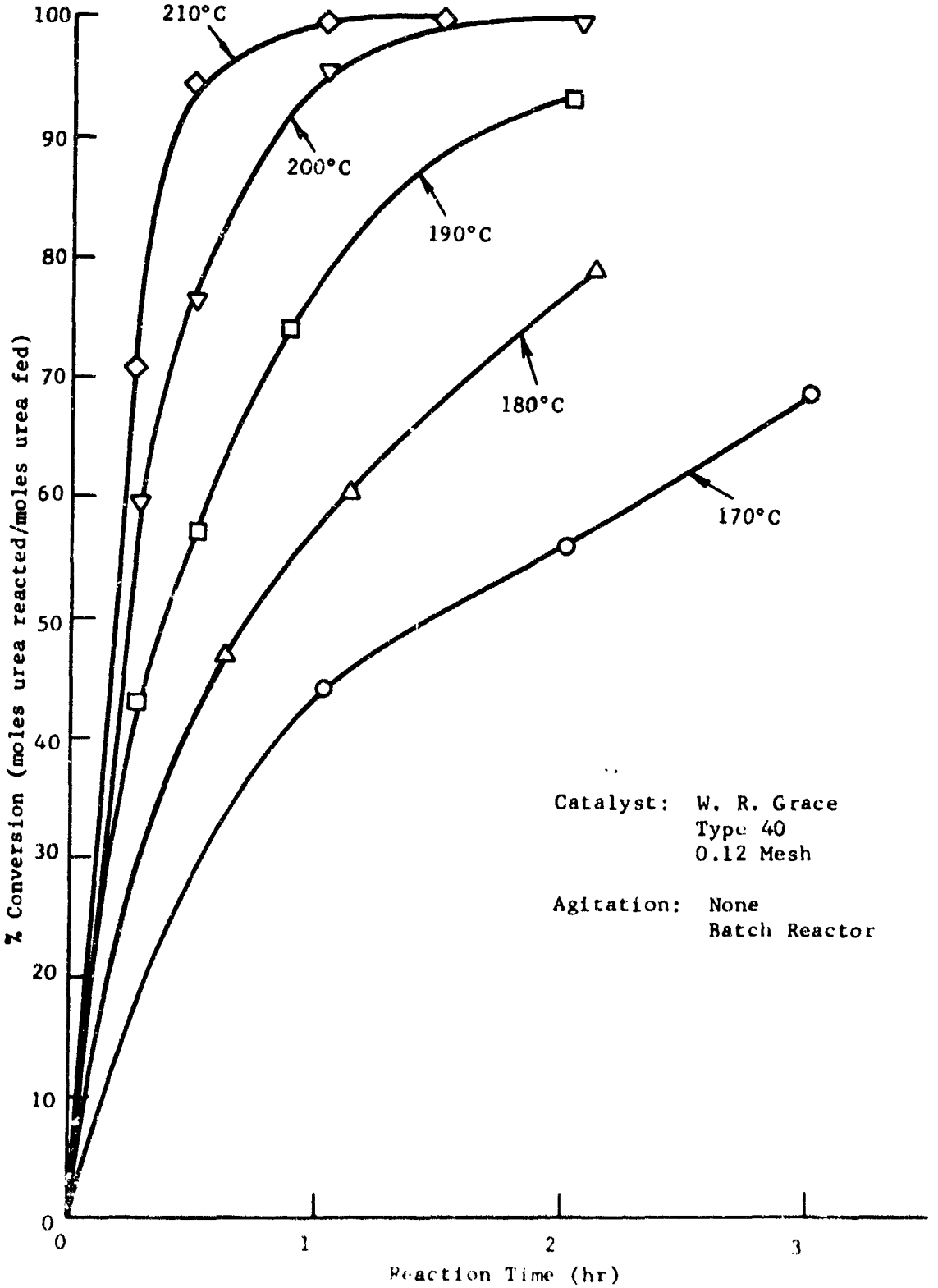



Figure 3. Conversion vs Reaction Time 2/2/1.7 (AN/U/SG)

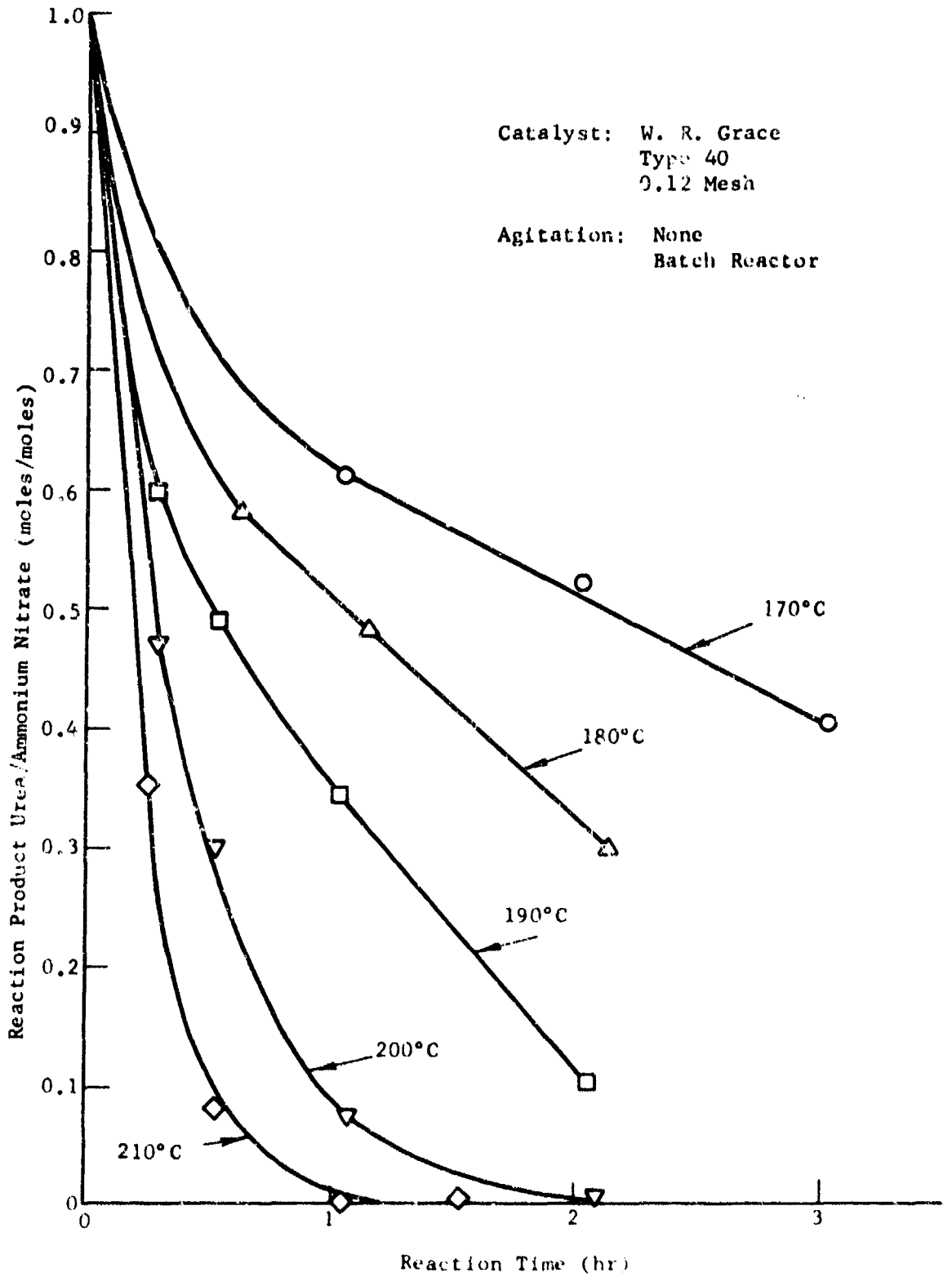
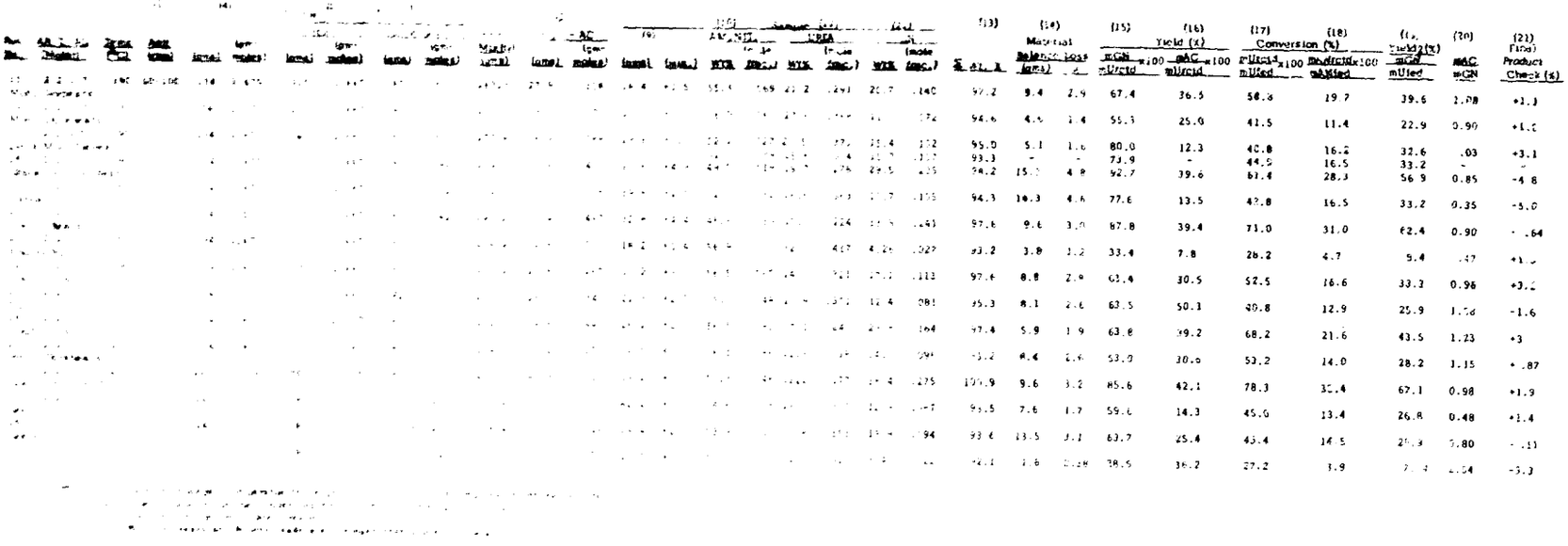



Figure 4. Urea/Ammonium Nitrate vs Reaction Time 2/2/1.7 (AN/U/SG)

## TABLE 3

## GUANIDINE NITRATE REACTION STUDIES - CATALYST SURVEY



Other explanatory notes are given on pages 35 and 36.

(1) Grace grade 59 Silica Gel - Davison Chemicals Division of W. R. Grace, Inc.

(2) Mobil Sorbeads R - Mobil Oil Corp.

(3) Houdry Macroporous Silica Beads CP-532 - Houdry Division of Air Products Co.

Conversion and yield data for the above three catalysts are summarized in Table 4 for comparison with Grace grade 40 silica gel data. Both Grace 59 SG and Houdry CP-532 silica beads produced higher GN yields (based on urea reacted) than Grace 40 SG. The conversion with Houdry was comparable to that with Grace 40 while the conversion from the Grace 59 silica gel was somewhat less than that from Grace 40.

Because of its physical strength and improved performance, the Houdry bead catalyst was investigated further (see next section).

TABLE 4

COMPARISON OF CANDIDATE CATALYSTS

| Run No. | Type Catalyst | Reaction Time (min.) | % Yield (mole GN/ mole urea reacted) | % Conversion (mole urea reacted/ mole urea fed) |
|---|---|---|---|---|
| 9* | Grace 40 SG | 60 | 68 | 74 |
| 15 | Mobil Sorbeads | 62 | 67 | 59 |
| 18 | Grace 59 SG | 65 | 93 | 61 |
| 20 | Houdry CP-532 Beads | 64 | 88 | 71 |

*No agitation; other experiments employed 60-100 rpm agitation.

Note: The following conditions were held constant:

1. Reaction Temperature = 190°C
2. Molar ratio AN/U/SG = 2/2/1.7

d. Houdry Macroporous Silica Bead Experiments

A series of kinetic runs using Houdry beads (CP-532) was made in the laboratory batch reactor. The data are presented in Table 5. Typical specifications for Houdry beads are presented in Table 6. The method of operation and definition of column headings are the same as described previously.

Four isothermal batch experiments were conducted at 170°C, 180°C, 190°C, and 200°C with the AN/U/silica gel (Houdry Beads) ratio maintained constant at 2/2/1.7. In addition, two runs were made at different AN/U ratios (Run 33, 1.4/2.8/1.7; Run 36, 2.8/1.4/1.7) and one run at one-half the catalyst charge (Run 35,2/2/0.85). The temperature selected for these experiments was 190°C.

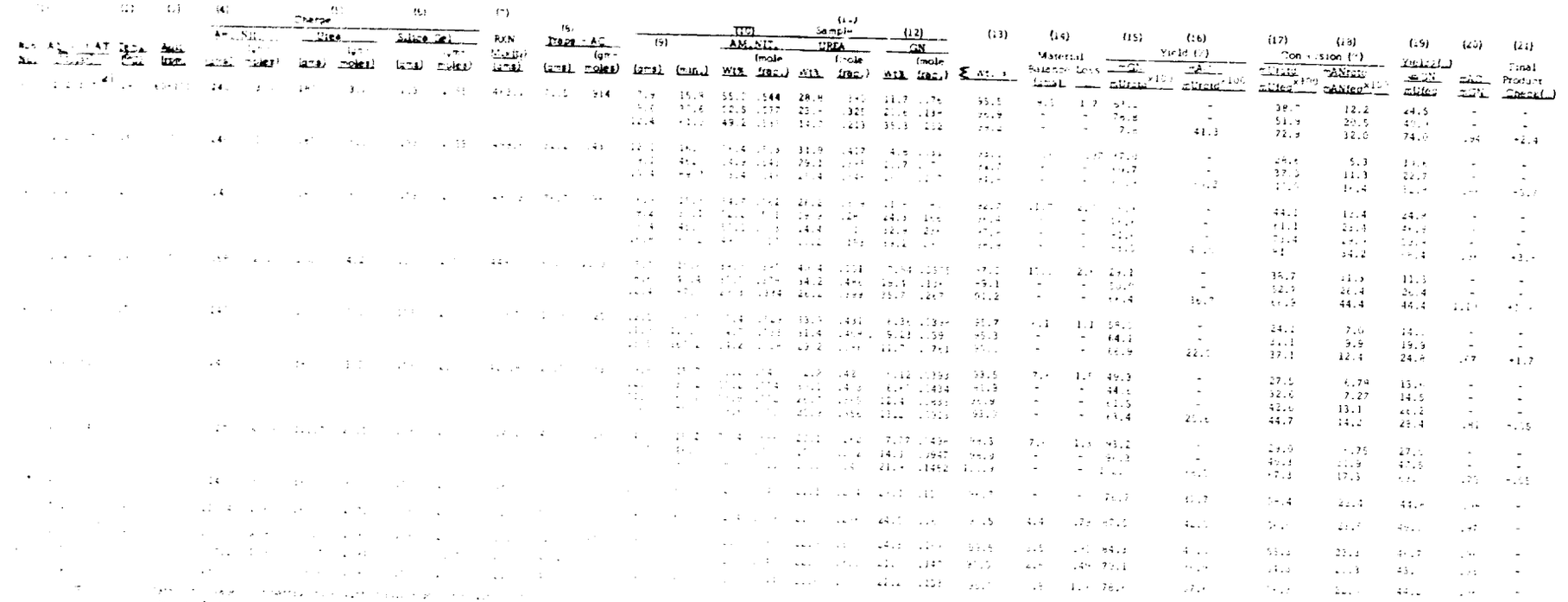
Figures 5 and 6 are plots of the yield as a function of reaction time for these experiments. Yield is again defined as moles of guanidine nitrate/2 moles of urea reacted. Diagrams of conversion (moles of urea reacted/mole of urea fed) as a function of reaction time are included in Figures 7 and 8. The data from these experiments serve as the basis for the mathematical model of the reaction kinetics which will be discussed later. Although these curves do not show maximum values, the reaction times are considered adequate for scale-up purposes and economical operations.

The yields and conversions at one-hour reaction time for the isothermal experiments are replotted in Figure 9 as functions of temperature. The one-hour yields increase from about 58% at 170°C to about 85% at 200°C, and the conversions also increase from 24% to 80% over this same temperature range. Except for the data from Runs 20 and 30, the yield and conversion appear to vary uniformly with increasing temperature between 170°C and 200°C. Run 20 is taken from the catalyst survey presented in Table 3. In conducting the Houdry bead experiments, three different catalyst batches were used. The catalyst for Runs 20 and 30 was taken from the same batch, and the catalyst for all other runs was taken from the remaining two batches. Differences in catalyst activity between batches may account for the apparent deviation exhibited by Runs 20 and 30 from the proposed straight line relationship. Data from Runs 20 and 30 were not considered in drawing the correlation line because their omission resulted in a more conservative interpretation of the catalyst performance.

The relationship between yield and the AN/U feed ratio is summarized in Figure 10. The yield increased from 58% to 98% as the AN/U ratio was increased from 0.5 to 2. All runs were conducted at 190°C with the same amount of catalyst, and the yields plotted are at one-hour reaction time.

# TABLE 5

## GUANIDINE NITRATE REACTION STUDIES - HOUDRY BEADS



For explanatory notes, see pages 35 and 36.

TABLE 6

CHARACTERIZATION OF HOUDRY MACROPOROUS SILICA BEADS

HOUDRY CATALYSTS



**MACROPOROUS SILICA BEADS (Experimental)**
(Catalyst support No. 532 CP)

*DESCRIPTION*

These beads are characterized by good physical strength, high purity, high absorptivity and surface area. The beads will not shatter when immersed in water and therefore can be easily impregnated with metal salts. Typical properties are tabulated below:

*TYPICAL PROPERTIES*

Chemical Analysis

| | | |
|---|---|---|
| $SiO_2$ | >99 | Weight percent (ignited basis) |
| $Al_2O_3$ | <0.1 | Weight percent (ignited basis) |
| $Fe_2O_3$ | <0.1 | Weight percent (ignited basis) |
| $Na_2O$ | <0.1 | Weight percent (ignited basis) |
| $NO_3$ | <0.01 | Weight percent (ignited basis) |
| Cl | <0.1 | Weight percent (ignited basis) |

Physical Properties

| | |
|---|---|
| Surface Area | 350 $m^2/g$ (Typical value – areas in excess of 700 $m^2/g$ available by special processing.) |
| Packed Bulk Density | 0.4 to 0.5 kg/l (Typical range after an air calcination at 1050°F. Values of 0.35 to 0.75 kg/l under same calcination conditions available by special processing.) |
| Particle Size | 4.0 mm avg. diameter (particles as small as 1 mm available by special processing.) |
| Particle Shape | Oblate Spheroids |
| Hardness | Min. 8 lbs. (Single particle plate to plate crushing strength. Value depends on both particle diameter and processing procedures.) |
| Porosity | 60 to 75 vol. % depends on processing procedure |
| Water Absorption | 60 to 125 wt. % depends on processing procedure |
| Particle Density | 0.68 to 0.90 g/cc. depends on processing procedure |
| True Density | 2.14 to 2.25 g/cc. depends on processing procedure. |

*AVAILABILITY*

Pilot plant quantities of macroporous silica beads are available for development work.

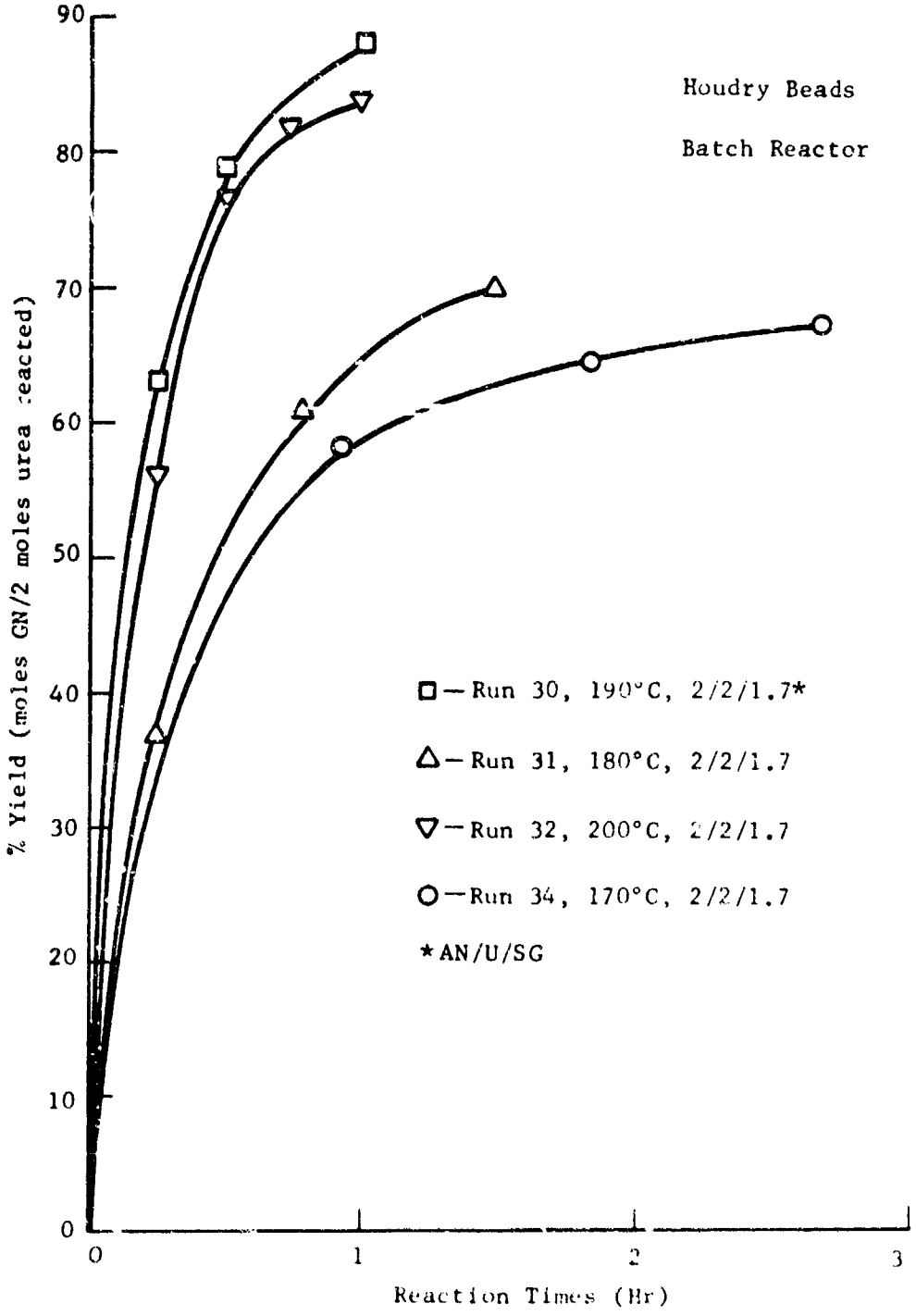



Figure 5. GN Yield vs. Reaction Time

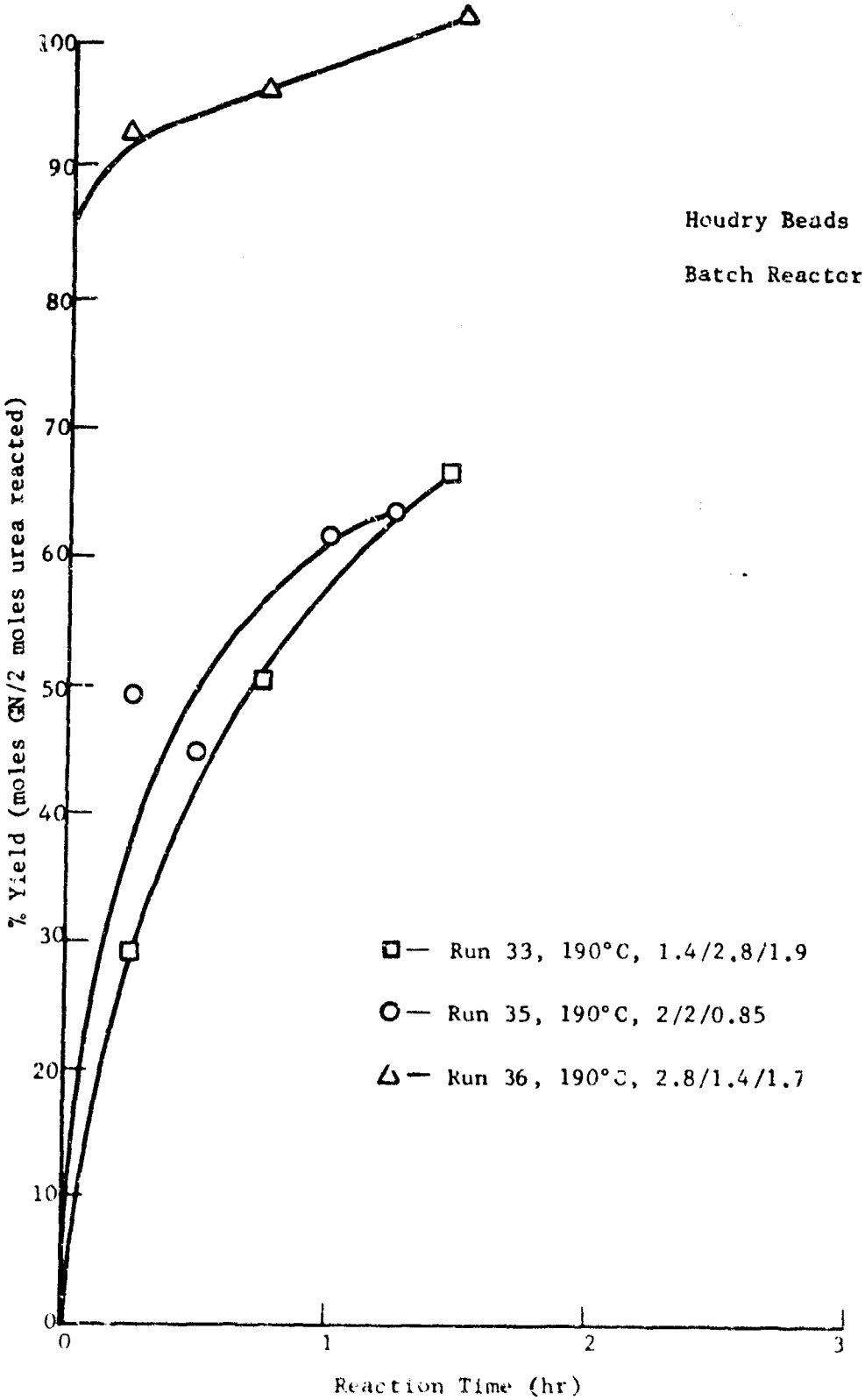



Figure 6. GN Yield vs. Reaction Time

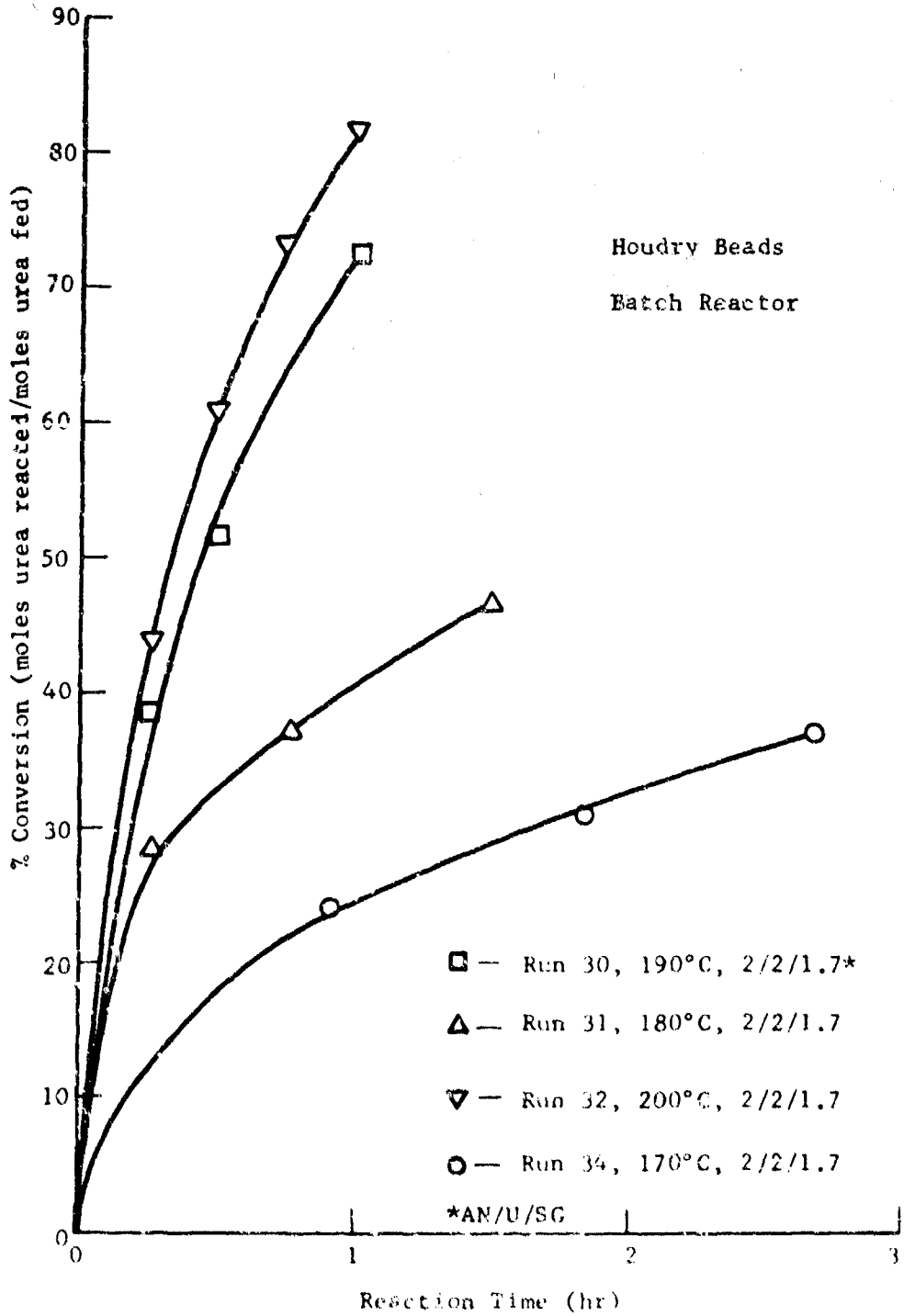



Figure 7. Urea Conversion vs Reaction Time

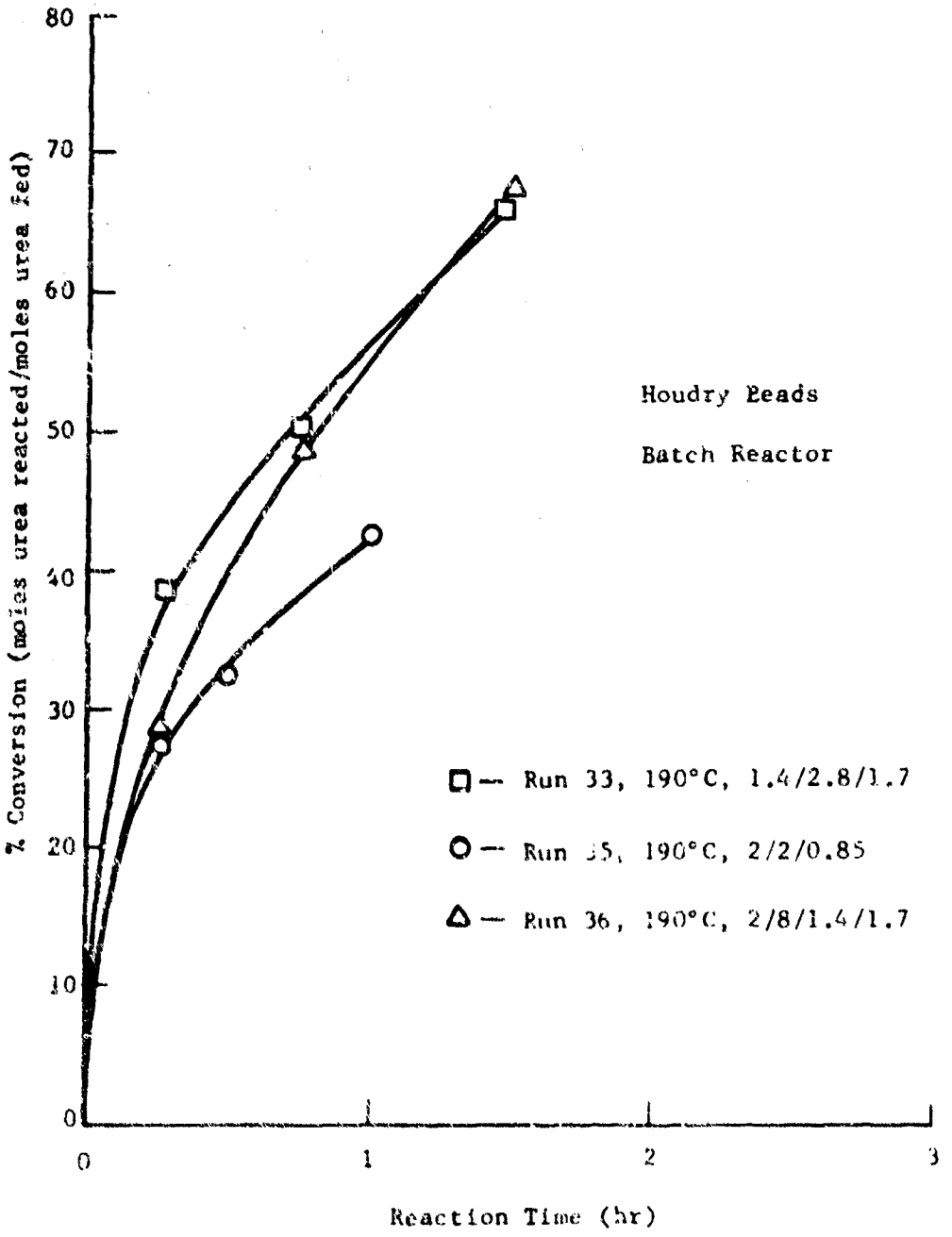



Figure 8. Urea Conversion vs Reaction Time

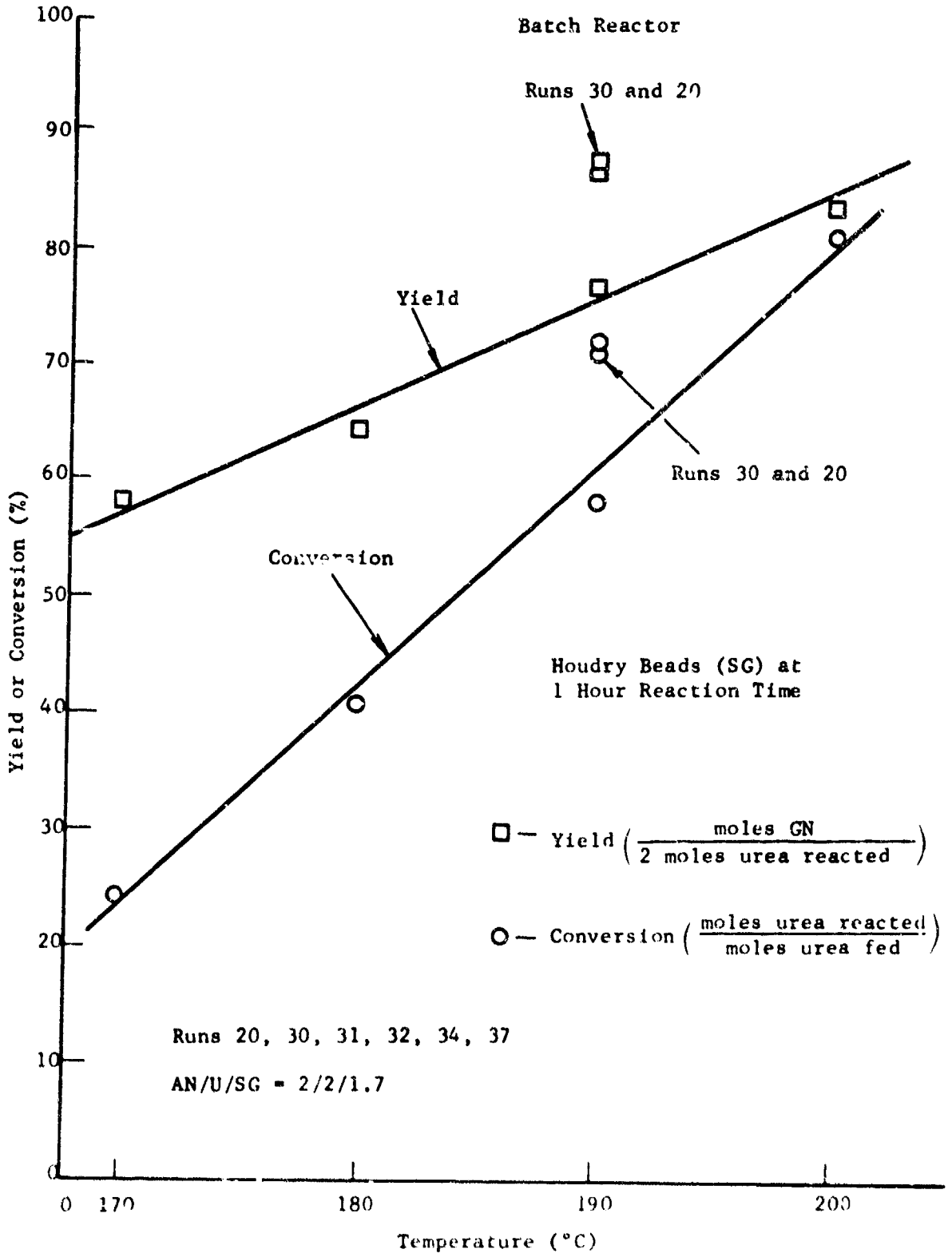



Figure 9. GN Yield and Urea Conversion vs Temperature

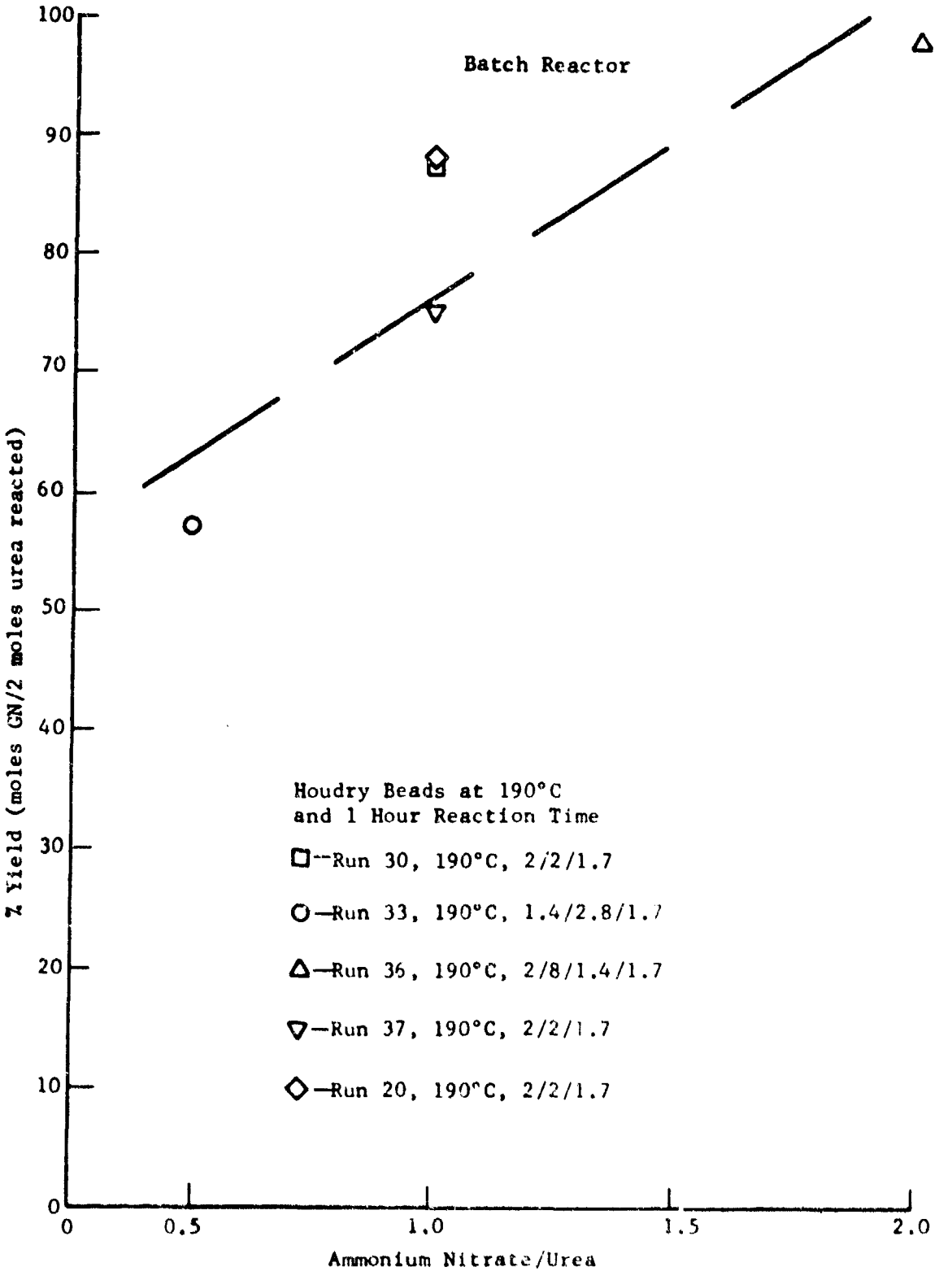



Figure 10. GN Yield vs Ammonium Nitrate/Urea Ratio

The conversions for the same experiments are plotted as a function of the AN/U ratio in Figure 11. The conversion of urea is not as strong a function of the AN/U ratio as is the yield over this range.

e. Supplementary Studies

1 Noncondensable Products

To identify more precisely the noncondensable products of a typical reaction, an experiment was conducted in which air was excluded from the apparatus. In this experiment, the apparatus consisted of a one-liter (working volume), stirred glass reactor equipped with a thermocouple and a manometer. The off-gases passed from the reactor through two dry ice traps in series and then to a large empty plastic bag where noncondensables were collected. The plastic bag was contained in a 22-liter vessel filled with water; and as gas entered, the water was displaced. Samples of the noncondensable gases were taken with evacuated gas bulbs just after the second trap. It was expected that gases coming from the second trap would contain little $NH_3$ and $CO_2$, since past experience had shown that the dry ice traps collected these gases quantitatively as solid ammonium carbamate.

Air was excluded from the system by displacing it with argon after charging the urea and AN. When the operating temperature was reached, the catalyst was charged through an air lock device. Since no samples were taken during the run, and the system remained closed, any air in the system was limited to that which could leak through the agitator seal, the catalyst air lock device, and the various tubing connections.

For the first 15 minutes after the beads had been charged to the 190°C reactants, about 850 ml of gas entered the collector. This was argon being displaced from the reactor and the first trap. Noncondensable gases then ceased to flow into the collector for the remainder of the one-hour experiment. In fact, the pressure in the reactor was below atmospheric (2 to 4 inches of water) much of the time. The partial vacuums apparently resulted from the condensation of most of the off-gas as solid carbamate. To increase the system pressure above atmospheric for purposes of taking a sample without drawing gas from the traps and reactor, the line from the second trap to the gas collector was closed for the last 37 minutes of the run. It was never possible to obtain pressures of more than an inch or two of water in the reactor. These pressures were quickly reduced to partial vacuums after sampling. Before the run, the system had been pressure tested at 10 inches of water.

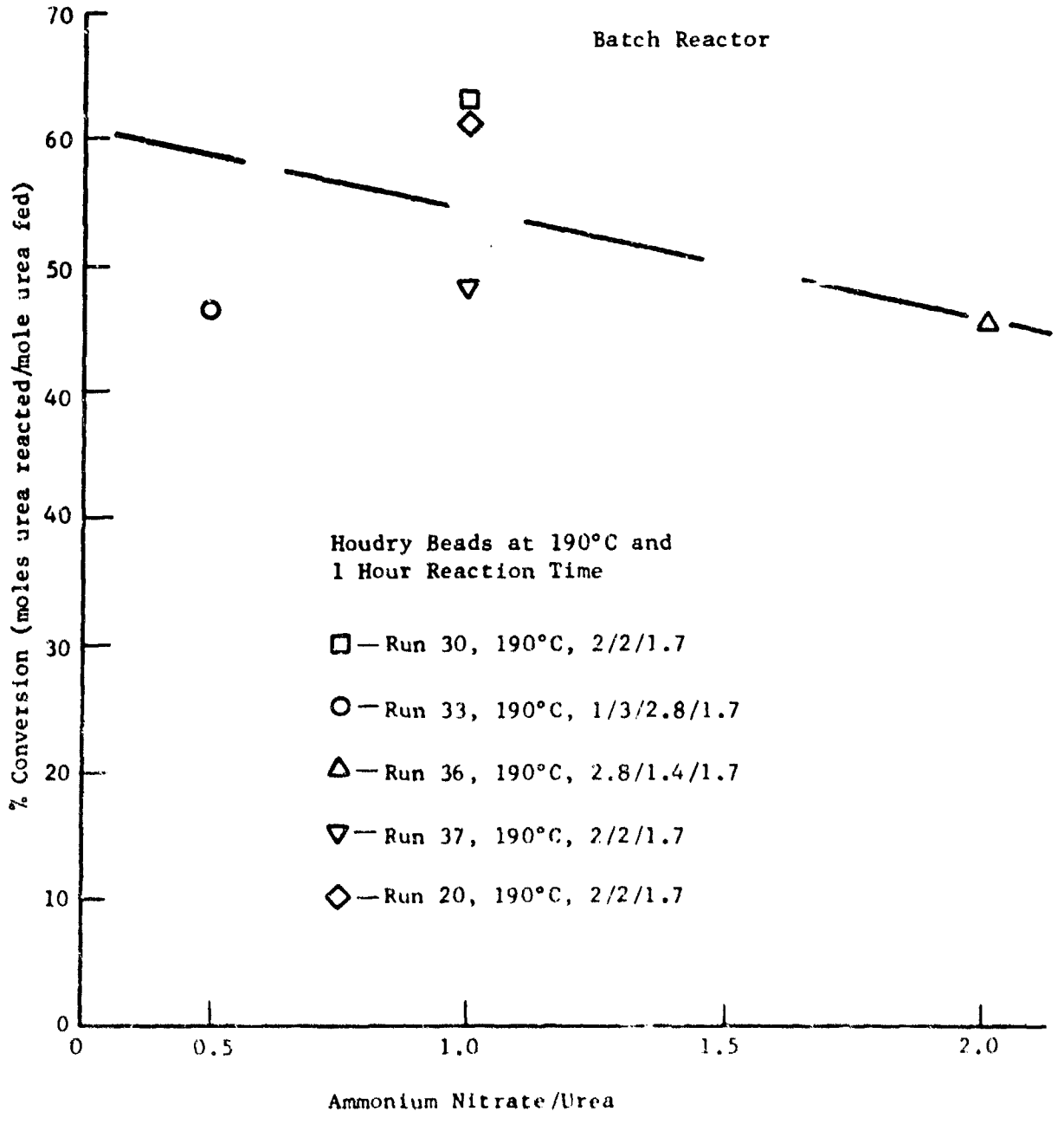



Figure 11. Urea Conversion vs Ammonium Nitrate/Urea Ratio

The fact that a closed system was operated without build-up in pressure was conclusive evidence that negligible amounts of non-condensable gases were generated. This conclusion is supported by the analyses of the four gas samples which are presented in Table 7.

## 2 Commercial Ammonium Nitrate and Urea vs Reagent Grades

The objective of these experiments was to determine whether commercial grades of urea and AN would yield satisfactory results (similar to those from runs using reagent-grade U and AN). Four complete runs were made, including aqueous workup of the reaction product. The results are given in Table 8.

The experimental procedures were a combination of those used previously. Crystalline urea and AN were first mixed and then melted. The melt was vacuum filtered using a medium glass frit (10 μ m) filter to remove insolubles* from the melted AN prills. It was thought that these insolubles might otherwise collect in the catalyst bed. The filtered melt was charged to a preheated reactor, and a one-hour run was made at 190°C. At the end of the run, the product melt was decanted, sampled and poured into cold water. The final temperature of the quench solution was usually 70-90°C. This solution was heated for about 10 minutes to dissolve any GN that might have precipitated during the water quench. The hot solution contained very fine white particles which gave the solution the appearance of thin skim milk. These water insolubles were removed by vacuum filtration from the hot solution using a medium frit filter. The clear filtered solution was then put in the controlled temperature bath and cooled at ca. 1°C/min. In Runs 38 and 39, the GN slurry was cooled to 20°C. In Runs 40 and 41, it was cooled to 11°C and 16°C, respectively, in an attempt to improve the yield and to determine that temperature at which significant amounts of urea and AN first precipitated. The GN crystals were then vacuum filtered and washed with fresh water (the water weight usually equal to the weight of cake). This amount of wash covered the cake. The cake and wash were stirred slightly to remove the holes in the cake formed when the wash was added. The washed GN was then dried in an oven at 110°C to a constant weight. Purification is discussed in greater detail in a subsequent section of this report.

Several grades of urea and AN were available commercially. These materials are summarized in Table 9 and Table 10. Since the industrial feed and agricultural grades of urea were all about the same

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*Clay, talc, Petro Ag., etc.

TABLE 7

ANALYSES OF MASS SPECTRA OF OFF-GASES
FROM BATCH REACTOR RUN 37

| Sample Number | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Sample Time, Min. | 19 | 34 | 52 | 59 |
| Gas Analysis (Mole %) | | | | |
| Argon | 98.12±1.0 | 98.2±1.0 | 96.7±1.0 | 96.6±1.0 |
| $CO_2$ | - | - | - | 0.05 |
| $O_2$ | 0.10±0.05 | 0.18±0.05 | 0.50±0.05 | 0.52±0.05 |
| $N_2$ + CO | 1.3±0.1 | 1.4±0.1 | 2.5±0.1 | 2.6±0.1 |
| $H_2O$ | 0.1 | 0.1 | 0.1 | 0.1 |
| $H_2$ | 0.27±0.05 | 0.22±0.05 | 0.20±0.05 | 0.22±0.05 |

NOTE: Reaction flask and traps purged initially with argon.

TABLE 8

RESULTS OF REACTION RUNS MADE WITH COMMERCIAL GRADES OF UREA AND AMMONIUM NITRATE AT 190°C

| Run Number | 37 | 38 | 39 | 40 | 41 |
|---|---|---|---|---|---|
| Urea Charged | Reagent grade | Grace prills | Kaiser flake | Grace prills | Kaiser flake |
| AN Charged | Reagent grade | Hercules LD prills | Hercules LD prills | duPont prills | duPont prills |
| Reaction Time (min.) | 71 | 65 | 66 | 66 | 66 |
| Urea Conversion (%) | 58.4 | 56.0 | 55.3 | 54.3 | 56.3 |
| GN Yield based on Urea Reacted (mole %) | 76.7 | 87.5 | 84.3 | 79.1 | 78.6 |
| Wt. % Insolubles in Product | 2.9 | 1.4 | 1.5 | 1.1 | 1.3 |

NOTE: All runs were prepared in a glass batch reactor at 190°C and using a 2/2/1.7, AN/U/Catalyst ratio. The catalyst was Houdry Macroporous silica beads.

# TABLE 9

## AVERAGE ANALYSES OF AMMONIUM NITRATE AND UREA

| | Ammonium Nitrate | | | | | Urea | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Hercules Prills (low density) | | Commercial Grade Prills | | Commercial Grade Grained | Industrial Grade Prills* | Solid | | | |
| | Maximum | Minimum | Low Density | High Density | | | Industrial | Feed** | Agricultural | Crystal |
| Ammonium Nitrate (wt. %) | - | 98.2 | 97-98 | 97 | ~ 99 | - | - | - | - | - |
| Moisture (wt. %) | ~ 25 | - | 0.2 | 0.2 | NA | 0.23 | 0.3-0.6 | 0.3-0.6 | ~ 0.5 | ~ 0.1 |
| Additives (wt. %) | | | | | | | | | | |
| (a) Organic (Free AC Material & Diatomaceous) | 0.2 | 0.04 | 0.03-0.1 | 0.03-0.3 | None | - | - | - | - | - |
| (b) Inorganic (Calcium Silicate) | 1.0 | 0.4 | 0.5-1.0 | 1.0-2.0 | None | - | - | - | - | - |
| Total Nitrogen (wt. %) | - | - | - | - | - | 46.5 | > 46 | > 46 | 45 | > 46 |
| Ammonia (wt. %) | - | | - | - | - | 15 | - | - | - | - |
| Free Ammonia (wt. %) | - | - | - | - | - | 80 | - | - | - | - |
| Biuret (wt. %) | - | - | - | - | - | 1.2 | ~ 1 | ~ 1 | ~ 1 | 0.1-0.25 |
| Insolubles (wt. %) | - | - | - | - | - | - | None | None | 1% Clay | None |

Ref. 5, Chap.

**Same as industrial grade but with narrow particle distribution.

price, viz., $65/ton, there would be no significant cost incentive in using an agricultural grade. Two kinds of industrial grade urea were used: prills made by W. R. Grace and flake made by Kaiser. The principal commercial form of AN is prills. Low-density AN prills from the Hercules' Donora plant and duPont's Seneca plant were tested. Typical detailed specifications for the urea and AN used in the reaction runs are given in Table 10. The Kaiser urea contained the standard 46% nitrogen and the duPont AN prills are > 97% AN.

Table 8 shows the results for the four commercial runs in comparison with Run 37. In general, the results were comparable in every way to those of runs made with reagent feed. Nominal water contents of ~ 0.5% (max.) for urea and ammonium nitrate did not appear to affect the GN reaction.

The problems encountered later with catalyst poisoning by the additives (phosphates) in prills were not observed in these laboratory experiments. This is due to (a) the absence of the habit modifiers in prills at that time and (b) the inherent low-exposure (AN/catalyst ratio) in a batch reaction. It would take many recycle passes in a batch reaction to show the effect of cumulative high mileage catalyst effects. See Section II-D.

### 3 Insolubles in Reaction Product

In previous work on the BMR process, it was common to report insolubles as a weight per cent of the reaction product. It was also stated that the insolubles were by-products, either ammelide or ammeline. The Pittsburgh Coke study isolated water-insoluble materials. In Roberts' work, it was not clear whether he was reporting melt insolubles, water insolubles, or both. It should be emphasized that "insoluble" is a relative term. For example, the amount of water used in workup will affect the fraction of insolubles obtained. Furthermore, in the BMR process, insolubles can have two basic constituents: by-product compounds and catalyst fines. Previous workers on the BMR process implied that their insolubles were all by-product compounds.

In this work, materials insoluble in the reaction melt and in water were isolated. To obtain information on melt insolubles, the reaction melt was filtered. It was found that the melt insolubles in two runs were 25% and 75% ash, presumably catalyst fines. Melt insolubles (26% ash) from Run 33 were analyzed for elemental carbon, hydrogen, nitrogen. Oxygen was obtained by difference. The elemental analysis results on an ash-free basis, presented in Table 11, agree well with those for ammelide. These results are interpreted to mean that the insolubles reaction product is, in fact, ammelide, confirming the findings of Roberts.

TABLE 10

ANALYSIS OF UREA AND AMMONIUM
NITRATE FOR RUNS 1 THROUGH 27

SUPPLIER: Mallinckrodt Chemical Works

GRADE: Analytical Reagent

| | Urea | Ammonium Nitrate |
|---|---|---|
| Chloride ($Cl^-$) | 0.0005% | 0.0005% |
| Heavy Metals (as Pb) | 0.001 | 0.0005 |
| Insoluble Matter | 0.010 | 0.005 |
| Iron (Fe) | 0.001 | 0.0002 |
| Nitrite ($NO_2$) | - | ca. 0.0005 |
| Phosphate ($PO_4$) | - | 0.0005 |
| Residue after ignition | 0.01 | 0.01 |
| Sulfate ($SO_4$) | 0.001 | - |

TABLE 11

ELEMENTAL ANALYSES OF MELT INSOLUBLES FROM RUN 33

| Element | Measured Value (wt. %) | Theoretical for Ammelide (wt. %) |
|---|---|---|
| C | 25.80 - 27.20 | 28.1 |
| H | 3.23 - 3.61 | 3.1 |
| N | 43.65 - 43.53 | 43.7 |
| O | 27.32 - 25.66 | 25.0 |

Data on the amounts of water-insoluble materials were obtained for most of the kinetic runs made with Houdry silica beads and for all four of the runs made with commercial feeds, by working up the melt in water and then filtering.

Table 12 summarizes all of the results obtained for the insolubles content from various reaction runs. Values for the percent melt insolubles were based on the combustible portion of the insolubles isolated and on the quantity of melt filtered. In the runs where melt insolubles were isolated (Runs 33 to 37), the insoluble fraction was very small except in Run 33 where the stoichiometric amount of urea was used. In all of the other runs shown in Table 12, the reaction product was worked up directly in water so that the percent total water insolubles were also the total insoluble fraction.

Two important assumptions were made in reporting the water insolubles. First, it was assumed that the insoluble content of reaction product in the beads was the same as that decanted off and worked up in water. This assumption was tested in Run 33 where the percent total insolubles of product in the beads was 3.2% compared with 4.6% in the decanted product. Secondly, it was assumed that the water insolubles contained no catalyst fines. In Run 37, for example, the water insolubles were 3.5 wt. % ash. Both of the assumptions should cause the reported values for water and total insolubles to be on the conservative side. Experimentally, the weights of the insoluble fractions were 2 grams or less out of 100 grams or more. Based on the results from Runs 35 to 41, made with at least equimolar urea and AN feeds at 190°C, it can be reliably concluded that the insolubles level in the reaction product at these conditions will be about 1-2 wt. %.

TABLE 12

INSOLUBLES CONTENT OF REACTION PRODUCTS
FROM HOUDRY SILICA BEAD RUNS

| Run No. | Reaction Temperature °C | Feed Mole Ratio AN/U/Houdry Beads | Wt. % Melt-Insolubles | Wt. % Water-Insolubles | Wt. % Total Insolubles |
|---|---|---|---|---|---|
| 20 | 190 | 2/2/1.7 | - | 6.9 | 6.9 |
| 32 | 200 | 2/2/1.7 | - | 2.2 | 2.2 |
| 33 | 190 | 1/2/1.2 | 1.4 | 3.3 | 4.6 |
| 34 | 170 | 2/2/1.7 | 0.05 | nil | 0.05 |
| 35 | 190 | 2/2/0.85 | 0.03 | 1.02 | 1.1 |
| 36 | 190 | 2/1/1.25 | 0.20 | 1.04 | 1.2 |
| 37 | 190 | 2/2/1.7 | 0.20 | 2.17 | 2.4 |
| 38 | 190 | 2/2/1.7 | - | 1.2 | 1.2 |
| 39 | 190 | 2/2/1.7 | - | 1.4 | 1.4 |
| 40 | 190 | 2/2/1.7 | - | 0.6 | 0.6 |
| 41 | 190 | 2/2/1.7 | - | 1.0 | 1.0 |

NOTE: Reactions performed in glass batch reactor.

## 4 Biuret In Reaction Product

Biuret is a known impurity in most grades of urea, and it can be formed during the reaction step. In the runs conducted, the reaction product was routinely analyzed for its major constituents, urea, ammonium nitrate and guanidine nitrate. The sum of the three major weight fractions was generally less than 1.0. It was believed that the primary reason for a closure of the U, AN, and GN of less than 1.0 was that biuret was present in the product.

To determine the amounts of biuret in typical reaction products, they were analyzed for biuret by the classical method. This method involved the formation of a six-membered ring with copper. The resulting complex is colored, and the intensity of the color is a measure of the biuret content. It was found that AN and GN interfered with the biuret analysis, but that this interference could essentially be removed by making the system basic. After heating, all of the AN was removed as $NH_3$. Tests showed that the GN interference no longer existed after being treated as described above.

Duplicate biuret analyses for nine runs are presented in Table 13 along with the analytical closures. The results obtained appeared to be consistent. In some cases, the sum of the biuret content and the closure exceeded 100% (e.g., Runs 30, 32, and 36). Since the U, AN, and GN analyses were quite reliable, this suggested that the biuret procedure may need some refinement.

The analyses shown did show some expected trends. For example, in Run 33, made with stoichiometric feed ratio, the biuret level was abnormally high - especially in the first sample. The level of biuret in the third sample was lower. This can be expected, since biuret has been shown to react with AN over $SiO_2$ catalysts to give GN. Run 36 also demonstrated the consistency of the data. This run was made with 2 moles of AN to one mole of urea. The low biuret content, expected because of excess of AN, was verified by the analyses.

## 5 Carbon Balance

Yields of GN based on the amount of urea reacted were usually in the range of 70 to 80% for the Roudry head experiments. This means that a portion of the urea reacted to form other species. It had been assumed that the urea which reacted to form other compounds could be accounted for in terms of the by-products produced, principally biuret and ammelide. To verify that all of the reacted urea could be accounted for, a carbon balance was made on Runs 31, 33, and 37.

TABLE 13

BIURET IN THE REACTION PRODUCT FROM
SEVERAL HOUDRY SILICA BEAD RUNS

| Run No. | Biuret (Wt. %) | AN, U, GN Closure (Wt. %) |
|---|---|---|
| 30 | 2.8, 1.5 | 99.2 |
| 31 | 2.6, 1.7 | 95.4 |
| 32 | 2.0, 2.0 | 98.9 |
| 33-1 | 6.4, 6.8 | 86.9 |
| 33-3 | 3.5, 4.2 | 91.2 |
| 35 | 4.7, 4.9 | 93 |
| 36 | 0.7, 0.9 | 100.9 |
| 37 | 1.6, 1.8 | 97.6 |
| 40 | 3.1, 3.6 | 95.9 |
| 41 | 2.7, 3.2 | 95.5 |

The amount of carbon put into an experiment was simply the amount of carbon in the charged urea. To determine the amount of carbon in the product, actual weights and analyses for U, GN, biuret, and insolubles were used. Runs 31 and 33 were chosen for evaluation because analyses of the reaction product were available for materials both inside and outside of the catalyst beads. Since it had been shown that the insolubles have a carbon content equal to that of ammelide, the insolubles on an ash-free basis were assumed to be ammelide. In all three of the runs, the biuret content of product inside the beads was assumed to be the same as that in the bulk. Run 37 was included, since no samples were taken during the run, which meant fewer contributions to the total carbon output, a factor which should help reduce the error in the balance. However, in Run 37, an analysis of the product in the beads was not available; thus it was assumed to be the same as that in the bulk.

The carbon balance results are presented in Table 14. This table contains, in addition to the balance calculated as discussed, a carbon balance based solely on GN yield and on the percent urea reacted.

## 6 Guanidine Nitrate - Analytical Determination

Work was done to improve and evaluate the proposed thermal assay method for purified guanidine nitrate. The method was based on the calculation of mole percent purity from melting point curves obtained by use of a differential scanning calorimeter (DSC). The calculations were based on the Van't Hoff equation, and a computer program was written to process the melting point curve data.

A laboratory sample of guanidine nitrate was analyzed by the DSC method, and assay values of 98.50 and 98.59 mole % were obtained. Recrystallization of this sample from water gave two crops of crystals that assayed 99.72 and 99.07 mole %, respectively. Differences between the melting curves of these two samples were readily apparent. It is estimated that a difference of 0.2-0.3 mole % can be visually detected without measurement or calculation. One experimental difficulty was encountered. Each sample must be premelted two or three times before analysis to eliminate a small endothermic peak that occurs at the beginning of the GN melting endotherm. The source of this interfering peak is unknown, but it may be related to a crystal phase transition.

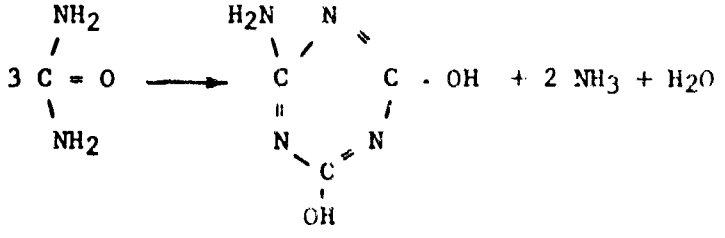
TABLE 14

CARBON BALANCE

| Run No. | Carbon Found[1] in U, AC, (N both in bulk and beads (Wt. %) | Carbon Found[1] in Ammelide and Biuret (Wt. %) | Closure (A & b) (Wt. %) | Carbon Unaccounted for (Wt. %) |
|---|---|---|---|---|
| 31 | 86 | 9.5 | 95.5 | 4.5 |
| 33 | 80 | 16.6 | 96.6 | 3.4 |
| 37 | 86 | 12.2 | 98.2 | 1.8 |

[1]Values calculated from experimental weights and analyses for batch reactions. It was assumed, based on previous analyses, that all of the insolubles were ammelide. Biuret contents were by actual analysis.

Ammelide (6-amino-s-triazine-2, 4-diol) is an insoluble and is formed by the condensation of urea as follows:



Urea Ammelide

## f. Process Studies

### 1 GN Recovery (Two-Stage Process)

#### a Recovery of GN from Reaction Melt by Melt Crystallization

The first-stage of a two-stage process for obtaining a pure dry GN is to crystalize a crude GN from the reaction melt diluted with additional urea. For this work, a reaction melt with additional urea was simulated by mixing appropriate proportions of reagent grades of urea, AN, and GN.

Melt crystallizations were performed in stirred 150-ml beakers placed in a controlled temperature bath. In a typical experiment, 100 grams of crystalline feed of the desired composition was added to the beaker and heated on a hot plate for melting. The beaker of melt was then transferred to a controlled temperature bath where it was cooled at a controlled rate. The temperature at which crystals first appeared was noted. After the final temperature for the experiment had been reached, the slurry from the beaker was filtered in a heated 4-cm-diameter coarse frit filtering funnel using vacuum. Filtration rates were measured. The weights of filter cake and filtrate were determined; the cake was analyzed for GN, U, and AN; and the approximate range of the crystal particle sizes was measured using a 75X microscope with a calibrated objective.

The procedures for recrystallizing the crude GN from water solutions were the same as given above except that the size of the feed charge was 20-30 grams, and a 10-ml water wash of the pure GN cake was used.

The eight complete melt crystallizations made are summarized in Table 15.

The primary variables in this study were the U/AN ratio, cooling rate, and final crystallizer temperature. The runs made showed the relative importance of these variables. Four runs were made with U/AN ratios of 42/58, three runs with a ratio of 47/53 and one run with a ratio of 52/48. The actual noted feed compositions are based on the assumption of a reaction melt composition of 15% urea, 50% AN, and 35% GN to which urea must be added to obtain the desired U/AN ratios.

TABLE 15

GUANIDINE NITRATE MELT CRYSTALLIZATION RESULTS

| Run Number | MC-1 | MC-2 | MC-3 | MC-4 | MC-5 | MC-6 | MC-7 | MC-8 |
|---|---|---|---|---|---|---|---|---|
| Feed Composition (Wt %) | | | | | | | | |
| [illegible] | 29.9 | 29.9 | 29.9 | 34.2 | 34.2 | 34.2 | 29.9 | 38.8 |
| [illegible] | 41.2 | 41.2 | 41.2 | 38.7 | 38.7 | 38.7 | 41.2 | 36.0 |
| GN | 28.9 | 28.9 | 28.9 | 27.1 | 27.1 | 27.1 | 28.9 | 25.2 |
| U/AN Wt. Ratio | 42/58 | 42/58 | 42/58 | 47/53 | 47/53 | 47/53 | 42/58 | 52/48 |
| Precipitation Temp. (°C) | 111 | 110 | - | 107 | 100 | 106 | 105 | 90 |
| Final Cryst. Temp. (°C) | 72 | 80 | 65 | 60 | 62 | 70 | 66 | 50 |
| Cooling Rate (°C/min.) | 2.0 | 1.9 | 11 | 9.2 | 1.6 | 1.4 | 5.5 | 1.8 |
| Filter Vacuum (cm Hg) | 50 | 50 | 50 | 50 | ~50 | ~50 | ~50 | 60 |
| Filtration Rate ($ml/cm^2$-min) | 2.5 | 3.8 | 1.8 | - | 25 | 35 | 10 | 32 |
| Cake Composition (Wt %) | | | | | | | | |
| Urea | 5.8 | 4.3 | 15.8 | 16.3 | 15.5 | 16.8 | 12.0 | 15.7 |
| AN | 17.0 | 15.4 | 22.1 | 20.7 | 12.7 | 19.4 | 17.3 | 15.1 |
| GN | 76.4 | 80.4 | 61.7 | 62.7 | 71.3 | 63.2 | 69.7 | 69.3 |
| Nom. Cryst. Size ($\mu m$) | 40-140 | 40-100 | 1-20 | 1-40 | 20-60 | 20-40 | 20-40 | 20-60 |
| Filtration Material Balance (g) | | | | | | | | |
| Slurry Filtered | 94.6 | 93.3 | 92.6 | 93.5 | 97.1 | 97.3 | 92.4 | 92.5 |
| Cake Wt. | 26.7 | 20.3 | 33.1 | 33.9 | 21.2 | 29.6 | 28.6 | 25.3 |
| Mother Liquor | 67.7 | 71.8 | 58.7 | 51.9 | 67.6 | 67.0 | 63.2 | 66.5 |
| Vol. Mother Liquor (ml) | 47 | 52 | 42 | 39 | 45 | 48 | 45 | 45 |
| Material Lost (%) | 0.2 | 0.6 | 0.9 | 8.2 | 8.5 | 0.7 | 0.6 | 0.7 |
| GN Yield * | 75 | 62 | 76 | 84 | 57 | 71 | 75 | 75 |

* Product recovery yield.

The effect of the three primary variables will be discussed in terms of resulting GN yield and crude GN purity. Both yield and purity affect the overall efficiency of the Roberts workup (i.e., melt crystallization followed by recrystallization of the crude GN). The overall yield of GN for the Roberts workup is the product of the GN melt yield and the GN recrystallization yield. Crude GN purity is important, since it affects the yield of the recrystallization; thus, purity should be as high as possible.

(1) Final Crystallizer Temperature

The final crystallizer temperature variable affects yield, purity, and filtration rate. As this temperature decreased, so did the filtration rates as a result of increased viscosity. In addition, the GN yield increased and the purity decreased. The results of Runs MC-1 and MC-2 made at U/AN ratios of 42/58 and the same cooling rate but at 72°C and 80°C final temperatures showed the trends discussed. The most significant difference in the results of the two runs was that the yield for the lower temperature was 75% compared to 62% obtained at 80°C. Runs MC-5 and MC-6 at a U/AN ratio of 47/53 and the same low cooling rate should have also showed the same trends but they did not. In fact, the reverse of the expected was found for purity and yield. The yield for Run MC-5 was very low at 57%. The validity of this result is suspect, since the material balance for Run MC-5 is much poorer than that for Run MC-6.

(2) Cooling Rate

Crystal size and GN purity appeared to be predominantly functions of the cooling rate. As expected, the higher rates result in smaller crystals. The more important effect, however, is that the purity of the crude GN decreases significantly with increased cooling rates. Runs MC-3 and MC-7 were made with the same U/AN ratios and the same final crystallizer temperatures but with 11°C/min. and 5.5°C/min. cooling rates, respectively. The purity for the lower cooling rate was 70% compared to 62% at the higher rate. Runs MC-4 and MC-5 showed the same dependence on cooling rate.

(3) Urea-to-AN Weight Ratio

The influence of this parameter on yield and purity was minimal within the range studied. Runs MC-1, -7 and -8 were made at U/AN ratios of 42/58, 47/53, and 52/48 at good conditions for cooling rate and final temperature. The GN yield for all of these runs was essentially 75%. The purity was somewhat lower at the higher urea ratios, and filtration rates were definitely higher at the higher urea ratios.

### (4) Filtration of Crude GN

Filtration was not emphasized in this study, since the separation of solids from mother liquor was easy. The filter cakes were not very compressible, and plugging of the filter medium was not observed. All of the separations were made with a 10 psi pressure drop. In commercial filters or centrifuges, even the slowest filtration rates obtained in Runs MC-1 to MC-3 would be satisfactory. The rate of 1.8 $ml/cm^2/min.$ corresponds to 25 $gal/ft.^2/hr.$ This yields 80-100 lb cake/$hr/ft^2$, an economical range for commercial operation.

### (5) Preferred Conditions for Melt Crystallization

Based on the results discussed above, the lowest U/AN ratio (42/58) should be used, since there is no apparent advantage in going to a higher ratio. Cooling rates of 1-2 °C/min. with a final crystallizer temperature of 65°C appear to be optimum temperature conditions. These were essentially the conditions for Run MC-1. The expected crude GN yield will be 75% with a crude GN purity of about 75%.

It is interesting to note that the Roberts patent example (USP 3,043,878)[3] also reported a 75% yield but a 92% purity. Roberts' feed compositions were higher in GN but that alone does not explain the large difference in purity. This purity has a significant effect on the yield of GN from the recrystallization step.

## b Recrystallization of Crude GN

Recrystallization of the crude GN obtained from the melt crystallization is the second step of the Roberts workup scheme. The objectives of this step are to convert the crude GN to ≥ 97% GN in high yields, using a minimum amount of water.

Experimental procedures for these crystallizations were quite similar to those for melt crystallization. The feed for the experiments was the crude GN produced from the melt crystallization. These experiments were made on a smaller scale; the amount of crude GN available from each crystallization run was only 15 to 25 grams.

In a typical experiment, crude GN and the desired portion of water was charged to a 100 ml beaker which was heated on a hot plate to dissolve the crude GN. Water which evaporated during dissolution was added back before the hot beaker of aqueous solution was placed in a controlled temperature bath. After the crystallization cycle was completed, the beaker of GN slurry was reweighed before filtration to determine the amount of water evaporated during crystallization. The slurry

was then filtered, and the wet cake was washed with an equal weight of water. The washed cake was dried, and the percent solids were determined. The purity of the dry GN was analyzed by differential scanning calorimetry (DSC).

The results of four recrystallization experiments are summarized in Table 16.

(1) Results for Recrystallization Experiments

In this work, an attempt was made to obtain a realistic estimate of the maximum obtainable GN yield for the recrystallization step. A yield of > 90% was needed for the Roberts workup scheme to be competitive with a single aqueous crystallization, which has demonstrated overall 70-75% yields with > 99% purity. The one-step aqueous crystallization is discussed in the next section.

The best yield obtained was 78% using 0.30 part $H_2O$/part crude GN, Run RC-4. The final crystallizer temperature for RC-4 was 35°C. It is possible that by reducing this temperature, the yield could have been improved. This temperature, however, was not arbitrarily chosen but rather was the lowest temperature at which the slurry appeared to be filterable. In summary, it is doubtful that GN recrystallization yields can be raised to 90%. Roberts (USP 3,043,878) reports recrystallization yields of 98%; however, the starting crude GN from eutectic crystallization was 92% GN. On this basis, the overall GN recovery yield (eutectic plus recrystallization) is about 70%.

(2) Aqueous Workup - Crystallization

The alternative to the Roberts workup scheme is the original aqueous one used by MacKay in the Pittsburgh Coke and Chemical work.[4] This scheme is a simple crystallization of GN from water. The melt from the reactor is dissolved in water, and the GN crystallizes and separated by filtration or centrifugation. The mother liquor stream could be evaporated to remove all water and the solids subsequently recycled.

The objectives of this study were to find operating conditions which gave the best yield of GN (GN in product/GN in melt) consistent with good purity and feasible, economical operations. The principal variables were water-to-melt weight ratio and cooling rate. Feed composition and final crystallizer temperature are other factors considered in the study.

TABLE 16

CRUDE GUANIDINE NITRATE RECRYSTALLIZATION RESULTS

| Run Number | RC-1 | RC-2 | RC-3 | RC-4 |
|---|---|---|---|---|
| Feed Source | MC-1 | MC-2 | MC-7 | MC-8 |
| Feed Composition (Wt %) | | | | |
| Urea | 5.8 | 4.3 | 12.0 | 15.7 |
| AN | 17.0 | 15.4 | 17.3 | 15.1 |
| GN | 76.4 | 80.4 | 69.7 | 69.3 |
| Initial Water/Feed Ratio | 0.5 | 0.6 | 0.37 | 0.51 |
| Final Water/Feed Ratio | - | - | 0.28 | 0.30 |
| Precipitation Temp. (°C) | - | 76 | 90 | 92 |
| Final Cryst. Temp. (°C) | 27 | 30 | 23 | 35 |
| Cooling Rate (°C/min.) | 3-4 | 3-4 | 2 | 2 |
| Filter Vacuum (cm. Hg) | 25 | 25 | 25 | 25 |
| Filtration Rate (ml/cm$^2$-min) | Fast | Fast | Fast | Fast |
| Nom. Crystal Size ($\mu$m) | 60-100 | 60-100 | 100 | 100 |
| Purity (mole % GN) | 99.2 | 99.8 | 99.9 | 99.9 |
| Material Balance Data (g.) | | | | |
| Crude GN | 20.6 | 16.5 | 12.7 | 21.5 |
| Water Added | 10.3 | 9.9 | 4.7 | 11.0 |
| Water Evaporated | - | - | 1.1 | 4.6 |
| Slurry Filtered | - | - | 15.5 | 26.3 |
| Unwashed Cake (wet) | - | 13.0 | 8.0 | 15.3 |
| Mother Liquor | 11.1 | 11.3 | 6.1 | 11.3 |
| Vol. Mother Liquor (ml) | - | 11 | 10 | 10 |
| Water Wash Added | 15 | 15 | 6.1 | 10 |
| Washed Cake (wet) | 11.5 | 10.0 | 5.1 | 12.2 |
| Wash Solution Collected | 17.0 | 11.6 | 7.7 | 12.4 |
| % Solids in Cake | 93.0 | 90.7 | 93.5 | 90.1 |
| % Material Lost | 19 | 21 | 16 | 7.7 |
| GN Yield (%) * | 69.8 | 68.2 | 56.3 | 78.3 |

* Product recovery yield.

NOTE: Crude GN charged to recrystallization flask amounted to only 1-25 gm for each run.

Notes for Table 16:

Feed Source - Refers to melt crystallization run from which crude GN was obtained.

Final Water/Feed Ratio - Weight ratio of water to crude GN at the end of crystallization which accounts for water loss through evaporation.

Purity - Mole per cent GN in the dry recrystallized product as determined by DSC.

Crude GN - Weight of crude GN charged to the crystallizer beaker.

Water Added - Amount of water in the system just before crystallization is started. The number is determined by differencing the gross weight of hot solution and the crude GN charges.

Water Evaporated - Weight of water evaporated during the crystallization cycle; determined by initial and final gross crystallizer weights.

Cake Solids - Weight per cent solids in the washed cake determined by drying some of the washed cake at 110°C to a constant weight.

Material Lost - Check on handling losses and calculated by subtracting outputs from inputs and dividing by inputs.

GN Yield - This is a crystallization product yield; i.e., the fraction of GN in the crude feed that is found in the dry, pure product.

$$\text{Yield} = 100 \left[ \frac{(\text{Purity} \times \text{Cake Solids} \times \text{Washed Cake Wt.})}{\left(\frac{\text{Wt. Crude GN}}{(\text{Wt. Crude GN} + \text{final wt. Water})}\right) \times \text{Wt. Slurry} \times \%\text{GN in Crude}} \right]$$

Experimental procedures for the aqueous workup runs were the same as used in the recrystallizations of crude GN except that the initial charge of feed was varied from 20 to more than 100 grams. The first six runs were made with simulated feeds made up from reagent grade U, AN, and GN. These runs were made to determine suitable operating conditions. In Runs AC-7 to AC-15, actual crystalline reaction products from Houdry Bead reaction experiments were worked up.

In reviewing the results of these runs, reported in Table 17, it can be seen that the workup procedures were refined two different times. Starting with Run AC-6, the amount of water evaporated during crystallization was measured. This provided a more accurate solids content (expressed as the final water ratio) of the slurry to be filtered. Runs AC-7 and AC-8, although made with actual reaction product, did not include filtration to remove water insolubles. In these runs, it was found that the water insolubles plugged the filters, making filtration rates low. Starting with Run AC-9, the water insolubles were removed before crystallization.

The results in Table 17 provide insight into the effects of water/feed ratio and GN concentration in the feed on the GN yield for an aqueous workup system. By taking data from runs with the same GN feed concentration, the effect of the water/feed ratio on yield is shown in Figure 12. These results show that water/feed ratios in the range of 0.2 to 0.3 result in GN yields of 75 to 30%. Larger portions of water result in lower yields because of the larger fraction of charged GN in the mother liquor.

It is also evident from Table 17 that the GN concentration in the feed (reaction product) strongly affects the yield. Figure 13 summarizes the yield versus feed concentration results. The GN yield for aqueous crystallization increases from about 30% to about 80% as the GN concentration in the reaction melt increases from 15% to 35%. Although no multicomponent solubility data were available to support these empirical results, the results are indeed qualitatively what would be expected; i.e., a greater fraction of the GN in a lean feed is lost to mother liquor than in a rich feed.

In summary, the most desirable conditions for aqueous workup appear to be:

(1) Water to feed ratios of 0.15 to 0.25
(2) GN feed concentrations ~ 35%
(3) Cooling rates of 1-2°C/min.
(4) Final crystallizer temperatures of 15 to 20°C.

# TABLE 17

## LABORATORY REACTION PRODUCT AQUEOUS WORKUP RESULTS

| | AC-1 | AC-2 | AC-3 | AC-4 | AC-5 | AC-6 | AC-7 | AC-8 | AC-9 | AC-10 | AC-11 | AC-12 | AC-13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | # | #2 | #3 | #4 | #5 | #6 | #7 | #8 | #9 | #10 | #11 | #12 | #13 |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | |

Notes for Table 17:

Filtration - Material Lost - For Runs AC-1 through AC-5, the noted values for lost material were for the entire workup process. For Runs AC-6 through AC-19, the losses are for the filtration step only.

GN Yield (or Recovery) - The GN yield is the per cent of GN in the feed that is found in the dry product. However, since the workup procedure involved several steps, the formula used to calculate yields contained many factors to account for as many of the handling losses as possible. The formula used for runs with removal of insolubles via filtration was as follows:

$$\text{Yield} = \frac{(\text{Wt. wet cake})\ (\text{fraction solids in cake})\ (\text{purity})}{(\text{Wt. slurry filtered})\ (\text{fraction solids in slurry})\ (\%\ \text{GN in XL feed})}$$

where:

$$\text{Fraction Solids in Slurry} = \frac{\left(\begin{matrix}\text{initial solids}\\ \text{fraction}\end{matrix}\right)\ \left(\begin{matrix}\text{wt. hot solution}\\ \text{filtered}\end{matrix}\right) - \begin{matrix}\text{Dry wt of}\\ \text{insolubles}\end{matrix}}{\text{Wt. hot solution filtered}} \times \frac{\text{Wt. solution to crystallizer}}{\text{Wt. solution to crystallizer - evaporation loss}}$$

(In Runs AC-1 through AC-5 yield was based on the feed dissolved.)

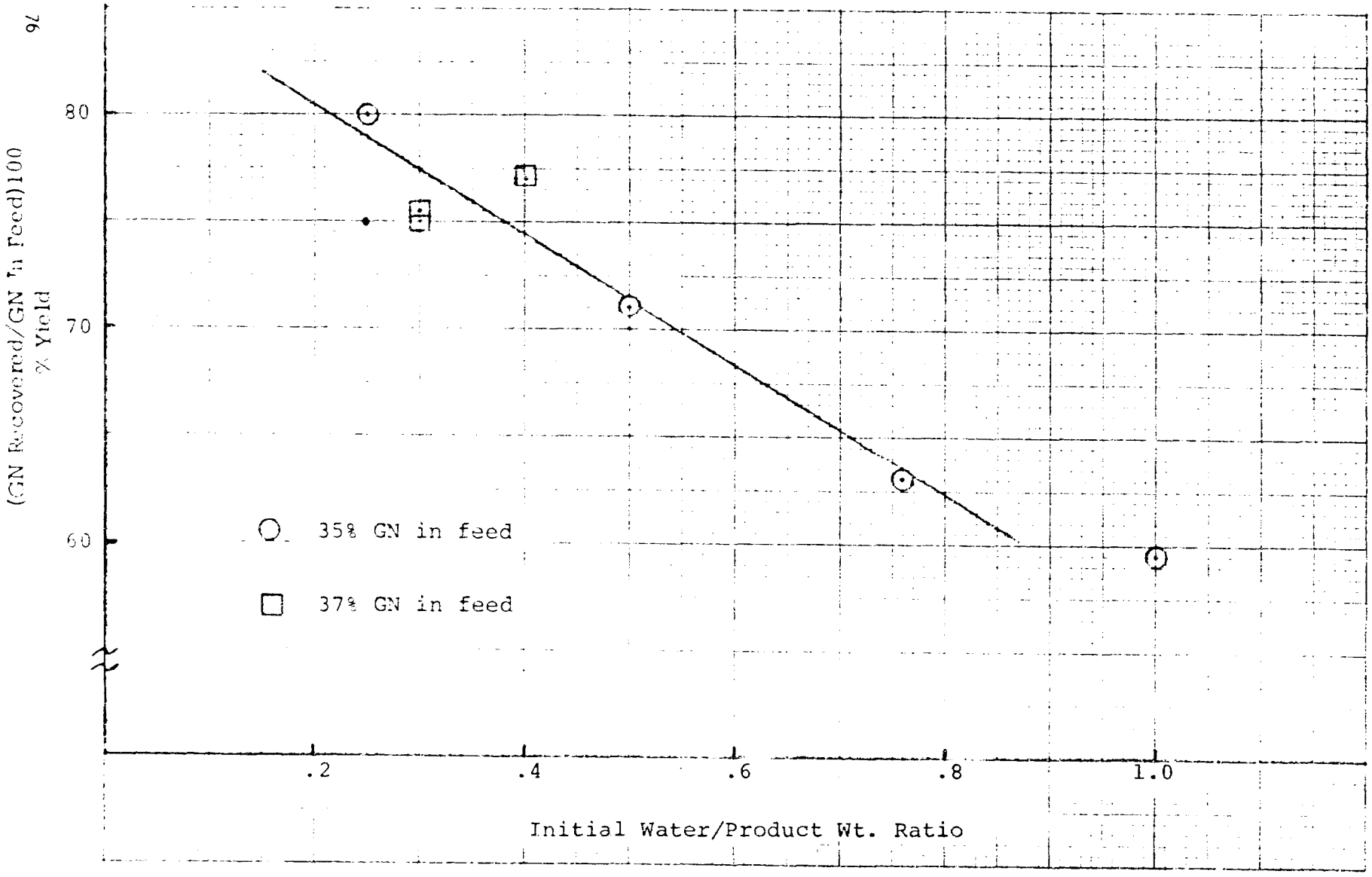



Figure 12. Effect of Water/Product Ratio on Yield from Aqueous Workup

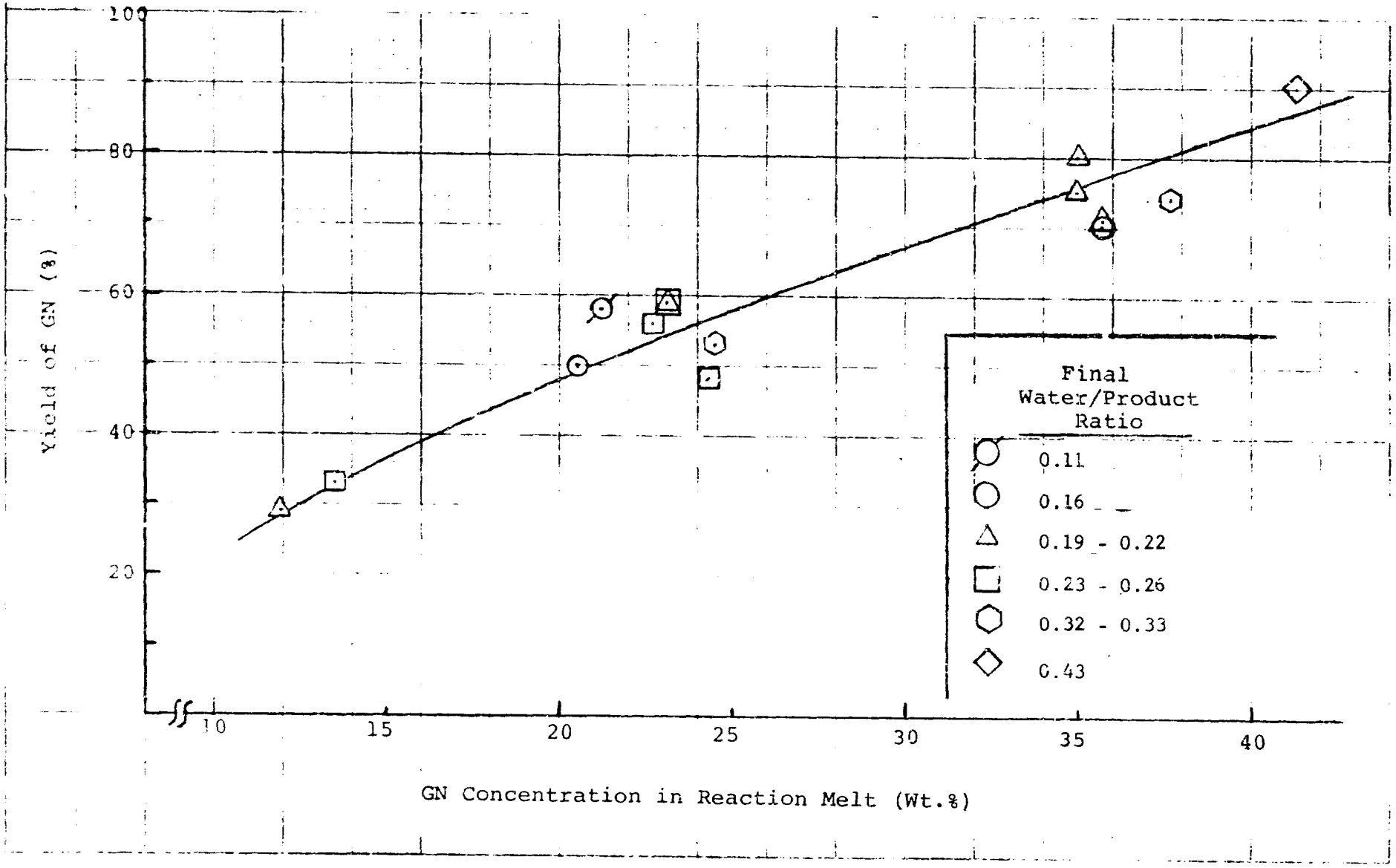



Figure 13. Effect of GN Concentration in Reaction Product on Aqueous Workup Yields

At these conditions, the yield of GN from the aqueous workup was in the range 70 to 80%, and filtrations were generally rapid and made without difficulty.

## 2 GN Drying

The purpose of these experiments was generally to assess guanidine nitrate drying characteristics and to obtain data for pilot plant dryer design.

In a typical drying experiment, dry GN from an aqueous workup run was slurried in water and filtered in a 4-cm-diameter fritted filter funnel. In this way, a wet cake of uniform thickness was formed. The filter (with the cake on it) was then put into an oven without forced air circulation and dried. The weights of the filter and cake were measured as a function of time. Experiments were conducted at ~ 60°C and ~ 44°C. Drying rates for two cake depths (6-7 mm and 12-13 mm) were determined at each temperature.

Drying data for one run (D-1) are presented in Figure 14. These data were plotted in the standard way: i.e., moisture content (grams water in the cake/g dry GN) as a function of drying time. Figure 15 shows a plot of drying rate versus time for Run D-1. This rate curve clearly shows that an initial constant rate period is followed by the falling rate period as is found for all normal systems.

To estimate the magnitude of the drying rates which might be obtained, the slopes of the drying curves during the constant rate period were used. Table 18 gives the drying rates in engineering units which result from the constant rate data for each of the four runs. The drying rates are commercially reasonable in magnitude and could be realized with indirect rotary dryers with moderate heat transfer area. Note that the rates reported should be conservative, since commercial dryers would be agitated and have forced air circulation. Agitation will definitely be required, since the GN caked severely.

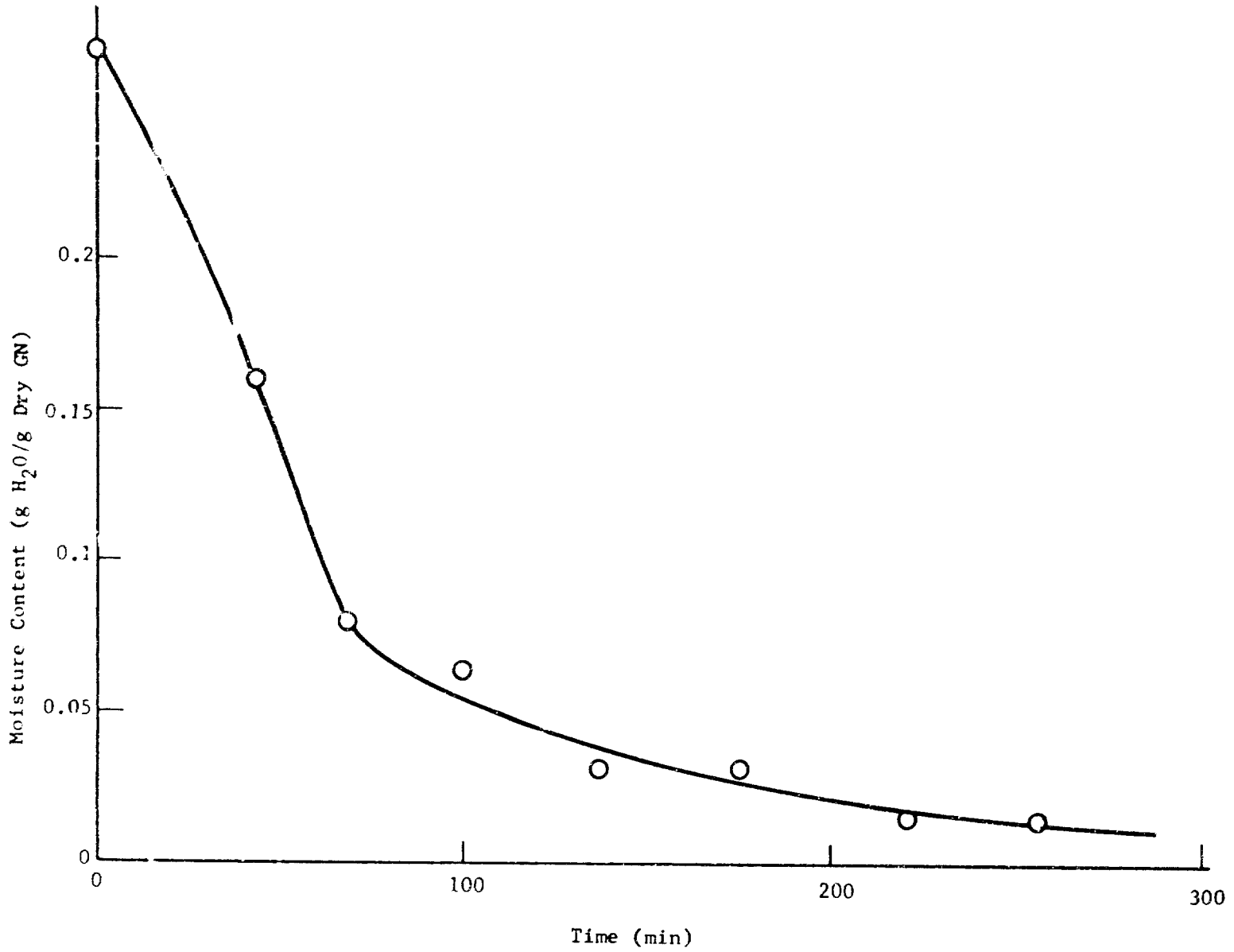



Figure 14. Drying Curve for Run D-1 (7 mm. Cake @ ~ 60°C)

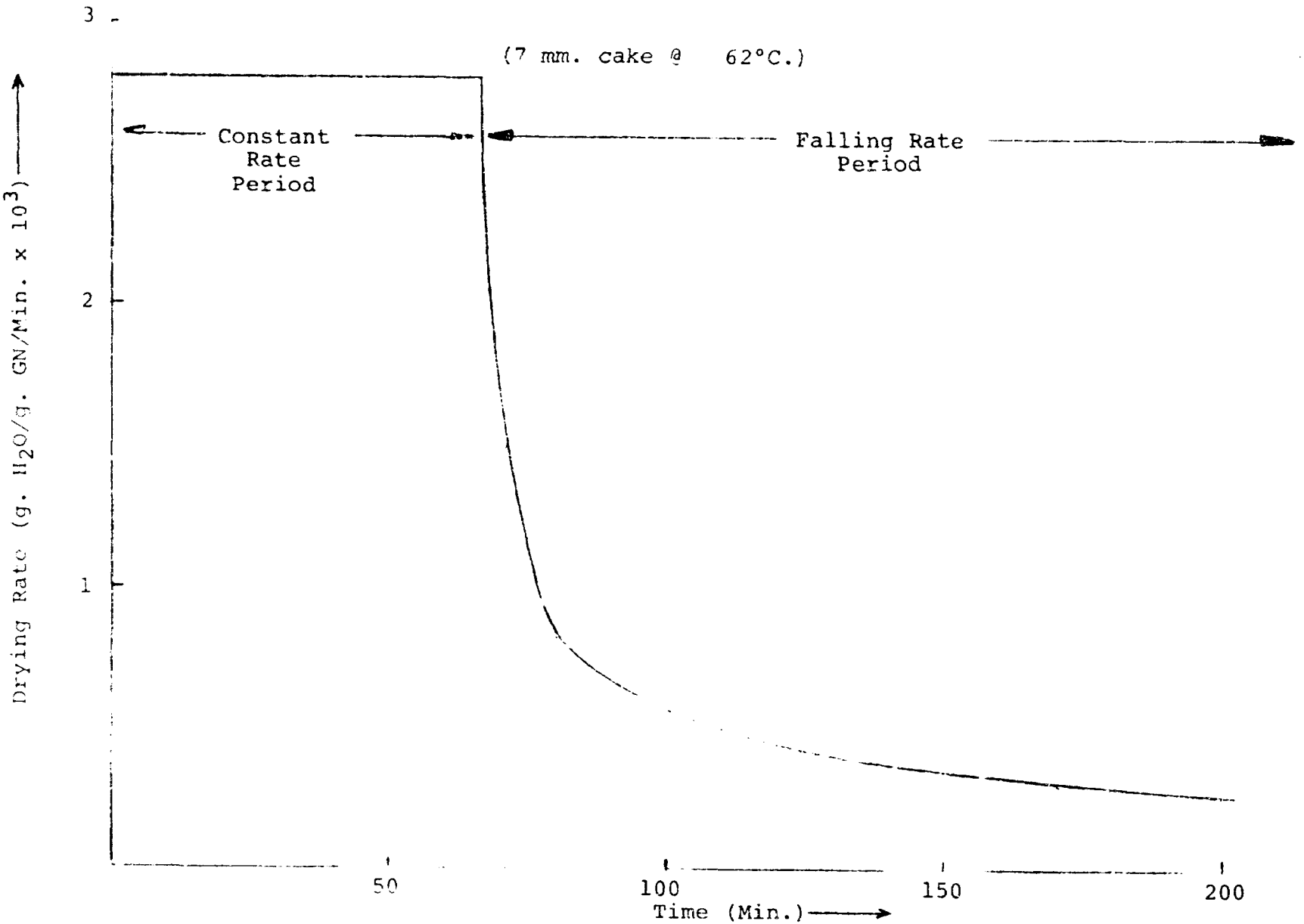



Figure 15. Drying Rate Curve for Run D-1

TABLE 18

SUMMARY OF DRYING RESULTS

| Run No. | Drying Temp. (°C) | Cake Depth (mm) | Drying $\left(\frac{\text{lb Dry Cake}}{\text{hr ft}^2}\right)$ (1) |
|---|---|---|---|
| D-1 | 62 | 7 | 59 |
| D-2 | 62 | 13 | 25 |
| D-3 | 44 | 6 | 19 |
| D-4 | 44 | 12 | 11 |

(1)This rate assumed a cake with an initial moisture content of 15%.

g. Waste Disposal and Pollution Control

Process development reports by Roberts and MacKay have strongly suggested that the BMR process is remarkably free from waste streams. The work done in Phase I of the contract corroborated the earlier reports. The results show that, stopping short of continuous recycle operation, there are no process waste streams which pose pollution control problems.

By-products or waste streams can arise potentially in two main areas in this process: gas evolution from the reaction, and solid and liquid streams from product and recycle workup.

As reported in an earlier section, the off-gas from the reaction is essentially pure ammonia and carbon dioxide. There are no impurities detectable by mass spectrography, a sensitive method. This result was confirmed using argon blanketing in the reactor. The off-gas stream is therefore totally recoverable and may be used to regenerate urea or ammonium nitrate.

During the reaction, the insoluble by-product ammelide is found; it is isolated by filtering the aqueous crystallization feed. Results show that with commercial feeds the preferred reaction conditions for GN production give about 1% ammelide based on reactor effluent or 3% based on product rate. Therefore, about 150 lb ammelide/hr could be expected at a production rate of 5000 lb GN/hr. Ammelide is potentially valuable as a slow-release nitrogen fertilizer. It has been tested extensively by the Tennessee Valley Authority and generally found to compare favorably with urea-type slow release fertilizers. These latter

materials sell at about $180/ton. Although ammelide would not sell at that price without market development, it should be possible to sell it in the fertilizer market.

The remaining waste stream will be a purge, probably from the bottom of the mother liquor evaporator, and will consist basically of AN, U, GN, together with their condensation products and perhaps tars or polymers. This material, once it is obtained and characterized, can be disposed of in one of three ways: it can be sold as fertilizer; it can be incinerated in a carbon-rich environment such as that in a sewage sludge incinerator, or it can be subjected to disposal by cylic nitrification-denitrification in a biological medium along lines recently discussed in a Federal Water Quality Administration paper. The probable small amount and high quality of the purge make the first alternative most likely.

h. Process Corrosion

To assess corrosion potential in future pilot plant or commercial plant equipment, a brief corrosion study was carried out in Phase I. Samples of 5052 aluminum and 304 and 316 stainless steel were made up in testing spools at the Research Center, exposed in a column reactor system at Kenvil, and returned to the Research Center for analysis. The results are summarized in Table 19. All materials showed very low corrosion rates in mils per year (mpy), the highest rate being that of aluminum in the reactor effluent (0.34 mpy).

Materials of construction were previously evaluated briefly by MacKay in his 1955 work.(4) The present results verify his findings that 304 stainless steel would be the preferred material for the reaction and workup stages. The 304 stainless steel, because of its low corrosion rate and low cost among stainless steels, was selected for all components of the pilot plant design except for one tubular reactor and most of the process pumps which were fabricated of 316 stainless steel. Corrosion coupons of different types of stainless steel and aluminum were installed in one of the reactor liquid-gas separators and the aqueous quench tank. Additional corrosion data will be available upon completion of the pilot plant operation.

TABLE 19

CORROSION OF POSSIBLE MATERIALS OF CONSTRUCTION

Specimen Exposed in Feed Tank

4.16 Day's Results or 100 hours @ 120°C.

| Specimen Design | Weight (gms) | Weight Loss (mg) | (a) $mg/dm^2$ | (b) mdd | (c) mpy | Evaluation |
|---|---|---|---|---|---|---|
| 16C48 AP (316 SS) | 6.2345 | .2 | 1.31 | .314 | .06 | No evidence of corrosion. |
| 35D8 B (5052 AL) | 2.1062 | .3 | 1.93 | .465 | .25 | General even corrosion - very light |
| 15C26 CP (304 SS) | 4.7898 | .1 | .68 | .16 | .03 | No evidence of corrosion |

Specimen Exposed in Reactor Effluent

2.08 Day's Results or 50 hours (Reactor Operation)

| | | | | | | |
|---|---|---|---|---|---|---|
| 16C48 AO (316 SS) | 6.4544 | .2 | 1.31 | .63 | .11 | No evidence of corrosion. |
| 35D8 A (5052 AL) | 1.8269 | .8 | 5.16 | 2.48 | 1.34 | General even corrosion - very light. |
| 15C26 CO (304 SS) | 4.8717 | .2 | 1.35 | .65 | .12 | No evidence of corrosion |

Note: Weighing accuracy with our Mettler Balance is ± 0.2 mg
(a) $mg/dm^2$ = milligram per decimeter squared
(b) mdd = milligram per decimeter per day
(c) mpy = mils per year

## 3. Part 2 - Mathematical Modeling

Part 2 of Phase I involved the preparation and use of mathematical models to describe the reaction step of the process.

### a. Kinetic Expressions

To aid in the selection of the mode of reactor operation best suited for guanidine nitrate production, mathematical models describing a packed bed and a series of continuous stirred tanks were written. Such models provide a means for evaluating the advantages and disadvantages of each type of operation. In addition, the effects on yield and conversion of such operating parameters as recycle ratio, feed composition, feed temperature, jacket temperature, equipment size, and residence time can be ascertained. This information will be of obvious value in further design work.

The first step in constructing such models is determining a set of reaction rate expressions that adequately describe the kinetic behavior of the system as functions of the system concentrations and the system temperature. In the case of guanidine nitrate, these expressions would have a firm basis, since the batch experiments conducted were designed to provide data appropriate for constructing such models.

Of several sets of equations tested, the one set that best fits the experimental data for all conditions was the following:

$$r_{GN} = \frac{1}{W_c}\frac{dN_{GN}}{dt} = k_{GN} \cdot x_U \cdot x_{AN} \qquad (1)$$

$$r_U = \frac{1}{W_c}\frac{dN_U}{dt} = -x_U \cdot x'_U \cdot x_{AN} \qquad (2)$$

$$r_{AN} = -\frac{1}{W_c}\frac{dN_{AN}}{dt} = -r_{GN} \qquad (3)$$

with

$$k_{GN} = k^{o}_{GN}\, e^{-E_{GN}/RT} \qquad (4)$$

$$k_U = k_U^o e^{-E_U/RT} \quad (5)$$

where r = reaction rate, moles/(time)(gram of catalyst)

$N_i$ = number of moles of component i.
$x_i$ = mole fraction of component i.

$W_c$ = weight of catalyst
t = time
k = specific rate constant
$k^o$ = frequency factor
E = activation energy
T = temperature, $^oK$
AN = ammonium nitrate
U = urea
GN = guanidine nitrate

A digital computer program, utilizing a parameter estimation technique known in the literature as quasilinearization, was used to fit the numerically integrated solutions of equations (1), (2), and (3) to the experimental data of Runs 30 through 36. These experiments were conducted at a variety of temperatures, ammonium nitrate/urea ratios and catalyst charges. The estimated rate constants are given in Table 20.

Figures 16, 17, 18, 19, 20 and 21 show comparisons of the experimental data from the batch runs and the curves predicted by the mathematical model (Equations 1, 2, 3) using the estimated rate constants given in Table 20. The fits are reasonable in all cases. The computed data were based on the same time increments as the experimental data. Extension of reaction times does not add substance to the comparisons.

The temperature dependence of the rate constants (Equations 4 and 5) can be ascertained by an Arrhenius plot of the rate constants.

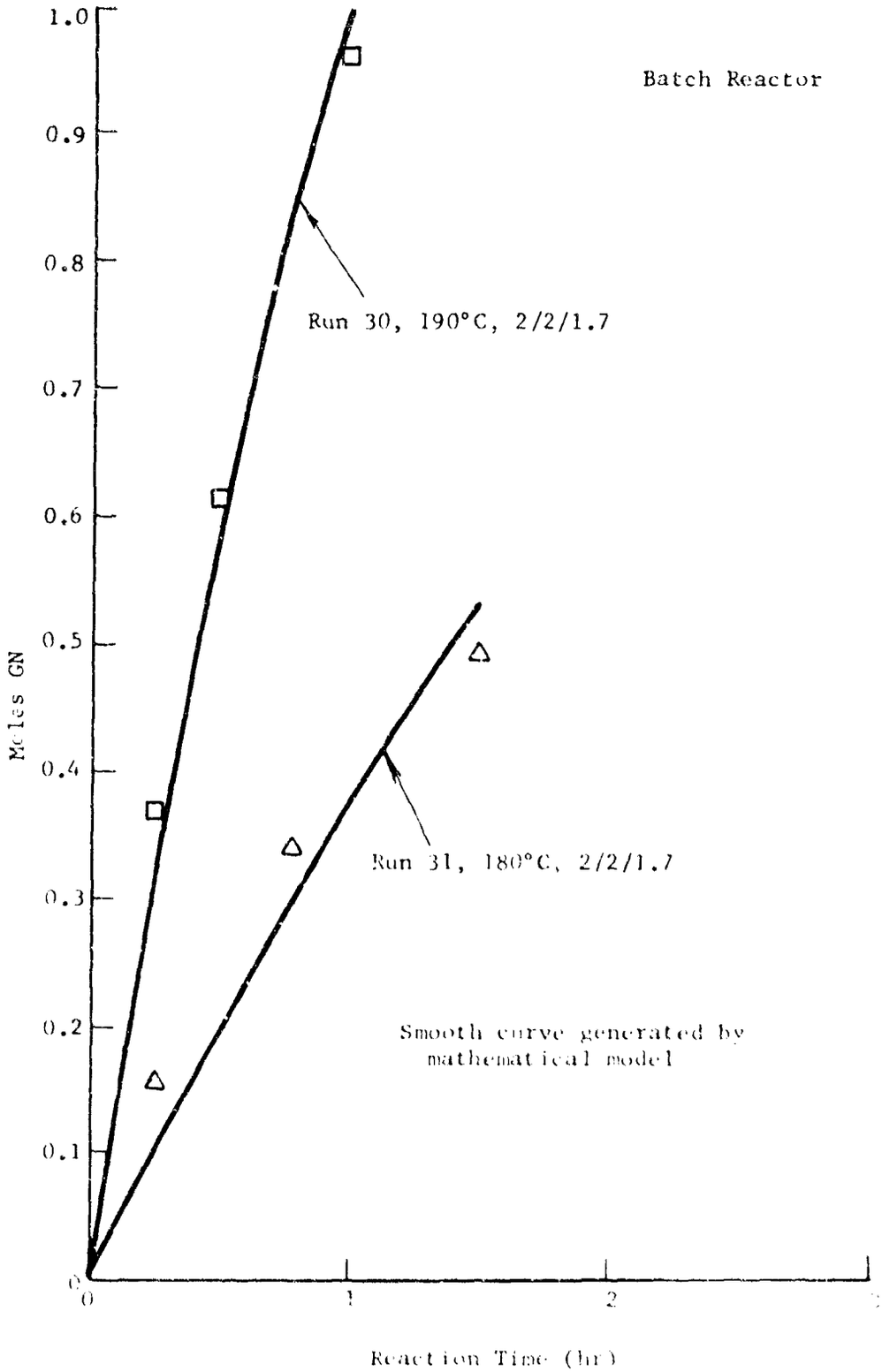



Figure 16. Moles GN vs Reaction Time Boudry Beads

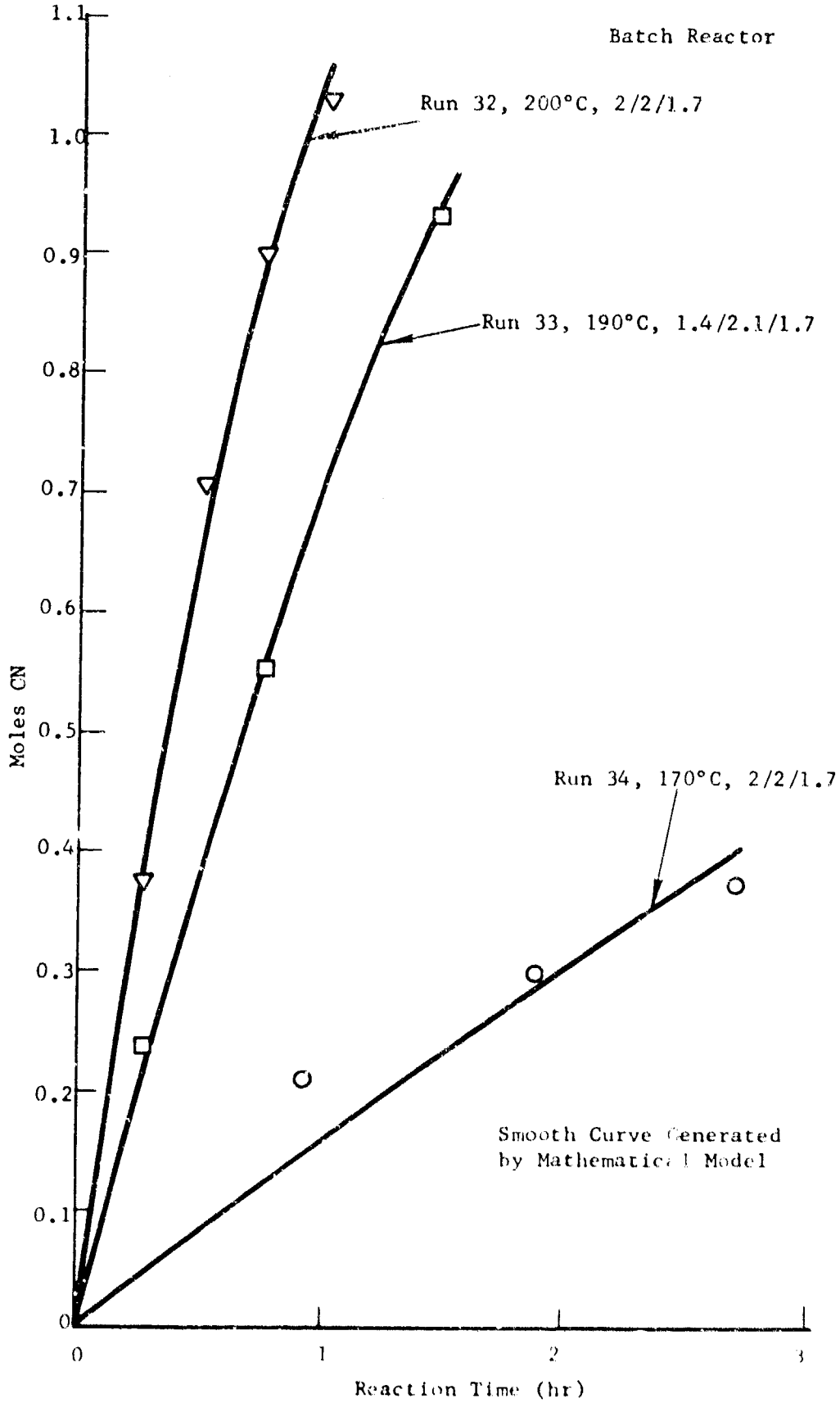



Figure 17. Moles Guanidine Nitrate Vs. Reaction Time (Houdry Beads)

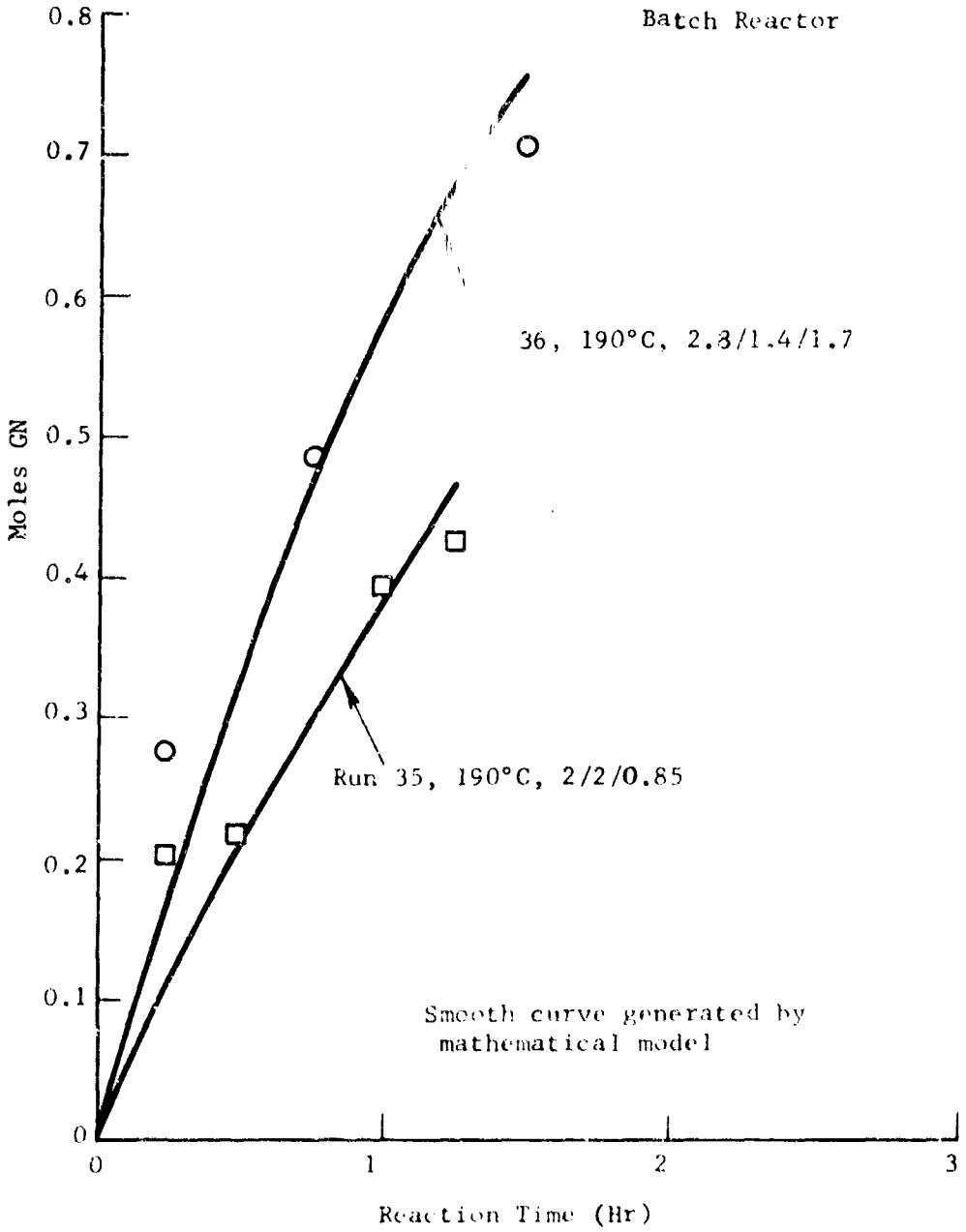



Figure 18. Moles GN vs Reaction Time Houdry Beads

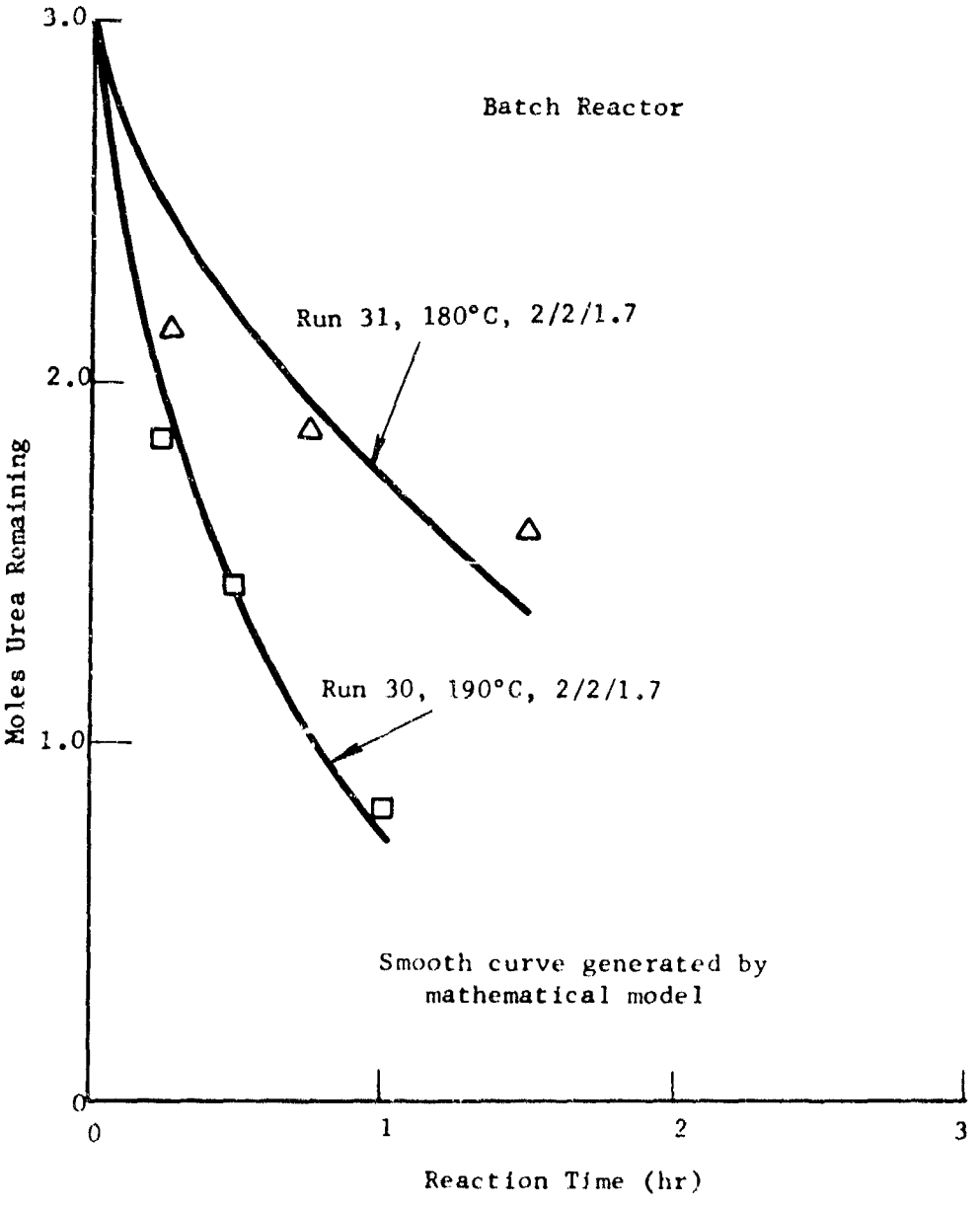



Figure 19. Moles Urea vs Reaction Time
Houdry Beads

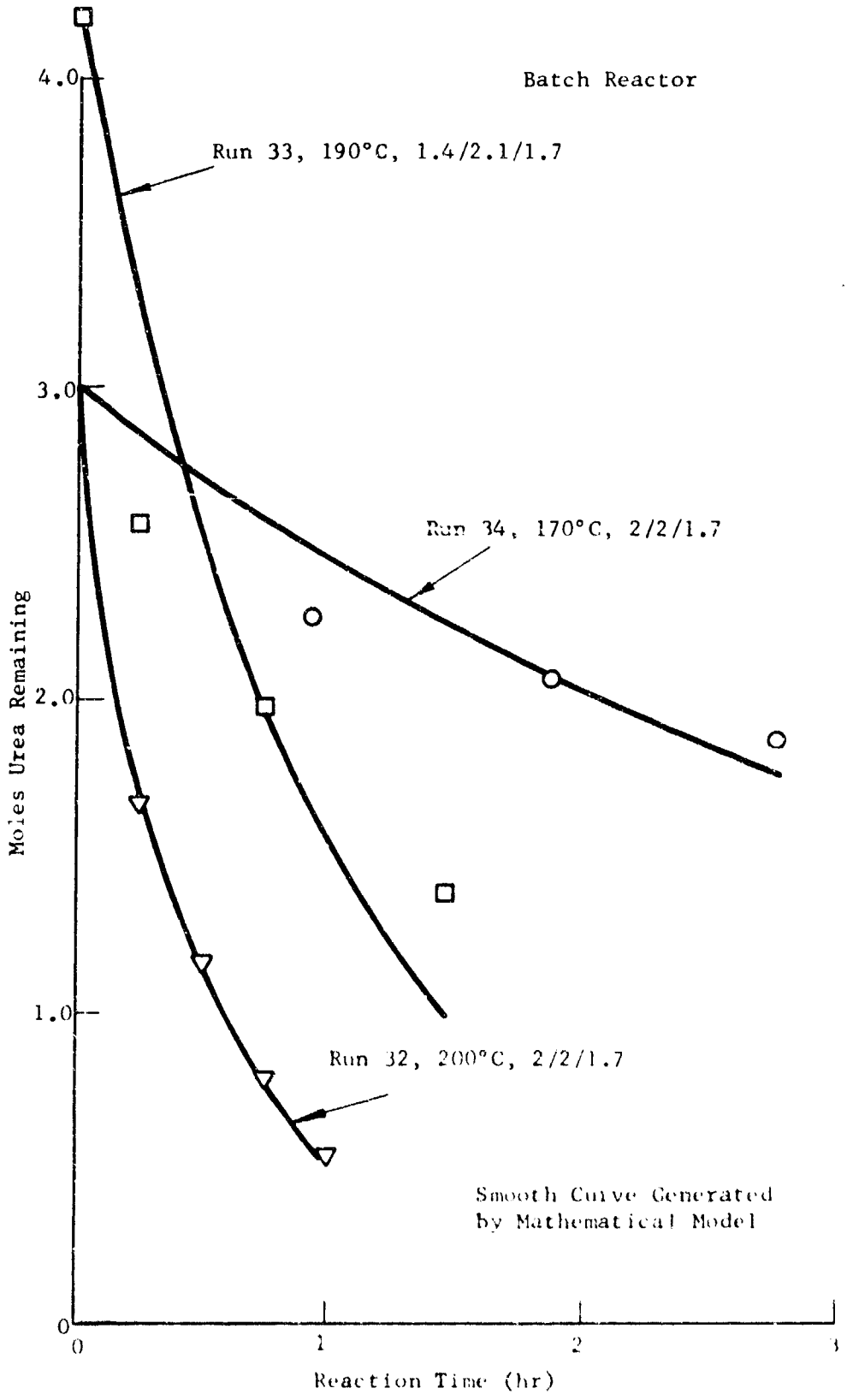



Figure 20. Moles Urea vs Reaction Time Houdry Beads

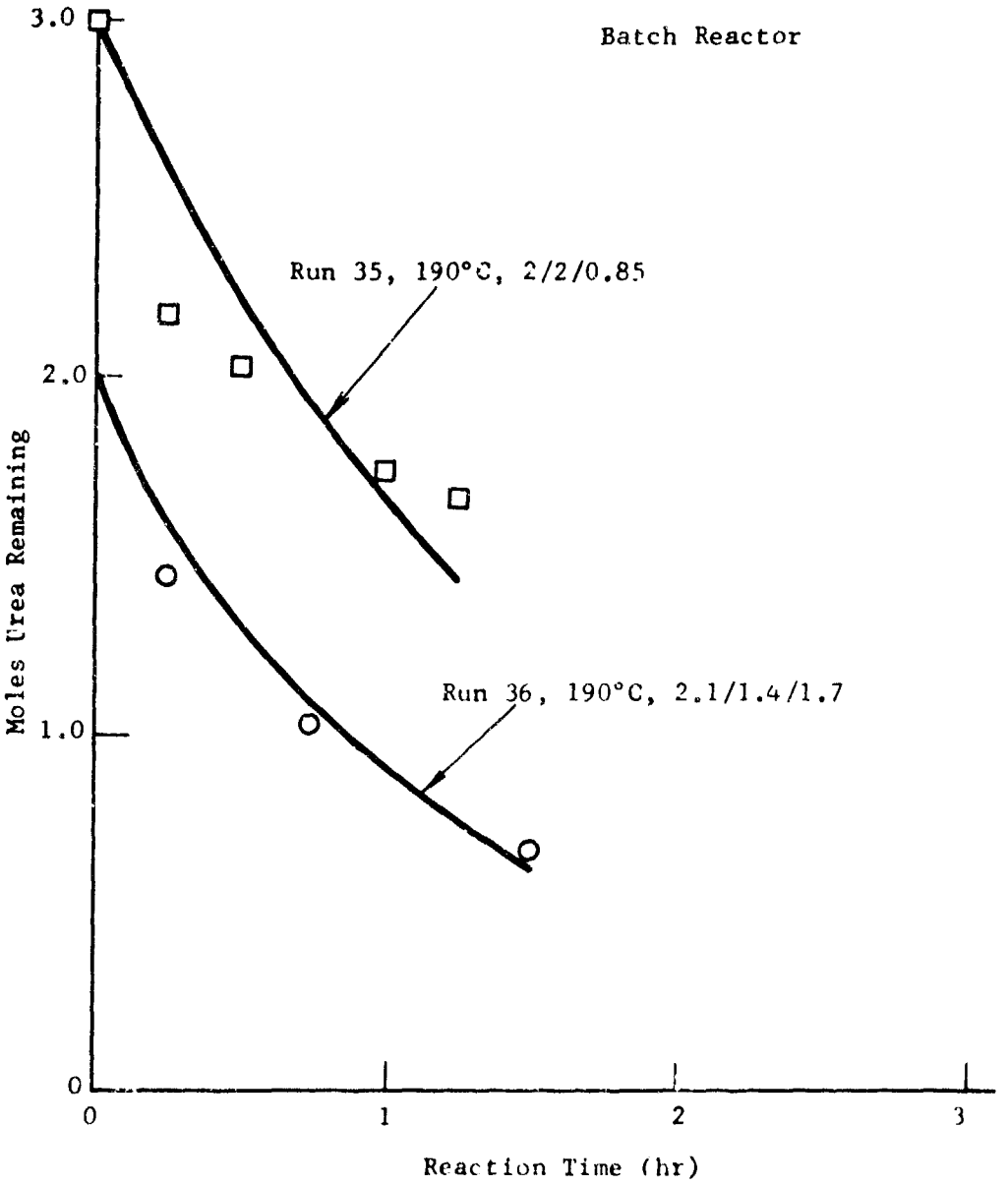



Figure 21. Moles Urea vs Reaction Time Houdry Beads

TABLE 20

ESTIMATED RATE CONSTANTS

| Run | Description | $k_{GN}$ | $k_U$ |
|---|---|---|---|
| 30 | 190°C, 2/2/1.7 | .0005935 | .003957 |
| 31 | 180°C, 2/2/1.7 | .0001791 | .001352 |
| 32 | 200°C, 2/2/1.7 | .0007113 | .005174 |
| 33 | 190°C, 1.4/2.8/1.7 | .0003795 | .002551 |
| 34 | 170°C, 2/2/1.7 | .00007240 | .0005035 |
| 35 | 190°C, 2/2/0.85 | .0003692 | .002962 |
| 36 | 190°C, 2.8/1.4/1.7 | .0003632 | .003164 |

Figures 22 and 23 are Arrhenius plots of $k_{GN}$ and $k_U$, respectively. Note that in each case one data point does not follow the linear relationship as well as does the rest of the data. These points are the rate constants for Run 30 whose deviation from the norm was due to a finer catalyst particle size as discussed in the previous section. However, even with these data points included, the rate constants in the Arrhenius plots follow straight lines with simple correlation coefficients in excess of 0.97 in both cases. It is important to note that the three points grouped closely together at 190°C (1/463°K) in Figures 22 and 23 represent the rate constants for the batch runs conducted at the different ammonium nitrate/urea ratios and the different catalyst levels(Runs 33, 36, and 35). The close grouping of these points indicates that the model adequately describes the response of the system to variations in these operating conditions.

Least-squares fits to the rate constants on the Arrhenius plots yield the following parameters:

$$E_{GN}/R = 16{,}550°K$$

$$k^{\circ}_{GN} = 1.31 \times 10^{12} \text{ moles/(gram of catalyst) (minute)}$$

$$E_U/R = 16{,}890°K$$

$$k^{\circ}_U = 2.01 \times 10^{13} \text{ moles/(gram of catalyst) (minute)}$$

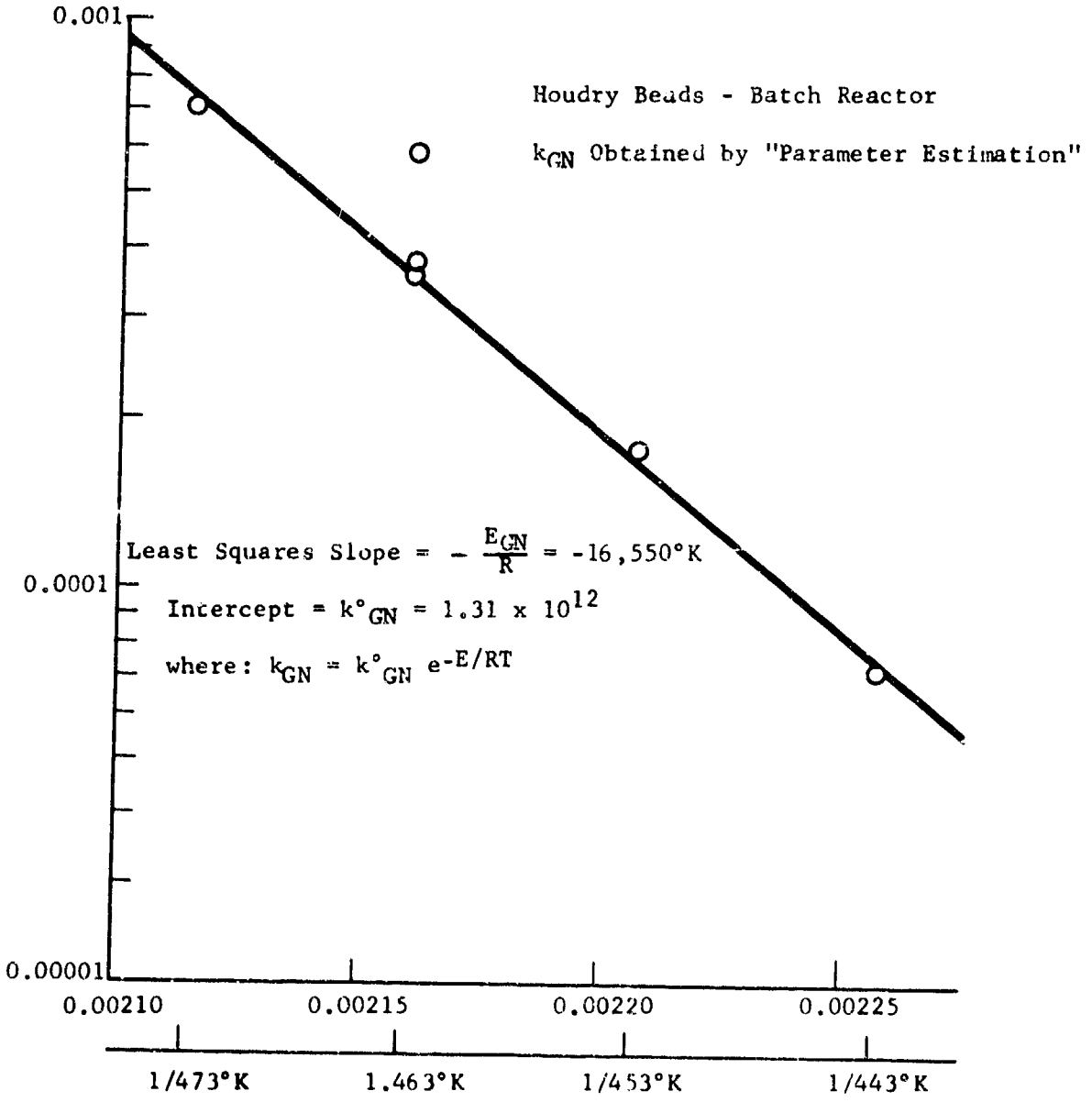



Figure 22. $\ell n\ k_{GN}$ vs 1/Temperature

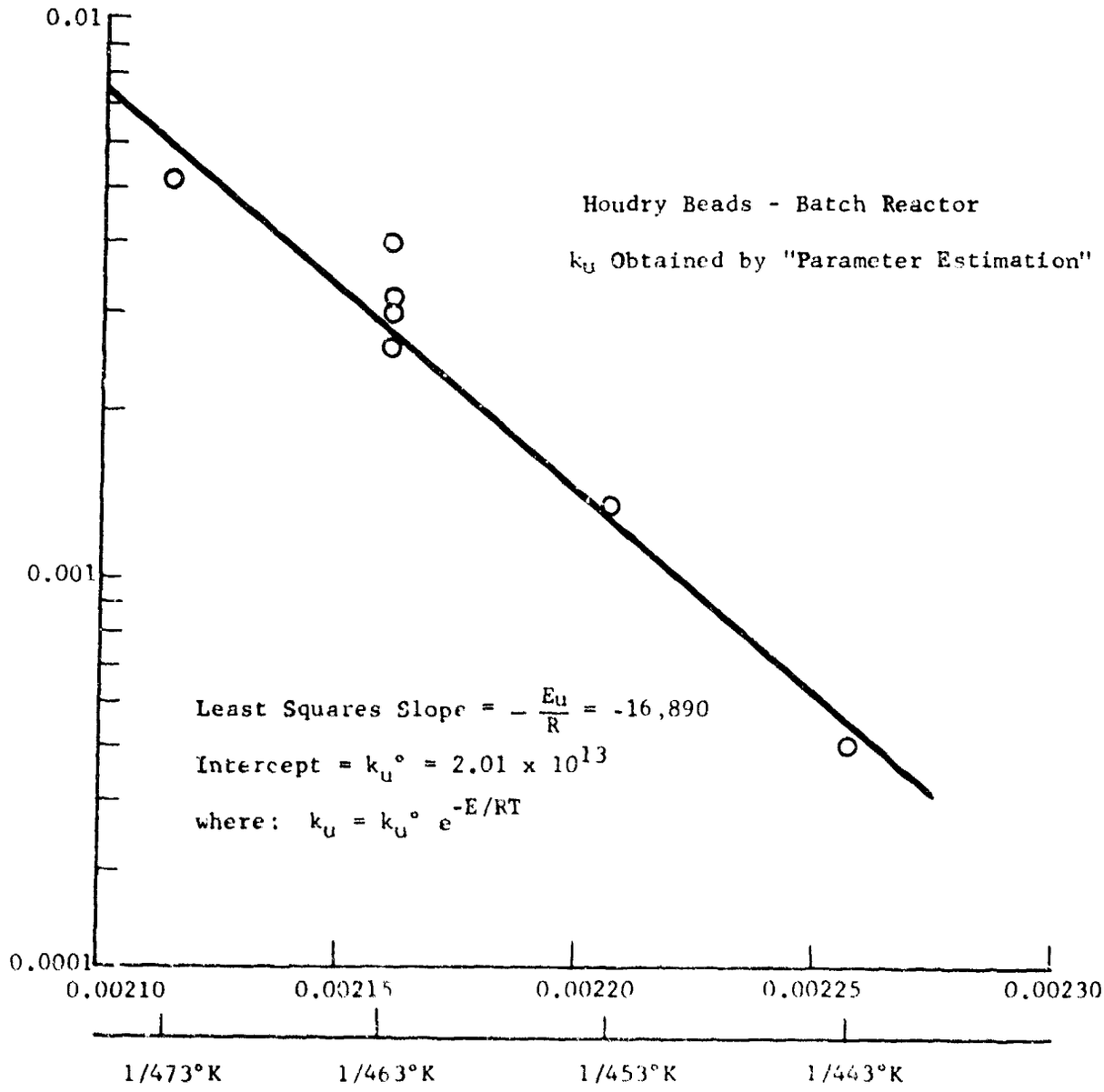



Figure 23. $\ln k_u$ vs 1/Temperature

b. Packed-Bed Model and Bench-Scale Reactor Predictions

A mathematical model of a packed-bed reactor was written to evaluate the performance of such a reactor for producing guanidine nitrate and to determine the effect of various operating conditions on yield and conversion. This model takes into account the variation of the melt volume with conversion and predicts the gas production rate. The model also includes heat transfer from a heating jacket and predicts the axial temperature profile (temperature gradient along the longitudinal axis of the reactor). The details of the derivation and differential equations themselves are presented in Appendix I-1. A listing of the computer programs is given in Appendix I-2.

The program determines the axial concentration profiles and final product flow rates and concentrations.

A computer run simulating a packed-bed reactor 2 inches in diameter and 4 feet long and having a 6-lb/hr feed rate was performed. This was the size of the bench-scale reactor to be employed in scale-up studies as discussed in a subsequent section. The feed was equimolar in ammonium nitrate and urea and contained 9.05 wt. % recycled guanidine nitrate. The computer printout for this run is shown in Table 21.

Additional computer predictions were performed on this 2-inch reactor but at different feed rates and GN feed contents. (The printouts are given in Appendix I-6.) The effect of feed rate on yield and conversion with and without recycled guanidine nitrate is given in Figures 24 and 25, respectively.

At a melt feed rate of 2 lb/hr, the data indicate the yield is in excess of 100% (see Figure 24). It is possible to obtain yields greater than 100% because of the ratio of assumed stoichiometric coefficients (i.e., 2 moles of urea react to form 1 mole of guanidine nitrate) used in the definition of yield. This stoichiometry has not been demonstrated and it was used here so that the results of this report can be compared to those of Roberts and MacKay who also used this factor of 2. Yields in excess of 100% have been obtained experimentally (see Run 36). A melt feed rate of 2 lb/hr corresponds to a residence time of about three hours which constitutes an extrapolation of the batch experimental data.

The data from the 2-inch column run are again plotted in Figures 26 and 27, but here yields and conversions are shown as a function of the nominal residence time. The nominal residence time is defined as the total reactor volume (packing plus voids) over the volumetric feed rate.

TABLE 21

EXAMPLE OF COMPUTER OUTPUT
FOR PACKED BED TUBULAR REACTOR MODEL

```
NI(IORY BEADS
   BULK DENSITY =  2.47 GRAMS/CU. IN.
   VOID FRACTION = .447
TUBE DIAMETER =  2.00 INCHES
FEED TEMPERATURE = 100.0 C.
JACKET TEMPERATURE = 195.0 C.
OVERALL HEAT TRANSFER COEFFICIENT =  1.00 CAL./SQ.IN.-MIN.-C.
```

| DISTANCE INCHES | MOLAR FLOW RATES MOLES/MINUTE MELT | GAS | MOLE FRACTIONS AMMONIUM NITRATE | UREA | GUANIDINE NITRATE | CONVERSION % OF REACT. % OF FED | YIELD % GAS / % OF REAC | TEMPERATURE DEG. C. |
|---|---|---|---|---|---|---|---|---|
| .000 | .624 | .000 | .4730 | .4740 | .0540 | .0000 | .0000 | 191.0 |
| .500 | .620 | .004 | .4741 | .4700 | .0550 | .0113 | .2861 | 189.6 |
| 1.000 | .616 | .008 | .4751 | .4671 | .0578 | .0233 | .2870 | 189.3 |
| 1.500 | .613 | .009 | .4761 | .4643 | .0597 | .0344 | .2874 | 189.1 |
| 2.000 | .610 | .012 | .4770 | .4615 | .0615 | .0452 | .2881 | 188.9 |
| 2.500 | .607 | .014 | .4780 | .4587 | .0633 | .0557 | .2888 | 188.7 |
| 5.000 | .592 | .027 | .4824 | .4454 | .0722 | .1151 | .2941 | 188.1 |
| 7.500 | .578 | .040 | .4865 | .4323 | .0812 | .1715 | .2984 | 188.1 |
| 10.000 | .565 | .052 | .4904 | .4193 | .0903 | .2254 | .3027 | 188.2 |
| 12.500 | .553 | .064 | .4943 | .4064 | .0993 | .2771 | .3071 | 188.3 |
| 15.000 | .541 | .076 | .4982 | .3936 | .1081 | .3266 | .3115 | 188.4 |
| 17.500 | .530 | .088 | .5020 | .3809 | .1169 | .3745 | .3160 | 188.5 |
| 20.000 | .520 | .099 | .5058 | .3683 | .1258 | .4208 | .3206 | 188.6 |
| 22.500 | .510 | .111 | .5095 | .3559 | .1346 | .4658 | .3252 | 188.7 |
| 25.000 | .500 | .121 | .5131 | .3437 | .1432 | .5095 | .3299 | 188.8 |
| 27.500 | .491 | .132 | .5167 | .3317 | .1516 | .5519 | .3347 | 189.0 |
| 30.000 | .483 | .141 | .5202 | .3200 | .1598 | .5930 | .3395 | 189.1 |
| 32.500 | .475 | .151 | .5236 | .3086 | .1678 | .6327 | .3444 | 189.2 |
| 35.000 | .467 | .160 | .5269 | .2975 | .1756 | .6711 | .3493 | 189.4 |
| 37.500 | .460 | .169 | .5301 | .2867 | .1831 | .7082 | .3542 | 189.5 |
| 40.000 | .454 | .177 | .5333 | .2762 | .1905 | .7441 | .3591 | 189.6 |
| 42.500 | .447 | .185 | .5364 | .2661 | .1975 | .7788 | .3640 | 189.8 |
| 45.000 | .442 | .193 | .5394 | .2564 | .2043 | .8124 | .3689 | 189.9 |
| 47.500 | .436 | .200 | .5423 | .2470 | .2107 | .8448 | .3738 | 190.0 |
| 48.000 | .435 | .211 | .5429 | .2452 | .2119 | .8511 | .3748 | 190.1 |

```
MELT FEED RATE =  0.00 LB./HR.
FEED WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5102
                                    UREA =  .3908
                          GUANIDINE NITRATE =  .0990
PRODUCT RATE =  4.800 LB./HR.
PRODUCT WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .4441
                                    UREA =  .1728
                          GUANIDINE NITRATE =  .1429
TOTAL CATALYST WEIGHT = 1111.12 GRAMS
NOMINAL RESIDENCE TIME =  61.25 MINUTES
RATE CONSTANT FOR RN
    FREQUENCY FACTOR =  .1311E 14
    ACTIVATION ENERGY =  .1655E 05
RATE CONSTANT FOR UREA DECOMPOSITION
    FREQUENCY FACTOR =  .2000E 14
    ACTIVATION ENERGY =  .1880E 05
```

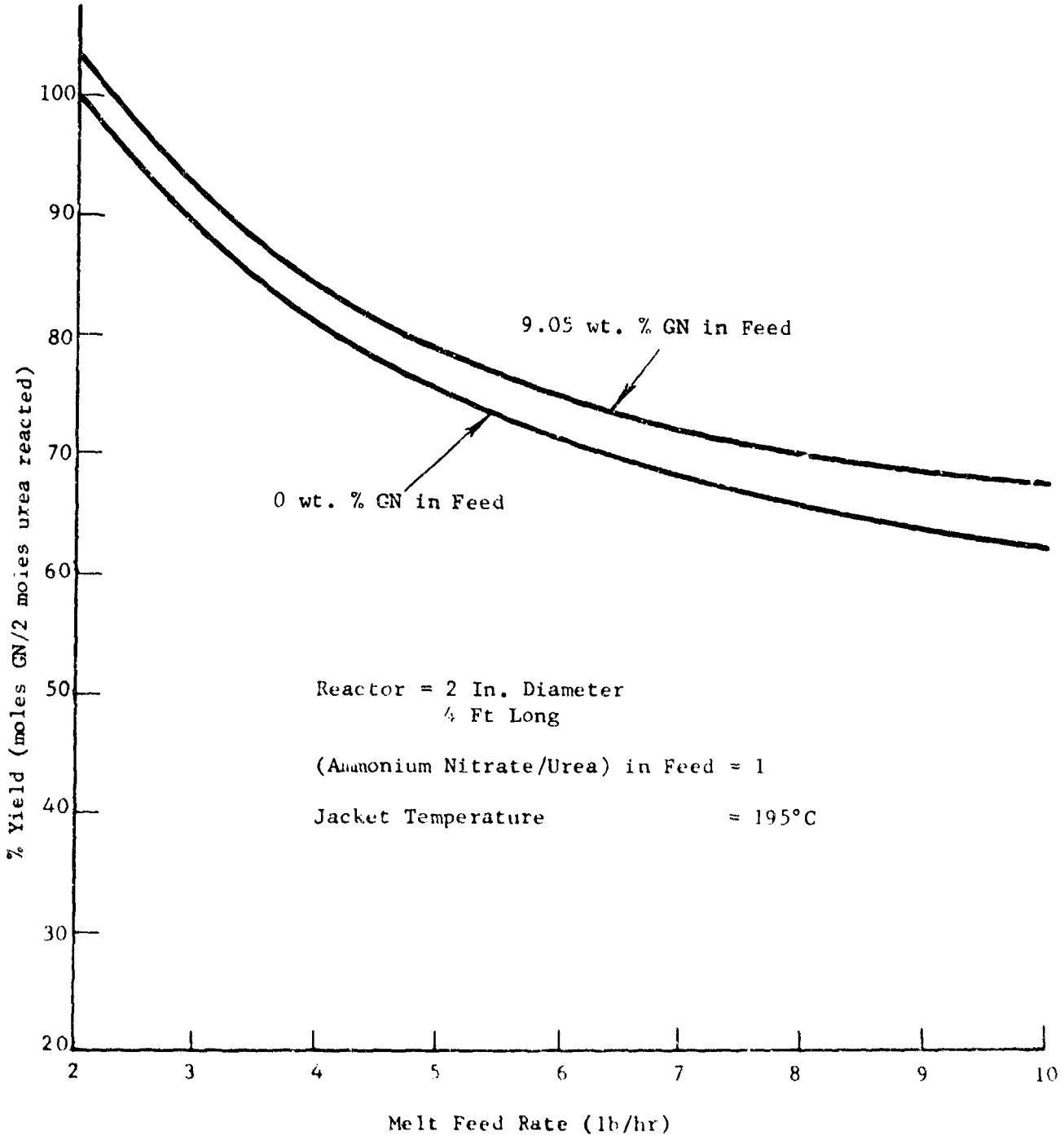



Figure 24. Predicted GN Yield vs Feed Rate

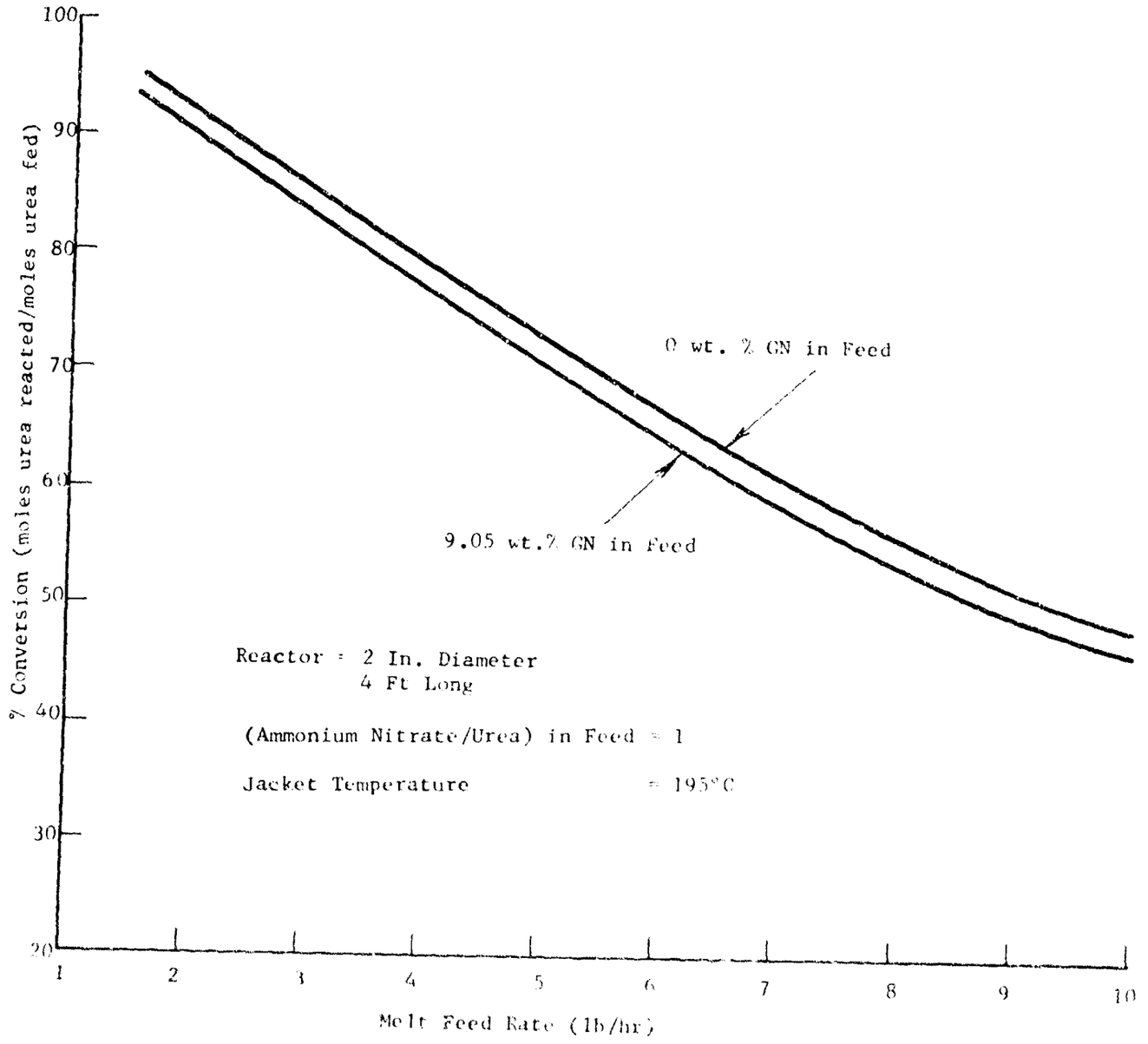



Figure 25. Predicted Urea Conversion vs Feed Rate

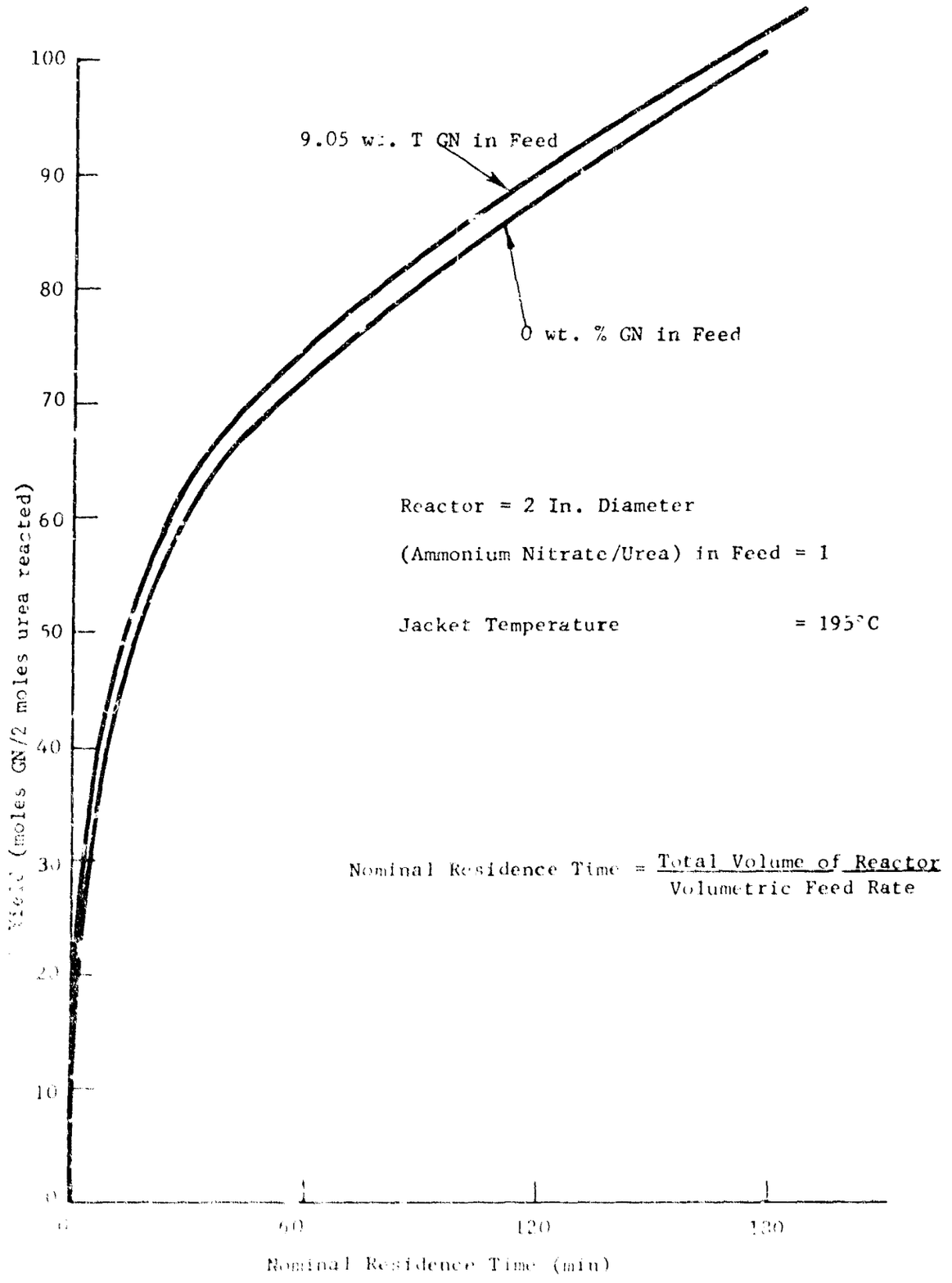



Figure 26. Predicted GN Yield vs Nominal Residence Time

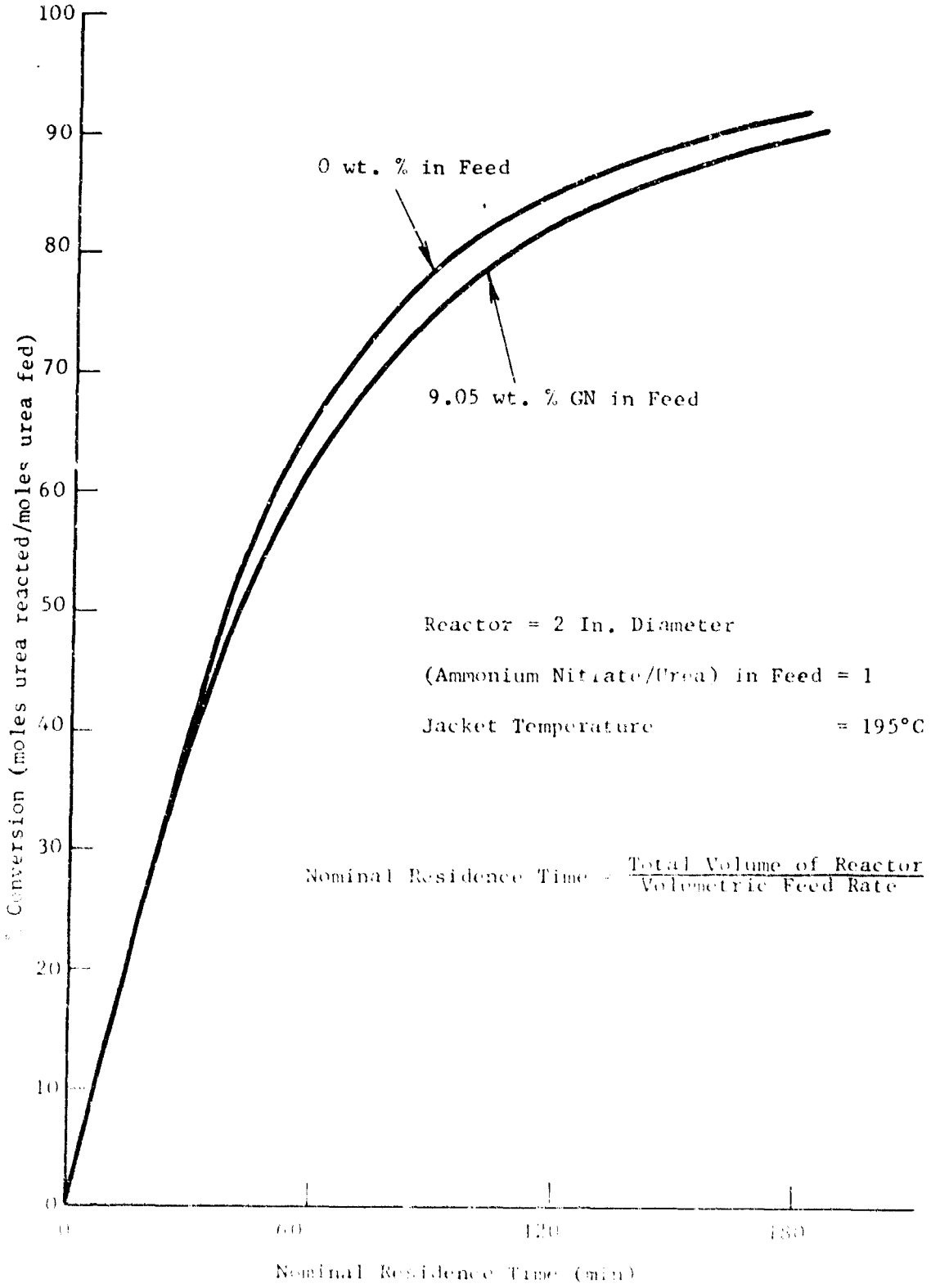



Figure 27. Predicted Urea Conversion vs. Nominal Residence Time

The curves in Figure 28 predict the temperature vs axial position for three different feed rates at a 195°C jacket temperature. All three curves show an initial temperature drop due to the high endothermic heat of reaction. The temperature recovers as the reaction slows down and the heat transfer improves.

Figure 29 shows the variation in overall yield with changing ammonium nitrate/urea ratio in the feed. It should be noted that this overall yield passes through a maximum at an AN/U ratio of 1/1. Above and below the 1/1 ratio, more feed material and therefore larger equipment is required to produce the same quantity of guanidine nitrate.

Several other parameters are of interest in the design and operation of a packed-bed reactor for this system. Since a large volume of gas is generated during a pass through the tubular reactor, the fraction of the void volume occupied by the liquid will vary with axial position. The Reynolds number will therefore also vary with axial position and will give rise to a change in the heat transfer properties of the bed down the length of the reactor. The change in volume of the melt upon reaction also makes a contribution to this phenomenon. The radial temperature profiles and the resulting yields and conversions will be directly affected by such considerations. Prediction of these factors and their effects on the behavior of the system was included in the mathematical model of the packed bed. Numerical results for these parameters are presented in the following section which discusses a candidate for a pilot plant utilizing packed-bed reactors.

### c. Pilot Plant Predictions Using Packed-Bed Model

A mathematical model of a packed-bed reactor was used to obtain data for the design of a pilot plant. The computer output is presented in Table 22.

The following inputs were programmed into the computer run:

| | | |
|---|---|---|
| (1) | Reactor diameter | - 4 in. |
| (2) | Reactor length | - 10 ft |
| (3) | Melt feed rate | - 30 lb/hr |
| (4) | Guanidine nitrate in feed | - 9% by weight |
| (5) | AN/U ratio | - 1/1 |
| (6) | Feed temperature | - 190°F |
| (7) | Jacket temperature | - 195°F |
| (8) | Catalyst per tube | - 11,260 gm (24.8 lb) |
| (9) | Nominal residence time (empty tube volume/volumetric feed rate) | - 125 minutes |

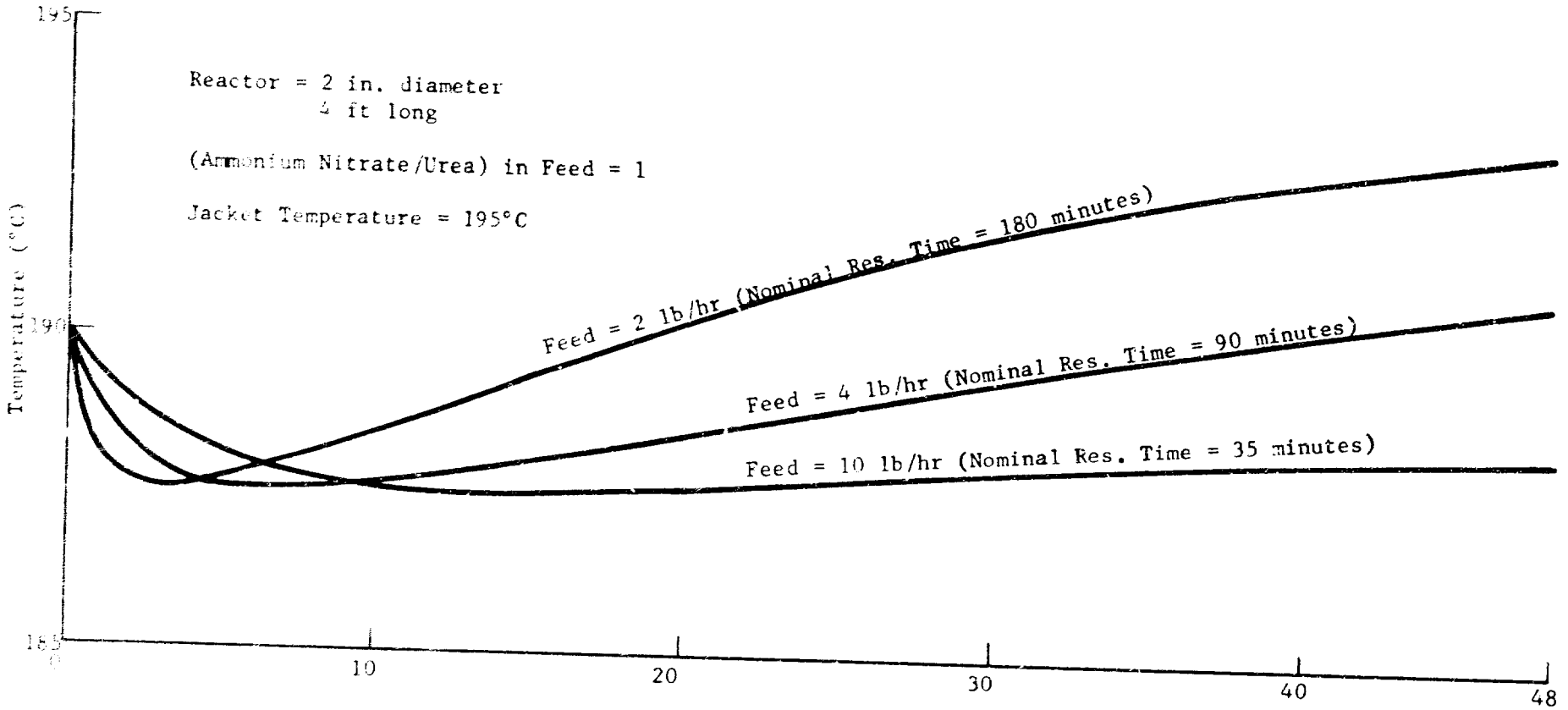



Figure 28. Predicted Temperature vs Distance

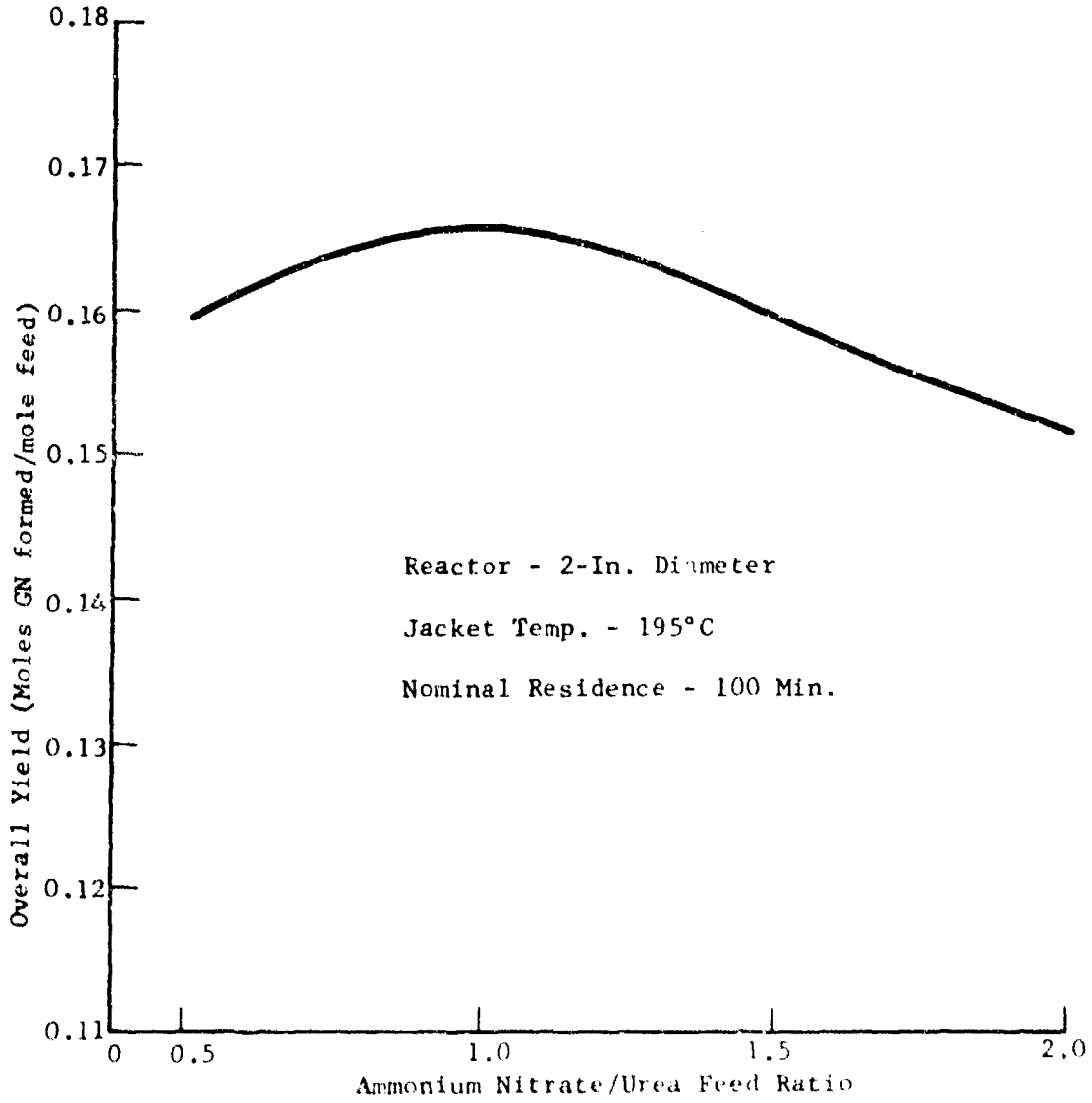



Figure 29. Calculated Overall Yield vs Ammonium Nitrate/Urea Ratio for Tubular Reactor

TABLE 22

MATHEMATICAL MODEL GENERATED COMPUTER OUTPUT
FOR 4-INCH-DIAMETER PACKED BED REACTOR

GUANIDINE NITRATE PROJECT
PACKED BED TUBULAR REACTOR

NOUDRY BEADS
BULK DENSITY = 7.37 GRAMS/CU. IN.
VOID FRACTION = .437
TUBE DIAMETER = 4.03 INCHES
FEED TEMPERATURE = 190.0 C.
JACKET TEMPERATURE = 195.0 C.
OVERALL HEAT TRANSFER COEFFICIENT = 1.08 CAL./SQ.IN.-MIN.-C.

| DISTANCE INCHES | MOLAR FLOW RATES MOLES/MINUTE MELT | GAS | MOLE FRACTIONS AMMONIUM NITRATE | UREA | GUANIDINE NITRATE | CONVERSION M.U REAC/ M.U FED | YIELD M. GN/ M. U REAC | TEMPERATURE DEG. C. |
|---|---|---|---|---|---|---|---|---|
| .000 | 3.115 | .000 | .4730 | .4730 | .0540 | .0000 | .0000 | 190.0 |
| .040 | 3.114 | .001 | .4731 | .4726 | .0541 | .0008 | .2852 | 190.0 |
| .080 | 3.113 | .002 | .4731 | .4726 | .0543 | .0016 | .2852 | 189.9 |
| .120 | 3.112 | .003 | .4732 | .4724 | .0544 | .0023 | .2853 | 189.9 |
| .160 | 3.110 | .004 | .4733 | .4722 | .0545 | .0031 | .2853 | 189.9 |
| .200 | 3.109 | .005 | .4733 | .4720 | .0546 | .0039 | .2854 | 189.8 |
| 6.200 | 2.988 | .129 | .4859 | .4470 | .0712 | .0995 | .2940 | 186.8 |
| 12.200 | 2.855 | .235 | .4886 | .4250 | .0864 | .1764 | .3014 | 186.1 |
| 18.200 | 2.754 | .335 | .4946 | .4038 | .1016 | .2454 | .3087 | 186.1 |
| 24.200 | 2.660 | .431 | .4998 | .3829 | .1173 | .3096 | .3161 | 186.3 |
| 30.201 | 2.575 | .525 | .5043 | .3624 | .1333 | .3668 | .3237 | 186.5 |
| 36.200 | 2.496 | .618 | .5081 | .3422 | .1497 | .4203 | .3315 | 186.7 |
| 42.199 | 2.424 | .704 | .5111 | .3227 | .1662 | .4692 | .3394 | 187.0 |
| 48.198 | 2.358 | .789 | .5133 | .3038 | .1829 | .5138 | .3475 | 187.3 |
| 54.197 | 2.298 | .871 | .5147 | .2857 | .1996 | .5543 | .3556 | 187.6 |
| 60.196 | 2.244 | .951 | .5153 | .2685 | .2161 | .5910 | .3639 | 187.8 |
| 66.196 | 2.196 | 1.027 | .5152 | .2523 | .2325 | .6241 | .3721 | 188.1 |
| 72.197 | 2.151 | 1.100 | .5145 | .2370 | .2485 | .6540 | .3804 | 188.4 |
| 78.198 | 2.112 | 1.169 | .5131 | .2227 | .2642 | .6808 | .3886 | 188.7 |
| 84.200 | 2.076 | 1.236 | .5112 | .2093 | .2795 | .7051 | .3967 | 189.0 |
| 90.201 | 2.044 | 1.300 | .5087 | .1969 | .2943 | .7268 | .4048 | 189.2 |
| 96.202 | 2.015 | 1.362 | .5058 | .1854 | .3087 | .7464 | .4127 | 189.5 |
| 102.203 | 1.989 | 1.420 | .5027 | .1748 | .3225 | .7640 | .4204 | 189.7 |
| 108.205 | 1.966 | 1.476 | .4993 | .1649 | .3358 | .7799 | .4281 | 190.0 |
| 114.206 | 1.945 | 1.529 | .4956 | .1559 | .3486 | .7942 | .4355 | 190.2 |
| 120.007 | 1.926 | 1.578 | .4918 | .1478 | .3604 | .8068 | .4425 | 190.4 |

MELT FEED RATE = 30.00 LB./HR.
FEED WEIGHT FRACTIONS = AMMONIUM NITRATE = .5107
UREA = .3894
GUANIDINE NITRATE = .0905
PRODUCT RATE = 23.488 LB./HR.
PRODUCT WEIGHT FRACTIONS = AMMONIUM NITRATE = .4488
UREA = .0982
GUANIDINE NITRATE = .4770
TOTAL CATALYST WEIGHT =11259.34 GRAMS
NOMINAL RESIDENCE TIME = 125.11 MINUTES
RATE CONSTANT FOR GN
FREQUENCY FACTOR = .1311E 13
ACTIVATION ENERGY = .1895E 05
RATE CONSTANT FOR UREA DECOMPOSITION
FREQUENCY FACTOR = .2000E 14
ACTIVATION ENERGY = .1860E 05

The computer output (Table 22) provided the (1) molar gas and melt flow rate; (2) mole fractions of ammonium nitrate, urea, and guanidine nitrate; (3) conversion of urea (moles of urea reacted/mole of urea fed); (4) yield (moles of guanidine nitrate formed/mole of urea reacted); and (5) area-weighted average radial temperature as functions of the axial position in the column.

Note that the yields shown in Table 22 do not contain the ratio of the assumed stoichiometric coefficients. To be comparable to yields previously presented, these values should be multiplied by 2.

The product flow from the reactor was 23.5 lb/hr. It consisted of 42.7 wt. % ammonium nitrate, 9.6 wt. % urea and 47.7 wt. % guanidine nitrate. The yield was 88.5%, and the conversion was 80.7%. The guanidine nitrate produced during a pass through this reactor was 8.5 lb/hr. For a pilot plant producing 50 lb/hr of guanidine nitrate, six such tubes in parallel would be required.

The computer model was also programmed to give output data regarding (1) fraction of the void volume occupied by liquid ($R_L$), (2) Reynolds number for the melt based on $R_L$, and (3) radial temperature profiles, all as a function of axial position in the reactor column.

A computer printout of the radial temperature profiles vs axial position is given in Table 23. These and other output data are also presented in the following graphical plots:

(1) $R_L$ vs axial position (Figure 30)

(2) Reynolds Number vs axial position (Figure 31)

(3) Radial Temperatures vs axial position (Figure 32)

(4) Average Radial Temperature and Centerline Temperature vs axial position (Figure 33)

(5) Mole Fractions of AN, U, and GN vs axial position (Figure 34)

The following conclusions were drawn from these data:

(1) The $R_L$ dropped rapidly from 1.0 to 0.1 in moving just one-half the distance up the tube due to the large volume (0.95 mole/min) of gas generated in this section.

TABLE 23

COMPUTER OUTPUT PREDICTING RADIAL TEMPERATURE PROFILE
AS FUNCTION OF BED HEIGHT FOR 4-INCH-DIAMETER PACKED BED REACTOR

| DISTANCE | RADIAL TEMPERATURE PROFILES | | | | | |
|---|---|---|---|---|---|---|
| | R = .000 | R = .403 | R = .805 | R = 1.208 | R = 1.610 | R = 2.013 |
| .000 | 190.000 | 190.000 | 190.000 | 190.000 | 190.000 | 190.000 |
| .040 | 189.934 | 189.934 | 189.934 | 189.934 | 189.939 | 190.161 |
| .080 | 189.868 | 189.868 | 189.868 | 189.869 | 189.893 | 190.221 |
| .120 | 189.803 | 189.802 | 189.802 | 189.806 | 189.859 | 190.248 |
| .160 | 189.737 | 189.737 | 189.737 | 189.746 | 189.831 | 190.260 |
| .200 | 189.672 | 189.672 | 189.673 | 189.690 | 189.806 | 190.264 |
| 6.200 | 185.520 | 185.620 | 185.918 | 186.419 | 187.127 | 188.065 |
| 12.200 | 184.757 | 184.866 | 185.196 | 185.747 | 186.518 | 187.508 |
| 18.200 | 184.734 | 184.844 | 185.176 | 185.729 | 186.502 | 187.494 |
| 24.200 | 184.923 | 185.032 | 185.358 | 185.900 | 186.658 | 187.630 |
| 30.201 | 185.180 | 185.286 | 185.603 | 186.132 | 186.870 | 187.816 |
| 36.200 | 185.466 | 185.569 | 185.877 | 186.389 | 187.105 | 188.023 |
| 42.199 | 185.760 | 185.868 | 186.166 | 186.661 | 187.354 | 188.242 |
| 48.198 | 186.081 | 186.177 | 186.465 | 186.944 | 187.612 | 188.469 |
| 54.197 | 186.400 | 186.492 | 186.760 | 187.230 | 187.874 | 188.700 |
| 60.196 | 186.720 | 186.818 | 187.044 | 187.508 | 188.147 | 188.941 |
| 66.196 | 187.055 | 187.140 | 187.306 | 187.822 | 188.416 | 189.178 |
| 72.197 | 187.381 | 187.453 | 187.706 | 188.115 | 188.685 | 189.415 |
| 78.198 | 187.703 | 187.781 | 188.016 | 188.406 | 188.951 | 189.650 |
| 84.200 | 188.018 | 188.093 | 188.317 | 188.690 | 189.212 | 189.880 |
| 90.201 | 188.326 | 188.397 | 188.612 | 188.968 | 189.467 | 190.105 |
| 96.202 | 188.624 | 188.692 | 188.896 | 189.237 | 189.713 | 190.323 |
| 102.203 | 188.912 | 188.977 | 189.173 | 189.497 | 189.951 | 190.533 |
| 108.205 | 189.189 | 189.251 | 189.437 | 189.747 | 190.180 | 190.736 |
| 114.206 | 189.453 | 189.513 | 189.690 | 189.985 | 190.400 | 190.930 |
| 120.207 | 189.694 | 189.750 | 189.920 | 190.203 | 190.598 | 191.115 |

NOTES:

R = .000 is the centerline

R = 2.013 is the wall.

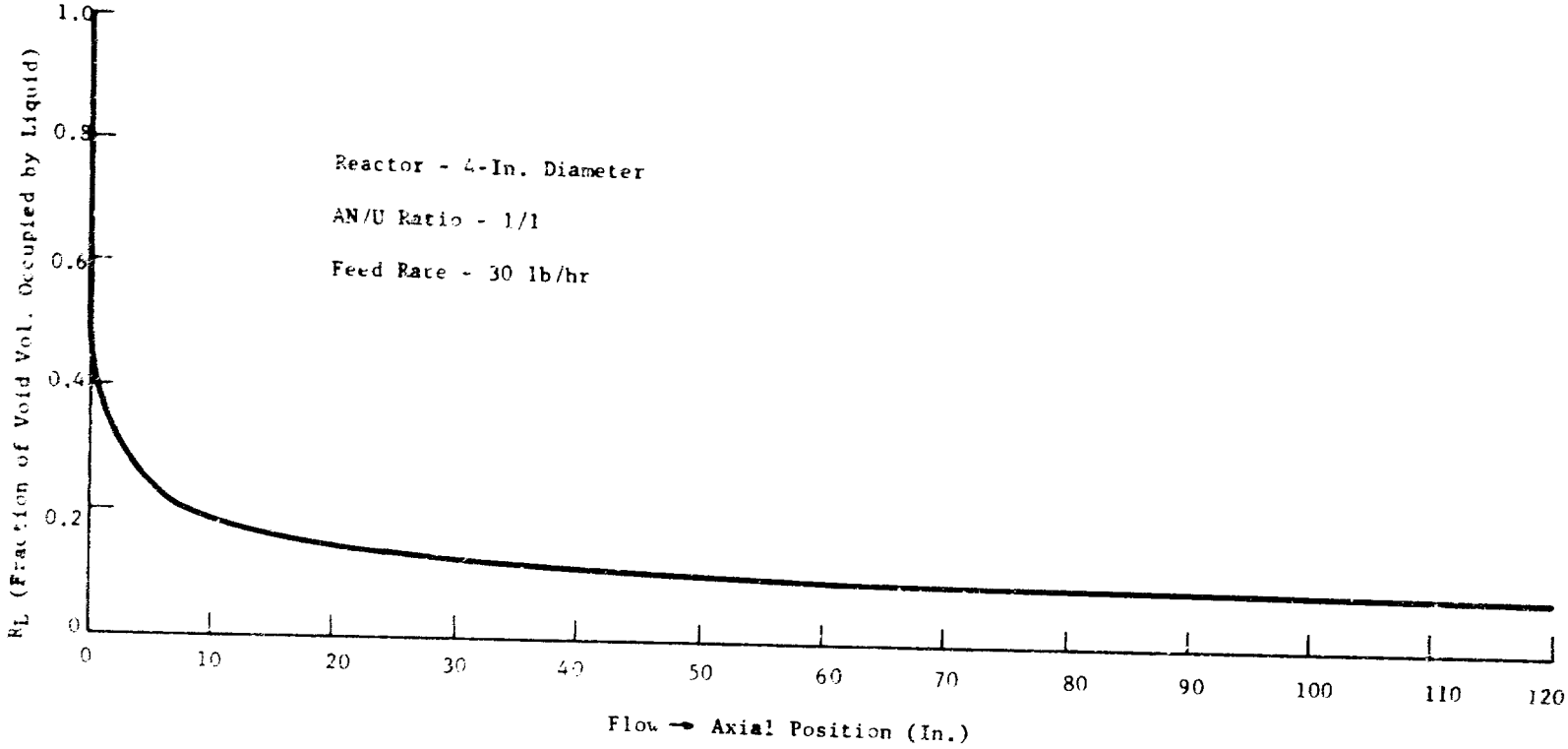



Figure 30. Calculated Fraction of Void Volume Occupied by Liquid ($R_L$) Vs Axial Position in a Tubular Reactor

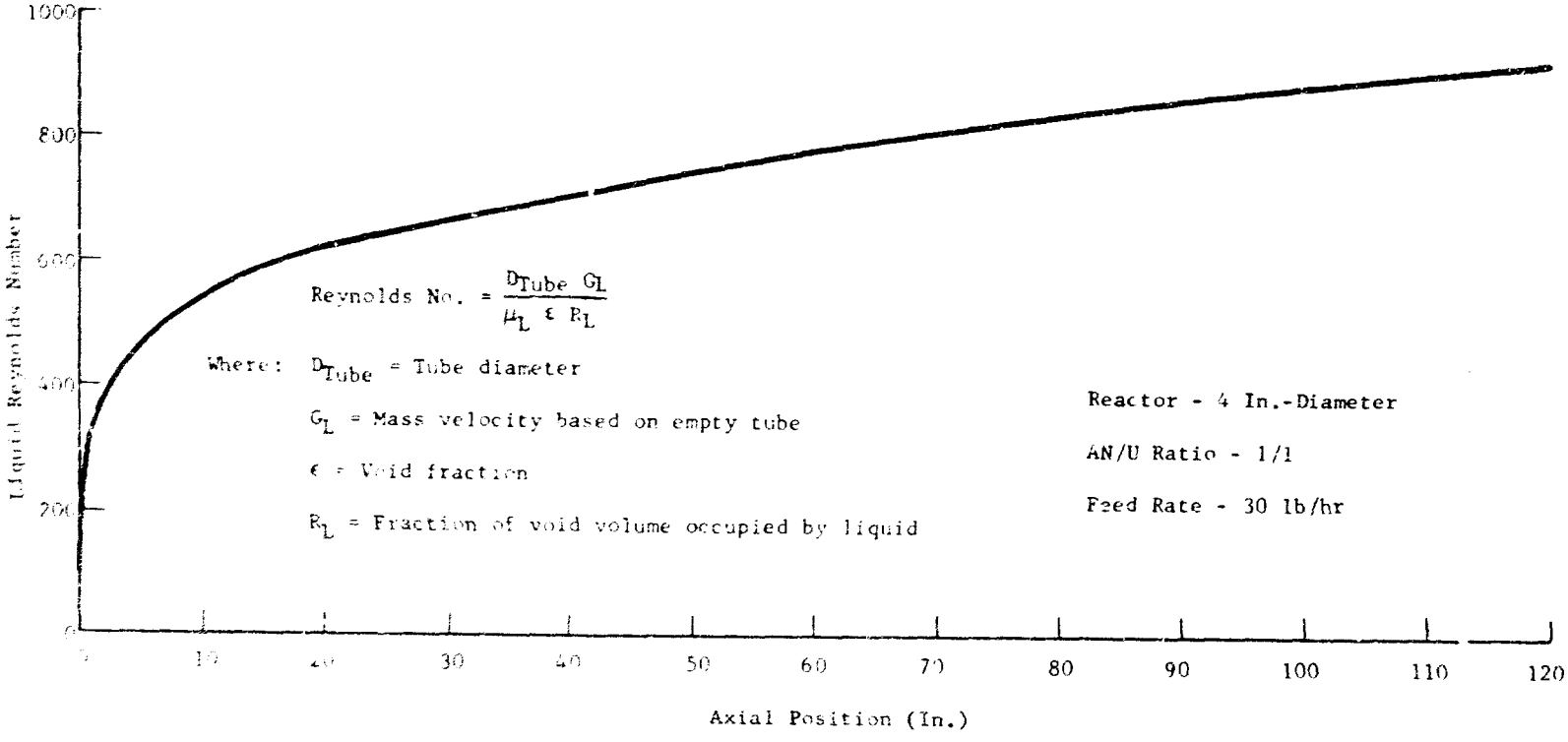



Figure 31. Calculated Liquid Reynolds Number Vs Axial Position for Tubular Reactor

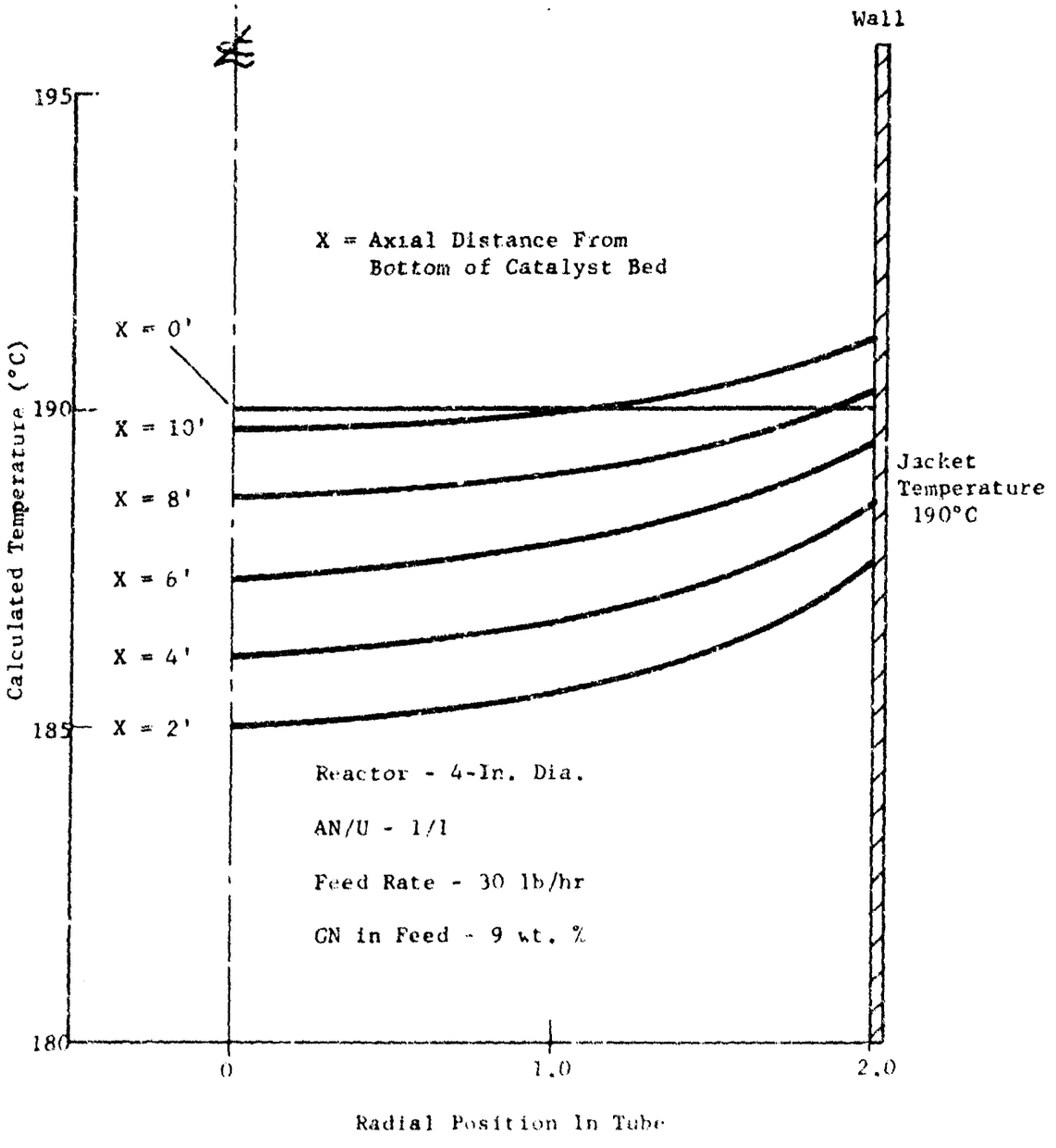



Figure 32. Calculated Radial Temperature Profiles for Tubular Reactor

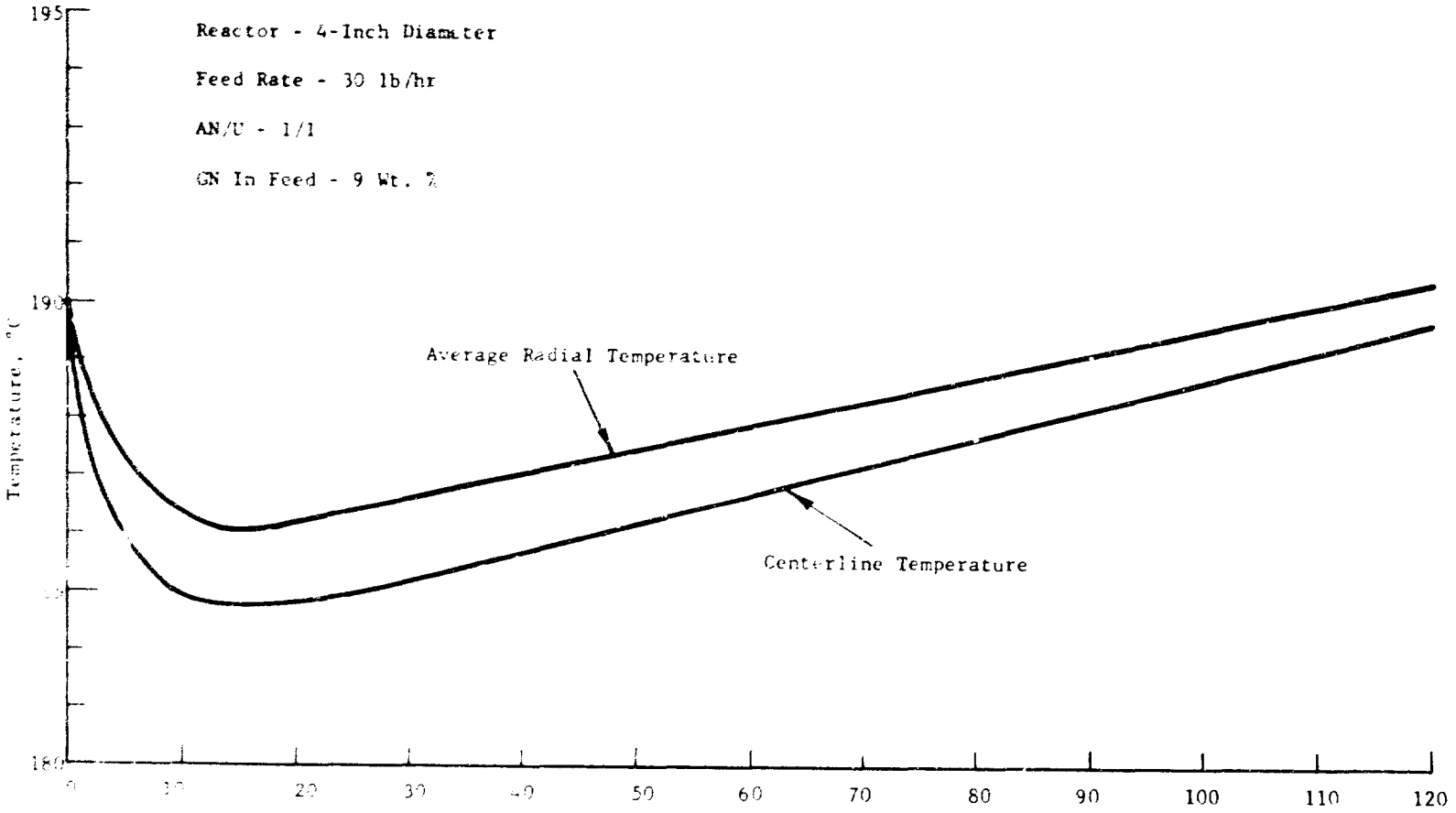



Figure 33. Calculated Average Radial and Centerline Temperatures Vs Tubular Reactor Axial Position

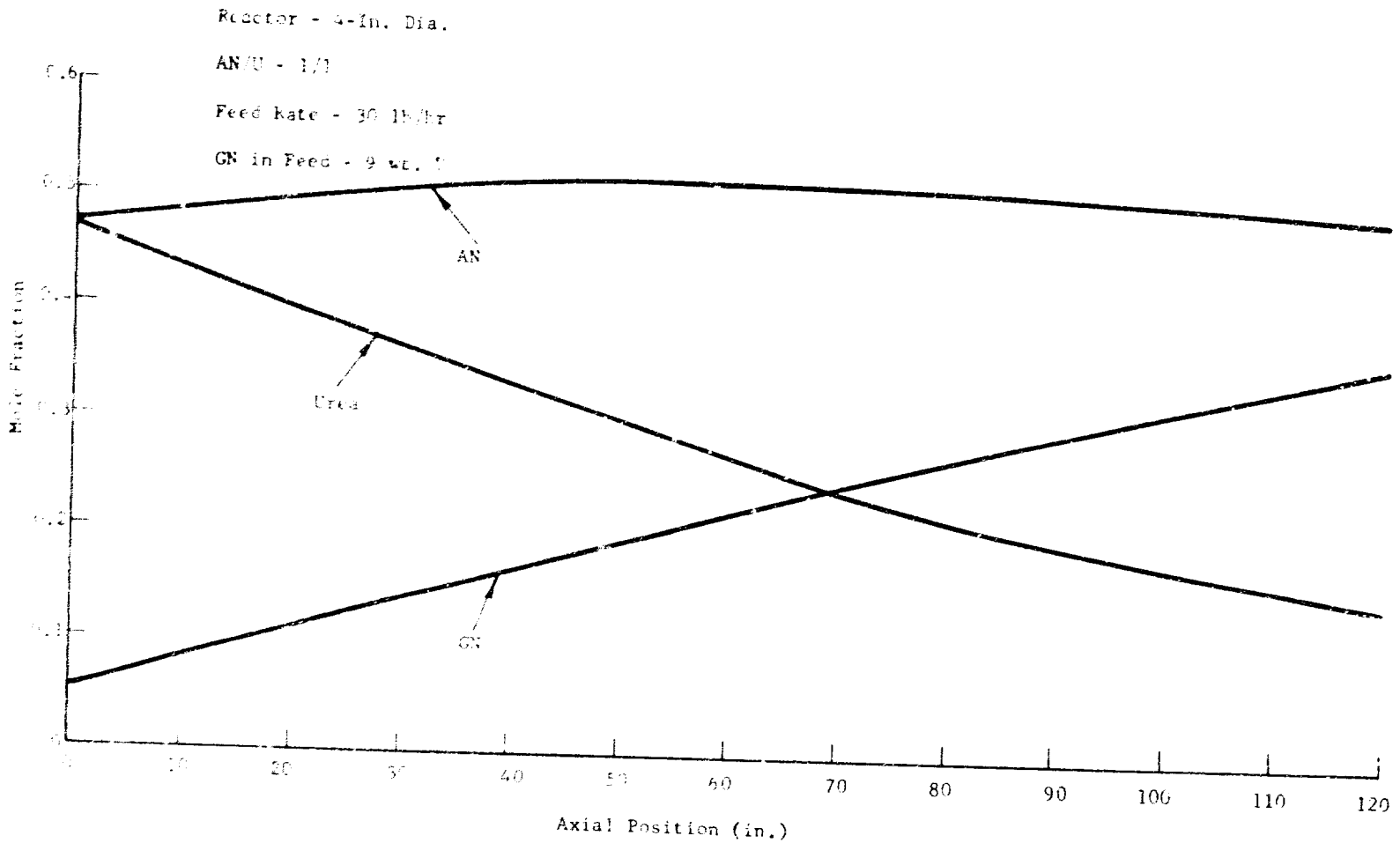



Figure 34. Calculated Axial Concentration Profiles for Tubular Reactor

(2) The Reynolds number increased by nearly an order of magnitude in proceeding up the reactor. Such an increase was advantageous in providing improved radial mixing and greater effective heat and mass transfer in the radial direction. The radial temperature profiles reflected this behavior.

(3) If the feed was introduced at 190°C, the centerline temperature dropped to 185°C at the 2-ft level. From this point the temperature steadily increased to approximately 190°C at the 10-ft level.

(4) The radial profiles became increasingly flat with an increasing axial position. This is due in part to the increase in radial mixing.

d. Continuous Stirred Tank Model

A computer model was prepared simulating the performance of one to three identical stirred tank reactors in series.

1 Conversion and Yield

A detailed description of the model is given in Appendix I-3. A listing of the computer model is given in Appendix I-4.

The model was programmed to give information on yield and conversion as a function of AN/U ratio and catalyst/feed ratio. The melt feed rate was held constant at 1 mole/minute for all simulations.

The computer runs produced data which are shown in graphical form as follows:

(1) GN Yield[a] vs AN/U Ratio at Different Catalyst/Feed Ratios (Figure 35)

(2) Urea Conversion[b] vs AN/U Ratio at Different Catalyst/Feed Ratios (Figure 36)

(3) Inverse of Overall Yield[c] vs AN/U Ratio at Different Catalyst/Feed Ratios (Figure 37)

---

[a]Yield - (moles GN/2 moles urea reacted) 100

[b]Conversion - (moles urea reacted/mole urea fed) 100

[c]Overall Yield - (moles GN formed/mole of feed) 100

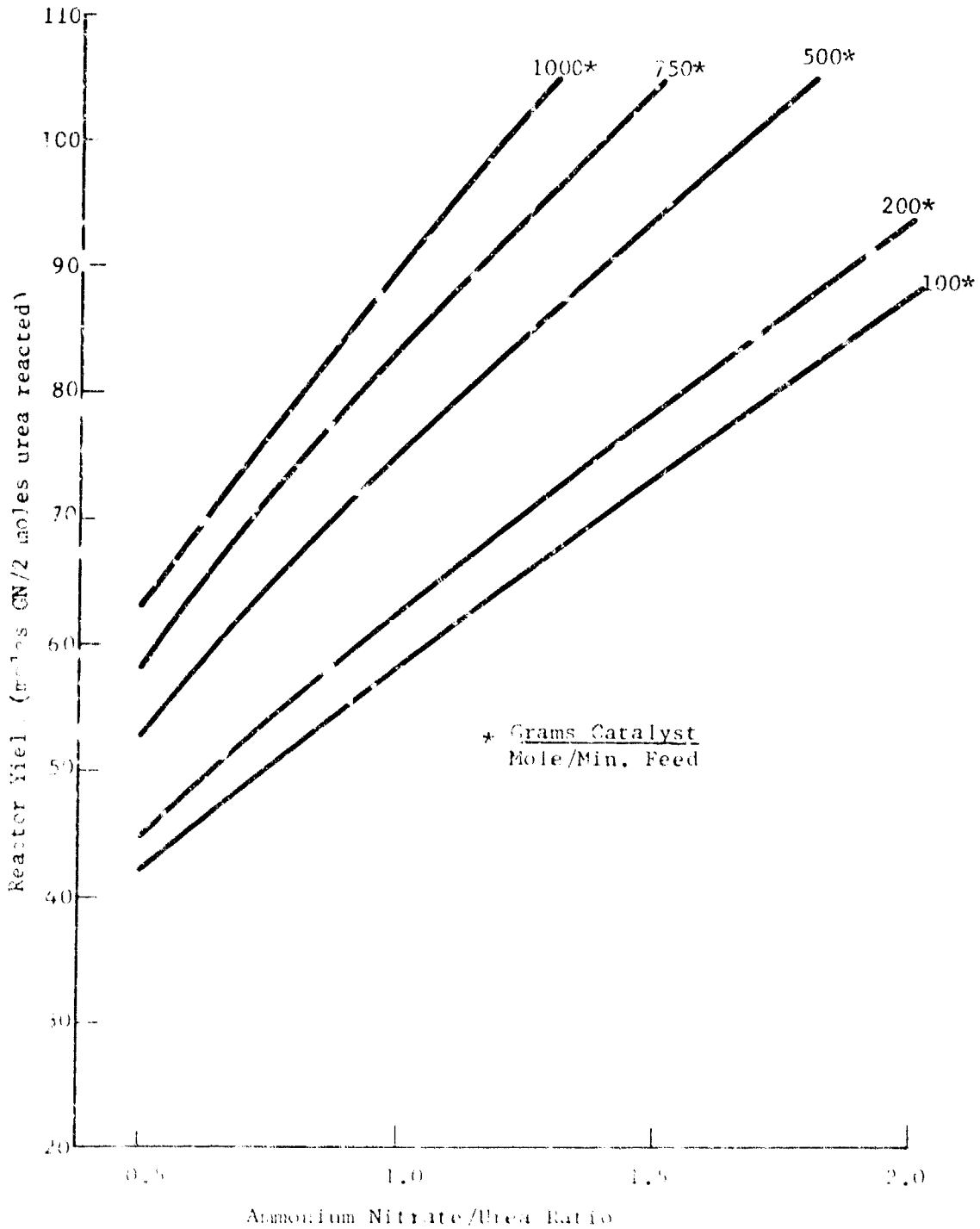



Figure 15. GN Yield (Calculated) vs Ammonium Nitrate/Urea Ratio for Series Stirred Reactors at Different Catalyst Levels

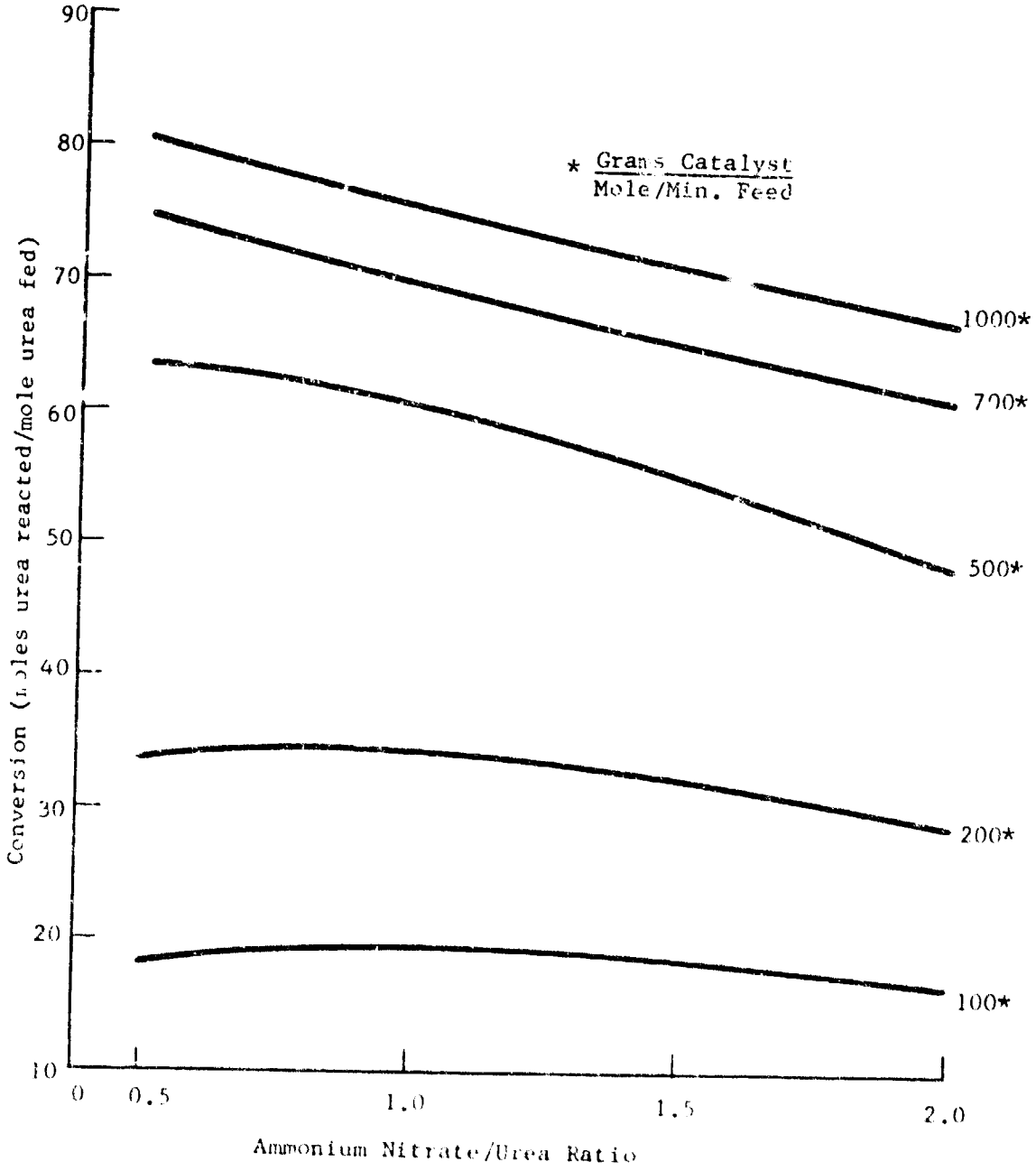



Figure 36. Urea Conversion (Calculated) vs Ammonium Nitrate/Urea Ratio for Series Stirred Reactors at Different Catalyst Levels

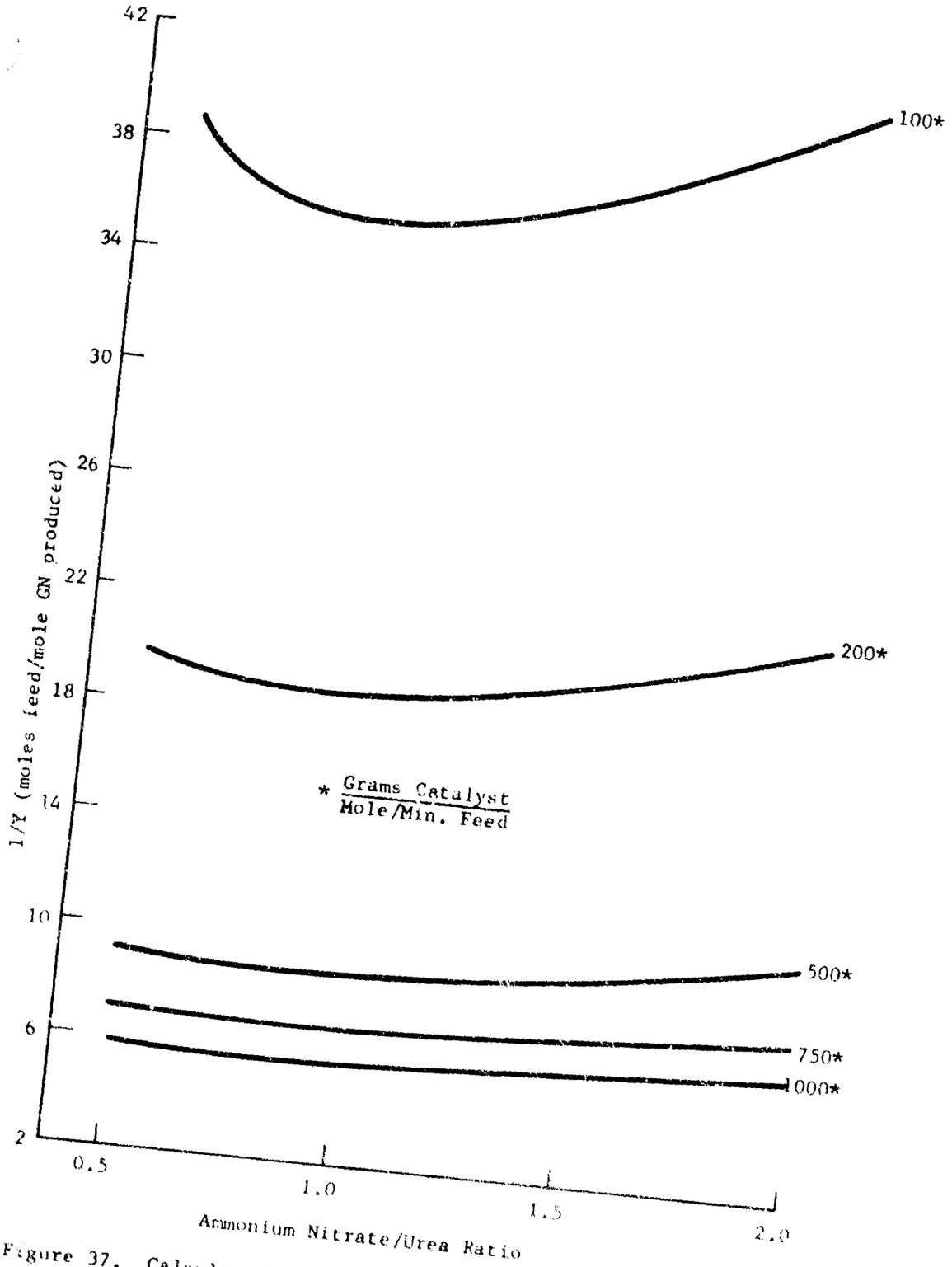



Figure 37. Calculated 1/Overall Yield vs Ammonium Nitrate/Urea Ratio for Series Stirred Tank Reactors at Different Catalyst Levels

These graphs illustrate the following relationships:

(1) The yield increased as the AN/U ratio and catalyst/feed ratio increased.

(2) The conversion in general decreased with increasing ammonium nitrate/urea ratio and increased with increased catalyst charge.

(3) The overall yield passed through a maximum at about a 1/1 AN/U ratio. This was also the case in the packed-bed simulations.

## 2 Pilot Plant Simulation

The model was next programmed to simulate a pilot-plant design employing three stirred tanks. A temperature of 190°C was maintained in each tank. One thousand grams of catalyst (Houdry beads) were charged into each tank, and the feed rate to the first reactor was 1 mole/min. of AN/U - 1/1 containing 10% guanidine nitrate. The catalyst filled 50% of each of the 1.175-gallon reactors. The computer output (see Tables 24, 25 and 26) determined the overall conversion to be from 38.1% to 59.3% to 71.3% for the three tanks. The yield in each tank increased from 76.1% to 85.2% to 93.3%. The final product flow rate was 7.88 lb/hr per mole/min. of feed and contained 42.1 wt. % ammonium nitrate, 13 wt. % urea and 44.3 wt. % guanidine nitrate.

From this program it is concluded that to produce 50 lb/hr of guanidine nitrate, a pilot plant would have to be 20 times as large as the system simulated. Therefore, three 25-gallon reactors would be needed. The feed rate to the first reactor would be 193 lb/hr, and the product rate from the third reactor would be 158 lb/hr. The catalyst in each vessel would be 20,000 gm (44 lb).

### e. Comparison of Stirred Tank and Packed-Bed Reactors

A summary and comparison of the findings from the previous two sections are presented in Table 27.

These data, plus other considerations, were used in selecting the reactor system for the pilot plant. A discussion of the rationale for the final reactor design selection appears later under Phase II.

TABLE 24

COMPUTER OUTPUT FOR PILOT PLANT
STIRRED TANK REACTOR - FIRST REACTOR

```
  GUANIDINE NITRATE PROJECT
 CONTINUOUS STIRRED  TANKS

HOUDRY BEADS
  BULK DENSITY =  7.37 GRAMS/CU.IN.
  PACKING POROSITY =   .80 VOL.PCT.
NOTE = CATALYST WEIGHT, NOMINAL REACTOR VOLUME, AND PRODUCT FLOW RATES ARE GIVEN
    WITH RESPECT TO THE MOLAR FEED RATE TO THE FIRST REACTOR.


REACTOR 1      CATALYST =  1000.00 GRAMS,     .5873 GAL.
               TEMPERATURE = 190.0 C.
               NOMINAL VOLUME =    .1570 CU. FT.,   1.1747 GAL.

         MELT FEED RATE = 9.6720 LB./HR.                 WEIGHT FRACTIONS
                                                AMMONIUM NITRATE =  .5142
                                                        UREA =  .3857
                                               GUANIDINE NITRATE =  .1001

         MELT FEED RATE = 1.0000 MOLES/MINUTE             MOLE FRACTIONS
                                                AMMONIUM NITRATE =  .4700
                                                        UREA =  .4700
                                               GUANIDINE NITRATE =  .0600

         PRODUCT FLOW RATE = 8.6291 LB./HR.              WEIGHT FRACTIONS
                                                AMMONIUM NITRATE =  .4928
                                                        UREA =  .2675
                                               GUANIDINE NITRATE =  .2397

         PRODUCT FLOW RATE =  .8209 MOLES/MINUTE          MOLE FRACTIONS
                                                AMMONIUM NITRATE =  .4895
                                                        UREA =  .3544
                                               GUANIDINE NITRATE =  .1561

         GAS FLOW RATE =  .2045 MOLES/MINUTE
         TOTAL CONVERSION =  .3611 MOLES UREA REACTED/MOLE UREA FED
         TOTAL YIELD =  .3806 MOLES GN/MOLE UREA REACTED
         RATE CONSTANT FOR GN
              FREQUENCY FACTOR =   .1311E 13
              ACTIVATION ENERGY =   .1655E 05
         RATE CONSTANT FOR UREA DECOMPOSITION
              FREQUENCY FACTOR =   .2009E 14
              ACTIVATION ENERGY =   .1689E 05
```

TABLE 25

COMPUTER OUTPUT FOR PILOT PLANT
STIRRED TANK REACTOR - SECOND REACTOR

```
 GUANIDINE NITRATE PROJECT
 CONTINUOUS STIRRED  TANKS

REACTOR 2      CATALYST =  1000.00 GRAMS.      .5823 GAL.
               TEMPERATURE = 190.0 C.
               NOMINAL VOLUME =     .1570 CU. FT.,    1.1747 GAL.

          MELT FEED RATE = 9.6291 LB./HR.                  WEIGHT FRACTIONS
                                                  AMMONIUM NITRATE =   .4928
                                                              UREA =   .2675
                                                 GUANIDINE NITRATE =   .2397

          MELT FEED RATE =  .8239 MOLES/MINUTE             MOLE FRACTIONS
                                                  AMMONIUM NITRATE =   .4895
                                                              UREA =   .3544
                                                 GUANIDINE NITRATE =   .1561

          PRODUCT FLOW RATE = 8.1196 LB./HR.               WEIGHT FRACTIONS
                                                  AMMONIUM NITRATE =   .4576
                                                              UREA =   .1869
                                                 GUANIDINE NITRATE =   .3555

          PRODUCT FLOW RATE =  .7211 MOLES/MINUTE          MOLE FRACTIONS
                                                  AMMONIUM NITRATE =   .4859
                                                              UREA =   .2651
                                                 GUANIDINE NITRATE =   .2491

          GAS FLOW RATE =  .1522 MOLES/MINUTE
          TOTAL CONVERSION =  .5932 MOLES UREA REACTED/MOLE UREA FED
          TOTAL YIELD =  .4264 MOLES GN/MOLE UREA REACTED
          RATE CONSTANT FOR GN
               FREQUENCY FACTOR =    .1511E 13
               ACTIVATION ENERGY =   .1655E 05
          RATE CONSTANT FOR UREA DECOMPOSITION
               FREQUENCY FACTOR =    .2000E 14
               ACTIVATION ENERGY =   .1688E 05
```

TABLE 26

COMPUTER OUTPUT FOR PILOT PLANT
STIRRED TANK REACTOR - THIRD REACTOR

```
 GUANIDINE NITRATE PROJECT
CONTINUOUS STIRRED  TANKS

REACTOR 3      CATALYST =  1000.00 GRAMS.      .5873 GAL.
               TEMPERATURE = 190.0 C.
               NOMINAL VOLUME =     .1570 CU. FT..    1.1747 GAL.

          MELT FEED RATE = 9.1196 LB./HR.                    WEIGHT FRACTIONS
                                                  AMMONIUM NITRATE =  .4576
                                                              UREA =  .1869
                                                 GUANIDINE NITRATE =  .3555

          MELT FEED RATE =  .7211 MOLES/MINUTE               MOLE FRACTIONS
                                                  AMMONIUM NITRATE =  .4869
                                                              UREA =  .2651
                                                 GUANIDINE NITRATE =  .2481

          PRODUCT FLOW RATE = 7.5802 LB./HR.                 WEIGHT FRACTIONS
                                                  AMMONIUM NITRATE =  .4211
                                                              UREA =  .1357
                                                 GUANIDINE NITRATE =  .4433

          PRODUCT FLOW RATE =  .6647 MOLES/MINUTE            MOLE FRACTIONS
                                                  AMMONIUM NITRATE =  .4717
                                                              UREA =  .2027
                                                 GUANIDINE NITRATE =  .3257

          GAS FLOW RATE =  .1127 MOLES/MINUTE
          TOTAL CONVERSION =  .7134 MOLES UREA REACTED/MOLE UREA FED
          TOTAL YIELD =  .4566 MOLES GN/MOLE UREA REACTED
          RATE CONSTANT FOR GN
               FREQUENCY FACTOR =    .1311E 13
               ACTIVATION ENERGY =   .1655E 05
          RATE CONSTANT FOR UREA DECOMPOSITION
               FREQUENCY FACTOR =    .2009E 14
               ACTIVATION ENERGY =   .1689E 05
```

TABLE 27

COMPARISON OF PROPOSED PILOT PLANT GN REACTORS

| | PACKED BED REACTOR | STIRRED TANK REACTOR |
|---|---|---|
| Size | 6 units, each 4-inch diameter, 10 ft. long | 3 units, each 25 gallons |
| Total Catalyst Charge | 148.8 lb. | 132.0 lb. (11.7 gallons) |
| Melt Feed Rate | 180 lb./hr. | 193 lb./hr. |
| Melt Feed Composition | AN/U = 1/1<br>52.0 % Wt. AN<br>39.0 % Wt. U<br>9.0 % Wt. GN | AN/U = 1/1<br>51.4 % Wt. AN<br>38.6 % Wt. U<br>10.0 % Wt. GN |
| Product Rate | 141 lb./hr. | 158 lb./hr. |
| Product Composition | 42.7 % Wt. AN<br>9.6 % Wt. U<br>47.7 % Wt. GN | 42.1 % Wt. AN<br>13.6 % Wt. U<br>44.3 % Wt. GN |
| GN Production Rate | 51 lb./hr. | 51 lb./hr. |
| Conversion (1) | 80.7% | 71.3% |
| Yield (2) | 88.5% | 93.3% |

(1) Conversion = (Moles Urea Reacted/Mole Urea Fed)100
(2) Yield = (Moles GN/2 moles Urea Reacted)100

## 4. Part 3 - Bench-Scale Reactor Studies

### a. Equipment Description

A tubular reactor concept for reacting AN and urea to produce GN was proposed originally for the pilot plant and subsequent production plant scale-up. This type of design offers advantages with respect to simplicity of design, reliable scale-up, costs and safety. A 2 inch diameter x 4 ft tall tubular reactor was installed and operated to demonstrate the feasibility of this concept, to verify laboratory data, and to prepare for pilot-plant design.

A schematic of bench-scale reactor and auxiliary equipment is shown in Figure 38. A schematic of the reactor is shown in Figure 39. Solid AN and urea were charged to the feed tanks, melted and then pumped at a desired rate through a preheater and into the bottom of the reactor. The reactor was designed for a nominal production rate of 5 lb GN/hr. Off-gas ($NH_3$ and $CO_2$) from the reactor was collected as solid ammonium carbamate (AC) in a dry ice trap.

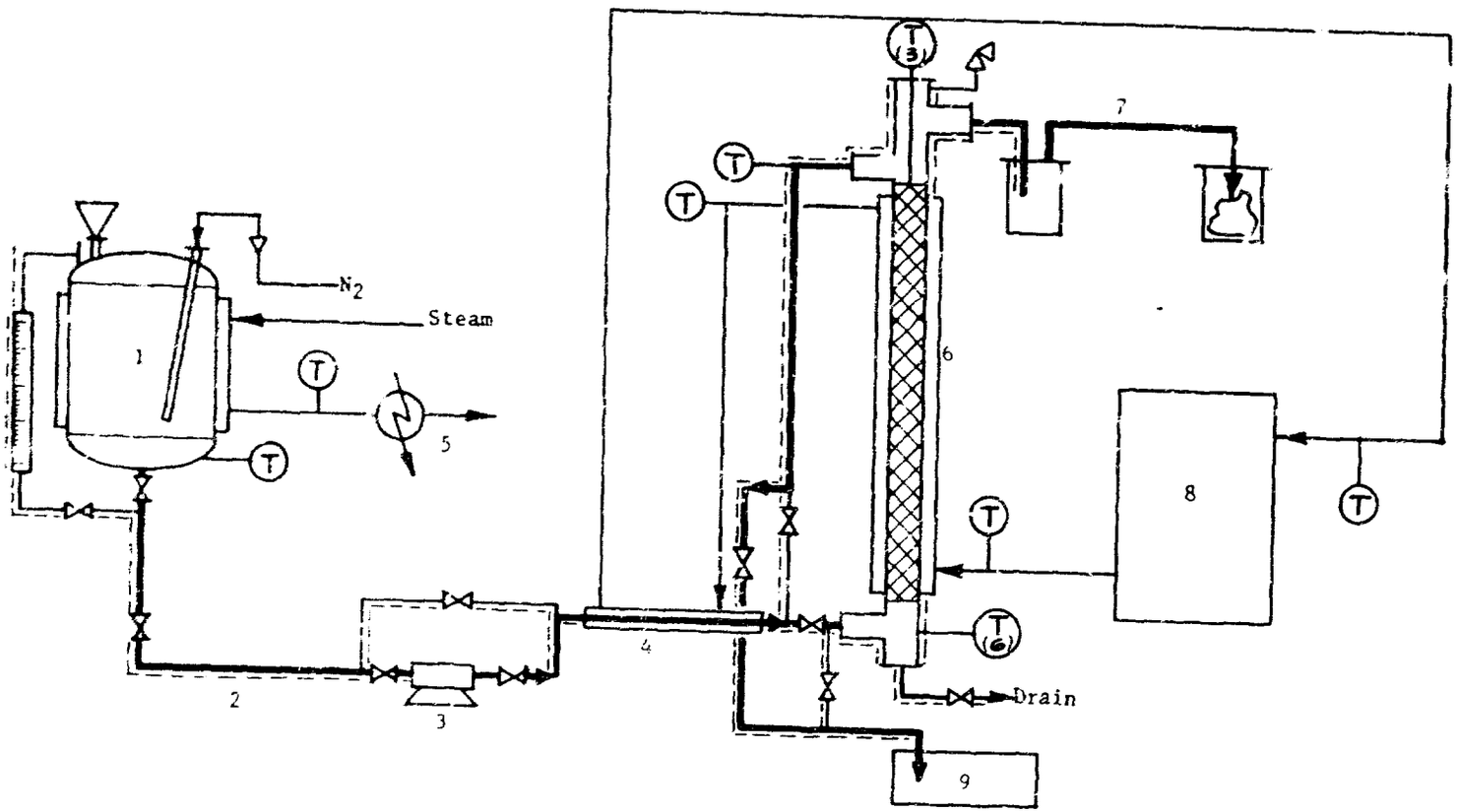
A 2 inch ID x 6 foot section of Pyrex pipe constituted the basis of the initial reactor. It was subsequently replaced with all stainless steel construction. Two-inch-diameter tees and/or crosses at each end of the reactor served as feed, product, off-gas and thermocouple connections. The bottom of the reactor was fitted with 100 mesh stainless steel screen to support the catalyst; the top was fitted with the same type screen to prevent overflow of the catalyst. Thermocouples were spaced throughout the reactor to measure axial and radial temperature profiles. All process lines were constructed of stainless steel. Heat for the preheater and reactor was supplied from an electric-fired, hot oil circulating system. The heat transfer medium employed was Union Carbide Grade L-40 silicone fluid, a dimethylpolysiloxane. This material is compatible with a mixture of AN/U/GN as was shown by the standard Taliani test. Houdry macroporous silica beads, predried at 225°C for two hours, were used for all experiments.

### b. Summary of Bench-Scale Reactor Operations

Twenty-one runs were made in the continuous-flow guanidine nitrate-packed bed reactor. The following objectives were achieved:

(1) The production of guanidine nitrate using the Boatright-MacKay-Roberts (BRM) process in a continuous-flow, packed bed reactor was demonstrated and shown to be feasible.

(2) Experimental data were obtained as a function of a number of process parameters (temperature, ammonium nitrate/urea feed ratio, flow rate, bed height, grades of reactants, upflow versus downflow, guanidine nitrate level in the feed).




1. Melt and feed tank, 25 gallon, jacketed, stainless steel.
2. Densitometer
3. Low capacity feed pump (FMI lab pump).
4. Feed preheater
5. Heating oil cooler (if required).
6. Packed bed tubular reactor, 2-inch diameter, jacketed, 4 to 5 ft bed depth, Pyrex glass (or 204SS) with 6 bottom entering and 3 top entering thermocouples
7. Dry ice off-gas collection system with liquid gas collection.
8. Silicone oil heat transfer circulation system.
9. Product receiver.

Figure 38. Guanidine Nitrate Bench Reactor Flow Diagram

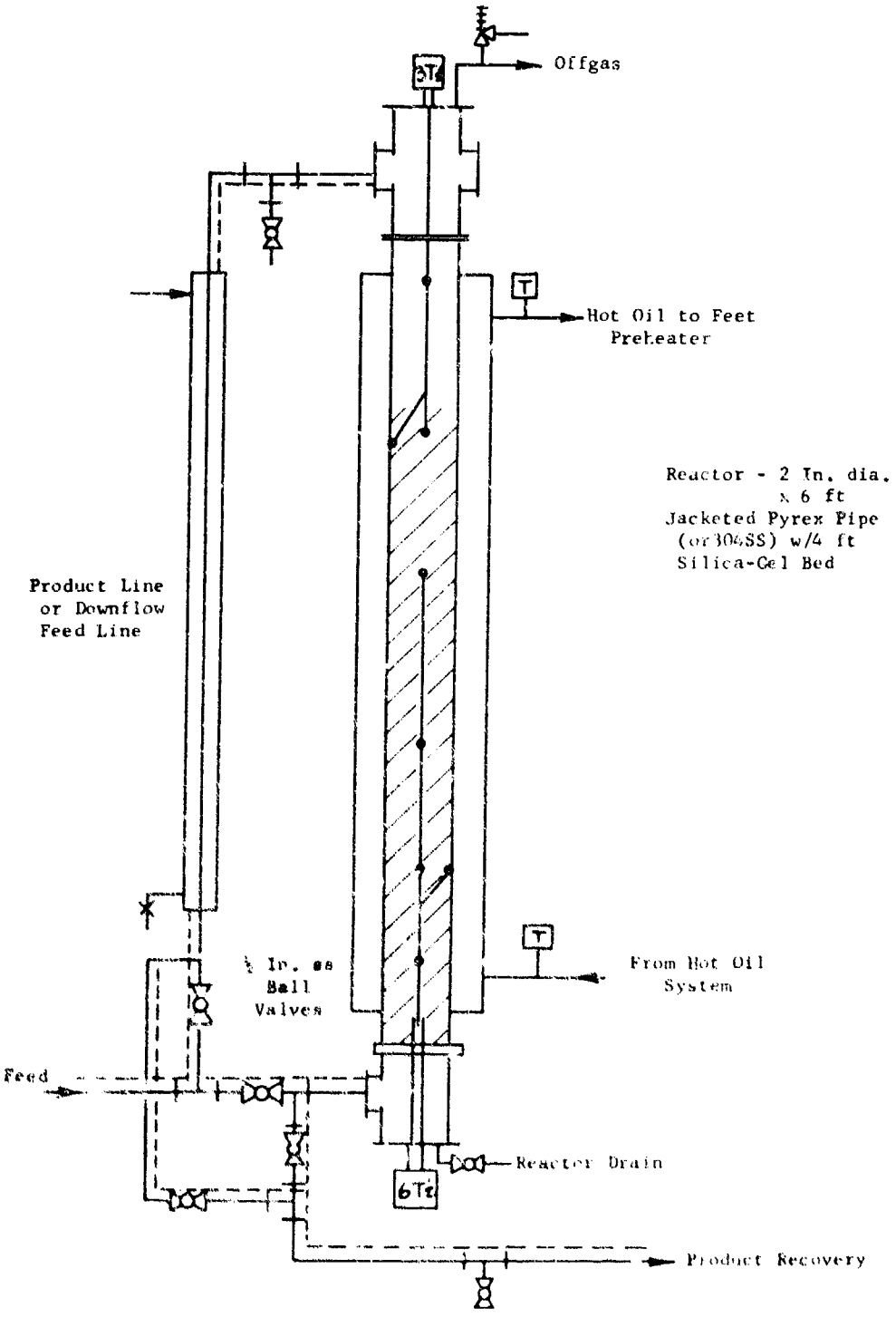



Figure 39. Kenvil GN Bench Scale Studies - Reactor

(3) The data from the columnar reactor were screened and compared on a preliminary level with the predicted values from the packed-bed reactor mathematical model in terms of product composition, temperature profiles, and fluid flow pattern in the reactor. This preliminary screening indicated that the model was quite accurate and could be used with confidence for the pilot plant reactor design.

(4) A number of process design questions were explored, and data obtained for the Phase II pilot plant design. Among the minor but important findings were the following:

(a) Mass transfer of reactants to the catalyst particle is not a significant factor in the reaction rate expression.

(b) The off-gas can be trapped completely, and no nitrogen oxides were generated in any of the runs.

(c) Water insolubles in the product were detected and measured routinely. The level confirmed the literature data.

c. Results and Conclusions

As noted above, 21 runs were made in the 2-inch-diameter columnar reactor. Complete sets of data were obtained for 12 runs, and partial sets of data were obtained for 9 runs. The runs made and calculated results are presented in Tables 28, 29 and 30, respectively. Two of the major efforts were (1) to demonstrate the feasibility of producing GN via the BMR process in a continuous, packed-bed reactor, and (2) to obtain experimental data to confirm the accuracy of the mathematical model for packed-bed reactors. Both objectives were accomplished. The experiments and results are discussed in detail in the following sections.

1 Effect of Process Parameters on Product Composition

The parameters varied in the continuous reactor runs were temperature, feed molar ratio (FMR) of ammonium nitrate:urea (AN:U), feed rate, flow direction (upflow versus downflow), bed height, grades of feed materials, and the level of recycle guanidine nitrate (GN) in the feed. The percent GN in the product increased with an increase in temperature and/or bed height and with a decrease in flow rate and/or FMR. The quantitative level of these increases versus that expected by theory can be assessed by comparing the Kenvil bench unit data with the predicted data from the packed-bed reactor mathematical model. Several computer runs were made with the mathematical model to provide data for product composition, conversion, yield, temperature, etc., as a function of catalyst depth for a 2-inch-diameter upflow reactor. Primary variables were mass

# TABLE 28

## RUNS MADE IN CONTINUOUS REACTOR

| Reactants | | | | | | | | | | Overall Results | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Type | Size | Type | Size | Molar Ratio AN/U | Flow Directions | Skin* Temp. °F | Flow Rate lbs/hr | Reactor Matl. of Construction | Run ** Duration Hrs | Performance |
| | | 24 inch | | | 3:2 | Upflow | - | - | Glass | 1.0 | Run aborted due to problems: (Plugs in feed sightglass, offgas lines low preheat level.) |
| | | | | | | | 350 | 6.6 | " | 1.0 | Run aborted - same reasons as above. |
| | | | | | | | | 7.4 | " | 2.1 | Samples of product taken, volatiles in product. |
| | | | | | | | 372 | 7.4 | " | 2.1 | Run stopped due to insufficient preheat. Samples taken. Bottom tee was subsequently traced with hot oil coil |
| | | | | | | | 358 | 8/3 | " | 3.1 | Run stopped due to insufficient preheat, samples taken. System being modified to provide more preheat. |
| | | | | | | | 383 | 6.2 | S.S. | 2.5 | Complete data taken. |
| | | | | | | | 342 | 3.9 | " | 2.5 | Run stopped due to plugged product line. |
| | | | | | | | 382 | 5.4 | " | 3.16 | Complete data taken. |
| | | | | | | | 381 | 4.0 | " | 3.50 | Run stopped due to miscellaneous problems. |
| | | | | | | | 366 | 5.2 | " | 2.75 | Complete Data taken |
| | | | | | | | 3[illegible] | 3.3 | " | 2.0 | Run stopped due to high MP Product |
| | | | | | | | 382 | 10.5 | " | 3.1 | Complete data taken. |
| | | | | | | | 37[illegible] | 3.41 | " | 4.3 | Complete data taken |
| | | | | | | | 374 | 3.74 | " | 2.0 | Complete data taken. |
| | | | | | | | 379 | 10.1 | " | 2.1 | Complete data taken. |
| | | | | | | | 381 | 10.1 | " | 1.7 | Complete data taken. |
| | | | | | 3:2 | " | - | 5.65 | " | 1.0 | Run stopped - frozen feed in bottom glass tee. |
| | | | | | 3:2 | " | - | 7.6 | " | 1.5 | Run stopped - frozen product line - high pressure. |
| | | | | | 3:2 | | 400 | 3.39 | " | 2.7 | Complete data taken. |
| | | | | | 3:2:2*** | " | 390 | 4.83 | " | 2.25 | Complete data taken. |
| | | | | | 3:2 | " | 362 | 3.84 | " | 4.0 | Complete data taken. |
| | | | | | 3:2 | Down | 380 | 16.00 | Glass | 1.84 | Gravity Flow |
| | | | | | | " | " | 15.97 | " | 0.84 | Pressure Flow |
| | | | | | | " | " | 7.96 | " | 0.50 | Pressure Flow |

* [illegible] ** Duration When Product was taken off Reactor. *** 5% Guanidine Nitrate in Feed.

# TABLE 29

## CALCULATED RESULTS FROM COLUMNAR RUNS

| Run No. | Feed | | Product | | | | | | | | | | Offgas Rate lbs/hr | Material Balances, % | | | Yields, % | | | Conversion Based on Urea (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Rate lbs/hr | Molar Ratio AN:U | Rate lbs/hr | Mole Fraction | | | % | | | | | | | | | | Based on AN | Based on Urea (actual) | Based on Urea (Theo.) | |
| | | | | AN | U | GN | AN | U | GN | Volatiles | $H_2O$ Insol. | Total | | AN | U | Total | | | | |
| 2 | 6.6 | 2:2 | 4 | - | - | - | 54.2 | 28.6 | 15.8 | - | .16 | 98.7 | - | - | - | - | - | - | - | - |
| 3 | 7.4 | 2:2 | 4 | - | - | - | 55.7 | 33.3 | 10.8 | 1.32 | .09 | 99.9 | - | - | - | - | - | - | - | - |
| 4 | 8.3 | 2:2 | 5 | - | - | - | 54.9 | 34.2 | 11.2 | .76 | .07 | 98.4 | - | - | - | - | - | - | - | - |
| 5 | 6.2 | 2:2 | 6.6 | .634 | .355 | .089 | 55.7 | 27.4 | 14.05 | 1.68 | .17 | 97.3 | .15 | 120.9 | 92.7 | 106.9 | - | 53.9 | 107.8 | 32.0 |
| 7 | 8.4 | 2:2 | 5.8 | .559 | .306 | .135 | 55.1 | 24.7 | 20.4 | 0.42 | - | 98.2 | .47 | 89.3 | 72.6 | 83.1 | 62.0 | 28.8 | 57.6 | 65.6 |
| 8 | 5.8 | 2:2 | 4.72 | .548 | .278 | .180 | 56.3 | 23.2 | 20.0 | .1 | .6 | 99.6 | .53 | 113 | 89.6 | 101 | 183 | 49.0 | 98.0 | 57.0 |
| 10 | 4.8 | 2:2 | - | - | - | - | 52.9 | 13.3 | 40.3 | .3 | ..62 | 98.1 | - | - | - | - | - | - | - | - |
| 11 | 7.8 | 2:2 | 11.1 | .593 | .355 | .084 | 57.4 | 2[illegible] | 13.7 | .14 | .32 | 98.2 | .35 | 126.3 | 92.0 | 113.8 | - | 55.8 | 111.6 | 31.1 |
| 12 | 5.4 | 2:2 | 5.14 | .187 | .143 | .327 | 40.0 | 9.75 | 44.5 | .15 | .55 | 103.8 | .29 | 127.7 | 94.0 | 101.8 | 241 | 60.7 | 121.4 | 78.8 |
| 13 | 6.7 | 2:2 | 2.42 | .548 | .[illegible]71 | .[illegible]78 | 46.55 | 7.15 | 51.5 | .9 | .4 | 106.6 | .93 | 95.8 | 68.1 | 78.1 | 90.5 | 30.6 | 79.2 | 91.9 |
| 14 | 5.1 | 2:2 | .[illegible] | .[illegible]224 | .[illegible]843 | .[illegible]187 | 58.[illegible] | 4[illegible].4 | 2[illegible].9 | .5 | .2 | 101.3 | 1.[illegible]5 | 98.7 | 91.9 | 95.1 | 99.3 | 42.6 | 85.2 | 47.8 |
| 15 | 5.3 | 2:2 | 6.4 | .[illegible]12 | .[illegible]783 | .[illegible]231 | 53.75 | 17.2 | 44.1 | .4 | .5 | 103.2 | .24 | 104.8 | 70.5 | 85.2 | 126.7 | 49.4 | 98.8 | 62.2 |
| 17 | 5.4 | 2:2 | - | .[illegible]21 | .[illegible]753 | .[illegible]334 | 52.71 | 2.05 | 47.[illegible] | .1 | .3 | 105.2 | .31 | 100.8 | 79.[illegible] | 82.9 | 102.1 | 55.7 | 111.4 | 05.4 |
| 18 | 4.[illegible] | 2:1.[illegible]* | 4.[illegible] | .[illegible]4[illegible] | .[illegible]11[illegible] | .[illegible]7[illegible] | 42.43 | 7.[illegible] | 54.05 | .3 | . | 104.6 | .47 | 112.[illegible] | 81.[illegible] | 87.6 | 137.5 | 61.4 | 132.8 | 93.2 |
| 19 | [illegible] | 2:2 | 5.[illegible] | .[illegible]43 | .[illegible]284 | .[illegible]285 | 57.[illegible] | 14.[illegible] | 33.7 | .2 | .3 | 101.3 | .14 | [illegible]2.7 | 79.[illegible] | 72.8 | 57.0 | 49.[illegible] | 98.0 | 75.[illegible] |
| 20[illegible] | 1[illegible].4 | 2[illegible]:2 | 11.[illegible] | .[illegible]5[illegible] | .[illegible]3[illegible]7 | .[illegible]094 | 57.7 | 24.5 | 34.3 | .5 | .08 | 96.6 | - | - | - | - | - | - | - | - |
| 21[illegible] | [illegible].[illegible] | 2:2 | - | .[illegible]71 | .[illegible]347 | .[illegible]181 | 57.3 | 20.1 | 18.5 | .4 | .1 | 96.0 | - | - | - | - | - | - | - | - |
| 22[illegible] | 5.[illegible] | 2:2 | - | .[illegible]86[illegible] | .[illegible]278 | .[illegible]136 | 57.4 | 21.[illegible] | 29.1 | .3 | .4 | 99.7 | - | - | - | - | - | - | - | - |

* Feed contains 5% guanidine nitrate.

TABLE 30

BENCH-SCALE DATA FROM COLUMNAR REACTOR PRODUCTION RATE AND INSOLUBLES

| Run No. | Bed Height Inches | A.N/U Molar | Skin Temp. °F | Product Flow lbs/hr | Product GN (%) | Product Urea (%) | Product Insolubles (%) | Lbs GN per Hr | Lbs Insolubles per Hr | Insoluble GN Ratio |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 16 | 2/2 | 335 | 4 | 15 | 28.4 | 0.15 | 0.60 | 0.0060 | 0.0100 |
| 3 | 18 | 2/2 | 340 | 4 | 10.5 | 33.3 | 0.09 | 0.42 | 0.0036 | 0.0170 |
| 4 | 18 | 2/2 | 355 | 5 | 11 | 34.2 | 0.07 | 0.55 | 0.0035 | 0.0060 |
| 5 | 25 | 2/2 | 380 | 6.6 | 14 | 27.4 | 0.16 | 0.92 | 0.0105 | 0.0114 |
| 7 | 25 | 2/2 | 384 | 4 | 20.4 | 23.4 | 0.42 | 0.82 | 0.0168 | 0.0205 |
| 9 | 25 | 2/2 | 384 | 4.8 | 26 | 20.2 | 0.6 | 1.25 | 0.0288 | 0.0231 |
| 11 | 25 | 2/2 | 382 | 11.6 | 13.7 | 26.7 | 0.32 | 1.59 | 0.0370 | 0.0235 |
| 12 | 48 | 2/2 | 378 | 3.2 | 43.6 | 9.8 | 0.63 | 1.40 | 0.0202 | 0.0145 |
| 13 | 48 | 2/2 | 374 | 2.7 | 51.5 | 5.2 | 0.8 | 1.39 | 0.0216 | 0.0156 |
| 14 | 48 | 2/2 | 379 | 8.6 | 20.8 | 26.3 | 0.5 | 1.78 | 0.0428 | 0.0242 |
| 15 | 48 | 2/2 | 392 | 8.4 | 34.4 | 17.2 | 0.8 | 2.90 | 0.0672 | 0.0232 |
| 18 | 48 | 3/2 | 400 | 2.5 | 47 | 2 | 0.2 | 1.175 | 0.0050 | 0.0043 |
| 19 | 48 | 2/2 * | 390 | 4.0 | 57* | 5.5 | 0.55 | 2.020 | 0.0220 | 0.0110 |
| 20 | 48 | 3/2 | 362 | 2.7 | 33.1 | 10.9 | 0.15 | 0.89 | 0.0041 | 0.0046 |

* 6% GN in Feed at 4.4 lbs/hr.

flow rate and feed compositions. Data from five of the bench-scale reactor runs are compared to predicted values in Table 31. The data for Run 5, made at an average feed rate of 6.2 lb/hr at 193°C reaction temperature, are compared to predicted values for a condition of 6.0 lb/hr at 190°C. The resulting product compositions are very close. Data for Runs 7, 11 and 14 were compared with data for samples which used lower feed rates and lower temperatures. Since the effects of these two parameters on the product composition counteract each other (higher feed rate - less conversion; higher temperatures - more conversion), the overall product composition should be close to the model. Inspection of Table 31 confirms this. Results for Run 12 (3.4 lb/hr and 379°F) are compared to a sample calculation (4.0 lb/hr and 374°F) in which the two experimental parameters would favor a somewhat higher conversion in the product. This was the case as shown in Table 31. The obvious conclusion from these five comparisons is that the packed-bed reactor model is capable of predicting quite accurately the resultant product compositions.

Two other parameters varied in the bench-scale runs were the grades of feed materials and the flow direction. Based on available information from other investigators (Hercules Research Center, etc.), one would not expect differences in yield, conversion, etc., when using commercial grades instead of reagent grades of urea and ammonium nitrate. Data from the bench-scale operations showed that there were no apparent effects on the reaction using commercial AN (Hercules/Kenvil, grained uncoated 1-G, see Table 32) or U (W. R. Grace). One effect, independent of the reaction, of using coated commercial feed stock is the necessity of in-line filtration to remove the anti-caking agents, etc. If this step is not added to the process, potential problems may result if impurities, such as talc or clay, are deposited in the feed pump check valves and/or in the catalyst bed.

The direction of flow through the catalyst bed was reversed to downflow for Run 21. This run was split into three parts so that gravity flow (21A) and pressure flow (two rates - 21B and 21C) could be explored. In Runs 21A and 21B, the feed rates were the same. The operational differences were that the overhead vent line valve was left open for Run 21A to provide gravity flow through the bed. The resultant conversions for Runs 21A and 21B were similar (14.3 versus 12.5% GN). When the flow rate was cut in half in Run 21C, the conversion increased to 24.1%. The actual bed temperature was not available in this run; however, based on the oil temperature and the estimated wall $\Delta T$ (based on Runs 1 through 4), it was estimated that the skin temperature in this run was $\sim$ 380°F. If so, these conversions appear in line with the upflow data.

## 2 Temperature Profile

Another objective of the bench-scale reactor work was to obtain temperature profile data for further confirmation of the packed bed mathematical model. A typical predicted axial temperature profile shows an initial decrease due to the inherent endothermic reaction. The axial temperature then recovers with a corresponding movement up the tube because of a slower reaction and improved heat and transfer resulting from higher fluid velocities.

TABLE 31

COMPARISON OF ACTUAL VS MODEL DATA FOR PACKED BED REACTOR

| | ACTUAL (2:2 AN:U) | | | | | | MODEL (2.2 AN:U) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Xenvil Run No. | Bed Height, inches | Flow Rate, lbs/hr | Skin Temp. °F | Product Mole Fraction AN | Urea | GN | Predicted Product Mole Fraction AN | Urea | GN | Flow Rate, lbs/hr | Feed Temp. °F |
| 5 | 25 | 6.2 | 380 | .539 | .355 | .089 | .552 | .361 | .087 | 6.0 | 374 |
| 7 | 25 | 5.4 | 382 | .558 | .306 | .135 | .565 | .298 | .136 | 4.0 | 374 |
| 11 | 25 | 10.5 | 382 | .563 | .350 | .088 | .542 | .395 | .063 | 8.0 | 374 |
| 12 | 48 | 3.4 | 379 | .537 | .143 | .320 | .564 | .172 | .264 | 4.0 | 374 |
| 14 | 48 | 10.1 | 379 | .523 | .343 | .134 | .565 | .305 | .130 | 8.0 | 374 |

TABLE 32

CHEMICAL ANALYSIS OF GRAINED, UNCOATED 1 G AMMONIUM NITRATE

(Contains no crystal habit modifiers)

| Property | Limits, % | Measured Value * |
|---|---|---|
| Moisture | .15 max | .02 |
| Ether Solubles | .10 max | .02 |
| Water Insolubles | .18 max | .02 |
| Insol. Mat'l Retained on #40 | .01 max | trace ( <.01) |
| Acidity, as $HNO_3$ | .02 max | none |
| Nitrites | none | none |
| Sulfates, as $(NH_4)_2 SO_4$ | .02 max | < 0.02 |
| Chlorides, as $NH_4 Cl$ | .02 max | < 0.02 |
| Ammonium Niteate | 99.0 min | 99.54 |
| Petro Ag | 0.08 - .15 | 0.10 |
| Zinc Oxide | 0.05 - 0.1 | 0.08 |
| Density, gms/ml | 1.63 min | 1.72 |
| Granulation: Thru No. 10 | trace | trace |
| On No. 40 | 51 | 53 |
| Thru No. 100 | 29 | 33 |

* Kenvil analyses of material from bag of Ammonium Nitrate 1G used in continuous reactor runs.

The initial comparison of actual vs predicted reactor temperature was made with bench-scale reactor Run 13 (2.5 lb feed/hr). The two sets of data were qualitatively similar; however, the predicted centerline temperatures were as much as 5°C higher than the actual values.

The heat of reaction used in the initial modeling work was 28.2 kcal/gmole GN. This value was determined experimentally by MacKay by measuring temperature drops and extents of conversion to GN. To show that this experimental value was reasonable, MacKay estimated the heat of reaction at 25°C using solid and gaseous standard state heat of formation data. His estimated value was 26.1 kcal/gmole GN.

Using the heat of formation data referenced by MacKay, the heat of reaction at 25°C was calculated to be 35.6 kcal/gmole. The large discrepancy between this value and MacKay's was apparently due to a sign error.

The estimate of the heat of reaction was further refined by using the most recent heat of formation data and by calculating it at 190°C based on liquid (melt) and gaseous standard states. To do this, it was necessary to estimate the heat capacities of crystalline urea, GN, and AN. It was assumed the heat capacities of the pure melts were not much different than those of the combined melt, which had a heat capacity of ca 9.45 Btu/lb/°F at 150°C. The estimated value for the GN heat of reaction, assuming the overall reaction of 2 moles of urea and 1 mole of AN to yield 1 mole of GN, 1 mole $CO_2$ and 2 moles $NH_3$ at 190°C, was 33.5 kcal/mole of GN. A value of 35 kcal/gmole of GN was used in the revised model.

The model for predicting the effective thermal conductivity of the bed consists essentially of two terms: one for the contribution of the thermal conductivity of the stagnant bed and the other for the contribution due to radial mixing. The value for the thermal conductivity of the stagnant bed that had been used was 7.03 cal/min-in.°K as suggested in the open literature by Wickman and Meyers.(6) These authors have correlated several sizes and types of packing material and have found that over a wide range of Reynolds numbers, a common value for the thermal conductivity of the stagnant bed for all of the various packings represented that data sufficiently well. At high Reynolds numbers, the contribution of the stagnant thermal conductivity to the effective thermal conductivity of the bed is small. However, at the low Reynolds number flow conditions that exist in the guanidine nitrate reactors, the stagnant thermal conductivity plays a much larger role and the values used should therefore reflect more accurately the properties of the bed material being utilized. Kunii and Smith(7) have measured the stagnant thermal conductivity of silica in various liquids and report it to be approximately 1.5 calories/min-in.°K. This is the figure now used in the guanidine nitrate reactor model.

With the above changes made, a simulation run was made for feed conditions of 10 lb/hr and ammonium nitrate/urea ratio of 1/1 in a 4-ft -long, 2-inch-diameter tube. These conditions duplicated those of Run 14 for the bench-scale packed bed unit. The centerline temperature for the simulation dropped to a minimum of 183°C at a distance of 17 inches from the start of a heated catalyst bed. This agreed well with the experimental results from the bench reactor in which a minimum temperature of 182°C was recorded at 15 inches from the bottom of the catalyst bed with a reference plane 2 inches above the steam jacket bottom. A comparison of the predicted vs the actual profiles is shown in Figure 40.

### 3 Gas-Liquid Pattern in Column Reactor

One of the objectives of the columnar reactor effort was to assess qualitatively the gas-liquid flow pattern in the packed-bed reaction zone. This was one of the two reasons a glass reactor was originally selected for the columnar work. The other reason was to observe the importance of foaming due to catalyst fines. The glass reactor was used for Runs 1 through 4 (upflow) and for Run 21 (downflow).

In the upflow runs, there was a distribution of a liquid dispersed in a gas phase at the bottom and throughout most of the bed. This condition changed to a gas bubbling through a liquid phase at the top of the column. The intensity of the foam was greatest at the bottom of the bed and became less and less as the gas moved up the column. The separation of gas from the liquid in the gas-liquid separator (glass cross at the top of the column) was very clean with no signs of foaming and no entrained liquid carried to the off-gas dry ice traps. The resultant holdup in the column was a gas-liquid mixture (a distribution of foam); this was expected to vary as the gas evolution rate varied. This was shown to be true by the weights of the material drained from the reactor at the end of the run and by the "settling" of the upper foam level, when either the flow rate or the temperature was reduced. The weights of the material drained from the reactor varied between 5 and 9 pounds. It was encouraging to note that the mathematical model of the packed bed reactor predicted the kind of foam pattern that was observed experimentally.

The downflow run (Run 21) was divided into three parts in an attempt to study two areas: (1) mechanism of gravity vs pressure flow and (2) conversion using pressure flow vs feed rate. The resulting gas-liquid patterns for the two types of downflow (gravity vs pressure flow) were as follows. In the gravity flow a liquid head resulted and there was a foam intensity pattern again from the top of the column (mostly liquid) to the bottom (mostly gas). The required liquid head increased as the temperature and gas evolution rate increased. Only a small fraction of the off-gas vented overhead, with the top vent valve open; i.e., countercurrent to the liquid flow. Most of the gas vented from the bottom of the reactor. The

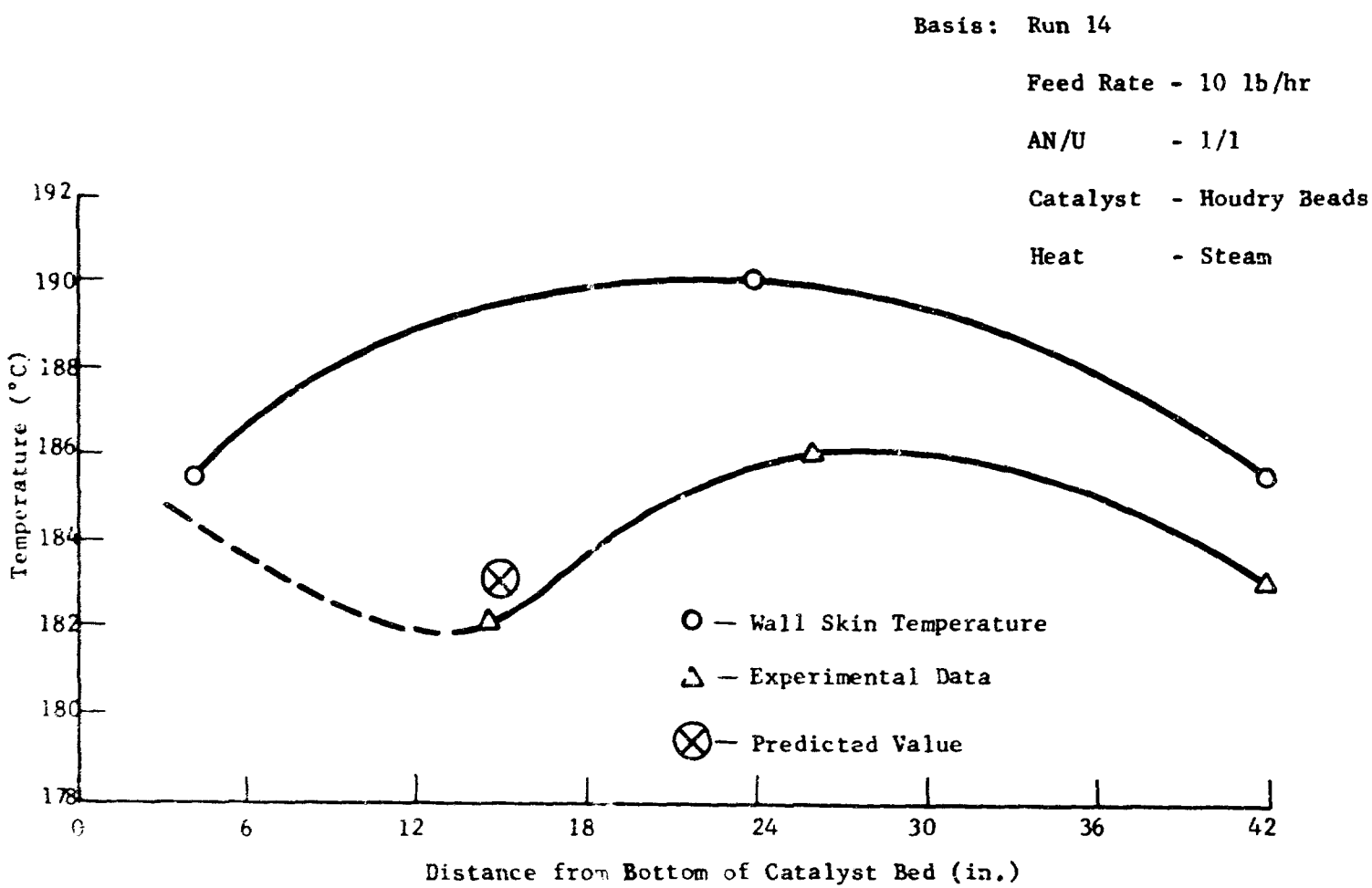



Figure 40. Predicted vs Actual Axial Temperature for 2-In. Diameter S/S Tubular Reactor

molten product dripped through the inert section at the bottom of the column. When the off-gas line at the top of the bed was closed, the feed pressure increased 2-3 psig (range 5 to 9 psig), the liquid head drained, and, as well as could be observed, the column became a trickle bed reactor. All of the off-gas was collected and vented from the bottom of the column. When the feed rate was reduced by 50% (Run 21C), the system remained as a trickle bed reactor.

## 4 Calculated Results

Table 29 presents, for each run, the total and component material balances and calculated yields and conversions. Inspection of this table reveals erratic and inconsistent results for the yields and conversions. The reason for the inconsistencies in these calculations is that the material balances in all runs but Run 14 were erratic.

Operational problems also contributed losses to the material balance. In the earlier runs, a plugged off-gas line forced much of the off-gas to go overhead with the molten product where it volatilized in the product container. In some of the later runs, off-gas losses from the product line were again experienced. In these runs, the product line consistently plugged because of the use of high melting point products (nominal 50% GN). To prevent this plugging, the product line was shortened and the gas seal loop eliminated so that the amount of product holdup and temperature loss in this line was slight. These two changes prevented complete collection of the off-gas.

The analytical procedures used in the product and feed workup were the same as those described in a previous section. These methods were quite adequate for most of the feed and product samples, but it became obvious, when results of the higher conversion runs became available, that some analytical refinements were necessary. Figures 41 and 42 present product closure (wt. %) as a function of product composition (AN or urea). The product closure appears to be a function of the guanidine nitrate (GN) or urea (U) level in the product. At GN levels of $\sim$ 55%, the closure approaches 108%. As the urea concentration increases from 0% to 38%, the product closure decreases from 107% to 98%.

There are valid reasons for the poor material balances. The contributing sources of error were the operational procedure, the system holdup, system losses, and the feed and product analyses. The operational procedure was to heat the system, pump it full, adjust conditions until steady state operation was reached, and then run for an additional 1-2 residence time units. The result of this procedure was that the system holdup (one volume) represented a large portion of the material processed through the system in the equilibrium period (one to two volumes). A pulsation in the system holdup

TABLE 33

CALCULATIONS FOR COLUMNAR REACTOR

Conversions and Yields

Basis: 1 hour — Run 14

IN:

| Compound | Wt. % | Lb | Lb. Moles | Mole Fraction |
|---|---|---|---|---|
| AN | 57.1 | 5.77 | 0.0721 | 0.5 |
| U | 42.9 | 4.33 | 0.0721 | 0.5 |
| Total | | 10.1 | 0.1442 | 1.0 |

OUT:

Product

| | | | | |
|---|---|---|---|---|
| AN | 53.5 | 4.580 | 0.0573 | 0.523 |
| U | 26.4 | 2.260 | 0.0376 | 0.343 |
| GN | 20.9 | 1.789 | 0.0147 | 0.134 |
| Volatiles | .5 | 0.043 | - | - |
| $H_2O$ Insol. | .5 | 0.043 | - | - |
| Total | | 8.56 | 0.1096 | 1.000 |

Offgas - 1.05 lbs (0.0134 moles AC)

Material Balances

| | | In (lb) | Out (lb) | % |
|---|---|---|---|---|
| (1) Total (per hour) | | 10.1 | 9.51 | 95.1 |
| (2) Ammonium Nitrate: | | | | |
| As AN | | 5.77 | 4.580 | |
| As GN | | - | 1.173 | |
| | Total | 5.77 | 5.753 | 99.7 |
| (3) Urea: | | | | |
| As U | | 4.33 | 2.260 | |
| As GN | | - | 0.880 | |
| As AC | | - | 0.841 | |
| | Total | 4.33 | 3.981 | 91.9 |

TABLE 33 (Continued)

Yields

(1) Based on AN = moles GN formed/moles AN consumed

= 0.0147/0.0148 x 100 = 99.3%

(2) Based on Urea = moles GN formed/moles U consumed (actual)

= 0.0147/0.0345 x 100 = 42.6%

(3) Based on Urea = actual urea yield x 2 = 85.2% (theoretical)

Conversion

Based on Urea = moles urea reacted/mole urea fed x 100

= (.0345/.0721) 100 = 47.8%

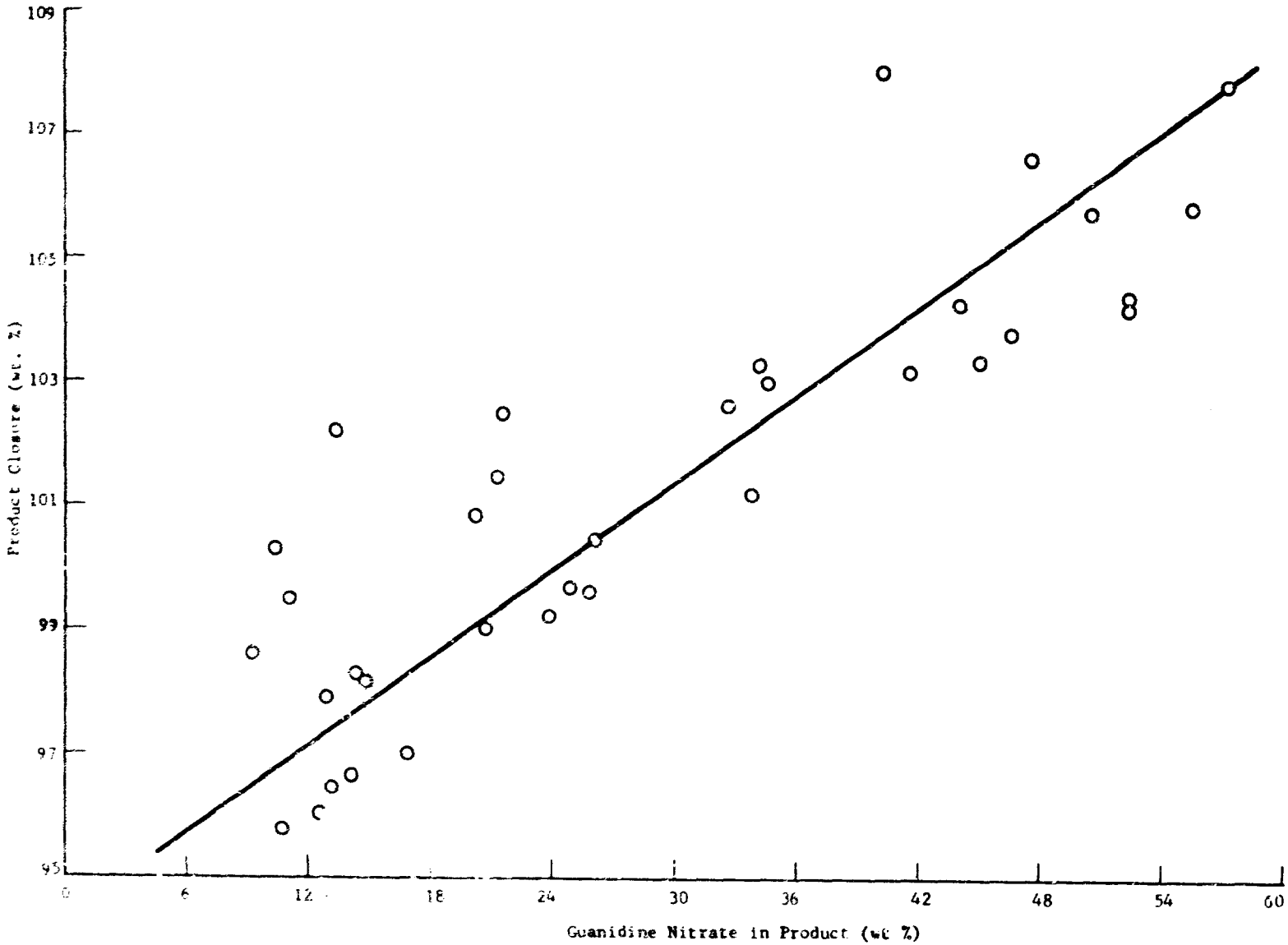



Figure 41. Product Closure Vs % Guanidine Nitrate in Product Continuous Reactor

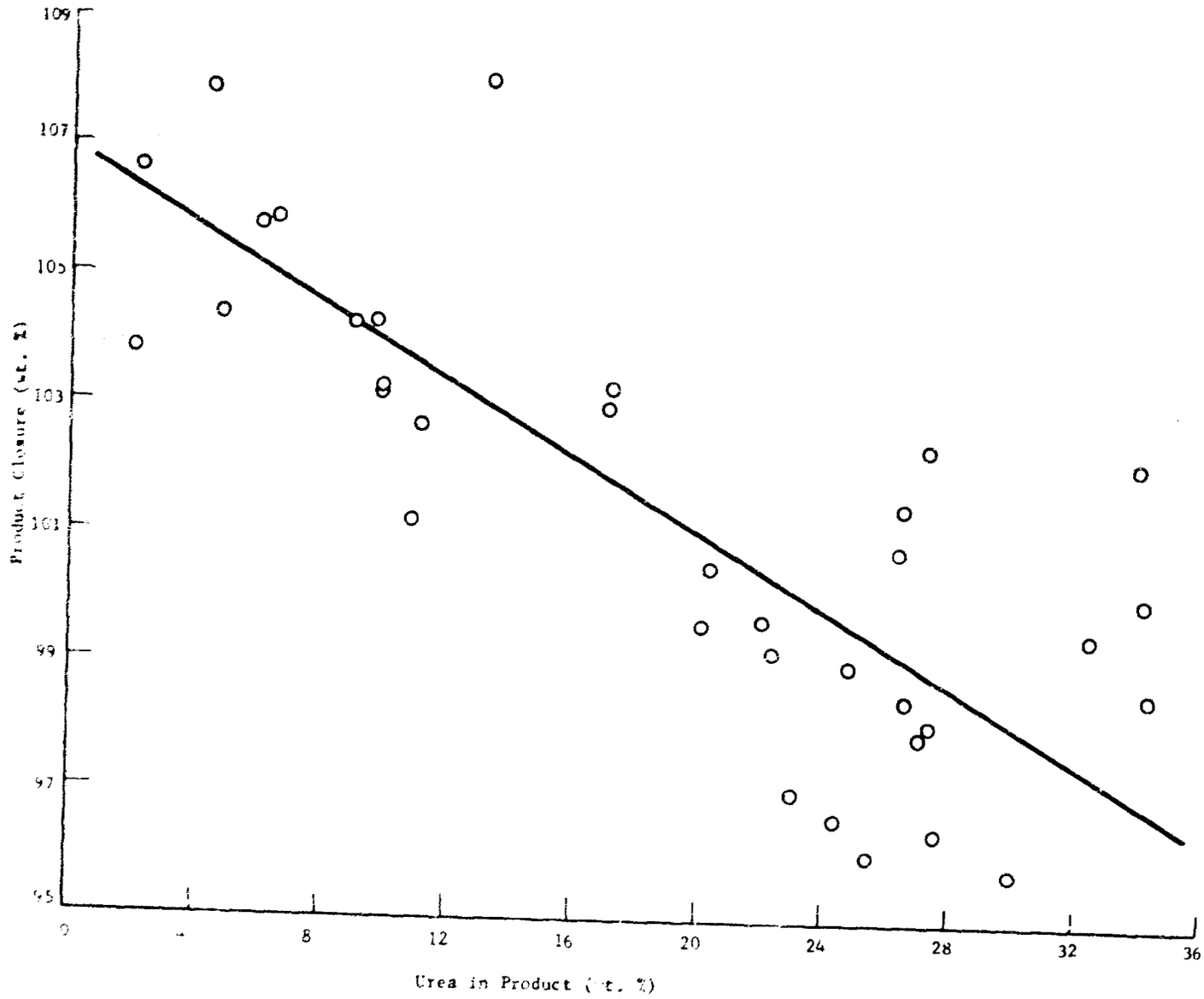



Figure 42. Product Closure Vs % Urea in Product Continuous Runs

(mostly foam) greatly changes the amount of product collected during the equilibrium period. Since the operation of the unit was constrained by an 8 to 12 hour operational cycle, it was not possible to operate the unit beyond 1 to 2 residence time units on a routine basis.

The resulting total weight of material pumped through the column in most of the runs was in the range of 8 to 20 lb (versus a system holdup of 5 to 9 lb). As this operation was a continuous, molten-flow, high-temperature gas-liquid system, there were unavoidable spills and vapor losses. The relative weight effect of these losses to the total material weight was significant.

Run 14 was made as a material balance run, and conditions were chosen to minimize the above error sources. Fresh feed was charged to the feed tank, melted and used immediately. A high feed rate was used, and the unit was operated for ~ 3 residence time units. A total of about 30 pounds of feed was pumped through the system. Reaction conditions were chosen so that a product containing about 20% GN would result. This product had a melting point which was easily handled in the product-gas line. Product with this GN concentration would be expected to have a product closure close to 100%, predicted from Figure 41.

The results of Run 14, with a product containing 20.9 wt. % GN, were a total weight material balance of 95.1% and component material balances of 99.7% for AN and 91.9% for urea. The urea yield was calculated to be 85.2%, and the ammonium nitrate yield was 100%. These numbers are quite consistent with the values resulting from the laboratory stirred reactor experiments. Calculations for Run 14 are shown in Table 33.

### 5 Catalyst Performance - Houdry Beads

Macroporous silica beads (4 mm dia.) were used as the catalyst for all of the runs. The catalyst bed was changed three times during the series of runs.

| Change No. | Bed Changed After Run No. | Cumulative Hours at Temperature | Description of Removed Catalyst | |
|---|---|---|---|---|
| | | | Color | Form |
| 1 | 4 | 7.2 | Black | Original |
| 2 | 11 | 19.0 | White | Original |
| 3 | 20 | 22.6 | White | Reduced in size |

The differences in recovered catalyst from the three bed changes were a result of the bed having been subjected to different conditions. Bed No. 1 picked up color but the beads retained their original shapes. It is theorized that the color was picked up from impurities left in the feed tank and feed lines even though the system was flushed thoroughly before startup. Catalyst beads in Bed No. 2 retained both their original shape and color. Recovered Bed No. 3 included about 5% of the beads with their original shape but the majority was finely divided silica. The reason for the reduction in catalyst particle size could have been one of the following:

(a) Effect of high GN content and insufficient flushing when reactor was shut down.

(b) Water cleanout.

During Run 17, the pressure drop through the bed reached a high of 35-40 psig in the first run in the series. It appeared as if it would be necessary to change beds at that point. It was decided to explore the possibility of flushing the bed with hot water to see if the pressure would decrease. It was theorized at that time that the higher pressure was being caused by a buildup of GN in the system and perhaps it could be dissolved out. After one hour of flushing at 210-300°F with tap water, the system pressure had dropped to 10 psig and clear water was overflowing from the column (at reduced temperature) at a rate of ~ 1.5 gallon/hour. Runs 18, 19, and 20 followed this flushing, but by the end of Run 20, the system pressure reached > 30 psig.

Contacting fresh Houdry Beads with water at room temperature did not change their physical size, but water close to steam temperature might have an effect. The other possibility for decrepitation was a gradual physical breakdown of the catalyst with time. It seems unlikely that this was the primary reason for the size reduction of Bed No. 3 since Bed No. 2 was used only four hours less and survived with minimal catalyst breakage. Based on the short runs made in the 2-inch-diameter columnar reactor, a long Houdry Bead physical life could be expected, barring unusual operating problems. Grace grade 40 silica gel decrepitated readily when contacted with water. This latter material would not be expected to retain its physical characteristics in prolonged tubular reactor operations. Originally a run had been planned using Grace 40 silica gel as the catalyst. Because of time limitations and because laboratory work had demonstrated the kinetic similarity between Houdry silica beads and silica gel, it was elected to eliminate the Grace grade 40 run from the program.

The chemical catalyst life of the Houdry beads should be comparable to that of the silica gel since they are both > 99% $SiO_2$. MacKay had used the silica gel for ~ 80 hours and encountered only physical reduction problems, so it is predicted that the macroporous silica beads will last as long as or longer than silica gel without physical attrition. More detailed discussions on catalyst behavior in a tubular reactor are presented in the Phase III section.

## 6 Production Rate and Mass Transfer

The guanidine nitrate production rate in the bench-scale unit at a given temperature and feed ratio was not too dependent upon feed rate. Runs 5, 7, 9, and 11, with a 25-inch bed and 382°F skin temperature, averaged 1 lb GN/hr although the ratio of the feed rates varied by a factor of two. Runs 12, 13, and 14 with a 48-inch bed and 378°F skin temperature averaged 1.5 lb GN/hour although the ratio of the feed rates varied by a factor of three. These data suggest that with these operating conditions, the unit was not in an area of mass transfer limitation. If it had been, then at the higher feed rates there would have been less GN formed because the flow rate of reactants from the bulk to the catalyst site would have been a significant factor in the reaction rate expression.

A set of runs was made to explore the possibility of mass transfer importance. Run 7 was made at a 25-inch bed height and a feed rate of 5.4 lb/hour. Run 14 was made at a 48-inch bed height and a feed rate of 10.1 lb/hour. The residence times in the catalyst bed in both cases were similar, but the liquid/gas flow rate through the bed in Run 14 was almost double that of Run 7. The resultant product formed in both cases was ~ 29.5% GN, indicating that the time required for the reactants to move from the bulk liquid to the catalyst site (mass transfer time) was insignificant in the overall reaction rate.

Doubling the bed length did not double the GN production rate. It increased about 50% in the 2-inch-diameter bench-scale reactor. This relationship fits well with theory since the major part of the reaction takes place in the first 12 inches of the bed. Without intermittent fresh feed, each incremental section of bed contributes a fraction less GN to the product than the previous bed increment.

## 7 Water Insolubles

The insolubles/GN ratio, which gives an indication of cleanliness of reaction, varied by a ratio of 6. There appeared to be a trend of increasing insolubles with temperature and urea concentration. This judgment is based on limited data, but it fits well with the other references on the

process. The product melt from the reactor during Run 20 was crystal clear, whereas the products from other runs were at times milky in appearance. A test tube experiment revealed that the water insolubles were soluble in the product melt at 170°C at levels of ~ 0.2% but not at levels of 0.8%. The level of water insolubles (0.15%) that produced a clear melt produced a very turbid, hot water solution. The fact that the water insolubles could be dissolved in the melt at a low level was encouraging since a buildup of insolubles on the catalyst bed could be minimized by proper selection of reaction conditions.

Insolubles levels of 0.5-2.0% in a commercial size plant represent about one ton/day of disposable by-products. This is of sufficient quantity that the economics of removing and disposing of these solids will have to be weighed against the economics of reducing their level by changing reactor operating conditions. One of the ways the level of insolubles could be reduced, if the economics of insolubles recovery warrant, is to use a staged reactor with intermittent urea feed. This would require a more expensive reactor system, but the other equipment in the process would stay at the optimum economic level based on an AN/U feed ratio of 1/1.

## 8 Product Color

As noted above, the product at different water insolubles levels has either a clear or a milky appearance. There was also a variance in color of the product. The product was normally white or tan, but during Runs 1 through 4 and in Run 18, the product was coffee-colored. It is theorized that this color was caused by metal salts contamination. In Runs 1 through 4, the system evidently was being cleaned out by the feed. This was evidenced by a visible change in catalyst color. In contrast, the recovered catalyst was always white in runs after Run 4. Before Run 18, the bed was flushed with tap water for about one hour. The impurities in the water evidently hung up in the system (probably on the catalyst, which is also used as a catalyst support for metal salts). The first product from Run 18 was again coffee-colored, but as the run proceeded the product became progressively lighter.

The product from the runs using the stainless steel reactor and the product from Run 21 using the glass reactor showed no difference in color.

## 9 Off-gas

The off-gas from the reactor passed through a dry ice trap and then to a liquid volume displacement bubbler. At no time during any of the runs did any gas accumulate in the liquid trap. There were no signs

of nitrogen oxides in any of the runs (in the stainless steel or glass reactor) as mentioned by the British investigators. If they did indeed find this gas, it is most likely that it came from overheating and decomposition of the ammonium nitrate in the feed system. A sample of the off-gas trap contents was analyzed for % volatiles at 70°C (99.85%), alkalinity as $NH_3$ (39.9%), and carbonate as $CO_2$ (59.0%). The latter two analyses are not free of interference so they are not completely accurate, but the finding checks well with this material being ammonium carbamate (56.2% $CO_2$ and 43.8% $NH_3$).

## 10. Packed-Bed Reactor Operation

When the original preheater was found to be insufficient, a second preheater was installed and the bottom of the catalyst bed was raised into the reactor jacketed section by placement of stainless steel balls on the support screen. After the equipment and start-up problems were resolved, the bench scale unit was shown to be capable of operating smoothly. There were, however, sets of operating conditions at which it was difficult to operate the unit. Primarily, these were conditions in which the equipment was operated close to its design limits. Most of the problems had to do with the feed pump and the heat control of the feed and product lines; many of the problems were caused by limited heat control (30 psig steam tracings) on the small feed, product and auxiliary lines. When runs at very low feed rates were attempted, these extreme problems become apparent. At 190°C and a feed rate below 4-5 lb/hour (1/1 AN/U feed), the conversion increased to the point where the melting point of the product was high enough (m.p. = 145°C at 40% GN) to promote plugging of the product line. Not only was the product melting point high, but the transportation lag through the product leg was long. There were occasional feed line plugging problems either at the reactor bottom tee or bed support as a result of low flow rates or AN/U feed ratios greater than 2/1. The off-gas lines in the earlier runs plugged often until the lines were more completely steam traced. By the end of the sixth run, it was standard shutdown procedure to blow out all of the feed, pump, product and off-gas lines with steam. This step greatly reduced subsequent start-up problems due to plugging.

The oil system and the melt tank system operated smoothly after the start-up problems were solved. The feed pump operated adequately in that it gave accurate rates at constant conditions. It was found, however, that its output was a function of downstream pressure. The feed rate had to be determined by measuring the weight and volumetric rates at 0 psig before filling the system and then periodically checking the volumetric rate during operation. The volumetric rate was determined by measuring the time for the feed level to drop 5 inches in the feed tank calibrated sightglass. This procedure turned out to be fairly accurate, but it was difficult to achieve the desired feed rate accurately because the resultant steady-state pressure level was not known until equilibrium was reached. Periodically, there were other small operational problems, but none of these were considered atypical (faulty thermocouples, etc.).

## 5. Part 4 - Economic Evaluation

### a. Approach

Economic dimensions were placed on the parameters involved in the proposed GN (guanidine nitrate) production to show the effect of economics on the engineering alternatives. Changes in parameters cause changes mainly in utilities, depreciation, and, in some instances, raw materials. Manpower changes are either zero or small.

To fully indicate the engineering effect of parameter change, the indicator used was an industrial accounting system in which the mill cost includes, in addition to labor and raw materials, the cost for depreciation and utilities at a smaller overhead reflecting only the fringe benefits for labor. In addition to giving full weight to the differences in the alternative engineering step, the GN transfer price which contains a value equal to 30% of T.O.A.* was used as a criterion. This transfer price over the mill cost could be referred to as the debt service which reflects amortization and interest terms. In addition, G&A costs** are contained in the transfer price. Since all cost terms in such a price are given their full value and weight, the curves based on these values showing parameter charges are sharper than when based on mill cost values only. The conclusions reached are the same and are valid since all are on the same basis. A more accurate calculation of GN manufacturing costs and capital requirements rightly awaits the pilot plant operation and design phase of the study.

It is recognized that the United States Government does not maintain its accounting system on the same basis as an industrial concern. In a Government accounting system, a mill cost includes raw material costs, labor plus overheads, maintenance and repair labor, utilities and packaging; does not include insurance, taxes, depreciation and profit. Since manpower, raw material requirements, etc., alone cannot adequately indicate the changes in the process engineering system at hand, it was elected not to use this accounting system as the primary indicator for parameter incremental differences but rather the one earlier referred to for the computer model and computer calculation. For each economic case study discussed further in this report, the mill and G% return costs by Government accounting technique were determined and included in a summary table.

---

* T.O.A. = Total operating assets which includes plant investment, allocated investment from existing facilities, and working capital.

**G&A = General and Administration, an overhead cost due to general direction of a company above the plant level. Generally includes top management salaries, legal, central purchasing, and engineering not chargeable to new fixed capital, traffic, and accounting, etc.

The latter 0% return cost does not include a corporate allocation but does include working capital and indirects.

The parameters considered in the economic evaluation included the following: (1) plant production capacities, (2) by-product credit value, (3) price of urea, (4) yields based on urea, (5) AN/U ratio, (6) melt crystallization workup of crude GN versus aqueous workup, and (7) tubular reactor versus an agitated kettle reactor.

Continuous operation with recycle, and Class 2 operation were also assumed. Figure 43 shows the flow sheet for the process using tubular reactors, and a melt crystallization with water recrystallization of the crude GN. Figure 44 has an alternative workup. The melt crystallization step is replaced with only an aqueous crystallization step. All equipment was assumed to be 304 stainless steel with aluminum storage vessels for the urea and ammonium nitrate ingredients.

b. Process

Case 100, Figure 45, was the basic case for a 40-million pound per year plant with packed-bed reactors. The process is based on use of a 190°C reaction temperature, Houdry macroporous silica beads, and a 1-hour residence time. Ammonium nitrate is fed to a melt tank where part of the required urea is mixed with it. The ammonium nitrate/urea/catalyst mole ratio is 2/2/1.7. After the feed has been filtered, it is mixed with the recycle stream and pumped to the reactors via a heat exchange (H-1). Following the reaction, the liquid phase is separated from the gas phase, and pumped to a mix tank (T-1) where sufficient urea is added to give the eutectic mixture of 47% urea, 53% ammonium nitrate. The GN is purified by a melt crystallization followed by an aqueous recrystallization. Most of the water in the mother liquor stream from the centrifuge (C-2) is removed in an evaporator before recycle. The GN product is dried in a rotary drier.

Off-gas, $NH_3$ and $CO_2$, is transferred to a recovery plant either for conversion to urea for recycle, or for conversion to $NH_4NO_3$ for external use. Since the off-gas is hot gaseous $NH_3$ and $CO_2$ and not ammonium carbamate, it can be piped to the recovery plant without further treatment. Ammonium carbamate does not exist at the operating pressure and temperature of the reactor.

The yield for this case based on urea is 80% at a 64.5% conversion. The ammonium nitrate yield is 100% at 32% conversion. Figure 45 gives the material balance for this case.

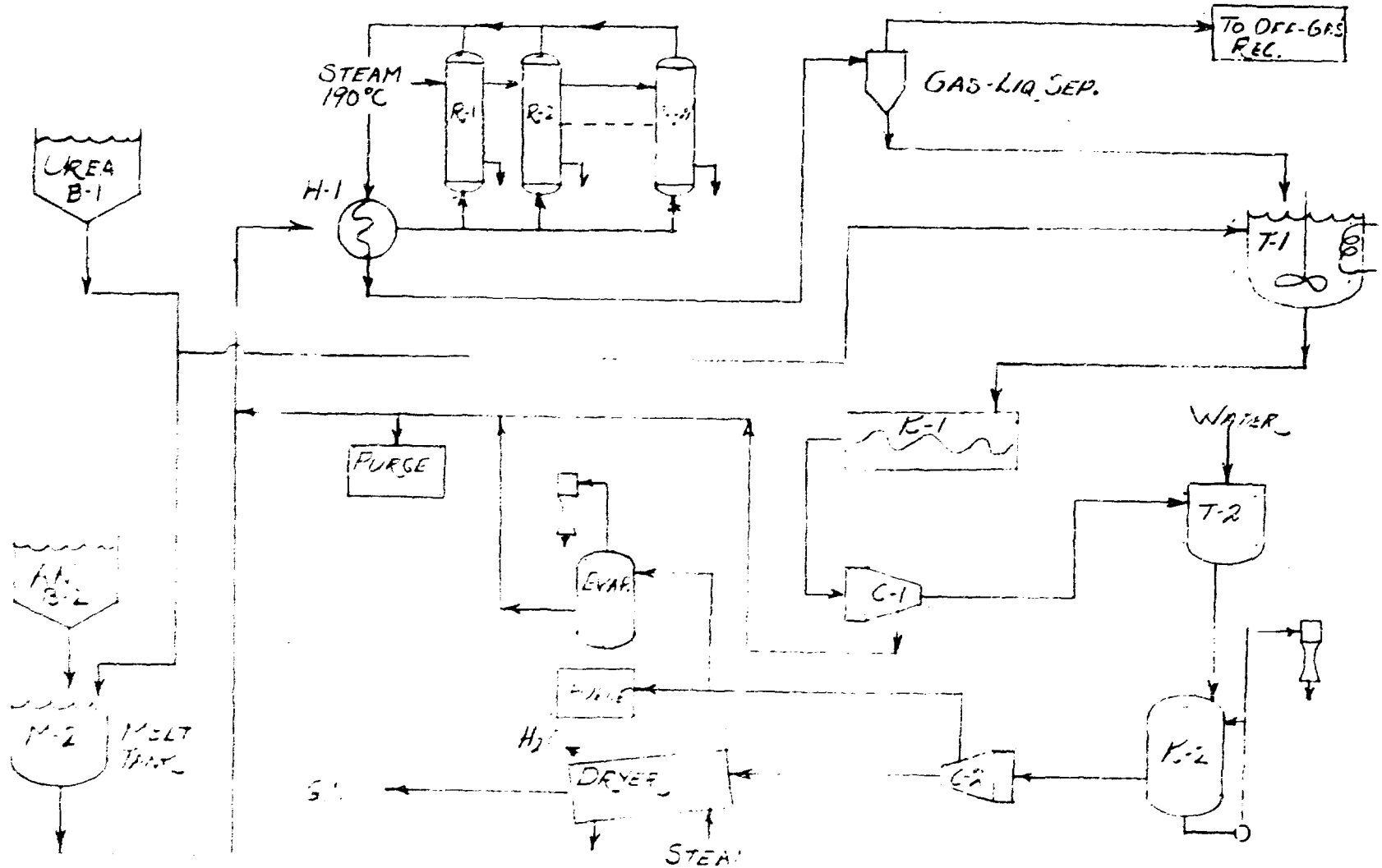



Figure 43. Flow Sheet for Guanidine Nitrate Production (Melt Workup)

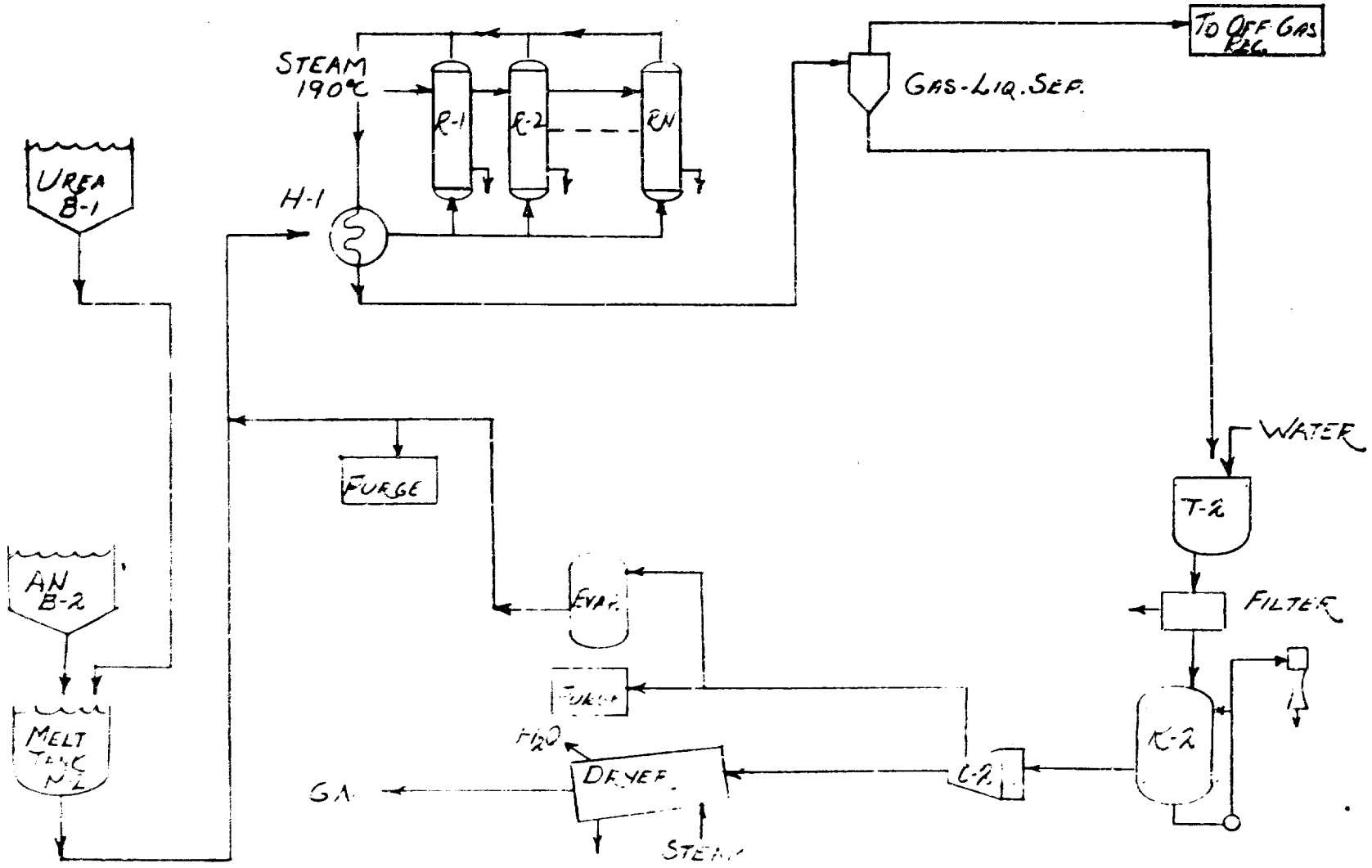
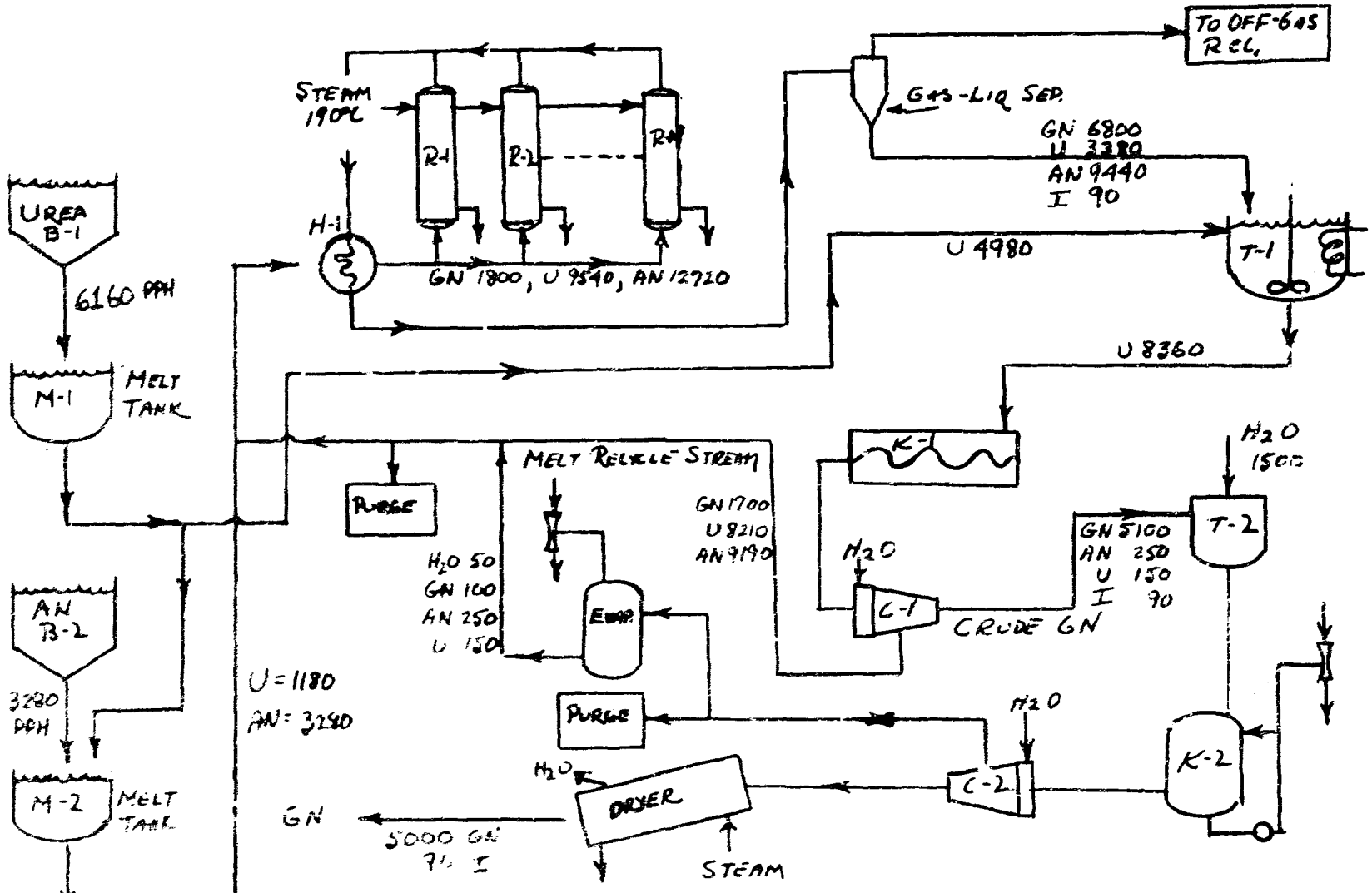



Figure 44. Flow Sheet for Guanidine Nitrate Production (Aqueous Workup)




Case 100

| | |
|---|---|
| Urea yield | 80% |
| Urea conversion | 64.5 |
| AN conversion | 32 |
| AN/U | 1.0 |
| Product | 98% |

$$U = \frac{6160}{5000} = 1.232 \text{ lb/lb GN}$$

$$AN = \frac{3280}{5000} = 0.656 \text{ lb/lb GN}$$

Figure 45. Material Balance for Case 100

c. Cost Sheet

Table 34 for case 100 gives the cost items included for each case investigated. The other cases investigated appear in Appendix I-5. Each item that enters into the mill cost and the sensitivity of such items are included. The lower the sensitivity index or number, the greater is the effect that the item has on the cost. For example, in Case 100, the plant investment and the urea most affect cost. For each 12% change in either the urea price or the quantity of urea required, the return on T.O.A. is changed 2%. In this manner, the items primarily concerned in the product economics are easily discernible.

d. Effect of Plant Capacity

The basic case was calculated at 40 million pounds per year. This was then scaled up to 80 million pounds and down to 20 million pounds. The scale-up is partly based on engineering judgment of consequences of equipment size changes and partly on equipment price volume using the 0.6 factor relationship.

Cases 100, 101 and 102 plotted in Figure 46 show cost changes with respect to plant capacity increases. The transfer price of GN drops 17% as the capacity increases from 20 million to 40 million pounds per year and 14% as the capacity doubles again to 80 million pounds per year. The cost advantage of large-scale operation appears to be leveling off at a 70 million to 90 million pounds per year plant size.

e. By-Product Credit

The by-product ammonium carbamate (AC) has been assigned a by-product credit of 0¢/lb in the basic case. The true value of this by-product is dependent on its final disposition. Based on Hercules' background in urea and ammonium nitrate manufacture and technology, and on selected data reported in the literature, it is predicted that the actual ammonium carbamate credit value will be in the range of 0 - 3¢/lb AC. By assigning the minimum credit value in the basic case, the most conservative mill cost results.

It is expected that the maximum credit value (3¢/lb AC) can be obtained if an adjoining urea plant (capacity = urea requirement for the GN plant of interest) is built. This prediction is based on a cost estimate, made in 1968 by Hercules, which assumed a low-tonnage urea plant using the Chemico low-ratio process. The capital cost of the urea plant would be about $1.3 million (based on a present ENR index of 1498) and its effect on the GN process would be to reduce the mill cost by 1.8¢/lb GN, exclusive of royalties (0.6 lb AC formed/lb GN X 3¢/lb AC value = 1.8¢/lb GN).

## TABLE 34

COST STUDY - GUANIDINE NITRATE
CASE NO.100

Basis: Basic Case
Cont. Process
AN/U/Cat. = 2/2/1.7
Yld. on U = 80% Conv. on U = 64.5%
Yld. on AN = 100% Conv. on AN = 32%

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

| | UNITS | RATE/UNIT | LIKELY | **SENSITIVITY PCT CHANGE | Gov't Acctg |
|---|---|---|---|---|---|
| INVESTMENT (MM $) | | | | | |
| BATTERY LIMIT | | | 4.22 | | 4.22 |
| OFFSITE AND ALLOCATED AUX. | | | 1.00 | | 1.00 |
| TOTAL (MM $) | | | 5.22 | 11 | 5.22 |
| PROCESSING COST (CENTS/LB) | | | | | |
| DEPRECIATION | | 10.0 PCT INVST | 1.30 | | - |
| MM AND RL | | 5.0 PCT INVST | .65 (2) | | .33 |
| OPERATING LABOR | 12.00 MEN | 8600.0 $/MAN-YR | .26 | 189 | .26 |
| CHEMICAL CONTROL | 4.00 MEN | 10000.0 $/MAN-YR | .10 | 471 | .10 |
| SUPERVISION | 4.00 MEN | 12000.0 $/MAN-YR | .12 | 399 | .12 |
| ELECTRICITY | .20 KWH/LB | 1.0 CNT/KWH | .20 | 294 | .20 |
| STEAM | 4.00 LB /LB | 75.0 CNT/M LB | .30 | 196 | .30 |
| WATER | 10.00 GAL/LB | 10.0 CNT/MGAL | .10 | 588 | .10 |
| FUEL | .01 GAL/LB | 7.0 CNT/ GAL | .10 | 560 | .10 |
| TOTAL (CENTS/LB) | | | 3.14 | | 1.51 |
| RAW MATERIAL COST (CENTS/LB) | | | | | |
| UREA | 1.23200 LB/LB | 4.00 CNT/LB | 4.93 | 13 | 4.93 |
| AMMONIUM NITRATE | .65600 LB/LB | 2.50 CNT/LB | 1.64 | 35 | 1.64 |
| CATALYST | .00100 LB/LB | 150.00 CNT/LB | .15 | 384 | .15 |
| TOTAL (CENTS/LB) | | | 6.72 | | 6.72 |
| PLANT OVERHEAD (CENTS/LB) | | | .27 | | .27 |
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS | | | 10.13 | | 8.50 |
| BY-PRODUCT CREDIT (CENTS/LB) | | | | | |
| AMMONIUM CARBAMATE | .60000 LB/LB | .00 CNT/LB | .00 | | .00 |
| TOTAL (CENTS/LB) | | | .00 | | .00 |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS | | | 10.13 | | 8.50 |
| | | | | Indirects | 1.78 |
| | | | | Price 0% return | 10.28¢/lb |

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT RETURN BY 5 PERCENTAGE POINTS

(1) Based on total operating assets.

(2) 50% is maintenance material.

RETURN CALCULATIONS

| | | |
|---|---|---|
| PLANT INVEST | $ | 5.2 MM |
| CORP ALLOC | $ | .2 MM |
| WORKING CAP | $ | .6 MM |
| TOT OP ASSETS | $ | 6.0 MM |

| | |
|---|---|
| PRICE FOR 0 PCT RETURN | 11.9 CENTS/LB (1) |
| PRICE FOR 20 PCT RETURN | 15.4 CENTS/LB |
| PRICE FOR 30 PCT RETURN | 17.2 CENTS/LB |

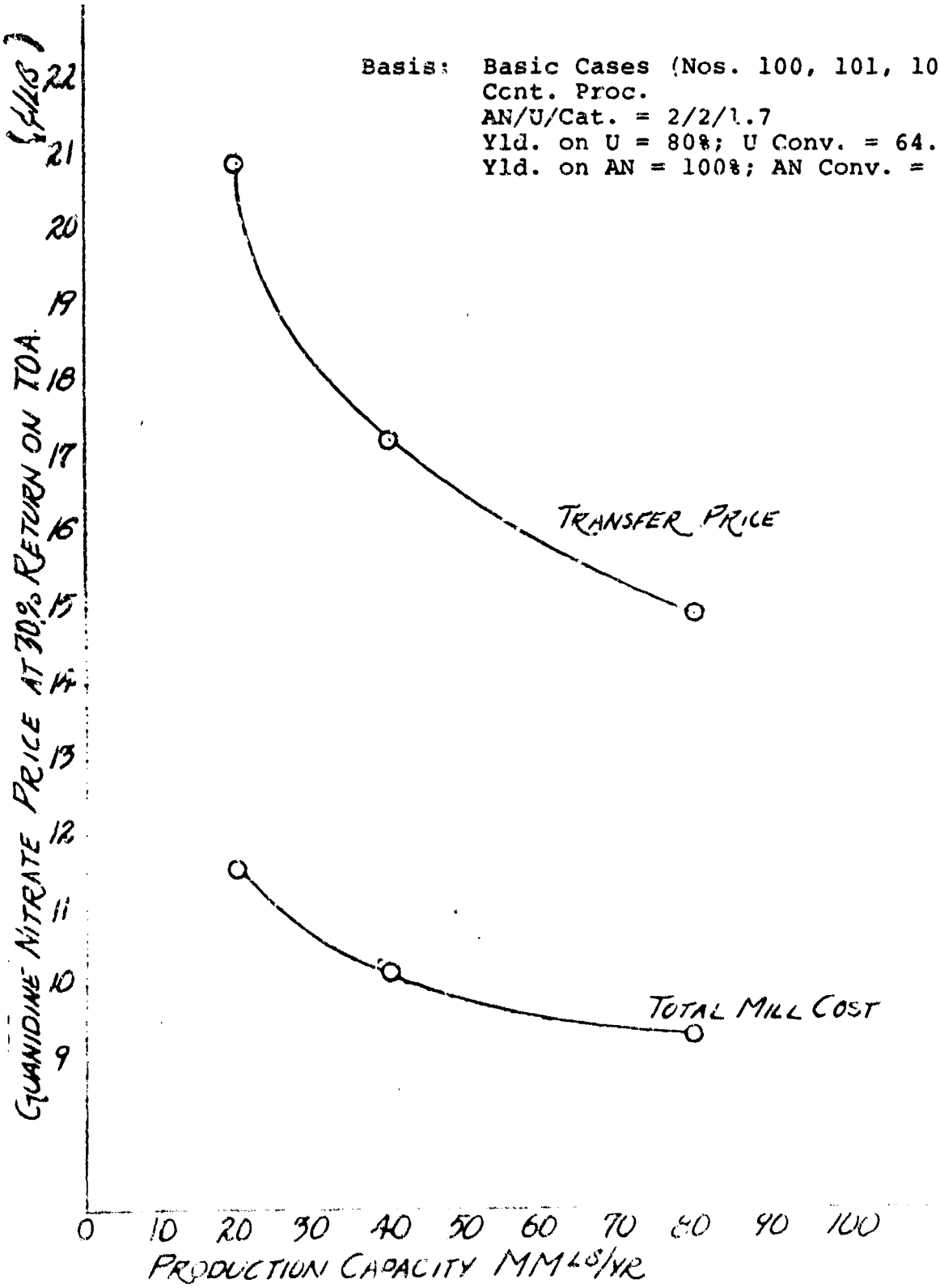



Figure 46. Effect of Plant Capacity on Costs

The minimum zero credit value represents situations in which the ammonium carbamate is sold to off-site urea or ammonium nitrate manufacturers or disposed of on-plant for ecology reasons. The former case is assigned a value of zero because AC does not have an established transfer price. The latter situation is a remote alternative which could become necessary if the material cannot be handled in any other manner.

There are a number of alternative dispositions for the ammonium carbamate which should result in credit values intermediate to those above. One of these is the use of the $NH_3$ (43.6%) portion of the ammonium carbamate for the production of ammonium nitrate. The additional plant investment to recover the $NH_3$ as $NH_4NO_3$ would be small. The resulting credit is estimated at 1¢/lb $NH_3$ or 0.25¢/lb GN based on the formation of 0.25 lb $NH_3$/lb GN. A second intermediate credit disposition method for the AC is the utilization of a less efficient urea plant. There are numerous processes for urea manufacture. The resulting mill cost of the urea from these processes is a function of the capital investment and tonnage. The basic urea reaction scheme is simple and well known but has a low conversion per pass (~ 50%). The differences between the various urea processes involve the recycling of the unconverted gases. Recycling improves yield but also increasesinvestment costs. The once-through process has no gas recycle and a low yield. It involves simultaneous compression of $NH_3$ and CO2 (molar ratio of 2/1 or greater to 2500-3000 psig) and contact at elevated temperature (~ 350°F) in a reactor. This is followed by a pressure reduction through a let-down valve, decomposition of unconverted AC by passage through a heat decomposer ($T_{out}$ ≈ 140°F), and then gas-liquid separation. In the high-pressure urea synthesis reactor, the gases are converted to ammonium carbamate, which in turn dehydrates at reaction conditions to urea and water. The liquid from the gas-liquid separator is an 80% urea solution.

As the preceding discussion points out, the credit that can be assigned to AC is wholly dependent on the additional capital investment required for recovery. Since this was not defined at this point in the program, it was elected to apply a zero AC credit for the basic economic analysis. This is constant for all parameter cases except those specifically directed toward evaluating the effect of by-product credit (Cases 810, 820, 830). Figure 47 shows the effect of such by-product credit on the value of GN. For each 1¢ credit for ammonium carbamate by-product, the mill cost decreases 0.6¢/lb GN and the transfer price at 30% of T.O.A. decreases 0.6¢/lb of GN. The net range (cost of recovery minus value) of the by-product value probably lies between 0.5¢ and 1.5¢/lb of ammonium carbamate.

f. Effect of Urea Price

The price of urea used here (5¢/lb delivered) is the price

Basis: Cont. Process. 40 MM lb./yr.
AN/U/Cat = 2/2/1.7
U Yld. = 80% U Conv. = 64.5%
AN Yld. = 100% AN Conv. = 32%
Cases: 100, 810, 820, 830

* Based on industrial accounting with transfer price at 30% on T.O.A.

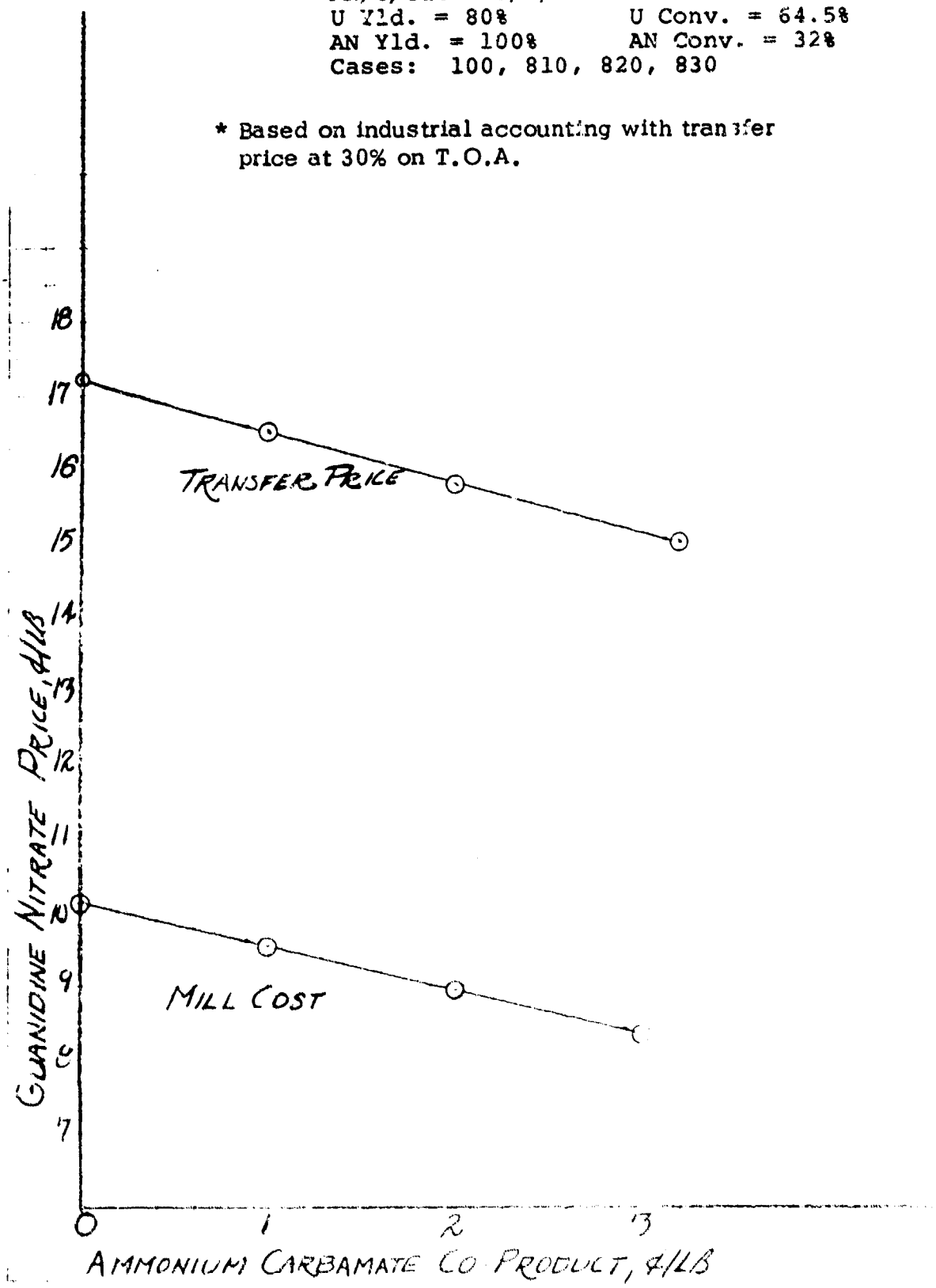



Figure 47. Effect of By-Product on Costs*

of commercial grade urea obtained by the Hercules' purchasing department. It is not necessarily the price that a GN producer will pay for his urea. Final urea (as well as ammonium nitrate) prices are dependent upon contracts for large volumes and will have to be determined at a later stage when the design of the plant has begun. To indicate the effect of urea costs on the GN prices, Cases 910 and 920 were calculated and plotted in Figure 48. Both GN mill cost and transfer price are a linear function of the urea price. For each 1¢ decrease in the urea price, the GN mill cost decreases 1.23¢/lb and the GN transfer price based on 30% of T.O.A. decreases 1.5¢/lb.

### g. Effect of Urea Yield on Costs

The mole ratio of AN/U/catalyst used is 2/2/1.7. The ratio of the two reactants to the catalyst is fixed for a plug flow reactor since the catalyst must be wet and excess liquid is not in contact with the catalyst. Under these conditions, the urea yield can be increased for a particular catalyst only by increasing the length of the reaction time, which means increasing the reactor size. The tradeoff is the saving of raw material versus greater investment. Table 35 summarizes increased urea yields obtained by increasing the reaction time.

TABLE 35

EFFECT OF UREA YIELD ON COSTS

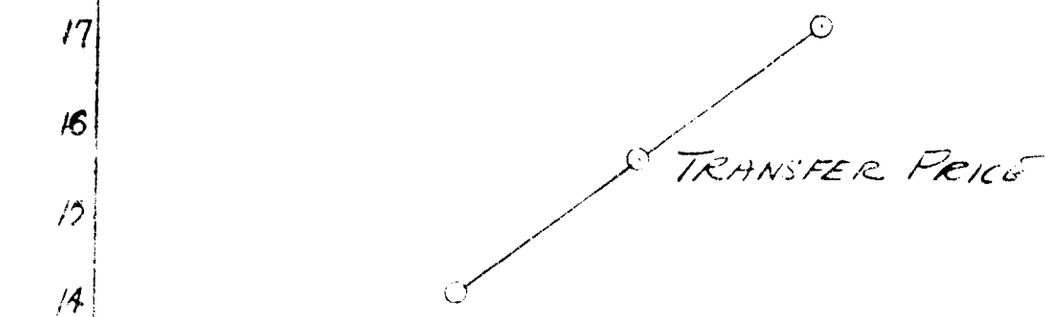
| Case | Urea Yield (%) | Urea Conversion (%) | Reaction Time (hr) | Mill Cost ¢/lb GN | Transfer* Price ¢/lb GN | Plant Investment $ Million |
|---|---|---|---|---|---|---|
| 100 | 80 | 64.5 | 1 | 10.1 | 17.2 | 5.2 |
| 210 | 87 | 88 | 2 | 10.1 | 17.8 | 5.8 |
| 220 | 88 | 98 | 3 | 10.5 | 19.0 | 6.6 |

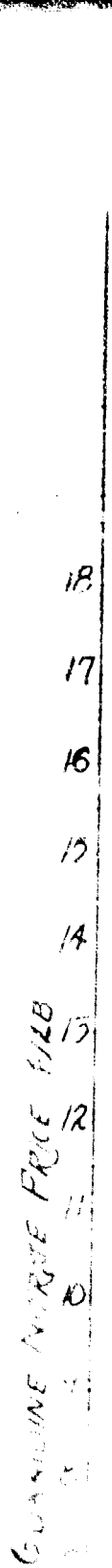
*Transfer price at 30% on T.O.A.

Plotting these values in Figure 49 indicates that the most economical operation is obtained by operation based on a 1-hour residence time at a lower urea yield (80% here). This is based on the urea cost of 4¢/lb. If cheaper urea is used, the effect is more pronounced since the sensitivity due to the urea price is decreased. Again, this is verified by the sensitivity index. When the reaction time is one-hour, the sensitivity due to urea is calculated as 12% (Case 100). This changes to 16% for a 3-hour reaction time (Case 220), indicating that it is less sensitive at the higher yield level.

Basis: Cont. Process. 40 MM lb./yr.
AN/U/Cat. = 2/2/1.7
U Yld. = 80% U Conv. = 64.5%
AN Yld. = 100% AN Conv. = 32%
Cases: 100, 910, 920

* Based on industrial accounting with transfer price at 30% on T.O.A.




GUARANTEE PRICE $/LB

MILL COST

PRICE OF UREA $/T

Basis: Cont. Proc.
AN/U/Cat. = 2/2/1.7

| Case | U Yld. | U Conv. | Time (Hr.) |
|---|---|---|---|
| 100 | 80 | 64.5 | 1 |
| 210 | 87 | 88 | 2 |
| 220 | 88 | 98 | 3 |

* Based on industrial accounting with transfer price at 30% on T.O.A.

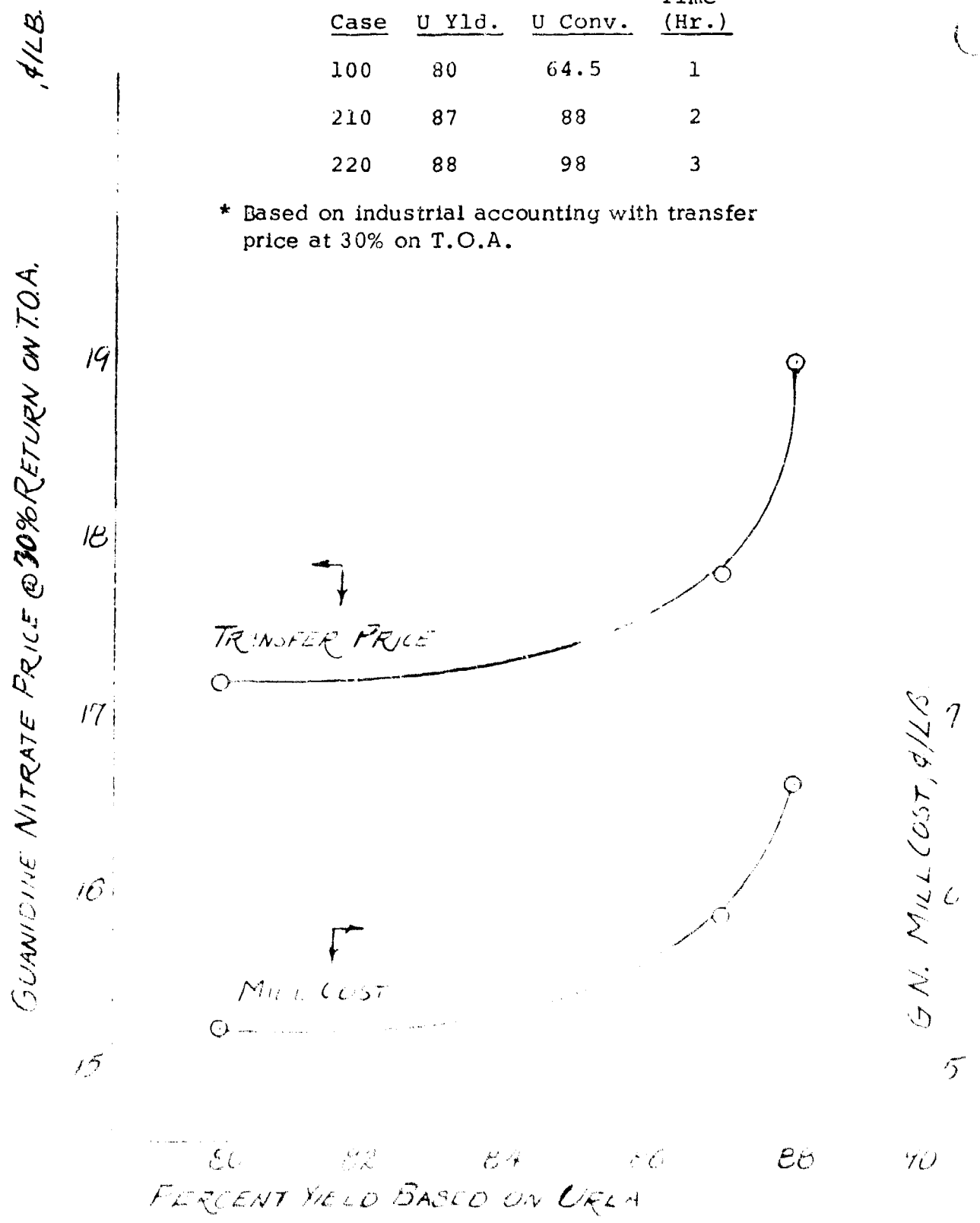



Figure 69. Effect of Urea Yields on Costs*

h. Workup of Crude GN

Two alternatives appear possible for recovery and purifying the GN from the reactor product. In one flow sheet (Figure 43), the GN is crystallized from the melt mixture and the crude GN is then recrystallized from a water solution. The alternative route (see Figure 44) is to take up the reactants directly into water, crystallize out the GN, and recover it by centrifugation.

The laboratory work indicates that the product purity and yield are roughly the same for both methods with the aqueous route being slightly better. The aqueous workup eliminates a mix tank (T-1), a crystallizer (K-1) and centrifuge (C-1).

The results on GN costs are as follows:

| Case | Workup | Plant Investment ($ Million) | Mill Cost (¢/lb) | Transfer Price* (¢/lb) |
|---|---|---|---|---|
| 100 | Melt | 5.2 | 10.1 | 17.2 |
| 301 | Aqueous | 4.6 | 9.8 | 16.2 |

*Price at 30% on T.O.A.

There is, therefore, a substantial incentive for one-step aqueous recovery. These results are shown graphically in Figure 50.

i. Effect of AN/U Ratio on Costs

The laboratory work has shown that increasing the amount of ammonium nitrate with respect to urea will increase yields. When large quantities of ammonium nitrate are used, it acts as a diluent and in a continuous system, where it is recycled, larger equipment results. Utility demands also increase since more water must be evaporated before recycle can be accomplished. As the amount of ammonium nitrate decreases, the equipment size decreases but at the expense of urea yield loss. Economic calculations were made to indicate the optimum range for these offsetting factors. These cases are all compared using the aqueous workup system, since at a large ratio of AN/U a eutectic mixture cannot be obtained for a melt workup. A 40-million pound per year plant with tubular reactors is the basis in all cases.

The results are summarized in the following table:

Basis: Cont. Process
AN/U/Cat. = 2/2/1.7
Reaction Time = 1 hr.
U Yld. = 80%
U Conv. = 64.5
40 MM lb./yr.

* Based on industrial accounting with transfer price at 30% on T.C.A.

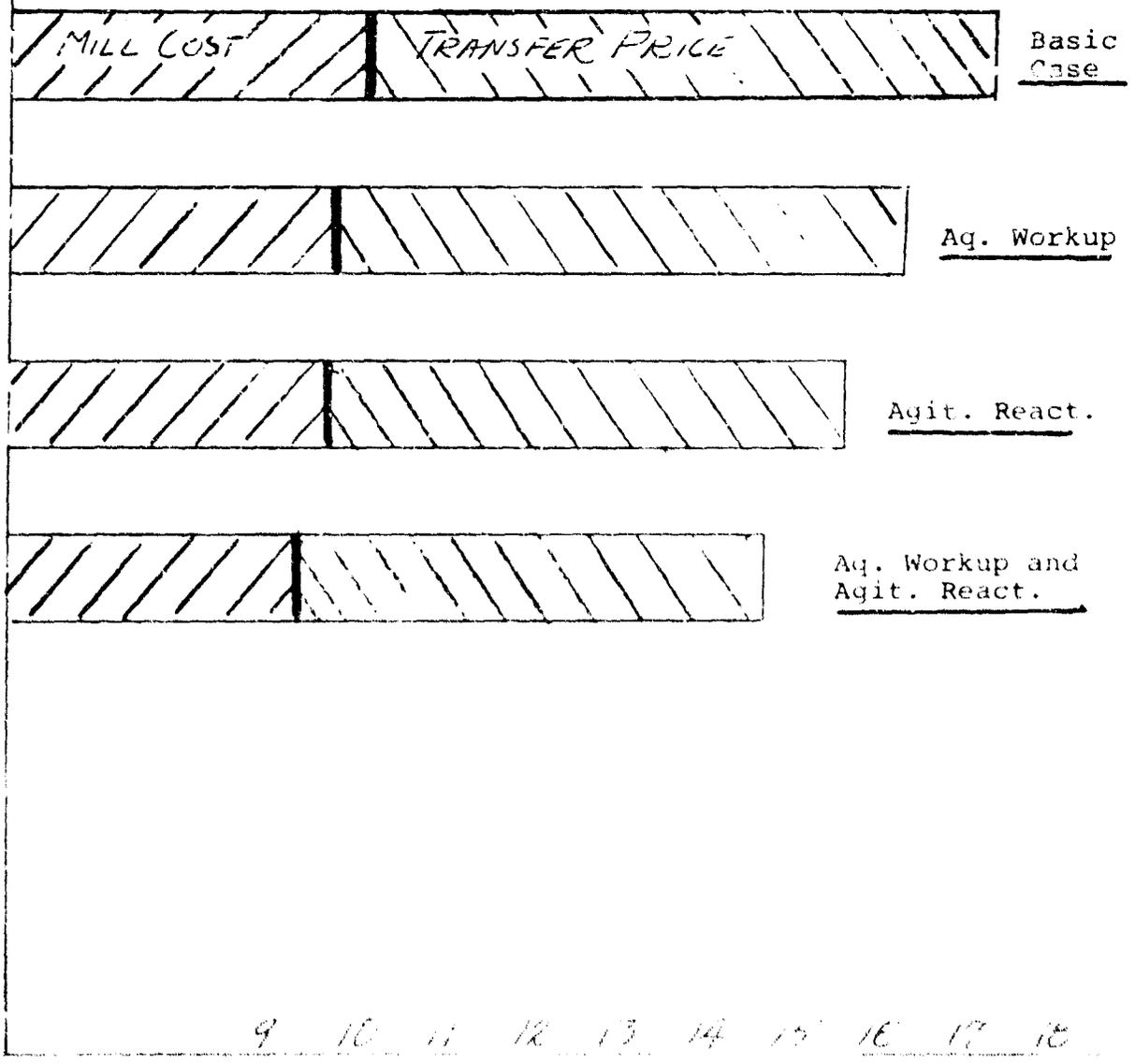



Figure 50. Effect of Reactor and Workup on Costs*

TABLE 36

EFFECT OF AN/U RATIO ON GN COST

| Case | AN/U | Urea Yield (%) | Urea Conversion (%) | GN Mill Cost (¢/lb) | GN Transfer* Price (¢/lb) | Plant Investment ($ Million) |
|---|---|---|---|---|---|---|
| 630 | 0.5 | 59 | 68.5 | 11.5 | 18.2 | 4.5 |
| 620 | 0.56 | 62.5 | 68 | 11.1 | 17.8 | 4.5 |
| 610 | 0.75 | 71 | 66.5 | 10.3 | 16.8 | 4.5 |
| 301 | 1 | 80 | 64.5 | 9.8 | 16.2 | 4.6 |
| 650 | 1.5 | 92.5 | 60 | 9.5 | 16.4 | 5.2 |
| 640 | 2 | 99 | 55.5 | 9.8 | 17.7 | 6.2 |

*Transfer price at 30% on T.O.A.

This is graphically illustrated in Figure 51 showing that the optimum AN/U on an economic basis is near 1/1.

j. Reactor Type

All economic evaluations are based on use of a packed tube. A 2-inch-diameter tube was chosen as a basis because the early reports indicated that this might be the more reasonable size. Later kinetic work indicated that 2- to 4-inch pipe size can be used. The cost of 3-inch-diameter reactors is about 80% of the cost of the 2-inch reactors; the cost of 4-inch-diameter reactors is about 65% of the cost of the 2-inch reactors.

Neglecting for the moment the point that safety may decide whether one can use an agitated type of reactor, calculations were made to indicate whether there is an economic incentive for the choice of an agitated reactor over packed tubes.

The costs are based on a system containing three agitated vessels in series, with the reactor volume approximately double the catalyst volume and the gas vented following each reactor. It is assumed that the catalyst is contained in a basket and that the catalyst life is approximately the same as that of the plug flow reactor. It was further

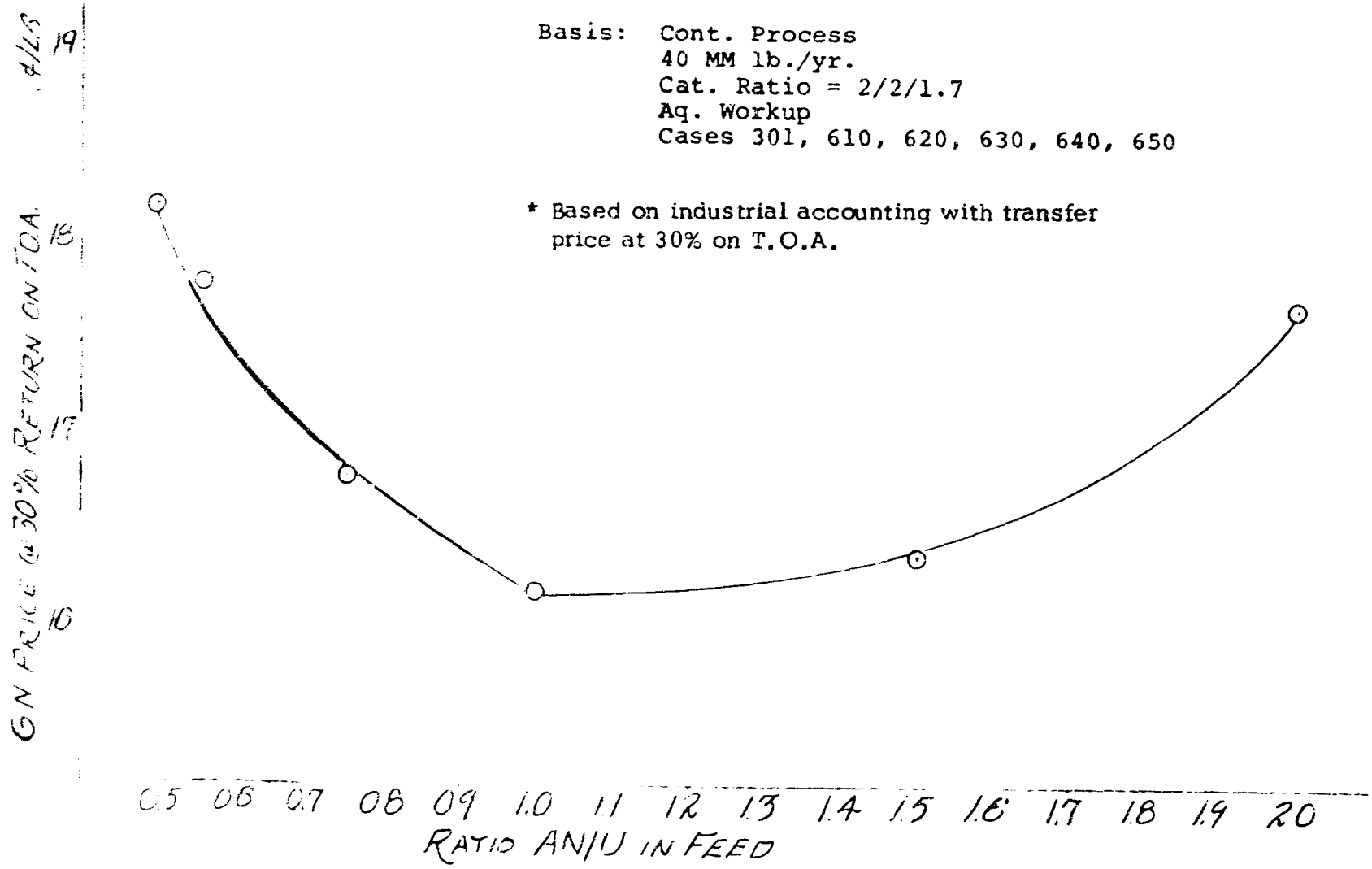



Figure 51. Effect of Ammonium Nitrate/Urea Ratio on Costs*

assumed that the agitated reactor costs were 20% of the cost of tubular reactors. Further analysis during Phase II (discussed in a future section) showed that this was not the case. However, the overall economics, based on the earlier assumption, are summarized as follows:

| Case | Reactor | GN Mill Cost (¢/lb) | GN Transfer Price (¢/lb) | Plant Investment ($ Million) |
|---|---|---|---|---|
| 100 | Packed Tube | 10.1 | 17.2 | 5.2 |
| 501 | Agitated Autoclave | 9.7 | 16.2 | 4 |

Figure 50 contains a graphical representation of these values. In addition, a case is included, and shown in the same graph, for a combination using agitated autoclaves and aqueous workup of the GN. If it is assumed that agitated reactors are lower in cost, as noted above, this case gives the most favorable economics picture.

| Case | Mill Cost (¢/lb) | Transfer Price (¢/lb) | Plant Investment ($ Million) |
|---|---|---|---|
| 710 | 9.3 | 14.6 | 3.4 |

k. Catalyst Life

A catalyst life of six-months was assumed for the Houdry macroporous silica beads for calculations. Based on a price of $1.50 per pound for this catalyst, the incremental cost to the GN product is 0.15¢ per pound of GN (Table 34) with the sensitivity index showing that its cost is negligible. Even with a two-month life, the catalyst cost portion would be only 0.45¢ per pound of GN, which can still be tolerated. Since silica gel catalyst is priced at about 35¢ to 50¢ per pound, the catalyst life leeway is greater for this catalyst before it becomes a significant cost item.

Basis for the cost study is presented in Table 7. Mill costs, industrial accounting GN transfer prices, plant investments, and Government accounting GN prices at 0% return for each case studied, are summarized in Table 38. Capital costs and plant equipment costs for a 40 million pounds per year GN plant are outlined in Tables 39 and 40, respectively.

TABLE 37

COST STUDY BASIS

1. Basic Case: AN/U/Catalyst mole ratio: 2/2/1.7
   40-million pound per year plant
   80% yield based on urea
   Urea conversion = 64.5%
   100% yield based on ammonium nitrate
   Ammonium nitrate conversion = 32%

2. Continuous process, Plant Operation = 8000 hours per year

3. Reactor: Tubular reactors, 2-inch tubes packed with catalyst.
   Reaction temperature = 190°C
   Assumed gas volume in reactor = liquid feed volume
   Residence time = 1 hour
   Endothermic reaction; 28Kcal/g mole GN (about 410 BTU per pound)

4. Catalyst: Houdry macroporous silica beads with assumed life approximately 1/2-year

5. Workup (basic case): Melt crystallization followed by recrystallization from water. Eutectic (for melt crystallization) taken as 47/53 = U/AN (wt. per cent)

6. A zero by-product credit was taken for ammonium carbamate for the basic cost calculations. However, values of 1 to 3¢/lb were assigned in Cases 810, 820, and 830 to indicate the effect on GN costs. See pp. 149 and 152 for discussion pertaining to by-product credits

7. Assumed existing plant site.

8. All equipment assumed 304 SS except for storage vessels.

9. Raw material prices (delivered)
   Urea = 4.0¢ per pound
   Ammonium nitrate prills = 2.5¢ per pound
   Houdry macroporous silica beads = $1.50 per pound
   (Cases 910 and 920 charges urea in at 2 and 3¢ per pound, respectively to indicate effect of urea price on GN price)

TABLE 37 (Continued)

10. Depreciation: 10 year, straight-line

11. Plant overhead: 25% of total labor plus 0.5 of plant investment for works accident.

12. Transfer price contains 15% indirects. Transfer prices at 30% on T.O.A. (total operating assets) are used for curves as well as mill cost. Values at 0% and 20% on T.O.A. are included in the detailed computer tables.

13. Definitions:

$$\text{Urea Conversion} = \frac{\text{moles urea reacted}}{\text{moles urea fed}} \times 100$$

$$\text{Urea Yield} = \frac{\text{moles GN formed}}{\text{moles urea reacted}} \times 100$$

14. Working capital is based on the following inventories:

| | |
|---|---|
| Raw Material | 1 month |
| Finished Material | 1 month |
| Maintenance Material | 6 months |

15. Corporate allocation in T.O.A. represents corporate allocated facilities equal to 3% of plant investment.

# TABLE 38

## INDUSTRIAL ACCOUNTING COST SUMMARY - GUANIDINE NITRATE

| Basis | | GN Total Mill Cost (¢/lb) | GN Transfer Price (¢/lb)* | Plant Investment (MM$) | Case | Government Accounting GN Price @ % Return (¢/lb) |
|---|---|---|---|---|---|---|
| Basic Case - [illegible] MM lb/yr | % Yield = 80<br>% Conversion = 84.5 | 10.1 | 17.2 | 5.2 | 100 | 10.3 |
| Basic Case - [illegible] MM lb/yr | " " | 9.3 | 14.9 | 7.6 | 101 | 9.8 |
| Basic Case - [illegible] | " | 11.6 | 20.9 | 3.7 | 102 | 11.3 |
| Effl[illegible] Yield - [illegible] yr | % Yield = 87<br>% Conversion = 88 | 10.1 | 17.8 | 5.8 | 210 | 10.1 |
| [illegible] yr | % Yield = 88<br>% Conversion = 96 | 10.[illegible] | 19.[illegible] | 6.6 | 220 | 10.3 |
| Elimination [illegible] Mill Crystallization | % Yield = 85<br>% Conversion = 84.5 | 9.8 | 16.2 | 4.6 | [illegible] | 10.1 |
| [illegible] | % Yield = 80<br>% Conversion = 84.5 | 9.7 | 15.5 | 4.0 | 501 | 10.2 |
| AN [illegible] 9.3% [illegible] Aqueous Ammonia | % Yield = 71<br>% Conversion = 66.2 | 10.3 | 16.8 | 4.5 | [illegible]0 | 10.8 |
| | % Yield = [illegible]<br>% Conversion = 68 | 11.1 | 17.8 | 4.5 | 620 | 11.7 |
| | % Yield = [illegible]<br>% Conversion = 68.5 | 11.9 | 18.3 | 4.5 | 630 | 12.1 |
| | % Yield = 99<br>% Conversion = 59.7 | 9.8 | 17.7 | 6.2 | 640 | 9.7 |
| | % Yield = 92.7<br>% Conversion = [illegible] | 9.7 | 16.4 | 5.2 | 650 | 9.5 |
| [illegible] | % Yield = [illegible]<br>% Conversion = [illegible].7 | 9.3 | [illegible].[illegible] | 3.4 | 710 | 9.9 |
| [illegible] A.C.** | [illegible] % | [illegible] | 16.[illegible] | 5.2 | 810 | 9.6 |
| | [illegible] % | 9.9 | 15.8 | 5.2 | 820 | 8.9 |
| | [illegible] % | 8.3 | 15.[illegible] | 5.2 | 830 | 8.2 |
| [illegible] | [illegible] % | 7.7 | 14.2 | 5.2 | 910 | 7.4 |
| | [illegible] % | 8.9 | 15.7 | 5.2 | 920 | 8.9 |

*[illegible]

**Ammonium carbamate by-product credit.

TABLE 39

PRELIMINARY ESTIMATE OF CAPITAL COST FOR 40 MM POUNDS/YR DRY GN BASED ON ENR INDEX-1465 AND USING TUBULAR REACTORS

| | in thousands |
|---|---|
| Purchased Equipment | $ 1,052 |
| Installation | 369 |
| Installed Equipment | $ 1,421 |
| Piping @ 60% | 853 |
| Building @ 30% | 427 |
| Electrical @ 7% | 100 |
| Instrumentation | 142 |
| Insulation & Painting @ %% Material and Labor | 71 |
| | $ 3,014 |
| Engineering & Supervision @ 10% | 301 |
| | $ 3,315 |
| Contractor's Fee at 15% | 498 |
| | $ 3,813 |
| Contingencies at 10% | 381 |
| | $ 4,194 |
| Catalyst (Houdry macroporous silica beads) | 25 |
| Battery Limit | $ 4,219 |
| Offsite & Allocated Facilities | 1,000 |
| Plant Investment | $ 5,219 |

TABLE 40

PRELIMINARY ESTIMATE OF PLANT EQUIPMENT COSTS (304 STAINLESS STEEL)
FOR CASE 100 - 40 MM POUNDS/YR DRY GN, BASED ON ENR INDEX-1465

| Ref. | Equipment | Purchase Cost |
|---|---|---|
| R-1 | Reactors; 2-inch (nominal) tubing, 35,000 ft total | $ 382,000 |
| H-1 | Reactor feed heat exchanger 250 sq. ft. | 13,000 |
| | Liquid-gas separator | 5,000 |
| T-1 | Mix tank, 2500 gal., agit, coil | 19,000 |
| T-2 | Crude GN dissolver, 1000 gal., agit. | 11,000 |
| T-3 | M.L. (from cent.) hold tank, 1500 gal. | 9,000 |
| T-4 | M.L. (from cent.) hold tank, 250 gal. | 2,500 |
| C-1 | Primary centrifuge, cont. (w/motor & controls) | 41,000 |
| C-2 | Secondary centrifuge, cont. (w/motor & controls) | 41,000 |
| | 3 - Conveyors | 11,000 |
| W-1 | Aqueous M.L., falling film evap., vac. | 35,000 |
| K-1 | Primary Crystallizer, cont. - Swenson Walker type, 300 ft. | 125,000 |
| K-2 | Secondary Crystallizer, cont.-growth type-Oslo or Krystal (6OTO) | 100,000 |
| | Cooler - refrigeration 35 tons, 0°F | 20,000 |
| D-1 | Dowtherm, 8.7 MM BTU/hr. | 50,000 |
| M-2 | U-AN Melt Tank, 2500 gal., 50 sq. ft. coil | 19,000 |
| S-1 | U - Air conveyor system | 10,000 |
| S-2 | AN - Air conveyor system | 10,000 |
| B-1 | U - Storage (Al) 25,000 gal. | 29,000 |
| B-2 | AN - Storage (Al) 10,000 gal. | 20,000 |
| B-3 | GN - Storage 25,000 gal. | 29,000 |
| D-2 | Rotary Dryer | 41,000 |
| | 2 - Metering Pumps | 6,000 |
| | 10 - Transfer Pumps | 10,000 |
| | 2 - Metering Feeders & Belt | 14,000 |
| | | $ 1,052,000 |

## B. PHASE II - PILOT PLANT DESIGN

### 1. Summary

The objectives of this phase of the program were to provide (a) a complete pilot plant design, with specifications, and (b) proposed methods of operation. In addition to a production capability of 40,500 pounds of guanidine nitrate (GN) for subsequent conversion to nitroguanidine (NQ), the pilot plant design was to have operating flexibility for investigating process variables and process upset conditions as related to overall process technology, GN quality, safety and full-scale production design.

The above objectives were met during this phase of the program. A pilot plant was designed having a nominal GN production rate of 50 lb/hr and the capability of producing 40,500 pounds of GN for delivery to the Contract Project Officer. This production rate was chosen to allow fulfillment of the production in about two months and to permit the use of prototype equipment sufficiently large to establish process feasibility. Two months is a conveniently short interval that in Hercules' experience provides the optimum balance between operating cost and pilot plant investment for the production commitment noted.

Highlights of Phase II activities were as follows: pilot plant equipment design and selection; equipment quotations; process equipment layout; preparation of a process flow sheet complete with material balance, operating conditions and equipment specifications; definition of utilities specifications, design and placement; instrumentation definition; preparation of general operating procedures; establishmen. of required building modifications; and equipment hazards analysis. The minor details of the pilot plant design, e.g. specific piping sketches, piping supports, etc., were not completed as they were planned activities during the early portion of Phase III. Decisions on equipment design and/or operating concepts were based on process technology generated throughout the program, hazards analysis, value engineering, state-of-the-art GN process knowledge, as well as Hercules' safety, process design and operating experience. The pilot plant design effort was conducted jointly between the Hercules Research Center Chemical Engineering Division, Kenvil Systems Group and ABI's Hazards Analysis Group personnel. The pilot plant was designed for placement at the Hercules/Kenvil, N. J. plant. Quotations were received for all process equipment, including instrumentation.

Each specified piece of equipment was subjected to a hazards analysis; i.e., comparing the in-process potential and material reactant energy potentials. After certain design changes had been made, all of the specified pilot plant equipment showed adequate margins of safety under normal operating conditions. In instances of zero margin of safety (abnormal operating condition), in-process material could ignite but its

burning would not transit to an explosion. Reactor mixture and GN will propagate an explosive reaction if sufficiently boostered. Other process materials will not sustain an explosive reaction in 1-inch-diameter pipe lines. In testing of a simulated packed tubular reactor 2 inch diameter x 12 feet long, burning did not transit to an explosion. A logic model (Fault Tree) simulation of the pilot plant design over 300 hours of operation resulted in a probability of initiation of $4.6 \times 10^{-3}$ or a corresponding probability of no initiation of 0.9953.

## 2. Equipment Selection

### a. Design Approach

The basic unit operations for the nominal 50 lb dry GN/hr pilot plant were as follows:

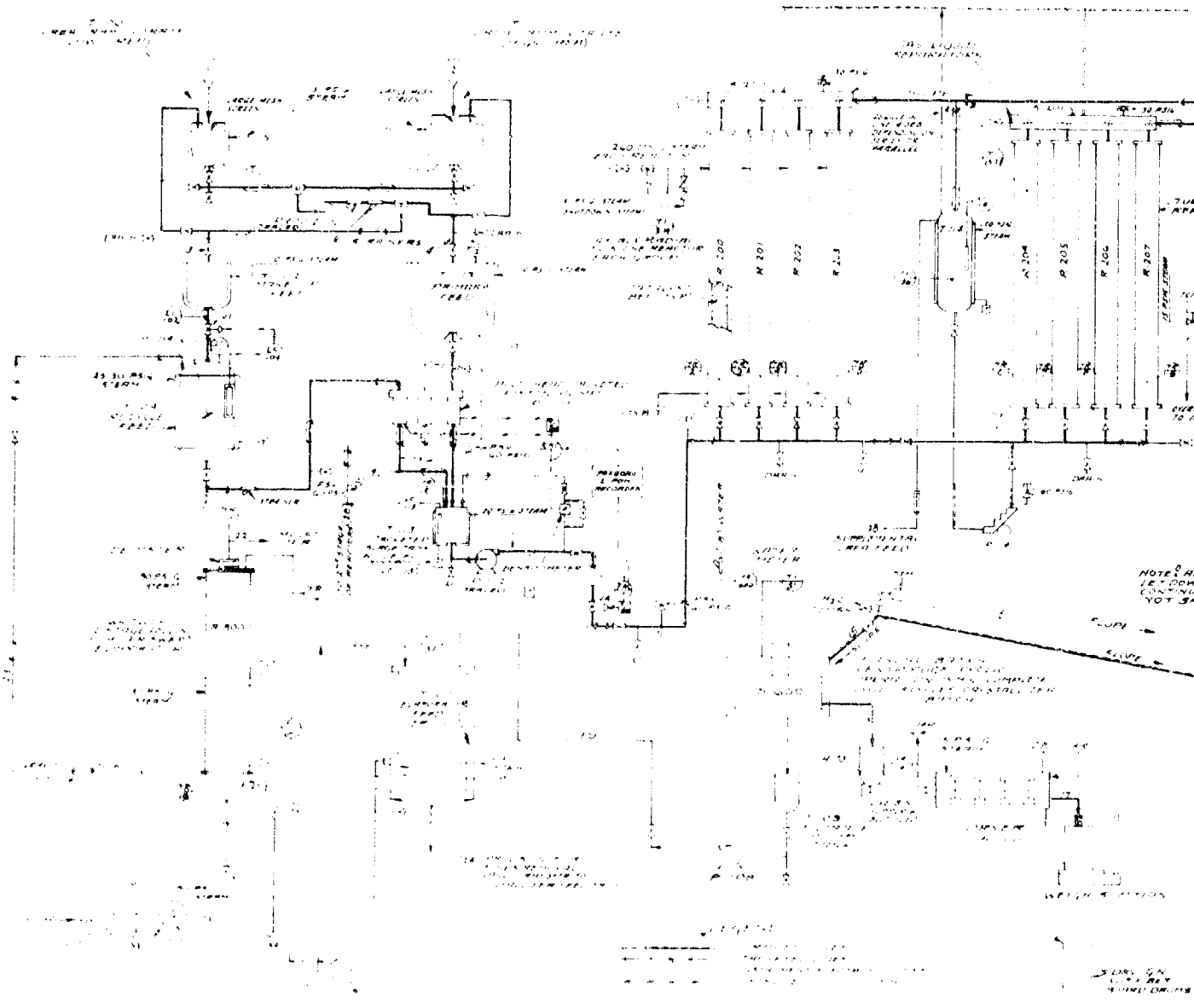
(1) Reactor feed system with varying AN/U ratio control flexibility.
(2) Packed tubular reactors arranged for operating flexibility and using Houdry CP-532 Silica Bead catalyst.
(3) Off-gas ($NH_3$ and $CO_2$) collection system.
(4) Single stage aqueous crystallization system consisting of an aqueous quench step, an insolubles separation step, and a vacuum crystallization step.
(5) GN solids/mother liquor separation operation.
(6) An evaporation system with GN/U/AN recycle to the reactor feed system.
(7) GN dryer-packout system.

The following constraints were imposed in selecting and/or designing equipment for the GN pilot plant:

(1) Operations associated with feed blending/metering, U/AN reaction, reactor off-gas collection, reactor product melt quenching, water insolubles removal, mother liquor evaporation and GN drying to be continuous.
(2) Urea and AN melting, vacuum crystallization and GN centrifugation operations to be done on a batch basis.
(3) All process equipment to be fabricated from stainless steel (type 304 or 316).
(4) All process heating to be done with saturated steam and hot water.
(5) Electrical requirements to be defined consistent with a 440V/3 phase building electrical system.
(6) The process equipment to be sized consistent with the 50 lb GN/hr dry product rate and to be compatible with an existing process building (Bldg. 2204).
(7) All equipment to be reviewed in terms of hazards potential and in-process energy potential to provide an adequate safety margin.

### b. Flow sheet and Equipment Layout

Heat and material balances were determined for the GN pilot plant. A process flow diagram was generated which is presented as Figure 52. Table 41 defines the referenced equipment depicted in Figure 52.



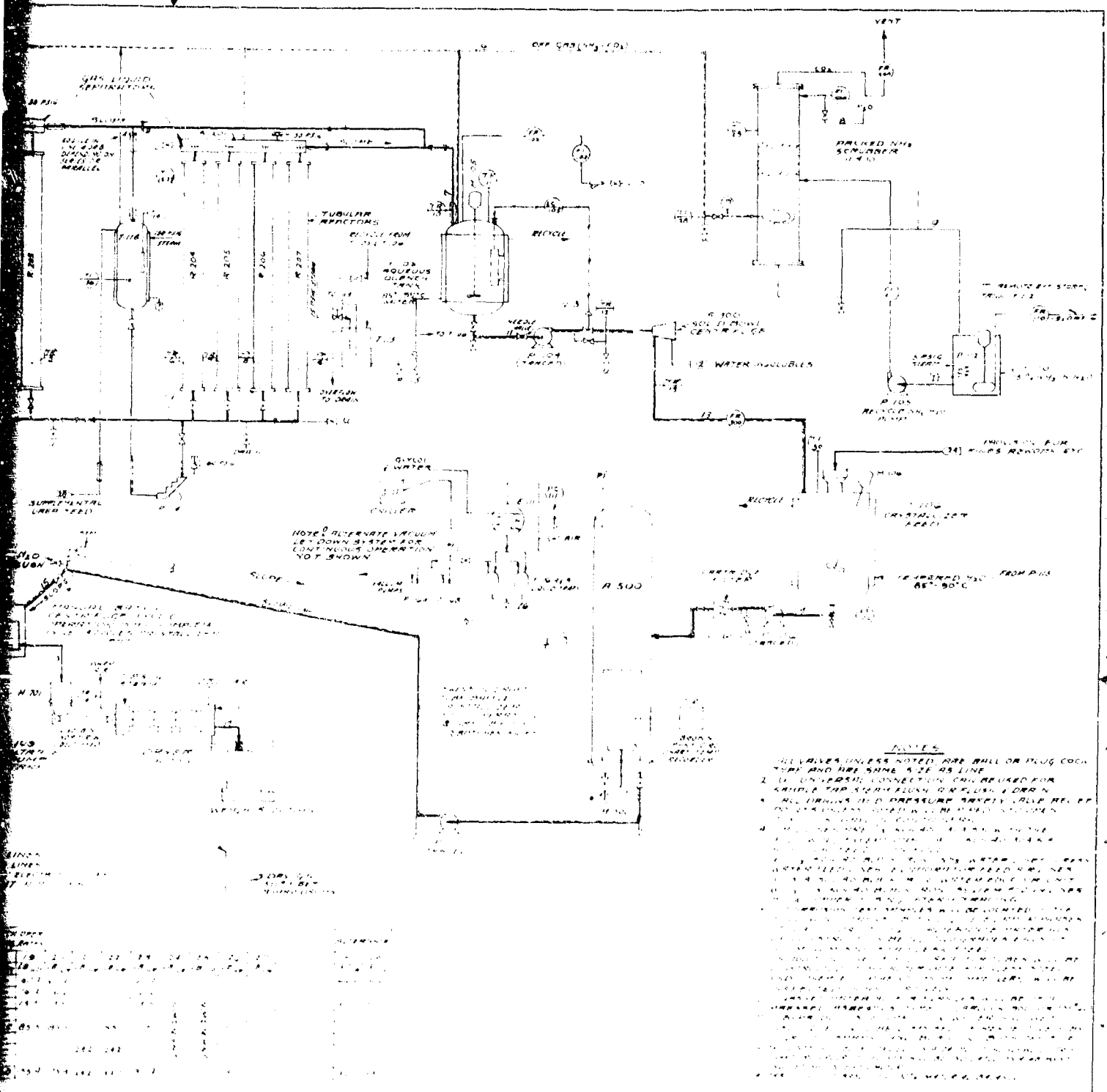



Figure 52. Guanidine Nitrate Pilot Plant Process Flow Sheet

TABLE 41

EQUIPMENT DESCRIPTION SHEET

| FLOW SHEET DESIGNATION | TITLE | DESCRIPTION |
|---|---|---|
| A-400 | Off Gas Scrubber | 6" diameter x 10 feet plexiglass flanged column packed with 1/2" raschig rings ( + 1.3K BTU/HR) |
| A-500 | GN Crystallizer | Swenson 100 gallon evaporative cooling draft tube crystallizer - 304 s.s. ( + 25K BTU/HR average) |
| A-700 | GN Dryer | Strong Scott 535-8-4 continuous 8' Solidaire Paddle Dryer - 304 s.s. ( - 27.5 BTU/HR) |
| A-800 | Evaporator | Whitlock #99 Pilot Plant - two stage falling film air swept evaporator - 304 s.s. ( - 120K BTU/HR average) |
| C-800 | Blower | 1 HP - 50 SCFM Whitlock Blower |
| CRC-1 | Composition Recorder - Control System | a) Automatic Products - "Dynatrol" density cell type CL-10HYT-jacketed 316 s.s.<br>b) Foxboro 62H - 5E Electronic Consetrol Controller<br>c) Foxboro 6420H 2-pen Milliampere Recorder (shared with FRC-1)<br>d) Foxboro 69TA Current - to-air converter |
| E-111 | Eductor Loop Cooler | American Standard 84 $ft^2$ single pass 316 s.s. heat exchanger or equivalent ( + 70K BTU/HR) |
| E-800 | Evaporator Air Heater | Whitlock type 3-Y-48, AET, heat exchanger ( - 13K BTU/HR) |

| FLOW SHEET DESIGNATION | TITLE | DESCRIPTION |
|---|---|---|
| FI-105 | Quench Tank Water Rotameter | Brooks Sho-Rate #150, Model 1355 Rotameter |
| FI-300 | Scrubber Fresh Water Rotameter | Brooks Sho-Rate #150, Model 1355 Rotameter |
| FI-401 | Scrubber $NH_3$-Water Rotameter | Brooks Sho-Rate #150, Model 1355 Rotameter |
| FI-800 | Evaporator Feed Rotameter | Brooks B55-8800 304 s.s. Flow Controller/ Integral Rotameter |
| FR-105 | Quench Water Flow Meter | Buffalo Meter Co - B-5/8" x 1/2" meters |
| FR-110 | $NH_3$ Water Flow Meter | Buffalo Meter Co - B-5/8" x 1/2" meters |
| FR-600 | Centrifuge Wash Meter | Buffalo Meter Co - B-5/8" x 1/2" meters |
| FR-300 | Aqueous Quench Flow Meter | Undefined |
| FR-400 | $CO_2$ Flow Meter | American Meter size 25B Sewage Gas Meter |
| FRC-1 | Feed Flow Control Loop | a) Foxboro E13 DM DP Transmitter W/Integral Orifice<br>b) Foxboro 62H-5E Electronic Consotrol Controller<br>c) Foxboro 6420 H 2-Pen Milliampere Recorder (shared W/CRC-1)<br>d) Foxboro 69TA I/air Transducer<br>e) V-4 |
| H-701 | Dryer Feeder | Vibra-Screw 5 cubic foot live bin feed hopper coupled with a belt feeder - 304 s.s. |
| H-702 | Scale | Platform Scale, 200 lbs. nominal capacity. |
| J-111 | Water Chiller for Vacuum Eductor System | Edwards Eng. Corp. 1½ ton packaged water chiller (+ 70 BTU/HR). |

| FLOW SHEET DESIGNATION | TITLE | DESCRIPTION |
|---|---|---|
| LC 105 | Level Controller for Aqueous Quench Tank | Foxboro Model 17BT-S41 Buoyancy Transmitter |
| LC 113 | Level Controller for Feed Surge Tank | Foxboro Model 17BT-S41 Buoyancy Transmitter |
| LI 102 | Level Indicator on Make-up Feed Tank | Air Bubbler System with 0-30" water gauge |
| LI 104 | Level Indicator for Recycle Feed Tank | Foxboro Model 17BT-S41 Buoyance Transmitter - Reverse Output |
| LI 105 | Level Indicator on Aqueous Quench Tank | Foxboro Model 17BT-S41 Buoyancy Transmitter |
| LI 106 | Level Indicator on Aqueous Quench Tank | Air Bubbler System with a 0-60" water gauge. |
| LI 113 | Level Indicator on Feed Surge Tank | Foxboro Model 17BT-S41 Buoyancy Transmitter |
| LI 114 | Level Indicator on Interstage Feed Tank | Foxboro Model 17BT-S41 Buoyancy Transmitter |
| M-104 | Agitator on T-104 | Lightning 5" flange mounted 1/3 HP N33-33 Mixer - 304 s.s. |
| M-105 | Agitator on T-104 | Lightning 5" flange mounted 1/3 HP N33-33 Mixer - 304 s.s. |
| M-106 | Agitator on T-106 | Lightning clamp mounced 1/3 HP Model ND-2 Mixer - 304 s.s. |
| M-500 | Agitator on Crystallizer | Lightning flange mounted, bottom entering, 3/4 HP N33-GDS75 Mixer - 304 s.s. |
| P-100 | Melt Transfer Pump | Goulds Model 3199- 1 x 1 x 5 centrifugal pump - W/Teflon filled packing; operating at 1750 RPM. |

TABLE 41 (CONT'D.)

| FLOW SHEET DESIGNATION | TITLE | DESCRIPTION |
|---|---|---|
| P-101 | Composition Blend Pump | Hills-McCanna 3-headed K-type metering pump with jacketed head and check valve assemblies - 316 s.s. with pneumatic stroke adjustment and speed control units. |
| P-102 | Feed Pump | Goulds Model 3199- 1 x 1 x 5 centrifugal pump W/Teflon-filled packing; operating at 3500 RPM |
| P-104 | Aqueous Quench Transfer Pump | Goulds Model 3199- 1 x 1 x 5 centrifugal pump W/Teflon - filled packing; operating at 1750 RPM. |
| P-105 | Recycle $NH_3$ Water Pump | Roper IK10-14 Gear Pump - cast iron (on hand from Phase I) |
| P-106 | Crystallizer Feed Pump | Goulds Model 3199- 1 x 1 x 5 centrifugal pump W/Teflon - filled packing; operating at 1750 RPM |
| P-107 | Crystallizer Slurry Pump | Goulds Model 3199- 1 x 1 x 5 centrifugal pump W/e Mechanical Seal; operating at 3500 RPM |
| P-108 | Mother Liquor Transfer Pump | Goulds Model 3199- 1 x 1 x 5 centrifugal pump W/Teflon - filled packing; operating at 1750 RPM |
| P-109 | Evaporator Feed Pump | Goulds Model 3199- 1 x 1 x 5 centrifugal pump W/Teflon - filled packing; operating at 3500 RPM |
| P-112 | $NH_3$ - Water Storage Level Control Pump | Penberthy Iron Guard 5 GPM Sump Pump |
| P-114 | Interstage Feed Pump | Hills-McCanna, Model UM-IF Piston Pump, 316 s.s., to deliver 30 GPH at 375°F |

TABLE 41 (CONT'D.)

| FLOW SHEET DESIGNATION | TITLE | DESCRIPTION |
|---|---|---|
| P-115 | Tempered Water System Pump | Crane #1 - SA6 - Figure 4001 Centrifugal Pump - On Hand |
| P-116A<br>P-116B | Mechanical Vacuum Pumps | Stokes 40 CFM Microvac Mechanical Vacuum Pumps |
| PG-111 | Crystallizer Vacuum Control | Manual Air Bleed |
| R-200 | Reactor | 304 s.s. Reactor, 4" I.D. x 12 ft. with 11-1/2 ft. of catalyst (Houdry Beads). Jacketed with 304 s.s. for 300 psig operation. Equipped with 6 dual radial entering thermocouples for profile measurement. ( - 10K BTU/HR EACH) |
| R-201<br>&<br>R-202 | Reactor | 304 s.s. Reactors, 4" I.D. x 12 ft. with 11-1/2 ft. of catalyst (Houdry Beads). Jacketed with 304 s.s. for 300 psig operation. ( - 10K BTU/HR EACH) |
| R-203 | Reactor | 304 s.s. Reactors, 4" I.D. x 12 ft. with 11-1/2 ft. of catalyst (Houdry Beads). Jacketed with 304 s.s. for 300 psig operation. ( 10K BTU/HR EACH) |
| R-204 | Reactor | 304 s.s. Reactors, 4" I.D. x 12 ft. with 11-1/2 ft. of catalyst (Houdry Beads). Jacketed with 304 s.s. for 300 psig operation. Equipped with 6 dual radial entering thermocouples for profile measurement. ( 10K BTU/HR EACH) |
| R-205 | Reactor | 304 s.s. Reactors, 4" I.D. x 12 ft. with 11-1/2 ft. of catalyst (Houdry Beads). Jacketed with 304 s.s. for 300 psig operation. ( - 10K BTU/HR EACH) |
| R-206 | Reactor | 304 s.s. Reactors, 4" I.D. x 12 ft. with 11-1/2 ft. of catalyst (Houdry Beads). Jacketed with 304 s.s. for 300 psig operation. ( - 10K BTU/HR EACH) |

TABLE 41 (CONT'D.)

| FLOW SHEET DESIGNATION | TITLE | DESCRIPTION |
|---|---|---|
| R-207 | Reactor | 316 s.s. Reactors 4" I.D. x 12 ft. with 11-1/2 ft. of catalyst (Houdry Beads). Jacketed with 304 s.s. for 300 psig operation. ( - 10K BTU/HR EACH) |
| S-106 | In-line Cartridge Filter | Filterite Corp. LM020S-3/4 In-line polishing on cartridge filter-316 s.s., 100 μ |
| S-200 | Gas-Liquid Separators | Custom Built - 6" diameter x 5 ft. horizontal separator jacketed - 304 s.s. |
| S-201 | Gas-Liquid Separators | Custom Built - 6" diameter x 5 ft. Horizontal separators jacketed - 304 s.s. |
| S-300 | Insolubles Separator | DeLaval Model 12 ATM Laboratory solid bowl centrifuge - 20 GPH @ 1 micron - 316 s.s. |
| S-600 | GN Basket Centrifuge | DeLaval ATM Mark III link suspended 22" x 16" centrifuge - 304 s.s. 250-350 lbs/hr @ 100-200 micron |
| T-100 | Low Urea Melt Tank | 60 gallon - 304 s.s. dished bottom jacketed tank with lift-off cover and internal coil - Lee Metal Products. ( - 11K BTU/HR average) |
| T-101 | High Urea Melt Tank | 100 gallon - 304 s.s. dished bottom jacketed tank with lift-off cover and internal coil - Lee Metal Products. (-11K BTU/HR average) |
| T-102 | Make-Up Feed Tank | 30 gallon 304 s.s. dished bottom jacketed tank with lift off cover - Lee Metal Products |
| T-103 | Primary Feed Tank | 60 gallon 304 s.s. dished bottom jacketed tank with lift off cover - Lee Metal Products |
| T-104 | Recycle Feed Tank | 60 gallon 304 s.s. dished bottom, bolted on head jacketed tank - Lee Metal Products. |

TABLE 41 (CONT'D.)

| FLOW SHEET DESIGNATION | TITLE | DESCRIPTION |
|---|---|---|
| T-105 | Aqueous Quench Tank | 50 gallon 304 s.s. dished bottom, bolted on head jacketed tank - Lee Metal Products |
| T-106 | Crystallizer Feed Tank | 200 gallon 304 s.s. flat bottom, jacketed tank with lift off cover - Lee Metal Products. |
| T-107 | Evaporator Feed Tank | 200 gallon 304 s.s. flat bottom tank with heating coil and baffles, and with lift-off cover - Lee Metal Products |
| T-109 | Filtrate Pump Tank | 30 gallon 316 s.s. drum bomb - (on hand from Phase I) |
| T-110 | $NH_3$ - Water Hold Tank | 53 gallon steel drum with plastic insert - Container Corp. of America 2S-0505, 18 ga., Type A |
| T-113 | Feed Surge Tank | United Utensils 30 gal. 316 s.s. Drum W/Jacket |
| T-114 | Interstage Feed Tank | Terriss-Consolidated custom made 8 gal. s.s. vessel W/jacket |
| T-115 | Tempered Water Feed Tank | 30 gal. insulated steel drum - on hand |
| T-116A<br>T-116B | Crystallizer<br>Condenser Traps | 8 gal. s.s. custom built<br>Traps - on hand |
| T-112 | $NH_3$ - Water Storage Tank | 30,000 gallon tank - on hand |
| V-1 | Make-up Feed Control Valve | Research Controls Miniature Diaphragm Motor Valve, 1/2" 316 s.s. |
| V-2 | Interstage Feed Control Valve | Research Controls Miniature Diaphragm Motor Valve, 1/2" 316 s.s. |

TABLE 41 (CONT'D.)

| FLOW SHEET DESIGNATION | TITLE | DESCRIPTION |
|---|---|---|
| V-3 | Aqueous Quench Control | Research Controls Miniature Diaphragm Motor Valve, 1/2", 316 s.s. |
| V-4 | Flow Control Loof Valve | Research Controls Miniature Diaphragm Motor Valve, 1/2", 316 s.s. |

It had been defined in a pre-contractual award safety audit that the selected process building (Bldg. 204) would require expansion in order to house the anticipated pilot plant equipment. To determine the extent of this expansion and to show that the equipment placement could be achieved consistent with both Hercules' and the Government's safety and engineering standards, a building layout was prepared. This equipment arrangement is shown in Figure 53. Approvals of the Government Contract Project Officer for the flow sheet and equipment arrangement drawings were received at the end of Phase II.

c. Specific Process Equipment Selection

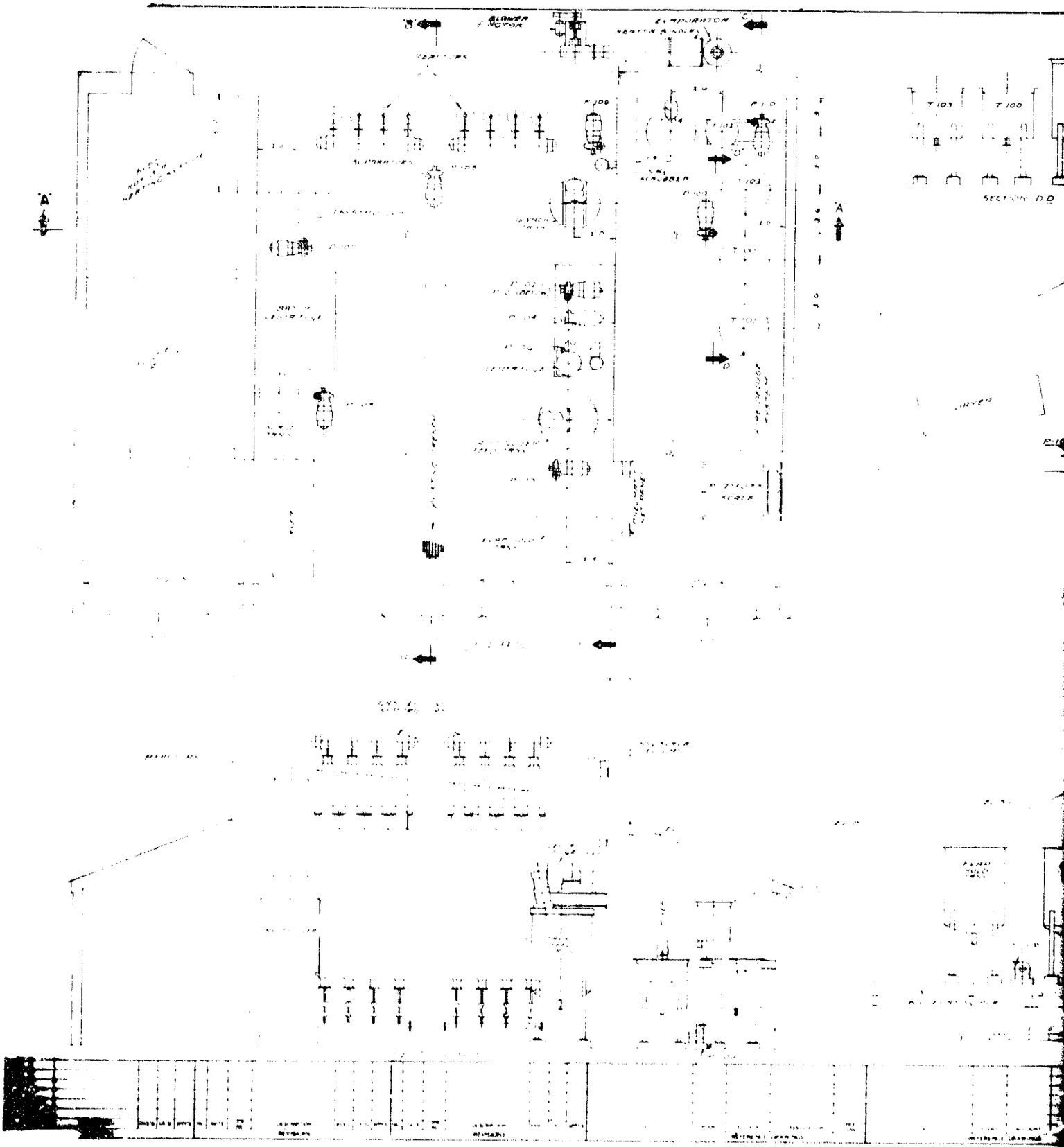
The following subsections present discussions of the individual units of the pilot-plant process equipment. In general, these subsections include the following: description of unit operation, design criteria, general method of operation, design constraints, and procurement/fabrication specifications. Reference to the process flow sheet (Figure 52) will be helpful to the reader.

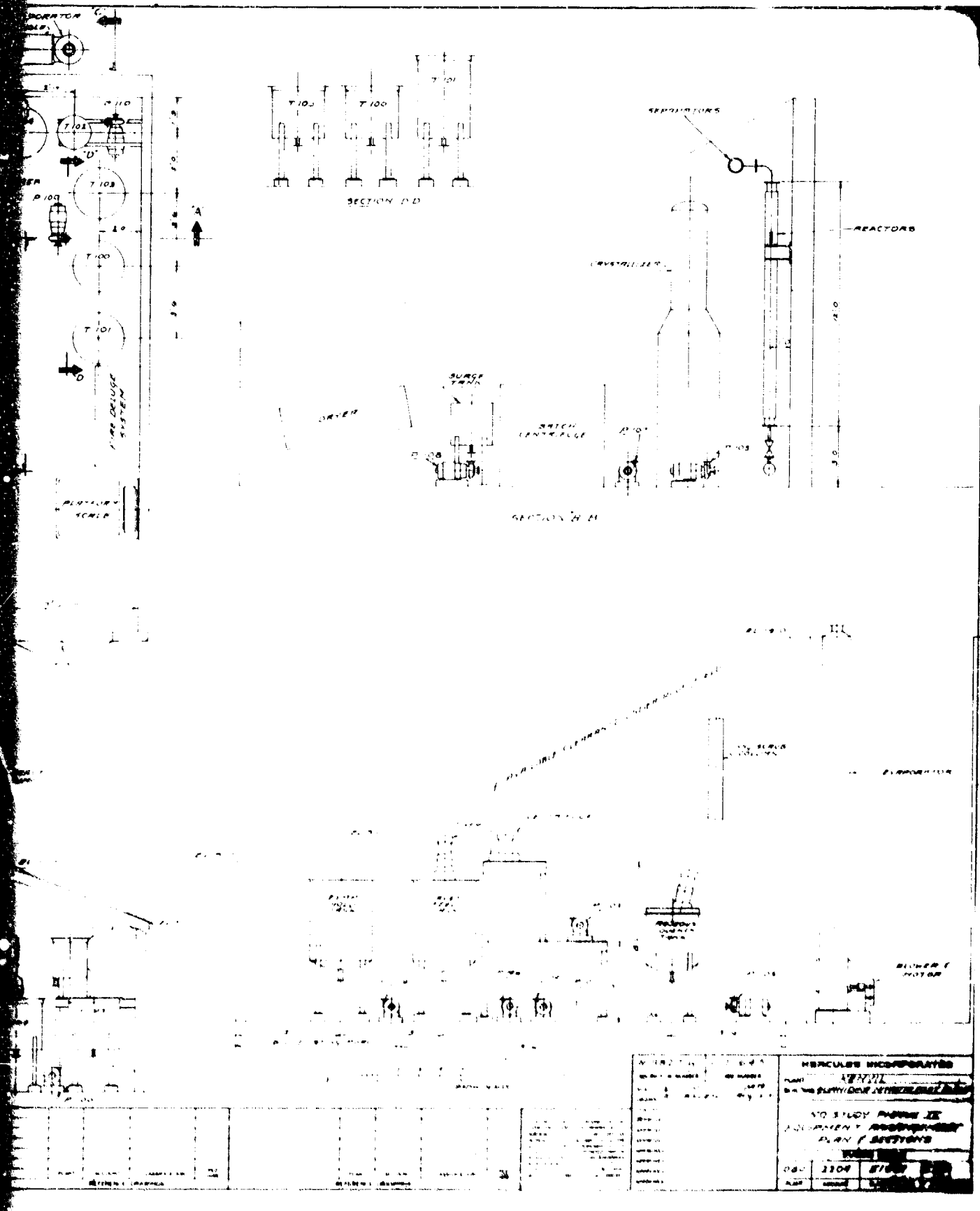
1 Reactor Feed System

Design of the reactor feed system was extremely important in establishing both operational and process control. The design of this system was more complex than usual for such a unit since the system must correctly proportion a two-component fresh feed stream (AN, U) with a three-component recycle stream (AN, U, GN) to achieve a predetermined AN/U motor feed ratio for the reactors. Known reactor feed compositions are required for process variable studies, kinetics, yield-conversion determinations, etc.

a Design Criteria

(1) Minimize possibility of operator error.
(2) Size the feed melters so that urea (U) and ammonium nitrate (AN) are charged only one or two times per shift.
(3) Select controls so that temperature, composition, and flow rate can be easily and quickly adjusted within suitable control ranges.
(4) Design a system with maximum reliability.
(5) Select materials of construction based on information gained in previous corrosion studies.
(6) Include safety human engineering considerations when designing equipment.
(7) Utilize uncoated and prilled urea and AN.


BLOWER MOTOR
EVAPORATOR
SECTION DD


T-101
T-103
T-100
SECTION D-D
SEPARATORS
REACTORS
CRYSTALLIZER
SURGE TANK
DRYER
BATCH CENTRIFUGE
FIRE DELUGE SYSTEM
HERCULES INCORPORATED

b General Description of Proposed Feed System Operation

(1) Charge feed melting tanks (304 stainless steel) 1-2 times per shift with a 4:1 weight ratio of U to AN and 1:4 U to AN in the respective tanks. Modify the makeup composition as required.
(2) Control temperature in the melters by low pressure (5-10 psig) steam in coils or jackets.
(3) After melting, transfer feed into heated hold tanks, again with the temperature controlled by low pressure steam.
(4) Transfer make-up feed to the recycle feed tank from a gravity flow tank with the rate governed by a level control (LC) system on the recycle feed tank.
(5) Mix high AN recycle from the evaporator (originating from the reactors) with 4 to 1 (AN/U) fresh feed.
(6) Control the proper ratio of high and low AN feed streams to achieve the desired reactor feed composition with an automatic variable stroke and speed piston pump.
(7) Discharge the make-up and recycle materials from the proportioning piston pump to a small surge tank, equipped with an LC system to control the piston pump speed and thus ensure sufficient feed supply for the reactors.
(8) Measure the density of the blended feed material in the surge tank with a densitometer.
(9) Transmit a signal from the composition sensor to a three-mode controller to adjust the individual stroke lengths of the proportioning piston pump.
(10) Control the feed rate to the reactors with a pneumatic flow control system.

c Description of Equipment Selected for Reactor Feed System

(1) Feed Melters (T-100, T-101) and Feed Hold Tanks (T-102, T-103)

The purpose of the feed melters and feed hold tanks is to provide feed melt of the proper urea/ammonium nitrate (U/AN) composition to the feed pump. The urea and AN virgin feeds are mixed during the melting step to reduce urea degradation and to keep melter temperatures low. The melter-hold tank arrangement is used to ensure that a totally melted feed is available to the blend pump. In a commercial plant, continuous solids feeding and melting or evaporation of water solutions would be used. Because of the small rates, solids feeding and continuous melting would not have been justifiable in the pilot plant.

The melters and hold tanks were sized so that bag quantities of urea and ammonium nitrate solids could be charged only once per shift. Since unc[illegible] AN prills were used, no feed filtration was necessary If it becomes [illegible]sary to use coated prills for a commercial plant, selection of a suita[illegible]lter will be easy since the melted AN feed characteristics are well kn[illegible]

[illegible] feed compositions of 4:1 and 1:4 AN to U (wt. basis) were selected [illegible]ve a good range for composition control and to limit the melter hold ta[illegible] temperatures to about 110°C. Another reason for selecting the 4:1 AN to [illegible]atio was that the predicted recycle melt from the evaporator had a simil[illegible]mposition. Matching of the two high composition AN streams is useful i[illegible] event of a failure in the composition control loop. In this event, [illegible]lend pump stroke length is set with the composition controller in th[illegible]al mode to proportion the 4:1 and 1:4 feeds to give the desired reac[illegible]ed composition.

The high composition AN melter (T-100) was sized to handle 320 pounds of ammonium nitrate and 80 pounds of urea per charge or about a one-day supply. A 60-gallon standard tank with a loose cover was selected for this service. The loose cover would facilitate charging of the solids which is accomplished by emptying a selected number of bags containing AN and U. In addition to the lid, there is a large mesh stainless steel screen across the top of the vessel to trap loose paper, etc. The vessel is jacketed and has an internal steam coil which provides adequate heat transfer area for melting.

The high concentration AN hold tank (T-102) was sized to handle a one-shift supply of feed melt - about 15 to 25 gallons. A 30-gallon jacketed tank operating at one-half capacity was selected. Since the feed melt is a true solution, no mixing is needed to improve heat transfer.

The high concentration urea melter (T-101) was sized to handle 160 pounds of ammonium nitrate and 640 pounds of urea per charge. Since this amounts to about 80 gallons of melt, a jacketed 100-gallon melter was selected. This melter also has a loose cover, an internal steam coil, a stainless steel mesh cover but no mixer. Feed melt is circulated back to the melters through a pump loop using the feed melt transfer pump (P-100) whenever convective mixing is not adequate.

The high urea content feed melt hold tank (T-103) was also sized to hold about a one-shift supply of feed melt. Since the flow rate from the hold tank is about 8 gallons per hour, a 60-gallon tank was selected.

(2) Evaporator Recycle Feed Tank (T-104)

This vessel is used for mixing the recycle melt (AN, U and CN) from the evaporator with fresh AN feed and for providing some surge capacity for the recycled melt. This tank also acts as a buffer to damp out composition fluctuations in the recycle melt.

The agitated vessel was designed to provide good mixing of the two feeds and to maintain a desired feed melt temperature.

A 60-gallon, closed, jacketed tank equipped with an internal float-type level sensor was selected for this service. This tank size provides for about five hours of recycle melt holdup. Agitation is provided by a fixed-mounted Lightnin N33-33 mixer (1750 rpm) bolted to a nozzle on the tank. The level in this tank is controlled by regulating the flow of fresh melt from the high concentration AN hold tank (T-102). To do this, a top-mounted Foxboro Force Balance Buoyancy Transmitter actuates a control valve in the gravity feed line from the high concentration AN hold tank (T-102). This level controller has a float-type sensor and integral pneumatic controller. It is mounted on a nozzle of the tank and puts out a proportional 3 to 15 psig air signal to the Research Controls Miniature Diaphragm Pneumatic control valve in the high concentration AN makeup line.

(3) Feed Blending and Metering System (P-101, P-102, FRC-1, and CRC-1)

The purpose of this system is to blend the high-urea and high-AN feeds in the proper ratio and to pump the blended feed at the proper rate to the reactor tubes.

The design philosophy for this system was to minimize the possibility of human errors by controlling both the feed composition and the feed rate with feedback control loops. Therefore, to adjust either the composition or feed rate, the operator simply adjusts a controller set point. Hardware reliability and control system stability were also important considerations in the design. Manual operability of this system in the event of control loop failure was also considered important.

Two basic methods of feed blending were considered: (a) one based on use of metering pumps and (b) one based on use of flow control loops on the discharge lines from the feed hold tanks. Because of the continuously changing hydrostatic head in the feed tanks, flow control loops using differential pressure (dp) cells and air-operated control valves would tend to result in cycling flows. For this reason, piston metering pumps were selected to blend the two feeds. These pumps are operationally stable and result in positive flows with very little variation.

A Hills-McCanna Type K piston pump (P-101) was selected for use in the feed blending operation. This pump has three hydraulically operated heads, all operating at the same stroke speed. The two heads used for feed blending of the high-AN and high-urea melts have pneumatic stroke adjustment capabilities. The third head contemplated for interstage reactor feeding has a manually adjusted stroke length. The heads, including the check valves, are fully jacketed. In addition, the pump speed is pneumatically controlled.

To obtain blended feed in sufficient quantity, the blend pump speed must be controlled. This is done by pumping blended feed into a surge tank (T-113) equipped with a level controller. This surge tank supplies feed to the centrifugal reactor feed pump (P-102). If the level in the surge tank becomes too low, the level controller calls for a higher blend pump rate.

The surge tank (T-113) is a 30-gallon stainless steel drum with a strap-on steam jacket and a loose lid. Mounted on the lid is a pneumatic Foxboro 2-mode Force Balance Transmitter which sends an air signal to the pneumatic speed controller in the blend pumps.

To control composition, the blended feed stream from P-102 must be monitored by a process variable that reflects the AN/U ratio. Since there is a significant density difference between U and AN melts, it was decided to use density as a measure of composition. A Dynatrol density cell was selected for this application.

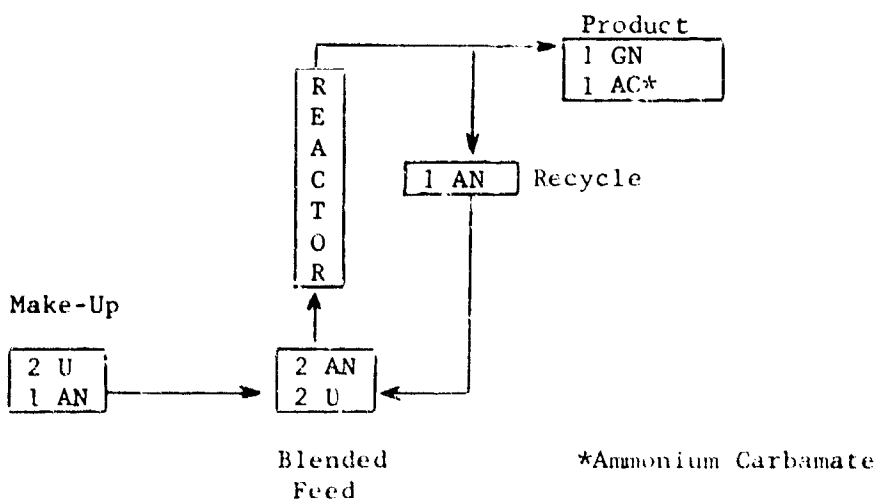
The Dynatrol is essentially a vibrating tube with melt flowing through it. As the unit mass of the melt changes, the frequency of vibration of the tube also changes. The Dynatrol has excellent sensitivity in the expected density range of 1.2-1.4 gm/cc with an accuracy of $\pm$ 0.0005 specific gravity units. The Dynatrol transmits a milliamp signal to the three-mode Foxboro 62H controller (CRC-1). The controller generates a 10-50 milliamp signal which is fed to a Foxboro 69TA-2R electric-to-air converter. The air signal from the converter is then split and sent to the pneumatic stroke controllers on the two blend heads of P-101. The stroke controllers are set so that one piston is an air-to-increase and the other piston is an air-to-decrease. The melt composition signal from the Dynatrol is recorded by a Foxboro 6400 two-pen recorder.

The final part of the feed blending and metering system is a flow control loop to regulate the feed rate to the reactor tubes. The flow sensor in this loop is a Foxboro E13DM integral orifice dp cell. The dp cell transmits a 10-50 milliamp signal to a Foxboro 62H three-mode controller. The 10-50 milliamp signal from the controller is sent to a

Foxboro 69TA-2R electric-to-air converter. The 3-15 psig signal from the converter operates the Fisher flow control valve (FRC-1). The signal (proportional to flow) from the dp cell is also recorded on the Foxboro 6400 two-pen recorder.

One of the purposes of the composition control system is to be able to demonstrate the effects of feed composition upsets on the overall process. Theoretically, the process is self-compensating and is not necessarily dependent upon controlling the composition of the makeup feed stream. The composition and quantity of material in the recycle loop are dependent primarily upon conversion of urea in the reactor. At an assumed urea conversion and yield, the makeup stream composition can be predetermined.

The following sketch shows the BMR guanidine nitrate process in its simplest form and assumes complete conversion of urea, 100% yield and no GN in the recycle stream. Note that values are in moles.




Under the above conditions, a steady state condition will be established. If the recycle stream composition changes, then the reactor feed composition will change. This will result in a kinetic change where the reaction rate will favor the higher concentration component. Consequently, the recycle stream composition will gradually return to its original composition. The effects of the self-compensating feature of the process are somewhat dependent upon the lags of the system. If the recycle stream compositional changes are small, an elaborate control system may not be necessary. On the other hand, the estimated lag of 16 hours for the recycle loop could make the control system mandatory, or at least beneficial.

### (4) Melt Transfer and Feed Pumps (P-100 and P-102)

The pump (P-100) used to transfer melt from the melters to the hold tank is a Goulds Model 3199 1x1x5 centrifugal pump. This pump has a fully open impeller, contains a stuffing box filled with Teflon packing, is rated at 10-gallons/minute against a 22-foot head of water and is driven by a 1/2-hp 1750 electrical motor. The reactor feed pump (P-102) is the same model pump but with a higher rating (25-gallons/minute against a 60-foot head) because of its higher speed motor (3/4-hp, 3450 rpm).

## 2 Reactor System

Packed bed tubular reactors, designed for flooded upflow operation, were selected for the pilot plant since they were so successfully demonstrated and modeled on a 2-inch-diameter scale in Phase 1. Stirred tank reactors were considered for the pilot plant but were not selected because of the potential safety hazards associated with large quantities of hot reactor melt. (A discussion on Stirred Tank Economics and Safety is given in a later section in this report.) The process economics for tubular reactors and stirred tanks were comparable.

### a Design Criteria

(1) Provide sufficient heat and catalyst surface area to yield 50 pounds of GN per hour.

(2) Select material of construction based on previous corrosion studies.

(3) Provide for easy catalyst charging and cleanout.

(4) Minimize bypassing of individual reactor tubes by having inlet and outlet pressure to all tubes identical for each stage.

(5) Measure reactor temperature profiles and the differential pressure across the tubes to provide data for mathematical model comparison and full-scale plant design.

(6) Provide for operating controls on the reactor temperature so that overheating cannot occur.

(7) Design reactors consistent with safety and hazards analysis.

b Reactor Design Constraints

After it had been decided to employ tubular reactors, the dimensions of a reactor tube were determined consistent with several constraints. The principal constraint on the reactor tube diameter was one of heat transfer. Since the reaction is endothermic, it is necessary to transfer heat through the tube wall to the contents of the tube. Simulation work showed that in tubes larger than 4 inches in diameter, the temperature profile was too steep across the tube. The reactor tube simulation work did verify that 4-inch-diameter tubes operated with a 200°C wall temperature had a satisfactory temperature profile. Therefore, 4-inch-diameter tubes were selected for the pilot plant. This diameter is consistent with commercial designs.

The length of the pilot plant reactor tubes was limited by the 18 feet of available head room in Building 2204. Another consideration was that the catalyst packing should remain wetted. If the reactor tubes were too long, then at some point there would be too much gas and not enough liquid to wet the packing. The other factor affecting tube length which will be pertinent in the design of the commercial plant is the economic balance between the value of production from an incrementally longer reactor and the cost of this additional reactor length. In the first 1-1/2 feet (~ 10 minutes for parallel operation) of the reactor tubes, the feed is preheated from ~ 120°C to the reaction temperature of 190°C. The remaining 10 feet of the reactor tube space provides the approximate 2-hour reaction time required. For example, a urea conversion of ca. 50% is obtained in the initial 5 feet of reactor length. At the 8 to 10 foot level, conversion changes at a nominal rate of about 1-2% per foot. The use of the bottom 1 to 2 feet of the reactor for a preheat zone was believed to be more efficient than a separate preheater, and will have only a small effect on the temperature in the tubes. (The sensible heat of preheat represents only ~ 10% of the endothermic heat of reaction.) Another favorable aspect of this scheme is that, at reaction temperature and in the absence of catalyst, it reduces feed residence time to zero.

A computer run was made to explore the feasibility of using the bottom section of the reactor tube as a preheater. Since the melt velocity through the tubes is low (7-15 minutes residence time for the first 2 feet), it was found that the feed temperature increases rapidly as soon as it is exposed to the 195-200°C jacketed reactor. Within 1 to 1-1/2 feet, the temperature has reached its desired value. Since two additional feet were added to the reactor for the preheat effect, the result is still a 10 foot plus reactor section with the advantages of limited feed contact time at elevated nonreactive temperatures.

After allowing for the feed manifolds, the gas-liquid separators, and clearances for maintenance, reactor tubes measuring 12 feet

in length with an 11-foot jacket were specified for the pilot plant. Simulation results showed that the single-stage urea conversion in an 11-foot, 4-inch-diameter tube fed with cold feed (100°C) and with a 200°C wall would be about 77.9% and the yield would be about 85.9%. The data from the 11-foot tubes will be more than adequate to refine the simulation program which can then be used to design tubes of any length for the commercial plant.

Eight reactor tubes (R-200 - R-208) were required to produce at least 50 pounds of dry GN per hour.

### c Reactor Configuration (R-200 - R-208)

The eight reactor tubes were installed in parallel as two sets of four tubes each (see Figure 54). These two sets of reactors were designed so that they could be operated in either parallel or in series. The simplest reactor configuration would be all eight tubes in parallel. However, by operating the two stages in series, i.e., feeding one-half of the urea to each stage, it was believed it would be possible to obtain higher yields by minimizing the formation of water insolubles. Another reason for series-staged operation is to use the reactor volume more efficiently by removing gas between stages. During stagewise operation, melt from the first stage gas-liquid separator would gravity-flow to an interfeed tank (T-114). For total parallel operation, the melt from the two separators flows directly to the quench tank (T-105).

### d Details of Reactor System Construction

There were several important design considerations affecting the design of the reactor system. One of the most important was that the dynamic pressure drop across each reactor tube in a stage should be identical to minimize liquid feed bypassing any one tube. It was later realized (Phase III operation) that the dynamic pressure drop was so small in relation to the static pressure drop (bed plus liquid heights) that uniform splitting of feed to the individual reactors is a problem without a separate control loop for each reactor. Ease of dismantling the reactor tubes and in-place catalyst charging or dumping were also very important considerations. Further, a positive indicator showing a flow or no-flow condition was needed in each tube. Temperature profile and pressure drop data are also needed for comparison with the simulated results. Lastly, fabrication costs were to be minimized by using schedule 10 pipe for the headers since the operating pressure is low.

A 2-inch feed header was specified to minimize dynamic pressure drop in the header between reactor tubes. The header design included almost total steam jacketing, valved nozzles for reactor draining, shutoff valves to each reactor and a flexible connection with valve to

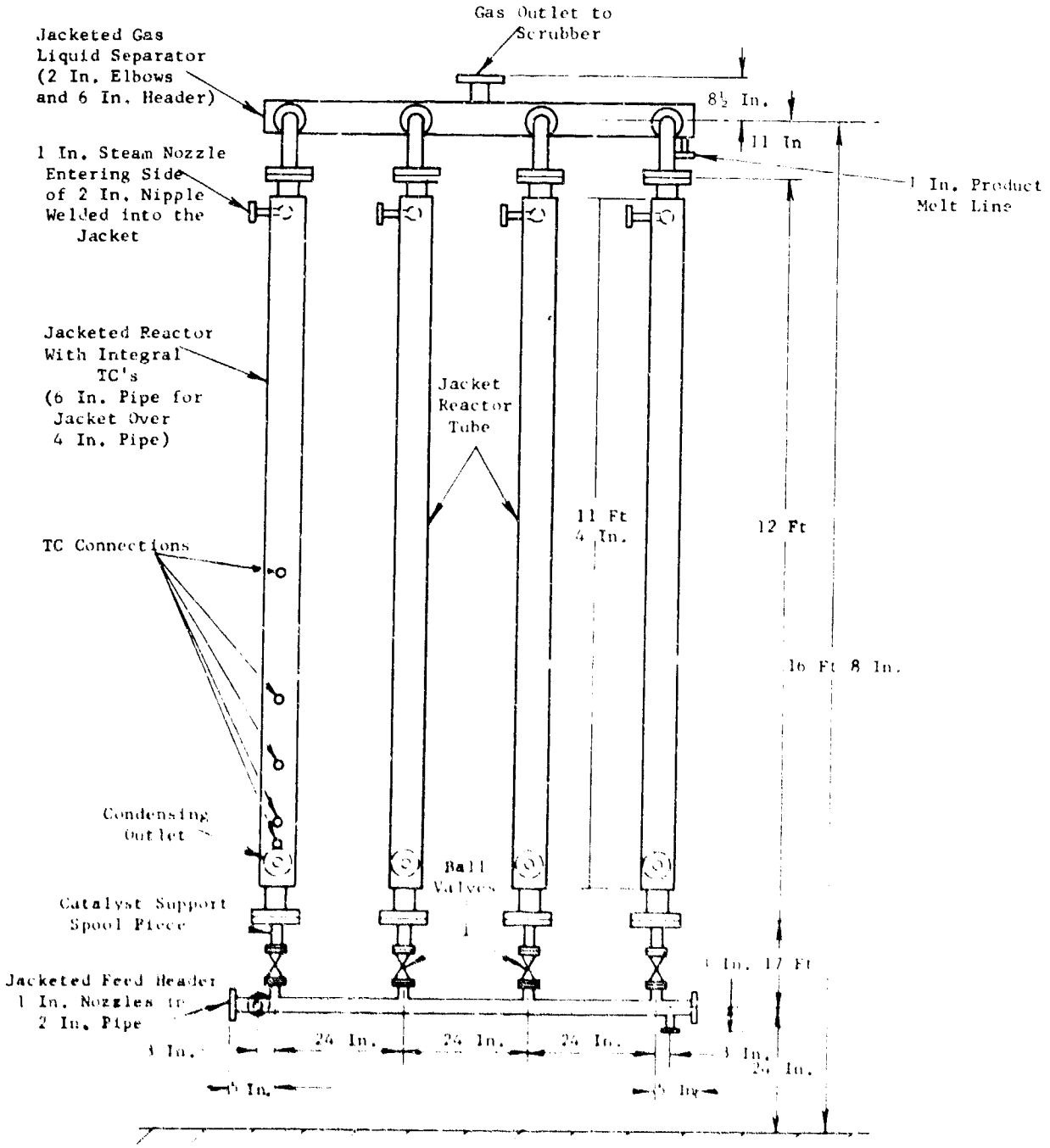



Figure 54. Guanidine Nitrate Reactor System Schematic

isolate the two banks of reactors. The shutoff valves were specified so that when a plug or partial plug developed in a particular tube during a run, flow to the affected reactor could be terminated, the flow rate decreased, and the run continued with the results evaluated on a reduced tube operation basis. Catalyst support spool pieces were provided to adapt the 1-inch feed nozzles to the 4-inch reactor tubes and retain the catalyst in place when the feed header is disconnected.

The eight reactors were fabricated from Schedule 40, 4-inch-diameter pipe with Schedule 10, 6-inch jackets (11-1/2 feet long). Seven of the tubes were constructed of 304 stainless steel and the eighth one was constructed of 316 stainless steel. The all stainless construction was specified because of the difference in the thermal coefficient of expansion between carbon steel and stainless steel. The use of a carbon steel jacket would have necessitated expensive expansion joints. Two of the reactors (R-200 and R-204) were designed with a series of thermocouple connections (12 each) for temperature profile data while the remaining six reactors were designed with a single thermocouple in each reactor (18 inches from the bottom flange).

Temperature profile measurements were required to confirm the kinetics model that was developed during Phase I. The thermocouples were strategically located based on observed and calculated temperature profiles. Thermocouples were more closely spaced at the bottom of the reactor since the endotherm is the greatest at this point.

The reactors were designed for 350 psig rating and conformed to the ASME Boiler code. The jacket steam inlets were designed to prevent steam impingement on the reactor tube, so that hot spots would not result

The outlet headers, which also double as gas-liquid separators, were designed so that the pressure drops between the tubes and the separators would be identical. Two-inch-diameter, Schedule 10, 304 stainless steel elbows are used for the connections between the reactor tubes and the separators, which are jacketed horizontal pieces of 6-inch-diameter, Schedule 10 stainless steel pipe. The use of elbows rather than a straight-in construction allows the reactor tubes to be charged or dismantled without moving the separators. The 4-inch off-gas line and 1-inch product melt line were amply sized to handle the gases and melts from four reactors. Low-pressure (30 psig) stainless steel rupture discs were also specified for each gas-liquid separator.

The separators were adequately sized based on the results observed in the 2-inch-diameter glass tee used in the Phase I work.

The 2-inch-diameter reactor work showed that the separation problem was one of breaking the foam in the reactor melt. Velocity in the 6-inch separator should have been one-half of that observed in the 2-inch-diameter bench-scale separator. Residence would be doubled. This separator design has one important advantage over a tee-type design in that the reactor product enters well above the liquid level, thus preventing backward drainage into an inoperative tube.

The entire reactor system was well heated (jacket and tracing) and insulated. The reactor tubes have about 2 inches of insulation covering. The elbows, spool pieces, gas-liquid separators, off-gas lines and reactor product melt lines were steam traced and insulated. A heat transfer cement was used in conjunction with tracing to improve overall heat transfer.

The system was designed to explore the interstage feeding concept. When the two banks of reactors were to be operated stagewise with fresh urea interfeeding, the melt from the first stage separator would flow to the interfeed surge tank (T-114). This surge tank is a custom-built, 304 stainless steel, 8-gallon tank fitted with a Foxboro force-balance bouyancy level transmitter. A small Hills-McCanna piston pump (P-114) is located below this tank to transfer melt from the interfeed surge tank to the second reactor stage. The melt in T-114 would be a combination of the first reactor stage melt overflow and fresh feed. The fresh feed is supplied to this system via the third head (manual stroke head) of the feed blending pump (P-101).

### 3 Melt Product Workup System

The effluent stream from the reactor is a hot (~ 190°C) melt containing GN, biuret, ammelide and unreacted AN and U. Two methods for recovering the GN from the melt were investigated during Phase I: (1) eutectic plus aqueous crystallization, and (2) single-stage aqueous crystallization. It was found that a 99 mole % purity product (GN) resulted from the dual eutectic-aqueous crystallization operation with an overall GN recovery (eutectic plus aqueous) of about 70%. Numerous experiments were performed where only aqueous crystallization was employed to recover GN from crude melt. Guanidine nitrate of 98 to 99 mole % purity was obtained from a single aqueous cyrstallization with an overall recovery or crystallization yield of 75% to 80%. The total water addition to the recovery system was about the same for both processes. Preliminary cost analyses indicated that the single aqueous crystallization operation results in a reduced mill cost of about 0.3¢/lb GN. This cost reduction is primarily the result of reduced plant investment and elimination of excess urea recycle. It should be noted that single aqueous crystallization also eliminates a potential hazard in the form of a hot, mechanically agitated eutectic mixture of energetic materials.

It was elected to gravity discharge the hot reactor effluent directly into temperature-controlled (80°C) water contained in an agitated tank (T-105). The purpose of the 80°C temperature was to maintain everything but water insolubles (e.g., ammelide) in solution. Water makeup to the tank is continuous and proportioned to the reactor melt flow. Residence time in the water quench tank is not critical.

The water solution in the quench tank is pumped at a rate proportional to its level in T-105, to an insolubles separator and then to a crystallizer hold tank. Pump rate is determined by a level controller with an output signal to a control valve. From the crystallizer hold tank, batch charges are drawn and fed to the vacuum crystallizer at a time cycle proportioned to the plant capacity. At full operating capacity, a transfer would be made every four hours.

a Design Criteria

1) Aqueous Quenching of Reactor Product Melt

(a) LC system same as for feed surge tank.
(b) Hot aqueous quench solution pump to feed water insolubles separator to be an open impeller centrifuge with a packed stuffing box rated for 10 gpm against a 22-ft head.
(c) Water quenched product to be fed to a tank at a rate proportional to the expected reactor melt rate.
(d) Jacketed 304 stainless steel vessel with agitation required to hold 30-60 minutes of quenched solution.
(e) A tempered water system to control tank contents at 80-95°C.

2) Separation of Water Insolubles from Aqueous Quench Material

(a) Known data on insolubles separation problem.

(1) Hot aqueous solution to be about 21 gph and contain ~ 0.5 wt. % insolubles particles.
(2) Solution temperature to be maintained at 85°C to prevent crystallization.
(3) Particle size of water insolubles to be 1-2 micron.

(4) Particle of water insolubles to have a density of ca 1.7 gm/cc.
(5) Aqueous quench solution density to be ca. 1.3 gm/cc.

(b) Basis for Selecting Centrifuge Instead of Filter for Insolubles Separations

(1) Laboratory work performed during Phase I showed that the insolubles particles were fine and compressible and that they plugged filters easily.
(2) Insoluble solids could be removed by filtration; however, operating problems would be encountered because of the physical characteristics of the material. Filtration would require sophisticated equipment and/or costly operations.
(3) Since there is a significant difference in density between particles and the solution, a solid bowl centrifuge would clarify the solution efficiently and predictably.

(c) Solid Bowl Centrifuge Specifications

(1) Low flow rates and solids content require a small laboratory size machine.
(2) Solids holding capacity should be 0.1 to 0.2 $ft.^3$ (2-4 hrs.).
(3) Decanted solution should be clear.
(4) The DeLaval Laboratory, 316 stainless steel, variable-speed bowl (12 inch) centrifuge met the above specifications.

3) Crystallizer Feed Hold Tank

(a) Bubble-type indicator to be used for level monitoring.
(b) Crystallizer feed pump to be an open impeller centrifuge similar to the aqueous quench solution pump.
(c) Capacity of tanks to be sufficient for about two batch crystallizer charges (200-300 gallons).

4) Crystallizer For Recovery of Guanidine Nitrate

(a) Supersaturation to be achieved by evaporative cooling, thus eliminating heat transfer surfaces which can foul due to crystal growth.
(b) Mechanical pumps or water eductor to be used to provide vacuum.
(c) Circulation in the crystallizer must be good.
(d) Operation to be done on batch basis only since the correct batch data can be reliably used for design of continuous crystallizers.
(e) Material of construction to be selected so unit is compatible with Phase I corrosion results.

b Description of Equipment Selected For GN Recovery

1) Aqueous Quench System

The function of the quench tank is to dissolve the liquid melt from the reactors in water to produce a hot aqueous solution. After processing to remove insoluble compounds, this hot aqueous solution is fed to a crystallizer. Although the actual quenching of melt in water is a simple operation, the two streams must be mixed in definite proportions. Too much water decreases the crystallizer yields, and too little water results in low purity and potentially precipitation in transfer lines. Good temperature control during the quench operation is required. High temperatures facilitate urea hydrolysis, and temperatures too close to the crystallization point would cause operational problems. In addition to its quenching function, this vessel also serves as a hold tank for the insolubles separator (S-300). This buffer tankage is necessary since the solid bowl centrifuge operates on a semi-continuous basis. When the solid bowl centrifuge is operating, the rate of feed to it is regulated to prevent overloading. Overloading the centrifuge results in passage of insolubles to the crystallizer.

The selected agitated, jacketed quench tank (T-105) has a capacity of 50 gallons. This size provides sufficient buffer capacity and allows for the installation of an internal level controller (LC-105). Agitation is necessary to provide a uniform solution and good heat transfer. The hot aqueous solution from the quench tank is about two parts of melt and one part of fresh water. Since the product melt and quench water go to another buffer tank (T-106) after mixing (2-hour holdup), only an average blend is required in T-105. These factors eliminate a costly control system.

The fixed, mounted agitator (M-105, 1750 rpm) specified for the quench tank is the same as that for the recycle feed tank. The level controller is identical to the one use for the recycle feed tank. A No. 6 Brooks Sho-Rate 150 rotometer (FI-105) with a R-6-15-B tube and B55 flow controller is used to monitor and control the water feed rate to the quench tank. A size B, 5/8 x 1/2 American water meter is used to measure the accumulated volume of water charged to the tank (T-105). A Goulds centrifugal pump (P-104) is used to transfer hot solution from the quench tank to the solid bowl centrifuge (S-300) and subsequently to the crystallizer feed tank (T-106). The control valve after the transfer pump, which is actuated by level controller (LC-105), is a Research Controls type similar to ones used in the feed system.

The quench tank has a bolted-on head and is vented to the reactor off-gas system. The solution in the quench tank is maintained at about 90°C by circulating hot water (85-95°C) through the jacket. This hot water is supplied by a tempered water system.

2) Insolubles Separator (S-300)

Due to urea-urea side reactions, some by-product compounds are formed. These compounds are members of the cyanuric acid family, the principal one being ammelide. They are relatively insoluble in the hot aqueous solution and their particle size is as small as 1-2 microns. If not removed, these insolubles may provide sites for nucleation in the crystallizer and would come out of the system as a product impurity. Excessive quantities of nuclei will tend to produce small guanidine nitrate crystals and plug the filter media during centrifugation of the GN slurry.

Both filtration and centrifugation were considered as a means of removing the insolubles. However, because the particle sizes were small and the particles tended to compress and blind filters, removal by filtration would probably be troublesome and require too much manpower. Removing the insolubles in a solid bowl centrifuge is a much simpler solution. The centrifuge operates on a semi-continuous basis. Clear solution is continuously decanted from the centrifuge until solids fill the bowl and reach a level where the separation becomes unacceptable.

The centrifuge was sized to minimize the number of times per shift a bowl must be changed. Since the solids rate was expected to be about 0.05 $ft^3/hr$, a bowl with 0.1 to 0.2 $ft^3$ of solids capacity was selected. The centrifuge is able to handle feed rates of about 20 gph, producing a nearly complete separation of the solids. A DeLaval/ATM Model 12 laboratory basket centrifuge was selected for the insolubles separator (S-300). This machine holds up to 0.2 $ft^3$ of solids and produces centrifugal forces of 450-1800 g. Almost complete rejection of particles of one micron in diameter is expected. Bowl changes may be as often as four times per shift. The variable speed option enables the best conditions for separation to be determined.

Since this centrifuge is a small laboratory machine, it was mounted over the crystallizer feed tank. Clear solution from the centrifuge flows by gravity and centrifugal force through a steam-traced pipe into the crystallizer feed hold tank (T-106). It was not necessary to trace this machine since the temperature drop across it will be only 5°C.

### 3) Crystallizer Feed Tank (T-106)

The primary purpose of this tank is to accumulate and hold aqueous crystallizer feed solution at 90°C. In addition, this tank is the main buffer zone between the continuous reactors and the quench tank system and the GN workup steps which operate batchwise.

A 200-gallon jacketed and agitated tank was specified for this service. It holds two crystallizer batches of solution (enough for slightly more than 8 hours of production). The tank is equipped with a loose metal cover and a portable N33-33G gear-driven Lightnin mixer (1750 rpm). The level in the crystallizer feed tank was monitored with a gas bubbler connected to a water manometer. A Goulds centrifugal pump (P-106) is used to transfer solution from the feed tank to the crystallizer. The solution transferred is pumped through Fulflo polishing filters (S-106). Model L203-3/4 filter housings are used. This type of housing holds 20-micron Cotton honeycomb tubes. These filters remove any miscellaneous contaminants as well as any insolubles which pass through the solid bowl centrifuge.

### 4) Guanidine Nitrate Crystallizer (A-500)

The main design criterion for the crystallizer was that supersaturation was to be obtained by evaporative cooling, thus eliminating heat transfer surface fouling problems. In addition, operation of the crystallizer was to be versatile so that GN crystal size could be varied. The crystallizer is operated on a batch basis, but the data obtained are applicable for design of either batch or continuous full-scale crystallizers. Another important design consideration is the degree of circulation of mixing in the crystallizer required to achieve uniform results.

A Swenson, pilot-plant size, draft tube crystallizer was selected. The crystallizer is 2 feet in diameter and 12 feet high, with a 100-gallon working capacity (about one-third of the total volume). The blade of a bottom-mounted agitator is positioned at the bottom of a 12-inch-diameter draft tube. This provides thorough circulation up through the tube to the boiling surface and back down between the tube and the vessel walls. Vacuum service for the crystallizer is provided by a set of mechanical vacuum pumps (Stokes 40 CFM Microvac units; P-116A and P-116B). The pressure in the crystallizer is controlled by manually adjusting an air bleed in the vacuum system. The crystallizer operating pressure (atmospheric to

10 mm Hg absolute) determines the crystallizer temperature. The water evaporated is condensed and collected in a set of 8-gallon stainless steel receivers (T-116A and T-116B). The condensers are cooled by an ethylene glycol water recirculating system that is chilled with a 10-ton Edwards Engineering packaged water chiller (J-111). The chiller is located in the utility building, approximately 120 feet from the process building.

The product from the crystallizer after completion of a cooling cycle is pumped to a basket centrifuge (S-600). The pump selected for this step is a Goulds Model 3199-1x1x5 centrifugal pump with a mechanical seal and a fully open impeller. The open impeller design minimizes excessive crystal size reduction in the transfer operation. Since the slurry from a crystallizer batch cannot be all processed in one centrifuge batch (four are required), a circulating loop is provided to keep the slurry in motion through the lines during the intermediate periods.

### 4 GN Product Recovery

The guanidine nitrate crystals are removed from the crystallizer slurry via a GN Basket Centrifuge (S-600). The recovered wet solids are then fed to the feed hopper of the GN dryer (A-700). The centrifuge mother liquor containing water, AN, U and GN is pumped to an evaporator feed hold tank (T-107).

#### a Design Criteria

##### 1) GN Centrifuge

(a) A 25% GN solids slurry to be centrifuged and thoroughly water washed to yield wet cake with a GN purity of $\geq$97% (dry basis).

(b) Total time to centrifuge a crystallizer batch to be one hour.

(c) The machine to be easy to operate and intrinsically safe.

(d) Material of construction to be selected recognizing the findings of corrosion studies.

(e) The slurry content and production levels in both the pilot plant and the commercial plant to be suitable for batch-operated (either manual or automatic) basket centrifuges. Batch operation also gives the option for a very efficient water wash, if necessary. One such type of centrifuge is the inverted (vertically mounted) basket centrifuge. Solids are discharged out the bottom by using a plow.

(f) A basket about 26 inches in diameter was required for the pilot plant.
(g) Cycle times of 5-10 minutes were desirable (15-25 gallon of feed).

2) GN Dryer

The design approach taken to select the dryer for the guanidine nitrate pilot plant is slightly different than Hercules' normal approach. The procedure normally followed would have been to determine drying rates, particle size and qualitative handling characteristics in bench scale studies and then to conduct candidate dryer vendors' tests during pilot plant operation with "real" process material. The result of this procedure is a dryer selection suitable for a commercial plant. The advantages of performing drying tests in vendor's equipment are to assess the effect of physical handling on the product and to determine any tendencies of the product to cake, dust, etc. Because the product is a Class 7 Explosive, it was not practical to consider testing different type of dryers at vendor sites. Rental of some units for in-plant trials could have been arranged; however, the timing of the pilot plant program (in conjunction with planned production plant design) precluded this course of action. A pilot plant GN dryer selection was based on laboratory drying data, analys s of problems that often producers have had in drying GN, contact with qual' fied dryer vendors, and engineering judgment.

b Description of Selected Equipment for GN Recovery

1) GN Centrifuge

A centrifuge is used to remove GN crystals from an aqueous slurry containing crystalline and dissolved GN, ammonium nitrate and urea. The crystals separated should be as pure and dry as possible. Purity, of course, can be improved by efficient washing. One of the main reasons for using a centrifuge instead of a filter is that the high acceleration loads and windage through the cake result in low cake moisture levels ($\leq$10%). Moisture levels in this range have been demonstrated by others. As a rule, it is more economical to remove water mechanically rather than in a dryer. Because of overall manpower requirements in the pilot plant, the GN centrifuge (S-600) was sized so that it requires only about 2 hours of operation per shift. The two crystallizer batches completed per shift would produce about 400 pounds (8 $ft^3$) of wet centrifuge cake. For reference, each crystallizer batch (4-hour cycle) contains 100 gallons of slurry or about 200 pounds of GN. Centrifugation requires four batches or cycles of 50 pounds GN/cycle and 15 minutes/cycle. Batch time for a basket centrifuge is 15 minutes at most; therefore, a centrifuge with about a 1 $ft^3$ basket was needed. Since purity and drainage rates for the GN cake were unknown, flexible charge, spin, wash and spin cycles were provided. To have an extremely flexible centrifuging cycle, a batch basket machine, namely, the DeLaval ATM Mark III link-suspended centrifuge, was selected. This centrifuge

has a perforated 22 inch x 26 inch (1-1/2 $ft^3$ solids capacity) basket and a variable-speed hydraulic drive. It is equipped with safety interlocks on the lid, a wash nozzle and a manually actuated plow. Solids are discharged from a bottom port. Another feature of this machine is that process material cannot enter bearing areas. All internal bolts and nuts are wired, and all clearances carefully evaluated. The link suspension feature keeps the basket from hitting the curb (housing) in the case of imbalance.

2) GN Dryer (A-700)

During Phase I, only a limited amount of drying work was done since it was believed that rotary steam tube dryers had been tested and used successfully in the British aqueous fusion process. However, an English report on drying of guanidine nitrate centrifuge cakes in rotary steam tube dryers noted that problems were encountered in handling both wet and dry GN. The report stated that wet feed clogged the dryer if the relative humidity of the exit air was higher than 60% at 60°C. As the ammonium nitrate concentration of the feed increased, so did the clogging problems. At the discharge end of the dryer it was observed that the steam tubes became glazed when the operating temperatures were greater than 115°C. This glazing was apparently due to the melting of a eutectic mixture of GN and AN. As little as 1% AN in the final product aggravated this problem. Another observation made was that both the wet and dry material tended to stick to all types of surfaces they tested, including polished metals. (Note: Confirmatory results are reported later in this report on the above systems based on work done during Phase III of this program.) The report concluded that steam tube dryers could be successfully used to dry GN if proper operating conditions were used. This meant that the relative humidity of the countercurrent air must be limited to prevent clogging at the feed end of the dryer and the tube wall temperature should not exceed 115°C to prevent glazing of the tubes. Formation of GN clumps between the tubes was also a serious problem.

During a trip to England by Hercules Incorporated and the U. S. Government personnel, it was learned that a steam tube dryer performed poorly during British aqueous fusion plant trials. The primary problem was severe clogging.

A plain rotary dryer with concurrent flow of hot air was considered next since during a trip to Cyanamid at Welland, it was learned that on occasion that facility had used such a dryer for custom batches of GN. Mr. D. Roy of Cyanamid at Welland stated that about 20 years ago rotary dryers were tried on GN centrifuge cakes, but that this type of dryer did not work because the flights and the baffles tended to plug. He also recalled that two years ago, a heated screw-type dryer was successfully used. The fact that this screw-type dryer had worked indicated that a suitable dryer must have positive mechanical agitation to break lumps and minimize caking.

A Stokes rotary vacuum dryer would provide good agitation and was considered. This dryer is essentially a large drum with internal rotary helical ribbon agitators. This dryer, of course, operates under a vacuum and is a batch type. The dryer drum is jacketed, and a solid-gas separator is a necessary auxiliary. Although this rotary vacuum dryer would, no doubt, handle the drying problem, it was not selected because its use requires batch operation and a vacuum system. The batch mode operation would mean that a significant inventory of material would be in the dryer at a given time, resulting in a potential safety hazard. The Stokes dryer would also be larger and thus more expensive than a continuous dryer.

Two fluidization-type dryers (Wolverine Jet Zone and Rex-Carrier Vibratory Dryers), which have been used successfully in the explosives industry, were considered. These units have the advantages of high heat transfer coefficients and gentle physical handling and operate best with a uniform feed particle size. However, since it was expected that the wet GN from the centrifuge would have both lumps and fines, the use of either of these dryers would have required both an inlet deagglomerator unit and an off-gas fines removal and recycle system. With either of these dryers, the system would have been more complex than the system selected below. They would not have accepted a feed with a large particle size range and would have larger dryer holdups.

Moving belt dryers were also considered (Sargent Tunnel Conveyor), but these units require preformed, uniform feed to obtain good circulation of air through the feed. Therefore, the wet GN centrifuge cake would have to be pelletized or granulated in some fashion. Moreover, because of the low water content of the GN centrifuge cake, granulation may not be possible. In view of these potential problems, this type of dryer was not considered further.

As a result of Cyanamid's successful experience with screw dryers, close consideration was given to a Holo-Flite dryer made by the Western Precipitation Division of Joy. In the Holo-Flite dryer, basically a double-screw conveyor, both the screws and the screw trough are steam heated. It was learned that Western Precipitation makes a laboratory-size dryer with double 3-inch screws. This unit would easily handle 50-pounds/hour of wet GN cake and produce dry material $\leq$ 0.5 wt. % water. The basic pilot plant model would cost about $5,000. A plant-size unit capable of handling 5,000-pound/hour of wet GN would require 1000 $ft^2$ of screw area based on Cyanamid's runs. This unit would cost about $70,000. The principal advantage of screw-type dryers is that they can convey hard-to-handle materials. However, heat transfer coefficients tend to be low - on the order of 10 Btu/hour/°F. Poor heat transfer is due to relatively mild mixing (screw speeds of only 2-20 rpm), the lack of an air purge to keep the relative humidity low, and the rather large cake depths (measured in inches).

The dryer can be designed, however, for countercurrent air sweep. The Holo-Flite dryer was seriously considered for the pilot plant. However, it did have disadvantages (e.g., poor heat transfer and possible short circuiting) that placed it second in choice when compared to the Scott Solidaire dryer discussed below.

The dryer selected for the pilot plant was a Strong-Scott Solidaire. This dryer is essentially a jacketed pipe with an internal rotor carrying an array of radial paddles. These paddles throw solids to the wall where heat transfer takes place. The paddles are pitched to impart axial and forward motion; the overall motion of the solids is one of a helical path down the length of the dryer to the discharge. A small stream of air flows countercurrent to the solids to sweep out water vapor. The only function of the air is to keep the water vapor concentration low. Volumetric rates are on the order of 2-5 cfm so that a solid-gas collection system was not necessary for the pilot plant.

This type of dryer combines many of the advantages of a fluid bed dryer, a steam-tube dryer and a screw-type dryer. Good circulation of air around the particles is obtained, the use of steam heat allows the wall temperatures to be limited, and the action of the paddles gives positive conveyance and prevents lumping and clogging.

Other important characteristics of the Solidaire dryer are short residence times, small holdup, and very thin solids layers. The holdup of solids is small because the material in the dryer occupies little more than the annular space between the tips of the paddles and the dryer wall. This space or clearance is 1/8 inch. Because the maximum thickness of solids is only 1/8 inch, heat transfer is very efficient as is the removal of water vapor to the countercurrent air stream. The maximum retention time in a Solidaire dryer is 15 minutes. This short time is due to the low holdup and the conveying capacity of the high-speed paddle. The resultant low holdup is advantageous for Class 7 GN.

Before the Solidaire dryer was specified, drying tests were made to verify that a 15-minute retention time in the dryer was sufficient. The procedures for the test were obtained from the Solidaire factory representative. The test consisted of spreading a small amount of wet GN on an aluminum weighing dish and putting it in an oven at 115°C. The thickness of the cake was approximately 1/8 inch, and the moisture content of the cake was initially 10-11%. After 5 minutes in the oven at 115°C with no forced circulation of air, the water content of the cake was about 0.2 wt. %. These results were not surprising since hydrates of guanidine nitrate are not known, and therefore, the water removed is merely surface water. At 115°C, this water should flash off quickly. In the pilot plant, the centrifuge cake has, at most, 15% water; and in view of the above results, it should easily dry in less than 15 minutes.

A Strong-Scott SJS-8-4 Solidaire was specified for the pilot plant. This is an 8-inch-diameter unit and it has more than enough capacity to produce 50 pounds of dry GN per hour. It is constructed of 304 stainless steel and has a variable speed motor to allow operation between 152 and 1520 rpm. The jacket is equipped to handle 14.9 psig steam. The unit is equipped with roller bearings and has given good commercial service including drying of ammonium nitrate in government facilities (e.g., U.S. Navy Ammunition Supply Plant, Indiana). Since the paddles are attached to the rotor with lock nuts, it is very improbable that they could come loose; however, they were examined and modified. The paddles were tack welded to the shaft to prevent this occurrence.

## 5 Mother Liquor Recycle System

Mother liquor removed from the crystallized slurry via the GN centrifuge is collected in a pump tank and batch transferred by a pump to the evaporator hold tank. This tank is a buffer tank between the batch mother liquor collection step and the continuous evaporation step. A continuous stream is pumped from the evaporator feed tank to the evaporator. The evaporator concentrates the mother liquor to about 0.5% water, and this concentrate (AN/U/GN) is then recycled back to the feed system.

### a Design Criteria

#### 1) Evaporator Feed Tank (T-107)

(a) Since it functions as a buffer tank between batch and continuous steps of the process, the evaporator feed tank should have a design similar to T-106.

(b) Since the potential contents of this tank do not have an elevated melting point, a non-jacketed tank would be satisfactory. However, an internal coil could be advantageous to guarantee hot feed to the evaporator.

#### 2) Evaporator (A-800)

(a) The evaporater was required to accept a continuous flow of mother liquor from the centrifuge and to increase its temperature so that the bottoms (urea, ammonium nitrate and guanidine nitrate) from the unit are molten.

(b) To evaporate system water from the mother liquor so that the bottoms stream from this unit will contain less than 0.5% water.

(c) To limit the residence time of the process stream in contact with the heating units in the evaporator when water is present so that urea hydrolysis is limited.
(d) To accomplish the above at lowest cost in proven equipment.
(e) To be constructed of materials compatible with previous corrosion studies.

## b Description of Equipment Selected for Mother Liquor Concentration

### 1) Evaporator Hold Tank (T-107)

The mother liquor from the centrifuge drops by gravity into a 30-gallon pump tank (T-109) and is then pumped to the evaporator feed tank (T-107). This tank, a baffled 200-gallon, 304 stainless steel unit with an internal steam coil, serves as the feed supply tank for the evaporator. The internal coil was added to this tank to dissolve fines (AN, GN, U) if needed. The inlet line to this tank is circumferential and is directed towards one of the baffles. Any large solids, therefore, will be disengaged and allowed to settle. A continuous stream is removed from the hold tank and fed to the evaporator. The rate of this transfer is monitored and regulated using a Brooks B55-8800 Flow Controller/Integral Rotameter (FI-800).

### 2) Mother Liquor Evaporator (A-800)

The evaporator selected for concentrating the mother liquor was a two-stage, Whitlock 99 pilot plant, air-swept falling-film evaporator. This unit is capable of accepting a 20-gph continuous feed stream composed of ca. 50% water and stripping it to less than 0.5% water with a short residence time. This unit is a proven unit for ammonium nitrate and urea systems, is easily scaled up and is low in cost because of the absence of moving parts. Temperatures of 120°-130°C are necessary to keep the bottom stream from this unit molten. The evaporator is not under vacuum.

The evaporator system consists of a 304 stainless steel evaporator, an air heater (type 3-Y-48 AHT heat exchanger), and a 50 scfm motor-blower combination. The evaporator provides for a two-stage process with both stages contained into a single unit. Each stage consists of four 2-inch-diameter tubes for counter-current falling liquid film and hot air. The feed stream is concentrated from 51% total solids at 68°F to 90% solids at 300°F in the first stage using 125 lb/hr of 90 psig steam. The second stage concentrates the stream from 90% total solids at 300°F to 99.5% total solids at 266°F using 10 lb/hr of steam at 30 psig. Air is preheated from ambient conditions to 266°F using 13.3 lb/hr of 90 psig steam. It is then blown countercurrent to the falling liquid, passed through

a mist eliminator and then vented to the atmosphere. The bottoms of the evaporator flow by gravity to the recycle feed tank (T-104). The bottom transfer line contains a seal loop to prevent blowback of air.

### 6 Reactor Off-Gas System

The by-product, ammonium carbamate, from the AN/U reaction decomposes instantaneously at the reaction temperature and pressure to form gaseous ammonia and carbon dioxide. These gases are separated from the reaction melt in the two overhead gas-liquid separators (S-200 and S-201). The disposition of these gases in the commercial plant has not yet been defined, but the options are: (1) reconversion of the combined gases to urea, (2) conversion of the $NH_3$ to ammonium nitrate and dry ice collection, (3) a combination of options (1) and (2). Regardless of which option is selected, it was not necessary to demonstrate the gas disposition method at the pilot plant scale. For the pilot plant, the primary concern of the gas disposition was one of safety and working conditions. A number of options were considered in terms of ease and safety.

The decision was made to treat the gases in the following manner. The hot ammonia and carbon dioxide gases (decomposed ammonium carbamate) from the reactor flow through a heated line to a water-scrubbing column. The scrubbed gas ($CO_2$) passes through a sewer meter (FR-400) and is vented to the atmosphere. The scrubber bottoms (15% $NH_3$ water) passes to an intermediate storage vessel (a 55-gallon drum) from which it is intermittently pumped (using a small sump pump (P-112)) to a large storage vessel. The aluminum column, 7 inches in diameter x 9 feet high, is packed with 1/2-inch Raschig rings. The water feed to the column consists of fresh water feed (ca. 20°C) and recycled water via pump P-105. The recycling is necessary to keep the packing wet. The fresh water feed flows through a rotameter for monitoring purposes. The bottom water from the sump pump storage drum is sampled occasionally for its $NH_3$ content.

## d. Pilot Plant Auxiliaries

Although an existing building was available for the proposed pilot plant, it was necessary to modify this building to make it suitable. Additional utilities were also necessary since the requirements of the unit operations far exceeded its existing capabilities.

### 1 Pilot Plant Utilities

#### a Electric Substation

The pilot plant process building had an existing electrical service of 27.5 kva. An estimate was made early in the design phase of the power required to handle the multiple unit operations of the U/AN process.

It was estimated that at full load, a power usage of ca. 160-200 kva was required. Allowing for future equipment requirements and using a design factor of 150%, a 300 kva electrical substation was selected. The design of the selected 300-kva electrical substation was completed in Phase II. Quotations on the major equipment pieces of the substation were received. The transformer portion of the substation was ordered in Phase II. This was necessary because it was a very long delivery item (18-20 weeks), and this procurement time was not compatible with the allowed Phase III construction time frame. Permission was granted by the government for early purchase of this item.

The resultant substation design consisted of a Hevi-Duty power transformer and the necessary high and low voltage accessories. This substation was designed in accordance with the rules of the local power utility company and the design approved by them prior to construction. The selected transformer converted the electrical service from 34,500 volt, 3 phase, down to 440 volt, 3 phase. A service voltage of 440 volts was selected for the low voltage side so that delivery times of the selected process equipment would be minimal.

b Thermal Heat Source

Heat load requirements were estimated for the pilot plant and determined to be about 500,000 Btu/hr (about 15 boiler horsepower). Low pressure steam was available to the process buildings for some of the process units, but an additional heat source capable of providing ca. 300,000 Btu/hr was necessary. The major demands for the additional heat were the GN reactors and the falling film evaporator. Both of these units required temperatures higher than that of plant steam.

High pressure steam (300 psig) was selected as the heating medium for the additional pilot plant process demands. A number of factors were considered in making this decision. Steam was an attractive heat source selection because it offered safety advantages (compatible with reaction mix), because pressure regulators could be used for temperature control, because condensate recycle was not an absolute necessity, and because its use entailed lower costs. The disadvantage of using steam was that full-time licensed personnel would be required to operate a high pressure boiler. Several alternate thermal energy sources were investigated. Table 42 lists the options that were considered. These alternatives were reviewed and discussed with the Hercules Corporate Engineering steam power group. They in turn made several inquiries as to the interpretation of the New Jersey State Labor Laws for use of high pressure boilers. Their resultant conclusion was that Option 9 was the most feasible option. It was determined that limiting the boiler size to less than six (6) boiler horsepower (bhp) negates the necessity of licensed operating personnel. The decision was made to utilize a pair of 5.75-bhp, high-pressure steam boilers as the alternate heat source. With these two modules (11.5 bph) plus the existing plant low pressure

TABLE 42

HEATING OPTIONS FOR GN PILOT PLANT

| Options | Remarks |
|---|---|
| 1. Employ Stationary Engineers to operate 15 BHP Steam Boiler. | Option would add a labor cost of about $60,000 to program. |
| 2. Locate 15 BHP steam boiler at powerhouse and install high pressure steam line to GN facility. | Cost of high pressure line estimated at $21,000. |
| 3. Utilize a steam compressor to increase pressure of existing plant steam supply at GN facility site. | This operation results in superheated steam which has very little thermal value. |
| 4. Install 15 BHP steam boiler at GN facility and install instrumentation for remote control of unit by powerhouse operators. | This system may not be legal. |
| 5. Install a hot oil heat transfer system. | Heat transfer temperature control and process piping tracing not as satisfactory as steam. Also, hazards of compatibility of organics and AN. |
| 6. Same as above but use existing low pressure steam for noncritical steam tracings. | Same as above. |
| 7. Install an organic vapor phase heat transfer system - with or without complementary use of existing low pressure steam. | Systems such as Dowtherm, p-cymene, etc., require condensate return systems. These may be difficult to design with existing facilities. Also hazards of compatibility of organics and AN. |
| 8. Generate high pressure steam indirectly by cooling a hot oil via water coolers. | This system will produce the required quantity and quality of required steam; however, it may not satisfy the New Jersey laws. |
| 9. Employ a multiple number of small high pressure steam boilers. | This system has merit and is being investigated. |

steam (4-5 bhp), sufficient thermal energy was available for the pilot plant. The selected boilers were Ebcor Model 6-445-4, electrode-type steam generators and were complete with water level controls, boiler feed pump and motor, and automatic blowdown conductivity control. Each unit has a maximum capacity of 207 pounds steam/hour for operation on 460 volt, 3 phase, 60 cycle. This equipment was, of course, built to ASME code and bears the Underwriters label. The design pressure on these units is 445 psig, and safety relief valves were built on the units so that the maximum steam pressure is limited to 395 psig (229°C). The pressure was high enough to allow for pressure drops through the high-pressure lines, regulators and piping and still provide 215-220°C steam to the reactor jackets. Thermal stability tests have shown that no decomposition problems occur in the reactor until a temperature of ca. 240°C is attained. There are, of course, lower pressure regulators and safety relief valves in the building in addition to those mentioned above.

The electrode-type steam generator is a demand unit that should require little attention. It operates on the same principle as a household vaporizer with current passing through the water between the electrodes. The rate of current flow is a function of the water conductivity and the exposed electrode surfaces. A conductivity control system is provided to control water conductivity. The exposed electrode surface is a function of the demand. As more steam is used, more fresh water enters the boiler chamber to be vaporized and the boiler electrode chamber water level rises, thereby exposing more electrode surface and raising the amperage required.

c Vacuum/Brine/Air/Water

The other utilities provided for in the pilot plant require little discussion. The vacuum system had been discussed in a previous section. It consists of a set of two 40-cfm Stokes Microvac mechanical vacuum pumps. These units were existing equipment and are housed in the utility building. A vacuum line was constructed from this building to the process building. The vacuum was controlled via an air bleed at the crystallizer. The crystallizer was cooled by water evaporation created by the vacuum system. Since oil-seal mechanical vacuum pumps were used, it was necessary to condense the water vapor from the crystallizer consistent to ensure good vacuum pump performance. This water was condensed in a heat exchanger (E-111) using circulating brine as the cooling medium. The brine (ethylene glycol-water solution) was cooled by an Edwards Model CC10A water chiller (J-111).

The air demand for the process was very small. Air is required for the pneumatic instruments and for the dryer and evaporator. The air source for the evaporator was a built-in blower. The source of air for the instruments and for the dryer was the existing plant air supply with a reservoir tank as a backup.

Water was required for the steam boilers (50 gph) and for the aqueous workup steps (10 gph). This is a total of 1 gpm which is drawn from the well system. The purity of the water was deemed sufficient for these uses. It was later found, during the pilot plant operations, that the boiler feed water had to be pre-treated in order for the boilers to operate at close to design capacity.

## 2 Process Buildings

Figure 55 shows a topographic map pointing out the area layout of the guanidine nitrate pilot plant. The key items on this map are the relation of the pilot plant building to adjacent buildings, the location of the electric substation and utility building (housing the chiller, vacuum pumps and steam boilers), the placement of the ammonia-water storage tank and the siting of necessary waste disposal and safety provisions.

With 750 pounds of Class 7 material in Building 2204, the placement of the buildings on this layout fulfills quantity distance restrictions. A front barricade was built to satisfy these restrictions.

Building 2204 was selected as the site for the GN process building. The building consists of a main operating bay, a control room, and an auxiliary side room suitable for equipment installation. The structure is reinforced concrete with barricades on three sides. An expansion was added to the original building to house the GN pilot plant. Additional buildings in the immediate area are used for intermediate ingredient and product storage (Building 2210). An existing building (Building 2260) on the plant was selected for the utilities. This portable building was moved to the GN area in Phase III.

## 3. General Operating Procedures for the Pilot Plant

The following general operating procedures are not intended for operational use. Specific operating procedures were written during the Phase III operation phase. They are, of course, much more detailed and are not included in this report. These general operating procedures were prepared as guidelines for checking the pilot plant design and as an aid to the reader in understanding the operating methods. Equipment designations have been omitted intentionally since the procedures were prepared for information purposes only. The equipment names, lines, etc.,are readily recognized in the process flow sheet (Figure 52).

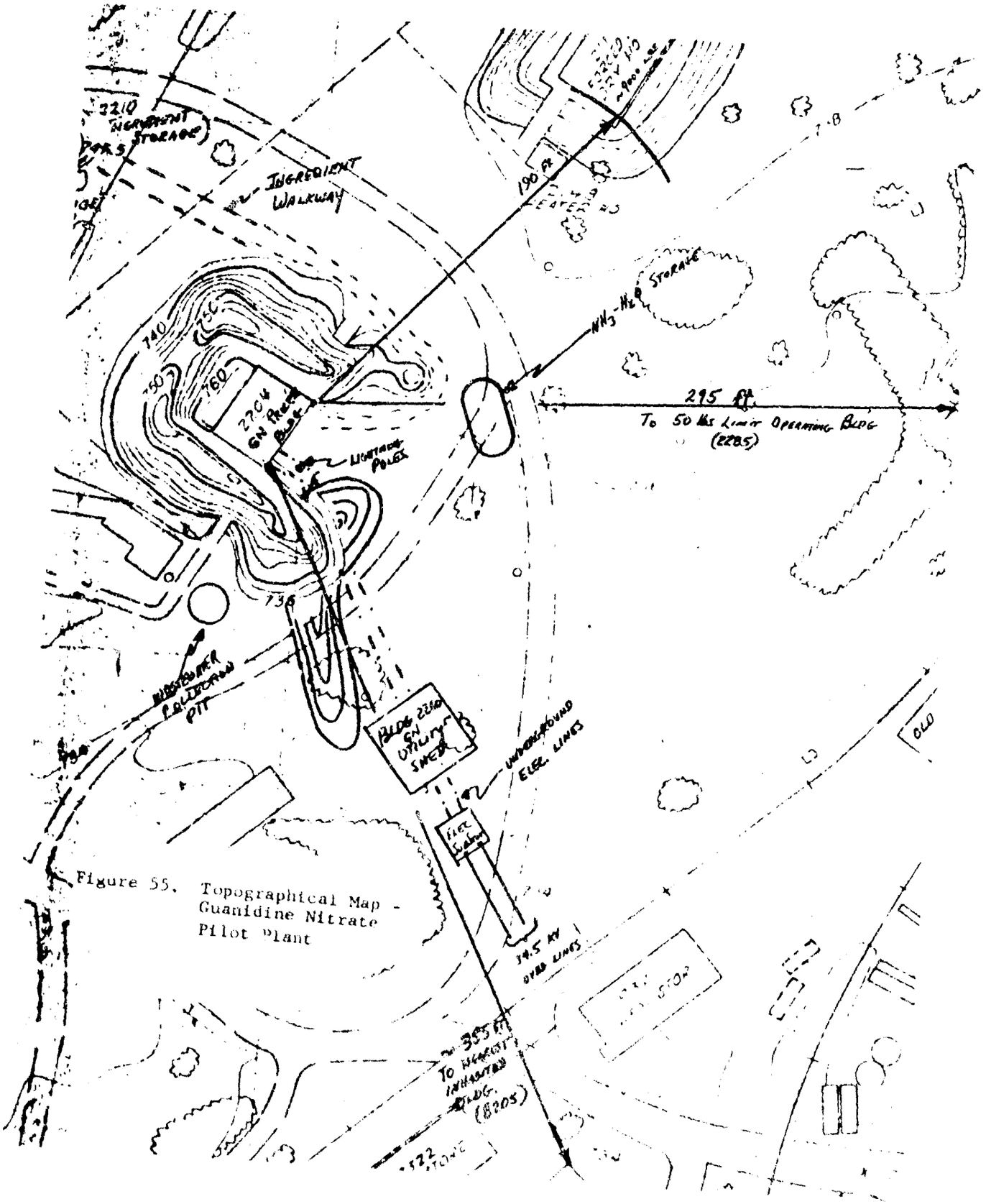



Figure 55. Topographical Map - Guanidine Nitrate Pilot Plant

a. Start-Up

1 Preliminaries

(a) Turn on building fan.
(b) Check the Building Class 7 inventory to confirm that it is not overloaded.
(c) Turn on electric power to the instruments and recorders.
(d) Turn on the instrument air.
(e) Start steam generator.
(f) Apply steam to the following items at the indicated pressures.

| Steam Pressure Distribution (psig) | Items |
|---|---|
| 260 | Reactor tube jackets, gas liquid separators, interfeed tank and lines |
| 125 | Melt product lines |
| 90 | Evaporator first stage |
| 25-30 | Melt tanks, feed hold tanks, recycle feed tank, blend pump jacket, feed line tracings, off-gas line, evaporator second stage, evaporator bottoms line |
| 15 | Dryer jacket |
| Atmospheric | Workup transfer lines and crystallizer feed tank |

(g) Apply 90-95°C hot water to the quench tank jacket and crystallizer feed tank.

2 Feed System

a Melt Tank and Hold Tanks

(1) These tanks need attention twice during one shift - once to adjust the level in the melt tank and charge solids to the melters and once to transfer the contents to the hold tank.
(2) Charge 1 bag of urea and 4 bags of AN (80-pounds AN or U/bag) to the high AN melter.
(3) Charge 8 bags of urea and 2 bags of AN to the high-urea melter.
(4) When charging the melters, always charge one bag of urea first, followed by one bag of AN.

The urea and AN in contact melt faster than either one separately.

(5) When melting is complete, transfer approximately 60-gallons of the high-urea feed to the high-urea hold tank via the transfer pump. If the melt is not well mixed, circulate through the melter pump loops before transferring.

(6) Charge about 32-gallons of the high AN feed to the high AN hold tank, using the feed transfer pump. During this transfer, be certain that the tank does not overflow. This tank is equipped with a level indicator.

(7) After charging the hold tanks, blow out the transfer pumps and lines with low pressure steam, then purge the lines with air. This will be a typical line cleanout practice.

(8) Before charging the melters with more solid AN and urea, reduce the volume of the heel in the melters to 8 gallons in the high AN melter and 10 gallons in the high urea melter.

(9) Leaving a heel in the melters makes the next melting operation proceed more rapidly.

b Recycle Feed Tank

(1) Adjust the set point of the level controller to control the level at about 1/2 capacity.

(2) To start up, an entire melter batch must be charged through to the recycle feed tank. After this has been done, another high AN melter batch must be prepared and charged to the hold tank.

(3) During operation, the tank temperature should be monitored and the proper operation of the level controller should be checked.

c Feed Blending and Pumping

(1) With the composition controller in the manual mode, set the piston stroke lengths to yield a 2:1 feed ratio.

(2) Adjust the set point on the composition controller and the flow controller to the desired level.

(3) Close the feed line valve between the feed pump and the flow control loop.

(4) Open the valves on the feed hold tanks and start the feed blend pump.

(5) When the feed surge tank has filled, start the reactor feed pump and recycle feed through the pump-around loop.
(6) Notice whether the Dynatrol composition controller is functioning properly. Adjust set-point at the desired density.
(7) When the level controller starts to reduce the feed blend pump speed, open the valve in the feed line to the reactor feed manifold. Have individual valves at reactor inlet open.
(8) Feed melt is now being pumped to the reactors; check to see that the flow rates and compositions are correct.
(9) On startup of the feed system, watch closely for plugged lines.

3 Reactor Operations - Catalyst Charging

(a) Remove the elbows that connect the top of the reactors to the gas-liquid separators.
(b) Charge pre-dried, pre-screened catalyst to the reactor tubes. Fill to levels even with the top of the reactor jackets. Record weight of charged catalyst.
(c) Replace the top elbows and bolt down uniformly.

4 Quench Tank Operation

(a) Charge 10 gallons of cold water to the quench tank.
(b) On startup, let melt flow into the quench tank until the total volume is about 25 gallons. Note the time it takes to add the 15 gallons of melt.
(c) Turn on water to the quench tank; set rate to provide one part of water to two parts of melt. The melt rate can be determined from the reactor feed rates and also from the time it took to charge 15 gallons of melt to the quench tank.
(d) Set the tank level controller for one-half of full operation and adjust temperature to 90-95°C.

5 Separation of Water Insolubles

(a) Preheat the centrifuge bowl with hot water or steam and then add about 2 inches of water to bowl.

(b) After the quench tank is one-half full, start the centrifuge and the solution transfer pump feeding the centrifuge.

6 Crystallizer Feed Tank

(a) Monitor the crystallizer feed tank level; maintain the temperature at 90°C.
(b) After collecting 2 hours' production of hot aqueous solution, stop charging hot solution from the quench tank and record the level in the feed tank.
(c) Charge the crystallizer with hot solution.
(d) Record the level of the crystallizer feed tank and determine the amount of solution charged to the crystallizer.
(e) Start transferring solution again from the quench tank.

7 Dryer

(a) After the dryer has been heated to the operating temperature of about 115°C, turn on the air purges.
(b) Charge a batch of centrifuged GN cake to the dryer feed hopper.
(c) Start the dryer rotor and then the feeder.
(d) Adjust the feed rate and dryer rotor speed to obtain dry product (with $\leq$ 0.5 wt. % water).

8 Evaporator

The continuous guanidine nitrate pilot plant will be started up without recycle feed. Feed blending will be accomplished by utilizing the low urea makeup feed system until recycle feed is available. Two hours before the first batch of mother liquor is available in the evaporator hold tank, the following steps are to be implemented:

(a) Turn on steam to the jacketed heat exchanger in the first stage of the evaporator. Regulate at 90 psig.
(b) Turn on steam to the second steam of the evaporator. Regulate at 30 psig.
(c) Turn on the steam to the air heater. Regulate at 90 psig.
(d) Confirm that steam to product line, level controller, and sump pump is on and regulated at 90 psig.

(e) Turn on air blower. Regulate air damper so that a pressure drop of 20 inches of water results (the blower at 20 inches of water provides for the desired air rate of 50 scfm).
(f) Allow system to heat up. Air will be at steady state when outlet air temperature reaches 266°F. Allow one hour for stages to reach steam temperature.
(g) When steady state temperature has been reached, start evaporator feed pump and set rotameter at predetermined setting.

9 Vacuum System

(a) In the process building, turn off the vacuum system valve between the heat exchanger (E-111) and the condensate traps (T-116A and T-116B).
(b) Turn on the power to the vacuum pumps. The vacuum gage at the pumps should begin to read and, within one minute, should be down to 29-30 inches of vacuum. If not, check for line leaks and/or pump operating guide.

10 Off-Gas Scrubber

(a) Set rotometer reading at predetermined setting so that the inlet scrubbing water flows at 11.0 gph.
(b) Confirm that all of the steam tracings on the off-gas lines from the gas-liquid separator to the water scrubber are turned on. If not, turn on and wait one-half hour before proceeding.
(c) Turn on the sump pump in the $NH_3$-water receiver.
(d) Turn on the small recirculating pump and increase this water rate to a maximum level of 70 gph. Any additional recirculation will flood the packed column.

b. Operation (Continuous Units)

1 Feed System

(a) As required, repeat steps for start-up, feed system (a.2), noted above.
(b) Check and record melt temperatures twice per shift.
(c) Check the flow and composition records once per hour and report any set point deviation.

## 2 Reactors

(a) Periodically check to ensure that melt is flowing through all the tubes. To do this, check the inlet thermocouple temperature on the tubes. This temperature should be 20-30°C below the jacket temperature. If a no-flow condition exists in a reactor tube, the inlet temperature will be the same as the steam temperature.
(b) Regularly check and record temperatures in the two instrumented tubes.
(c) Adjust the steam pressure to the reactor jackets to control the center line reactor temperature at $\leq$ 190°C.
(d) Verify that off-gas is flowing to the scrubber and melt to the quench tank.
(e) Interfeeding (Special Experiment)

(1) Set the stroke length on the third piston of the blend pump to provide one-half of the urea requirement to the second reactor stage.
(2) When the interfeed surge tank has filled with melt from the first stage, start the interfeed pump and the third piston of the blend pump.
(3) Check the combined flow rate to the second stage.
(4) When interfeeding, the melt from the first stage separator will flow to the interfeed surge tank. Otherwise, it will flow directly to the quench tank.

## 3 Quench Tank

(a) Periodically check the melt/water rate as noted in start-up, quench tank operation (a.4) above.
(b) Note and record quench temperature periodically.

## 4 Insolubles Separator

(a) Notice whether the aqueous solution to the crystallizer feed tank is clear. Sample this solution for insolubles and per cent water.
(b) As the centerfuge bowl fills, the solid-liquid separation will become less efficient. When the aqueous solution turns cloudy, shut off the transfer pump and quench tank bottom valve and stop the centrifuge. Remove the centrifugal bowl and install a new one.

(c) Start the centrifuge, blow 5 psig steam through the centrifuge for 5 minutes, add water to the bowl, open the quench tank valve, and start the transfer pump.
(d) Determine the weight of insolubles collected in the centrifuge bowl and sample.
(e) During operation, periodically check the liquid exit temperature from this unit. If the temperature drops below 80°C, stop feeding and begin a 10 minute steam sparge to increase the temperature.

5 Crystallizer Feed Tank

(a) Check the tank temperature periodically. It should always be higher than 85°C.
(b) Note and record liquid level before each crystallizer transfer.

6 Dryer

(a) Check often for signs of plugging in the dryer and watch for caking and bridging in the feed hopper.
(b) Package the product for 50 lb per drum. Weights can be adjusted at the scale.

7 Evaporator

The evaporator is a self-contained unit which operates by itself and with no moving parts (except the blower). The following items, however, will be routinely checked to ensure proper operation.

(a) Check the feed rotometer reading every hour.
(b) Check feed availability every three hours.
(c) Check the steam pressure to the two stages and air heater every two hours.
(d) Check the temperatures of the feed, molten product, air in and air out every hour.
(e) Once every four hours, analyze a sample of the evaporator bottoms to determine % $H_2O$. (Once a history of evaporator performance is available, the frequency of this step can be reduced to once per day).
(f) Check to see that evaporator bottoms are flowing to the recycle tank.

8 Vacuum System

(a) During operation, periodically check the system vacuum and the condenser (E-111) jacket temperatures.
(b) Prior to each crystallizer batch, drain the condensate traps (T-116A and T-116B). Record weight of collected condensate.

c. Operation (Batch Units)

1 Crystallizer

(a) Start the crystallizer agitator after it becomes covered with solution.
(b) Start the vacuum system.
(c) After the crystallizer has been charged, start to lower the temperature by reducing the pressure in the crystallizer using the vacuum system.
(d) Without bumping the crystallizer contents, cool as rapidly as possible, to the crystal point.
(e) Cool at a low rate, about 1°C in 3 minutes, through the crystal point.
(f) Continue cooling to 20°C at about 1-3°C per minute.
(g) The vacuum level is controlled by bleeding air into the vacuum at the condensate traps.
(h) Record pressure and temperature data for the run.
(i) When temperature has decreased to 20°C, break vacuum by bleeding in air, but keep the agitator running.

2 GN Centrifugation

(a) Start the slurry pump and circulate slurry to the centrifuge.
(b) Start the centrifuge and set the speed for slurry charging (500-600 rpm).
(c) Start the filtrate pump.
(d) Open the slurry valve, and charge slurry until the basket is nearly full of cake.
(e) Raise the centrifuge speed to the spin-out level 1200 rpm, and spin until little mother liquor remains in the cake. The spin-out cycle will take 2 minutes.
(f) While the centrifuge is operating at the spin speed, wash the cake with about one cake volume of water (about two gallons).

(g) Spin out the wash until the cake is dry as possible.
(h) Reduce the speed to the discharging level (or 100 rpm) and plow the cake into a weigh drum.
(i) Repeat this cycle until all of the slurry is processed. There will be about four batches per crystallizer batch.

d. Shutdown Procedures

(1) Drain and thoroughly flush all melt transfer lines and hot aqueous solution lines with water and/or steam. Blow lines with air.
(2) If the tanks in the reactor feed, aqueous quench, crystallizer systems are not to remain heated, then they must also be drained and thoroughly flushed.
(3) Drain the reactor tubes and the interfeed lines and interfeed tank.
(4) Flush the off-gas line to the scrubber.
(5) Drain the recycle melt line and the surge tank on the bottom of the evaporator.
(6) After all lines and vessels have been drained and flushed, the steam to these vessels and lines may be shut down.

e. Special Procedures

1 Catalyst Dumping (When Required)

(a) After draining and cooling the reactor tubes, remove the top elbow and the feed manifold. This provides access to the top and bottom of the reactor tube.
(b) Lift out the catalyst retainer and unbolt the catalyst spool piece.
(c) With a little prodding, the catalyst should flow from the reactor tube.
(d) If the tube is severely plugged, steam and/or hot water may be used to break plugs in the reactor.

2 Reactor Flush

(a) Increase pump rate two to three times the normal rate.
(b) Decrease reactor temperature by 30°C.
(c) Continue pumping fresh feed for one hour.

(d) After a one-hour flush, turn off the feed pump and open the reactors and feed line drain valves.
(e) After molten material stops draining, connect an air line to reactor overhead system and apply 40-50 psig air to the reactor tubes. The product melt and off-gas line valves must also be closed. Maintain air pressure until molten material stops draining from the reactor.
(f) Release pressure and close the reactor feed valves. Apply 10 psig steam to the feed line, and blow back to the drain valve below the feed pump.
(g) Cool down reactor.

3 Emergency Shutdown

a Electric Failure

(1) Blow out lines with steam or air.
(2) Drain the reactor as in 2(e) through (g) above.
(3) Turn off electric equipment switches.
(4) Leave steam on tracings, etc.

b Steam Failure

(1) Isolate tanks and drain lines immediately wherever possible.
(2) Blow out lines with air.
(3) Drain reactor and blow down with air.
(4) Turn off equipment motors.

c Air Failure

An air reservoir tank is available as a backup air supply. If building air is lost, switch over to this tank. If air failure is long term, follow shutdown procedures.

d Water Failure

If the water pressure in the building becomes too low, the fire system low-pressure alarm will be energized. Since a water failure eventually results in a steam failure, follow the above procedure for a steam failure.

4. Safety Design Considerations

Sensitivity testing, engineering analysis of pilot plant equipment, preparation of a Logic Model (Fault Tree) and performance of a

risk analysis for the GN pilot plant were interrelated functions and were performed during Phases I, II and III. For the purpose of continuity, the results from all three phases are discussed in this section. A final Hazards Analysis summary report is presented in Appendix IV.

### a. Sensitivity Testing

Initiation testing of simulated process materials was completed, and the results are presented in Figure 56 and Table 43. These tests consisted of subjecting in-process materials to impact, friction and electrostatic discharge (ESD) stimuli to determine threshold initiation levels (TIL's) for each material. An inspection of the data shows that the process materials are relatively insensitive. Many samples could not be initiated at the limits of the standard test machines (these materials can be identified by the equal to or greater than ($\geq$) sign preceding the sensitivity value in Table 43). The limit of the impact test machine is reached when a sample fails to initiate when a 2-Kg weight is dropped on it from a height of 120 cm (over a known impact area). A friction TIL value was obtained for AN/GN/U = 45/40/15 while all other combinations exceeded the limits of the test. The ESD threshold values ranged from 0.075 to 1.26 joules. They are above the energy region that could be available from a human being (0.013 joule maximum). A Lira Analyzer (Model 300) was used in all sensitivity testing to determine if initiation occurred. This instrument detects the presence of decomposition gases CO, $CO_2$, $NO_2$ and NO. Therefore, initiation does not necessarily mean that a flash fire or smoke will occur, but rather that some gaseous decomposition occurs. Differential Scanning Calorimeter tests showed that high temperatures (266 to 295°C) were required for any exothermic reaction.

#### 1 Transition Testing

Transition tests were performed to determine the effect of initiation on the ability of a material to transit from flame initiation to an explosive reaction in terms of material height under specific environmental conditions.

Tests on the reactor mixture were performed at both ABL and Kenvil. Initial tests were run in containers smaller than pilot plant reactor tubes with the intent of extrapolating data to determine if the reactors would transit to an explosion if the material was initiated. However, no reaction occurred in a 1 inch x 48 inch container. Therefore, a 2 inch x 12 foot container was used for a test performed at the Kenvil Plant, and no explosive reaction occurred. Since material height required for explosion to occur increases as the diameter increases, it was concluded from the Kenvil tests that an explosive reaction would not occur in the 4 inch x 12 foot pilot plant reactors if initiation occurred.

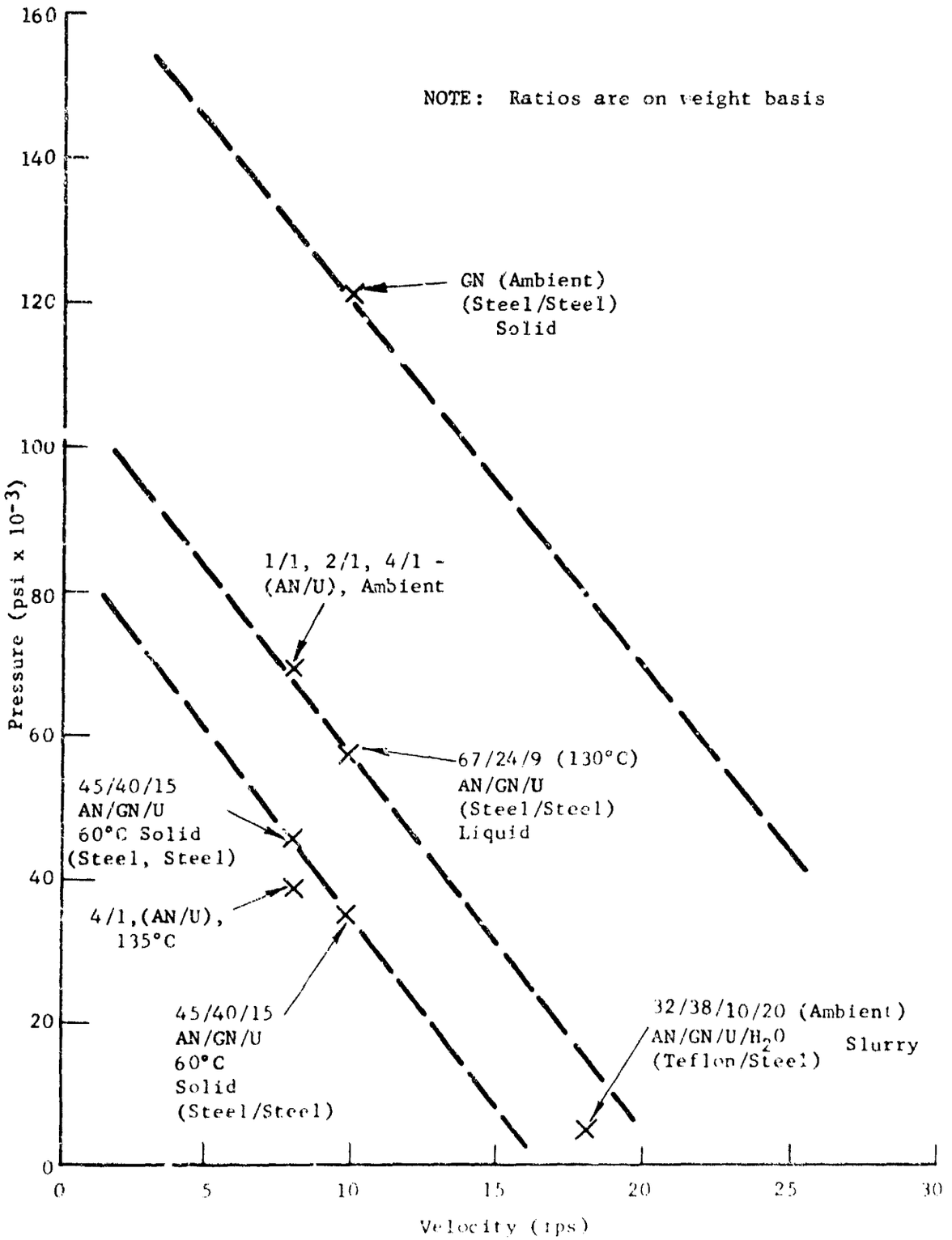



Figure 56. Friction Sensitivity Data Velocity vs Pressure

TABLE 43

SUMMARY OF SENSITIVITY DATA (bMR PROCESS)

| Sample (Wt. Ratio) | Temperature | Threshold Initiation Level** | | | |
|---|---|---|---|---|---|
| | | Impact ($ft\text{-}lbs/in^2$) | Friction (psi/ft/sec) | ESD (Joules) | Materials |
| AN/U 1/1 | Ambient | -- | ≥ 69,000/8 | | Steel/Steel |
| AN/U 2/1 | Ambient | -- | ≥ 69,000/8 | | Steel/Steel |
| AN/U 4/1 | Ambient | ≥ 59.7 | ≥ 67,000/8 | 0.5 | Steel/Steel |
| AN/U 4/1 | 135°C | $84 \times 10^3$* | ≥ 39,090/8 | | Steel/Steel |
| AN/GN/U 45/40/15 | 60°C | > 77.6 | 45,614/8<br>35,185/10 | | Steel/Steel<br>Steel/Steel |
| AN/GN/U 67/24/9 | 130°C | | ≥ 58,870/10 | | Steel/Steel |
| GN - Pure | Ambient | ≥ 59.7 | ≥122,400/8 | 1.26 | Steel/Steel |
| GN - Technical Grade | Ambient | 31.6 | >105,800/8 | 0.075 | Steel/Steel |

* ft-lbs/sec

** Level above which initiation can occur as a result of 20 consecutive failures at that level.

Transition tests were also performed on guanidine nitrate, and no explosive reaction occurred in a 1 inch x 24 inch container. Again, after considering pilot plant equipment dimensions, it was concluded that no transition hazard existed in pilot plant equipment handling guanidine nitrate.

Because of the importance of determining the safety of the packed bed tubular reactors, the full-scale transition tests are discussed below in detail.

Six transition tests were conducted. General conditions for the first three tests are outlined below:

(1) Pipe - 1 inch diameter x 12 foot tall, carbon steel, top vented.
(2) Catalyst - Houdry silica beads packed full length of pipe.
(3) Pipe position - 30° from vertical.
(4) Method of heating - External electrical heating tapes.
(5) Feed material - 1/1 molar ratio of urea and ammonium nitrate. Pipe filled to 12-foot height.
(6) Ignition - High-resistance Pyrofuze, 0.004-inch diameter, 30 to 40 feet coiled, installed at bottom of pipe.
(7) Time of ignition - Approximately 30 minutes after reaching 190°C.
(8) Temperature measurement - Top and bottom thermocouples.
(9) Velocity profile measurement - Two externally mounted pressure chronograph sensors.

Of the first three tests completed, two were valid tests with no burning or explosion following flame initiation. One of the tests was not valid because of a premature gas release before ignition. No attempt was made to ignite the Pyrofuze, since the gas release expelled the pipe contents.

Three additional tests were made after the pipe diameter was increased to 2 inches to prevent gas evolution problems. Two of these tests were invalid because of equipment failures. The tests did point out areas of design consideration; e.g., adequate venting of reactors and lack of radial plugs on startup.

The six tests are discussed in more detail in the following paragraphs.

a Test No. 1

For this test, the Pyrofuze electrical leads and the top and bottom thermocouple wires entered the test pipe from the top. The bottom of the pipe was closed with a standard pipe cap. The molten urea/ammonium nitrate mixture was added to the catalyst-packed pipe, and the contents were heated to 190°C. Reaction was evident from the odor of ammonia in the atmosphere. After 25 minutes of reaction at 190°C, the Pyrofuze was ignited. Thirty minutes after flame initiation and elimination of heat input via electric tapes, the contents of the pipe were expelled from the open end as a result of gas release. It is assumed that the diameter of the packed pipe was insufficient to handle the gas evolution. The bottom of the pipe was significantly hotter than the middle or upper sections. Removal of the bottom pipe cap revealed charred catalyst - evidence that there had been a fire within the pipe. Transition did not occur.

b Test No. 2

The equipment setup and test procedure for this test were essentially the same as for Test No. 1 except that the bottom thermocouple (sheathed stainless steel) and the Pyrofuze electrical leads were installed through a bottom tee arrangement. After approximately 30 minutes of reaction time at 190°C, the Pyrofuze circuit was energized. The bottom thermocouple (located 2-1/2 feet from the bottom) registered a 45-50°F temperature rise within 1 to 2 minutes. Charred catalyst was found in the bottom of the test pipe, indicating that the Pyrofuze ignited and burned. Catalyst and reaction mix located about midway in the pipe were clean. Transition did not occur.

c Test No. 3

This test was planned as a repeat of Test No. 2 with respect to equipment assembly, test procedure, etc. Due to a late start, the pipe contents were heated more rapidly than normal to the 190°C reactor temperature. After 18 minutes of reaction at 190°C, the pipe contents were expelled as a result of gas evolution. The Pyrofuze circuit was not energized. Examination of the pipe interior and material found on the ground did not disclose evidence of a fire. It is believed that the rate of gas formation was too great for the 1-inch-diameter pipe. This was not a valid test.

d Test No. 4

For this test, the pipe diameter was changed from 1 inch to 2 inches, and the material of construction of the 13-foot-long

pipe was changed to 304 stainless steel. The Pyrofuze (source of flame initiation) was wrapped in aluminum foil before it was installed in the bottom of the pipe. Temperatures were monitored with both top and bottom-entering thermocouples. After the pipe had been loaded with Houdry silica beads and a new 1/1 U/AN melt, the temperature was raised to 190°C over a period of about 60 minutes. Pyrofuze failed to ignite when the system was energized. It is presumed that the Pyrofuze circuit was short-circuited by either the thermocouple or the aluminum wrap.

The reactor contents were subsequently raised to a temperature of 240°C and held at this level for 30 minutes. There was no exothermic reaction.

This transition test was considered invalid because of the fuze failure.

e Test No. 5

The test pipe and its contents from the No. 4 test were used for this test. The new Pyrofuze igniter was wrapped in polyethylene rather than aluminum foil. After the contents of the simulated reactor had leveled out at reaction temperature (190°C), there was a loud report from the bomb butt. Ignition of the Pyrofuze was never attempted. Examination of the test setup showed that the thermocouple Conax adaptor and the bottom carbon steel plug had been blown clear of the pipe. There was no evidence of a fire. A pressure buildup in the pipe resulted in failure of the bottom fittings. Subsequent examination of the pipe interior showed that the pipe was plugged about midway along the axial length. Past review of the experiment recalled the fact that the center heating tape had been taken out of service due to a malfunction. This would have prohibited the melting of material in this location. This test was invalid.

f Test No. 6

A new piece of 2-inch-diameter, 13-foot-long section of 304 stainless steel pipe was obtained for this test. Thermocouples and Pyrofuze leads were installed from the top (open end) while the bottom was capped off. Various Pyrofuze igniter designs were evaluated to determine the system that would yield the greatest assurance of success. The pipe was loaded with nondry silica beads and a new 1/1 U/AN melt. Temperature of the pipe contents was raised to 190°C. During the heatup, the rate of temperature rise increased from the normal slope, and consequently, the material was at reaction temperature for only 15-20 minutes before the Pyrofuze circuit was energized. It is believed that this is sufficient time to obtain a satisfactory conversion of the raw materials.

Following cooldown of the pipe, the bottom pipe cap was removed. Approximately 75% of the Pyrofuze (50 feet had been charged to the fuze circuit) had been consumed, indicating that a fire had existed in the pipe. There was some evidence of darkened catalyst beads. This was a valid test.

## 2 Materials Testing - Bonfire Tests

To determine the potential problems that may be encountered in the event of a building fire, selected bonfire tests were performed. The tests were designed to simulate either reactor product or reactor contents. Active ingredients were Cyanamid of Canada guanidine nitrate and analytical grades (Mallinckrodt) urea and ammonium nitrate. The various combinations tested are shown below:

| Test No. | GN/AN/U (Wt. %) | Other | Remarks |
|---|---|---|---|
| 1 | 30/50/20 | - | Simulate reactor product |
| 2 | 30/50/20 | - | Simulate reactor product |
| 3 | 15/25/10 | 50 wt. % silica gel | Simulate reaction mix with catalyst |
| 4 | 30/50/20 | 1 wt. % micro-balloons | Simulate reaction mix with gas bubbles |

Testing of the above systems consisted essentially of charging the blend of materials (about 4 pounds) to a 1-gallon paint can and suspending the filled can over a wood fire. The cans were fitted with a loose lid and contained a thermocouple. All tests were viewed from a distance.

The following conclusions were made based on the results of the four bonfire tests:

(1) None of the mixes subjected to the bonfire environment detonated.
(2) All of the mixtures burned but only when the contents of the can spilled into the flames, generally at temperatures >500°F
(3) The faster rise in temperature for Tests 3 and 4 was attributed to improved heat transfer and/or improved mixing as a result of the added silica gel or micro-balloons.

### 3 Propagation Tests

Propagation tests determine explosive propagation characteristics of a material in terms of the diameter of the material when it is subjected to a shock stimuli. The results showed that guanidine nitrate and the material in the reactors will propagate an explosive reaction, since both of their critical diameters are less than one inch. However, it must be remembered that the transition tests demonstrated that these materials, under the pilot plant conditions, would not transit to an explosion. In other words, the pilot plant process materials are not capable of supplying a shock stimulus for propagation to occur.

Propagation tests performed on other samples show that no propagation would occur in the one-inch piping used in the pilot plant.

### 4 Dust Explosibility

Dust explosibility tests were performed in an effort to determine the minimum concentration and minimum energy required to initiate guanidine nitrate in a dusty atmosphere. The guanidine nitrate was screened to < 53 micron, and two different sources of initiation were used. Initially, a continuous sparking electrode was attempted; however, no initiation of a GN/air dust cloud could be obtained. The test was rerun using as an ignition source fibrous nitrocellulose which is a more violent source of initiation than the sparking electrodes. In both cases, the guanidine nitrate dust/air mixture could not be initiated at the standard test limits of the machine (4.1 $oz/ft^3$).

## b. Hazard Evaluations

The engineering analysis for selected equipment was based on equipment drawings, specifications and maximum operating parameters furnished by Kenvil and the Research Center. Since no on-site measurements (i.e., forces, pressures, and velocities) were made, tensile strengths or yield points of materials involved were used to obtain safety margins. In general, the safety margins found on equipment are representative of "worst case" condition, so the analysis would be conservative from a safety point of view.

In the process in which equipment handles a water slurry, the analysis was based on water-free material response data, since testing was not done with water slurries. The use of water-free material values would render conservative results since the water would most likely act as an extinguisher for any initiation. This type of an analysis, using water-free sensitivity data, would apply to start-up or shut-down modes of operation or a process "upset condition" in which a sufficient amount of water would not be present.

A hazards analysis was performed on pilot plant pumps, mixers, reactors, valves, centrifuge, crystallizer and dryer in which in-process potentials and material response data (expressed in similar engineering terms) were compared to obtain quantitative safety margins for normal and abnormal conditions. The initial pilot plant design specified high-speed ECO centrifugal pumps for almost all applications. Analysis showed that this type of pump could cause initiations at the seal faces and, to overcome this problem, the speed must be reduced to 2800 rpm. Required heads and rates prohibited a reduction in speed. Consequently, Gould pumps were selected whereby reduced shaft and seal speeds could be obtained. Pump speed and impeller diameter were selected for each application. For example, a 3450-rpm centrifugal pump with a carbon/ceramic mechanical seal was selected to pump material to the crystallizer. Velocity of the rotating seal parts was calculated to be 16.9 ft/sec with a normal pressure of 30 psi and an abnormal pressure of ~ 8000 psi (yield point of carbon). Extropolation of the friction data for this process material showed no positive safety margin at 16.9 ft/sec. A pump with a reduced speed (1750 rpm) and a Teflon packing gland was substituted. The in process potential for this pump was 24 psi (normal) to ~ 5000 psi (abnormal) at a velocity of 8.6 ft/sec. Material response at 8.6 ft/sec is ~ 43,000 psi. Consequently, safety margins of 8.6 to 1797 were realized by this change.

The "Lightnin" Fixed-Mount mixers presented no problems under normal conditions. It was recommended that mixer shaft seals be placed outside the tanks and the impellers be attached positively to the shaft. The latter condition was accomplished by spot welding.

The Strong Scott rotary, counter-current dryer was analyzed and found to present no hazard under normal operating conditions. Since the blade tip speed in the dryer would be about 56.3 ft/sec foreign objects must be eliminated and metal-to-metal contact between the blades and the dryer body must be prevented. The blades were subsequently spot welded to the rotor. Should the dryer bearings become contaminated with GN, initiation most likely would occur. Such initiation could cause bearing deterioration and, ultimately, an unbalance along the dryer axis, resulting in frictional contact between dryer blades and body. If ignition should occur, the material (GN) would not transit to an explosion.

The Specified Swenson Draft Tube Crystallizer contains a bottom entering agitator operated at 0-350 rpm. Analysis showed a safety margin for this agitator assembly (mechanical seal faces) of 25.7. The DeLaval Link Suspended Centrifuge for separating GN from the crystallizer slurry was of particular concern from a hazards analysis viewpoint. Under normal conditions, the charging of slurry to a rotating basket and plowing the wet cake from the basket would present no problems. Of primary concern was that of the plow hitting the basket at full speed of the centrifuge. Under this abnormal condition, there would be no safety margin. Corrective

action consisted of designing into the system a positive plow lock device to prevent the blade from moving into the basket and an interlock to prevent cake plowing above a preset basket speed (e.g., 50-70 rpm).

In general, all normal and some abnormal operations have adequate safety margins. Abnormal occurrences such as impellers or mix blades breaking and hitting metal parts would cause initiation (no safety margin), but would not result in transition. The probabilities of such events occurring over the life of pilot plant operations are $5 \times 10^{-4}$ to $5 \times 10^{-5}$.

Examples of calculating in-process potentials and safety margins for pumps, dryer, and centrifuge are presented in Table 44. A hazard evaluation summary for the pilot plant equipment is presented in Table 45.

c. Logic Model

A logic model (Fault Tree) is a concise and orderly description of various combinations of events that can lead to a predefined "undesired" event. The logic model is presented in a diagram or blueprint form and results in an engineering capability to identify and evaluate the overall effect of component failure, controls or human actions on the system. The logic model constructed for analysis of the pilot plant (described in detail in the Appendix) yielded a total of 352 potential failure modes. Of these, only 21 were considered to be significant or critical. These failure modes would result, at most, in initiation and not transition to explosion. The basic failure modes are impeller, shaft, and/or alignment. Continuous operation of 800 hours was assumed.

The probability of initiation then becomes the product of the probability of failure, times the proportion of operating time the failure rate applies, times the material response probability. For example, the impeller, shaft and shaft packing for the Goulds Pump (mixing system) had a combined failure rate of seven per million operating hours ($7.10^{-6}$). Thus, after 800 hours, the probability of failure becomes $7.10^{-6}$ times 800 or $5.6 \cdot 10^{-4}$. Multiplying this probability of $5.6 \cdot 10^{-4}$ times the proportion of operating time it applies, times material response probability gives an overall probability of initiation, or $5.6 \cdot 10^{-4}$ times 1.0 times 0.98 or $5.6 \cdot 10^{-4}$. The overall probability for the pilot plant is $4.6 \cdot 10^{-3}$. The overall reliability of the pilot plant system is 0.99536. It must be emphasized that this probability assumed 800 hours at continuous operation without repairs or maintenance. Any such action within the 800 hours would tend to reduce this probability to a much smaller quantity.

TABLE 44

HAZARDS ANALYSIS OF GN PILOT PLANT EQUIPMENT

1. P-100 - U/AN Melt Transfer Pump

Type Pump - Gould Centrifugal, 1750 rpm, asbestos-filled Teflon packing, 1.25" Diameter Shaft, 4.875" Diameter Impeller, 304 S.S.

Shaft Velocity - 8.6 ft./sec

Impeller Velocity - 37.2 ft./sec

Process Material - 80%/20%, AN/U melt @ 120°C

Hazards Analysis

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| **Normal** | | |
| Friction In Shaft Packing Not totally defined (ca. 20 psig @ 8.6 fps*) | 35,185 @ 10 | > 7.8 based on abnormal condition |
| **Abnormal** | | |
| a. Friction in Shaft Packing 5000 psig @ 8.6 ft./sec (yield strength of Teflon) | > 39,090 @ 8 | > 7.8 |
| b. Friction impeller to case 45,000 psig @ 37.2 ft./sec (yield strength of stainless steel) | > 39,090 @ 8 | None(1) |

2. P-104 & P-106 - Quenched Reactor Product

Type Pump - Same as P-100

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*Pressure between packing and shaft will equal pump NPSH (net positive suction head) + 20% of maximum discharge pressure.

(1) Possibility of impeller coming loose very remote. If ignition does occur, there will be no transition.

TABLE 44 (CONT'D.)

Shaft Velocity - 8.6 ft./sec

Impeller Velocity - 37.2 ft./sec

Process Material - 26%/29%/6%/39%, AN/GN/U/$H_2O$ @ 90°C

Hazards Analysis

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| **Normal** | | |
| Friction In Shaft Packing Not totally defined (ca. 20 psig @ 8.6 ft./sec)* | 35,185 @ 10 | > 7 Based on abnormal conditions |
| **Abnormal** | | |
| a. Friction In Shaft Packing 5000 psig @ 8.6 ft./sec (yield strength of Teflon) | 5,185 @ 10 | None(1) |
| b. Friction impeller to case 45,000 psig @ 37.2 ft./sec (yield strength of stainless steel) | | |

3. P-108 - Filtrate Transfer Pump

Type Pump - Same as P-100

Shaft Velocity - 8.6 ft./sec

Impeller Velocity - 37.2 ft./sec

Process Material - 34%/9%/8%/49% AN/GN/U/$H_2O$ @ 20°C

---

*Pressure between packing and shaft will equal pump NPSH (net positive suction head) + 20% of maximum discharge pressure.

(1)Possibility of impeller coming loose very remote. If ignition does occur, there will be no transition.

TABLE 44 (CONT'D.)

Hazards Analysis

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| **Normal** | | |
| Friction In Shaft Packing Not totally defined (ca. 20 psig @ 8.6 ft./sec* | 35,185 @ 10 | > 7 |
| **Abnormal** | | |
| a. Friction In Shaft Packing 5000 psig @ 8.6 ft./sec | 35,185 @ 10 | 7 |
| b. Friction impeller to case 45,000 psig @ 37.2 ft./sec (yield strength of stainless steel) | 38,185 @ 10 | None(1) |

4. P-107 - GN Slurry Transfer

| | |
|---|---|
| Type Pump - | Gould's Centrifugal, 1750 rpm, Double Mechanical Seal (Carbon - Stainless Steel), 1.25" Diam. Shaft, 3.75 diameter impeller, 304, S.S. |
| Shaft Velocity - | 8.6 ft./sec |
| Impeller Velocity - | 28.6 ft./sec |
| Mechanical Seal Velocity (outer - edge) | 11.9 ft./sec |
| Seal Spring Loan - | 16 pounds |
| Process Material - | 28%/32%/6%/34%, AN/GN/U/$H_2O$ (Use 60°C, 40/45/15, AN/GN/U solid data) |

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*Pressure between packing and shaft will equal pump NPSH (net positive suction head) + 20% of maximum discharge pressure.

(1) Possibility of impeller coming loose very remote. If ignition does occur, there will be no transition.

TABLE 44 (CONT'D.)

Hazards Analysis

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| **Normal** | | |
| Mechanical seal friction** ca. 35 psig @ 11.9 ft./sec | ~ 25,000 @ 12 | 714 |
| **Abnormal** | | |
| a. Mechanical Seal Friction, Abnormal wear 8800 psi @ 11.9 ft./sec (yield strength of carbon) | ~ 25,000 @ 12 | 2.8 |
| b. Friction impeller to case 45,000 psig @ 28.6 ft./sec (yield strength of stainless steel) | ~ 25,000 @ 12 | None(1) |

5. P-102 - Reactor Feed Pump

| | |
|---|---|
| Type Pump - | Goulds Centrifugal, 3500 rpm, asbestos-filled Teflon packing, 1.125" diameter shaft, 4" diameter impeller, 304 S.S. |
| Shaft Velocity - | 17.2 ft./sec |
| Impeller Velocity - | 61 ft./sec |
| Process Material - | 52%/9%/39%, AN/GN/U @ 120°C |

---

**Based on spring load and contact area of mechanical seal faces.

(1) Possibility of impeller coming loos very remote. If ignition does occur, there will be no transition.

TABLE 44 (CONT'D.)

Hazards Analysis

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| **Normal** | | |
| Friction in shaft packing Not totally defined (ca. 20 psig @ 17.2 ft./sec)* | (22,000 @ 17.2 by extrapolation) | (1100 based on extrapolation) |
| **Abnormal** | | |
| a. Friction in shaft packing 5000 psig @ 17.2 ft./sec (yield strength of Teflon | (22,000 @ 17.2 by extrapolation) | (4.4 based on extrapolation) |
| b. Friction impeller to case 45,000 psig @ 61 ft./sec (yield of stainless) | $\geq$ 58,870 @ 10 | None(1) |

6. P-109 - Evaporator Feed Pump

| | |
|---|---|
| Type Pump - | Same as P-102 |
| Shaft Velocity - | 17.2 ft./sec |
| Impeller Velocity - | 61 ft./sec |
| Process Material - | 34%/9%/8%/49%, AN/GN/U/$H_2O$ @ 20°C |

Hazards Analysis

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| **Normal** | | |
| Friction in shaft packing Not totally defined (ca. 20 psig @ 17.2 ft./sec)* | $\geq$ 4900 @ 18 (Teflon/Steel) | (250 based on 20 psig @ 17 ft./sec) |

---

*Pressure between packing and shaft will equal pump NPSH (net positive suction head) + 20% of maximum discharge pressure.

(1) Possibility of impeller coming loose very remote. If ignition does occur, there will be no transition.

TABLE 44 (CONT'D.)

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| Abnormal | | |
| a.Friction in shaft packing 5000 psig @ 17.2 ft./sec (yield strength of Teflon) | 22,000 @ 17.2 (67/24/9 @ 130°C data) | 4.4 |
| b.Friction impeller to case 45,000 @ 61 ft./sec (yield strength of stainless steel) | ≥ 58,870 @ 10 | None(1) |

7. A-700 GN Dryer

Description - Strong-Scott Solidair Rotary Dryer, fixed paddles, Neoprene lip seals each end of dryer, sealed external bearings, 304 S.S.

Speed - 19 - 1520 rpm (Normal - 350 rpm)

Shaft Diameter - 1.5 inches

Paddle Diameter - 8.375 inches

Shaft Velocity - 2.3 ft./sec (Normal); 9.9 ft./sec (Max.)

Paddle Velocity - 12.56 ft./sec (Normal); 55.3 ft./sec (Max.)

Hazards Analysis

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| Normal | | |
| a.Friction lip seal 4000 psig @ 2.3 ft./sec (yield strength of neoprene) | > 122,800 @ 2.3 | > 30.5 |

(1)Possibility of impeller coming loose very remote. If ignition does occur, there will be no transition.

TABLE 44 (CONT'D.)

| Initiation Mode & In-Process Potential | Material Response (psig @ ft./sec) | Safety Margin |
|---|---|---|
| b.ESD in dryer 0.04 joules | 0.075 joules (worst case - commercial grade) | 1.9 |
| Abnormal | | |
| a.Friction lip seal, max. vel. 4000 psig @ 9.9 ft./sec (yield strength of Neoprene) | ≥ 122,800 @ 10 | ≥ 30.5 |
| b.Paddle hit shell (normal velocity) 4500 psig @ 12.5 ft./sec (yield strength stainless steel) | ca. 110,000 @ 125 | ca. 2.4 |
| c.Paddle hit shell (max. vel.) 45,000 psig @ 55.3 ft./sec (yield strength of stainless steel) | ca. 0 @ 55.3 (assume linear extrapolation) | None*** |

8. S-600 GN Centrifuge

| | |
|---|---|
| Description - | DeLaval Link Suspended, 22-inch diameter perforated basket, variable speed, hydraulic drive, interlokced for low speed plowing, 304 S.S. wetted parts. |
| Speed - | 0-1600 rpm range (70 rpm plowing speed) |
| Shaft Diameter - | 2 inches |
| Basket velocity - | 303 ft./sec (Max.); 6.7 ft./sec (Plowing) |

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***Speed of dryer will be limited by positive stop on speed adjustment. Extrapolation of friction data to 17.5 ft./sec for GN yields a dryer speed of 500 rpm for a safety margin of about 2.

TABLE 44 (CONT'D.)

Shaft Velocity - 13.8 ft./sec (Max.); 0.58 ft./sec )Plowing)

Process Material - 85%/15%, GN/$H_2O$ @ 20°C

| Initiation Mode & In-Process Potential | Material Response psig @ ft./sec | Safety Margin |
|---|---|---|
| a.Plow hits basket (Plow vel.) 4500 @ 6.7 ft./sec (yield strength of stainless steel) | ca. 140,000 @ 6.7 | 3.1 |
| b.Plow hits basket (Max. Vel.) 45,000 psig @ 303 ft./sec (yield strength of stainless steel) | ≥ 122,000 @ 10 | None*** |
| c.Friction of contaminated teflon bearing seal (Max. vel.) 5000 psig @ 13.8 ft./sec (yield strength teflon) | ca. 100,000 @ 13.8 | 20 |
| d.Friction of contaminated teflon bearing seal(plow speed) 5000 psig @ 0.58 ft./sec (yield strength of teflon) | ca. 150,000 @ 0.58 | 30 |

NOTE: For the Gould pumps with Teflon packing, it was assumed that under normal conditions, the packing would be adjusted so that water or process fluid could flow through the shaft-packing annulus. In this case,the applied pressure between the packing and shaft would approximate the sum of the pumps NPSH (net positive section head) and 20% of the dead head pressure.

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***Centrifuge equipped with interlock device to prevent plowing at speed greater than 50-70 rpm. Centrifuge also equipped with positive stop to prevent plow from hitting basket.

TABLE 45

HAZARD EVALUATION SUMMARY

| Operation | Initiation Mode | In-Process Potential | Material Response | Hazardous | Safety Margin |
|---|---|---|---|---|---|
| Pumping Initial AN/U Mixture | | | | | |
| a. Normal | Friction in shaft packing (teflon/316SS) | ~24 psi @ 8.6 ft/sec | ~36,000 psi @ 8.6 ft/sec | No | ~1500 |
| b. Abnormal | Friction in shaft packing (teflon/316SS) | ~5,000 psi @ 8.6 ft/sec (yield point of teflon) | >36,000 psi @ 8.6 ft/sec | No | ~7.2 |
| | Impeller scrapping pump case (316SS/316SS) (shaft or impeller breaks) | ~45,000 psi @ 37.2 ft/sec (yield point of 316SS) | >39,090 psi @ 8 ft/sec | Yes | |
| Pumping Reactor Feed Mixture | | | | | |
| a. Normal | Friction in shaft packing (teflon/316SS) | ~24 psi @ 17.2 ft/sec | ~21,000 psi @ 17.2 ft/sec | No | ~875 |
| b. Abnormal | Friction in shaft packing (teflon/316SS) | ~5,000 psi @ 17.2 ft/sec (yield point of teflon) | ~21,000 psi @ 17.2 ft/sec (steel/steel) | No | ~4.2 |
| | Impeller scrapping pump case (316SS/316SS) (shaft or impeller breaks) | ~45,000 psi @ 61 ft/sec (yield point of 316SS) | >58,870 psi @ 10 ft/sec | Yes | -- |

TABLE 45 (Continued)

| Operation | Initiation Mode | In-Process Potential | Material Response | Hazardous | Safety Margin |
|---|---|---|---|---|---|
| Pumping Inter-stage Reaction Mixture | | | | | |
| Normal | Friction in ball check valves (Hastelloy D/Durimet) | ~40,000 psi @ 0.03 ft/sec (yield point of Durimet) | ~87,000 psi @ 0.03 ft/sec | No | ~2.2 |
| | Friction between plunger and packing (alumina-ceramic/Garlark) | 20,000 psi @ 0.33 ft/sec (yield point of 85% alumina-ceramic) | ~85,000 @ 0.33 ft/sec | No | ~4.3 |
| Pumping Aqueous Quench Tank Mixture | | | | | |
| a. Normal | Friction in shaft packing (teflon/316SS) | ~24 psi @ 8.6 ft/sec | 43,000 psi @ 8.6 ft/sec | No | ~1792 |
| b. Abnormal | Friction in shaft packing (teflon/316SS) | ~5,000 psi @ 8.6 ft/sec (yield point of teflon) | 43,000 psi @ 8.6 ft/sec (steel/steel) | No | 8.6 |
| | Impeller hits pump casing (316SS/316SS) (shaft or impeller breaks) | ~45,000 psi @ 37.2 ft/sec (yield point of 316SS) | 35,185 psi @ 10 ft/sec | Yes | None |
| Pumping Crystallizer Feed Mixture | | | | | |
| a. Normal | Friction in shaft packing (teflon/316SS) | ~24 psi @ 8.6 ft/sec | 43,000 psi @ 8.6 ft/sec | No | 1797 |
| b. Abnormal | Friction in shaft packing (teflon/316SS) | ~5,000 psi @ 8.6 ft/sec (yield point of teflon) | 43,000 psi @ 8.6 ft/sec (steel/steel) | No | 8.6 |
| | Impeller hitting pump case (316SS/316SS) (shaft or impeller breaks) | ~45,000 psi @ 37.2 ft/sec (yield point of 316SS) | 35,185 psi @ 10 ft/sec | Yes | None |

TABLE 45 (Continued)

| Operation | Initiation Mode | In-Process Potential | Material Response | Hazardous | Safety Margin |
|---|---|---|---|---|---|
| Pumping Centrifuge Feed Mixture | | | | | |
| a. Normal | Friction between mechanical seal faces | ~35 psi @ 11.9 ft/sec | ~25,000 psi @ 12 ft/sec | No | 714 |
| b. Abnormal | Friction between mechanical seal faces (carbon/stellite) | ~8,800 psi @ 11.9 ft/sec (yield point of carbon) | ~25,000 psi @ 12 ft/sec (steel/steel) | No | 2.8 |
| | Impeller hitting pump case (316SS/316SS) (shaft or impeller breaks) | ~45,000 psi @ 28.6 ft/sec (yield point of 316SS) | ~25,000 psi @ 12 ft/sec | Yes | None |
| Pumping Mixture to Evaporator Feed Tank | | | | | |
| a. Normal | Friction between shaft and packing | ~24 psi @ 8.6 ft/sec | ~63,000 psi @ 8.6 ft/sec | No | ~2625 |
| b. Abnormal | Friction in shaft packing (teflon/316SS) | ~5,000 psi @ 8.6 ft/sec (yield point of teflon) | ~63,000 psi @ 8.6 ft/sec (steel/steel) | No | 12.6 |
| | Impeller hits pump case (316SS/316SS) (shaft or impeller breaks) | ~45,000 psi @ 61 ft/sec (yield point of 316SS) | >58,870 psi @ 10 ft/sec | Yes | None |
| Pumping Mixture to the Evaporator | | | | | |
| a. Normal | Friction between shaft and packing | ~24 psi @ 17.2 ft/sec | ~22,000 psi @ 17.2 ft/sec | No | ~ 916 |
| b. Abnormal | Friction in shaft packing (teflon/316SS) | ~5,000 psi @ 17.2 ft/sec (yield point of teflon) | ~22,000 psi @ 17.2 ft/sec (steel/steel) | No | 4.4 |
| | Impeller hits pump case (316SS/316SS) (shaft or impeller breaks) | ~45,000 psi @ 37.2 ft/sec (yield point of 316SS) | ~58,870 psi @ 10 ft/sec | Yes | None |

TABLE 45 (Continued)

| Operation | Initiation Mode | In-Process Potential | Material Response | Hazardous | Safety Margin |
|---|---|---|---|---|---|
| Operation of Centrifuge | | | | | |
| Abnormal | Plow hits basket wall (316SS/316SS) | ~45,000 psi @ 6.7 ft/sec (yield point of 316SS) | ~146,000 psi @ 6.7 ft/sec | No | ~3.2 |
| | Plow hits basket wall at maximum centrifuge speed (316SS/316SS) (interlock fails and plow stop fails) | ~45,000 psi @ 303 ft/sec | ≥122,000 psi @ 10 ft/sec | Yes | |
| | Friction in contaminated bearing seal at maximum speed (teflon/316SS) | ~5,000 psi @ 13.8 ft/sec (yield point of teflon) | ≥114,000 psi @ 13.8 ft/sec | No | 22.8 |
| Operation of Dryer System | | | | | |
| a. Normal | Friction in sprocket & chain drive of vibra-feeder | ~120,000 psi @ 0.03 ft/sec (yield point of 4130 steel) | ≥167,000 psi @ 0.03 ft/sec | No | ≥1.4 |
| | Friction between neoprene belt & doctor blade of vibra-feeder | ~4,000 psi @ 0.03 ft/sec (yield point of neoprene) | ≥167,000 psi @ 0.03 ft/sec | No | ~41.7 |
| | Friction between belt and roller support of vibra-feeder | ~4,000 psi @ 0.03 ft/sec (yield point of neoprene) | ≥167,000 psi @ 0.03 ft/sec | No | ~41.7 |
| | Friction between neoprene air boot and dryer shaft (350 rpm) | ~4,000 psi @ 2.3 ft/sec | ≥157,000 psi @ 2.3 ft/sec | No | ≥39 |
| b. Abnormal | Friction between neoprene air boot and dryer shaft (max speed of 1520 rpm) | ~4,000 psi @ 9.9 ft/sec (yield point of neoprene) | ≥122,000 psi @ 10 ft/sec | No | ~30.5 |

TABLE 45 (Continued)

| Operation | Initiation Mode | In-Process Potential | Material Response | Hazardous | Safety Margin |
|---|---|---|---|---|---|
| Operation of Dryer System b. Abnormal (continued) | Paddle hits dryer wall at normal velocity (350 rpm) (316SS/316SS) | ~45,000 psi @ 12.5 ft/sec (yield point of 316SS) | ≥110,000 psi @ 12.5 ft/sec | No | ≥2.4 |
| | Paddle hits dryer wall at max. dryer speed (1520 rpm) (316SS/316SS) | ~45,000 psi @ 55.3 ft/sec (yield point of 316SS) | ≥110,000 psi @ 12.5 ft/sec | Yes | None |
| | ESD in vibra-feeder hopper (assume 15,000 charge & loss of ground) | ~0.0069 joules | ~0.075 | No | ~10.9 |
| | ESD in dryer (assume 15,000 charge and loss of ground) | ~0.012 joules | ~0.075 | No | ~6.3 |

It has been shown that no transition is possible for guanidine nitrate material. Thus, the maximum expected losses to be experienced are those related to a localized initiation.

d. Safety

The process flows, material balances, equipment specifications, building layout, etc. are shown in Figures 52 and 53 and Table 41. The equipment was analyzed by the Hercules Hazard Analysis Technique. In addition to this analysis, as well as general safety considerations in designing and selecting equipment, other safety requirements must be fulfilled. Some of the safety requirements considered for this program are listed below.

(1) The facilities were designed to comply with DOD 4145.26M, the DOD Contractors' Safety Manual. Among the pertinent safety practices in this publication are those referring to the quantity-distance requirements, lightning protection, building ventilation, and building personnel limits and safety equipment.

(2) The equipment motors and starters were selected based on the national electrical code for special occupancies. Since there is a possibility of dust in the feed and dryer system, the classification of Class 2, Group G, was specified.

(3) The process input energies and failure modes for the selected equipment under planned operating conditions were calculated by the Hazards Analysis group. These values were compared with the Phase I initiation data (friction, impact, etc.). If any equipment item exhibited an inadequate safety factor by this analysis, either it was replaced by an alternate or its operating condition was altered to increase its safety factor.

(4) Design of all equipment and selection of operating conditions were made with full regard to the safety requirements on handling urea and ammonium nitrate and their mixtures. For example, temperatures in feed lines, melters, feed tanks, etc., were controlled with steam to prevent overheating and decomposition. Raw materials with organic oils, etc., were not used.

(5) The use of steam as a heating medium provides an additional safety margin to the equipment design. Since steam temperature is constant for any pressure, and since the steam pressure can be easily regulated and controlled, maximum temperature limits (e.g., 240°C decomposition in reactor) can be easily maintained. Also, since the use of steam provides for high heat transfer coefficients, a minimum heating Delta T is necessary, which in the case of a pump failure, limits the resultant temperature increase of a stream to a few degrees and renders overheating improbable.

(6) The equipment layout was planned so that a 12-in. reinforced wall separated the melt and feed tanks from the rest of the equipment. This allowed the inventory of material in this bay to be accounted for separately as Class 2 material.

(7) The Chemical Propulsion Division Standards were implemented in the design and setup of the pilot plant. Among the items in the Hercules Standards are maintenance procedures for explosive operations. The three most pertinent items in this area are listed as follows (there are of course others too numerous to mention):

(a) Maintenance personnel will not be allowed to work in an explosives process building while the operation is in progress.

(b) Maintenance personnel will not be allowed to work on equipment in or near an explosives operation until it has been fully decontaminated and fully checked by operating, safety and management personnel. On fulfillment of this procedure, an appropriate label will be provided for the equipment.

(c) All joints in an explosives process operation are to be designed to prevent accumulation points where explosives can hang up. This suggests flanged or quick disconnect fittings. Threaded fittings can be used on selected operations provided the process hazards are well defined and an appropriate maintenance procedure is provided so that these joints are well cleaned and inspected before reassembly.

(8) Safety relief valves are designated in certain process lines - particularly downstream of a positive displacement pump.

e. Product and Process Classification

Testing in accordance with TB-700-2 was conducted on guanidine nitrate. The findings from these tests were as follows:

| Test | Result |
|---|---|
| Detonation test (No. 8 Blasting Cap) | No deformation of pressure plate or cylinder |
| Ignition and unconfined burning test | Burning reaction only |
| Thermal stability test | No color or visible change in 48 hours at 75°C |
| Card gap test | Failure at zero cards |
| Impact sensitivity test | No ignition at 47.3 inches (120 cm) |

These results show that guianidine nitrate should be classified as a Class 2 material for storage. Since guanidine nitrate will propagate if sufficiently boostered, the government tentatively classified guanidine nitrate (less than 25% water) as Class 7 for storage and as an oxidizing agent for shipping.

The process classification was evaluated in terms of individual units of equipment. Each equipment unit was evaluated in terms of its contents, temperature, and hazards and given a process classification. It was decided that the Class 7 process units in the operation were the reactors, the GN dryer, the GN dryer-feeder, and the GN centrifuge. These units were selected because under their operating conditions, they contain material capable of being propagated. (Reactors contain oxygen-balanced AN/U/GN mixes at elevated temperatures; the other units contain, potentially, guanidine nitrate with less than 25% water.) The selected process building (Building 2204) has an explosive limit of 750 pounds. In the units designated as Class 7, there is a holdup of 450 pound of material; i.e., 180 pound in the reactor, 20 pound in the dryer, 200 pound in the dryer-feeder, and 50 pound in the GN centrifuge. There was, therefore, a limit of 300 pound of dry GN storage for the building.

f. Picatinny Arsenal Sensitivity Testing

Propagation testing was conducted by Picatinny Arsenal's Manufacturing Technology Directorate (Chemical Process Technology Division) with various pseudo samples of process streams occurring in the AN/U process. Picatinny Arsenal personnel will prepare and distribute an independent report, complete with test procedures, results and conclusions.

## 5. Alternate Reactor Considerations

One of the objectives of the Phase II design effort was to select a reactor design based on the results of the laboratory studies, normal safety and design considerations, and predicted economics.

### a. Performance of Alternate Reactor Types

During Phase I of this program, reaction studies were performed in both a laboratory, stirred batch reactor and a 2-inch-diameter tubular reactor with continuous flow. Based on reaction kinetic data, reactor models were constructed and used to predict the performance of both tubular and stirred tank reactors. Calculations showed that both urea conversion and guanidine nitrate yield (based on urea consumed) increased as a function of catalyst charge for stirred tank reactors. Calculations based on 1000 gm catalyst per tank per mole per minute of feed and 190°C showed overall urea conversions increasing from Tank 1 to Tank 3 as follows: 38.1%, 59.3%, and 71.3%. Respective GN yields were 76.1%, 85.2%, and 93.3%. These data indicate that three stirred tank reactors installed in series are sufficient to obtain practical and realistic urea conversions and GN yields. For a single train of reactors, 1000 gm catalyst per gm mole feed per minute per reactor, and a one-hour residence time per reactor, the required catalyst in each stirred vessel for 50 pound GN per hour would be 44 pound or 11.7 gallons based on a 7.37 gm/in.$^3$ bulk density. Theoretically, the required reactor working volume would be 11.7 gallons (catalyst volume); however, due to practical limitation of design, it was estimated that the total working volume would be increased by at least a factor of two (e.g., 25 vs 11.7 gallons). This estimation was based on a preliminary reactor design in which the catalyst would be contained in a basket which in turn would be suspended from a drive shaft for rotation. Clearances between the basket and the reactor wall for baffles and liquid flow plus a central inside diameter for liquid flow would be required. Design of stirred tank reactors must also take into consideration an effective circulation system (internal and/or external) as well as possible additional heat transfer area other than the vessel's jacket. Scale-up of this type of reactor to a 5000 pound GN per hour production rate would result in three 2500-gallon units. The size of stirred tank reactor units can be decreased by installing multi-train systems.

Experimental results obtained from the 2-inch-diameter fixed-bed reactor at Kenvil during Phase I indicated that the mathematical model did well in predicting concentration profiles, conversions, and yields for the production of guanidine nitrate. However, the temperature profiles recorded at Kenvil exhibited a larger temperature drop because of the endothermic heat of reaction than was predicted by the model. Two parameters associated with the heat balance, namely, the heat of reaction and the thermal conductivity of the stagnant bed, were altered to bring the predicted and the experimental temperature profiles into closer agreement.

The value of the heat reaction had the greater influence on the temperature profile. The heat of reaction of 28,000 cal/mole of GN reported by MacKay and used in the mathematical model in its original form was erroneous. The revised figure was 35,000 cal/mole of GN. The thermal conductivity of the stagnant bed was changed from 7.03 to 1.5 cal/min-in. °K. This was done based on a re-evaluation of the effect on various liquids of the flow conditions and thermal conductivity data of silica.

With the above changes, a simulation run was made for a 2-inch-diameter, 10-foot-long reactor and with a 6.6 lb/hr feed rate. These conditions duplicated those of Run 14 for the packed bed unit at Kenvil. The centerline temperature for the simulation run dropped to a minimum of 183°C at a distance of 17 inches from the entrance to the tube. This agrees well with the experimental results from the Kenvil reactor in which a minimum temperature of 182°C was recorded at 15 inches from the entrance to the tube.

The model was used to simulate the behavior of the 4-inch-diameter fixed-bed reactors proposed for the pilot plant. A number of cases were investigated. A comparison of the performance of 2-inch- and 4-inch-diameter reactors is shown in Table 46. Results are for 10-foot-long tubes with the same residence time. It can be seen that the conversion decreases from 84.6% to 81.2% in going from a 2-inch to a 4-inch tube. Likewise, the yield is reduced from 93.7% to 89.4%. These changes are due to the poorer heat transfer in the 4-inch reactors. The minimum average radial temperature dropped to 183°C at 18 inches from the entrance for the 4-inch tube, as compared to 186°C at 12 inches for the 2-inch tube. However, for the same guanidine nitrate production rate, approximately 3.6 times as many 2-inch tubes as 4-inch tubes are required. The increased cost and equipment space required for the 2-inch tubes are not justified for the relatively small increases in conversion and yield. Four-inch tubes were, therefore, selected for the pilot plant.

An annulus tube reactor which has the same volume as a 4-inch-diameter packed tube would have a substantially larger surface area than the straight 4-inch tubes and, therefore, probably a higher yield and conversion. However, the cost of such a reactor (odd pipe sizes, construction, jacket tube seals, flow arrangements) and the resulting operational problems (seal leakage, catalyst rejuvenation) greatly outweigh the marginal yield increase. If larger tubes are selected for commercial reactors, the yield difference as well approaches zero.

A reactor configuration consisting of two sets of fixed bed reactors, in series, with venting of the product gases between stages was also examined. By delaying the addition of one-half of the urea reactant to the second set of tubes, the ammonium nitrate/urea ratio is maintained at a high level in each tube. This condition favors the production

TABLE 46

COMPARISON OF 2-INCH AND 4-INCH DIAMETER REACTOR TUBES
USING CORRECTED MATHEMATICAL MODEL

| | 2-Inch Reactor | 4-Inch Reactor |
|---|---|---|
| Tube Length | 10 ft | 10 ft |
| Feed rate/tube | 6.6 lb/hr | 25 lb/hr |
| Urea Conversion[1] | 84.6% | 91.2% |
| GN Yield[2] | 93.7% | 89.4% |
| Reactor Product rate/tube | 5.14 lb/hr | 19.6 lb/hr |
| GN in product | 52.0 wt.% | 48.1 wt.% |
| GN producted/tube | 2.1 lb/hr | 7.2 lb/hr |
| Number of tubes required to product 50 lb/hr of GN | 24.1 | 6.95 |
| Average Radial Temperature | 186°C at 12" from entrance. | 183°C at 18" from entrance. |

(1) Based on urea fed.

(2) Based on urea consumed.

of guanidine nitrate in high yields. Results of this simulation with two sets of 10-foot-long tubes in series are shown in Table 47. To serve as a comparison, results are also shown for a single, 20-foot tube with the same total amount of feed. It can be seen that, although the yield is increased by about 14%, the GN production rate remains about the same since the conversion rate is reduced at the higher ammonium nitrate/urea ratio. It may be recalled that the GN yield (based on urea) of 104% is not unreasonable and was demonstrated experimentally in Phase I. An added potential advantage to inter-stage feeding is a reduction in the formation of the insoluble by-product (ammelide). An apparent yield of > 100% is possible due to the calculation procedure used for this parameter.

$$(\text{GN yield} = \left(100 \times \frac{\text{moles GN formed}}{\text{moles U consumed}}\right) \times 2).$$

This reaction assumed that the side reaction of urea hydrolysis is instantaneous and occurs completely. If this reaction is not included in the stoichiometry on which the above calculation is based, the yield is one-half the above results (52% for the case in point). Since, at very high urea conversion (low concentration), it is conceivable that the hydrolysis no longer is complete and since small water evaporation losses are possible, at these extreme cases the apparent yield referred to above can exceed 100%.

An added advantage to feeding the urea to both stages of reactors is that the number of tubes in the second set may be reduced by one-third to take advantage of the reduction in volume of the melt upon reaction. An overall saving of 6% in reactor volume (and, therefore, catalyst charge) is realized for the same GN production rate.

b. Economics of Alterate Reactor Types

Eighteen preliminary cost analyses were performed and reported in the Phase I section. These case studies were designed to show the effect of process variables (e.g., ingredient costs, ingredient feed ratio, product workup, type of reactor) on the mill cost of guanidine nitrate. The costs were based on 20-, 40- and 80-million pound per year plants with the assumptions - in each case - that there was only one (single train) plant. In establishing prices for equipment, standard handbook values were used. Examination of the reported cost data for a stirred tank reactor plant (3 units in series) versus a fixed bed tubular reactor plant (2400, 2-inch-diameter tubes) indicated a 1.4¢/pound mill cost advantage for stirred tank reactors. The plant capital investment for stirred reactors was $1.2 million less than for tubular reactors at 40 million pound per year production rate. Even though the above data favor stirred tank reactors, packed tubular reactors were selected for the pilot plant. The criteria were: safety, design simplicity, and demonstrated performance for tubular reactors.

TABLE 47

COMPARISON OF SINGLE-POINT REACTOR FEED VS INTER-STAGE REACTOR FEED

| | | |
|---|---|---|
| Reactor Design: | Two 10-foot long tubes in series (4-inch diameter) | One 20-foot tube (4-inch diameter) |
| Feed Rate: | (a) 1st Tube: 40.26 lb/hr mixed feed<br>(b) 2nd Tube: 9.75 lb/hr urea | 50.0 lb/hr<br>- |
| Mixed Feed Composition: | AN - 64.6 wt. %<br>U - 24.2 wt. %<br>GN - 11.1 wt. % | AN - 52.0 wt. %<br>U - 39.0 wt. %<br>GN - 9.0 wt. % |
| Urea Conversion:(1) | 70.2% | 81.7% |
| GN Yield:(2) | 104% | 90.0% |
| Reactor Product Rate: | 41.3 lb/hr | 39.1 lb/hr |
| GN in Reactor Product: | 46.0 wt. % | 48.9 wt. % |
| GN production rate: | 14.5 lb/hr | 14.6 lb/hr |

(1) Based on urea fed.

(2) Based on urea consumed.

Hercules utilizes the same preliminary cost analysis technique as used in this program when reviewing new corporate products and processes. Our experience has shown that mill and capital investment costs are within ± 10% and ± 25%, respectively, when compared to actual final values. To arrive at a more realistic equipment cost, a 60% engineering design would be required. This level of design is not normally conducted this early in a development program.

A further analysis of plant capital investment was made during Phase II. Specifically, the effects of multiple train plants on equipment and total capital investments were estimated for both stirred tank and packed tubular reactors. Comparisons were made only at an 80 million pound per year rate. For tubular reactors, both 2-inch and 4-inch diameters were considered, since the initial work reported in Phase I was based on 2-inch-diameter tubes. Extrapolations were based on original estimated equipment costs and cost analysis cases 100, 101, 102, 301, 501 and 710. Equipment costs, other than the tubular reactors, were estimated for production rates other than 40 million pounds per year by using the Williams six-tenths factor, viz.,

$$\left(\frac{C_1}{C_2} = \frac{S_1}{S_2}\right)^{0.6}$$

where $C_1/C_2$ is the ratio of costs $C_1$ and $C_2$ for capacities or sizes $S_1$ and $S_2$, respectively. Costs of tubular reactors were varied linearly with capacity.

Nine new cases are shown in Table 48 for the following major sub-groups:

(1) Single 80 million pounds per year plant for 2-inch and 4-inch-diameter tubes and stirred reactors;
(2) Three separate 28 million pounds per year plants for same reactors as above;
(3) One plant with three trains with capacity of 28 million pounds per year per train.

The data in Table 48 (columns A and B) show that the tubular reactors with 4-inch-diameter tubes have an advantage over reactors with 2-inch-diameter tubes with respect to total plant investment regardless of plant configuration. Also, the economic advantage (Table 48, column B) of stirred tank reactors disappears as the operation is divided into multiple production units. When multi-train plants are considered (a design which offers flexibility of operation and lower loss probabilities),

TABLE 48

EXTRAPOLATION OF PHASE I CAPITAL INVESTMENT COSTS
2- AND 4-INCH TUBULAR REACTORS, MULTI-TRAIN PLANT & REVISED STIRRED TANK REACTOR COST
BASIS: 80 MM LBS GN/YEAR

| Group | Case No. | Type Plant & Capacity | Reactor System | A - Extrapolation of Phase I Costs (Reference 40 MM lbs/Yr)(1) Equipment Cost ($MM) Reactor | Other | Total | Plant Investment ($MM) | B - Plant [illegible]ent(2) Based on Revised Stirred Tank Reactor Cost ($MM) |
|---|---|---|---|---|---|---|---|---|
| I | K-1 | One plant Single Train 80 MM lbs/yr | 2" Tubes (4800) | 0.76 | 0.69 | 1.45 | 6.9 | 6.9 |
| | K-4 | " | 4" Tubes (1200) | 0.50 | 0.69 | 1.19 | 5.8 | 5.8 |
| | K-6 | " | 3 Stirred Tanks | 0.11 | 0.69 | 0.80 | 4.2 | 5.3 |
| II | K-3 | Three plants Single Train 28 MM lbs/yr | 2" Tubes (4800) | 0.80 | 1.15 | 1.95 | 10.8 | 10.8 |
| | K-5 | " | 4" Tubes (1200) | 0.48 | 1.15 | 1.62 | 9.6 | 9.6 |
| | K-7 | " | 3 Stirred Tanks | 0.17 | 1.15 | 1.32 | 8.4 | 10.2 |
| III | K-8 | One plant, three trains 28 MM lbs/yr | 2" Tubes (1600) | 0.80 | 1.15 | 1.95 | 8.9 | 8.9 |
| | K-9 | " | 4" Tubes (400) | 0.48 | 1.15 | 1.62 | 7.5 | 7.5 |
| | K-10 | " | 3 Stirred Tanks | 0.17 | 1.15 | 1.32 | 6.3 | 8.1 |

(1) Reference Case 100 and equipment costs in Appendix of March 1971 Guanidine Nitrate Report. Equipment cost scaled by 0.6 factor except for tubular reactors which was linear extrapolation.

(2) Stirred tank reactor for 40 MM lb GN/year adjusted from $25,000 to $80,000/reactor.

Note: Following conditions assumed constant: 1-hour residence time, zero by-product credit, 4¢/lb urea, AN/U = 1/1, aqueous workup.

the plant with stirred reactors has a higher capital cost than one with tubular reactors with 4-inch-diameter tubes. In addition, safety predictions are much more reliable for tubular reactors than for stirred tank reactors.

The tubular reactor costs employed in the original work were based on standard tube and shell designs and appear to be realistic. As noted previously, there appeared to be a plant capital investment advantage for stirred tank reactors. Since the original stirred tank reactor costs were based on standard reference data for stirred tanks, a second look or reevaluation of the reactor costs was undertaken. In Phase I, stirred tank reactors were estimated at $25,000 each (2500 gallons each) for a 40 million pounds per year plant (single train, 3 stirred tanks in series). A new stirred tank reactor estimate was made based on the following conditions:

1. Design Volume: 2500 gallons
2. Vessel: Closed top pressure vessel with capability to support catalyst basket and drive system.
3. Jacket: Capable of operating at $>$ 300 psig.
4. Catalyst: Rotating basket containing approximately 2 tons of catalyst.
5. Material of Construction: 304 stainless steel vessel, carbon steel jacket.
6. Drive: Capable of rotating basket containing 2 tons of catalyst and 4 tons of reactant at 50-100 rpm against baffle arrangements designed to effect liquid pumping.

Based on the purchase of similar reactors for a Hercules commercial operation (without rotating catalyst basket) in 1968 and adjusted to 1971 basis, it was estimated that this type of reactor would cost about $60,000 compared with the original estimate of $25,000. The added cost is due primarily to the agitation system, baffle design, high pressure operation and weight support requirements.

The above estimate assumes that the required endothermic heat of reaction is supplied via the reactor jacket. Calculations have shown that the heat transfer surface area available for three 2500-gallon reactors is about 650 square feet whereas tubular reactors

(600 tubes, 4 inch x 10 foot tubes) for the same GN production rate have a total heat transfer area of about 6300 square feet. Assuming that the heat transfer coefficient for a stirred reactor is 2 to 3 times that for a tubular reactor, the stirred tank reactor system is still deficient by about 3000-4000 square feet of heating surface. Installation of internal coils would be difficult. Use of an external heating system with a 1000 square foot heat exchanger and a high capacity circulating pump per reactor was assumed. The heat exchanger cost was estimated at $15,000 ($15/square foot) and pump estimated at $5000. When these units are added to the above basic costs, a more realistic total reactor cost is obtained - $80,000.

The plant investments for the conditions in Table 48 as noted above were revised on the basis of the new estimate of $80,000 for a 2500-gallon stirred tank reactor (40 million pounds per year basis). The modified capital investments are shown in column B of Table 48. These data show that the capital cost difference between the two reactor systems has decreased considerably, particularly for multi-train plant systems. If the ± 25% estimating accuracy is taken into consideration, then there is essentially no difference in costs between the two reactor systems.

c. Predicted Safety of Tubular and Stirred Tank Reactors

As noted in the Hazards Analysis Section, 2-inch-diameter, 12-foot-tall packed tubular reactors with reaction melt at ca. 200°C did not transit to a propagation as a result of bottom ignition. Therefore, tubular reactors of this configuration were considered to be intrinsically safe.

The reaction mixer (AN/U/Silica Gel) contained in Schedule 40 pipes for transition tests were at reaction temperature, but there was not physically induced agitation of the material. Thus, the transition data were not directly applicable to stirred tank reactor designs. One of the major differences between stirred and static reactors is that in a stirred reactor a point source flame probably would be dispersed readily throughout the reactor. This could, in effect, amplify transition from flame ignition to propagation. Another factor when comparing the two types of reactors is the potential sources of ignition. Both systems have common sources of potential ignition such as undetected feed impurities, adiabatic gas compression, and gas cavitation. Because of its inherent design, a stirred reactor has added potential ignition sources; e.g., friction from agitator seal, impact of rotating basket against the reactor wall, thermowells, and/or baffles, failure of shaft retention systems, and subsequent dropping of catalyst basket, motion of foreign materials accidentally dropped into the reactor.

Considerable thought was given to the extrapolation of transition data for stirred tank reactors. It would be necessary to test an actual model of the reactor complete with catalyst basket, drive system and heating capabilities. Because of the predicted diameters of stirred reactors (approximately 5 to 7-1/2 feet which would cover single or multi-train production plants), it would be necessary to perform transition tests at a 3-4 foot diameter. The quantity of AN/U/GN (~ 2000 pound) that would be contained in a stirred t .k test vehicle is large enough to necessitate testing in a remote area. The cost of the power and heat source lines alone would itself represent a large investment. Since transition testing of stirred tank reaction could not be accomplished in the present program, and since the reaction kinetics had been demonstrated in tubular reactors and tubular reactors have a great advantage in design simplicity, the decision was made to proceed to the pilot plant with packed tubular reactors.

## C. PHASE III, PART 1 - GUANIDINE NITRATE PILOT PLANT CONSTRUCTION AND OPERATION

### 1. Summary

Phase III of this contract consisted of the following tasks:

(a) Procure Pilot Plant equipment.

(b) Expand Phase III design into specific piping and lay-out sketches.

(c) Construct Pilot Plant.

(d) Operate Pilot Plant for:

(1) Start-up

(2) Process variable studies

(3) Process upset run

(4) Production run

(e) Perform parallel laboratory studies to demonstrate satisfactory guanidine nitrate conversion to nitro-guanidine.

(f) Determine specifications for guanidine nitrate product.

The above seven tasks were to be completed in an 11-month time frame which meant that the execution of the first three tasks must be well coordinated (six months) in order to complete the remaining tasks in the desired time frame.

Five of the above tasks were completed as programmed within the Phase III time period. The pilot plant operation task was not completed because of chemical process development problems. The parallel laboratory conversion step was not completed since it was to parallel the latter part of the operation task. A similar step, however, was completed at Cyanamid of Canada (nitroguanidine manufacturing facility) with guanidine nitrate made in the Kenvil pilot plant.

As noted above, the four-part pilot plant operation phase was not completed. The start-up of the pilot plant portion of this task required a longer time than expected but was accomplished after problems typical of new operations had been resolved. It was found that successful operation of the pilot plant necessitated a seven-day per week continuous mode of operation. The longer period required for start up was due mainly to the recurrence of problems in the original five-day operation schedule.

The Process Variable Study and Process Upset Runs were envisioned to be perturbations of variables from a smooth steady state operation. Because of the time limitations imposed by the longer start-up and the catalyst failures, these studies were completed on a more random basis during periods of equipment failures or during production attempts. The data available from the five-month operation period covered a host of operating parameters across all of the equipment in the pilot plant except the guanidine nitrate dryer. Separate runs were made later in alternate dryer units to provide design data for this unit operation.

The production step in the operation task was not completed because of catalyst problems. Only about 2,000 pounds of guanidine nitrate were made in the pilot plant operation. This material had a nominal purity of 96+% GN. The program objective was to make 40,500 pounds of material for conversion to nitroguanidine at Cyanamid of Canada facilities. Two production attempts were made, but in both cases, a decrease in reactor productivity occurred. The contributors to this productivity decline were catalyst attrition (leading to loss of flow) and catalyst chemical poisoning.

To ascertain what was poisoning the catalyst, the emphasis of the pilot plant operation was changed from production to a set of carefully controlled research experiments on catalyst life. The program suggested for the pilot plant to best aid in defining the source of the catalyst activity loss was to conduct, under carefully controlled conditions, a series of single-tube continuous runs at mild reaction conditions (180°C, 2/1 AN/U molar ratio) so that the formation of ammelide by-product would be minimized and the catalyst would not be shocked initially. Three runs, made to examine three different types of silica gel-type catalyst, were deemed necessary. Single tube runs were selected to eliminate flow distribution problem between reactors and to minimize batch steps, thereby allowing operators to concentrate on the reaction step. Three catalysts were selected for investigation (Houdry CP-532 Macroporous Silica Beads, Mobil Sorbeads R, and Davidson Grace 59 Silica Gel). Three single-tube runs were initiated and completed successfully. In all three cases, the catalyst activity decreased, confirming that there was a catalyst poisoning problem. A program extension was recommended to explore this problem, it was implemented and is the subject of the next section (Phase II - Part 2, Resolution of Catalyst Poisoning Problem).

Although the pilot plant operation was not completed as proposed, major progress was made in the development of the U/AN process for manufacture of guanidine nitrate. Among the accomplishments were the following.

(1) The U/AN process does indeed make GN of a high purity.

(2) The workup of the product melt (quench, insolubles separation, crystallization, centrifugation and drying) is very efficient in that it cleanses the product

of its operational history; that is, the operation of the plant reactors does not significantly affect the end product because the workup system controls the ultimate product purity.

(c Once the plant is operating, operation continues smoothly.

(d) Thermal cycling of the catalyst bed along with improper draining and/or semicontinuous flow through the bed are undesirable and will lead to catalyst attrition and ultimately will force a shutdown because of loss of flow through the tubes.

(e) The catalyst beds, if allowed to break down as noted above, become very hard to drain and, on cooling, become a solid mass which cannot be easily dumped. It was found that tubes in this condition can, however, be cleaned by use of a high-pressure water jet.

(f) All of the process equipment selected for the pilot plant, except for the reactors and dryer, operated as designed. The non-performance of the reactors was due to failure of the catalyst. The operation of the dryer was not optimized because of limited guanidine nitrate production.

(g) Fifty pounds of typical U/AN process guanidine nitrate of high quality was shipped to Cyanamid of Canada where it was subsequently converted in the laboratory to nitroguanidine (NQ) comparable to normal production NQ.

## 2. Procurement and Detailed Equipment Design

The sequence of events in Phase III was extremely important because of the tight target time schedule. There were a number of activities required prior to equipment ordering, and planning was necessary to compensate for variable delivery times. Table 49 shows the sequence of activities for both the major and the auxiliary equipment. The major equipment had to be phased into the ordering program first because of the necessary government approvals and also because most of these items were long delivery items (6 to 12 weeks). The minor equipment design and specifications were scheduled to fill in the time slots available in the major equipment delivery periods. These items (e.g., piping and fittings, rotameters, etc.) were generally stock delivery items and, being low cost items, required only a general approval to purchase. The major equipment items each required specific approvals. The Defense Industrial Equipment Center (DIPEC) search and DCAS approvals in Table 49 refer to contract requirements. The former requirement is that any major equipment item with a value > $1000 must be screened through the DIPEC to ensure that a comparable unit is not available in government used-equipment storage. This search generally required a lead time of 4 to 6 weeks. The purpose of the latter requirement (DCAS Approval) prior to purchase was to demonstrate to the administrative contracting officer (ACO) that the purchased items were compatible with the contract and to demonstrate that standard purchasing practices (e.g. multiple quotes) were employed.

One event that occurred parallel to the major equipment quotations is not noted in Table 49. This activity was a search through the Hercules Incorporated Investment Recovery and the Kenvil Plant equipment files for available surplus equipment. Details of some of the activities referred to in Table 49 follow:

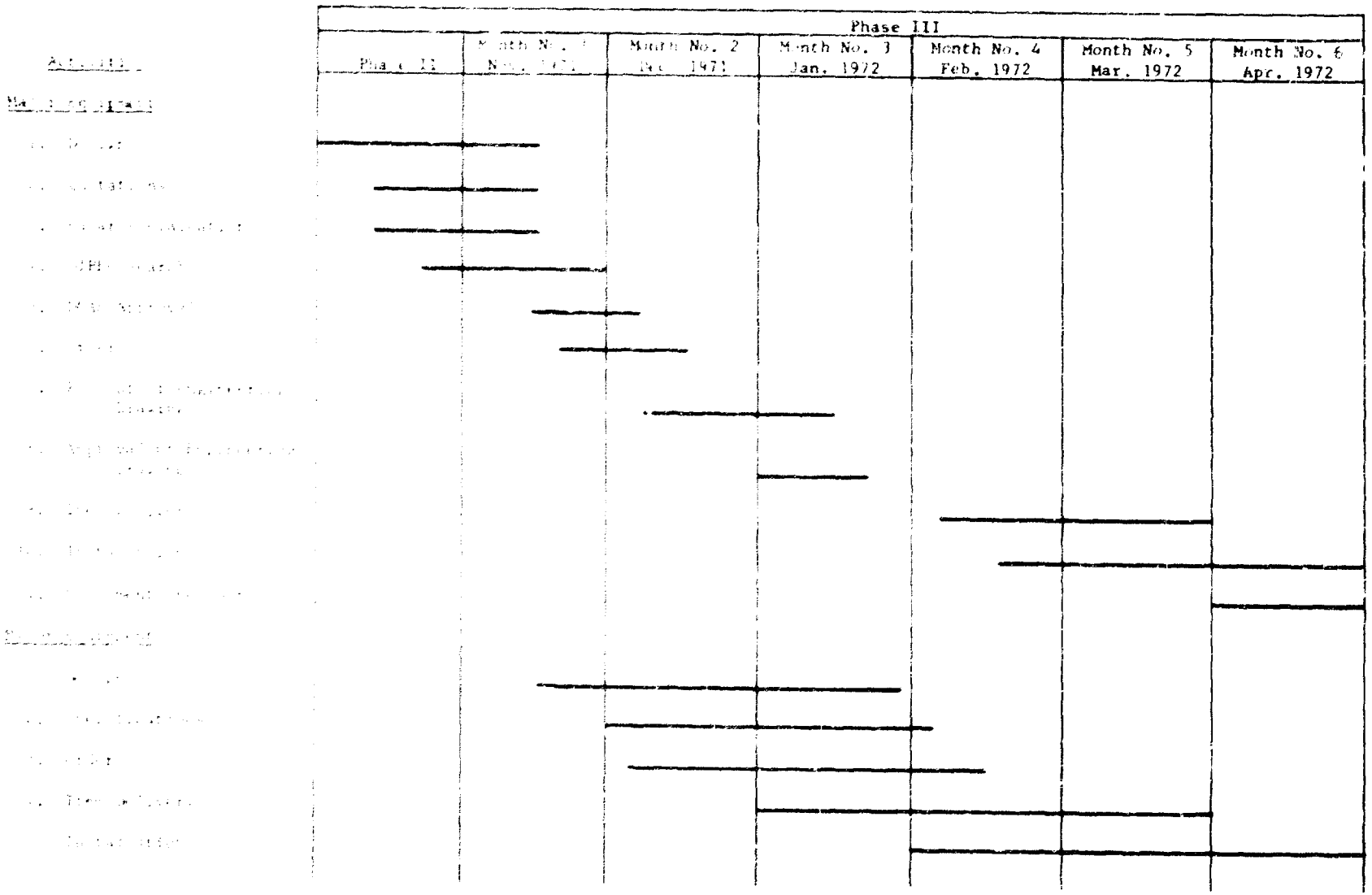
### a. Equipment Ordering, Drawing Approval, and Deliveries

All of the major equipment items, exclusive of the reactors, were placed on order within the first month of Phase III. Since much of the equipment was custom designed and had to be inspected for compliance with Hercules' standards, engineering drawings were requested for Hercules approval prior to fabrication. The following equipment items were subjected to the drawing approval step:

(1) GN Batch Centrifuge (22-in. Delaval Mark III)
(2) Swenson Batch/Continuous Crystallizer (A-500)
(3) Strong-Scott Dryer (8-in. Solidaire) (A-700)
(4) Whitlock Falling Film Evaporator (A-800)
(5) Seven Stainless Steel tanks (T100, 101, 102, 103, 104, 105, 106, 107)
(6) Reactor Assemblies (R-200 - R-207)
(7) Hills-McCanna Feed Blend Pump (P-101)
(8) Interstage Feed Tank (T-114)

TABLE 49

PHASE III - SEQUENCE OF PILOT PLANT EQUIPMENT
PROCUREMENT AND INSTALLATION ACTIVITIES



Some of the more pertinent design changes and/or comments, relative to a typical piece of equipment, are outlined below.

The 22-in. Mark III Centrifugal is a batch centrifuge driven with a hydraulic motor. The cake plow (operable only at low speed) is also operated hydraulically. In the latter case, the plow has a positive stop that prevents contact of the plow with the screen and/or basket. Vibration of the basket (as a result of uneven loading) is transmitted to the curb (housing) which in turn transmits any motion to an external link suspension system. The annulus between the basket bottom discharge and the filtrate curb baffle is approximately 1-1/2-in. wide. The vendor representative assured us that the link suspension system would limit lateral movement of the basket to about ±.010-in., thus eliminating the need for plastic bumpers, etc.

As a result of the drawing review, the following changes and/or additions were imposed:

(1) Addition of curb inspection door.
(2) Installation of interlocking device to prevent access to the centrifuge interior while in motion.
(3) Positive locking of all internal bolts and nuts.
(4) Substitution of stainless steel with Teflon-filled asbestos for lubrication of the oil seal backup plate.
(5) Supply centrifuge with installed cloth.

These changes were believed necessary after reviews with DeLaval engineers and with Hercules' safety and engineering personnel. Modified centrifuge drawings were received 1 month after these changes were imposed. The modified changes reflected the requested changes and a slight cost impact.

A similar exercise, as noted in the centrifuge discussion in the preceding paragraph, was conducted for all the equipment with approval drawings. Details of changes on these other items are documented in monthly reports.

As might be expected with the volume of equipment ordered, shipment date problems developed for a few items, viz., the Hills-McCanna three-headed blend pump, the evaporator, and three of the Goulds pumps. In an attempt to resolve the delivery problems, contact was made with the appropriate DCASD industrial specialist and Hercules' Expert Purchasing Department personnel. The result was a reduction in the delivery delay of one week for the Hills-McCanna pump, 2-1/2 weeks for the evaporator, and 1 to 3 weeks for the Goulds pump. All of the necessary equipment was on hand within two weeks of the proposed schedule. This two-week period was made up during the installation period, by overtime and overlap of equipment loading and troubleshooting during the latter stages of installation.

b. Additional Equipment Design

1 Selection of Alternate System Pumps

Hazards analysis showed that some of the initially specified process pumps presented problem areas in terms of possible initiation sources. The rotating seal face at a pump speed of 3600 rpm generates sufficient frictional energy to create a condition of a zero safety margin. The hazards analysis recommended a reduction of the pump speed to $\leq$ 2800 rpm to achieve an adequate safety margin.

The pumps previously specified were small Eco 1 x 3/4 stainless steel end suction centrifugal pumps with a 3-3/4-in. fully open impeller and mechanical seals. These pumps are rated at 10 gallons per minute at a net output head of 60 feet. In this line of pumps, the motor speeds offered are 1750 and 3450 rpm. The use of the lower speed results in an adequate safety margin in terms of hazards,but the resultant pump head drops to less than 30 feet. Since the head requirements for the reactor and evaporator feed pumps are very close to this value, utilization of the Eco 1 in. x 3/4 in. x 3 3/4 in. pump at 1750 rpm for these uses would offer no design capacity factor. Therefore, the pump specifications were changed. The new specifications are discussed below:

a Reactor Feed Pump - (P-102)

A Goulds 3196, 1 x 1-1/2 end suction AVS pump with an 8-in. impeller and with a jacketed stuffing box was selected for feeding the reactors. It is nominally rated at 20-30 gpm with an output head of 60 feet. The design of the casing was such that it can be easily traced. This pump is an industrial type that is suitable for long continuous service. Because of the location of this pump in the system, it is necessary that an extremely reliable and flexible pump be selected. Speed of this pump is 1750 rpm.

b Evaporator Feed Pump - (P-109)

The solution to be transferred by this pump is a 50% water solution containing dissolved urea, ammonium nitrate and UO$_2$ at ambient temperatures. The hazards analysis friction data which were applied to this pump in determining its safety margin were the same data for a no-water condition at an elevated temperature. It was concluded that the safety margin for this area was very conservative. Because of the need for a high head on this pump and its relatively mild service requirements, a 3500 rpm pump could be employed. The necessary backup frictional data for this stream at its expected temperature and composition were obtained to confirm that an adequate safety margin does exist. A Goulds 3196 pump was also selected for this application.

c Melt Transfer Pump (P-100); Aqueous Quench Transfer Pump (P-104); Crystallizer Feed Pump (P-106); Centrifuge Filtrate Transfer Pump (P-108)

Goulds pumps, similar to those above but at a slower speed (1750 rpm) and with conventional Teflon packing were selected for these applications. These pumps are more rugged than the previously selected ECO pumps and are also compatible with the reactor feed and evaporator feed pumps.

2 Vacuum System

The guanidine nitrate crystallization system depicted in an initial pilot plant process flow sheet incorporated a water eductor system for vacuum. This system required a continuous flow (350 gpm) of water through an eductor coupled with a cooling system (water chiller and heat exchanger) to reach the desired jet temperature (35°F) which at the above flow would result in the necessary vacuum in the crystallizer. A storage tank was also required for the eductor water. The total vacuum system was expensive and made an in-process water balance difficult.

Two Stokes 40-cfm Microvac Mechanical vacuum pumps (Model 148-H) were substituted for the eductor system. These pumps, complete with traps and piping, were available on the plant site, and permission was granted for their use. Use of high-capacity vacuum pumps simplifies measurement of condensed water from the crystallizer; using the existing equipment resulted in a net savings of about $7890.

3 Hot Water

Hot water is required to control the temperatures in both the aqueous quench and crystallizer feed tanks. It had originally been planned to use steam-water mixers, but it was believed that they would have required too much operator attention. A tempered water system (55 gallon drum, temperature controller, circulating pump, etc.) was substituted for the individual mixers.

4 Reactor Feed

The initial reactor feed system included a level control unit as a surge tank for recirculation of feed from the densitometer. It was decided that it would not be a good policy to operate the feed pump (particularly a Gould 3500 rpm pump) without a recirculating loop. Since the previously selected LC-2 unit (a Fisher Level-trol) had a free volume of only one-half gallon, it was elected to replace it with a 15-20 gallon jacketed tank equipped with a separate float level controller. The new tank designation was T-113 with a corresponding level controller designation of LC-113.

5. Inter-Stage Feed

The pilot plant had been designated for flexibility. One option was to operate the two sets of reactors (four reactors per set) in series with inter-stage feeding of fresh urea. The original inter-stage feed design was based on a Fisher Leveltrol unit coupled with a centrifugal pump. Since centrifugal pumps were presenting a problem with respect to Hazards Analysis, the system was redesigned to utilize a low-velocity Hills-McCanna positive displacement pump (new designation - P-114). The Fisher Leveltrol unit (LC-3) was replaced with a 15-gallon jacketed tank (T-114), and a level indicator (LI-114). Urea would be pumped directly to T-114 and mixed with the reactor product.

c. Utilization of Used Equipment

As noted above, the major equipment items costing more than $1000 were screened through the government's DIPEC system prior to purchase approval. These searches resulted in two equipment offers: a substitute solid-bowl centrifuge and a substitute Strong-Scott Solidaire dryer. The former item was rejected because it was too small in capacity (1/10 that desired) and the latter item was rejected because it was oversized (6 to 8 times the desired capacity). Use of the oversized dryer would have created floor space problems, and it would have resulted in a higher Class 7 material holdup.

The files of the Hercules Corporate Investment Recovery Group were examined for potential excess equipment that could be used in the pilot plant. No suitable items were found.

Circular chart recorders for reduced pressure and temperature applications plus a 24-point temperature recorder were obtained from the Hercules/Kenvil, New Jersey, excess property inventory, as well as the vacuum pumps and hot water system discussed above.

3. Construction

The construction of the pilot plant consisted of five major areas of activities. These areas overlapped both in function and construction time periods. These activities will be discussed in the following sequence.

(a) Utilities Preparation
(b) Building Modifications
(c) Safety Requirements
(d) Equipment Stands and Piping Sketches
(e) Equipment Installation

Figures II-1 through II-11 in Appendix II show photographs of the equipment and the buildings during the construction phase.

a. Utilities Preparation

1 Electric Substation

Since the power requirements for the guanidine nitrate pilot plant exceeded the available electrical service to the Building 2204 area, a 300 KVA electric substation (34,000/400 volt system) was designed and installed at the site. The services of the corporated Engineering Department were used for the design and preparation of material lists. In addition to the substation, electric layouts and equipment requirements for the utilities (vacuum, steam boilers, chiller, etc.) and the process equipment were determined. The substation site was subsequently defined, the area was graded, footings and electrical ground system were installed, and a confinement fence was built. A subcontract was granted for the electrical installation of the substation. The installation of the substation and its low voltage switchgear was completed in the desired time frame. (See Figure II-1.)

2 Utility House

Permission was obtained from plant management personnel to utilize an existing 20 ft x 20 ft x 8 ft eave height metal building to house utilities. The building (No. 2260) was relocated to the Building 2204 area. The location of the utility shed was positioned so that the quantity-distance requirements of an existing propellant manufacturing facility were not affected.

The sequence of events in preparing this building for use was as follows: installation of underground water and electrical lines, pouring of a concrete pad, movement of the metal building to the site and its construction, installation of lights and heat, equipment placement, and equipment installation.

All of these events were completed in the desired time frame. (The utility shed is shown in Figure II-1 directly behind the electrical substation).

3 Off-Gas Collection

Ammonia and carbon dioxide gases from the reactors are passed through a water scrubber. Ammonia is absorbed in the water, and carbon dioxide (metered) is vented to the atmosphere above the building. The ammonia water (ca. 15-20% by weight $NH_3$) is stored and periodically disposed of by ground spraying. Permission was granted by plant management to utilize an

existing excess 20,000-gallon tank for storage of the ammonia water. The tank was located outside of the barricade and was installed for temporary service. This method of disposal is in accordance with ecology practices.

This 20,000-gallon storage tank was moved to its selected location, and its piping was completed early in Phase III. (This tank is shown in Figure II-1 on extreme right of photograph.)

### 4 Waste Water Collections

In-process chemical spills, samples, excess chemicals, etc., are normally disposed of by burning at the plant's burning ground. There are, on occasion, spills which inadvertently end up in the floor drain. It is also necessary to water-wash equipment and floors. In such instances, chemicals are collected for eventual disposal. A waste collection system has been designed to conform to DOD 4145.26M requirements. A standard concrete septic tank was selected for the collection of all process building waste waters. It is located outside of the barricade and connected to the process building floor drain. Its overflow free drains to a large open field. Since all the expected waste waters are soluble nitrates, this disposal method satisfies pollution and ecology standards.

### 5 Air, Water, and Auxiliary Steam Systems

Air is supplied to the pilot plant from the Kenvil plant's air supply. An air distribution system was set up in the process building to feed the process instruments and to blow out the lines. A large air reservoir tank was also installed outside of the building as a backup air supply. Water for the process is obtained from the Kenvil well system. Water manifolds were installed in each room of Building 2204 to supply water to the quench, off-gas, and wash systems.

An auxiliary steam system was installed in the process building to supply heat to the low temperature operations (melters, dryer, tracings, tempered water, etc.) and for building heat. The auxiliary steam was also used to back up the pilot plant reactor boilers (to prevent reactors freezeup if these boilers fail) and to serve as the source of steam for line blowouts. Fifty psig steam was regulated to the building.

### 6 Vacuum System

As noted in a previous section, vacuum for the crystallizer was supplied by a pair of mechanical vacuum pumps. These were installed in the utility shed, early in Phase III.

### 7 Brine System

Brine for the crystallizer overhead condenser (E-111) is supplied by an Edwards Eng. CC10A water chiller. This unit was installed in the utility shed early in Phase III. Lines were installed from this unit to the process building through the barricade. The condenser to which this brine is fed was located in the main room of the process building.

### 8 Pilot Plant Steam Boilers

The main electrical load and utility required by the pilot plant was for the steam boilers. These units were received and installed in the utility shed in the latter part of the construction time period. Feedwater for the boilers was drawn from the well system. Steam lines had to be constructed to extend the distance of 150 ft between the utility shed and the rear of Building 2204 (where the regulators were located). These lines had to be also supported and covered with lagging. (Figure II-2 in the Appendix shows a photograph of the installed boilers in the utility shed.)

## b. Building Modifications

The building selected for the pilot plant was deficient in floorspace for the conceived process equipment. An equipment layout was conducted during Phase II to define the extent of the required building expansion that was needed. (Figure 53 shows this layout.) As a result of the layout and the actual equipment space requirements, Building 2204 was remodified in the following ways:

(1) The front wall of the building was moved out about 8 ft to the edge of the existing porch, and enclosed. This resulted in approximately a 30% increase in floor space for process equipment and electric switch gear.

(2) The process building was also modified by an addition of a roof cupola over the crystallizer. This provided sufficient room below this unit to allow removal of the bottom-entering agitator.

(3) An instrument panel was installed in the front wall of the process building and an instrument shed (4 ft x 4 ft x 8 ft high) added to the exterior front of the building to provide rear access to the instruments for maintenance.

(4) The building ventilation system, safety sprinkler systems, and lighting systems also had to be modified to provide these services to the expanded portions of the building.

c. Safety Requirements

The pilot plant equipment and auxiliaries were designed in accordance with the following standards:

(a) Government Pre-Award Safety Audit
(b) DOD Contractors Safety Manual (DOD 4145-26M)
(c) Hercules Safety and Engineering Standards

The Pre-Award Safety Audit required three modifications in the proposed process building. One of the modifications requested was to increase the floor space of the process building. As noted in the previous section, an equipment layout was performed to determine the extent of this modification. The resultant building expansion was then implemented. The other two deficiencies pointed out dealt with the absence of an approved lightning protection system and the presence of overhead electrical lines within 50 ft of the process building. In Phase II, both of these deficiencies were corrected. A single pole lightning protection system was installed in compliance with section 8.12 of AMCR 385-100. The overhead electrical lines were removed and replaced with underground service from the new substation.

The DOD Contractors Safety Manual was reviewed, and the facilities were designed to conform with this document. The important requirements of this manual deal with the quantity-distance requirements and waste disposal provisions. To satisfy the former, it was necessary to construct a barricade between the utility house (Building 2260) and the process building (2204). To satisfy the latter, a waste water pump tank and an ammonia-water tank were installed as noted in a prior section.

d. Equipment Stands and Piping Sketches

Detailed equipment placement and process piping drawings were prepared. Isometric drawings were constructed from the building layout (Figure 53) and from the equipment engineering drawings. These additional piping drawings helped itemize and expedite the equipment/piping procurement and installation. It should be noted that these layout-piping sketches were for in-house use only and are not included in this report.

A number of the equipment items required stands and platforms before their placement in the process building. These stands were designed, built, and installed before receipt of the functional equipment. Among the process items requiring stands were the recycle feed makeup tank (T-102), the feed table containing the densitometer and blending feed tank (T-113), the reactors, the crystallizer (A-500), the solid bowl centrifuge (S-300), the GN centrifuge (S-600), the evaporator (A-800) and the dryer-feeder (H-701). In Figures II-3 to II-11 in the Appendix, the resultant equipment supports can be seen.

e. Equipment Installation

After the major process equipment items had been received, the following steps were taken:

(1) The equipment was positioned by fastening to the floor or to a stand.

(2) The equipment was electrically installed and grounded (for static electricity protection).

(3) Inlet and outlet piping was installed.

(4) Instrumentation was installed.

The piping in many cases required steam tracing and insulation. After the above steps were completed, the equipment items were checked for mechanical and electrical performance, cleaned internally and then calibrated. The cleaning step was necessary to insure that foreign contaminants were absent. The calibration steps involved defining operating levels in the tanks, defining line pressure drops for the pumps, etc., so that normal operating performance of the equipment was established.

Ammonium nitrate and urea were not admitted to the pilot plant during this period. Upon completion of the electric substation and wiring hookup of all electrical equipment, captive electric power was turned into the area. Subsequently, all pumps, agitators, etc., were checked for proper rotation and current draw. In some cases, it was necessary to repack and/or align the pumps.

Process equipment and associated piping were thoroughly cleaned with a hot aqueous detergent solution. The equipment was subsequently washed with clear water and then dried by a combination of heat (via steam jackets and tracers) and air purging. This water cleanout operation also served as an opportunity to check controllers, automatic valves, and pump performances and to spot gross leaks.

All of the above procedures were completed within the desired six-month setup and "debugging" time schedule.

## 4. Pilot Plant Start-up

### a. Preparation

Before the pilot plant was started up, a number of activities had to be completed in the areas of training, procedures, and equipment understanding. Among these activities were the following:

(1) Equipment calibration and definition

(2) Checkout of laboratory analytical methods

(3) Preparation of specific operating procedures

(4) Operator training

(5) Safety Review

Also in this period, the first shipments of chemicals to be used in the process were received and the reactors were charged with catalyst.

#### 1 Equipment Calibration and Definition

As noted in the previous section, during the last month of the equipment installation, some of the equipment (e.g., tanks, pumps) were calibrated during the cleaning process. In addition to this effort, each piece of utility equipment was given a preliminary checkout for functionality. For reference, the equipment items included the brine chiller, the vacuum pumps, the high-pressure electric steam boilers, and the tempered water system. No serious problems were encountered.

Specific gravity data were determined for various combinations of AN/U/GN at elevated temperatures. The resulting data were utilized for start-up of the in-line densitometer. These data plus known AN-water density data were used in calibrating this unit.

The calibration was followed by a similar determination of the feed flow-rate of the control system and control settings. A 50% AN in water solution was used for this calibration.

#### 2 Checkout of Analytical Methods

It was projected that during the pilot plant operation, eight types of samples would routinely be analyzed to determine process performance and control. Table 50 lists the eight samples and the requested

TABLE 50

ANALYTICAL SCHEDULE FOR GN PILOT PLANT
USING THE U/AN PROCESS

| Type Sample | Designation | % Urea | % AN | % GN | % $H_2O$ | % T.S.* | % $H_2O$ Insol.** | % Ash |
|---|---|---|---|---|---|---|---|---|
| Reactor Feed | 1S- | x | x | x | x | - | - | - |
| Reactor Product | 2S- | x | x | x | x | - | x | - |
| Solid Bowl Centrifuge Product | 3S- | x | x | x | - | x | x | x |
| Crystallizer Feed | 4S- | x | x | x | - | x | - | - |
| Wet GN From Centrifuge | 5S- | x | x | x | - | x | x | - |
| Dry GN | 6S- | x | x | x | x | x | x | x |
| Evaporator Feed | 7S- | x | x | x | - | x | - | - |
| Evaporator Bottoms | 8S- | x | x | x | x | - | - | - |

---

*T.S. = Total Solids.

**$H_2O$ Insol. = Water Insolubles.

analysis required per sample. The frequency of the sampling was variable during the different tasks of Phase III. The most frequent sample type analyzed was the reactor product.

In Table 50, the methods referenced that were used for determining the urea, ammonium nitrate, and guanidine nitrate contents were the same used in Phase I. These methods are discussed in a previous section of the report. The water content is determined by the standard Karl Fischer analysis. Total solids is measured by drying the samples of water. The percentage of water insolubles is obtained by dissolving the sample in water, filtering this solution, and then weighing the insolubles. The ash content is found by the standard method of burning off the combustibles in a muffle furnace and then obtaining the weight of the residue.

### 3 Operating Procedures

Prior to starting up the pilot plant, detailed operating procedures were written for each unit operation. The bases for these procedures were the operating methods presented in the Phase II section, the specific equipment operating instructions, and Hercules Safety and Standards regulations. These procedures were revised as necessary during the operation, as operating experience was gained. The purpose of the specific operating procedures was to provide the operators of the plant with a rule-book and guideline to use as they are operating the plant. They are specific to the pilot plant and not of general use and are not contained in this report.

### 4 Operator Training

Before the pilot plant was started up, the assembly of technicians, whose responsibility it was to operate this plant, were trained. This training was accomplished by use of the specific operating procedures, group meetings, and on-the-job training. The latter was achieved during the equipment cleaning and calibration stages and by working with the process engineers during the early start-up phases. By the end of the operating period, a few of these technicians had qualified as shift leaders. This is significant when the complexity of the intertwined multiple unit operations is realized.

### 5 Safety Review

Also before the pilot plant was started up, the process and its planned operation had to be reviewed with corporate safety officers to show that it was consistent with Hercules safety and government safety regulations. These reviews were accomplished with only minor process modifications.

On-site inspections and safety reviews were conducted by Hercules Industrial Systems Division personnel; namely, Mr. R. C. Tucker, Director of Operations; Mr. J. A. Ruth, Manager of Process Engineering; and Dr. R. S. Voris, Manager of Research. Subsequently, a formal design review was held at Hercules/Kenvil with emphasis on equipment and building design, operating procedures, and waste disposal, as related to Hercules Chemical Propulsion Standards and Hercules Major Facility Project Management System. The following corporate groups were represented at this meeting: Safety, Engineering, Departmental Research, Research Center, and Allegany Ballistics Laboratory. Authorization was granted to introduce ammonium nitrate and urea into the system.

The first shipments of chemicals being used in the pilot plant were received during the last month of the construction phase. Tables 51, 52, 53, and 54 contain the pertinent specifications of the ammonium nitrate prills, urea, and Houdry Silica Bead catalyst.

Uncoated, additive-free ammonium nitrate prills were ordered. In Table 51 it can be seen that the only trace impurities that the AN contained were ~ 0.34% of salt additives. These salts are added to the ammonium nitrate as crystal habit modifiers. These salts or substitutes are contained in several commercial grades of AN to prevent prill breakage. Reagent grade or solutions of AN are minus these components but were not sufficiently compatible in price or process for use in the pilot plant. Phase I runs indicated no reaction conversion penalties due to use of commercial grades of AN. (Note: it was found later in this portion of the program that these salts are indeed harmful to the catalyst and that only reagent grade AN could be used.)

Table 52 shows the specifications for the commercial grades of urea used in the pilot plant. The major variable specifications in commercial grades of urea are the biuret content and the nitrogen content. Since biuret is believed to be consumed in the U/AN process as a reagent, the U/AN urea specification was based on the nitrogen content requirement. Again for the pilot plant, uncoated prills were requested so that a filtering step to remove these coatings was not a pilot plant requirement. Phase I runs showed no deleterious effects of using commercial grades of urea.

A 1000-lb shipment of Houdry Silica Beads (catalyst) was received. At the request of Hercules/Kenvil, Air Products and Chemicals, Inc., forwarded a screen analysis and crushing data for this material. A comparison was also made to similar material purchased during Phase I of the program. The Air Products and Chemicals, Inc. letter is presented in Table 54. The Houdry Silica Bead properties are shown in Table 53. After the reactor had been cleaned and dried, the top elbows were removed for catalyst charging. Since there was concern regarding dry loading breakage of the Houdry Silica Beads, a free-fall drop test was performed where a

TABLE 51

ANALYTICAL RESULTS FOR UNCOATED AMMONIUM NITRATE PRILLS

**HERCULES INCORPORATED**

LOUISIANA, MISSOURI 63353

**CERTIFICATE OF ANALYSIS**

3/3/72

AMMONIUM NITRATE PRILLS, UNCOATED

**CUSTOMER:** Hercules Incorporated
Kenvil, NJ 07847

Attention: Mr. Fred Friend

**DATE SHIPPED** 3/2/72 **CARRIER** [illegible]

**NET WEIGHT** 35,000# **LOT NUMBER** [illegible]

**CUSTOMER'S ORDER NO.** -- **HERCULES ORDER NO.** [illegible]

| | |
|---|---|
| Moisture, % | [illegible] |
| Ether Soluble, % | [illegible] |
| Water Insoluble, % | [illegible] |
| a. Retained on [illegible] micron, | [illegible] |
| b. Retained on [illegible] micron, | [illegible] |
| Acid, as nitric, % | [illegible] |
| Nitrites, | [illegible] |
| Chlorides, as $NH_4Cl$, % | [illegible] |
| Phosphates, as DAP, % Diammonium phosphate | [illegible] |
| Sulfates, as DAS, % Diammonium sulfate | [illegible] |
| Boric Acid, % | [illegible] |
| Ammonium nitrate, % | [illegible] |
| Density: Particle, g/ml | [illegible] |
| Bulk, g/cc | [illegible] |
| Bulk, lbs/cu. ft. | [illegible] |
| Distribution: | |
| Through 1360 micron (No. 14) | [illegible] |
| Retained on 1.80 micron (Co. 120) | [illegible] |
| Retained on 840 micron (Co. 20) | [illegible] |
| Through 500 micron (No. 40) | [illegible] * |

* through 40

HERCULES INCORPORATED

By: [illegible]

JJL

TABLE 52

ANALYTICAL RESULTS FOR INDUSTRIAL GRADE PRILLED UREA

# SUNOLIN CHEMICAL COMPANY

**CLAYMONT, DELAWARE 19703**

TELEPHONE AREA CODE 302 798-6801

March 2, 1972

OAP 10-0263-

Mr. Fred Fremd
Hercules, Inc.
Kenvil, N.J. 07847

CERTIFICATE OF ANALYSIS

This is to certify the analysis of a truck shipment of prilled urea, industrial grade, on March 1, 1972 to Hercules, Inc., Kenvil, N.J.

| | |
|---|---|
| .24 | % Moisture |
| .94 | % Biuret |
| 46.5 | % $N_2$ |
| 0.1 | ppm Fe |
| 150 | ppm Free $NH_3$ |
| 4 | ppm Ash |
| < 5 | turbidity |
| 9.6 | pH |
| < 5 | APHA Color |
| | |
| 0.0 | % on 6 mesh |
| 2.1 | % thru 6 mesh on 8 mesh |
| 97.1 | % on 20 mesh |
| 0.8 | % thru 20 mesh |

O. L. Norder
Chief Chemist

TABLE 53

CHARACTERIZATION OF HOUDRY MACROPOROUS SILICA BEADS






**MACROPOROUS SILICA BEADS (Experimental)**
(Catalyst support No. 532 CP)

*DESCRIPTION*

These beads are characterized by good physical strength, high purity, high absorptivity and surface area. The beads will not shatter when immersed in water and therefore can be easily impregnated with metal salts. Typical properties are tabulated below:

*TYPICAL PROPERTIES*

Chemical Analysis

| | | |
|---|---|---|
| $SiO_2$ | >99 | Weight percent (ignited basis) |
| $Al_2O_3$ | <0.1 | Weight percent (ignited basis) |
| $Fe_2O_3$ | <0.1 | Weight percent (ignited basis) |
| $Na_2O$ | <0.1 | Weight percent (ignited basis) |
| $NO_3$ | <0.01 | Weight percent (ignited basis) |
| Cl | <0.1 | Weight percent (ignited basis) |

Physical Properties

| | |
|---|---|
| Surface Area | 350 $m^2/g$ (Typical value ... areas in excess of 700 $m^2/g$ available by special processing.) |
| Packed Bulk Density | 0.4 to 0.5 kg/l (Typical range after an air calcination at 1050°F. Values of 0.35 to 0.75 kg/l under same calcination conditions available by special processing.) |
| Particle Size | 4.0 mm avg. diameter (particles as small as 1 mm available by special processing.) |
| Particle Shape | Oblate Spheroids |
| Hardness | Min. 8 lbs. (Single particle plate to plate crushing strength. Value depends on both particle diameter and processing procedures.) |
| Porosity | 60 to 75 vol ... depends on processing procedure |
| Water Absorption | 60 to 125 wt ... depends on processing procedure. |
| Particle Density | 0.68 to 0.90 g/cc ... depends on processing procedure |
| True Density | 2.14 to 2.26 g/cc ... depends on processing procedure. |

*AVAILABILITY*

Pilot plant quantities of macroporous silica beads are available for development work

TABLE 54

SCREEN ANALYSIS OF HOUDRY SILICA BEADS

Air Products and Chemicals INC.

CHEMICALS GROUP

Five Executive Mall, Swedesford Road, Wayne, Pa. 19087

HOUDRY DIVISION

W. J. Cross, Jr., General Manager
R. G. Craig, Mkt. Mgr.
Tel: (215) 687-6150
Twx: 510-668-2034

March 2, 1[illegible]

M[illegible]. John Doyle
Hercules, Inc.
Kenvil, N[illegible]

Dear Mr. Doyle:

About a week ago you asked me to [illegible] on the recent ship[illegible] At the time, I was not [illegible] process of the material appears to [illegible] particles, which evaporated most of [illegible] to obtain. A few [illegible] to [illegible] was [illegible] the past [illegible] The [illegible] of the [illegible]:

| | |
|---|---|
| [illegible] | [illegible] |
| [illegible] | [illegible] |
| [illegible] | [illegible] |
| [illegible] | [illegible] |
| [illegible] | [illegible] |
| [illegible] | [illegible] |

We screened out a [illegible] cut from our earlier production runs and measured the crushing strength on both. These were respectively [illegible] lbs. which is well within the experimental error of the test. Consequently, we conclude that the hardness of the two runs is the same. Other pertinent data from the most recent run are the density of [illegible] lbs per liter, a surface area of [illegible], and an ignition loss of approximately 1.[illegible] when calcined at 1400°F.

I trust all of the above is adequate for your use but if there are any other questions, I would appreciate your getting in touch with us.

Yours very truly,

[signature]

J. W[illegible]
Manager, [illegible]

quantity of beads was dropped through a 1-in.-diameter pipe into an aluminum tub. There was no visible breakage of beads. Each reactor was then loaded with about 30 pounds of silica beads. The final level in each reactor coincided with the top of the steam jacket. Circular pieces of stainless steel screen were welded to ¼-in.-thick stainless steel rings (diameter ¼-in. less than reactor diameter). These assemblies were placed on top of the individual catalyst beds for retention.

b. Pilot Plant Startup Equipment Problems

After the above preparations had been completed, the plant was started up with introduction of "live" reagent AN and U) ingredients and with full intent to operate the entire plant. Typical start-up problems were encountered which were not completely solved until five or six weeks later. At this point, operation of the total integrated pilot plant could be achieved. The start-up period required more time than had been predicted, but this time was necessary because of the complexity of the pilot plant and also because of the five-day per week operation mode. Proper start-up of the entire plant required one and a half days and orderly shutdown of the plant required a day. In a five-day week, therefore, half of the available operating time was lost. A seven-day a week operation was implemented after the start-up to minimize the plant downtime.

The equipment problems faced on start-up were typical of those encountered in other processes of this type. The major problems encountered are listed below with a brief discussion.

1 Line Plugging Due to "Cold Spots"

The two AN/U melters (different AN/U ratios) operated as designed, i.e., sufficient heat transfer area to melt ingredients as required. Some problems were encountered as a result of insufficient heat on the transfer lines, but additions of more steam tracers, improved insulation and/or application of heat transfer cement were beneficial.

2 Molten Mixtures of AN and U

Occasional problems were encountered in pumping the molten mixtures of ammonium nitrate and urea.

Gases formed in the melters (presumably ammonia) would build up in the centrifugal pump casing and make transfer almost impossible. The first approach to solving the problem consisted of installing a vertical tube on the suction side of the pump (P-100) for disengagement of the gases from

the melt. This action was not completely satisfactory. By the end of the start-up, the tube was replaced with a vented 9-gallon stainless steel container and the pump suction lines were changed from ½-in. diameter to 1-in. diameter pipe. Melt transfers were then made with relative ease.

The source of the gases was presumed to be the hydrolysis of urea. The water necessary for the hydrolysis came from three sources: moisture in the solids, recycle, and from the air (the AN/U molten mixture is quite hygroscopic).

### 3 Electric Steam Boilers

Problems using the packaged boilers were of three types: conductivity control, sensitivity to loads, and blowdown losses. These boilers operate on the principle of electric conductivity. This conductivity must be maintained at a certain level to obtain the design output. Too high a conductivity resulted in shutdown due to high amperage. Too low a conductivity resulted in undercapacity. Installation of a deionizer and a condensate recycle system provided better control of this variable than was achieved with the well water.

The boilers were found to be extremely sensitive to load swings, primarily due to the low steam holdup in the boiler. Installation of back pressure regulating valves reduced the effect of this variable to an acceptable level.

When well water was being used as the feedwater for the boilers, the boilers had to be continuously blown down to maintain the conductivity at an acceptable level. This was due to the high mineral content of the well water. The resultant high frequency of blowdowns severely lowered the effective capacity of the boilers. Utilization of the deionized water and recycled condensate greatly decreased the blowdown frequency and minimized this problem.

### 4 Reactor Feed, Catalyst, and Product

One major operational problem which surfaced when the plant became operational was the inability of the feed system to distribute the flow equally between the eight reactor tubes. Most of the pressure drop in the feed and reactor system was hydrostatic head. With the low flows involved (~ 2 gph/tube), the dynamic pressure drop was very small and the flow could not be throttled. The reactor feed system had been designed so there would be an equivalent drop in flow pressure through all eight tubes. However, since most of the $\Delta P$ is hydrostatic, a small change in the condition

of a bed (due to such actions as plugging and settling) severely changes the pressure drop and resultant flow through that bed. The apparent solution was to add dynamic pressure drop to the system which could be throttled as required. To confirm this, orifice plates were added to four of the reactors in an attempt to add 10-15 psi additional $\Delta P$ to the flow system. This was a "quick fix," and homemade orifices were used. The result was that only two of the four orifices demonstrated the desired effect; the other two had burred orifices and a pressure drop higher than available by the feed pump.

Once the principle of adding a throttling pressure drop was shown to be effective, miniature needle valves with vernier dial handles were purchased and added to the reactor feed system in a bypass loop around the main 1-in. ball valves. The ball valves were left in the system for the purpose of draining the reactors. After the microvalves had been used for a period of time, it was shown that they did solve the problem but were not optimum because they required constant attention.

Before the end of the production run attempts, it was decided to purchase a flow control loop for each reactor. This equipment was procured but was not installed. It will be utilized if an additional production program is requested.

It was found that the conditions of the catalyst in the reactors was quite sensitive to thermal cycling. In the periods of five-day operation and boiler problems, the temperatures of the reactors were necessarily up and down, causing catalyst weakening and attrition. This catalyst degradation was followed by a non-flow condition and over-reaction. The result was inoperative tubes filled with a hard, fused material which was difficult to remove. Implementation of the seven-day operation, better boiler operation and improved reactor flushing and draining techniques essentially eliminated this problem.

During early operations, it was found that catalyst was being carried overhead of the reactors and being trapped in the gas-liquid separators and overhead lines, leading to line plugging. Installation of a positive hold-down screen at the top of each reactor eliminated this problem.

### 5 Solid Bowl Centrifuge

A laboratory-size solid bowl centrifuge was selected for use in the pilot plant because of the anticipated small amount of insolubles load. Being a laboratory model, it was sensitive to the operating conditions and when flow-rate or insolubles level cycled to high values, some separation

problems occurred. Careful control of the flow rate and reduction of the insolubles level (by changing the reactor operating parameters) resulted in a much smoother operating unit.

### 6 Ammonia Leaks

The by-product ammonia leaked into the operating room from loose seals in the off-gas scrubber and by dissolution from the melt and water streams. Installation of a tight metal scrubber, gas seal loops in pertinent product lines, and additional building fans greatly reduced the above problem.

### 7 Guanidine Nitrate Crystallizer

Because a heat wave occurred during the start-up period and because most of the equipment in the pilot plant utilized steam heat, the process room containing the crystallizer reached an ambient room temperature of approximately 110°F. The crystallizer solution was cooled by evaporative cooling. It was found that under the above conditions the vacuum system was undersized and instead of cooling down to about 65-70°F as designed, the crystallizer temperature could be reduced only about 10°F below ambient. To help resolve this problem, cooling coils were added to the crystallizer. After the temperature due to vacuum cooling leveled out, the coils were used to decrease the temperature an additional 25°F. Eventually, the vacuum system will be modified to offset the higher ambient temperatures.

### 8 Guanidine Nitrate Centrifuge

During the first use of the large centrifuge, it was learned that plow-to-cake drag was stopping the basket in the plow mode. It was necessary to (1) fabricate a new plow blade with a sharp edge and (2) increase the plow speed from 50 rpm to 100 rpm. These changes solved the drag problem.

5. Production Run Attempts

After the start-up problems of the pilot plant had been partially resolved, the operation was directed toward production of the required quantity of guanidine nitrate. Two attempts were made at production runs before it was realized that the catalyst was becoming deactivated. Detailed discussion of these two runs follows.

a. Catalyst Run No. 1

The first catalyst run, defined as that run employing the first catalyst charge, represented a futile attempt to start up and sustain the operation to make production. The period of operation covered by this run was June 8 to July 10. The plant ran well on occasions during this period, but in general, it was a period of frustration because of the following constraints and problem areas.

(1) Start-up/shutdown times represented 50% of the operational time.

(2) Erratic steam boiler operation.

(3) Equipment limitations (feed distribution, insolubles separation, vacuum).

Although this period of operation was not smooth, a great deal of valuable information was learned about the operation, the process variables and component performance.

The available data from this run are shown in Table II-1 in Appendix II. Calculated results are shown in Figures II-12 and II-13 in Appendix II and Figure 57. As can be seen from Table II-1, the operation during this run was variable in regard to the number of tubes used, the feed rate, reaction temperature and feed mole ratio. Table 55 lists the guanidine nitrate that was formed during this effort.

The data in Table II-1 represent a host of operating conditions and alone show few trends. However, in the perspective of the total data on hand and experience from the operation, several insights can be drawn from this run. (Initial reactivity is defined as that occurring in the first 2-3 hours.)

(1) The initial reactivity from a fresh bed of catalyst appears to be higher than its steady state value.

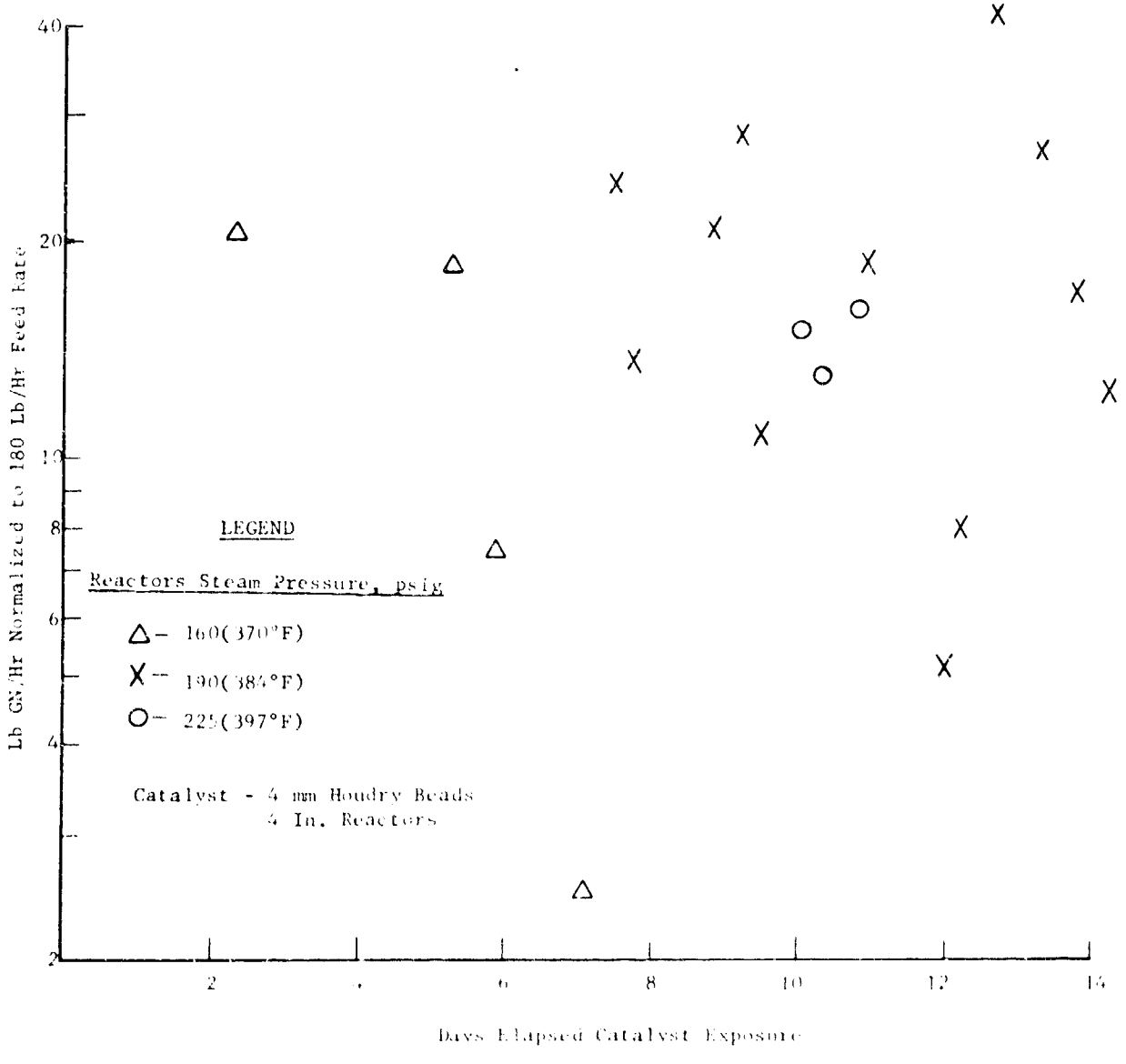



Figure 57. Normalized Productivity/Hour Vs Time - First Catalyst Run

# TABLE 55

## GUANIDINE NITRATE PRODUCT

RUN NO. 1

| Crystallizer Batch No. | Date | WET CAKE | | | | | | DRIED PRODUCT | | | | | | Notes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Wet Weight, lb. | Analyses, Wt. (Dry Basis) | | | | | Batches | Analyses, Wt. % | | | | | |
| | | | U | AN | GN | Insolubles | T.S. | | U | AN | GN | Insolubles | T.S. | |
| 1 | 6/4 | [illegible] | 0.11 | [illegible] | 99.7 | 0.39 | 99.86 | - | - | - | - | - | - | - |
| 2 | 6/4 | 1.0 | 1.41 | 0.49 | 93.2 | 4.5 | 86.3 | - | - | - | - | - | - | - |
| 3 | 6/5 | [illegible] | [illegible] | 3.74 | 95.4 | 3.5 | 88.9 | - | - | - | - | - | - | - |
| 4 | 6/5 | [illegible] | [illegible] | [illegible] | 93.4 | 5.1 | 85.7 | - | - | - | - | - | - | - |
| 5 | 6/13 | [illegible] | 1.35 | 3.4 | 92.1 | 1.4 | 87.9 | - | - | - | - | - | - | - |
| 6 | 6/13 | 25.0 | [illegible] | [illegible] | 95.6 | 1.0 | 99.1 | 5,6,7 | 0.5 | 2.0 | 95.6 | 1.0 | 99.1 | - |
| 7 | 6/14 | 32.5 | - | - | - | - | - | - | - | - | - | - | - | - |
| 8 | 6/14 | 21.5 | - | - | - | - | - | - | - | - | - | - | - | - |
| 9 | 6/14 | [illegible] | - | - | - | - | - | 8,9,10,11 | 0.8 | [illegible] | 96.7 | 0.6 | 99.3 | Drum No. 1 |
| 10 | 6/15 | [illegible] | - | - | - | - | - | 8,9,10,11 | 0.9 | 2.0 | 93.9 | 1.6 | 99.1 | Drum No. 2 |
| 11 | 6/15 | 19.5 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| 12 | 6/15 | 8.5 | [illegible] | [illegible] | [illegible] | [illegible] | 98.2 | - | - | - | - | - | - | - |
| 13 | 6/15 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| 14 | 6/21 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | 0.4 | 0.8 | 97.7 | 0.22 | - | m.p. = 208°C |
| 15 | 6/21 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| 16 | 6/21 | 37.3 | 0.7 | 0.8 | 97.8 | 0.16 | 90.2 | 15,16,17 | 0.6 | 1.2 | 98.0 | 0.29 | 99.6 | Labeled X2138-49-1,50# Shipped to Cynamid, 50# Retained |
| 17 | 6/22 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |

TABLE 55 (Continued)

| [illegible] | [illegible] | [illegible] | Analyses, Wt. % (Dr. Basis) | | | | DRIED PRODUCT Analyses, Wt. % | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Batches | | | | | | |
| | | | | | | | | P | AN | GN | Insolubles | T.S. | Notes |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - | - | - | - | - |
| [illegible] | [illegible] | [illegible] | - | - | - | - | - | - | - | - | - | - | - |

(2) Either the flow distribution to the eight tubes must be maintained or the total feed rate must be adjusted. Otherwise, the effectiveness of the plant decreases with time. The history of Run No. 1 was a gradual loss of tubes.

(3) As the theory and Phase I work showed, the level of insolubles formed is indeed a function of urea concentration and temperature. The higher the two of these variables, the more ammelide recovered.

(4) The stripping of water from the recycle mother liquor is extremely important from both an operational and a yield standpoint. Residual water in the feed creates pumping problems. It also reacts with feed urea in the reactor (the carbamate side reaction), thereby lowering the guanidine nitrate yield.

Figure II-12 (Appendix II) shows the resultant lb GN/lb feed for Run No. 1; Figure II-13 shows the actual hourly GN productivity for this run, whereas Figure 57 shows productivity normalized to 180 lb/hr in eight tubes. Because of the data scatter and host of variables represented by these data, no lines were drawn through these curves. The productivity, however, does not appear to be decaying with time.

The major equipment operational problem during this run was encountered with the electrode steam boilers. Problems were associated with the boiler's operating principle of conductivity. Steam problems affect the plant drastically because loss of steam leads to plugged lines, loss of reaction heat and incomplete mother liquor evaporation. Incomplete evaporation results in excess water in the recycle feed which contributes to pumping and yield problems.

Since the loss of steam so drastically affects the operation of the pilot plant, it was the major contribution for down-time. Other equipment items which gave less than optimum performance were the solid bowl centrifuge, the vacuum pumps and the dryer. The solid bowl centrifuge problems were caused by its limited (laboratory-size) capacity. When the operating conditions chosen resulted in a high insolubles fraction, a high frequency of bowl changes became necessary, and as the solids level approached the bowl capacity, the ability of the machine to separate the ammelide efficiently was strained. Since the unit was designed for use in batch laboratory operations and not for continuous pilot plant use (at elevated temperatures and in a corrosive atmosphere), its maintenance frequency was high. The vacuum pump problems were primarily due to a high ambient building temperature

and contamination of water in the seal oil. The latter drastically lowers the pump performance in the 10-20 torr range. This contamination can be minimized and essentially eliminated by very careful manual control, but this had not been the case in this period. Some modification of this system will be necessary for the full-scale production run.

The guanidine nitrate dryer was not operational. A run was made in July using cocurrent heated feed air and was encouraging in that its run length was the longest experienced yet. The dryer operated efficiently for six continuous hours before the run was terminated. It was stopped as were previous runs when the shaft began thumping because of material caked between its paddles. The shaft was sprayed with Teflon to prevent this material adhesion, but the available Teflon spray was not effective. A decision was then made to remove the dryer shaft and have it commercially coated with a nonstick coating (Teflon FEP).

Modifications were made in the steam boilers system to improve reliability. The following modifications greatly improved boiler performance:

(1) Installation of back pressure regulators downstream from the boiler so that, in operation, if the pressure dropped below a preset value (300 psig) because of load demands, these control valves closed, preventing the boiler from supplying steam at a lower pressure. The result is that the system, instead of the boiler, takes the major load swings and the boiler has only minor swings.

(2) It had been decided that the feedwater sources for the boiler would be those with low mineral content, either the condensate recycle or the deionized water. Later in the operation, a decision was made to use only recycle condensate.

(3) Periodic cleaning of the boiler interior using sulfamic acid and/or trisodium phosphate appeared to improve reliability by removing build-up scale and sludge, even though the manufacturer stated that it was not necessary to do this frequently.

In addition to the above modifications, it was decided to procure equipment to increase the pressure in the plant steam line, which feeds the building for heating and for the melt kettles, from 50 psig to 120 psig. This will allow use of this steam source for the evaporator and high pressure tracings. The steam load required for the evaporator is the major demand (~50%) on the EBCOR boilers. This modification was not made during this program but will be necessary before the pilot plant is started again.

b. Catalyst Run No. 2

Catalyst Run No. 2 was conducted using the second charge of catalyst and covered the operational period of July 17 to August 1, 1972. This run was continuous; that is, the operation was never shut down in this period and all eight tubes were used in the run. Major events of Run No. 2 are shown in Table 56.

The first 2½ to 3 days of operation were successful in that the mechanical operation of the plant went smoothly, and the product of good quality was made (See Table 57). However, by July 20, the quantity of GN recovered from each successive crystallizer batch was decreasing, and it was postulated that the catalyst had lost its activity. Since one of the likely reasons for this was that the bed was loaded with ammelide coating the catalyst surfaces, it was elected to flush the beds at nonreaction conditions with high AN feed in an attempt to wash the catalyst. After the flushing step, it was planned to restart the run and program the conditions to start forming GN again but in the absence of ammelide.

Three days after this poisoning theory, it was learned, when analyses of the reaction product became available, that the beds had not lost all their activity as postulated but had, in reality, leveled out at a lower reactivity. An attempt was then made to stabilize the reaction conditions by operating on recycle with just incremental addition of urea (equivalent to the urea being consumed). By August 1, when sufficient analytical data were available and calculated (Figure 58), it was apparent that the catalyst activity had not leveled off but was decaying so the decision was made to shut down the operation. A meeting was scheduled for the first week in August to review the operation and the apparent catalyst decay and to formulate a plan of action for future work.

As noted in Table 56, multilayer cakes were becoming a problem near the end of the operation. The heel on the centrifuge cake consisted of two distinct crystals - a very fine whited colored one and a larger tan crystal. The fine crystal blinded the centrifuge cloth and created centrifuging problems. The source of the two crystals had not yet been identified, but the following possibilities were considered:

(1) A decision had been made a day or two before the multilayer problem occurred to charge wet product available from earlier runs, whose quality was less than desirable (from runs in which problems had occurred) and from centrifuge heels, back to the workup system in the quench or crystallizer feed tank. This material would have been recrystallized and dried.

TABLE 56

JULY 1972 CHRONOLOGICAL HISTORY OF PILOT PLANT

| Date | Event |
|---|---|
| July 1, 2 | Operation on Catalyst Bed No. 1 |
| July 3, 4 | Holidays |
| July 5-7 | Boiler checkout; visit by EBCOR |
| July 8 | Restarted pilot plant |
| July 10 | Shut down pilot plant due to high pressure drop and fines in product |
| July 11-15 | Boiler modification and distribution valve modification |
| July 14-15 | Repacked beds |
| July 17 | Restarted pilot plant - Run No. 2 |
| July 19 | Steady state operation and first data collection |
| July 20 | Catalyst appeared to have become inactive |
| July 21-22 | Flushed reactors at low temperature and with high AN (primarily recycle) feed |
| July 22 | Restarted reactor with programmed feed rate and temperature |
| July 24 | Increased temperature |
| July 25 | Operating on recycle with urea solids addition to recycle tank (rate equal to urea being consumed) |
| July 26 | Increased temperature again (185-190 psig). Sets FRC-1 on manual and controlled blend of recycle and fresh makeup |
| July 28 | Increased makeup recycle ratio. Increased feed rate. |
| July 30 | Centrifuge problems of multilayer cake |
| July 31 | Recycle holdup increasing to maximum. Still multi-cake problems. Feed pump pressure requirement increasing. |
| August 1 | Shutdown |

# TABLE 57

## GUANIDINE NITRATE PRODUCT

RUN NO. 2

| Centrifuge Batch Number | Date | Wet Weight lb | Wet Cake Analyses, Wt. % (Dry Basis) | | | | |
|---|---|---|---|---|---|---|---|
| | | | U | AN | GN | Insolubles | T.S. |
| 51 | 7/26 | 67.4 | .80 | .24 | 93.5 | 0.14 | 93.86 |
| 52 | 7/26 | 65.3 | .14 | .08 | 97.5 | 0.22 | 93.16 |
| 53 | 7/27 | 76.0 | .16 | 0.1[illegible] | 97.3 | 0.58 | 93.40 |
| 54 | 7/27 | 51.5 | .67 | .40 | 94.6 | 2.84 | 90.14 |
| 55 | 7/28 | 27.3 | .42 | .31 | 94.2 | 4.50 | 89.27 |
| 56 | 7/28 | 46.8 | .51 | .34 | 96.6 | 2.30 | 92.27 |
| 57 | 7/28 | 65.2 | .18 | .21 | 97.7 | 1.44 | 91.62 |
| 58 | 7/29 | 71.9 | .43 | .33 | 94.1 | 1.75 | 91.90 |
| 59 | 7/29 | 81.0 | .25 | .25 | 97.3 | 2.30 | 90.20 |
| 60 | 7/30 | 49.5 | 6.8 | 23.7 | 63.3 | 1.49 | 97.56 |
| 61 | 7/30 | 76.5 | 1.16 | 0.44 | 92.9 | 2.92 | 81.2 |
| 62 | 7/31 | 23.3 | 0.26 | 0.24 | 93.2 | 2.41 | 90.13 |
| 63 | 7/31 | 45.2 | 0.51 | 2.8 | 94.3 | 2.69 | 89.43 |
| 64 | 7/31 | 55.2 | - | - | - | - | - |
| 65 | 7/31 | 66.6 | 2.8 | 8.6 | 75.4 | 3.70 | 83.11 |
| 66 | 8/1 | None | - | - | - | - | - |
| 67 | 8/1 | None | - | - | - | - | - |
| 68 | 8/1 | 1.5 | 3.3 | 8.4 | 75.0 | 14.2 | 72.8 |

TABLE 57 (Continued)

| Crystallizer Batch Number | Date | Wet Weight lb | Wet Cake Analyses, Wt. % (Dry Basis) | | | | | Centrifuge Batch Number | Date | Wet Weight lb | Wet Cake Analyses, Wt. % (Dry Basis) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | AN | AN | Insolubles | T.S. | | | | U | AN | GN | Insolubles | T.S. |
| [illegible] | [illegible] | 22.0 | 0.20 | 0.11 | [illegible] | 0.68 | 91.74 | | | | | | | | |
| 59 | [illegible] | [illegible] | 0.00 | 0.03 | [illegible] | 0.55 | 92.97 | | | | | | | | |
| TOTAL | | | | | | | | | | 1500 | | | | 95.43* | |

*Excluding Lot #60, 65, 68

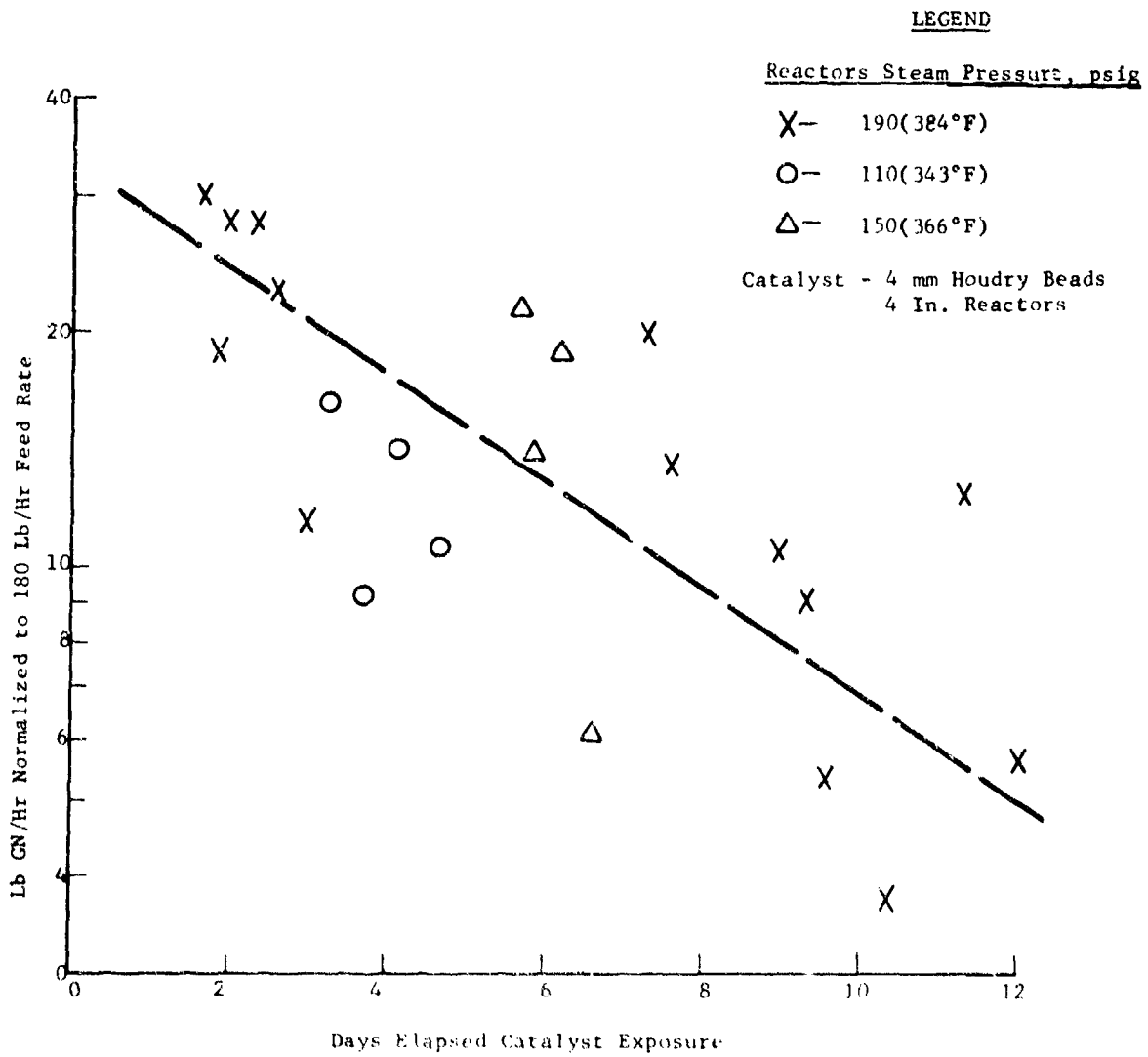



Figure 58. Normalized Productivity Vs Time - Second Catalyst Run

It has been postulated that some of the solids charged did not dissolve. This would have meant a slurry feed to the crystallizer and a resultant two-crystal growth pattern.

(2) At about this same time an inadvertent error was made in charging the crystallizer. A cold heel was left in the crystallizer, and hot feed was dumped in on top of it, thereby quenching the incoming material. This would have generated fines.

Table II-2 in Appendix II lists the data and calculated results for Run No. 2, Figures II-14, II-15, and II-16 in the Appendix and Figure 58 show the plotted productivity, productivity/hr, yield, and productivity/hr normalized to 180 lb/hr feed, respectively. The operation during Run No. 2 was mechanically smoother than previously; that is, down-time periods due to boiler problems, etc., were minimal. The flow distribution was not as poor as in the previous run, but over the two-week operation, the number of effective tubes was reduced because of uneven flows. By the end of the run, the pressure drop required to maintain flow could not be provided. It was speculated that the beds at this time were broken up again into fines. (When the beds were dumped in August, it was learned that this was true for only two tubes and that actually the high $\Delta P$ differential was due to the upper screens being plugged with insolubles.) Since the pilot plant was experiencing operational problems due to feed and product plugged lines, steam failures and flow problems, material balances could not be made on the reactors. A method had to be developed, in the absence of a material balance, which would give a rapid indication of the reactor performance. Since there is a total conservation of nitrate moles across the reactor (assuming little or no ammonium nitrate decomposition), it was elected to use a method based on the reactor feed and product sample analyses normalized in regard to total nitrates. The accuracy of the calculations and results obtained by this method is strongly dependent on the accuracy of the sampling and analytical technique. However, with a large number of samples, definite trends indicating reactor performance can be rapidly developed with minimum data workup. A sample calculation utilizing this method is shown in Table II-3 in the Appendix. The results in Tables II-1 and II-2 in Appendix II were obtained by these methods.

## 6. Pilot Plant Results

### a. Conclusions

Although the production attempts were hindered because of catalyst activity problems, a number of the program objectives were met and the process reached a higher level of development in this period.

The important results from Run No. 1 and Run No. 2 were the following:

(1) The U/AN process does indeed make GN of a high purity.

(2) The workup of the product melt (quench, insolubles separation, crystallization, centrifugation and drying) is very efficient in that it cleanses the product of its operational history, i.e., it does not matter how the plant reactors are operated because the workup system controls the ultimete product purity.

(3) Once the plant is operating, the operation is a smooth one. It is recommended that the plant be operated on a continuous basis. The plant was operated as an integrated unit as designed.

(4) The process concept has been demonstrated and the selected process equipment has performed as designed.

(5) The operating performance of the wet end of the process was determined; the findings confirm assumptions made in the alternate GN process. (British Aqueous Fusion Contract No. DACA 45 71 C0121).

(6) Approximately one ton of 96% GN was produced.

(7) A 50-pound sample of typical U/AN process guanidine nitrate was sent to Cynamid of Canada at the request of Picatinny Arsenal. The material produced satisfactory nitroguanidine.

(8) Thermal cycling of the catalyst bed, improper draining and/or semicontinuous flow through the bed are all undesirable and lead to bed attrition and ultimately force a shutdown due to loss of flow through the tubes involved.

(9) The catalyst beds, if allowed to break down as noted in (8) above, become very hard to drain and, on cooling, become a solid mass which cannot be easily dumped. Tubes in this condition can, however, be cleaned by use of high pressure water jets.

Most of these results were discussed in earlier sections of the report. Detailed discussions follow for the 50-pound sample shipment to Cynamid and for the performance of individual pieces of equipment.

b. Shipment of Guanidine Nitrate to Canada

Picatinny Arsenal had requested that Hercules Incorporated ship to Cyanamid of Canada 50 pounds of typical U/AN process guanidine nitrate. This was agreed upon and implemented on July 5, 1972. This material was to be examined by Cyanamid and converted in the laboratory to nitroguanidine to establish operating procedures for converting the 40,500 lb to be shipped at the end of Phase III and to assess the chemical quality of the nitroguanidine to be made.

The guanidine nitrate shipped was made in the pilot plant under representative conditions. The material had the following analyses:

| | % Total | % Dry Basis |
|---|---|---|
| Guanidine Nitrate | 97.4 | 98.0 |
| Ammonium Nitrate | 1.2 | 1.2 |
| Urea | 0.6 | 0.6 |
| Insolubles | 0.3 | 0.3 |
| Moisture | 0.4 | |

A 50-pound sample of material from the same lot was retained at Kenvil.

The above material designated as X2138-49-1, was shipped as an oxidizer material (DOT Lading Bill of Material) as per the shipping reclassification made under the contract modification DAAA21-71-C-0193 - P00005, dated June 30, 1972.

It was later learned that this material on conversion made very acceptable nitroguanidine.

c. Equipment Performance

During the periods of smooth pilot plant operation in June and July, the process equipment selected was evaluated. This section presents discussions of the performance of certain components, i.e., evaporator, densitometer, solid bowl centrifuge, GN centrifuge and dryer.

1 Whitlock Evaporator (A-800)

The evaporator design had been based on similar ammonium nitrate/urea systems, as the falling-film, air-swept unit is typical for AN and urea concentrators. Table 58 shows the resultant design and experimental data.

TABLE 58

WHITLOCK EVAPORATOR DATA

| | Whitlock Design Prediction | Typical Experimental Data(6/14-1:15 p.m.) |
|---|---|---|
| Feed Rate, lb/hr. | 175 | 200 |
| Feed Composition, % AN | 51 | 59 |
| Feed Temperature, °F | 68 | Ambient |
| Bottoms Composition, % $H_2O$ | 0.5 | 0.41 |
| Bottoms Temperature, °F | 266 | 259 |
| Air Temperature In., °F | 266 | 260 |
| 1st Stage Temperature, °F | 331 | 331 |
| 2nd Stage Temperature, °F | 274 | 274 |

Since the basis of the design of the evaporator is a number of 2-inch-diameter tubes at the above stage temperatures, this equipment can easily be scaled up by Whitlock and other vendors with confidence.

2 Densitometer (CRC-1)

The densitometer is used as the composition analyzer in the feed composition control system (CRC-1). This control system was found to function very well. Table 59 lists typical feed analyses and density readings.

TABLE 59

DENSITIES OF VARIOUS AN/U/GN MIXTURES

| Date | Sample | % U | % AN | % GN | Density* | T, °F |
|---|---|---|---|---|---|---|
| 6/7 | 1S-2 | 39.8 | 57.7 | - | 1.35 | 254 |
| 6/8 | 1S-1 | 28.7 | 61.4 | 8.0 | 1.375 | 258 |
| 6/8 | 1S-2 | 27.3 | 62.4 | 10.9 | 1.37 | 255 |
| 6/12 | 1S-1 | 40.3 | 56.6 | - | 1.35 | 255 |
| 6/13 | 1S-2 | 41.5 | 54.0 | 3.3 | 1.35 | 262 |
| 6/14 | 1S-1 | 39.8 | 52.9 | 6.2 | 1.35 | 257 |
| 6/14 | 1S-2 | 44.1 | 47.7 | 8.6 | 1.35 | 257 |
| 6/15 | 1S-1 | 28.7 | 53.4 | 11.8 | 1.365 | 256 |
| 6/15 | 1S-2 | 28.2 | 53.7 | 12.7 | 1.365 | 258 |
| 6/16 | 1S-1 | 56.1 | 36.9 | 3.2 | 1.315 | 250 |
| 6/21 | 1S-1 | 43.4 | 50.2 | 5.5 | 1.335 | 249 |
| 6/21 | 1S-2 | 42.6 | 50.1 | 3.5 | 1.335 | 250 |
| 6/21 | 1S-3 | 43.1 | 52.7 | 4.8 | 1.35 | 250 |
| 6/21 | 1S-4 | 36.7 | 58.1 | 4.2 | 1.35 | 252 |
| 6/21 | 1S-5 | 39.3 | 55.6 | 2.4 | 1.35 | 250 |
| 6/21 | 1S-6 | 34.8 | 57.3 | 6.0 | 1.35 | 250 |
| 6/22 | 1S-1 | 45.2 | 48.8 | 5.8 | 1.325 | 250 |
| 6/22 | 1S-2 | 44.9 | 48.6 | 2.9 | 1.325 | 250 |
| 6/22 | 1S-3 | 37.6 | 55.3 | 5.9 | 1.35 | 246 |
| 6/22 | 1S-4 | 32.2 | 60.7 | 5.6 | 1.35 | 247 |
| 6/23 | 1S-1 | 27.0 | 61.8 | 8.0 | 1.37 | 249 |
| 6/23 | 1S-2 | 25.8 | 63.3 | 7.4 | 1.37 | 248 |
| 6/23 | 1S-3 | 26.5 | 61.1 | 8.5 | 1.37 | 250 |
| 6/27 | 1S-1 | 28.2 | 58.6 | 10.5 | 1.365 | - |
| 6/27 | 1S-2 | 26.7 | 60.5 | 10.3 | 1.37 | - |
| 6/27 | 1S-3 | 25.6 | 61.6 | 9.7 | 1.36 | - |
| 6/28 | 1S-1 | 32.0 | 57.2 | 6.6 | 1.35 | - |
| 6/28 | 1S-3 | 28.5 | 61.0 | 4.9 | 1.35 | - |
| 6/28 | 1S-4 | 32.7 | 55.5 | 6.7 | 1.35 | - |
| 6/29 | 1S-1 | 33.2 | 57.9 | 4.6 | 1.35 | - |
| 6/29 | 1S-2 | 34.6 | 57.5 | 3.4 | 1.35 | 238 |
| 6/29 | 1S-3 | 33.2 | 62.3 | 1.4 | 1.35 | 250 |

*Values measured by densitometer

In the control system, the density set point was satisfied as long as the Hills-McCanna blend pump (P-101) operated well. The major problem was plugged suction lines to P-101 resulting from the low flow rates.

Although the CRC-1 control system has shown satisfactory performance, it is apparently not an absolute process requirement. The set point is based on a certain urea consumption, but if the reactors are not performing to the assumed reactivity, excess urea or ammonium nitrate goes through the system and builds up in the recycle inventory. This deviation plus variations in the makeup feed tank prevents fine control of the feed stream, but slight variation in the blended feed due to use of manual control does not affect the reactor performance. It was later demonstrated that suitable reactor feed control could be attained using the Hills-McCanna feed blend pump on manual control.

### 3 Solid Bowl Centrifuge (S-300)

The DeLaval Solid Bowl Centrifuge used for insolubles separation is a laboratory machine. It was selected because a commercial unit was not available for the small flow rate required. It was predicted during the design phase that an insolubles formation rate much greater than that designed for would strain the capacity of the unit and result in a loss in efficiency. This did indeed happen, and the result was a reduction in the product purity. For the commercial plant, obtaining a machine in the proper size range will be no problem so the above event will not occur.

The important finding gained from using the solid bowl centrifuge in the pilot plant is that a solid bowl machine (operating at 1200-1500 g) does very effectively remove the insolubles. One set of data in June showed that the insolubles level had been reduced from 0.38% to 0.06% in the solution on one pass through the separator.

### 4 GN Centrifuge

As Tables 55 and 57 show, the wet GN recovered from the centrifuge contains in the range of 10% to 12% water and a fraction of a per cent of AN and U. These figures coincide with the data used for design. Mechanically, this centrifuge was the most trouble-free unit in the pilot plant. Except for the plow modification noted earlier, this unit has been operational since being installed.

### 5 GN Dryer (A-700)

The Strong-Scott dryer has not yet been shown to operate for long periods. During June it was started up on a number of occasions with

only limited success. Its major weakness has been that wet material tends to build up on the shaft between the paddles. The resultant effect of this is that the dryer within 1-1/2 to 2 hours begins to thump (caused by paddles hitting accumulations of material in the feed position of the dryer). A number of changes were tried in an attempt to improve its performance. The inlet feed funnel was coated with an adhesive-backed Teflon tape, cocurrent air was introduced at the feed injection port, and dry/wet blended feeds were used. The result of all these changes was that the dryer could be operated for 3 to 4 hours before material accumulated on the shaft.

One important parameter relating to the apparent gu. line nitrate caking property is the resultant angle of repose of the dry product. The dry product in the recovery drum forms a cone whose height is 3 to 4 times its base width.

An air heater was also constructed to provide heated cocurrent air, and the dryer hazards were reviewed to determine whether a higher paddle shaft speed could be used. These modifications did not appreciably increase the dryer run time so the dryer shaft was removed and covered with a nonstick coating. Additional dryer tests were planned and conducted in the Phase III extension program.

## 7. Single 4-Inch Tube Catalyst Runs

As reported in the previous section, after two attempts to operate the pilot plant for guanidine nitrate production, it became apparent that the Houdry Bead silica gel catalyst was losing its activity at a rapid rate.

Status meetings were held in this period between Hercules and Picatinny Arsenal personnel to review these runs and to determine the most logical course of action. From these meetings, it was elected to suspend GN production in the pilot plant and utilize the pilot plant facilities for about 3 to 4 weeks to conduct controlled research experiments on catalyst life.

The program suggested for the pilot plant to best aid in defining the source of the catalyst activity loss was to conduct, under carefully controlled conditions, a series of single-tube continuous runs at mild reaction conditions (180°C, 2/1 AN/U) such that the formation of the by-product ammelide would be minimized and the catalyst would not be initially shocked. Three runs, looking at three different types of silica gel catalyst, were deemed necessary. Since the Houdry beads were still a development product and it appeared that its superior catalyst activity might be evident only in the initial portion of a run, it was believed that this was the appropriate time to look at other suitable forms of silica gels.

It was decided to conduct single-tube runs so that there would be no flow distribution problem and so that batch steps would occur infrequently, thereby allowing the operators to concentrate on the reaction step.

A five-step startup approach was used so that the catalyst would not be initially shocked. These steps were as listed in Table 60.

The three catalysts selected were the three most active in Phase I laboratory catalyst studies:

(a) Houdry Macroporous Silica Beads (Experimental)
(b) Mobil Sorbeads R (Commercial)
(c) Davidson Grace 59 Silica Gel (Commercial)

Table 61 lists the pertinent physical properties for these three catalysts.

The three catalyst life pilot plant runs were initiated on August 12, 1972 and completed August 31, 1972. Figures 59, 60, and 61 and Table 62, 63, and 64 show the data and calculations from these runs. In the figures, productivity (lb GN/hr/tube) is plotted versus time on semilog paper.

TABLE 60

CATALYST LIFE STUDIES - START-UP CONDITIONS

CONSTANT: Feed Mole Ratio AN/U = 2/1

Feed Temperature 110°C - 120°C

| Step | Jacket, °C | Run Duration (hrs.) | Comments |
|---|---|---|---|
| 1 | 160 | - | Preheat dry packing to 150°C |
| 2 | 160 | 4 | Run and discard product |
| 3 | 170 | 4 | Run and discard product |
| 4 | 180 | 3-4 days (until recycle is available) | Collect Product |
| 5 | 180 | 4-5 days | Recycle operation |

TABLE 61

CATALYST PHYSICAL PROPERTIES

| Physical Characteristics | Type Catalyst: Houdry 532 CP Silica Beads | Sorbead R | Grade 59 Silica Gel |
|---|---|---|---|
| Size, mm. | 4-6 | 1-4 | 2-7 |
| Density, G/cc (Packed Bulk) | 0.43 | 0.80 | 0.40 |
| Pore Volume, cc/gm | 0.60 | 0.34 | 1.15 |
| Average Pore Diameter, $A^{o}$ | 60-70 | 21 | 140 |
| Surface Area, M 2/gm | 398 | 630 | 340 |
| Total Volatiles, % at 1750° F | 1.1 | - | 5 - 6.5 |
| Analyses, % Wt. | | | |
| $SiO_2$ | > 99 | 97 | 99.7 |
| $Al_2O_3$ | < 0.1 | 3 | 0.1 |
| Other | Macropores | Micropores | Macropores |
| Reactor Charge | 25 lbs. | 50 lbs. | 25 lbs. |

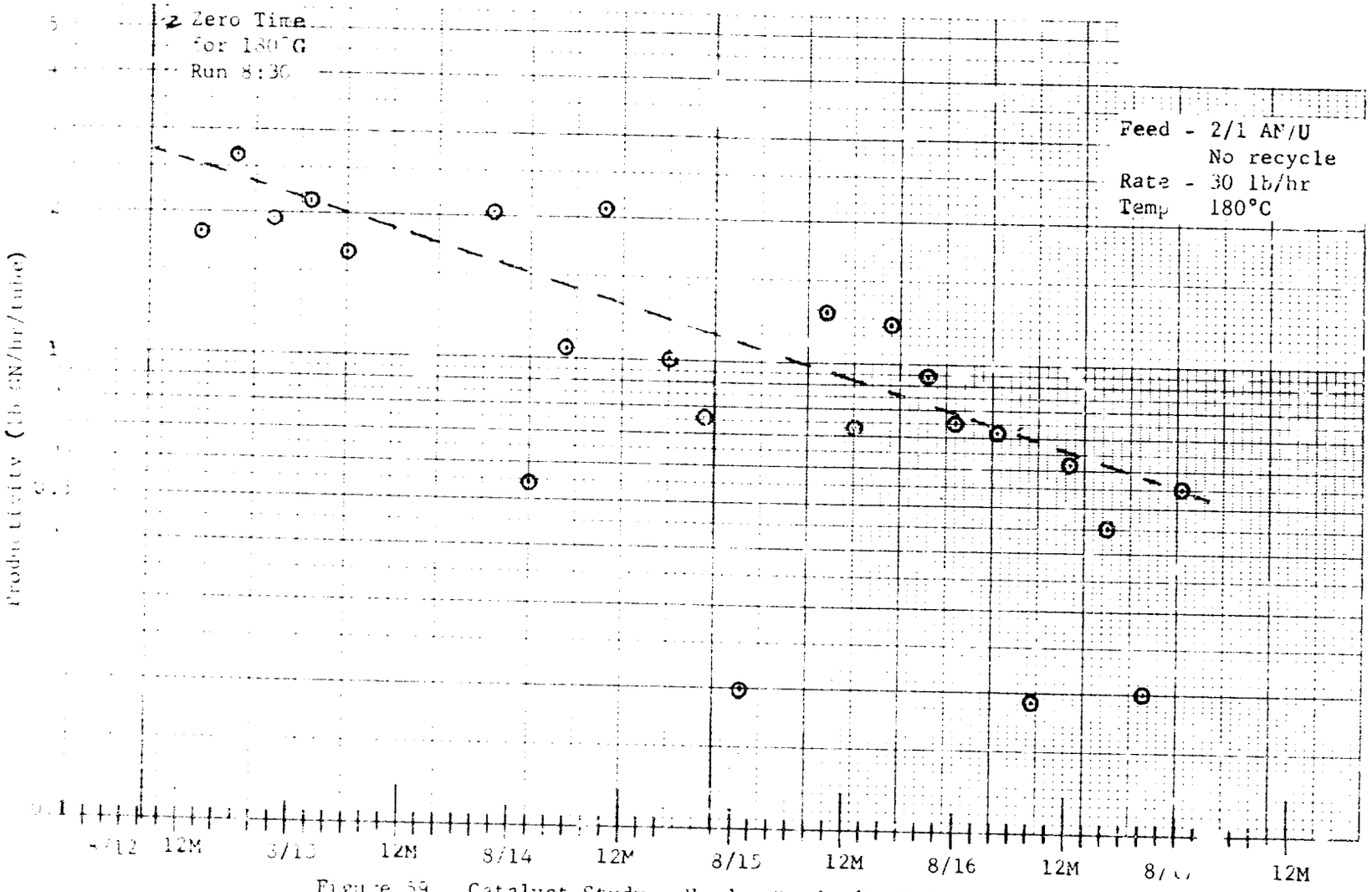



Figure 59. Catalyst Study - Houdry Beads (K-200), Single Tube

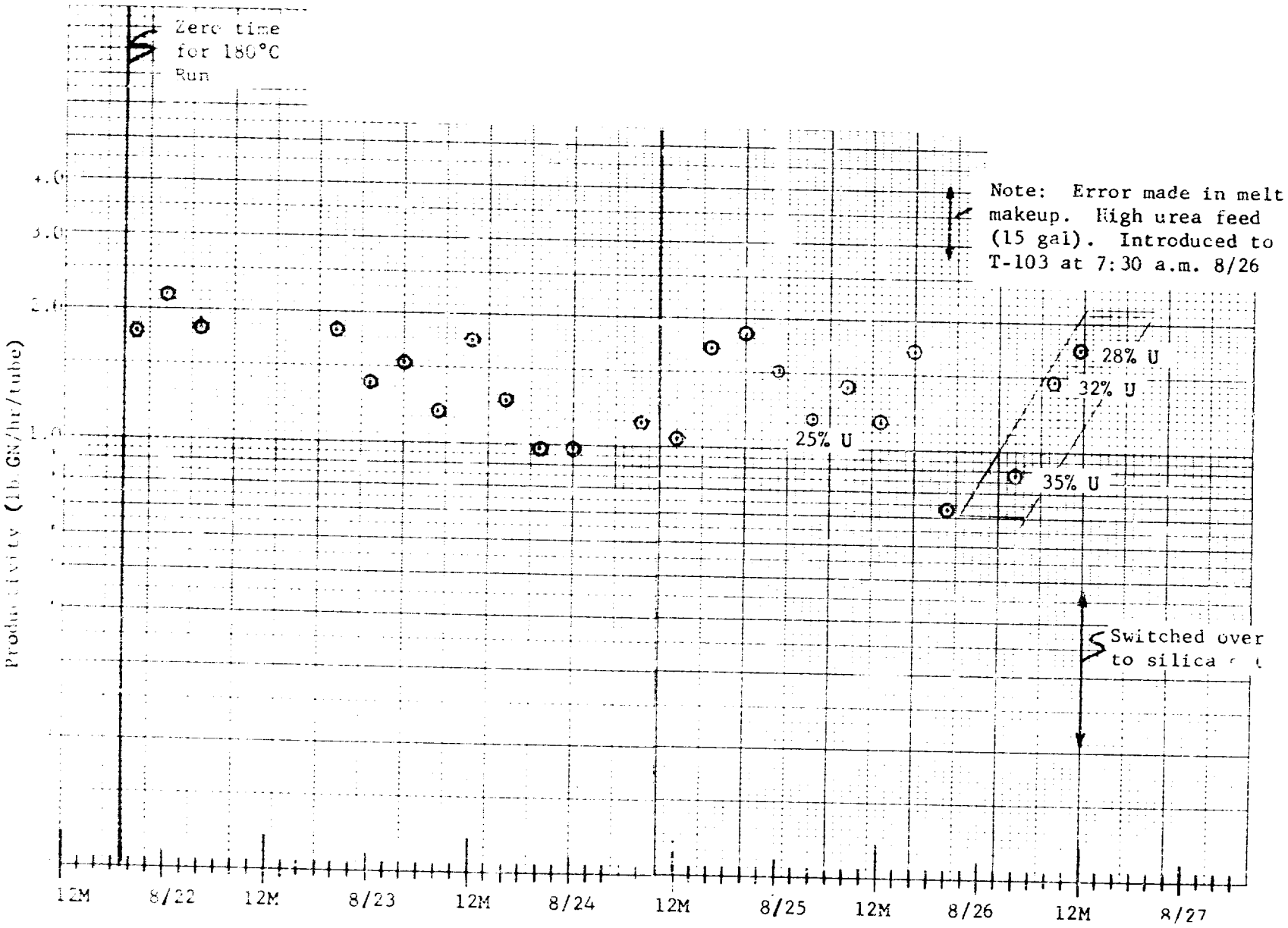



Figure 60. Catalyst Study - Mobil Sorbeads, Single Tube

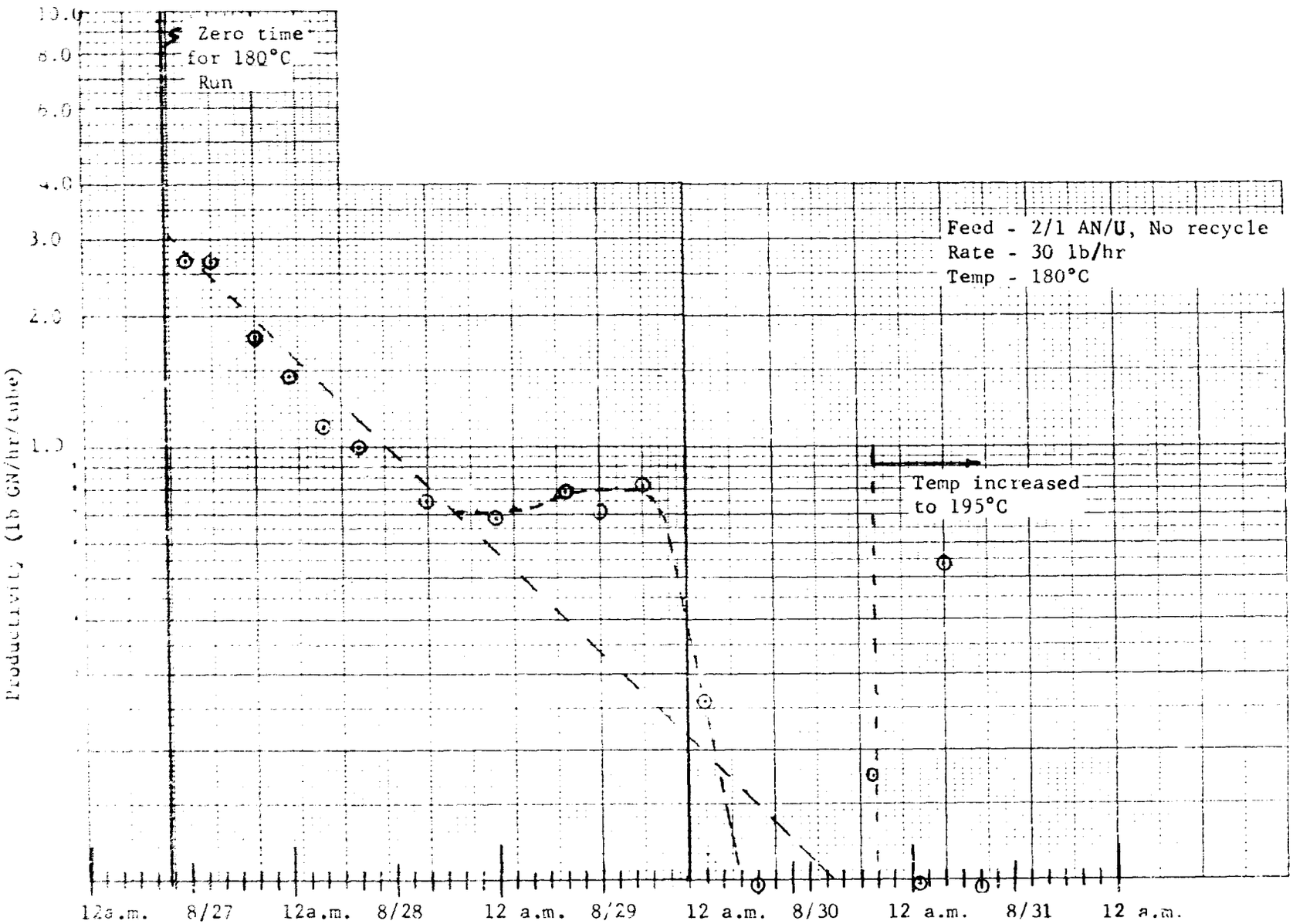



Figure 61. Catalyst Study - Grace Grade 59 Silica Gel, Single Tube

TABLE 62

## HOUDRY BEAD CATALYST LIFE RUN

| SAMPLE | | | FEED | | | | PRODUCT | | | Yield | Productivity |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Date | Time | % U | % AN | % GN | % H20 | % U | % AN | % GN | % | #GN/Hr. |
| 1 | 8/12 | 1:30 PM | 20.2 | 75.6 | 0 | 1.5 | 18.9 | 75.1 | 5.0 | 246 | 1.45 |
| 2 | 8/12 | 5:30 PM | 17.9 | 74.1 | 1.3 | 0.8 | 16.8 | 79.2 | 3.2 | 69.4 | 0.50 |
| 3 | 8/12 | 10:00 PM | 22.1 | 74.3 | 0 | 2.0 | 13.6 | 78.3 | 7.4 | 67.0 | 2.00 |
| 1 | 8/13 | 2:00 AM | 24.0 | 71.6 | 2.4 | 2.0 | 12.9 | 77.7 | 9.6 | 46.0 | 1.82 |
| 2 | 8/13 | 6:00 AM | 23.7 | 72.1 | 1.9 | 1.8 | 15.0 | 75.3 | 12.2 | 81.6 | 2.64 |
| 3 | 8/13 | 10:00 AM | 23.9 | 71.7 | 3.0 | 3.3 | 16.1 | 74.0 | 9.4 | 88.4 | 1.95 |
| 4 | 8/13 | 2.00 PM | 25.0 | 72.7 | 2.6 | 1.5 | 15.9 | 74.2 | 9.6 | 76.6 | 2.13 |
| 5 | 8/13 | 6:00 PM | 26.1 | 71.4 | 2.1 | 0.6 | 17.7 | 73.8 | 7.7 | 75.8 | 1.66 |
| 1 | 8/14 | 10:00 AM | 25.2 | 69.5 | 4.7 | 2.04 | 13.9 | 74.9 | 12.7 | 48.2 | 2.04 |
| 2 | 8/14 | 2:00 PM | 22.8 | 72.7 | 1.9 | 2.89 | 17.7 | 79.0 | 4.0 | 30.8 | 0.54 |
| 3 | 8/14 | 6:00 PM | 24.5 | 74.2 | 0.9 | 0.98 | 16.2 | 77.8 | 5.2 | 40.4 | 1.10 |
| 4 | 8/14 | 10:00 PM | 24.7 | 72.7 | 1.5 | 1.53 | 16.0 | 74.4 | 8.6 | 69.0 | 2.09 |
| 1 | 8/15 | 5:00 AM | 25.2 | 71.8 | 2.4 | 2.59 | 15.3 | 78.8 | 6.2 | 29.0 | 1.00 |
| 2 | 8/15 | 9:00 AM | 24.6 | 72.0 | 2.2 | 1.36 | 17.4 | 77.2 | 5.6 | 31.4 | 0.76 |
| 3 | 8/15 | 1:00 PM | 22.7 | 70.0 | 2.9 | 6.04 | 13.1 | 83.6 | 3.5 | 5.6 | 0.20 |
| 4 | 8/15 | 9:00 PM | 25.0 | 71.5 | 3.3 | 1.33 | 15.3 | 78.1 | 8.7 | 36.8 | 1.29 |
| 1 | 8/16 | 1:00 AM | 24.3 | 70.3 | 2.3 | 0.63 | 16.5 | 78.3 | 5.4 | 24.2 | 0.73 |
| 2 | 8/16 | 5:00 AM | 24.9 | 77.5 | 0 | 0.93 | 16.8 | 79.9 | 4.3 | 43.4 | 1.21 |
| 3 | 8/16 | 9:00 AM | 24.0 | 73.9 | 1.7 | 0.52 | 19.1 | 75.9 | 5.1 | 84.4 | 0.94 |
| 4 | 8/16 | 12:00 Noon | 24.6 | 73.3 | 2.0 | 0.44 | 20.3 | 74.2 | 4.7 | 46.6 | 0.75 |
| 5 | 8/16 | 4:30 PM | 24.7 | 73.4 | 1.5 | 0.92 | 19.0 | 75.1 | 4.1 | 36.4 | 0.72 |
| 6 | 8/16 | 8:30 PM | 24.3 | 74.0 | 2.5 | 0.85 | 22.1 | 75.0 | 3.2 | 24.4 | 0.19 |
| 1 | 8/17 | 12:30 AM | 25.9 | 72.8 | 1.3 | 0.97 | 21.0 | 75.2 | 4.2 | 35.0 | 0.62 |
| 2 | 8/17 | 4:30 AM | 24.7 | 72.9 | 2.9 | 1.12 | 21.1 | 75.1 | 4.6 | 33.0 | 0.45 |
| 3 | 8/17 | 8:30 AM | 25.2 | 72.6 | 2.4 | 0.96 | 19.8 | 75.6 | 3.2 | 10.2 | 0.20 |
| 4 | 8/17 | 12:30 PM | 23.5 | 74.1 | 3.0 | 0.82 | 19.3 | 75.7 | 5.0 | 37.2 | 0.55 |

TABLE 63

## MOBIL SORBEADS CATALYST LIFE RUN

| SAMPLE | | | FEED | | | | PRODUCT | | | Yield | Productivity |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Date | Time | % U | % AN | % GN | % $H_2O$ | %U | % AN | % GN | % | #GN/Hr. |
| 1 | 8/22 | 2:00 AM | 23.9 | 72.3 | 3.0 | 2.30 | 18.6 | 78.5 | 5.8 | 30.8 | 0.67 |
| 2 | 8/22 | 5:15 AM | 21.9 | 76.1 | 2.1 | 1.52 | 19.0 | 76.3 | 6.7 | 104.8 | 1.29 |
| 3 | 8/22 | 8:30 AM | 24.5 | 73.3 | 3.3 | 0.96 | 15.3 | 75.7 | 10.1 | 56.0 | 1.78 |
| 4 | 8/22 | 12 Noon | | | | | 15.2 | 74.1 | 10.1 | 64.4 | 2.16 |
| 5 | 8/22 | 4:00 PM | 24.5 | 72.7 | 2.2 | 1.21 | 15.4 | 70.9 | 8.5 | 62.0 | 1.82 |
| 6 | 8/22 | 8:00 PM | | | | | | | | | |
| 1 | 8/23 | 12 Midnight | | | | | | | | | |
| 2 | 8/23 | 4:00 AM | | | | | | | | | |
| 3 | 8/23 | 8:00 AM | 24.1 | 72.5 | 2.4 | 1.19 | 15.4 | 75.3 | 9.2 | 59.4 | 1.83 |
| 4 | 8/23 | 12 Noon | | | | | 17.6 | 75.2 | 7.1 | 52.8 | 1.38 |
| 5 | 8/23 | 4:00 PM | 26.0 | 72.6 | 1.9 | 1.23 | 18.7 | 74.4 | 7.5 | 58.6 | 1.53 |
| 6 | 8/23 | 8:00 PM | | | | | 19.5 | 74.6 | 6.3 | 60.0 | 1.18 |
| 1 | 8/24 | 12 Midnight | 25.5 | 72.5 | 0.0 | 1.46 | 19.6 | 73.7 | 6.2 | 78.4 | 1.73 |
| 2 | 8/24 | 4:00 AM | | | | | 18.7 | 73.9 | 6.6 | 60.0 | 1.26 |
| 3 | 8/24 | 8:00 AM | 25.4 | 72.4 | 0.0 | 1.39 | 19.5 | 74.7 | 5.2 | 44.0 | 0.88 |
| 4 | 8/24 | 12 Noon | 25.3 | 73.6 | 1.0 | 0.40 | 19.5 | 74.8 | 4.1 | 43.4 | 0.88 |
| 5 | 8/24 | 4:00 PM | | | | | | | | | |
| 6 | 8/24 | 8:00 PM | 26.3 | 72.0 | 0.0 | 1.20 | 21.6 | 73.3 | 4.0 | 63.2 | 1.14 |
| 1 | 8/25 | 12:00 AM | | | | | 19.8 | 73.0 | 5.3 | 54.0 | 1.05 |
| 2 | 8/25 | 4:00 AM | 25.9 | 72.9 | 0.5 | | 19.7 | 73.2 | 6.5 | 72.0 | 1.71 |
| 3 | 8/25 | 8:00 AM | | | | | 19.8 | 72.5 | 7.2 | 103.0 | 1.83 |
| 4 | 8/25 | 12:00 PM | 24.3 | 73.1 | 1.5 | 0.41 | 19.4 | 73.7 | 7.0 | 84.6 | 1.53 |
| 5 | 8/25 | 4:00 PM | 25.5 | 72.1 | 1.9 | | 19.4 | 73.8 | 6.2 | 53.2 | 1.18 |
| 6 | 8/25 | 8:00 PM | 23.9 | 74.8 | 1.5 | | 20.8 | 73.4 | 6.2 | 130.0 | 1.40 |
| 1 | 8/26 | 12:00 AM | 22.2 | 77.4 | 2.9 | | 19.9 | 73.7 | 6.7 | 191.0 | 1.16 |
| 2 | 8/26 | 4:00 AM | 25.7 | 73.5 | 1.6 | | 20.0 | 73.1 | 7.6 | 84.3 | 1.70 |
| 3 | 8/26 | 8:00 AM | | | | | 19.1 | 74.1 | 4.6 | 36.0 | 0.73 |
| 4 | 8/26 | 12:00 PM. | | | | | | | | | |
| 5 | 8/26 | 4:00 PM | 35.2 | 60.6 | 2.8 | | 25.2 | 68.0 | 6.6 | 22.0 | 0.885 |
| 6 | 8/26 | 7:30 PM | 32.0 | 65.6 | 0.6 | | 26.4 | 65.2 | 7.2 | 135.2 | 1.72 |
| 7 | 8/26 | 11:30 PM | 28.2 | 68.5 | 1.8 | | 24.4 | 65.9 | 7.7 | 109.0 | 1.47 |

TABLE 64

GRADE 59 SILICA GEL CATALYST LIFE RUN

| SAMPLE | | | FEED | | | | PRODUCT | | | Yield | Productivity |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Date | Time | % U | % AN | % GN | % $H_2O$ | % U | % AN | % GN | % | #GN/Hr. |
| 1 | 8/27 | 4:30 AM | | | | | | | | | |
| 2 | 8/27 | 8:00 AM | | | | | | | | | |
| 3 | 8/27 | 12:00 PM | 25.8 | 71.8 | 1.8 | 1.26 | 19.2 | 69.9 | 10.9 | 115.4 | 2.68 |
| 4 | 8/27 | 3:00 PM | 25.1 | 70.5 | 2.4 | | 15.3 | 69.4 | 12.1 | 80.2 | 2.66 |
| 5 | 8/27 | 8:00 PM | 25.1 | 73.1 | 1.8 | | 17.2 | 73.3 | 8.2 | 66.2 | 1.78 |
| 6 | 8/27 | 11:59 PM | 22.3 | 75.6 | 2.2 | | 17.3 | 74.9 | 7.3 | 77.2 | 1.45 |
| 1 | 8/28 | 4:00 AM | 26.4 | 72.0 | 2.4 | | 17.7 | 75.6 | 5.5 | 37.6 | 1.11 |
| 2 | 8/28 | 8:00 AM | 25.6 | 71.7 | 2.5 | 1.80 | 18.1 | 75.0 | 6.3 | 37.4 | 1.00 |
| 3 | 8/28 | 12:00 Noon | | | | | | | | | |
| 4 | 8/28 | 4:00 PM | 23.4 | 72.7 | 2.2 | | 20.3 | 75.6 | 5.0 | 57.2 | 0.75 |
| 5 | 8/28 | 8:00 PM | | | | | | | | | |
| 1 | 8/29 | 12:01 AM | 24.1 | 73.8 | 2.2 | | 19.7 | 75.4 | 3.7 | 44.4 | 0.69 |
| 2 | 8/29 | 4:00 AM | | | | | | | | | |
| 3 | 8/29 | 8:00 AM | 25.5 | 73.4 | 1.6 | 0.29 | 20.9 | 74.3 | 4.4 | 48.2 | 0.79 |
| 4 | 8/29 | 12:00 Noon | 24.7 | 74.3 | 1.0 | 0.86 | 20.0 | 75.5 | 3.5 | 43.0 | 0.71 |
| 5 | 8/29 | 5:00 PM | 24.4 | 74.3 | 1.1 | 0.96 | 19.3 | 75.6 | 4.0 | 46.2 | 0.82 |
| 6 | 8/29 | 8:00 PM | 24.9 | 74.3 | 1.2 | | 20.6 | 76.9 | 1.4 | 0.9 | 0.001 |
| 1 | 8/30 | 12:00 Midnight | 25.6 | 74.0 | 1.2 | | 21.4 | 75.1 | 2.1 | 15.5 | 0.26 |
| 2 | 8/30 | 4:00 AM | 25.3 | 73.3 | 2.3 | | 21.1 | 74.7 | 1.7 | - | Negative |
| 3 | 8/30 | 8:00 AM | 25.0 | 71.9 | 1.5 | 2.35 | 18.0 | 79.3 | 2.0 | 3.5 | 0.093 |
| 4 | 8/30 | 12:01 AM | 21.4 | 74.0 | 3.07 | | 16.5 | 78.9 | 1.05 | - | Negative |
| 5 | 8/30 | 4:00 PM | 21.9 | 75.7 | 0.97 | | 17.2 | 77.4 | 5.90 | 75.8 | 0.89 |
| 6 | 8/30 | 8:00 PM | 21.7 | 73.6 | 1.65 | | 16.5 | 75.7 | 2.59 | 15.0 | 0.174 * |
| 1 | 8/31 | 12:30 AM | 23.7 | 73.5 | 2.26 | | 16.6 | 76.4 | 2.74 | 4.6 | 0.072 |
| 2 | 8/31 | 4:30 AM | 22.7 | 73.7 | 1.24 | | 16.8 | 76.6 | 3.99 | 36.4 | 0.54 |
| 3 | 8/31 | 8:00 AM | 27.0 | 72.7 | 2.50 | 1.06 | 19.8 | 76.7 | 1.80 | - | Negative |
| 4 | 8/31 | 12:00 AM | | | | | | | | | |

*Increased temperature to 195° C

The data workup procedure which was used was based solely on feed and product analyses. These calculations are, of course, strongly aligned to analytical variations, but a high frequency of samples has been shown to demonstrate trends.

a. Houdry 4mm Experimental Silica Beads - Catalyst Life Pilot Plant Run No. 1

This run was initiated on August 12, 1972. The major data collected are summarized in Table 62, and the productivity data are plotted in Figure 59. Although the data are scattered because of sampling and analytical errors and the method of calculation, a definite decaying trend can be seen. Within five days, the average tube productivity (at 2/1 AN/U feed ratio, 180°C) was down to ~ 15% of its original value. This entire run was operated with virgin feed (Hercules MCW AN prills, Olin commercial urea). It was planned to introduce recycle feed after three days, but the decaying pattern was already apparent. The catalyst bed for this run was not thermally cycled at all during the run. There were some periods when feed to the reactor was interrupted by feed line plugging at the low flow rate. The following findings and conclusions were derived from this run:

(1) One of the speculated possible catalyst fouling theories, that of pores plugging with ammelide, had to be considered unlikely. In the five days of operation at 180°C, only a trace amount of water insolubles, presumed to be ammelide, was collected (~ 0.001%). The theory that ammelide formation can be all but eliminated at 180°C and an excess AN concentration has certainly been verified.

(2) Another theory advanced to explain catalyst fouling, that the catalyst is poisoned when its surface active sites are lost because of adsorbed water or trace amount of decomposed reagents, appeared to be a strong possibility. The loss of feed to the tubes on a few occasions resulted in feed cooking in the reactors for longer periods and also required more feed line steam-outs (more possible water pickup by the feed). The gradual decay of the productivity data in Figure 59 suggests a gradual loss of catalyst "active" surface.

(3) The raw analysis in Table 62 indicates the need for refinement of the methods. Since virgin feed was used during this entire run, no guanidine nitrate should have been detected in the feed samples. It can be seen, however, that these feed samples average about 2% GN. The sample

results also show the strong hygroscopic effects of the samples. The product from the reactor cannot contain water. The results indicate that they do. This water is in the sample but is most probably picked up during the sampling and cooling period.

Yields are included in Table 62. As can be seen, the calculated yields showed extensive scatter. This scatter is attributed to yield losses caused by water in the feed and by the use of the feed and product analyses only in the calculation method. A 1 to 2% urea analysis variance, within the accuracy of the method, projects to a 6-12% change in the resultant yield. The yields were calculated for academic reasons only. Actual yields would have to be calculated from a material balance run.

(4) The melt from the reactor during the entire run was waterwhite in color. This is the same effect seen in the Kenvil bench scale column in Phase I when the ammelide formation was minimal.

(5) After the catalyst run was completed, the bed was drained of melt and then the heat turned off. When the reactor was dismantled, the beads were very easily removed, indicating that preventing over-reaction in the beds, eliminating thermal cycling and thorough draining, will facilitate easy catalyst changing.

(6) The initial productivity from this run is in line with that predicted from the computer program of Phase I. A few additional computer cases were run this month. The results are shown in Figures II-17 and II-18 in Appendix II and Figure 62. The GN production rates shown on Figure II-18 (180°C jacket) for a melt feed rate of 30 lb/hr is 3.4 lb/hr. Extrapolating Figure 59 to zero time results in a GN production rate of about 2.6-3.2 lb/hr.

b. Catalyst Life Pilot Plant Run No. 2 - Mobil Sorbead R Desiccant

Run No. 2 was initiated on August 22 and terminated on August 27, 1972. Table 63 and Figure 60 show respectively the raw data and productivity curve. Again a decaying activity was apparent, so recycle material was not introduced. The pilot plant operated mechanically very well during this run. There was no thermal cycling on the catalyst bed and a minimal amount of feed down-time. The first four conclusions that were made for the Houdry Bead run apply to this run. In addition, the following points can be made:

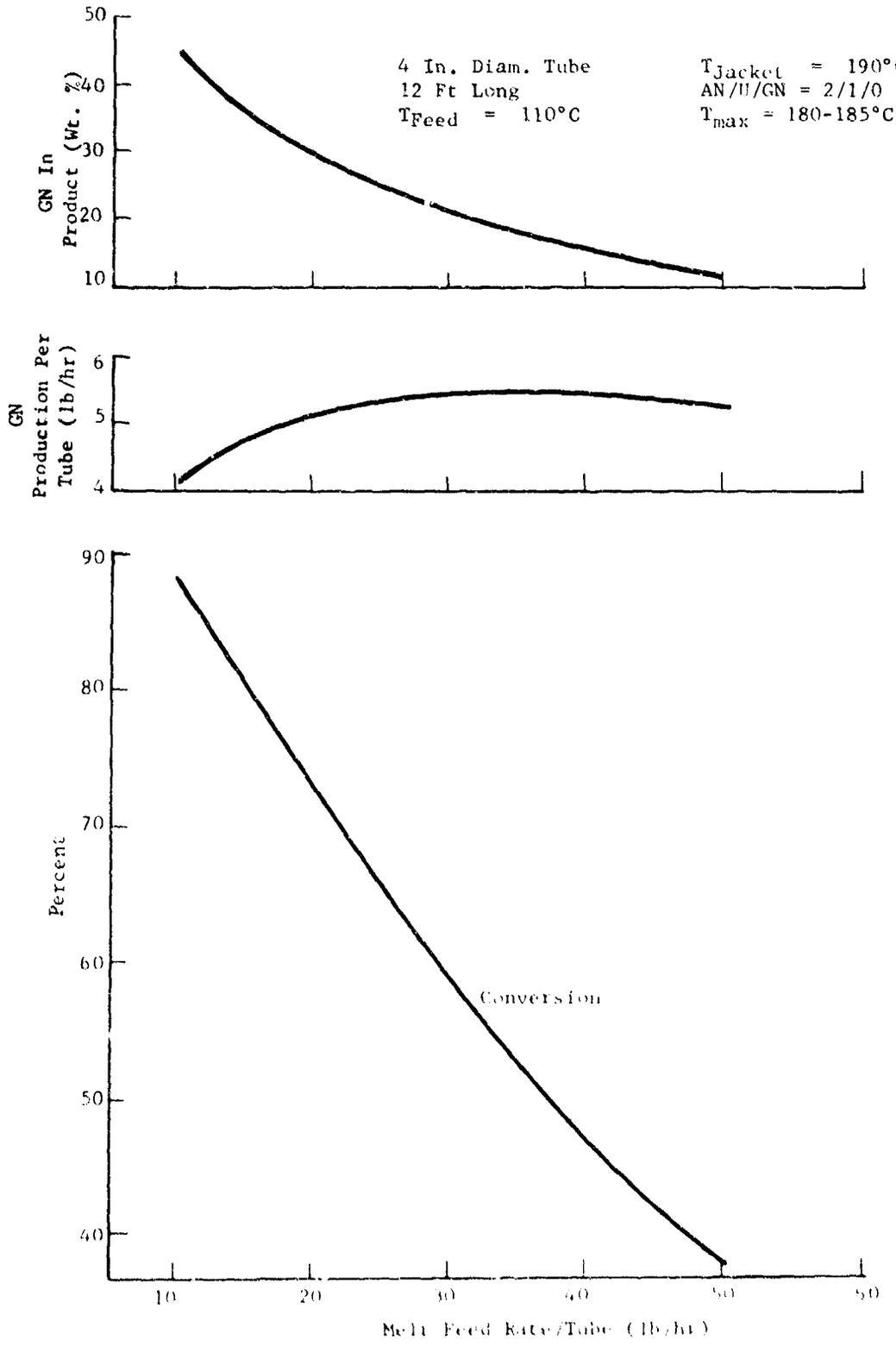



Figure 62. Computer Prediction

(1) The productivity curve in Figure 60 appears to cycle in a somewhat downward trend. It is postulated that the cycling effect is being caused by two factors. One of these factors is catalyst attrition. Operating personnel noted catalyst fines coming over with the product on the first upward swing of Figure 60 (12 midnight, 8/24). Also, on shutdown, approximately half of the bed was recovered as catalyst fines. The second factor for the cycling was an operator error on the feed makeup. A high U/AN fresh melt (120 lb urea/45 lb AN) was made up instead of the reverse during the latter part of the run.

(2) The original catalyst beads charged to the reactor were quite dark. The by-product collected in the solid bowl centrifuge was extremely dark (dark brown), suggesting an extraction of trace impurities from the beads. The recovered beads still were colored but not as dark as originally. This observation is in line with the Phase I batch runs of a colored product although the pilot plant product melt appeared clear.

(3) The original productivity was not as high as that obtained with the Houdry beads but the decay rate was lower. This might be explained by the effective catalyst surface theory.

c. Catalyst Life Pilot Plant Run No. 3 - Davidson Grace 59 Silica Gel

This run (No. 3) was initiated on August 27 and terminated on August 30, 1972. The major data collected are summarized in Table 64, and the productivity data are plotted in Figure 61. The decaying slope for this run is obvious and drastic. After 15 hours, the productivity had dropped to half its original value. Again this run was operated with virgin feed (no recycle) and the bed was not thermally cycled at all. Feed to the reactor was continuous at all times. The first four conclusions made for the Houdry bead run can also be made for this run. In addition:

(1) There is what appears to be a plateau in the productivity curve of Figure 61. This can be attributed to catalyst breakup. On the catalyst dump following this run, a portion of the silica gel (~ 10-20%) was recovered as fines.

(2) One speculation of the poisoning mechanism was adsorption on the catalyst surface of a product, by-product, or impurity followed by limited desorption. Since the decay slopes of the three catalyst study runs were greater than experienced in production Run No. 2 (Figure 58) and since these runs were at 180°C, rather than 190°-192°C, it was thought that a temperature increase might increase the desorption phenomenon and result in a change of the decay slope. Since the catalyst activity decay was apparent on 8/30/72 and one more operating day was available, the reactor temperature was increased to 195°C. As can be seen from the data in Figure 61, the data are erratic and do not suggest any change.

d. Catalyst Study Runs - Interpretation

One initial interpretation that is apparent from the data is the correlation between initial catalyst activity, pore diameter and rate of decay. The silica gel has the highest initial activity, probably because its pore diameter is by far the largest and all of the internal pore surfaces are available for reaction. It loses its activity the fastest, which is perhaps due to plugged pores. Its effective surface area then drops to a small fraction of its original value. The Houdry beads are next in line in this effect and then the Sorbeads.

After the three single-tube runs had been completed, a meeting was held between Picatinny Arsenal and Hercules personnel to review the above data. It was decided to curtail pilot plant operations and to further investigate the chemistry of the process via analytical methods, literature surveys, batch reactor experiments, and operation of a one-inch diameter continuous reactor. These efforts are discussed in the next section.

## D. PHASE III - PART 2, RESOLUTION OF CATALYST POISONING PROBLEM

### 1. Summary

The previous section (Phase III-Part 1) describes the two series of attempts to produce 40,500 pounds of guanidine nitrate. Since the operations were unsuccessful because of catalyst poisoning (confirmed with single, 4-inch-diameter reactor runs with three different types of catalysts), the program emphasis was diverted from production to process research. This latter emphasis involved laboratory reactor studies, analytical research, literature searches, 1-inch-diameter reactor studies, and pilot plant reactor operations related to resolving the catalyst poisoning phenomenon. In addition, some work was also performed to resolve the GN drying problem.

Thin-layer chromatography (TLC) analytical techniques were employed to determine the presence of impurities suspected of deactivating the silica gel type catalysts. Samples of spent Houdry CP-532 macroporous silica beads removed from one of the pilot plant reactors were extracted with water and a base. Analysis of the resulting solution by TLC definitely showed the presence of melamine, ammeline, ammonium nitrate and urea. Other possible contaminants were ammelide, cyanuric acid and biuret. None of these triazine compounds were detected in pilot plant feed and reactor product samples by the TLC method. A sample of pilot plant feed aged for four days at 110°C and displaying a dramatic loss of urea did not exhibit any of the above triazines by TLC. Samples of feed and product from the GN pilot plant operations (when employing Hercules' MCW ammonium nitrate and Olin urea) were analyzed for elemental boron and phosphates. The data showed that both elements were adsorbed initially onto Houdry Silica Beads and Grace 59 Silica Gel. Microscopic examinations of split Houdry beads at magnifications of 10X to 75X showed no obvious shells of insolubles encasing the catalyst beads.

Several one-liter batch reaction experiments were carried out as a part of the catalyst poisoning effort. The major results from these experiments were as follows: (a) Houdry silica beads recovered from the pilot plant reactors had lost their activity; (2) washing the used Houdry beads restored part of their activity but at the expense of particle attrition; (3) utilization of Hercules MCW ammonium nitrate resulted in lower catalyst performance as compared to reagent grade AN.

A 1-inch-diameter, 3-ft.-tall downflow reactor was fabricated and installed to investigate the catalyst poisoning problem. This reactor was sized to approximate that employed by MacKay of Pittsburgh Coke and Chemical Company. A critical path experimental program was developed and followed. For the initial nine experimental runs, Grace grade 59 silica gel catalyst was employed. Ammonium nitrate and urea of different types and/or treatment conditions were employed. The results of the experiments clearly demonstrated that the primary cause for pilot plant catalyst poisoning was due to the presence of a

crystal habit modifier (Permalene*) incorporated into the Hercules' MCW ammonium nitrate. It was further resolved that the actual poison was diammonium phosphate.

Confirmation of the above 1-inch-diameter reactor results was attempted in the 4-inch-diameter pilot plant reactor with Grace grade 59 silica gel and additive-free Hercules' Donora AN plus Olin urea. Four experiments were attempted, and in each case high pressures developed in the reactor feed line. In most cases, the silica gel had at least partially broken down. The physical breakdown was attributed to the presence of water in the feed. Subsequent 1-inch-diameter reactor and beaker experiments showed that both anhydrous and water-wet hot melt (AN and U) caused Grace 59 silica gel attrition. This was not the case with Houdry silica beads. A nominal 1% water in feed resulted in poisoning Grace 59 silica gel at a mileage of 13 gm GN/gm catalyst. These results decisively disqualified Grace 59 silica gel catalyst for use in packed bed tubular reactors.

A 338-hour experimental run in the 1-inch- diameter reactor with Houdry silica beads and feed melt containing about 1% by weight water resulted in a minimum catalyst mileage of 68 gm GN/gm catalyst, and 558 displacements (gm feed/gm catalyst). The beads showed no signs of poisoning or physical breakdown.

A single, 4-inch-diameter reactor, loaded with Houdry beads, was operated for five days (115 hours actual feed time) under conditions similar to those for the above 1-inch-diameter reactor run. Operation of this run (without recycle) produced the following results: (a) production rate of 9 lb GN/hr/tube, (b) 38 lb GN/lb catalyst mileage, (c) 83% urea conversion, (d) 95% GN yield, (e) 98% overall weight material balance, (f) no evidence of catalyst poisoning, (g) retention of Houdry bead physical characteristics and (h) very good agreement with temperature profile, conversion, yield and productivity values predicted using the packed bed tubular reactor mathematical model.

The results obtained from the latter 1-inch- and 4-inch-diameter reactor experiments were comparable to those obtained by previous researchers with virgin feed.

Experiments related to drying water-wet GN showed that indirect heated and agitated dryers such as the Strong-Scott and Littleford units are unsatisfactory. This type of equipment results in the formation of a GN-water paste

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*Boric acid, diammonium phosphate and diammonium sulfate

followed by evaporation of the water which leaves a hard mass of GN adhered to the dryer internal walls. Direct heated drying; e.g., a jet zone Wolverine dryer or cloth bags in a forced air dry house, produces a satisfactorily dried material.

## 2. Approach

Preceding sections entitled "Phase I," "Phase II," and "Phase III" presented discussions detailing laboratory studies relative to reaction kinetics, catalyst evaluations, GN purification, etc.; mathematical modeling; process economics; and pilot plant operations. The major problem encountered at that time was a rapid catalyst activity decay in terms of productivity (lb GN/hr) and catalyst mileage (lb GN/lb catalyst). Productivity and mileage results were such that continued operation of the pilot plant for GN production was not justified. Furthermore, no conclusive recommendations could be made regarding the design of a full-scale production plant. Consequently, the program emphasis was directed towards resolving the catalyst deactivation problem. This program redirection consisted of additional laboratory batch reactor experiments, analytical scouting experiments, literature searches, and scouting plus demonstration runs in both a 1-inch-diameter downflow reactor and a 4-inch-diameter pilot plant reactor. Miscellaneous activities consisted of guanidine nitrate drying and catalyst supplies. The results of these efforts are discussed in the following sections.

## 3. Catalyst Poison Scouting - Analytical Methods

To assist in solving the catalyst deactivation problems encountered in the pilot plant, the analytical group at the Research Center initiated a search for a method to identify trace impurities present in the Kenvil pilot plant feed, product and catalyst samples. The compounds considered likely as the poisoning impurities were biuret, melamine, ammeline and cyanuric acid.

The compounds referred to above and those extracted by water and base from beads supplied from the pilot plant were compared by thin layer chromatography (TLC). The best chromatographic system found consisted of Cellulose MN 300 plates and a methanol ammonia developing solvent. By this method it was shown that melamine, ammeline, AN and urea were present in the extracts from used pilot plant Houdry beads and possibly ammelide, cyanuric acid and biuret.

Analytical studies of contaminants and by-products in the Kenvil pilot plant reactor feed and product streams were performed.

Several samples of reactor feed taken at 12-hour intervals (AN and U) from a single 4-inch reactor run were analyzed by the TLC method (cellulose MN 300 plates and a methanol/ammonia developing system). Comparison of the

feed samples with control samples containing 1% add-backs of melamine, ammelide, ammeline, cyanuric acid and biuret showed that these compounds were not present at the 1% by weight level and probably not even at the 0.5% level.

Selected Kenvil aged samples of AN and U (2/1 molar ratio) shown in Table 65 were analyzed by the TLC method for possible contamination with triazine compounds. The samples analyzed are listed below:

Aged AN/U Feed Samples Analyzed by TLC

| Sample Designation | Hours Aged @ 110°C |
|---|---|
| X2130-77-1 | 3 |
| X2130-77-3 | 7 |
| X2130-77-5 | 25 |
| X2130-77-7 | 31 |
| X2130-77-9 | 96 |

The above individual samples were put into solution and spotted onto a 250-micron cellulose MN 300 TLC plate which was developed in a solution of methanol and 3N ammonia (60:75 ratio). Standard solutions of cyanuric acid, melamine, ammelide, ammeline and biuret were also spotted on the same plate. After the plate was developed and dried in an oven for a few minutes, a silver nitrate/ammonia spray was used to reveal the chromatogram. The mentioned triazines, which are detectable by this method at the 100 ppm level, were not found in the aged feed samples. Biuret also was not detected at this level. Two other spray reagents (dimethylamino benzaldehyde and Sakaguchi reagent) which are suggested in the literature for use with biuret were also tested with no success up to what would be equivalent to 0.3% biuret in the feed samples. Efforts were made to detect biuret with another chromatographic system which consisted of an acidic developing solvent - silica gel TLC plates but with no success.

Feed and product melt samples from a single 4-in.-diameter reactor run with Grace 59 silica gel catalyst were analyzed by TLC. The samples covered the time span from 12:00 noon, August 27 through 8:30 a.m., August 30. There was no evidence of cyanuric acid, melamine, ammeline or ammelide in any of the samples at the 100 ppm level.

Sodium hydroxide extracts of used Houdry beads and Grace 59 silica gel catalysts were spotted on cellulose MN 300 TLC plates along with the above noted triazine compounds as well as boric acid and diammonium hydrogen phosphate (DAP). While melamine was found in both extracts, the Grace 59 silica gel contained less than the Houdry beads. Since the Rf values for cyanuric acid and ammeline are almost the same, it is difficult to distinguish between the two. However, it did appear that one or both of these compounds had been

TABLE 65

STORAGE OF HERCULES' MCW AN AND OLIN UREA AT 110°C

| Sample X2130-77- | Time | Day | Storage (Hours) | Analysis (Wt. %) U | AN | GN (1) | Notes |
|---|---|---|---|---|---|---|---|
| - | 9:00 AM | 9-14-72 | 0 | 25.0 | 75.0 | - | Solids |
| -1 | 12 Noon | " | 3 | 20.0 | 77.4 | 4.2 | Melt * |
| -2 | 2:00 PM | " | 5 | 22.8 | 76.5 | 3.4 | " |
| -3 | 3:55 PM | " | 7 | 18.2 | 78.5 | 3.0 | " |
| -4 | 8:00 AM | 9-15-72 | 23 | 19.6 | 77.6 | 1.5 | " |
| -5 | 10:00 AM | " | 25 | 21.6 | 75.6 | 2.6 | " |
| -6 | 1:00 PM | " | 28 | 20.7 | 76.4 | 2.2 | " |
| -7 | 4:00 PM | " | 31 | 18.4 | 78.4 | 2.8 | " |
| -8 | 8:30 AM | 9-18-72 | 96 | 10.7 | 87.4 | 2.0 | " |
| -9 | 8:30 AM | " | 96 | 9.6 | 87.6 | 2.7 | " |

(1) Nitrates not attributed to AN (direct titration) calculated as GN

* $H_2O$ by KF ranged between .05% - .26%

extracted from both catalysts. DAP did not appear as a spot but as a broad streak on cellulose MN 300 plates when methanol/$NH_3$ was used as developing agents. Both extracts contained a material which streaked in the same manner and, therefore, could be presumed to be DAP. Boric acid was not detected.

As noted previously, it was learned that Hercules' MCW ammonium nitrate (used in pilot plant operations) contained boric acid, diammonium phosphate and diammonium sulfate. Samples of Kenvil pilot plant reactor feed and product melt streams were analyzed for elemental boron and phosphorous to determine if these materials were adsorbed by the silica gel catalyst. Data from two sets of samples are presented in Table 66. These results show that initially both boron and phosphorous are adsorbed onto the catalyst. Apparently, the catalyst becomes saturated as a function of time and then the concentration of boron and phosphorous in the effluent approximates that in the feed stream.

TABLE 66

ANALYSIS OF 4-INCH-DIAMETER REACTOR FEED AND PRODUCT SAMPLES FOR BORON AND PHOSPHOROUS

1. Houdry Bead Single Tube Run

| Sample | Kenvil No. | Date (1972) & Time | P (ppm) | B (ppm) |
|---|---|---|---|---|
| Feed | 1S-1 | 8/12; 1:30 P.M. | 290 | 100 |
| Product | 2S-1 | 8/12; 1:30 P.M. | 6 | 20 |
| Feed | 1S-4 | 8/17; 2:00 P.M. | 300 | 80 |
| Product | 2S-4 | 8/17; 2:00 P.M. | 170 | 200 |

2. Silica Gel Single Tube Run

| | | | | |
|---|---|---|---|---|
| Feed | 1S-3 | 8/27; 12:00 P.M. | 420 | 140 |
| Product | 2S-3 | 8/27; 12:00 P.M. | 12 | 30 |
| Feed | 1S-2 | 8/28; 8:00 A.M. | 490 | 150 |
| Product | 2S-2 | 8/28; 8:00 A.M. | 7 | 50 |
| Feed | 1S-3 | 8/30; 8:00 A.M. | 420 | 140 |
| Product | 2S-3 | 8/30; 8:00 A.M. | 730 | 100 |

4. Catalyst Poison Scouting - Batch Reactor Experiments

The overall objective of the effort conducted at the Chemical Engineering Division at the Research Center was to help resolve the catalyst deactivation that arose during the operation of the pilot plant. Specific objectives for this effort were as follows:

(a) Verify in a laboratory-batch experiment that the dry catalyst used in the pilot plant reactor had lost its activity.

(b) Determine if the spent catalysts can be reactivated by washing.

(c) Check out the initial activity of Mobil Sorbead R and Grace grade 59 silica gel for support of pilot plant runs.

(d) Explore whether or not the grades of AN and urea actually used in the pilot plant contribute to catalyst poisoning.

(e) Measure the solubility in reaction melt of the water insolubles from the solid bowl centrifuge.

(f) Examine spent Houdry beads microscopically for clues to deactivation.

The reactor was a 1-liter glass resin kettle fitted with a 5-port lid. The reactor was supported in a controlled temperature, silicone oil bath and stirred at ~ 60 rpm by a single-blade agitator. Off-gases were condensed in a series of dry ice traps. Reaction liquid samples were taken by drawing reaction melt by vacuum into a glass tube with a tapered tip. The procedure for a typical batch run was as follows:

(a) Preheat the oil bath to about 5-10°C above the desired reaction temperature.

(b) Charge solid urea and ammonium nitrate (usually reagent grade) to the reaction kettle.

(c) Melt the solids and heat to 5-10°C above the reaction temperature.

(d) Heat the catalyst to 190°C (30-45 minutes) and add to the reaction vessel. (Start the reaction time clock.)

(e) On addition of the catalyst, the reaction temperature drops to the desired level. The temperature is controlled with an oil bath thermostat.

(f) Take liquid samples several times during the run.

The reaction samples were analyzed for urea by the urease method, for AN by the formaldehyde precipitation method, and for GN by difference between total nitrate by UV and ammonium nitrate. GN yield and urea conversion were calculated as outlined in Phase I. The yield was based on urea reacted and the assumption that all the ammonium nitrate goes to guanidine nitrate.

Table 67 summarizes the batch runs made to check activity of used Kenvil catalyst, etc. Table III-1 in Appendix III gives the detailed data for these runs. Runs 42 and 43 were made to check out the equipment and confirm that the results were consistent with Phase I, Runs 30 and 31. The GN yields and urea conversions from these 180°C and 190°C Houdry bead runs were comparable with these parameters for Runs 42 and 43 made at the same conditions.

Runs 44 and 45 were made to confirm that the Houdry catalysts from a pilot plant run had lost activity.

Because the used beads contained quantities of reaction mixture, the catalyst charge to a batch run was made on a volumetric basis. About 335 ml of used beads were charged; this represents a volume of 153 gm of new beads. Since the composition of the 182 gm of Kenvil reaction mixture in the used beads was unknown, the amount of GN produced was based on assuming one mole of GN was made for each mole of ammonium carbamate recovered. Catalyst mileages (gm GN/gm catalyst) were then calculated and compared to results from a fresh bead run. The mileages from Runs 44 and 45 were 0.17 and 0.10 compared with 0.73 and 0.76 obtained with new beads.

After establishing that used Houdry beads had been deactivated, attempts were made to regenerate the catalyst using aqueous washes. Run 46 was made with a cold water-washed sample of the same beads as used in Run 44. The washed beads had a mileage of 0.31 gm GN/gm catalyst but the GN yield and urea conversion were lower than those in Run 42. Runs 50 and 51 were made to determine if $Na_2CO_3$ or KOH washes improved the activity of beads relative to the activity of untreated beads from Run 48. The results were similar to those obtained with straight water washing.

In all cases the aqueous washes seriously reduced the size of the beads. For this reason and the high costs of regenerating a $2/lb catalyst, it was felt an aqueous regeneration scheme would not be practical.

Run 47 was made to verify Run 15 made in Phase I at 190°C. The two runs were comparable. Run 49 was a Sorbead run at 180°C, made to provide a comparison for Kenvil pilot plant results. The yield for Run 49 (180°C) was higher than for Run 47 (190°C), but the latter run at 190°C had double the productivity.

A total of six additional batch reactor experiments were carried out to determine the effects of commercial grades of AN and U used in the pilot plant operations on yield and conversion. The runs made are summarized in Table 68, and the detailed data are presented in Table III-2 of Appendix III.

TABLE 67

SUMMARY OF KENVIL CATALYST PROBLEM STUDIES

(Stirred Batch Experiments with 2/2/1 AN/U/Cat)

| Run No. | RXN Temp. °C. | Catalyst Used | Run Time Min. | Urea Conv. % | GN Yield % | Molar Ratio of Carbamate to GN | Wt. GN / Wt. Cat. |
|---|---|---|---|---|---|---|---|
| 42 | 190 | New Kenvil Houdry | 62 | 67.3 | 90.7 | 0.93 | 0.73 |
| (30) | 190 | (New Houdry) | (61) | (72.9) | (87.8) | (0.94) | (0.76) |
| 43 | 180 | New Kenvil Houdry | 46 | 40.5 | 81.7 | - | 0.41 |
| (31) | 180 | (New Houdry) | (47) | (37.3) | (60.7) | - | (0.49) |
| 44 | 190 | Used Houdry (Top R-200) | 69 | - | - | 1.0* (*Assumed this ratio) | 0.17 |
| 45 | 190 | Used Houdry (Top R-201) | 150 | - | - | 1.0* | 0.10 |
| 46 | 190 | Water Washed(Top R200) | 61 | 49.0 | 52.0 | 1.1 | 0.31 |
| 48 | 190 | Used Houdry(Top Rxs | 61 | - | - | 1.0* | 0.15 |
| 50 | 190 | Hot $Na_2CO_3$(5%) Washed from Top Rxs | 62 | 44.0 | 47.0 | 1.1 | 0.36 |
| 51 | 190 | Hot Alc.-KOH Washed from Top Rxs | 61 | 48.0 | 68.0 | 0.79 | 0.35 |
| 47 | 190 | New Sorbead R | 61 | 65.1 | 65.4 | 1.28 | 0.51 |
| (15) | 190 | (New Sorbead R) | 60 | 58.8 | 67.4 | 1.1 | - |
| 49 | 180 | New Sorbead R | 136 | 66.0 | 71.0 | 1.14 | 0.56 |

TABLE 68

SUMMARY OF GRACE 59 SILICA GEL RUNS

(Stirred Batch Experiments with 2/2/0.85 Molar Ratio AN/U/SG at 190°C)

| Run No. | Feed Materials AN | Feed Materials Urea | GN Yield (%) | Urea Conv. (%) | Molar Ratio of Carbamate to GN | Wt. GN / Wt. S G | RXN Time (Min.) |
|---|---|---|---|---|---|---|---|
| 52 | Reagent | Reagent | 72.7 | 65.1 | | .566 | 61 |
| | | | 87.5 | 85.8 | .809 | 1.84 | 264 * |
| 53 | Heat Aged MCW | Heat Aged Olin | 60.4 | 70.2 | | .507 | 61 |
| | MCW | Olin | 57.0 | 62.2 | 1.63 | .847 | 143 * |
| 54 | MCW | Olin | 37.1 | 58.8 | 2.23 | .521 | 120.7 |
| 55 | MCW | Olin | 67.1 | 63.5 | | 1.02 | 121.0 |
| | | | 77.4 | 73.8 | 1.04 | 1.37 | 173.8 |
| 56 | Reagent | Olin | 53.1 | 52.9 | | .623 | 60.1 |
| | | | 78.5 | 69.2 | | 1.30 | 120.2 |
| | | | 86.1 | 77.8 | .929 | 1.60 | 180.6 |
| 57 | MCW | Olin | 57.8 | 44.5 | | .616 | 60.4 |
| | | | 70.2 | 61.8 | | 1.04 | 120.5 |
| | | | 75.3 | 74.8 | 1.14 | 1.34 | 180.5 |

*Second increment of AN & U (240 g & 160 g, respectively) added to catalyst after 120 minute reaction time.

Since a decision had been made to perform 1-inch-diameter down-flow reactor experiments (discussed in a later section) at Kenvil with Grace 59 silica gel catalyst, Run 52 was made to check Phase I results with this catalyst using reagent grades AN and U. Results from Run 52 duplicated those obtained for the previous Run 18. In Run 52 it was noticed that the standard 2/2/1.7 charge of urea, AN and SG did not adequately wet the Grace 59 catalyst. After two hours of reaction time, 240 gm AN and 160 gm urea were added to the reaction flask. About 25 minutes was required for the temperature to recover to 190°C. Yield and conversion data were then taken for another 100 minutes. Extra charge weights were used in subsequent experiments.

Run 53 was a duplicate of Run 52 made to show the effect of Olin urea and MCW grade AN heat aged at 130°C for 8 hours followed by similar materials without aging. The aged material was the first feed added to the reactor. The GN yield after one hour was 60% in Run 53 compared with 73% in Run 52. As expected, the urea conversion was higher in Run 53 and as a result, the catalyst mileages for the first hour were about the same. However, in the second part of Run 53, where fresh MCW grade AN and Olin urea were added to the reactor, GN yield and urea conversion values were clearly lower than those in Run 52. These data indicated that aging MCW grade AN in combination with Olin urea had a detrimental effect on catalyst performance.

Runs 54 and 55 were duplicate experiments made with commercial feeds from the Kenvil pilot plant operation. The molar feed ratios in these runs were 2/2/0.85 of AN/U/SG. The purpose of the runs was to give the Grace 59 silica gel, which was poisoned the fastest at Kenvil, increased exposure to Kenvil feeds. It was thought that additives to the MCW AN might be causing lower yields than those obtained with reagent grade AN and ureas. The low yield obtained in Run 54 was attributed to inaccurate analytical results. The results from Run 55 were similar to those obtained in Run 52 but not comparable because all of the urea and AN was not charged initially in Run 52. Based on the yield in Run 55 alone, it was not possible to say that the Kenvil feed stock (MCW AN and Olin U) gives lower yields and mileages than reagent grade feeds.

Runs 56 and 57 were designed to help pinpoint the poisons which deactivated the Kenvil pilot plant catalysts. Run 56 was identical to Run 55 or 57 except that reagent grade AN was used instead of the MCW material. Runs 55 and 57 are duplicates made with Kenvil raw materials, MCW ammonium nitrate and Olin urea. The GN yield after about 3 hours in Run 56 was 86% compared with 77.4% in Run 55 and 75.3% in Run 57. The mileage in Run 56 was 1.60 gm GN/gm SG compared with 1.37 and 1.34 in Runs 55 and 57, respectively. These results suggest that MCW grade AN with its additives causes the catalyst to start losing activity in about 2 hours.

The two minor objectives of the laboratory work were to obtain the "insolubles" solubility in the reactor melt and to microscopically examine the poisoned Houdry beads removed from the pilot plant reactors. The results of these efforts are discussed below.

Solids (water insolubles) from the Kenvil solid bowl centrifuge were washed, filtered and dried overnight at 80°C. The solubility of these solids in simulated reaction melt at 180°C was measured. About 0.12 gm of insolubles dissolved in 100 gm of melt. It is not clear whether the heat treating resultant from drying this cake overnight at 80°C altered the structure of the insolubles.

To determine if the pores of Houdry catalyst beads were plugged by insolubles, several lots of used beads were examined at magnifications of 10X to 75X. No obvious shell of insolubles was observed encasing the catalyst beads. In general, cross-sections of the beads appeared uniform, like a granular solid.

The above laboratory experiments can be summarized as follows:

(a) Two reactions were performed with Houdry beads at temperatures of 180°C and 190°C to establish a base line. The resulting GN yield and urea conversion values were consistent with those obtained during Phase I of this program when reagent grade feed materials were used.

(b) Catalyst mileage (gm GN/gm catalyst) was significantly lower with used Houdry beads from the Kenvil pilot plant reactor than with fresh Houdry bead catalyst.

(c) Regeneration of used Houdry bead catalyst via cold water and either aqueous $Na_2CO_3$ or KOH washes restored part of the activity but not sufficiently to justify regeneration as a standard practice. Washing also resulted in a serious size reduction of the beads.

(d) The results obtained with Mobil Sorbeads were similar to those in Phase I. Operation of the reaction at 180°C compared to that at 190°C resulted in a reduced productivity and a higher GN yield.

(e) The results obtained with Grace 59 silica gel were similar to those in Phase I.

(f) Lower conversions and yields were demonstrated when Hercules MCW AN and Olin urea were used compared to reagent grade AN and Olin urea.

(g) Solubility of water insolubles (obtained by washing residue removed from the Kenvil solid bowl centrifuge) was 0.12 gm per 100 gm of melt at 180°C.

5. Catalyst Poison Scouting - One-Inch Diameter Downflow Column

The objectives of this effort were as follows:

(a) To design, fabricate and install a 1 inch diameter x 2 ft long tubular reactor for continuous downflow operation.

(b) To operate the reactor continuously to "bridge the gap" between Hercules' 4-inch-diameter reactor runs and work performed by MacKay (Pittsburgh Coke and Chemical Company, 1956)(4) in a 1 inch diameter x 2 foot long column operated intermittently.

(c) To operate the 1-inch-diameter reactor with different types of feed (AN and U) in an attempt to pinpoint the catalyst decay problem.

A 1 inch diameter x 3 ft deep tubular reactor was designed, fabricated and installed in the Kenvil GN pilot plant. The jacketed 304 stainless steel reactor, shown in Figure 63, was equipped with a heated dropping feed funnel, an off-gas vent system and a bottom product collection system. Feed, a weighed blend of AN and U, was melted on a hot plate and then held at about 130°C in a sand bath until used. Hold time of feed melt averaged one-half hour except for special experiments in which it was held for an extended period of time to assess the effect of hot storage on yield, catalyst life, etc.

The unit was installed to simulate work performed by MacKay of Pittsburgh Coke and Chemical; however, the equipment and operation differ in the following respects: (a) the Hercules/Kenvil reactor was 304 stainless steel rather than glass, (b) off-gas from the Hercules reactor was not recovered, (c) the Hercules experiments did not utilize recycled AN and U, and (d) the Hercules reactor bed depth was 36 inches vs 24 inches for the MacKay reactor due to the use of a lower density silica gel (Grace 25 - 25 lb/ft$^3$ vs 45 lb/ft$^3$ for the MacKay silica gel).

The lower density Grace 59 silica gel was selected instead of a higher density catalyst, such as Houdry beads, Mobil Sorbeads or Grace 40 silica gel

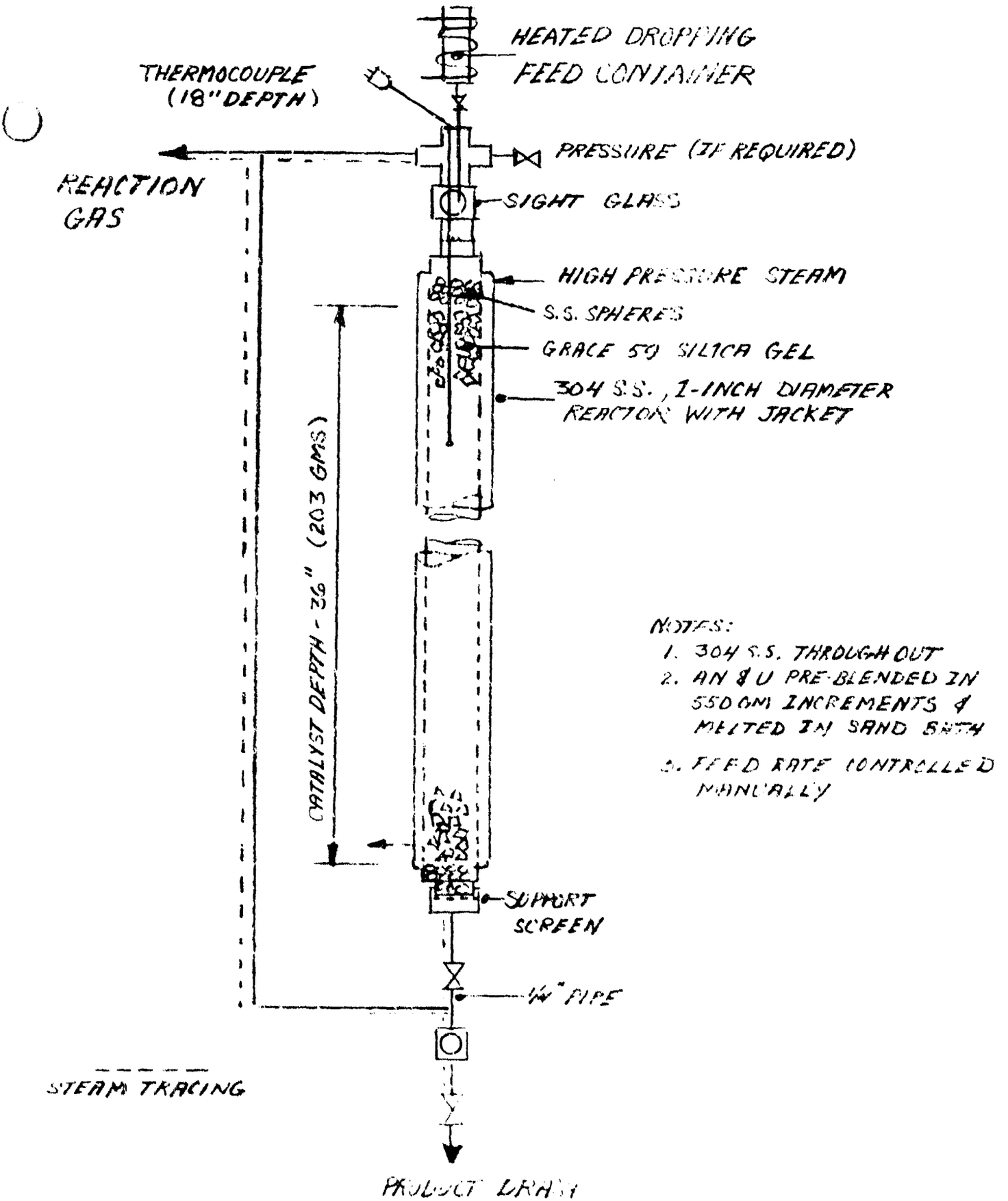



Figure 6.1. One-Inch-Diameter Reactor for Catalyst Work

because: (a) the poisoning effect of Grace 59 silica gel was more pronounced when compared with Houdry beads or Mobil Sorbeads in the 4-inch-diameter single-tube runs, (b) Grace 59 silica gel does not exhibit the decrepitating characteristics of Grace 40, and (c) Grace 59 silica gel was a likely catalyst candidate for a future production run. One of MacKay's major problems was attrition of silica gel which formed a layer of fine catalyst at the top of the bed and created downflow problems and nonreproducible operations. The Hercules' 1-inch-diameter operation was similar to that of MacKay's in that it employed down-flow feed, reagent grade AN and U with minimum melt hold time, similar feed rate, 2/1 - AN/U molar feed ratio and 190-195°C reactor temperature.

A critical path program in which each subsequent run is based on the results of a preceding run is presented in Figure 64. Table 69 is used in conjunction with Figure 64 to denote the types of materials associated with the individual runs (e.g., A, B, etc.). As an example, the initial run (A) was designed to employ both reagent grade AN and U, and its primary purpose was to duplicate MacKay's results in terms of displacements (total gm feed per gm catalyst) and catalyst life (60 hr). If the catalyst were to be deactivated rapidly, the process conditions would be changed. If catalyst activity were maintained, then Run B would be conducted, etc. The nominal length of an experiment was 80-85 hours unless there was an earlier sign of catalyst decay. Catalyst activity was based on productivity (gm GN/minute) as calculated from feed makeup and actual analysis of the product melt. Calculations utilized the nitrate conservation technique described earlier. It should be noted that the primary objectives of the 1-inch-diameter reactor work were to demonstrate catalyst life and to explore potential variables that lead to catalyst poisoning.

Nine runs were completed in the 1-inch-diameter reactor; however, departure was made from the critical path shown in Figure 64. The actual runs made are shown in Figure 65 and the results are summarized in Table 70.

In summary, it was demonstrated that both Permalene additives in Hercules' MCW ammonium nitrate (AN) and diammonium phosphate post-added to reagent grade AN had a pronounced effect on the deactivation of Grace 59 silica gel. Other variables investigated and their results are summarized below:

(a) A 61-hour run made with reagent grades of AN and U for direct comparison to the work of MacKay resulted in a minimum catalyst mileage (based on 61 hours) of 16.2 gm GN/gm catalyst for total displacements of 119 gm feed/gm catalyst. MacKay's approximate values were 14 gm GN/gm catalyst and 46 gm feed/gm catalyst, respectively, for presumably a total run time of 77 hours based on a quoted operation of 7 hr/day for 11 days.

TABLE 69

ONE-INCH-DIAMETER COLUMN RUNS

(Refer to Figure 64)

| Run No. | Type AN | Type U | Other |
|---|---|---|---|
| A | Reagent Grade | Reagent Grade | S. C. * |
| B | Hercules MCW Prills | Olin Commercial Prills | S. C. * |
| C | Hercules MCW Prills | Reagent Grade | S. C. * |
| D | Reagent Grade | Olin Commercial Prills | S. C. * |
| E | Cyanamid Tech. Prills | Olin Commercial Prills | S. C. * |
| F | Aged** Hercules MCW Prills | Aged** Olin Commercial Prills | S. C. * |
| G | Aged** Reagent Grade | Aged** Reagent Grade | S. C. * |
| H | Change Standard Conditions (e. g. Feed Temp., Silica Gel, Bed Depth) | | |

* S. C. = Standard Conditions

Feed Mole Ratio = 2/1 AN/U
Bed Temperature = 190-193°C.
Flow Rate = 2.5 cc/minute Downflow (Target)
Run Length = 85 hours or less
Feed Temperature = 130°C
Catalyst = Low Density Silica Gel (Grade 59), 36" deep bed.
Feed Residence Time = 15-30 minutes max.

** 8-10 Hour Melt Holdup at Feed Tempeature.

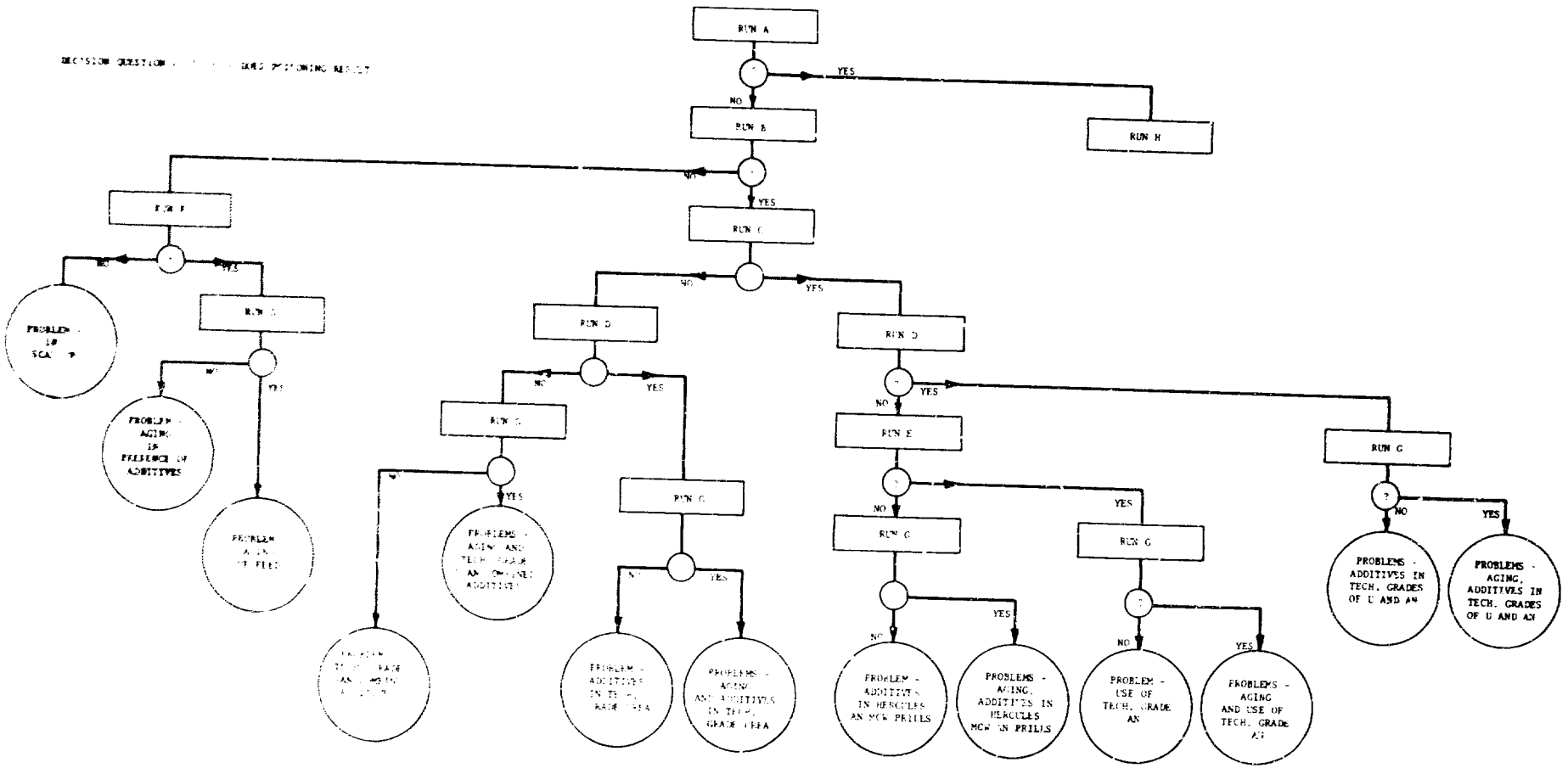



Figure 64. 1-Inch Column Run Sequence (Refer to Table 69)

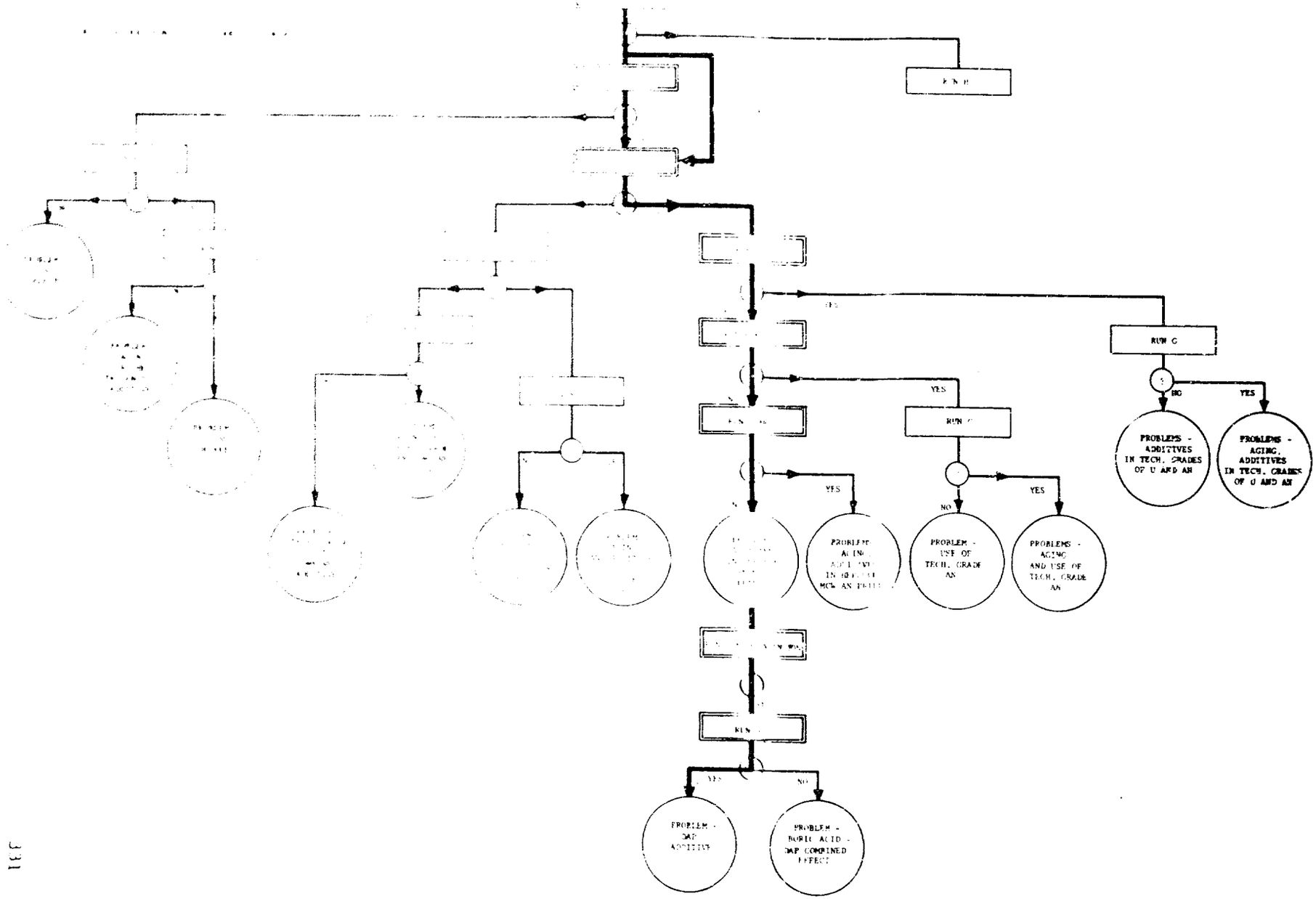



Figure 65. 1-Inch Column Run Sequence Actually Followed (Refer to Table 70)

# TABLE 79

## CATALYST POISONING STUDY IN ONE-INCH-DIAMETER DOWN FLOW REACTOR

| Run Letter | Performance Period | Type Experiments (1) AN | U | Run Time (Hours) | Total Displacement (gms Feed/ gm Catalyst) | Productivity (gms GN/min.) Initial | Final | Catalyst Mileage (gms GN/ gm Catalyst) | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| A | 1-4-72 | Reagent | Reagent | 61 | 119 | 0.90 | 0.90 | 16.9 (min.) | Feed preheated to 175°C - feed funnel plugged, run aborted, feed turned amber color. |
| | 1-[illegible]-72 | Reagent | Reagent | 168 | 184 | 0.99 | 0.18 | 12.7 | Repeat Run A with 130°C feed. No catalyst activity decay. |
| | [illegible]-17-72 | Reagent | Olin | 21 | | | | | Feed 130°C, Catalyst activity decay. Feed turned amber. |
| | 1-[illegible]-21-72 | Reagent | Olin | 57 | 119 | 0.95 | 0.95 | 16.0 (min.) | Lost reactor steam, run aborted |
| [illegible] | 1-24-1-27 | Cyanamid (3) | Reagent | 67 | 146 | 0.94 | 0.94 | 18.6 (min.) | Feed 130°C, No catalyst activity decay |
| [illegible] | 1-27-1-28-72 | Hercules Dow 26 | Olin | 4 | | | | | Feed 130°C, No catalyst activity decay. Small amount of talc coating plugged reactor. Run aborted |
| [illegible] | [illegible]-1-30-72 | Cyanamid | Olin | 66 | 127 | 0.95 | 0.95 | 18.0 (min.) | Feed aged 8 hrs. @ 130°C. No catalyst activity decay. |
| | 2-1-[illegible]-1-72 | Cyanamid | Olin | 24 | 37 | 0.95 | 0.45 | - | Normal feed residence @130°C, 0.5% diammonium phosphate added to AN, Catalyst activity decreased. |
| | [illegible]-1-[illegible]-1-72 | [illegible] | Olin | 12 | 24 | 0.45 | 0.45 | | Stopped adding DAP to melt. Catalyst activity levelled off. |
| | 2-[illegible]-[illegible]-72 | Reagent | Olin | 47 | 68 | 0.90 | 0.21 | 7.6 | 0.5% DAP added to AN, Catalyst activity decreased. |

1. [illegible] = Phosphoric acid
2. [illegible] AN = Ammonium nitrate; Reagent = [illegible] (phosphoric acid-diammonium sulfate)
3. [illegible] AN = [illegible]; Reagent = [illegible]

[illegible] Conditions identical to run with conditions and results as noted under "Remarks"

NOTE: Feed rate ranged between [illegible] Reactor temperature 130°C

It should be noted that in all Kenvil runs where catalyst activity did not decrease, the minimum catalyst mileages were in the range of 16.0 to 18.6 gm GN/gm catalyst at displacement values ranging from 119 to 146 gm feed/gm catalyst.

In summary, the Kenvil 1-inch-diameter reactor exceeded the mileage and displacement values obtained by MacKay. Run durations ranged from 57 to 67 hours at which times the experiments were voluntarily terminated.

(b) Commercial Olin urea in combination with reagent grade AN behaved the same as reagent grade urea.

(c) Cyanamid AN in combination with reagent grade urea yielded a satisfactory productivity with no sign of catalyst decay. A sample of this AN contained 0.16% by weight boric acid as determined by a Hercules' analysis. Confirmation of this analysis, as well as other additives, by Cyanamid Chemical Company is pending. Data presented earlier showed that silica gel absorbs boron; however, it did not affect catalyst life during a 67-hour continuous run. Regardless, use of this material is not recommended for two reasons; namely, (1) eventually a purge of the boric acid from the system would be required and (2) the supply of AN to a production plant would be via a captive and/or an imported boron-free aqueous AN solution.

(d) Aging Cyanamid AN and Olin urea for approximately 8 hours at 130°C did not affect productivity. This time element approximates the residence time of feed melt in the pilot plant.

(e) A 400-pound sample of AN was obtained from the Hercules' Donora plant to determine the effect of a commercial grade AN without any additives on catalyst activity. Inadvertently, the prills had a slight talc coating, which caused the reactor to plug. Additional material without any coating was subsequently obtained but not evaluated in this particular portion of the program. Evaluation of Hercules' Donora reagent grade is discussed in a succeeding section.

(f) Further evidence of the effect of diammonium phosphate (DAP) on the poisoning of Grace 59 silica gel was dramatized by adding 0.5% by weight DAP to an AN/U melt which had not shown any decrease in catalyst

activity for 66 hours. The addition of the DAP resulted in catalyst activity decay. When addition of DAP was stopped, productivity leveled off but at a level lower than initially obtained.

Certain observations were made while operating the 1-inch-diameter tubular reactor. MacKay (Pittsburgh Coke and Chemical Company)[4] noted that his successful "7-hr per day, 11-day run" utilized AN/U melt heated to 175°C. Our initial experiment (Run A) followed this procedure with reagent grades of AN and U, but the run was aborted after approximately 4 hours because of plugging of the feed funnel and discoloration of the feed melt, i.e., from colorless to amber. Analysis of the feed showed that the urea concentration had decreased from the initial level of 25% to ca 10% by weight. Consequently, the feed melt temperature was reduced to 130°C. Reactor feed, consisting of combinations of reagent grade of Cyanamid AN and reagent grade of Olin urea, was colorless when heated to 130°C for time periods up to 8 hours. A melt containing AN with either Permalene or post-added diammonium phosphate gassed and turned amber. Catalyst fines were not evident when the 1-inch-diameter reactor was emptied at the completion of each experiment.

In summary, it was concluded that the catalyst poisoning experienced in the operation of the pilot plant 4-inch-diameter reactors with Houdry macroporous beads, Mobil Sorbeads or Grade 59 silica gel resulted from the use of Hercules' MCW ammonium nitrate which contains Permalene.

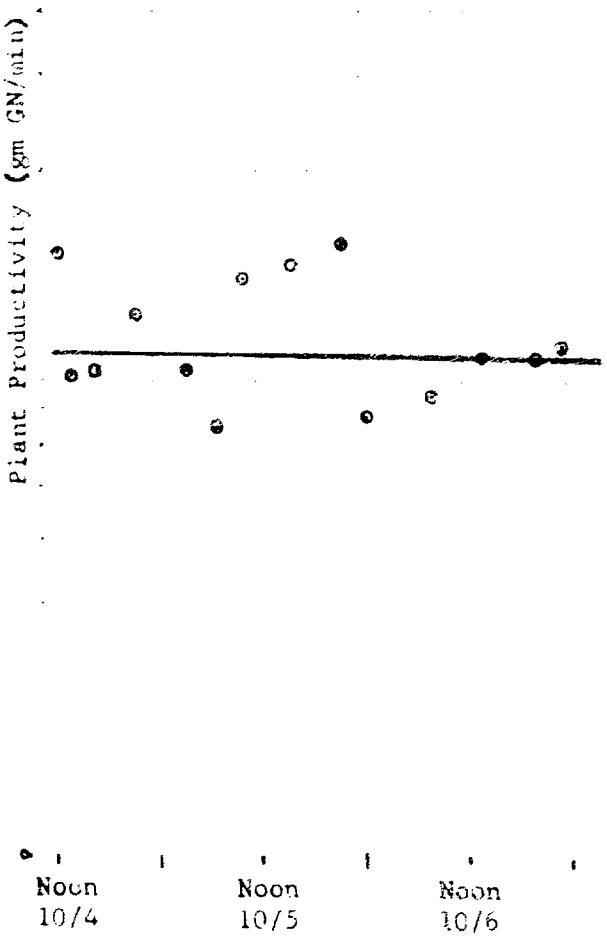
It was demonstrated in the 1-inch-diameter reactor that Permalene and one of its constituents, diammonium phosphate, poisons Grace 59 silica gel catalyst. Presumably, boric acid has no detrimental effect on catalyst activity as evidenced by the experiment employing Cyanamid AN. It is recognized that Permalene contains a third compound, diammonium sulfate; however, its effect was not investigated for two reasons: (1) it is present in AN at only a 0.01% by weight level, and (2) the use of AN with any additive has been ruled out.

Productivities, expressed as gm GN/minute, as a function of time are plotted for six different runs in Figures 66 through 71.

The general procedure for each run was as follows:

(a) As-received AN and U were weighed out at a 2/1 molar ratio for a total weight of 550 gm.

(b) The AN and U increments were dry blended in a Pyrex beaker and then heated on a hot plate until melted. The mix was stirred periodically to limit the maximum temperature to 130°C (except 175°C in Run A).




Reagent Grade AN
Reagent Grade Urea

Average melt hold time - 45 minutes

Run Summary

Run length - 61 hr
No displacements - 119 gm feed/gm catalyst
Catalyst mileage - 16.2 gm GN/gm catalyst

Reactor Conditions

Feed rate - 5-9 gm/min
Downflow operation
Feed mole ratio (AN/U) - 2/1
Reactor temperature - 193°C
Catalyst - 1 in. diameter x 36 in. high bed. Grace 59 silica gel (203 gm)
Feed temperature - 130°C

Figure 66. Plant Productivity Vs Time - 1-Inch Column Catalyst Study (Run A2)

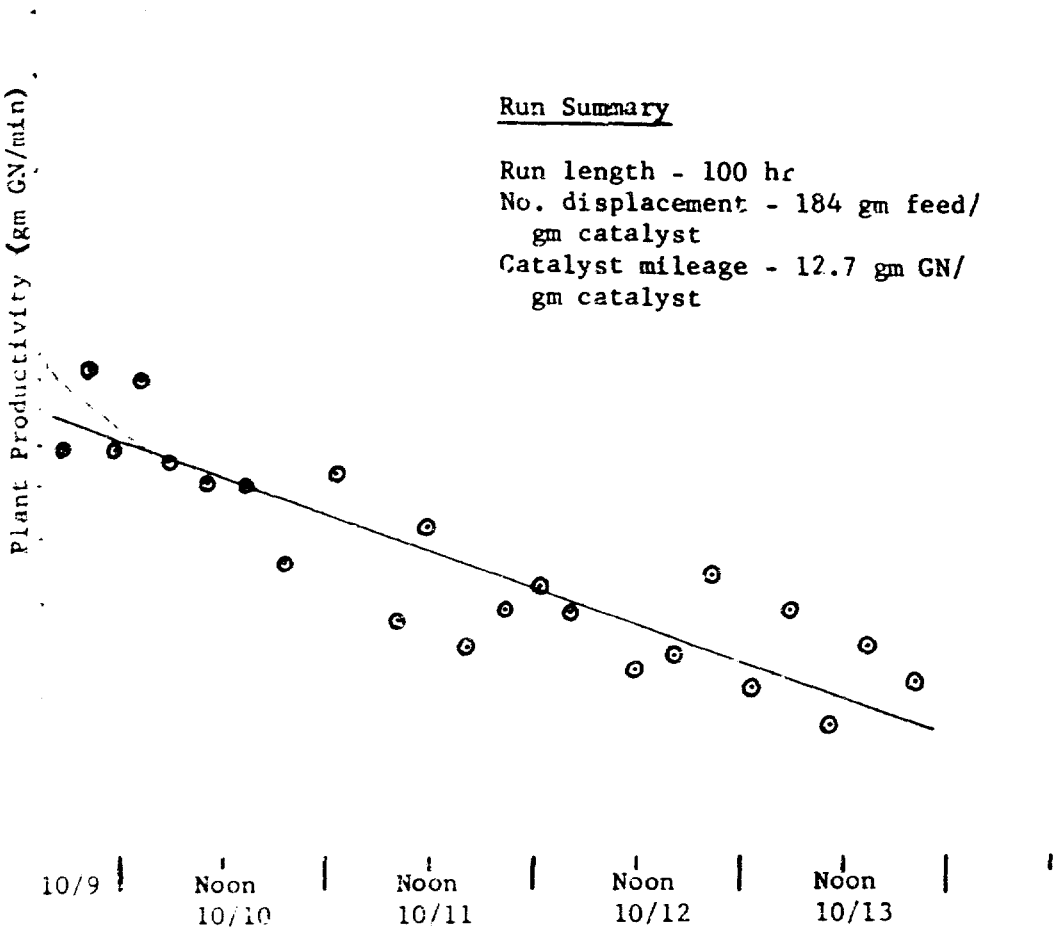
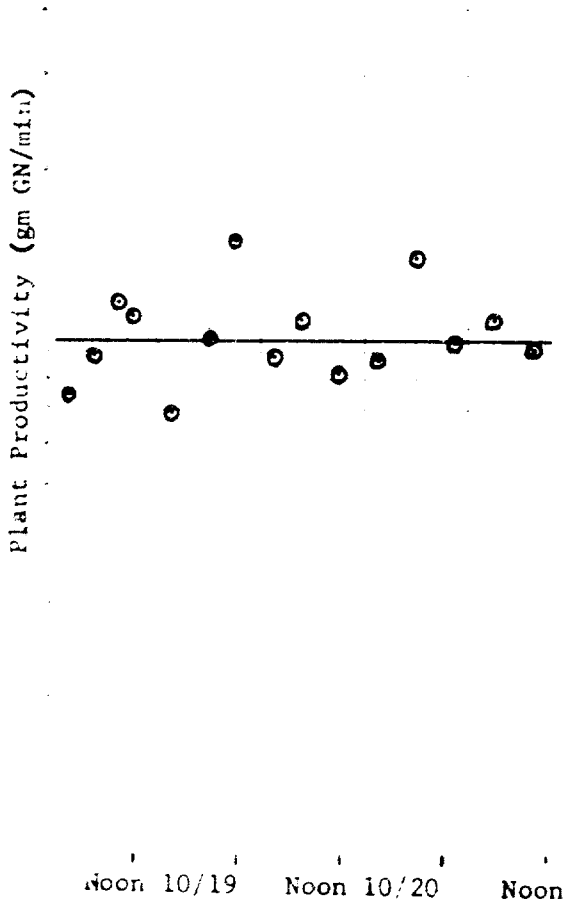



Figure 67. Plant Productivity Vs Time - I-Inch Column Catalyst Study (Run C)




Reagent Grade AN
Olin Commercial Urea

Average melt hold time -
45 minutes

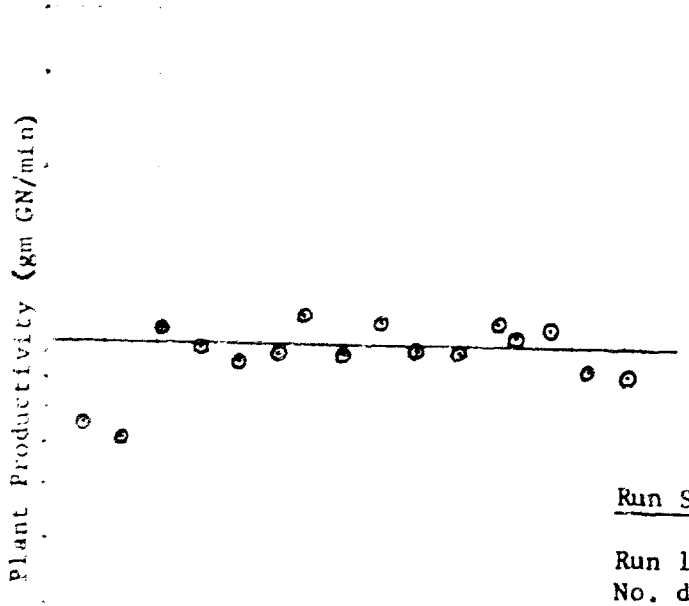
Run Summary

Run length - 57 hr
No.of displacements -
119 gm feed/gm catalyst
Catalyst mileage -
16 gm GN/gm catalyst

Reactor Conditions

Feed rate - 5-9 gm/min
Down-flow operation
Feed mole ratio (AN/U) - 2/1
Reactor temperature - 193°C
Catalyst - 1-inch-diameter x
36 inch high bed. Grace 59
silica gel (203 gm)
Feed temperature - 130°C

Figure 68. Plant Productivity Vs Time - 1 Inch Column Catalyst Study (Run D2)




Cyanamid Commercial AN
Reagent Grade Urea

Average melt hold time -
45 minutes

Run Summary

Run length - 67 hr
No. displacements - 146 gm feed/
gm catalyst
Catalyst mileage - 18.6 gm GN/
gm catalyst

Reactor Conditions

Feed rate - 5-9 gm/min
Down-flow operation
Feed mole ratio (AN/U) - 2/1
Reactor temperature - 193°C
Catalyst - 1 in. diameter x
36 in. high bed. Grace 59
silica gel (203 gm)
Feed temperature - 130°C

Figure 69. Plant Productivity Vs Time - 1-Inch Column Catalyst Study (Run E, Modified)

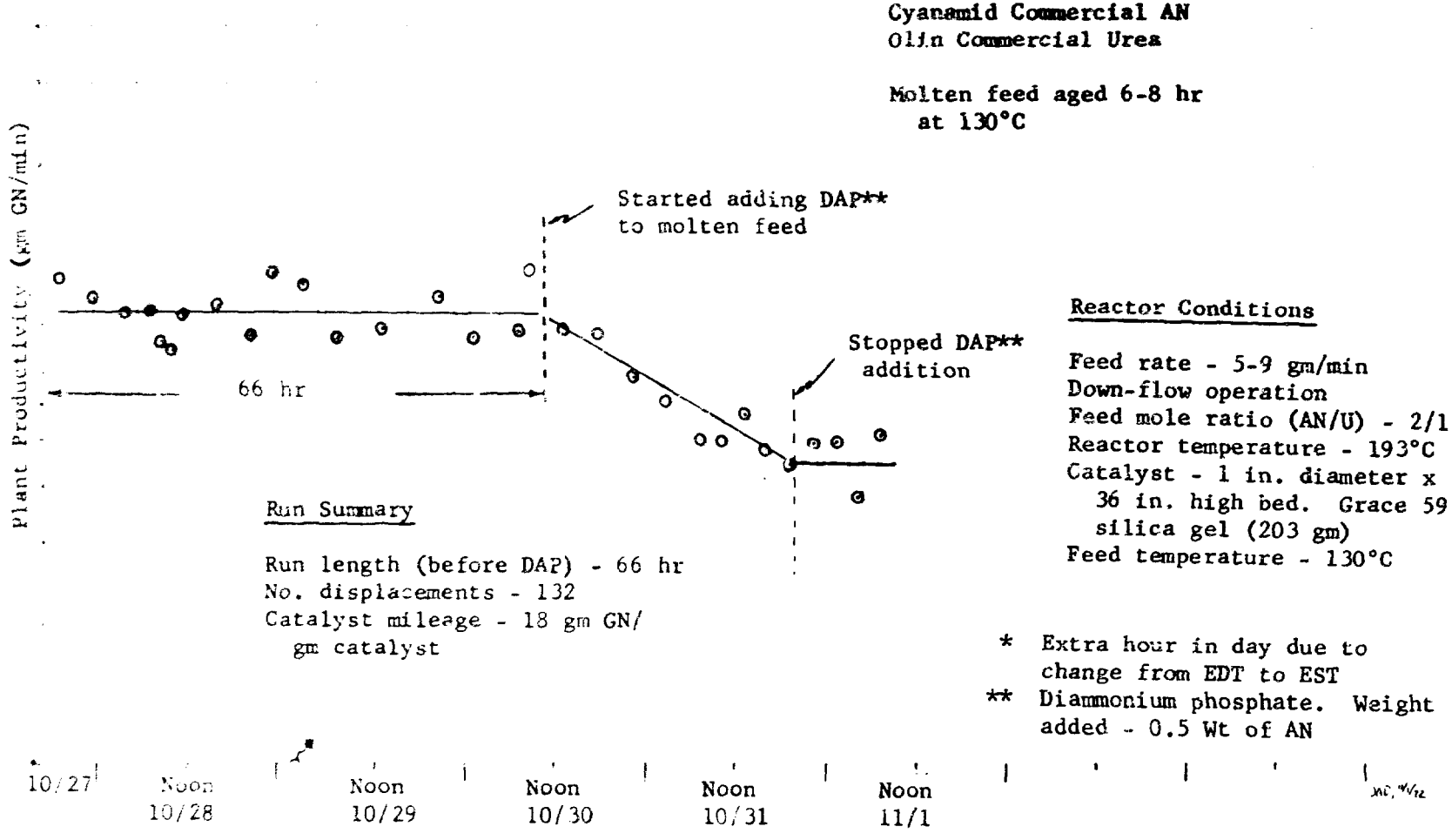
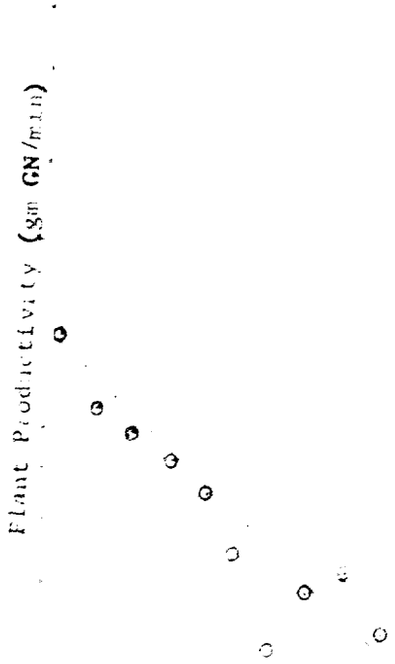



Figure 70. Plant Productivity Vs Time - 1-Inch Column Catalyst Study (Run G, Modified)

A.R. Grade AN w/DAP* added
Olin Commercial Urea

Melt feed hold time -
45 minutes average




Run Summary

Run length - 42 hr
No. displacements - 78.3 gm feed/gm catalyst
Catalyst mileage - 7 gm GN/gm catalyst

Reactor Conditions

Feed rate - 5-9 gm/min
Down-flow operation
Feed mole ratio (AN/U) - 2/1
Reactor temperature - 193°C
Catalyst - 1 in. diameter x 36 in. high bed. Grace 59 silica gel (203 gm)
Feed temperature - 130°C

* Diammonium phosphate. Wt. added - 0.5% wt. of AN



Figure 71. Plant Productivity Vs Time - 1-Inch Column Catalyst Study (Run J)

(c) The beaker of melt was then transferred to a sand bath maintained at 130°C. Normally, logistics were such that partial transfer of a new melt to the reactor feed funnel would occur within 10 minutes after it had melted. The final transfer would occur within 80-90 minutes, resulting in an average melt residence time of 30-45 minutes.

(d) Before the melt had been charged to the feed funnel, high-pressure steam (170 psig) was applied to the reactor jacket and 30 psig steam was applied to the feed funnel, discharge valve and off-gas line. The column had been loaded previously with 203 gm of Grace 59 silica gel predried at 225°F for 2 to 3 hours.

(e) The valve at the bottom of the feed funnel was adjusted for dropwise addition of melt to the reactor. Experience dictated the dropping rate and frequency of valve adjustment.

(f) Product was collected continuously in a stainless steel beaker. Samples for analysis were taken each 1-1/2 hours in open aluminum cups and then transferred to sealed bottles when solidified. No attempt was made to operate the column flooded, i.e., the bottom discharge valve was left fully open.

(g) Average feed rate was calculated on the basis of the time required to use a beaker of melt and assuming no change in feed funnel inventory between the first and final charge increment.

6. Four-Inch Diameter Reactor Scale-Up Run Following Catalyst Poisoning Studies

The 1-inch column work discussed above was successful in that it clearly identified the main contributor (diammonium phosphate) to the catalyst poisoning experienced in the pilot plant runs. However, before a recommendation for a pilot plant production run could be made, it was believed necessary to confirm these results with a single, four-inch column run. This confirmation was to show that the productivity would not be affected by scale-up or by system recycle. This experiment was started on November 8, 1972. Table 71 lists the conditions used for this run.

Hercules' Donora ammonium nitrate (uncoated) was employed with Olin urea. The reactors were charged with Grace grade 59 silica gel based on the results obtained with the 1-inch-diameter reactor and because a continuing supply of Houdry silica beads was not certain.

## TABLE 71

## CONDITIONS FOR SINGLE FOUR-INCH-DIAMETER REACTOR RUN FOLLOWING ONE-INCH-DIAMETER REACTOR STUDIES

| | |
|---|---|
| 1) START: | November 8, 1972 |
| 2) DURATION: | Approximately 10 days |
| 3) SEQUENCE: | a) 4-5 days virgin feed<br>b) 4 days virgin and recycle feed |
| 4) TYPE INGREDIENT: | a) AN - Donora (uncoated)<br>b) U - Olin<br>c) Grade 59 Silica Gel Catalyst |
| 5) FEED RATIO: | 2/1, AN/U (molar ratio) |
| 6) FEED RATE: | 25 lb /hr. |
| 7) REACTOR TEMP: | 180-185°C (measured @ 54" centerline) |
| 8) SAMPLING: | Feed and product every 3 hours |
| 9) QUENCH: | Melt/water ratio, 2/1 |

The following is a brief chronology of events for the 4-inch-column work performed in November 1972.

(a) Feed was started to R-200 at approximately 9:00 p.m. on November 8. From 2:00 a.m. until about 10:00 a.m. November 9, feed flow was intermittent. Since the feed line and header were determined to be clear as evidenced by steam sparging, it was assumed that the reactor was plugged (November, 4-inch-dia. reactor, Run 1).

(b) Feed was admitted to R-204 at 10:00 a.m. on November 9. Feed rate was continuous until about 5:00 p.m., at which time it stopped and an attempt to regain a flow of feed was unsuccessful. Consequently, operations were curtailed and steam was turned off in both reactors. (November, 4-inch-dia. reactor, Run 2).

(c) When the reactors were dismantled, catalyst fines were found beneath each catalyst support screen and in the 1-inch bottom valves. Considerable catalyst fines were found in the 2-inch-diameter feed header; however, their origin is questionable. (There is reason to believe the fines in the header resulted from the reactor dumps following the Grace grade 59 single column run in August.)

(d) Reactors R-200 and R-204 were emptied and recharged again with predried (150°F) Grace 59 silica gel. The support screens were modified to eliminate sifting of catalyst fines into the bottom valve.

(e) Melt was introduced to R-200 at 10:00 p.m. November 10. From about 3:00 a.m. until 3:00 p.m. on November 11, feed to the reactor was stopped because of several feed line plugs. Starting at 3:00 p.m. November 11, feed supply to R-200 was constant (except for two short periods) until 11:00 p.m. November 14. At that time, pressure in the feed line increased from the normal 10 psig to 35 psig and flow stopped. The pressure was released by draining the feed header, and feed was started again. Pressure in the feed line gradually increased to 35 psig and at 5:00 a.m. November 15, the run was terminated. The reactor was on stream for about 85 hours, discounting approximately 12 hours of feed stoppage due to plugged lines. (November, 4-inch-dia. reactor, Run 3).

(f) Feed was admitted to fresh catalyst in R-204 at 5:00 a.m. November 15. At 11:00 a.m., high pressure developed in the feed line. Attempts to eliminate the plug were negative; thus the experiment was aborted at 3:00 p.m. (November, 4-inch dia. reactor, Run 4).

When reactors R-200 and R-204 were dumped, it was learned that approximately 20% of the recovered catalyst from R-200 was present as fines. The reactor valves were not plugged as in Runs No. 1 and No. 2. The plug in R-200 (Run No. 3) was determined to be due to fines in the bed. Stoppage of Run No. 4 was determined to be due to a feed line plug.

On November 15, 1972, the reasons for the plugging of R-200 and R-204 were not yet known and a meeting was held between Hercules and Picatinny Arsenal personnel. The following alternatives were suggested for the remaining time allocated to experimental work.

(a) Clear melt from the bottom of R-204 and attempt to resume operations.

(b) Repack a 4-inch-diameter reactor with new Grace 59 silica gel and start a new run, taking precautions to minimize water in the feed melt.

(c) Repack a 4-inch reactor with Houdry beads and resume operations.

(d) Investigate the effect of water in melt by operatin the down-flow 1-inch-diameter reactor with Grace 59 silica gel.

It was decided that the most valuable data could be obtained by operating the 1-inch reactor again but under carefully controlled conditions. It was further agreed that a limited number of beaker experiments would be performed to determine the qualitative effects of hot melt, water in melt, etc., on silica gel and Houdry beads.

7. One-Inch-Diameter Reactor and Beaker Tests

Of the 4-inch column runs discussed above, three were terminated because of high pressure drop due to fines. Run No. 3 lasted 85 hours because care had been taken before the run to screen the catalyst and to modify the catalyst support plate. The pressure drop did, however, eventually build up to the point where the feed pump could no longer pump melt through the bed. This implied that the reported nondecrepitating Grace grade 59 silica gel may not be a suitable catalyst for a fixed bed reactor. These runs, however, used feed containing various amounts of water (0.5% to 3%). There was some belief that "dry" feed would eliminate Grace 59 catalyst physical attrition and lead to a long bed life. The 1-inch column work and the laboratory beaker tests were programmed in an attempt to answer this question.

Two 1-inch-diameter column runs, designated Runs K and L, were made to investigate the effect of 1% water in the feed on catalyst decrepitation. These runs employed: (1) Hercules' Donora ammonium nitrate, (2) Olin urea, (3) average 45-minute hold time of feed melt at 130°C, (4) feed rate of 6 gm/minute, (5) 190-193°C reactor temperature, (6) trickle bed operation, (7) 60 hours minimum run time and (8) feed mole ratio of 2/1 AN/U.

Run K used predried (225°F for two hours) Grace grade 59 silica gel which had been screened through an eight-mesh screen. Run L used predried (225°F for 2 hours) Houdry CP-532 silica beads which had been screened of fines. Run K was started on November 16, 1972.

Productivity data for Runs K and L are plotted on Figures 72 and 73, respectively. Figure 72 contains, in addition to productivity data, the analyzed water content of the feed. In both Runs K and L, a nominal 1% by weight water was added to blended AN and U solids before melting. Figure 68 is a productivity vs time plot for Run D-2 that was made in October 1972 in the 1-inch-diameter column using reagent grade AN, Olin urea, and Grace 59 silica gel, but without intentional addition of water to the feed. When Grace 59 silica gel catalyst was used, the effect of water on productivity is evident if one compares Figures 72 and 68. In Figure 72, the GN productivity was about 0.75 gm/minute, whereas without water added (Figure 68), the productivity was ca 0.95 gm GN/minute. The addition of water to the feed melt also resulted in poisoning the Grace 59 silica gel catalyst after about 48 hours of continuous operation. This resulted in a catalyst mileage of only 13 gm GN/gm catalyst. Silica gel fines in the reactor bed for Run K amounted to about 20 wt. %. Since water in the feed is inevitable, it is concluded that Grace 59 silica gel is not suitable for packed bed reactors because of its poor poisoning and attrition characteristics. The lower productivity for Run K (as compared to Run D-2) is attributed to hydrolysis of urea caused by water in the feed. Hydrolysis reduces the available urea and thus increases the AN/U ratio, resulting in a decreased urea conversion per pass. For reference, 1% water in the feed will increase the AN/U ratio from 2/1 to [illegible] assuming that hydrolysis is complete. It is assumed that the catalyst activity decay is related to attachment of water or urea hydrolysis products to the silica gel active sites. It appears that any type of silica gel catalyst will have a finite life, partly decay if water is present.

[illegible] Figure [illegible] were made [illegible] silica beads in the 1-inch-diameter [illegible] were identical to those used in Run K. The initial [illegible] was that the [illegible] to the bed to [illegible] the initial residence [illegible] flow rate. As feasible, the first [illegible] was made [illegible] and [illegible] productivity of Houdry [illegible] Run K, viz, [illegible] was [illegible] to [illegible]

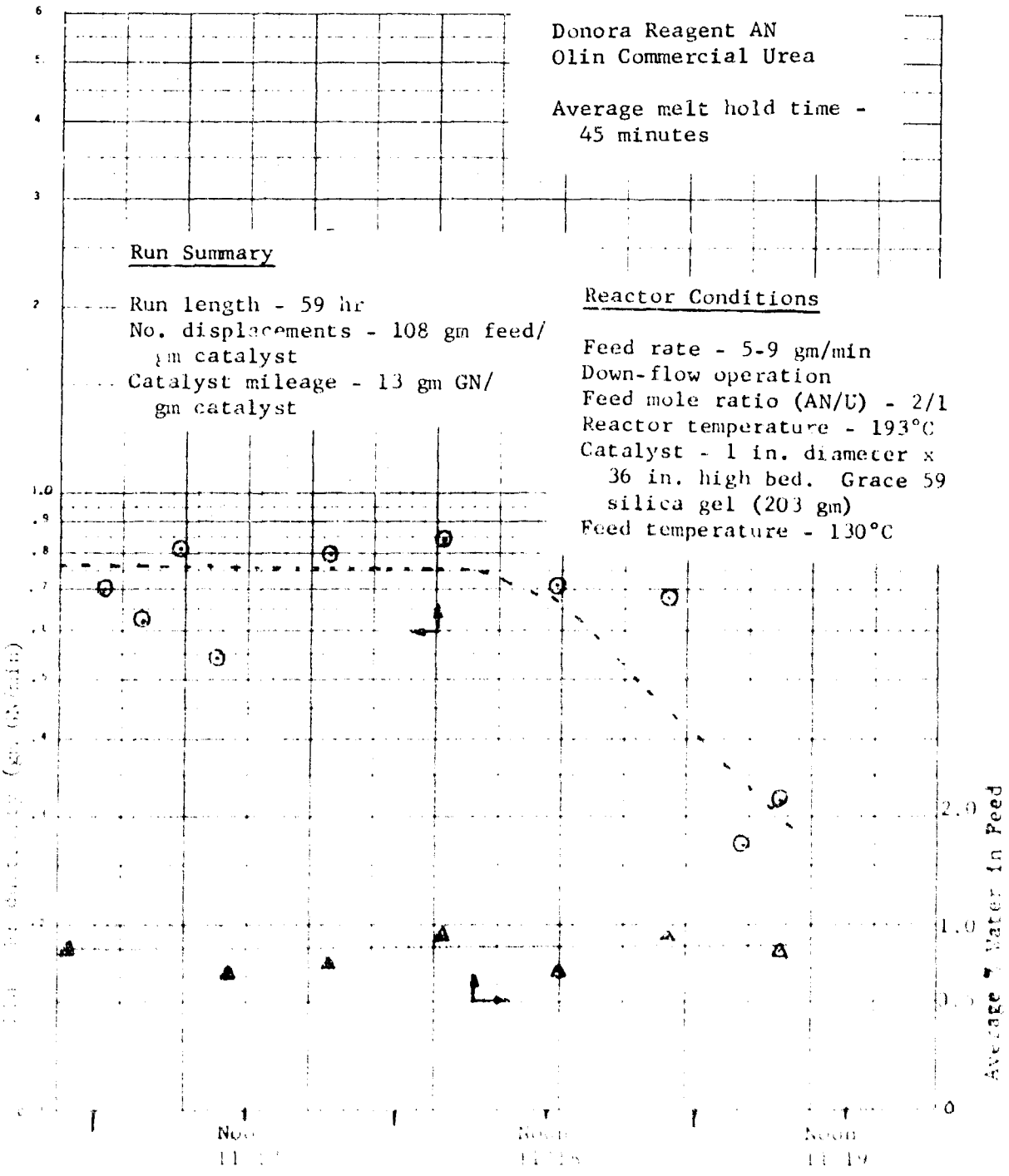



Figure 7. Plant Productivity Vs Time
Twin Column Catalyst Study (Run K)

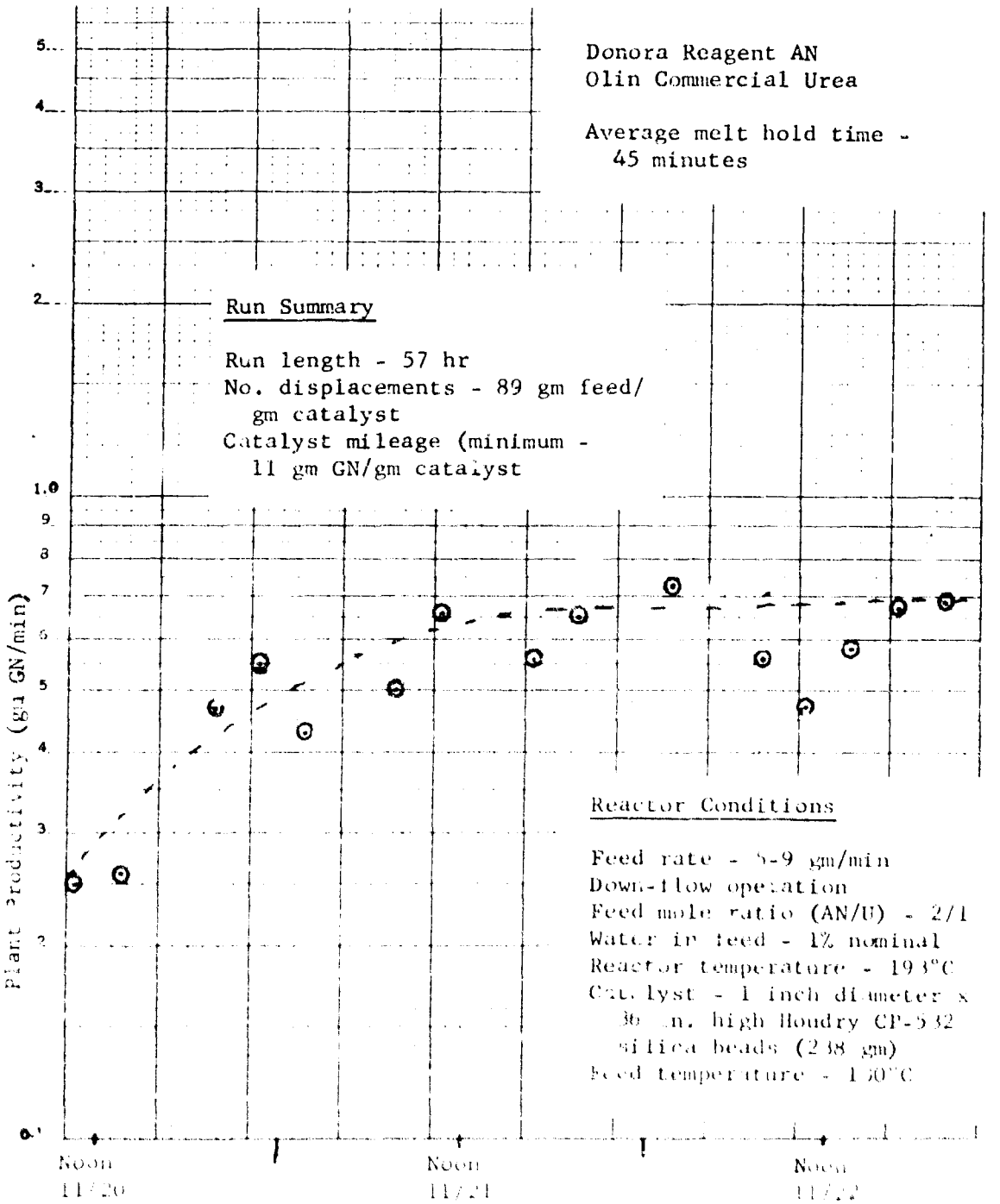



Figure 7a. Plant Productivity Vs Time - Telford Solution Catalyst Study (Run 1)

reactions during Phase I. Total run time for the Houdry beads was the same as for the Grace 59 silica gel, but a decay in catalyst activity was not noted. This could be a characteristic of Houdry beads. On the other hand, since the number of displacements (gm feed/gm catalyst) was lower (89) for the Houdry beads than for the Grace 59 silica gel (108), catalyst activity decay could have occurred if the run had been continued. Calculated minimum Houdry mileage was only 11 gm GN/gm catalyst. The purpose for making both Run K and Run L was to investigate the effect of water in feed on the attrition characteristics of the two different catalysts. Had the data presented in Figures 72 and 73 been available immediately, Run L would have been continued. An extended run (e.g., 15 days) in the 1-inch-diameter reactor using Houdry beads and water added to the feed melt was subsequently made. This extended run is discussed in the next section along with a final and successful 4-inch-diameter reactor experiment. It should be noted that there were no signs of Houdry bead fines when the reactor was dumped following Run L.

Five beaker tests were conducted in an attempt to assess the effect of contacting the silica gel catalysts being used in the GN program with hot AN/U melts containing various amounts of water. The objective of this work was to obtain insights into what had led to catalyst attrition problems in the pilot plant operation. These tests were meant to simulate the feed zone of the reactors where AN/U melts are preheated from 110° to 180°C and make initial contact with the silica gel catalyst. The observations made during these five tests resulted in the following conclusions:

(a) The "nondecrepitating" form of silica, Grace grade 59, did not physically break down when contacted with liquid water at ambient temperature. However, at elevated temperatures and when contacted with hot AN/U melts, the catalyst did suffer some attrition (5-20%). The attrition appeared to be due to a combination of thermal stresses, the pressure due to the venting of entrained gases, and a softening of the gel structure from the wetting of the AN/U melt.

(b) The experimental macroporous silica beads, Houdry CP-532, did not suffer any attrition either from water contact or from hot melt contact.

(c) The recovered Grace grade 59 silica gel particles from the beakers, while hot and wet with AN/U melt, were very soft and fractured very easily. The recovered Houdry beads appeared harder than unused beads.

(d) The presence of liquid water in the melt appeared to increase the level of the silica gel attrition. However, it is not believed to be the major contributor. A best guess is that the silica gel breaks down in two steps:

(1) A softening of the structure from contact with hot melt and then,

(2) Fracturing of its structure due to gas evolution resulting from:

a Entrained ai
b Steam (generated from water in the feed)
c Reaction gases ($NH_3$ and $CO_2$)

A sample of Houdry CP-532 silica beads stored for one-month in 140-150°C AN/U melt did not exhibit any signs of decrepitation.

Details of the catalyst beaker tests are presented in Table III-3 in the Appendix III.

## 8. Final One-Inch-Diameter and Four-Inch-Diameter Reactor Experiments

Based on the results from Runs K and L in the 1-inch-diameter reactor, a recommendation to proceed with pilot plant modifications and operations to produce an evaluation quantity of GN could not be made. The demonstrated Houdry catalyst mileage of 11 gm GN/gm catalyst was insufficient for extrapolation to a practical level of 200-300 lb GN/lb catalyst. A program was proposed to Picatinny Arsenal personnel whereby the 1-inch-diameter reactor loaded with Houdry silica beads would be operated continuously for 15 days to demonstrate a more meaningful catalyst mileage. This would then be followed by an identical 5-day run in a single 4-inch-diameter reactor (upflow) for scale-up purposes. Both of these experiments were completed on February 4, 1973. Results of the two experiments are discussed below.

### a. One-Inch-Diameter Reactor (Run M)

The 1-inch-diameter tubular reactor was charged with 250 gm of predried (120°C for 4 hours) Houdry CP-532 macroporous silica beads and then heated to the operating temperature of 193°C with high-pressure steam in the jacket. Increments of ammonium nitrate (Hercules' Donora) and urea (Olin) prills were weighed for a 2/1 molar ratio, dry blended and then melted. Precautions were taken not to exceed a 130°C melt temperature, and logistics were planned so that the average hold time of the feed melt was about 45 minutes. A volume of water, equivalent to 1% by weight of the total AN and U, was added to the dry materials before melting. The successive batches of feed melt were added incrementally to the feed funnel, and the discharge valve was adjusted to yield a feed rate ranging from 5 to 9 gm/minute. The feed and reactor product melts were analyzed for water content (Karl Fisher) and AN/U/GN, respectively. Productivity values (gm GN/minute) were calculated on the basis of the nitrate conservation technique described earlier.

The 1-inch-diameter reactor was operated continuously for 332 hours (13.8 days) with a 2/1 (AN/U) molar feed containing an average of 0.84% water by analysis (Figure 75). Pertinent results from this experiment were as follows:

- Catalyst mileage (minimum) - 68 gm GN/gm catalyst
- Displacements - 558 gm feed/gm catalyst
- Houdry Bead appearance - No breakage - slight discoloration

A plot of productivity vs time for Run M in the 1-inch-diameter reactor is presented in Figure 74. Catalyst poisoning was not evident.

b. Four-Inch-Diameter Reactor

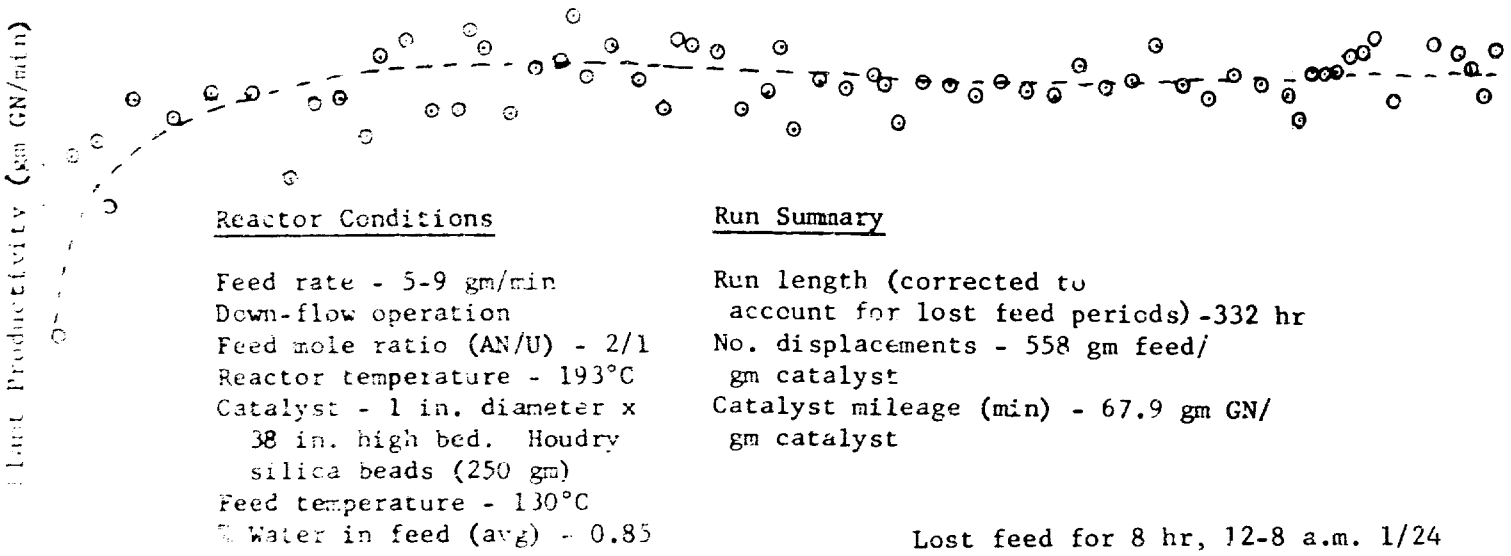
A single, 4-inch-diameter tubular reactor (R-200) was charged with predried (55°C for 12 hours) Houdry silica beads (26 pounds total) and then preheated with 250 psig steam in the reactor jacket. Ammonium nitrate (Hercules' Donora) and urea (Olin) prills were blended and melted in a batch melter for a 2/1 (AN/U) molar ratio.

Water was not added intentionally to the melt; however, melt feed to the reactor was analyzed periodically for per cent water as well as AN, U and GN. Analyses showed that absorption of water from the atmosphere and water introduced via the pump seal was sufficient to maintain the nominal 1% programmed level. To minimize water pickup, feed melt was transferred manually from the melter to the feed tank (T-113). Reactor product was analyzed periodically (normally each three hours) for AN, U and GN content. These data, in conjunction with the feed rate, were utilized to calculate reactor productivity values (lb GN/hr).

Melt (2/1, AN/U, molar ratio) was introduced to R-200 at 4:00 p.m., January 29, 1973, at a nominal rate of 25-30 lb/hr. After nine hours of operating time, feed to the reactor was stopped because of loss of plant steam to the melter, feed tank and feed lines. The reactor was drained pending the return of plant steam; however, 200-250 psig steam from the captive electric boilers was maintained on the reactor jacket. Operations were resumed but curtailed again within 37 hours because of a second plant steam failure. Reactor feed was stopped and the reactor was drained. On the third startup, the reactor feed makeup was changed from a 2/1 to 1/1 (AN/U) molar ratio to obtain a lower melting point material and, hopefully, not necessitate another shutdown in the event of low-pressure plant steam. The reactor was then operated for 70 consecutive hours at the 1/1 AN/U ratio. The run was voluntarily terminated at 2:30 p.m., February 4, 1973, resulting in an

Donora Reagent AN
Olin Commercial Urea

Average melt hold time -
45 minutes



Plant Productivity (gm GN/min)

Reactor Conditions

Feed rate - 5-9 gm/min
Down-flow operation
Feed mole ratio (AN/U) - 2/1
Reactor temperature - 193°C
Catalyst - 1 in. diameter x 38 in. high bed. Houdry silica beads (250 gm)
Feed temperature - 130°C
% Water in feed (avg) - 0.85

Run Summary

Run length (corrected to account for lost feed periods) -332 hr
No. displacements - 558 gm feed/gm catalyst
Catalyst mileage (min) - 67.9 gm GN/gm catalyst

Lost feed for 8 hr, 12-8 a.m. 1/24

1/11 1/12 1/13 1/14 1/15 1/16 1/17 1/18 1/19 1/20 1/21 1/22 1/23 1/24 1/25 1973
12 a.m.

Figure 74. Plant Productivity Vs Time - 1-Inch Column Catalyst Study (Run M)

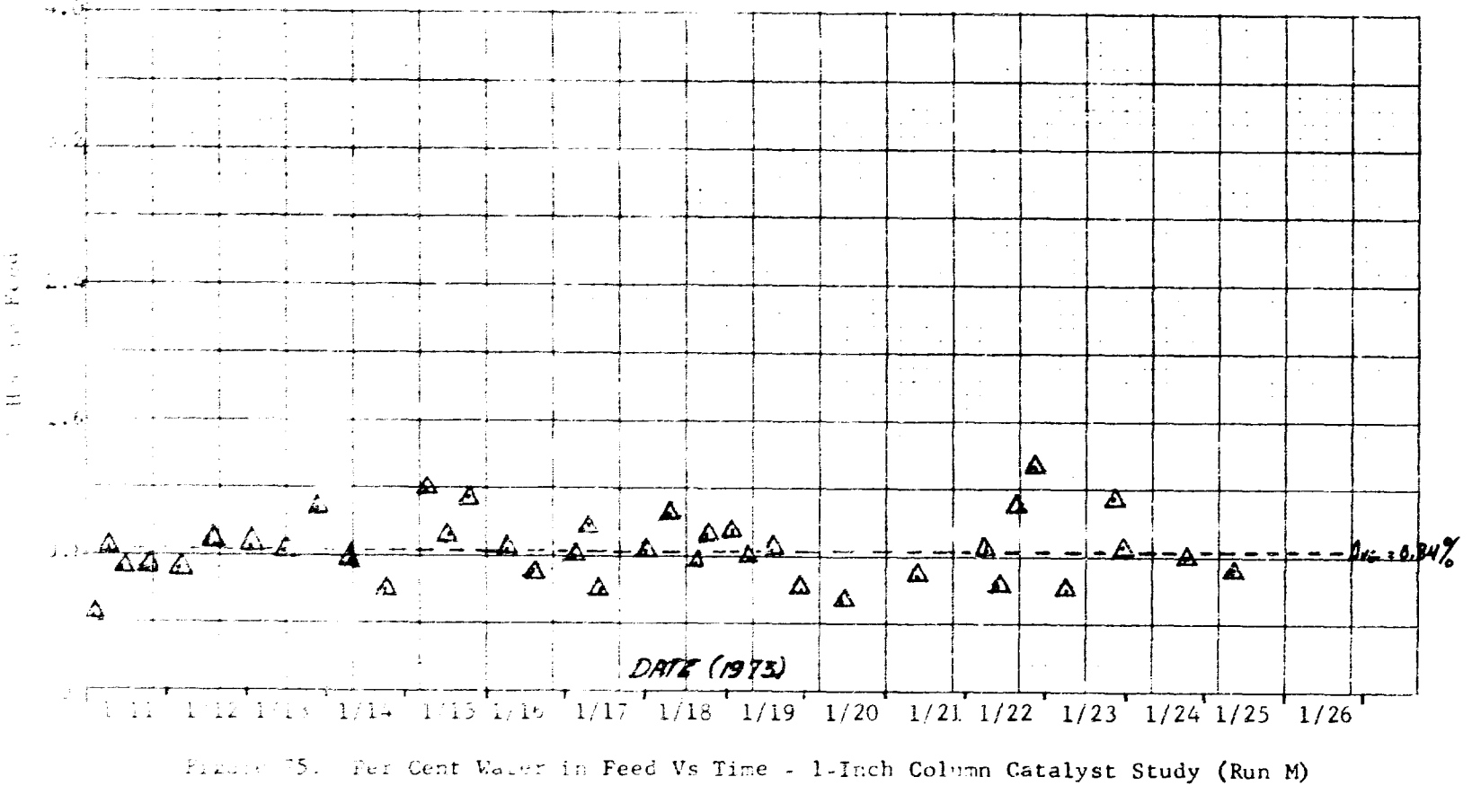



Figure 75. Per Cent Water in Feed Vs Time - 1-Inch Column Catalyst Study (Run M)

accumulated reactor feed time of 115 hours. Total elapsed time from initial introduction of feed to the reactor until termination of the run was 143 hours. The used Houdry bead catalyst drained freely from the reactor. The Houdry beads were less discolored than those recovered from the 15-day, 1-inch-diameter reactor run (Run M). Very few broken beads were noted.

Time, rates, analytical, etc.,data and calculated GN productivities for the above 4-inch-diameter reactor run are presented in Table III-4, Appendix III. Yield, productivity (lb GN/lb feed) and production rate (lb GN/hr) calculations were based on the nitrate conservation technique. For most of the cases, these calculations were based on both "actual" and "theoretical" analyses of the reactor feed stream. The difference between "actual" and "theoretical" analysis was the detection of a nitrate, other than ammonium nitrate, in the feed by actual analysis. This nitrate was credited as guanidine nitrate. An "actual" feed analysis results in lower GN productivity and production values.

The GN production values (lb GN/hr) based on "theoretical" feed analyses for this single-tube run are plotted in Figure 76 as a function of time. During the initial operating period when a 2/1 (AN/U) molar feed was used, the steady state production rate averaged 8 lb GN/hr. Towards the end of this initial period, the productivity decreased; however, this decrease was attributed to minor operating problems, i.e., interrupted feed, partial draining of reactor, etc. When a 1/1 AN/U feed stock was employed, the steady state productivity averaged about 9.4 lb GN/hr. This represents about a 50% increase when compared to the pilot plant design value of 6 lb GN/hr/tube. The calculated results for the latter 70 hours of operation with a 1/1 AN/U feed indicate a slight decline in GN productivity as a function of time (see Figure 76). However, one cannot place much credence in this observation because of the relatively short duration (115 hr total feed time) of the run.

During the latter period of operations, reactor product melt was weighed. These data, in conjunction with reactor product analyses, were used to calculate an average GN production rate over a steady-state period of 22.5 hours, independent of feed analysis and the nitrate conservation method for yield-productivity calculations mentioned above. The results showed that the nitrate conservation method of calculating yields and productivities is sound. Data and results are presented in Table 72 and summarized below.

| Method of Calculation | GN Production Rate |
|---|---|
| 1. Based on melt product rate and analysis (444 lb melt, 4 .% GN, 22.5 hr) | 9.0 lb GN/hr |
| 2. Nitrate conservation using actual feed analysis | 8.8 lb GN/hr |
| 3. Nitrate conservation using theoretical feed analysis | 9.2 lb GN/hr |

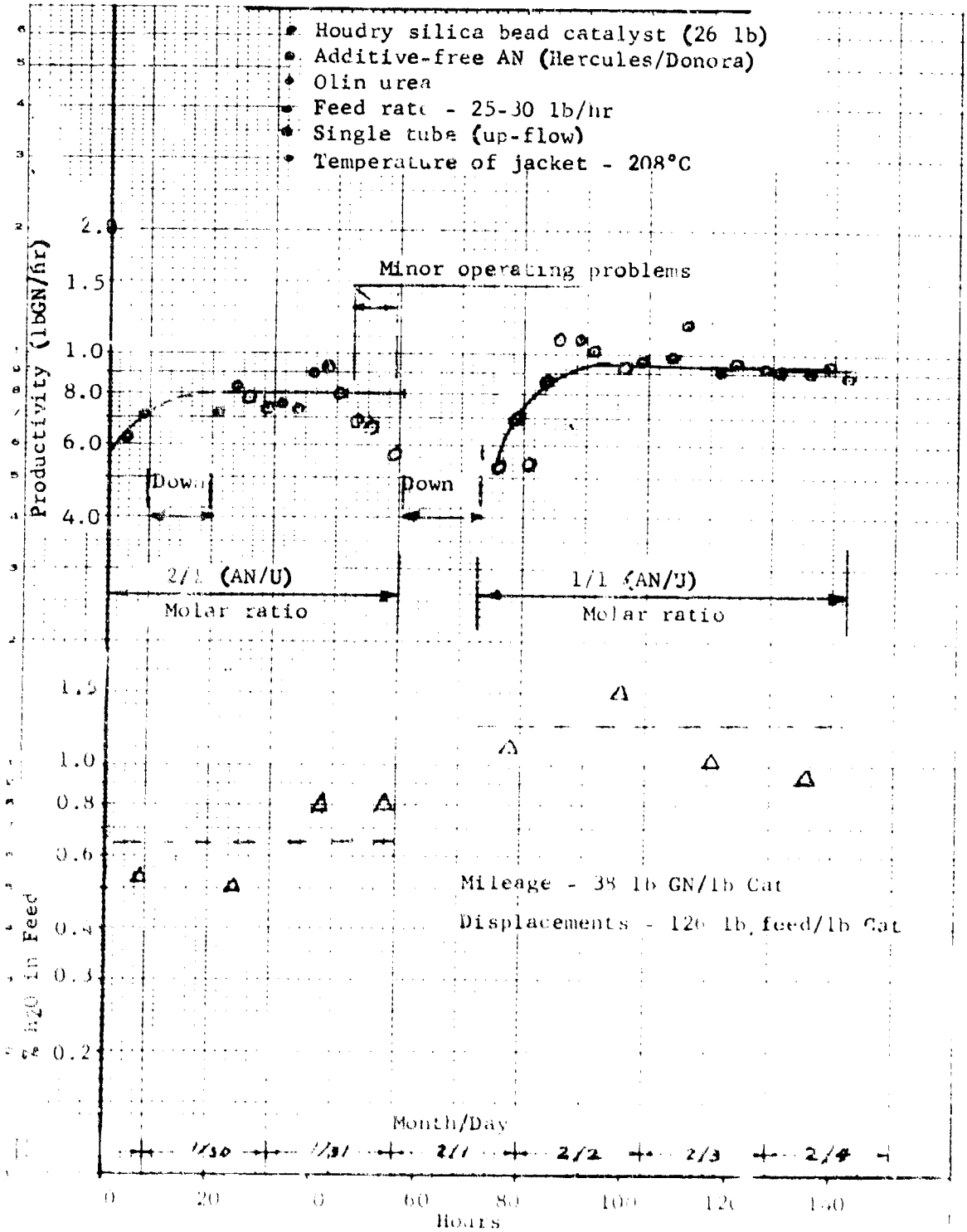



Figure 76. Performance of 4-Inch-Diameter Tubular Reactor

TABLE 72

## COMPARISONS OF GUANIDINE NITRATE PRODUCTION RATE CALCULATIONS

BASIS:

1. Four-inch diameter tubular reactor (R-200)
2. Houdry macroporous silica beads (26 lbs.)
3. Donora (Hercules) additive-free AN
4. Olin urea
5. AN/U ratio - 1/1
6. Reactor jacket temperature - 208°C
7. Recycle - None
8. Feed rate - 27 lbs./hr.

A. Sample operating period: 4:00 P.M., 2/3/73 - 2:30 P.M. 2/4/73

B. Operating time: 22.5 hours

C. Average GN content of reactor product: 45.5%
(based on 6 samples)

D. Reactor melt collected (total): 444 lbs.

E. Average GN production rate based on melt product rate and analysis: 9.0 lbs. GN/hr.
(444 lbs. x 0.455)/(22.5 hrs.)

F. Average GN production rates calculated by $NO_3$ conservation method (see Table III-4)

a) Based on actual feed analysis: 8.8 lbs. GN/hr.

b) Based on theoretical feed analysis: 9.2 lbs. GN/hr.

If one estimates from Figure 76 average GN production values of 8.0 and 9.0 lb/hr for the 2/1 and 1/1 (AN/U) periods of performance, respectively, the minimum catalyst mileage was 38 lb GN/lb catalyst [(45 hr x 8 + 70 hr x 9)/26 lb catalyst]. Table 73 contains data and calculations for determining an overall material balance, urea balance, etc. The total calculated GN formation was 962 lb which represents a minimum catalyst mileage of 37 lb GN/lb catalyst. Catalyst mileage values determined by the two methods agree very well.

When a 2/1 molar feed melt (72.7% AN, 27.3% U) was employed, the calculated GN yield [(moles GN formed/moles U reacted) 2] averaged 104% with a range of 91 to 123%. For the 1/1 molar condition, the GN yield averaged 96% with a range of 88 to 107%. In the latter case, calculated GN yields (52-67%) for the startup period were neglected in determining the average value. If one uses the material balance values from Table 73, the calculated overall reactor GN yield was 95.0%. This represents a very good yield and agrees fairly well with yields calculated from individual product analyses and reactor feed rates (Table III-4, Appendix III).

Table 73 contains data and calculations relative to a material balance for the entire period of performance for the 4-inch-diameter reactor run. Records were kept as to materials charged to the melters, materials removed from the melters and feed tank after terminating the run, weights and analyses of quenched reactor product, reactor drainings necessitated by plant steam failure and run termination, etc. Estimates of weights and/or analyses of material not directly accounted for were made in certain instances. The results from this material balance are detailed in Table 73 and summarized as follows:

- Overall weight balance - 98.3%
- Reactor urea balance - 102.9%
- Reactor AN balance - 94.8%
- Urea conversion - 82.8%
- GN yield based on urea - 95.0%

The packed bed tubular reactor mathematical model was employed to predict the temperature profiles, product rate, product analysis, urea conversion and GN yield for the 4-inch-diameter reactor. The model was refined to incorporate the actual weight of Houdry silica beads employed (26 pounds) and the actual catalyst bed depth (126 inch). The required input data consisted of the following experimental values: 120°C feed temperature, 27 lb/hr feed rate and 1/1 (AN/U) molar feed. The computer printout of predicted results is presented in Table 74. The temperature data in Table 74

TABLE 73

## MATERIAL BALANCE CALCULATIONS FOR FOUR-INCH DIAMETER REACTOR RUN

BASIS:

1. Reactor - R-200
2. Performance Period - 1/29/73 thru 2/4/73
3. Total Feed Time - 115 hours
4. Catalyst - Houdry CP-532 macroporous silica beads
5. Ammonium Nitrate - Hercules' Domora (additive-free)
6. Urea - Olin
7. AN/U Molar Ratio - a) 2/1 for initial 45.5 hrs.
   b) 1/1 for final 69.5 hrs.

A. Total Material Charged to System: AN - 2495 lbs.
U - 1381 lbs.
$H_2O$ - 31 lbs. (assumed 0.8 wt. % avg.)
3907 lbs.

B. Accounted for Material:

| | Weight (lbs.) | | | | | |
|---|---|---|---|---|---|---|
| | AN | U | GN | AC | $H_2O$ | Total |
| 1. Removed from melter & feed tank @ end of run | 378 | 158 | | | 4 | 540 |
| 2. Discarded $H_2O$ quenched Melt (815 lbs. - 41.5% AN, 4.6% U, 29.5% GN, 24.4% $H_2O$) | 338 | 37 | 240 | | | 615 |
| 3. $H_2O$ quenched product in T-1-6 (2110 lbs. - 42.7% AN, 7.6% U, 30.8% GN, 18.9% $H_2O$ | 901 | 160 | 650 | | | 1711 |
| 4. Discarded Reactor product (estimated 35 lbs. in 4 hrs. assume 45% AN, 7% U, 48% GN) | 38 | 5 | 42 | | | 85 |
| 5. Reactor product from dumping (est. 100 lbs. - assume 65% AN, 5% U, 30% GN) | 65 | 5 | 30 | | | 100 |
| 6. Discarded feed melt for rate checks (est. 60 lbs. - 30% U, 69% AN, 1% $H_2O$) | 41 | 18 | | | 1 | 60 |

TABLE 73 (Continued)

| | Weight (lbs.) | | | | | |
|---|---|---|---|---|---|---|
| | AN | U | GN | AC | $H_2O$ | Total |
| 7. Samples, pump leaks, etc. (neglect) | - | - | - | - | - | - |
| 8. Off-Gas $\left(\frac{962 \text{ lb. GN}}{122} \times 78\right)$ | - | - | - | 615 | - | 615 |
| 9. Urea hydrolysis loss from feed $H_2O$ $\left(\frac{26 \text{ lb. } H_2O}{18} \times 78\right)$ | - | - | - | 113 | - | 113 |
| Totals | 1761 | 383 | 962 | 728 | 5 | 3839 |

C. Overall Weight Material Balance

$$\frac{\text{Material Out}}{\text{Material In}} \times 100 = \frac{3839}{3907} \times 100 = \underline{98.3\%}$$

D. Reactor Urea Balance

$$[1381 - (158 + 18)]/60 = 1205/60 = 20.1 \text{ moles}$$

Urea Out

As Urea - 207 lb/60 - 3.45 moles

As GN Equivalents - 962 lb/122 - 7.90 moles

As AC Equivalents - 728 lb/78 - 9.35 moles

Total - 20.68 moles

Reactor Urea Balance $\frac{\text{moles Urea Out}}{\text{moles Urea In}} \times 100$

$\frac{20.68}{20.1} \times 100$

$\underline{102.9\%}$

TABLE 73 (Continued)

E. Reactor Ammonium Nitrate Balance

| AN In | AN Out |
|---|---|
| [2495 - (378 + 41)]/80 | As An = 1342 lb/80 = 16.75 moles |
| = 2076/80 | As GN = 962 lb/122 = 7.90 moles |
| = 26 moles | Total 24.65 moles |

$$\text{Reactor N Balance} = \frac{\text{Moles AN out}}{\text{Moles AN in}} \times 100$$

$$= \frac{24.65}{26} \times 100$$

$$= \underline{94.8\%}$$

F. Urea Conversion

$$\text{Conversion} = \frac{\text{moles U reacted}}{\text{moles U fed}} \times 100$$

$$= \frac{20.1 - 3.45}{20.1} \times 100$$

$$\underline{82.8\%}$$

G. Reaction GN Yield from Urea

$$\text{Yield} = \left[\frac{(\text{moles GN})}{(\text{moles U reacted})} 2\right] 100$$

$$\frac{7.90}{16.65} \times 2 \times 100$$

$$\underline{95.0\%}$$

TABLE 7-

PREDICTED RESULTS FOR COMPARISON WITH SINGLE FOUR-INCH-DIAMETER TUBULAR REACTOR RUN

ACTUAL BEADS
BULK DENSITY = 7.27 GRAMS/CU. IN.
VOID FRACTION = .437

TUBE DIAMETER = 4.05 INCHES
FEED TEMPERATURE = 120.0 C.
JACKET TEMPERATURE = 208.0 C.
Run made 1/29/73 through 2/4/73

| DISTANCE INCHES | MOLAR FLOW RATES MOLES/MIN. FEED | GAS | MOL /AMMONIUM NITRATE | FRACTIONS UREA | DIMETHYLOLUREA NITRATE | CONVERSION M.O FEED/ M.O FEED | YIELD M. GM/ M. O REAC | TEMPERATURE DEG. C. |
|---|---|---|---|---|---|---|---|---|
| .000 | 2.916 | .000 | .5000 | .5000 | .0000 | .0000 | .0000 | 120.0 |
| .040 | 2.916 | .000 | .5000 | .5000 | .0000 | .0000 | .0000 | 120.4 |
| .080 | 2.916 | .000 | .5000 | .5000 | .0000 | .0000 | .0000 | 120.7 |
| .120 | 2.916 | .000 | .5000 | .5000 | .0000 | .0000 | .0000 | 121.0 |
| .160 | 2.916 | .000 | .5000 | .5000 | .0000 | .0000 | .0000 | 121.4 |
| .200 | 2.916 | .000 | .5000 | .5000 | .0000 | .0000 | .0000 | 121.7 |
| 8.200 | 2.915 | .001 | .5002 | .4995 | .0003 | .0020 | .2921 | 151.9 |
| 12.200 | 2.895 | .020 | .5017 | .4981 | .0023 | .0158 | .2843 | 169.2 |
| 16.200 | 2.854 | .062 | .5053 | .4955 | .0061 | .0561 | .2822 | 179.1 |
| 20.200 | 2.755 | .159 | .5143 | .4886 | .0189 | .1244 | .2847 | 184.0 |
| 24.200 | 2.614 | .299 | .5242 | .4823 | .0335 | .2069 | .2903 | 186.1 |
| 28.200 | 2.482 | .433 | .5344 | .4758 | .0508 | .2908 | .2978 | 187.0 |
| 32.200 | 2.378 | .537 | .5439 | .4688 | .0694 | .3693 | .3063 | 187.5 |
| 36.200 | 2.274 | .641 | .5521 | .4587 | .0892 | .4407 | .3155 | 187.9 |
| 40.200 | 2.196 | .719 | .5590 | .4313 | .1097 | .5045 | .3252 | 188.2 |
| 44.200 | 2.140 | .774 | .5643 | .4054 | .1307 | .5611 | .3352 | 188.6 |
| 48.200 | 2.096 | .818 | .5679 | .3801 | .1520 | .6105 | .3456 | 189.1 |
| 52.200 | 1.962 | 1.024 | .5760 | .3567 | .1733 | .6547 | .3561 | 189.6 |
| 56.200 | 1.805 | 1.111 | .5797 | .3349 | .1944 | .6938 | .3667 | 190.1 |
| 60.200 | 1.807 | 1.109 | .5849 | .3142 | .2158 | .7287 | .3774 | 190.7 |
| 64.200 | 1.814 | 1.202 | .5879 | .2954 | .2367 | .7595 | .3882 | 191.2 |
| 68.200 | 1.727 | 1.302 | .5948 | .2797 | .2555 | .7811 | .3990 | 191.8 |
| 72.200 | 1.745 | 1.438 | .5978 | .2645 | .2747 | .8063 | .4098 | 192.4 |
| 76.200 | 1.717 | 1.516 | .6000 | .2505 | .2932 | .8284 | .4196 | 192.8 |
| 80.200 | 1.696 | 1.578 | .6006 | .2384 | .3110 | .8398 | .4300 | 193.2 |
| 84.200 | 1.671 | 1.664 | .6047 | .2270 | .3283 | .8543 | .4376 | 193.4 |
| 88.200 | 1.656 | 1.704 | .6067 | .2177 | .3457 | .8667 | .4495 | 194.0 |

FEED FLOW RATE = 27.00 LB./HR.
FEED WEIGHT FRACTIONS = AMMONIUM NITRATE = .5714
UREA = .4286
DIMETHYLOLUREA NITRATE = .0000
PRODUCT RATE = 20.127 LB./HR.
PRODUCT WEIGHT FRACTIONS = AMMONIUM NITRATE = .6681
UREA = .0782
DIMETHYLOLUREA NITRATE = .2537

RATE CONSTANT DATA
PRE-EXPONENTIAL FACTOR = .1813E 13
ACTIVATION ENERGY = .2218E 05
RATE CONSTANT FOR UREA DECOMPOSITION
PRE-EXPONENTIAL FACTOR = .2119E 14
ACTIVATION ENERGY = .1879E 05

TOTAL CATALYST WEIGHT = 1102.40 GRAMS
NOMINAL RESIDENCE TIME = 140.47 MINUTES

are weighted radial averages as a function of axial height. The pertinent results are summarized in Table 75 and are compared to experimental results obtained over the last 22.5 hours of operating time. During this period, all the reactor product melt was collected, weighed and analyzed for AN, U and GN. A comparison of the predicted and experimental results clearly demonstrates the accuracy and reliability of the mathematical model.

The predicted temperature profile data are plotted in Figure 77. Included on the graph are the experimental radial and wall temperature data. The experimental wall temperature data agree with the predicted values. The experimental radial temperature data fall, for the most part, on the calculated curve representing a distance of 0.8 inch from the reactor wall. The departure of the measured radial temperature from the predicted curve in the bottom section of the reactor can be explained The mathematical model predictions are based on feed entering the reactor at 120°C with both the catalyst bed and reactor jacket originating at zero axial height. However, in actual practice, feed enters the reactor at 120°C (zero axial height) and then travels through an 8-inch section of reactor that does not contain catalyst. This 8-inch section, in effect, serves as a preheat section, resulting in higher than predicted initial radial temperatures.

Several reactor product samples were analyzed for water insolubles (ammelide). These analyses, in conjunction with the analyses of the individual reactor product melts, were used to calculate the per cent water insolubles on a total GN basis. The results are shown in Table 76. Figure 78 is a plot of insolubles (on a GN basis) as a function of cumulative reactor feed time. When operating at a 2/1 (AN/U) molar feed ratio, the insolubles level was < 0.1% after 45 hours of reactor feed time. At the 1/1 feed ratio, the insolubles started at a level of about 0.55% and increased to 1.04% (0.49% on a total reactor melt basis) after operating for 70 hours at this feed ratio. The final steady-state insolubles value is unknown; however, it is assumed that it would level out at 2-3% based on GN.

c. Conclusions

The 1-inch and 4-inch-diameter reactor experiments completed during this report period were both gratifying and rewarding in that minimum catalyst mileages of 68 g GN/g catalyst and 38 lb GN/lb catalyst, respectively, were demonstrated. In addition to the improved demonstrated catalyst mileage values with commercial, additive-free AN and urea feed stocks (but no plant recycle), there was no apparent catalyst poisoning or physical breakdown of the catalyst. Material balance data reflects the accuracy of the assumption that one mole of ammonium carbamate (AC) is produced for each mole of guanidine nitrate. Conversion of urea to GN and AC was 83-85%, which is consistent with earlier developed mathematical model predictions. The GN yields, based on urea reacted, were in excess of 90% (average 95% for the 4-inch-diameter reactor operation).

TABLE 75

## COMPARISON OF EXPERIMENTAL & PREDICTED RESULTS FROM OPERATION OF SINGLE FOUR-INCH DIAMETER REACTOR

CONDITIONS:

1. Houdry Silica Beads (26 lb )
2. Feed Rate - 27 lb./hr.
3. Feed AN/U Molar Ratio - 1/1 (No Recycle)
4. Feed Temperature - 120°C.
5. Jacket Temperature - 208°C.

| | Experimental (1) | Predicted (2) |
|---|---|---|
| a) Product Analysis (%) | | |
| AN | 45.3 | 46.8 |
| U | 9.1 | 7.7 |
| GN | 45.5 | 45.5 |
| b) Urea Conversion (%) | 84.5* | 86.7 |
| c) GN Yield (%) | 89.3* | 89.9 |
| d) Melt Product Rate (lb/hr) | 19.7 | 20.1 |
| e) Productivity (lb. GN/hr.) | 9.0 | 9.1 |

*Urea fed = (27 lb. feed/hr. x 0.429) (22.5 hr.)/60 = 4.344 moles urea
Urea in reactor product = (444 lb. product x 0.091)/60 = 0.673 moles urea
GN in reactor product = (444 lb. product x 0.455)/122 = 1.656 moles GN

$$\text{Urea conversion} = \frac{4.344 - 0.673}{4.344} \times 100 = 84.5\%$$

$$\text{GN Yield} = \frac{1.656}{3.707} \times 2 \times 100 = 89.3\%$$

1. Based on 22.5 hours of operation during which time reactor product melt was weighed and analyzed (4:00 P.M. 2/3/73 - 2:30 P.M. 2/4/73)

2. Based on tubular reactor mathematical model developed during Phases I and II and using experimental feed rate, feed makeup and jacket temperature data.

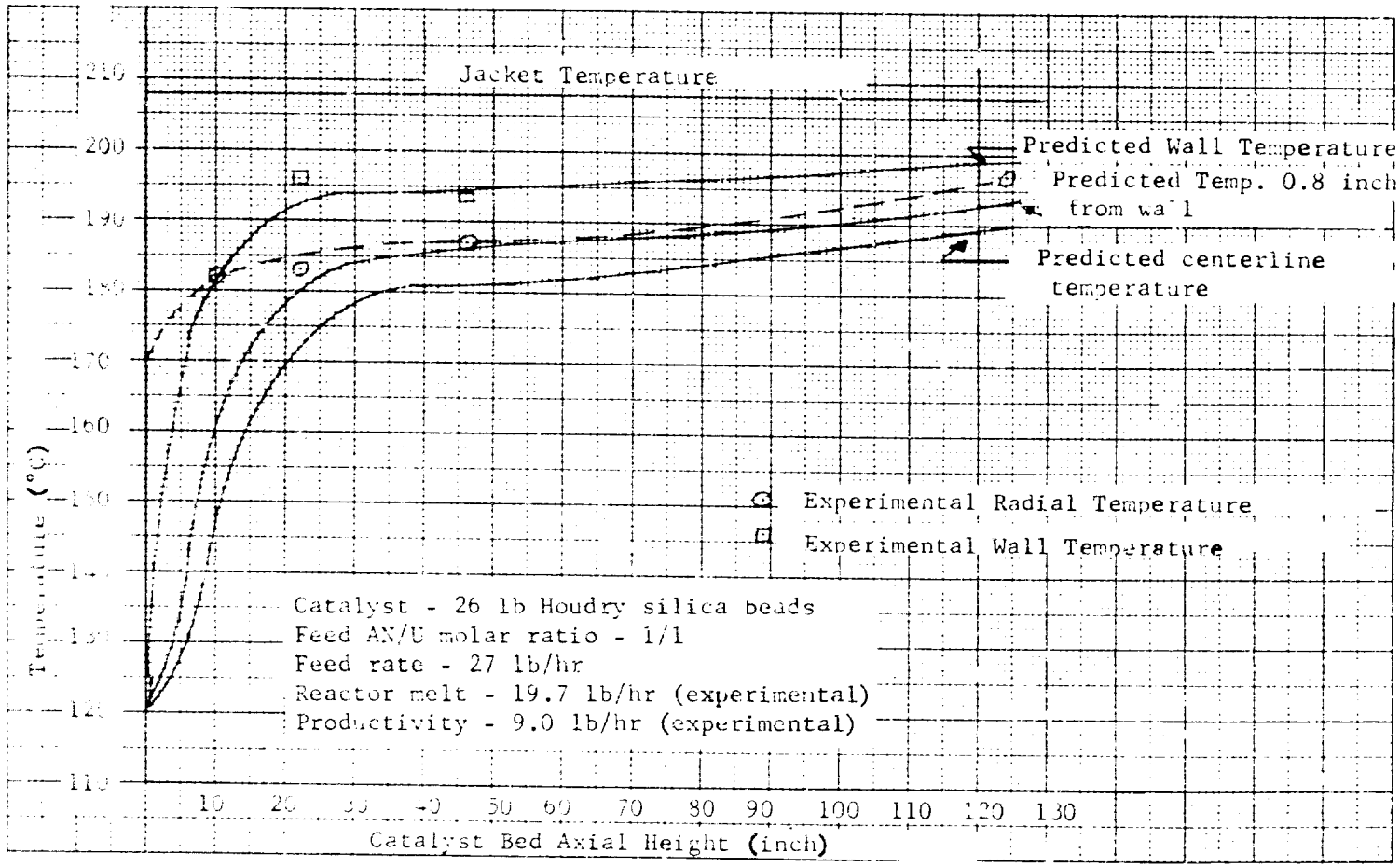



Figure 77. Comparison of Actual and Predicted Temperature Profiles for 4-Inch-Diameter Reactor Run (1/29/73 - 2/4/73)

TABLE 76

## WATER INSOLUBLES IN REACTOR PRODUCT MELT FROM FOUR INCH DIAMETER REACTOR CONTAINING HOUDRY BEADS

1. Additive-Free Hercules/Donora AN
2. Olin Urea
3. Reactor Jacket Temperature - 200°C.
4. Feed Rate - 25 - 30 lb./hr.

| Date | Time | Cumulative Feed Time (hrs.) | Feed AN/U Ratio | Insolubles In Melt (wt. %) | GN In Melt (Wt.%) | Insolubles Based on GN (Wt. %) |
|---|---|---|---|---|---|---|
| 1-31-73 | 7:30 AM | 22 | 2/1 | 0.01 | 29.4 | 0.034 |
| 1-31-73 | 11:00 PM | 44 | 2/1 | 0.05 | 27.1 | 0.084 |
| 2-2-73 | 4:30 AM | 57 | 1/1 | 0.27 | 45.5 | 0.602 |
| 2-2-73 | 7:30 AM | 60 | 1/1 | 0.35 | 51.2 | 0.680 |
| 2-3-73 | 7:30 AM | 84 | 1/1 | 0.39 | 48.7 | 0.792 |
| 2-4-73 | 10:30 AM | 111 | 1/1 | 0.49 | 46.9 | 1.035 |

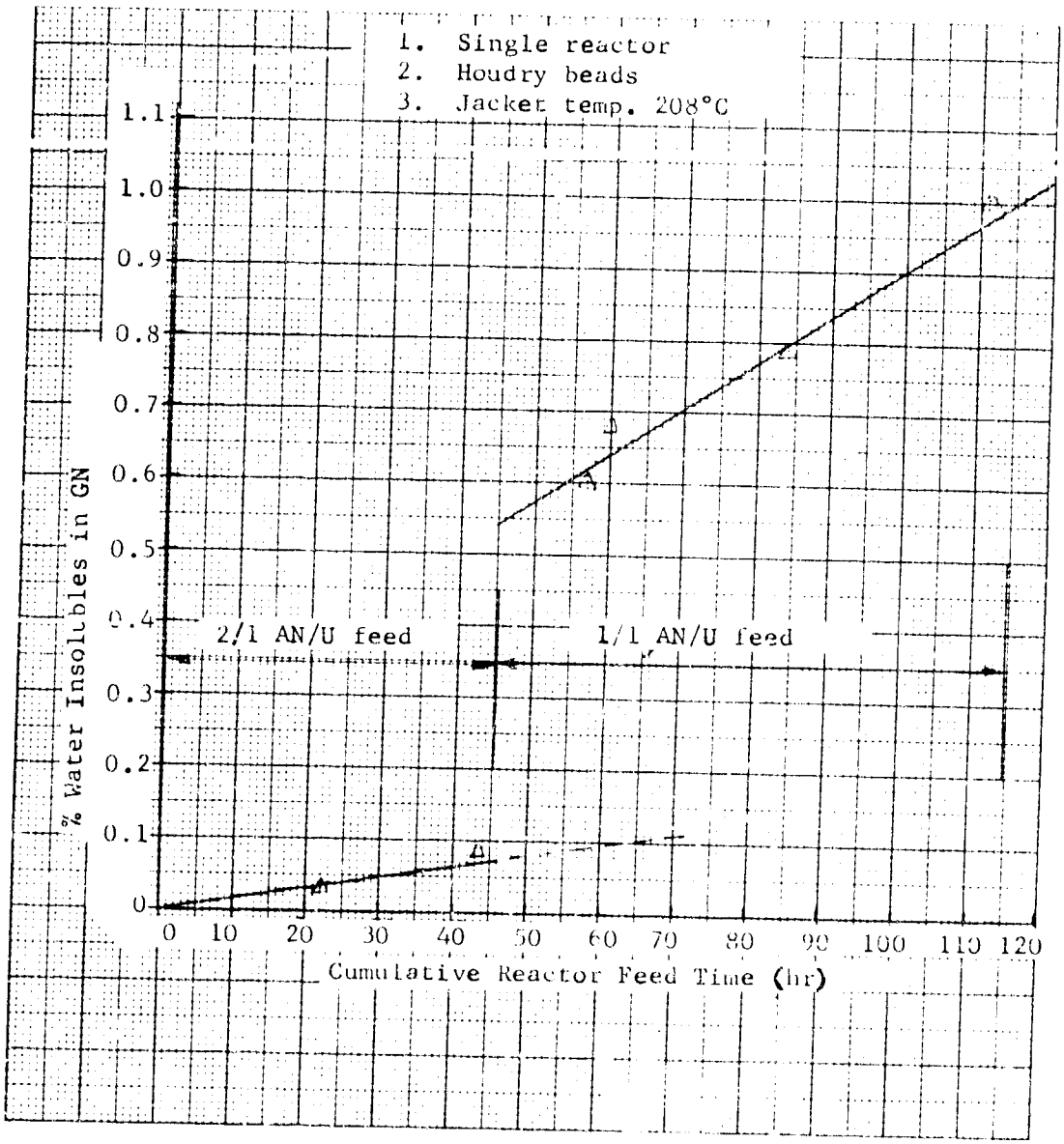



Figure 78. Reactor Product Water Insolubles for 4-Inch-Diameter Reactor Run (1/29/73 - 2/4/73)

The accuracy of the packed bed tubular reactor mathematical model developed earlier was demonstrated, i.e., predicted and experimental results were in almost total agreement. For example, predicted and experimental production rates were 9.1 and 9.0 lb GN/hr/tube, respectively.

On the basis of these two experiments, the practicality of the AN/U process for manufacturing GN appears to be technically sound. Additional data are required to establish the effect of plant recycle feed on GN productivity, insolubles formation, catalyst mileage, catalyst life, etc.

## 9. Chemical and Process Literature Search for Guanidine Nitrate Manufacture via Catalytic Reaction of Urea and Ammonium Nitrate

Two different literature searches were performed to (1) determine if the literature held any clues regarding the problems encountered in the pilot plant with catalyst poisoning, and (2) briefly review work done by other researchers on the U/AN process for manufacturing guanidine nitrate.

### a. Chemical Literature Search

A literature search related to production of GN from urea and ammonium nitrate was made with the following objectives: to assure that recent literature on the process had been covered and to develop information relative to production of by-products and their possible effects on catalyst performance. Chemical Abstracts was thoroughly checked from 1956 through October 16, 1972 and in some cases from 1947. The information was divided into four general categories: (a) Preparation of Guanidine Nitrate from Urea, (b) Reactions of Urea from 100°C to 200°C, (c) Formation of Melamine from Urea, and (d) Silica-Phosphate Reactions. The chemical literature search, which is the subject of a separate report presented in Appendix V, can be summarized as follows:

Little new information was found on the process for guanidine nitrate from urea and ammonium nitrate, but reaction characteristics and reaction mechanisms were reviewed. The catalytic reaction with silica gel leads to the formation of guanidine nitrate and small amounts of triazine by-products at temperatures which give cyanuric acid as the main product in a straight thermal reaction. The mechanism appears to involve: (1) formation of HNCO from urea; (2) complexing of HNCO with the catalyst, followed by disproportionation to $CO_2$ and a reactive carbodiimide-catalyst complex; and (3) displacement of the carbodiimide by ammonium nitrate to give guanidine nitrate.

The current Hercules procedure of holding the urea-ammonium nitrate feed at about 110°C for extended periods can be expected to involve the reactions: (1) hydrolysis of urea to give yield losses and (2) formation of

biuret. An experimental check should be made of the biuret formed, but amounts in excess of 5% would not be expected. Formation of biuret is readily reversed at reaction conditions so that its formation in small amounts would not be a serious problem. Significant amounts of triazine products would not be formed at the feed temperature.

Cyanuric acid, ammelide, ammeline, and melamine can all form at the guanidine nitrate process temperature. Maintenance of catalyst activity, optimum reactant ratios, and temperatures as low as compatible with practical rates can be utilized to minimize these by-products.

Recently developed processes for production of melamine from urea and ammonia appear to involve the same initial steps as production of guanidine nitrate from urea and ammonium nitrate, namely, formation of HNCO from urea and disproportionation on the catalyst. The melamine process is run at temperatures > 350°C which avoid formation of cyanuric acid, ammelide, and ammeline and give high concentrations of the reactive intermediate which then trimerizes to melamine.

Information on possible reactions of phosphates with silica gel was sought in view of the finding at Hercules Kenvil Plant that diammonium phosphate in the ammonium nitrate stabilizer decreases the activity of the catalyst. Adsorption of phosphates on mineral surfaces has frequently been reported but generally appears to involve Al or Fe in the mineral clays. Phosphoric acid-impregnated silica showed evidence of chemical reaction of phosphate groups with surface hydroxyls. Chemical reaction between $PCl_3$ and hydroxyl groups of silica gel has been demonstrated and offers an analogy to what appears to happen with diammonium phosphate. Specific references were not located for reaction of phosphates with silica gel under conditions of the guanidine nitrate reactions. However, the information in the literature is not inconsistent with surface reaction of phosphate to inactivate the catalytic sites on silica gel.

b. Correlation of Works By Other Researchers

Boatright and MacKay of Pittsburgh Coke and Chemical Company, U.S.A., patented(1) the urea/ammonium nitrate/silica gel method for manufacturing guanidine nitrate. In his early work,(4) MacKay noted problems of catalyst activity decay. However, his vintage Run 80-88 (1956) with downflow recycle feed to a 1 inch diameter x 24 inch deep bed for eleven days and seven hours per day did not exhibit catalyst deactivation. The column was fed with a 175°C, 2/1 molar melt (AN/U) at an average feed rate of 2.6 cc/minute. Pertinent results were: 85%-90% yield, ca 70 displacements (gm feed per gm catalyst) and a catalyst mileage of 14 (gm GN per gm catalyst). Presumably, reagent grade and/or non-contaminated AN and U were used.

Work by Martin and Roberts (E.R.D.E., England)[3] using four-cascade stirred reactors (30 gm $SiO_2$ each) with a 2.75-hour residence time demonstrated 264 displacements and a catalyst mileage of 69 gm GN per gm catalyst. This experiment was a prolonged trial using recycled mother liquor resulting from urea dilution of reactor melt, crystallization, GN separation and evaporation. Average feed rate (1/1 AN/U) was 113 gm per hour and the product averaged 35% GN. The run was carried out intermittently for 35 days at 8 hours per day. No drop-off in catalyst activity was noted.

Spasskaja and Kazarnovskii (U.S.S.R., 1963)[8] operated a special steel columnar reactor with upflow feed for 150 hours. It is not certain if the run was conducted in a continuous manner or intermittently. A 90% yield accompanied by 225 displacements and a mileage of 110 was obtained for the following conditions: feed rate 1.8 kg/hr (~ 4.0 lb/hr) at 80-100°C, 0.7/1.0 AN/U ratio and reactor temperature of 190°C. No reduction in catalyst activity was reported. Again, as was the case for both MacKay and Martin-Roberts, the types of AN and U are unknown.

For reference, when employing ammonium nitrate with a crystal habit modifier, the approximate catalyst mileage and total displacement values for a 14-day run of Houdry beads in the Kenvil pilot plant while utilizing eight 4-inch-diameter reactors were 6 lb GN per lb catalyst and ~ 300 lb feed per lb catalyst, respectively. For a single 4-inch-diameter reactor run with Mobil Sorbeads (5 days), the approximate mileage and displacement values were 2.5 and 60, respectively. When commercial, reagent grade AN was used, Hercules demonstrated a catalyst mileage of 68 gm GN/gm catalyst with 558 displacements (gm feed/gm catalyst) in a 1-inch-diameter downflow reactor. Operation of 4-inch-diameter reactor with the same AN resulted in mileage and displacement values of 38 and 126, respectively. Catalyst (Houdry CP-532 silica beads) was not evident in either of the latter experiments.

The literature indicates some decrepitation in the case of silica gel. Literature references relating to work performed by MacKay, Martin and Roberts and Sparskaya and Kazarnovskii note that catalyst poisoning was not a problem with fresh feed. MacKay also reported no poisoning when using recycled material. However, there are contradictory comments throughout the literature relating to catalyst regeneration.

Ammonium nitrate prills purchased from the Hercules' MCW plant contain a borate - phosphate crystal habit modifier. This modifier (boric acid, diammonium phosphate and ammonium sulfate, less than 0.5% total) is added to the ammonium nitrate melt prior to prilling to produce prills that are less subject to fracture as a result of crystal transitions. Ammonium nitrate undergoes volume expansion and contraction as it passes through its crystal transition temperatures during production and storage. Passing through a crystal transition results in breakdown of prills and granules to dust and fines. The habit forming modifier minimizes the size reduction and consequently improves their bulk handling properties.

Data presented by S. J. Gregg (Chemisorption, W. E. Garner, ed; Butterworths, London, 1957, p. 68) showed that silica gel dried at 200°C contains about 6.5% by weight water. More than one-half of this water is present as hydroxyl and not as adsorbed water as calculated from silica gel surface area and hydroxyl groups per unit surface area data. If there is about 1/4% borates and phosphates in the reactor feed and if each hydroxyl is inactivated by a borate or phosphate, ten to a hundred displacements (lb feed per lb catalyst) would consume all of the hydroxyls and yield a zero catalyst activity.

## 10. Guanidine Nitrate Drying

The guanidine nitrate pilot plant was operated in two successive campaigns to produce about one-ton of GN (dry basis). A portion of the GN was dried in the pilot plant Strong-Scott rotary dryer; however, its operation was not entirely successful because of a buildup of GN within the dryer. It became apparent that a satisfactory method for drying water-wet GN must be found to fulfill the pilot plant requirements as well as a design for a production plant, either the U/AN or BAF process. Tests were conducted using: (a) the modified (Teflon-coated paddles) Strong-Scott drier, (b) a Littleford steam jacketed dryer designed for back mixing, and (c) direct heat, jet zone dryer (Wolverine), and (d) canvas bags placed in a forced air dry house. The results from these drying tests showed that indirectly heated and mechanically agitated driers are unsatisfactory for drying GN. The wet GN progressed from a wet solid state to a paste followed by evaporation of the water which resulted in a hard cake adhering to the walls, etc., of the dryer. Drying GN in a direct-heat dryer (e.g., hot air, a jet zone Wolverine dryer or a static forced-air dryer) resulted in a free-flowing and/or a slightly agglomerated dry product. Consequently, indirect-heat dryers are not recommended for drying water-wet GN.

Seven drying tests were made in three types of mechanical dryers: (1) Strong-Scott, (2) Littleford, and (3) pilot model jet zone. In addition, water-wet GN was placed in canvas bags and dried in a forced-air (55°C) dry house. The tests are described below:

### a. Littleford Dryer (Model FM-130 D-1Z)

This type of dryer contains a rotor with plow shear-shaped blades to provide intimate mixing of solids within the dryer. This action results in a high percentage of dry solids throughout the dryer which should minimize particle bridging and adhesion of particles to internal parts. For reference, the Strong-Scott rotary dryer installed in the pilot plant has a number of pitched blades resulting in a pseudo plug flow of solids throughout the length of the dryer. The Littleford dryer was steam jacketed and gas purged.

### 1 Test X2121-29-1

Using 16 psig steam on the jacket and a small nonheated inert gas purge, a dryer test was conducted in this unit. The unit was charged half-full with 120 lb of wet GN containing 19.5% moisture. In about three hours, the moisture had been reduced to 2-3%.

The initial wet GN was wetter than typical wet GN from the pilot plant centrifuge (~ 12% $H_2O$). Its change in form during the drying test was very informative. The heat from the jacket of the mixer transferred to the solids, resulting in a solids temperature increase. Presumably, as the temperature of the solids increased, the water would have flashed off. However, as the solids became hotter, the GN solubility in water increased and the GN began to dissolve in the water. The result was a paste which coated all of the surfaces of the mixer. As the temperature increased and the water began to evaporate, the resultant coatings in the surfaces turned into hard, fused masses. The agitator scraped these surfaces and generated dry powder but a good percentage of the charged wet GN ended up as a fused coating.

The paste stage that was seen in this dryer explains why drying problems had been experienced in the Strong-Scott dryer. In the Strong-Scott unit, when the fused cake built up on the wall, the rotor would start to scrape it, resulting in a thumping action. This was the final symptom which terminated each of the previous drying tests in the Strong-Scott unit. This property of passing through the paste stage is in line as well with the problems experienced in steam tube dryers in previous Canadian tests.

### 2 Test X2121-40-1

This run was a repeat of X2121-29-1 in the Littleford dryer but without jacket heat and with a heated (200°F) hot air purge (~ 3 cfm). Its result was similar to X2121-29-1 with its paste stage and resultant buildup of solids on the wall. This test could have been more successful if a better and larger air distribution system were available on this dryer. The rotation of the Littleford agitator had a tendency to throw solids into the air inlet pipe, frequently choking off its flow.

## b. Strong-Scott Dryer

The Strong-Scott rotary dryer was disassembled, and the rotor and paddles were coated with a 3-mil layer of Teflon. Following assembly of the coated shaft, a test run (X2121-34-1) was made with wet GN. After two hours of continuous wet solids feeding, the dryer began to thump. Inspection of the internal walls showed that the surface was coated with fused GN. Further inspection of the interior surfaces showed that it contained indentations where the paddles had scraped through the solids buildup. The conclusions drawn from the Littleford dryer test were directly applicable to this test.

c. Hot Air Jet Zone Dryer

A Wolverine Jet-Zone dryer is used at Kenvil for drying smokeless powder. It is essentially a vibratory conveyor which conveys the feed solids along beneath a forest of downward-directed tubes inside which hot air flows and from which jets of hot air impinge upon the surface of the drying solids. The local turbulence of the hot air jets is believed to promote improved drying.

Figure 79 illustrates a pilot unit set up to develop data for jet-zone drying of smokeless powder. The unit was also used to test HMX drying. The action of the large-scale air jets is well duplicated, but the vibratory action of the conveyor is not a part of the pilot unit. The solids rest at the bottom of a windowed container and are essentially motionless, although there is some fluidization as the top part of the bed becomes dry.

A half-pound charge of 10% to 15% water-wet GN (3/4 inch bed) was added to the container, which was then clamped into place beneath the jet tubes. Two runs were made with unscreened feed, and two were made with screened feed. The data and drying results, given in Figure 80, show that screening and increased air flow (high Magnehelic readings) lead to increased drying rates.

The determination of the air flow from the Magnehelic readings is not clear. An estimated value is 10 cfm at a Magnehelic reading of 1 inch of water.

The outstanding result from the Jet-Zone dryer test at Kenvil was that the dry product was neither caked nor dusty and that there was only a slight adhesion of one particle to another. Just the slightest touch of the finger caused the aggregates to separate. There was no evidence of pasting as had been the case with the Littleford dryer. It was the best looking GN yet obtained from a dryer.

There was essentially no entrainment under these drying conditions nor was there any evidence of electrostatic effects such as powder clinging to the tubes.

The drying action, i.e., air flowing at or across the top surface of a bed of wet solids, is essentially that of a Wyssmont dryer. Both the Jet-Zone and the Wyssmont are examples of a "continuous tray dryer." In the tray dryer the solids are spread out on trays which are supported by shelves or brackets. Hot air circulates across the top of the solids. Water diffuses up through the cracks in the bed, first by capillary attraction, to keep the surface moist and cool. When a certain minimum water content is

reached, no more water is brought to the surface, and the solids begin to dry as the dry-moist interface works downward in the solid bed. It has been demonstrated that a "continuous tray dryer" will work.

Calculations for a rough design of a production unit using a Jet-Zone design dryer are shown in Table 77. The air flows are reasonable. The question of residence time is a problem and is related to the minimum velocity at which a unit can convey. The calculations show only 10-minute residence time at a conveying velocity of 5 feet per minute and a wet solids loading of 2 lb wet solids per square foot (3/4 inch bed). To obtain a 20-minute residence time, it would be necessary to convey at 2.5 feet per minute and at a wet solids loading of 4 lb per square foot (1-1/2 inch bed). Whether drying rate is limited by air flow or bed thickness is not yet known. In any case, more test work needs to be done before a dryer can be designed with assurance.

d. Forced Air Tray Drying

Canvas-type bags were filled with different weights (10, 25 and 40 lb) of water-wet ( $\sim$ 15%) GN and then placed on perforated trays in a 55°C forced-air dry house. After about 60 hours of drying time, the moisture contents of the materials had decreased to $< 0.5\%$. The dry GN, in all cases, consisted of some lumps but they were friable. In view of the time required to design, deliver and install a pilot model jet-zone type dryer, it is planned to utilize this type of a drying procedure for future pilot plant operations.

TABLE 77

ROUGH DESIGN CALCULATIONS FOR A PRODUCTION GN JET-ZONE DRYER

1. Assume 5,000 lb/hr wet GN at 89% solids.

2. Assume two parallel trains of two 4 foot wide by 25 foot long units in series.

3. Assume surface inlet leading at 2 lb (wet) per square foot of horizontal area. (Approximately 3/4 inch deep bed as at Kenvil.)

4. Assume conveying velocity at 5 ft/min.

   Then capacity = 2 units x 4 ft width x 5 ft/min x 60 min/hr x 2 lb/sq ft

   = 4,800 lb/hr versus 5,000 lb/hr assumed

5. Assume air flow from nozzles at 30 scfm/$ft^2$.

   Then total flow per dryer = (30 scfm/$ft^2$) (4 ft x 25 ft)

   = 3,000 scfm

6. What is minimum air flow to evaporate the water?

   Heat to evaporate 550 lb water/hr = 550,000 Btu.

   If air is cooled from 250°F to 150°F

$$Scfm_{minimum} = \frac{550{,}000 \text{ Btu/hr}}{(0.075 \text{ lb air/scf})\ (60 \text{ min/hr})\ (100°F)\ (0.24 \text{ Cp})}$$

   = 5,000 scfm

NOTICE: Total drying time is only 10 minutes here. We depend upon four factors to give improvement over pilot test results:

(1) Use of hotter air.
(2) Break-up of static cake at outlet of first unit.
(3) Vibration to give better heat transfer and mass transfer.
(4) Less heat losses in the plant-size unit.

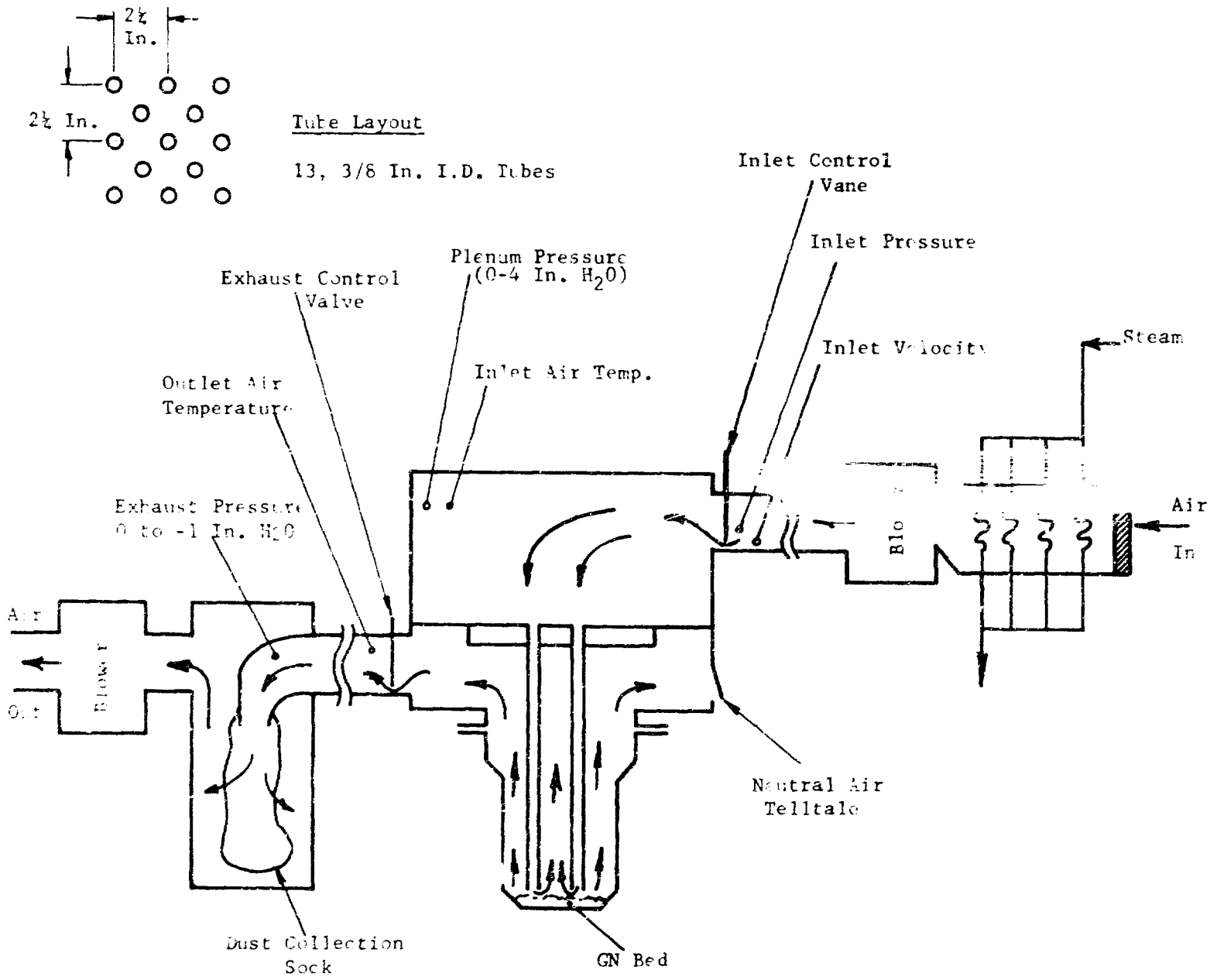



Figure 79. . Laboratory Fluid Bed Dryer

| GN | Symbol | Run No. | Air Temp., °F (In/Out) | Air Flow Δ P (in. Water) |
|---|---|---|---|---|
| Unscreened | □ | X2121-32-A | 175/100 | 1.4 |
| screened | X | X2121-32-B | 175/100 | 1.0 |
| Screened | ○ | X2121-33-A | 175/100 | 1.0 |
| Screened | △ | X2121-33-B | 160/80 | 0.3 |

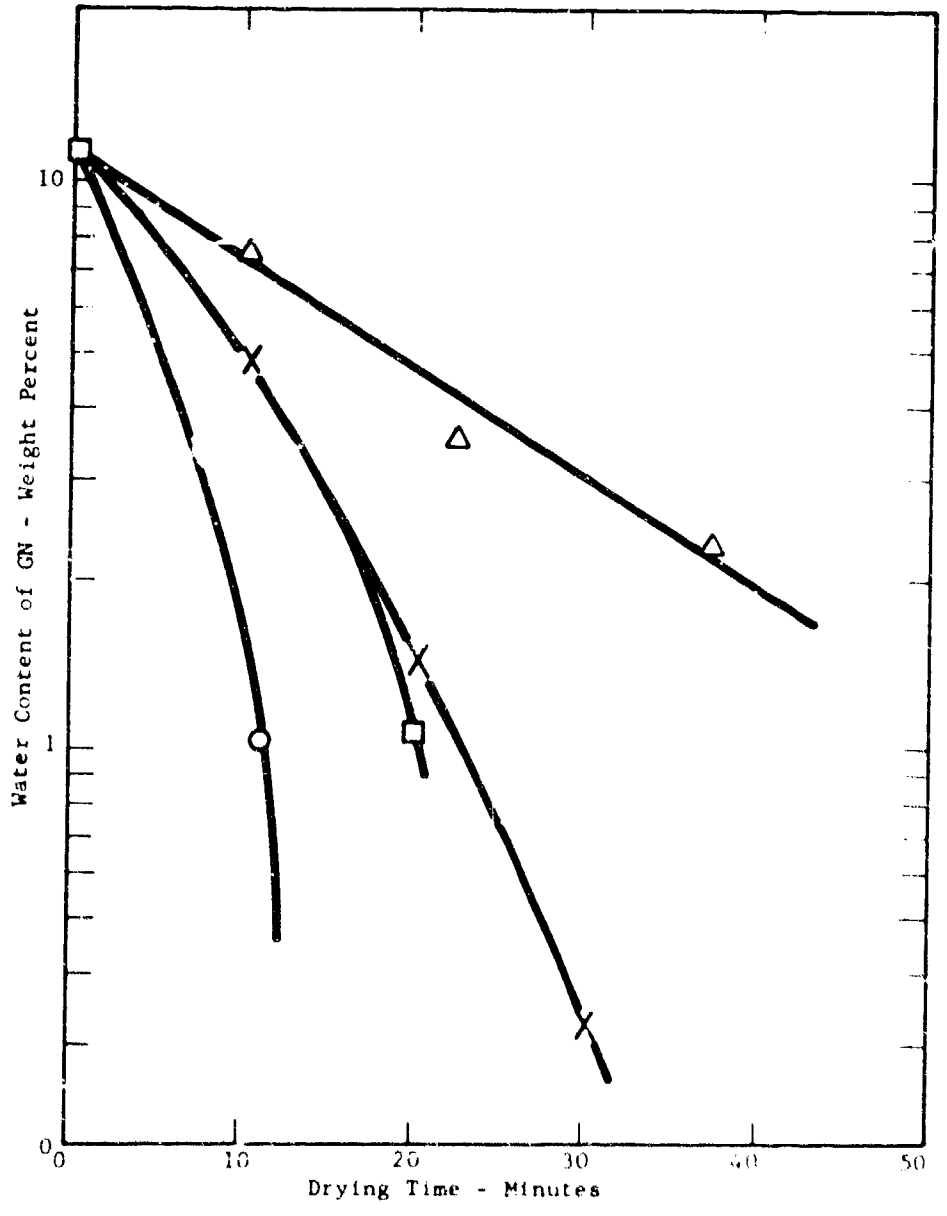



Figure 80. GN Drying Data - Kenvil Test Dryer Jet-Zone Type

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