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A 1/10 SCALE PILOT PLANT FOR THE ECOLOGICAL DEMILITARIZATION OF MK 25 MARINE LOCATION MARKERS/RED PHOSPHORUS COMPOSITION

NWSC/CR/RDTR-70

by

Frank E. Montgomery
James E. Short, Jr.

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NAVSEA (0332) under WR 74026 tasked NWSC Crane to develop a 1/10 scale pilot plant to reclaim phosphoric acid and other components from the disposal of Mk 25 Marine Location Markers. The typical pyrotechnic formulation for the Mk 25 and Mk 58 Marine Location Markers plus the Mk 6 Aircraft Smoke and Illumination Signal is 53 percent red phosphorus, 34 percent manganese dioxide, 7 percent magnesium, 3 percent zinc oxide and 3 percent linseed oil. The process includes

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breakdown equipment to extract the red phosphorus composition from the markers and an incineration complex to convert the composition to phosphoric acid suitable for fertilizer application. Processing the composition from the Mk 58 Marine Location Markers and that from the Mk 6 Aircraft Smoke and Illumination Signal through the incineration complex would be identical to that of the Mk 25 - only the composition extraction procedure would differ. As part of the overall development efforts by NWSC Crane, breakdown machines and an incineration complex were designed, fabricated and individually tested in order to obtain necessary data. After delivery, the incineration complex was installed in the pilot plant with the associated marker breakdown equipment and operated from May 1977 through August 1977 in order to obtain data on the total system.

The results of this demilitarization effort illustrate that the overall process developed by NWSC Crane offers a technically sound and ecologically acceptable approach for the reclamation of a fertilizer-grade phosphoric acid from the red phosphorus composition contained in the pyrotechnic devices mentioned above.

DISCLAIMER

At different points throughout this report, it has been necessary to identify commercial materials and equipment. In no case does such identification imply recommendation or endorsement by the Navy, nor does it imply that the material or equipment identified is necessarily the best avaliable for the purpose. Criticism of commercial equipment by the Navy does not imply that the equipment is generally inferior.

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SUMMARY

Disposal of obsolete, outdated, or unserviceable conventional ammunition items has been performed primarily by deep-water dumping or by open field burning. With these procedures, no salvage value of the constituent components of the ordnance can be realized. Two additional detracting factors are the considerable costs that may be incurred in deep-sea dumping and the atmospheric pollution that is generated by open burning.

As a result, NAVSEA instituted programs to develop methods to dispose of scrap or obsolete pyrotechnic items in environmentally acceptable ways. This particular program involves the design, fabrication and operation of a 1/10 scale pilot plant for the ecological demilitarization of red phosphorus compositions. These compositions are derived both from production scrap and unserviceable units. Currently there are approximately 500,000 pounds of red phosphorus composition on inventory for disposal. Historically each producer of red phosphorus markers has generated approximately 125 pounds of production scrap per day.

Machines were designed and built to take red phosphorus containing pyrotechnics apart (principally the Mk 25 Marine Location Marker) and incinerate the composition in an environmentally acceptable manner.

As part of the overall development efforts by the Naval Weapons Support Center, Crane, Battelle-Columbus Laboratories, Columbus, Ohio was requested to construct and test an incineration complex on a pilot plant scale and to develop design data for a production sized incineration complex.

An incineration complex capable of processing approximately 10 pounds of composition/batch was constructed. The complex consisted

of incinerator, scrubber, mist eliminator, gas pump, stack, stack gas sampler, and control panel. A total of 39 runs were made for calibration and equipment checkout, incinerator curing, exploratory operations, and test operations. The incineration complex was then combined with the breakdown machines. The total pilot plant was operated from May through August 1977.

The results of the operations confirmed that the incineration process concept was technically sound and feasible. The incineration unit was able to be operated in an environmentally acceptable fashion. The combustion residue was chemically stable after water treatment and the stack gas emission for P_2O_5 was below the current Ammunition Procurement and Supply Agency (APSA) Standard of 1 mg P_2O_5/scf when the pilot plant was operated at the optimal operating condition. Battelle-Columbus Laboratories, which operates the U.S. Fertilizer Technical Institute, feels that the phosphoric acid produced from the incineration process is fertilizer grade. The acid yield was approximately 41 percent, based on the total phosphorus in the feed composition without allowing for the recovery of condensed acid from the incinerator and process lines.

A preliminary design of a production facility capable of processing approximately 100 pounds of composition in a batch operation was made based on information obtained from the pilot plant operations.

It is concluded that the process described herein offers a method to demilitarize red phosphorus containing pyrotechnics such as the Mk 25 and Mk 58 Marine Location Markers as well as Mk 6 Aircraft Smoke and Illumination Signals. This process converts the red phosphorus compositions into phosphoric acid. Although this process does not realize a profit, it does offer a sound method of disposing of the above mentioned munitions in an environmentally acceptable manner.

INTRODUCTION

Disposal of obsolete, outdated, or unserviceable conventional ammunition items has been performed primarily by deep-water dumping or by open field burning. With these procedures, no salvage value of the constituent components of the ordnance can be realized. Two additional detracting factors are the considerable costs that may be incurred in deep-sea dumping and the atmospheric pollution that is generated by open burning.

NAVSEA instituted programs to develop methods to dispose of scrap or obsolete pyrotechnic items in environmentally acceptable ways because of:

a. The increasing, evident salvage value of both metallic and non-metallic constituents of ammunition.

b. The increasing cost associated with storage space occupancy, record keeping, and provision for security.

c. The increasing volume of material to be disposed of.

d. The increased awareness of environmental aspects of deep-water dumping and open burning. These programs were directed toward reclaiming valuable constituents whenever possible.

NAVSEA (0332) under WR 74026 tasked NWSC Crane to develop a 1/10 scale pilot facility to reclaim phosphoric acid and other components from the disposal of Mk 25 Marine Location Markers (MLM). Our task was to build and/or procure the equipment necessary to completely disassemble and process Mk 25 MLM's.

Of the approximately 500,000 pounds of red phosphorus composition on inventory for disposal, the majority of the composition is contained in Mk 25 Marine Location Markers. Most of the remainder is contained in Mk 58 Marine Location Markers and Mk 6 Aircraft Smoke and Illumination Signals. This, plus the fact that the red phosphorus composition in the three different munitions listed above is practically identical, led us to use the Mk 25 MLM in the process described herein. Table 1 lists the materials obtained from processing Mk 25 MLM's while Figure 1 is a process flow chart which briefly describes our process.

EQUIPMENT DESIGN

Figure 2 shows a cutaway model of the Mk 25 Marine Location Marker (MLM). The first series of operations consists of mechanically separating the red phosphorus pyrotechnic composition from the remainder of the hardware. Figures 3, 4, and 5 show the operator approaching the band saw with a Mk 25 MLM and loading it into the band saw. Figure 6 shows the Mk 25 MLM clamped in the band saw with the base removed. After removal of the base, the inner aluminum tube containing the pyrotechnic candle easily slips from the foam liner and outer tube. This operation is shown in Figure 7. Next, the inner tube is placed in the push out fixture (Figure 8). Figures 9 and 10 show the pyrotechnic candle being pushed from the inner tube through the paper tube slicer.

After push out, the plastic cap on the ignition end of the candle is removed and the loose ignition composition is poured into a separate container where it is stored for reuse, (Figures 11 and 12). The next step in the breakdown series involves sectioning the pyrotechnic candle in the radial arm saw. Figure 13 is an overall view of the radial arm saw.

In Figure 14 the candle is placed in the reservoir. Water is then pumped into the reservoir to cover the candle, and the saw is activated to section the candle. After sectioning, the pieces of candle are allowed to soak in the reservoir of the radial arm saw to facilitate paper tube removal from the composition.

After soaking 20 minutes, the water is drained from the candle sections and the dump door on the reservoir is opened. See Figures 15 and 16. This allows the candle sections to fall into the conveyor feed hopper as shown in Figure 17. At this station the paper is removed and the composition is loaded by means of a vibrating feeder into a conveyor bucket for transport to the incinerator (Figures 18 and 19).

Figure 20 shows the first operator conveying the composition toward the incinerator. Figures 21 and 22 show the composition dumping from the bucket into the charge pan. In Figures 23 and 24, the second operator is seen feeding the charge pan into the incinerator and closing the door.

After charging the incinerator the burner in the first chamber (No. 1 burner) is turned on long enough to achieve ignition of the composition (Figure 25). Upon ignition No. 1 burner is turned off. Phosphorus pentoxide (P_4O_{10}), the principal product of combustion of red phosphorus composition, is drawn through the second chamber of the incinerator. The second chamber (with No. 2 burner) has been preheated to ensure complete combustion of the product gases (Figure 26). From the second chamber of the incinerator, the product gases are drawn into the top of a concurrent water spray, ceramic packed, scrubber column as seen in Figure 27. The water spray containing the product gases forms phosphoric acid which is collected (Figure 28) and recycled through the scrubber.

Any remaining product gases and acid droplets travel from the second column of the scrubber into a mist eliminator seen in Figure 29. The mist eliminator performs a function true to its name. It removes any residual acid mist from the stack gas stream.

The machine that keeps the product gases traveling from the incinerator through the scrubber columns and the mist eliminator is an air pump shown in Figure 30. Its intake is connected to the mist eliminator and its exhaust is connected to the stack. Stack sampling equipment is attached to the stack to periodically monitor the exhaust gas stream. The console for this sampling equipment is shown in Figure 31.

The instrument panel shown in Figures 32 and 33 is monitored throughout the incinerator test burn. Pressure differentials as well as temperatures, are measured at various points throughout the incineration system to monitor the progress of the burn.

The incineration of the red phosphorus composition contained in Mk 58 Marine Location Markers and Mk 6 Aircraft Smoke and Illumination Signals would be handled exactly as the Mk 25 MLM composition. Breakdown of these units is feasible as shown in Figures 34 and 35. Figure 34 shows a Mk 58 MLM that has been sawed on a band saw and Figure 35 shows a Mk 6 that has been sawed on a band saw.

The various machines and auxiliary equipment discussed above are treated more thoroughly in the Operations Section.

PROCESS CONSIDERATIONS

1. Throughout the course of this project, several areas were investigated. The initial process concept was to demilitarize Mk 25 Marine Location Markers in an ecologically approved manner. This was to be accomplished by dismantling the markers and extracting

the red phosphorus composition for incineration. The concept involved combustion of the red phosphorus composition to reclaim a phosphoric acid product for use by the fertilizer industry. A preliminary evaluation of the incineration concept was conducted by Battelle-Columbus Laboratories, Columbus, Ohio, in an early study. The results indicated that the incineration concept proposed by Naval Weapons Support Center, Crane appeared technically sound and feasible. It was determined that a phosphoric acid product recovered from the incineration process would be suitable for use in the manufacture of a solid fertilizer, such as triple superphosphate, without purification. Based on this study, Battelle-Columbus Laboratories was requested to pursue the incineration concept through pilot plant scale to further examine the technical design data for a production facility. Appendices A and B are reports covering the above effort.

2. During the incineration study, it was found that a spontaneously combustible gas was released when the hot combustion residue (ashes) was quenched in water. Upon collection and analysis of this gas, it was found to be principally composed of phosphine (PH_3), which is toxic with a tolerance limit of 0.3 ppm in air.

The corrective action taken in eliminating this hazard was to install a water spray and drain in the first chamber of the incinerator. A drain was installed in the second chamber also. After combustion of composition appeared to be complete, the water spray was turned on and the No. 1 burner was ignited for approximately five minutes. The water spray generated phosphine and the burner flames combusted any phosphine generated. The resultant ashes were chemically inert to water. This series of tests is covered more thoroughly in Appendix B under Ash-Water Reaction Experiments, p. B-15.

3. Another area investigated during the incineration study was the disposal of the combustion residue or ashes from the incineration of red phosphorus composition. Battelle-Columbus Laboratories felt that the ashes might be used by the manganese industry. The ashes are typically 40 percent by weight oxides of manganese (MnO/MnO_2). Since the United States imports about 98 percent of the total manganese used, recycling the ashes is one possibility. This alternative is discussed more thoroughly in Appendix A, p. A-116.

Another possible use for the ashes is in the ceramic industry. It was found that by screening the ashes through a No. 60 mesh screen, they could be used as a portion of a ceramic glazing compound. When used as a glaze on a clay cup, the ashes imparted a spotted brown color to the surface. See Figure 45 and notice the difference between cups that were glazed with zero ashes, 4 percent and 10 percent ashes in the glazing compound.

Should the first two possibilities described above be nonfeasible economically, the ashes could be landfilled. They have been sprayed with water and "burned" a second time to ensure there is no possibility of phosphine being generated. They are chemically inert and will cause no problems in a landfill.

4. The fourth consideration was the preparation of a hazard analysis for the Mk 25 Marine Location Marker demilitarization process. NAVSEASYSCOM and local requirements dictate the preparation of an operations hazard analysis prior to the start-up of any process involving high energy materials. Appendix C is the operations hazard analysis. This document is included not only as information, but as an attempt to acquaint the reader with some of the paperwork necessary before engineering tests were run on the individual machines prior to design freeze and incorporation of the equipment into the pilot plant.

5. During the operation of the pilot plant the mist eliminator coalescing element was plugged from time to time. Our immediate solution was to provide a by-pass line which, simply stated, removed the mist eliminator from the system. The solution works, but the correct solution would be to have two mist eliminators connected in parallel - so that if one plugged the other could be used until the plugged element is cleaned. This approach is recommended for the scaled-up version (see Scaling Factors).

6. For ease of operation, our cooling water was discharged down a drain after use. The water could easily be passed through a cooling tower and recirculated. This approach is also recommended for consideration in the scaled-up version (see Scaling Factors).

7. The recent blackout in New York City prompted a test of the incinerator under a simulated power outage. After ignition of the composition in the incinerator, power to the burners and air pump was disconnected. The water spray over the burning composition was turned on. Smoke continued to roll from the edges of the incinerator door for 5-7 minutes. After the smoke cleared, and the composition was observed to be out, the water spray was shut off, the air pump was turned on, and the burners in the incinerator were again ignited to finish burning the composition.

8. Although this pilot plant was designed to demilitarize red phosphorus munitions, i.e., the Mk 25 and Mk 58 Marine Location Markers and Mk 6 Aircraft Smoke and Illumination Signals, the incineration unit is also capable of handling the red phosphorus scrap generated in the production of the aforementioned munitions. It is estimated that a producer of Mk 25 or Mk 58 Marine Location Markers would generate 125 pounds of scrap composition per day. In the event there were a large buy of red phosphorus munitions, there would be a sizeable quantity of red phosphorus scrap for disposal.

OPERATIONS

1. Test Plan

The pilot plant became operational in May 1977. The data is presented in Tables 2 through 9 and will be discussed in this section. Prior to start-up of the pilot plant, a test plan was devised which consisted of three alternate routes toward accomplishing our task.

These alternate routes consisted of utilizing different machines for the breakdown operation prior to incineration. The test plan is listed below:

SEQUENCE I	SEQUENCE II	SEQUENCE III
Pull down	Band saw	Band saw
Decrimper	Push out	Push out
Push out	Radial arm saw	Convey
Radial arm saw	Convey	Incinerate
Convey	Incinerate	
Incinerate		

a. Sequence I

In Sequence I the first step involved removing a rubber G-ring from the G-ring slot in the exterior circumference of the base fuze housing. The operator is shown doing this in Figure 36. (The purpose of the G-ring is to provide a gas seal between the marker and launcher barrel.) After the G-ring was removed, the marker was placed in the pull down machine (Figure 37) and clamped by means of the G-ring slot (Figure 38). The machine would first separate the outer tube and foam liner from the remainder of the marker (Figure 39). It would then shift and separate the inner tube containing the pyrotechnic candle from the base fuze housing (Figure 40). The inner tube would then be placed on the decrimper machine (Figure 41).

This operation rolled out the crimp that had held the inner tube to the base fuze housing and facilitated easy removal of the pyrotechnic candle from the inner tube on the push out fixture (Figure 8). As the candle was pushed from the inner tube, it was fed through a tube splitter. (The tube splitter cut the paper tube once to facilitate separation of the paper tube from the candle composition.) After being pushed through the tube splitter (Figure 9) the plastic starter cap with electric squib is removed and the loose ignition composition is dumped into a separate storage container. Now the candle is placed in the radial arm saw reservoir (Figure 14). The reservoir is filled with enough water to cover the candle and the saw is started. The saw automatically clamps and saws the candle into thirds.

A sufficient quantity of candles for one charge of the incinerator is sawed and allowed to soak in the reservoir. After soaking for twenty minutes, excess water is drained from the reservoir, the dump door is opened and the candle tube paper and candle composition fall into the conveyor feed hopper. See Table 2 for data on the pull down, decrimp, push out, and radial arm saw operations of Sequence I.

The paper is easily separated from the composition and placed in a container for disposal by incineration. The paper is not incinerated with the composition but rather it is accumulated and incinerated separately. The composition is fed into a conveyor bucket which transports the composition toward the incinerator. The conveyor bucket dumps into an incinerator charge pan.

Prior to feeding the charge pan into the incinerator, the incinerator system is brought "on-line" by heating the second chamber of the incinerator to 500°F, setting the air pump to pull approximately 125-150 CFM through the system, adjusting the scrubber column spray/recycle phosphoric acid, and ensuring that the cooling water is flowing through the heat exchangers. The three heat exchangers consist of water jackets on the process line leading from the incinerator, around scrubber column No. 1, and a finned tube exchanger mounted in scrubber column No. 2. The above procedure is depicted graphically in Figures 42, 43 and 44. These Figures are graphs of three typical test burns in the incinerator with notation of particular events as they occurred throughout the test burn. For data on test burns conducted May 1977 - August 1977, see Table 9. After the second chamber of the incinerator reaches 500°F, the charge pan is fed into the incinerator. The burner in the first chamber (burner No. 1) is used to ignite the composition and then is turned off. After combustion of the composition, water is sprayed on the combustion residue by means of a spray bar mounted inside the first chamber of the incinerator and burner No. 1 is ignited to dispose of any phosphine present. (The phosphine problem is discussed in Appendix A, pp. A-87 and A-88). The water spray and burner No. 1 are turned off after five minutes, the combustion residue is removed and the incinerator is ready for another charge.

Cycle time for the incinerator system was found to be approximately twenty (20) minutes per five (5) pound batch after the initial test burn of the day. See Figures 42, 43 and 44.

b. Sequence II

In Sequence II the marker was placed in the band saw (Figure 5.) The band saw was set to saw the base fuze housing from the rest of the Mk 25 MLM. In doing so, it also removed the portion of the inner tube which was crimped to the base fuze housing. The band saw replaced the pull down machine and the decrimper required in the Sequence I test plan.

After removal of the base fuze housing, the inner tube containing the pyrotechnic candle easily slipped from the foam liner and outer tube (Figure 7).

From this point in the process the procedure duplicated that of Sequence I. Tables 3, 4, 5 and 6 include data on the band saw, push out, and radial arm saw operations in Sequence II.

c. Sequence III

In Sequence III the band saw was programmed to remove the base fuze housing and wafer the remainder of the marker into thirds (Figure 5), see data in Tables 7 and 8. Once the marker was wafered, the section of inner tube and candle easily slipped from the section of foam liner and outer tube. The wafered section was then placed in the push out fixture to separate the section of candle from its corresponding section of inner tube. As seen in Table 8, difficulty was experienced in pushing the candle section from the section of inner tube. Some candle sections pushed out easily while others (31%) would not push out. A couple of sections held momentarily and then ejected from the inner tube violently. This part of Sequence III proved to be unsafe and not feasible. Tests under Sequence III were discontinued at this point.

2. Problem Areas

A number of problem areas surfaced during operation of the pilot plant. These problem areas together with proposed solutions are summarized below:

a. Pull down machine. In using the pull down machine it was found that the circumference of the cast aluminum base fuze housing differed considerably from unit to unit. This created difficulty in placing the marker in the pull down machine. Fifty to seventy-five percent of the markers used had to be filed to some degree in the G-ring slot. It is felt that this problem could have been eliminated by modifying the machine; however, results of tests conducted during the pilot plant run indicated that the band saw eliminated the requirement for both the pull dowr machine and the decrimper. The band saw was quicker and more efficient. Thus, this problem was eliminated.

b. Push out fixture

(1) The only problem experienced with the push out fixture was covered in the previous section under Sequence III. This involved pushing candle sections from sections of inner tube after they had been sawed on the band saw. A couple of sections ejected violently from the inner tube. Due to its unsafe nature and the difficulty in getting candle sections separated from sections of inner tube, Sequence III was abandoned as a feasible mode of operation.

(2) In the early days of operating the pilot plant, it was taking considerable time to soak the paper tube from the candle composition. (The problem of burning paper in this incineration system is discussed in Appendix A, pp. A-123 and A-124). Approximately 100-120 minutes soak time under water were required to loosen the paper from the candle composition. Based on recommendations by NAVSEA 0332 personnel, a paper tube splitter was constructed and installed at the aft end of the push out fixture (see Figure 7). This splitter made one longitudinal slice through the candle paper tube. After sectioning the candle in the radial arm saw, total soak time was reduced to 20 minutes for complete paper removal. See Table 2.

(3) After the candle has been pushed from the inner

tube and through the tube splitter, the plastic starter cap with electric squib is loosened sufficiently that it can be lifted from the candle and placed in segregated storage. To dispose of the starter caps with electric squibs, it is recommended that a batch of starter caps be placed in the incinerator and the temperature elevated enough to fire the electric squibs followed by landfill of the residue.

(4) After the plastic starter cap is removed from the candle, the loose ignition composition is poured into a grounded container and saved for reuse in other flares. Tests on a small number of units indicated the reclaimed ignition composition performed as reliably as standard ignition composition.

c. Radial arm saw

(1) The reservior on the radial arm saw serves two purposes. First, as a safety feature, it serves to ensure that the red phosphorus candle is kept under water during the sawing operation. Second, it has sufficient capacity to serve as a soak tank for the candle sections after sawing. After a 20 minute soak period, the paper and candle composition are dumped into the conveyor feed hopper. At this point the paper is separated by hand from the composition and placed in segregated storage.

(2) Disposing of the paper in the red phosphorus incineration system would be possible if the mist eliminator in the system was by-passed. Incineration of the paper in the present system would also be possible if there were two mist eliminators in parallel. As one became plugged, it could be switched out of the system and cleaned while the other mist eliminator performed its function. In the past the system has become plugged as a result of burning paper in the incinerator. See Appendix A, pp. A-61,

A-63, A-122 and A-124. A viable alternative to incineration would be enzymatic hydrolysis of the paper to yield fermentable sugars. This method is covered in the U.S. Army Natick Research and Development Command Report "Enzymatic Hydrolysis of Cellulosic Wastes to Fermentable Sugars and the Production of Alcohol," by L.A. Spano, January 1976.

d. Incineration

(1) Difficulties were experienced with the automated incinerator feed mechanism. The problem was by-passed for the operation of the pilot plant by constructing a table with runners, such that the loading and unloading operations could be performed manually. The automated incinerator feed mechanism will be corrected in the final documentation package.

(2) The problems encountered in the incineration system are covered in Appendix A. The principal problem in the system concerns the air pump used to pull the product gases from the incinerator through the scrubber columns and mist eliminator. The 302SS vanes in the air pump are eroding away after intermittent usage over the past two years. This problem can be solved by purchasing a larger air pump constructed entirely of 316L stainless steel.

This and other problems encountered with the red phosphorus incineration system are discussed in Appendix A, pp. A-120 through A-124. Some modifications prompted by the problems described in Appendix A are detailed in Appendix B.

USE OF DEMILITARIZATION PROCESS BY-PRODUCTS

The principal by-products of this demilitarization process are phosphoric acid, scrap aluminum and combustion residue (ashes).

Preliminary data indicates that the phosphoric acid would qualify as agricultural grade suitable for the manufacture of fertilizer. See Appendix A, p. A-116 for further discussion on this topic.

Scrap aluminum, generated at the rate of two pounds per Mk 25 MLM processed, is worth twenty-six cents per pound even though it is contaminated with rubber seals and foam liners. Although a profit will not be made on recycling the aluminum components from Mk 25 MLM's, realizing their value from the scrap yard is much better than landfilling them.

The combustion residue has three possible dispositions. It may be used as a manganese ore since it contains approximately 40% MnO. Further discussion of the combustion residue as an ore is covered in Appendix A, pp. A-117 and A-119.

Another viable use for the combustion residue is in a glazing compound for ceramic wares. Figure 45 is an example of some pots that have been glazed with a mixture, one portion of which was the combustion residue.

The final alternative disposition for the combustion residue would be to landfill it - if the first two ideas were not economically feasible. It contains no harmful heavy metal contaminants and is therefore ecologically acceptable for landfill.

Another by-product, is the silver and magnesium strips available in the sea water battery. The base fuze housing for each Mk 25 contains a sea water battery for functioning of the marker. Figure 46 shows a sea water battery positioned inside a base fuze housing that has just had the end removed in the band saw. Although each battery contains only 0.42 grams of silver and 1.7 grams of magnesium - if these metals were extracted from 100,000 sea water batteries, there would be 1350 troy ounces of scrap silver worth $5400.00 and 374 pounds of scrap magnesium worth $150.00.

SCALING FACTORS

This facility was designed to be a 1/10 scale pilot plant for recovering components from Mk 25 Marine Location Markers (MLM). Most of the breakdown equipment had to be scaled for full sized Mk 25 MLM's. Hence, all equipment up to the conveyor is adequate for production operations. The conveyor could be modified to serve in a production operation by increasing the number of buckets attached to the conveyor belt or by installing aluminum paddles periodically along the conductive belt in place of buckets. The times required for each operation are listed in Table 10.

As seen from Table 10, our pilot facility contained a fast cutting band saw, a push out fixture, a slow cutting radial arm saw, a conveyor, and a pilot sized incineration system. This facility was capable of processing 58 pounds of composition in an eight hour day. The sequence necessary to accomplish this is shown in Table 11.

The equipment required to scale up a facility capable of processing 472 pounds of composition per ten hour shift would be another radial arm saw, a new conveyor feed hopper that would receive composition from both radial arm saws to load the conveyor and a production sized incineration system. Times required for a scaled-up version as described above are shown in Table 12. A scaled-up version of the incineration system is discussed in Appendix A, pp. A-125 through A-143.

A recommended addition to the incineration system discussed in Appendix A would be another mist eliminator in parallel to the one already discussed. Once a mist eliminator element became plugged as a result of excess carbon from burning paper, plastic, etc., it could be switched from the system and cleaned while the other mist eliminator continued to function.

Another factor for consideration in a production sized incineration facility would be the inclusion of a cooling tower. In the pilot plant operation, the cooling water was discharged directly to the drain. However, the water could easily be passed through a cooling tower and recirculated to the heat exchangers.

ECONOMIC ANALYSIS

The cost of operating the pilot plant versus the cost of construction and operating a production plant are listed in Table 13. For a cost break-down of the production sized incineration system, refer to Appendix A, pp. A-135 through A-136.

It is shown in Table 13 that the disposal of Mk 25 Marine Location Markers in a production plant will cost approximately $4.20 per pound of composition processed. The decision to enlarge the plant will be based upon guidance from NAVSEASYSCOM.

CONCLUSIONS/RECOMMENDATIONS

It is concluded that this process offers a method to dispose of unserviceable Mk 25 Marine Location Markers in an ecologically acceptable manner. At the same time the process recovers a fertilizer grade phosphoric acid and scrap aluminum. It is recommended that consideration be given to scaling the present pilot plant into a production facility with the following recommendations incorporated:

Radial arm saw - an additional radial arm saw would be required to produce a desirable production rate. After sufficient de-bugging, the radial arm saw in the pilot plant operated satisfactorily; however, there is no way to increase its rate enough to supply a production sized incinerator with 54 sliced Mk 25 candles every 90 minutes.

Conveyor feed hopper - the conveyor feed hopper presently used in the pilot plant would require modification. Presently the sawed candles are soaked in the radial arm saw reservoir. In the production facility, the water soak would have to be done in the conveyor feed hopper adjoining each of the two radial arm saws. The conveyor feed hoppers would have to be designed to both empty into the conveyor.

Conveyor - the conveyor used in the pilot plant performed adequately. In a production operation, the conveyor would require more buckets attached to the conveyor belt or aluminum paddles attached periodically along the conductive belt in place of buckets.

Incineration system - in a production facility an incinerator capable of processing 100 lb. per batch rather than 5-10 lb. per batch would be a necessity. A larger incinerator would necessarily require appropriately sized scrubber columns, acid recycle tanks, heat exchanger, mist eliminator, and air pump. Mist eliminators in parallel would be ideal in a production facility to facilitate cleaning one while the system is running. If one becomes plugged, the other can be switched into operation - thereby avoiding shut down and the escapement of noxious P_4O_{10} vapors. A production sized incineration system is thoroughly discussed in Appendix A, pp. A-125 through A-143.

Phosphoric acid - Battelle-Columbus Laboratories, which operates the U.S. Fertilizer Technical Institute, feels that the phosphoric acid produced from the incineration process is fertilizer grade. Although there are trace metal contaminants (magnesium, manganese, zinc, chromium and nickel) in the phosphoric acid, there is no published specification on the maximum allowable concentrations of these metals for fertilizer applications (Appendix A, p. A-116). Manganese and magnesium in small concentrations are good micronutrients for the soil.

Although this process to demilitarize Mk 25 and Mk 58 Marine Location Markers does not realize a dollar profit, it does offer a sound method for disposing of the markers in an environmentally acceptable manner.

TABLE 1

Listing of Materials Obtained From Processed Mk 25 Marine Location Markers

Component	Suggested Reuse
Outer tube, inner tube, base fuze housing	Sale as scrap
Styrene packaging and foam liner	Landfill or sale as scrap
Metal banding	Sale as scrap
Pallet	Reuse as is
Plywood overpack	Reuse as is or sale as scrap
Sea Water battery	Sale as scrap
Paper tube contaminated with composition	Controlled incineration
Starter cap w/ electric squib	Controlled incineration followed by landfill
Ignition composition	Reuse in other markers
Phosphoric acid	Sell to fertilizer industry
Ash residue	Use as ore for Mn extraction, ceramic glaze, or landfill

TABLE 2
SEQUENCE I
PULL DOWN, DECRIMP, PUSH OUT, RADIAL ARM SAW

Unit No.	Pull Down (sec)	Decrimp (sec)	Push Out (sec)	Water Fill RAS^1 (sec)	RAS^1 Candle into Thirds (sec)	Water Drain RAS (sec)	Overall Time to Fill Water, Saw 3 Candles, Drain Water and Dump (min)
1	88	6	9		138		
2	75	3	8.5				
3	92	4	8.2				10.83
4	72	3	11		136		
5	95	3	11		136		
6	77	9	15				13.75
7	79	6	12				
8	114	4	11				
9	67	5	11				10.67
10	74	5	11.5				
11	73	5.2	8				
12	79	7	14		140		10.50
13	88	7	21	87	150		
14	78.5	5.1	9		135		
15	75.2	4	14		136	73	10.45
16	77	4	16	80.5	140		
17	75	8	8		122		
18	74	8	11.4		131	90	10.07
19	76	7	11	60	135		
20	74	5	11		133		
21	79	4.8	11		135	82	10.02
22	79	5	11	125	130		
23	75	6	15		137		

TABLE 2 (CONT'D)

24	79	7	11		134	84	11.08
25	70.2	4.5	9	94	135		
26	76	5	11		130		
27	77	8	10		131	73	10.23
28	77	4.5	12	77	135		
29	76	5	12		131		
30	75.4	6	12		132		
31	74	6	12		135	73	12.00*
9 each**	798**	168**					24.80**
9 each**	768**	306**	132.6**				21.75**
Average	78.7	5.5	11.5.	87.2.	134.6	79.2	10.8 (batch of three)

*Time includes sawing of four candles instead of three. Not used in averaging.

Average time for batch of three candles through Sequence I Breakdown:

$$\frac{78.7 \text{ sec} \times 3 + 5.5 \text{ sec} \times 3 + 11.5 \times 3}{60 \text{ sec/min}} + 10.8 \text{ min.} = 15.6 \text{ min.}$$

**Times include reservoir fill time, but no drain time. All of the nine candles were left to soak in reservoir to determine soak time required for candle tube separation. After soaking 100 minutes, approximately 85 percent of the paper peeled off easily. Later in the project a tube splitter was added to the push out fixture. This reduced the water soak time required to 20 minutes for complete paper removal from the composition. Times not used in averaging.

[1] - Radial Arm Saw

TABLE 3
SEQUENCE IIA
BAND SAW, PUSH OUT, RADIAL ARM SAW

Unit No.	Cut Off Base (Band Saw) (sec)	Push Out (sec)	Radial Saw (Candle into Thirds) (sec)	Saw 3 Candles (Thirds) Overall (min)
1	27.5	9.0	159	
2	32.2	7.8	142	
3	37.2	11.6	141	13.63*
4	29.3	11.6	144	
5	35.7	7.9	138	
6	40.7	12.1	139	10.82
7	35.5	11.5	173	
8	30.4	9.3	137	
9	31.2	9.4	165	12.53*
10	29.7	8.6	138	
11	32.2	9.4	177	
12	32.4	7.9	133	11.33
13	34.7	8.3	134	
14	36.2	8.3	134	
15	31.0	9.2	133	9.92
16	34.9	6.6	134	
17	28.6	7.5	134	
18	27.1	9.0	135	9.90
19	29.7	8.2	135	
20	29.2	9.0	134	
21	28.0	8.5	132.5	10.27
22	27.7	9.2	143	
23	27.8	8.0	133	
24	31.0	9.2	139	10.17
25				
26	225	70.2		13.23
27				
28				
29	135	64.8		10.98
30				
Average	37.3	11.7	141.9	11.28

NOTES:

Total time (band saw) for units 9 through 16 = 5.82 min. Fresh water fill (RAS) reservoir = 4.2 min. Units 1-30 sawed into thirds.

Average time for batch of three candles through Sequence IIA Breakdown: $\frac{37.3 \times 3 + 11.7 \times 3}{60 \text{ sec/min}} + 11.28 \text{ min} = 13.7 \text{ min}$

See notes on following page.

TABLE 3 (CONT'D)

NOTES:

Cut Off Base - Time includes loading of band saw, removal of the base and removal of inner tube afterward.

Push out - Time includes loading and unloading operation in addition to push out time.

Radial Saw - Time required for saw to slice one Mk 25 candle into thirds.

Saw Three Candles Overall - Time includes water fill of the radial arm saw reservoir, loading and sawing three Mk 25 candles, draining the water from the reservoir, and dumping the candle sections into the conveyor feed hopper.

TABLE 4
SEQUENCE IIB
BAND SAW, PUSH OUT, RADIAL ARM SAW

Unit No.	Cut Off Base (Band Saw) (sec)	Push Out (sec)	Radial Saw (Candle into Halves) (sec)	Saw 3 Candles (Halves Overall) (min)
1	33.3	8.2	74	
2	35.6	11.0	75.4	
3	33.8	16.7	72	6.97
4	36.1	9.5	130*	
5	34.8	7.2	75	
6	35.6	9.7	73.8	8.17
7	34.9	8.2	75	
8	34.6	8.3	74	
9	32.9	9.2	76	6.50
10	33.5	7.3	75	
11	34.9	7.9	73.5	
12	33.9	8.1	76	6.13
13	32.7	7.9	73.5	
14	34.2	9.2	75.5	
15	34.4	8.4	74.1	6.50
16	33.9	8.9	75.5	
17	33.9	8.6	77	
18	37.2	8.1	75.4	8.10**
19	36.1	8.6	75.2	
20	34.1	7.3	77	
21	37.8	9.7	83.2	7.30
22	34.1	9.9	81.2	
23	34.5	8.3	83	
24	36.9	9.8	72.5	7.53
Average	34.7	9.0	75.8	7.2 min

Total time (band saw) for units 1 through 8 = 5.78 min.
Total time (band saw) for units 17 through 24 = 5.95 min.
** Fresh water fill reservoir = 2.67 min.
Units 1-24 sawed into halves
Average time for batch of three candles through Sequence IIB
Breakdown: $\frac{34.7 \text{ sec} \times 3 + 9 \text{ sec} \times 3}{60 \text{ sec/min}} + 7.2 \text{ min} = 9.4 \text{ min}$

See notes on following page.

TABLE 4 (CONT'D)

NOTES:

Cut Off Base - Time includes loading of band saw, removal of the base and removal of inner tube afterward.

Push Out - Time includes loading and unloading operation in addition to push out time.

Radial Saw - Time required for saw to slice one Mk 25 candle into halves.

Saw Three Candles Overall - Time includes water fill of the radial arm saw reservoir, loading and sawing of three Mk 25 candles, draining the water from the reservoir, and dumping the candle sections into the conveyor feed hopper.

It was found that Mk 25 candles sawed into halves would not feed properly through the conveyor feed hopper. Therefore, this operation was discontinued.

TABLE 5
SEQUENCE II
BAND SAW, PUSHOUT

	Operation				
Unit No.	Load Band Saw (sec)	Cut Off Base (sec)	Remove Inner Tube (sec)	Push-Out (sec)	Saw 6 Candles (thirds) overall (min)
1	2.0	22.2	4.2	14.2	
2	2.2	24.3	6.5	8.0	
3	4.7	20.4	12.1	11.9	
4	3.7	19.5	11.2	9.4	
5	4.8	19.5	3.0	9.0	
6	4.6	23.2	3.5	9.6	9.50
7	2.9	23.0	7.5	10.5	
8	3.9	21.0	4.4	11.8	
9	4.2	20.0	7.0	9.7	
10	3.7	21.2	8.1	8.9	
11	4.8	16.2	4.9	9.5	
12	5.4	17.8	5.5	9.6	9.84
13	5.1	23.2	4.4	9.4	
14	5.0	18.3	5.8	12.7	
15	4.9	24.1	4.9	8.7	
16	5.4	20.8	4.9	14.6	
17	5.7	17.6	4.9	11.3	
18	6.8	18.2	5.5	11.4	9.39
19	6.3	18.5	5.9	12.3	
20	6.2	19.6	5.3	11.4	
21	5.9	21.5	4.8	8.0	
22	6.7	24.5	8.8	8.8	
23	6.2	21.9	5.8	7.6	
24	6.1	18.2	5.2	9.1	9.74
Average	4.9	20.6	6.0	10.3	9.62

TABLE 5 (CONT'D)

Notes:

Push-Out - Time includes loading and unloading operation in addition to push out time.

Saw 6 Candles Overall - Time includes water fill of the radial arm saw reservoir, loading and sawing six Mk 25 candles, draining the water from the reservoir, and dumping the candle sections into the conveyor feed hopper.

TABLE 6
SEQUENCE II
BAND SAW

Unit No.	Cut Off Base and Remove Inner Tube (sec)	Unit No.	Cut Off Base and Remove Inner Tube (sec)	Unit No.	Cut Off Base and Remove Inner Tube (sec)
1	27.0	20	27.4	39	26.8
2	26.9	21	26.8	40	32.0
3	29.7	22	27.9	41	29.7
4	26.2	23	27.3	42	25.2
5	30.2	24	28.3	43	26.8
6	28.2	25	34.6	44	26.4
7	27.3	26	26.8	45	26.8
8	27.1	27	27.1	46	26.3
9	29.0	28	26.5	47	27.8
10	27.4	29	27.3	48	25.5
11	30.6	30	29.2	49	25.5
12	26.3	31	25.8	50	25.0
13	31.0	32	25.8	51	26.5
14	29.6	33	25.8	52	25.1
15	Special*	34	26.7	53	25.5
16	Special*	35	38.5	54	24.2
17	31.4	36	26.8	55	25.0
18	26.5	37	28.5	56	27.2
19	29.1	38	27.0	Average	27.7

*These units were sawed through the middle of the base to show the feasibility of removing the sea water battery for reclamation purposes.

TABLE 7
SEQUENCE III
BAND SAW

Unit No.	Cut Off Base (sec)	Cut Off First Section (sec)	Cut Off Second Section (sec)	Remove Mk 25 Nose Section From Saw (sec)	Total Elapsed Time (sec)
1	26.7	14.0	13.2	10.7	64.6
2	34.8	15.6	15.5	6.6	72.5
3	28.2	12.2	13.6	14.0	68.0
4	31.8	16.2	15.0	6.0	69.0
5	30.0	16.4	13.7	8.1	68.2
6	30.1	17.1	14.6[2]		
7	30.4	15.3	16.7	7.7	70.1
8	29.8	15.2	15.7	11.0	71.7
9	26.7	15.1	15.0	7.6	64.4
10	29.2	14.8	15.5	7.2	66.7
11	73.9[1]	14.7	16.1	15.2	119.9[1]
12	24.6	14.3	14.8	7.9	61.6
13	31.1	14.3	14.9	9.4	69.7
14	27.5	15.0	14.6	10.6	67.7
15	31.8	14.7	13.1	9.0	68.6
16	30.8	14.2	15.5[3]	11.0	71.5
17	40.4[1]	14.1	14.0	10.1	78.6[1]
18	30.5	15.3	13.3	7.7	66.8
19	31.3	14.7[3]	15.0	8.6	69.6
20	26.5	14.2	15.3	8.4	64.4
21	40.2[1]	14.0	15.0	7.4	76.6[1]
22	31.9	13.9	14.8	7.2	67.8
23	29.0	14.6	14.1[3]	7.3	65.0
24	27.5	13.7	14.8	6.8	62.8
25	35.0	16.5	14.8	7.3	73.6
26	40.2[1]	15.8	15.3	5.6	76.9[1]
27	29.8	15.2	13.7	5.0	63.7
28	26.5	15.1	13.9	5.0	60.5
29	30.0	15.1	15.9	3.5	64.5
30	32.2	16.3[3]	14.3	6.2	69.5
31	30.6	16.4	14.9	6.6	68.5
32	32.7	16.3	15.6	5.2	69.8
33	30.3	14.6[3]	16.2	4.8	65.9
34	32.0	15.6	15.0	4.4	67.0
35	29.9	16.0	15.3[xx]	13.8	75.0
36	28.6	19.3[3]	17.1	7.2	72.2
37	36.5	17.1	15.0	5.8	74.4
38	37.1	17.9	16.6	6.4	78.0
39	32.9	17.1	16.5	6.6	73.1
40	32.6	17.2	17.1	8.9	75.8
41	31.3	17.5	16.8[3]	9.8	75.4
42	34.2	17.1	16.5	8.7	76.5

TABLE 7 (CONT'D)

43	34.8	17.7[3]	17.2	7.3	77.0
44	32.5	16.4	16.3	7.1	72.3
45	32.8	17.4	16.8	6.8	73.8
46	36.1	17.2	17.0	6.7	77.0
47	32.6	17.1	16.9	5.0	71.6
48	31.5	18.0[3]	16.5	10.1	76.1
Average	31.0	15.7	15.3	7.7	69.8

[1] Long time due to operator error. Not used in averaging.
[2] Saw blade came off track during cut.
[3] Puffs of smoke were noted during these operations. Approximately one third of these smokers also had a small flame which was quickly extinguished by the water spray mounted on the saw.

[xx]Units 35-48 - Saw blade very noisy during third cut.

Units 1-24 - Sawed with blade 6 teeth/inch.

Units 25-48 - Sawed with blade 11 teeth/inch.
(Eleven toothed blade averaged one second longer per cut.)

Remarks:

Step 1. Time started when unit dropped into saw channel.

Step 2. Cut off base time - taken when saw arm reached raised position after sawing base from unit.

Step 3. Cut off first section time- time from end of step 2 until saw arm reached raised position after sawing first section from remainder of unit.

Step 4. Cut off second section time - time from end of step 3 unit saw arm reached raised position after sawing second section from remainder of unit.

Step 5. Total elapsed time - time started when unit dropped into saw and stopped when nose section removed from saw.

TABLE 8
SEQUENCE III
PUSH OUT

Section No.	Push Out Time (sec)	Section No.	Push Out Time (sec)	Section No.	Time (sec)
1	7	26	12	51	11.0
2	6	27	6.3	52	
3	8	28		53	7.1
4		29	5.9	54	
5		30	13.4	55	
6	9.1	31	31.2**	56	6.9
7		32	23.0**	57	11.1
8	10	33		58	8.6
9	6	34	12.0	59	9.1*
10		35	6.2	60	10.1
11		36	6.5	61	5.9
12	12	27		62	6.4
13		38	7.5	63	8.9
14		39	5.8	64	7.2
15		40	10.0	65	7.8
16	27.3**	41	6.8	66	6.4
17	6.2	42	6.0	67	11.3
18	28.2**	43	15.0	68	6.6
19	6.2	44		69	6.6
20	8.3	45		70	8.2
21		46		71	8.1
22	6.0	47		72	7.0
23	14.8	48	8.7	73	7.2
24	11.6	49	25.5**	74	
25		50		75	
				76	
				77	6.8*

Average: 10.0 sec., 31% would not push out

NOTES:

Blank - Candle section would not come out of inner tube.
* Candle section violently ejected from inner tube.
**Long time resulted when candle section had to be reversed in fixture and/or when candle sections did push out, but at a very slow rate.

TABLE 9
OPERATION OF PILOT PLANT

Dates	6/9	6/10	6/22	6/22
Operating Condition				
Position of Burner 1	Lower	Lower	Lower	Lower
Charge Pan Opening				
Lid	100%	100%	100%	100%
Side Wall	50%	50%	0%	0%
Preheating Temperature, °F				
Chamber 1	~140	135	120	120
Chamber 2	~800	480	650	560
Load, lb	5.25 (wet, w/o paper)	5.25 (wet, w/o paper)	1.47 (wet, w/o paper)	2.93 (wet, w/o paper)
Combustion				
Preheating Period, min	NM	NM	25	9(6)[1]
Time to Ignition, min	2	2	1	2(1)[1]
Combustion Period, min	5	9	2	6(2)[1]
Maximum Temperature, °F				
Chamber 1 (Inside Charge Pan)	~1300	1360	650	980
Chamber 2	~900	760	720	740
Pressure in Both Chambers, inch of water vacuum	NE	NE	NE	NE
Recycle Acid for Gas Scrubbing				
Initial Conc., % by wt	NM	NM	NM	NM
Initial Volume, gal	NM	NM	NM	NM
Final Conc., % by wt	NM	3.60	NM	NM
Final Volume, gal	NM	3.52	NM	NM
Mist Elimination				
York Mist Elimination (ME) Drain				
Column 1 & 2 Volume, gal	NM	1.11	NM	NM
Conc., % by wt	NM	30.0	NM	NM
Stack Gas				
Flow Rate, acfm	NM	154	NM	155
Temperature, °F	NM	NM	NM	NM
Minimum Oxygen Content, % by vol	NM	NM	NM	NM
Acid Emission, mg P_2O_5/scf	NM	NM	NM	NM
Combustion Residue				
Quantity, lb	NM	NM	NM	NM
Total Phosphorus, % by wt	NM	NM	NM	NM
Incinerator Drain				
Vol, gal	NM	1.42	NM	NM
Conc., % by wt	NM	4.83	NM	NM
Remarks	Shakedown run w/o strip chart	Shakedown run	Strip chart recorder not operating properly. Small charge pan used.	[1]Candles placed on top of wet ashes from previous burn. Great difficulty in getting complete & continuous combustion. Small charge pan used.

TABLE 9 (CONT'D)
OPERATION OF PILOT PLANT

Dates	6/22	6/23	6/23	7/6
Operating Condition				
Position of Burner 1	Lower	Lower	Lower	Lower
Charge Pan Opening				
Lid	100%	100%	100%	100%
Side Wall	0%	50%	0%	50%
Preheating Temperature, °F				
Chamber 1	140	120	165	120
Chamber 2	560	650	700	500
Load, lb	4.4 (wet, w/o paper)	4.4 (wet, w/o paper)	4.4 (wet, w/o paper)	4.4 (wet, w/o paper)
Combustion				
Preheating Period, min	8	32	10	10
Time to Ignition, min	2	1	1	1
Combustion Period, min	9[2]	6	8	5
Maximum Temperature, °F				
Chamber 1 (Inside Charge Pan)	1010	1650	810	1230
Chamber 2	740	1340	600	1110
Pressure in Both Chambers, inch of water vacuum	NE	NE	NE	NE
Recycle Acid for Gas Scrubbing				
Initial Conc., % by wt	NM	NM	NM	NM
Initial Volume, gal	NM	NM	NM	NM
Final Conc., % by wt	NM	NM	NM	NM
Final Volume, gal	NM	NM	NM	NM
Mist Elimination				
York Mist Elimination (ME) Drain				
Column 1 & 2 Volume, gal	NM	NM	NM	NM
Conc., % by wt	NM	NM	NM	NM
Stack Gas				
Flow Rate, acfm	144	155	153	NM
Temperature, °F	NM	NM	NM	137
Minimum Oxygen Content, % by vol	NM	NM	NM	NM
Acid Emission, mg P_2O_5/scf	NM	NM	NM	1.65
Combustion Residue				
Quantity, lb	NM	NM	NM	NM
Total Phosphorus, % by wt	NM	NM	NM	NM
Incinerator Drain				
Vol, gal	NM	NM	NM	NM
Conc., % by wt	NM	NM	NM	NM
Remarks	[2] Flames & fumes noted in ash pan, burners re-ignited & had spray on for 15 min. Combustion complete. Recorder checked. Small charge pan used.	Recorder malfunctioning, erratic readings.	Approximately 1/4-1/3 composition not combusted.	

TABLE 9 (CONT'D)
OPERATION OF PILOT PLANT

Dates	7/7	7/8	7/9	7/12
Operating Condition				
Position of Burner 1	Lower	Lower	Lower	Lower
Charge Pan Opening				
Lid	100%	100%	100%	100%
Side Wall	50%	50%	50%	50%
Preheating Temperature, °F				
Chamber 1	120	140	125	120
Chamber 2	500	500	450	500
Load, lb	4.4 (wet, w/o paper)	4.4 (wet, w/o paper)	4.4 (wet, w/o paper)	4.4 (wet w/o paper)
Combustion				
Preheating Period, min	15	10	13	10
Time to Ignition, min	1	2	2	2
Combustion Period, min	11	8	11	8
Maximum Temperature, °F				
Chamber 1 (Inside Charge Pan)	1240	1382	1070	1510
Chamber 2	1070	1170	750	1205
Pressure in Both Chambers, inch of water vacuum	NE	NE	NE	NE
Recycle Acid for Gas Scrubbing				
Initial Conc., % by wt	NM	NM	NM	NM
Initial Volume, gal	NM	NM	NM	NM
Final Conc., % by wt	NM	NM	NM	NM
Final Volume, gal	NM	NM	NM	NM
Mist Elimination				
York Mist Elimination (ME) Drain				
Column 1 & 2 Volume, gal	NM	NM	NM	NM
Conc., % by wt	NM	NM	NM	NM
Stack Gas				
Flow Rate, acfm	128	128	122	120
Temperature, °F	135	NM	NM	134
Minimum Oxygen Content, % by vol	NM	NM	NM	NM
Acid Emission, mg P_2O_5/scf	0.75	NM	NM	(1.36)[3]
Combustion Residue				
Quantity, lb	NM	NM	NM	NM
Total Phosphorus, % by wt	NM	NM	NM	NM
Incinerator Drain				
Vol, gal	NM	NM	NM	NM
Conc., % by wt	NM	NM	NM	NM
Remarks				[3] Mist Eliminator by-pas line opened to demonstrate efficiency of mist eliminator to visitors (20 sec). Increased particulate conc. (stack gas acid emission reading)

TABLE 9 (CONT'D)
OPERATION OF PILOT PLANT

Dates	7/13	7/14	7/16	7/19
Operating Condition				
Position of Burner 1	Lower	Lower	Lower	Lower
Charge Pan Opening				
Lid	100%	100%	100%	100%
Side Wall	50%	50%	50%	50%
Preheating Temperature, °F				
Chamber 1	135	145	135	120
Chamber 2	500	460	500	560
Load, lb	4.4 (wet, w/o paper)	.5	4.4 (wet, w/o paper)	.5
Combustion				
Preheating Period, min	7	18	8	18
Time to Ignition, min	2	1	2	2
Combustion Period, min	6	6	6	4
Maximum Temperature, °F				
Chamber 1 (Inside Charge Pan)	1280	510	1195	565
Chamber 2	1100	780	955	630
Pressure in Both Chambers, inch of water vacuum	NE	NE	NE	NE
Recycle Acid for Gas Scrubbing				
Initial Conc., % by wt	3.54	NM	3.69	NM
Initial Volume, gal	3.83	NM	3.43	NM
Final Conc., % by wt	7.90	NM	7.47	NM
Final Volume, gal	3.37	NM	2.91	NM
Mist Elimination				
York Mist Elimination (ME) Drain				
Column 1 & 2 Volume, gal	3.36	NM	3.80	NM
Conc., % by wt	7.53	NM	7.18	NM
Stack Gas				
Flow Rate, acfm	120	128	135	NM
Temperature, °F	NM	NM	NM	NM
Minimum Oxygen Content, % by vol	NM	NM	NM	NM
Acid Emission, mg P_2O_5/scf	NM	NM	NM	NM
Combustion Residue				
Quantity, lb	NM	NM	NM	NM
Total Phosphorus, % by wt	NM	NM	NM	NM
Incinerator Drain				
Vol, gal	0.78		0.84	
Conc., % by wt	4.90		17.07	
Remarks		New operators, trial run. Small chunk of composition.		Small chunk of composition burned for movie run.

TABLE 9 (CONT'D)
OPERATION OF PILOT PLANT

Dates	7/22	10/13
Operating Condition		
Position of Burner 1	Lower	Lower
Charge Pan Opening		
Lid	100%	100%
Side Wall	50%	50%
Preheating Temperature,°F		
Chamber 1	125	730
Chamber 2	550	830
Load, lb	2.2 (wet, w/o paper)	4.4 (wet, w/o paper)
Combustion		
Preheating Period, min	6	92
Time to Ignition, min	1	2
Combustion Period, min	4(6)[4]	25(60)[5]
Maximum Temperature,°F		
Chamber 1 (Inside Charge Pan)	605	1240 (1440)
Chamber 2	640	900
Pressure in Both Chambers, inch of water vacuum	NE	NE
Recycle Acid for Gas Scrubbing		
Initial Conc., % by wt	NM	.04
Initial Volume, gal	NM	3.64
Final Conc., % by wt	NM	3.54
Final Volume, gal	NM	3.72
Mist Elimination		
York Mist Elimination (ME) Drain		
Column 1 & 2 Volume, gal	NM	3.62
Conc., % by wt	NM	12.74
Stack Gas		
Flow Rate, acfm	NM	129
Temperature,°F	NM	110
Minimum Oxygen Content, % by vol	NM	NM
Acid Emission, mg P_2O_5/scf	NM	0.14
Combustion Residue		
Quantity, lb	NM	NM
Total Phosphorus, % by wt	NM	NM
Incinerator Drain		
Vol, gal		3.19
Conc., % by wt		0.81
Remarks	[4] Power failure simulation study. Fire went out in less than two minutes water spray time.	[5] Approximately 1/4 composition not combusted. Burners ignited to ensure complete combustion. York Mist Eliminator plugged by carbon soot, by-pass opened to finish test.

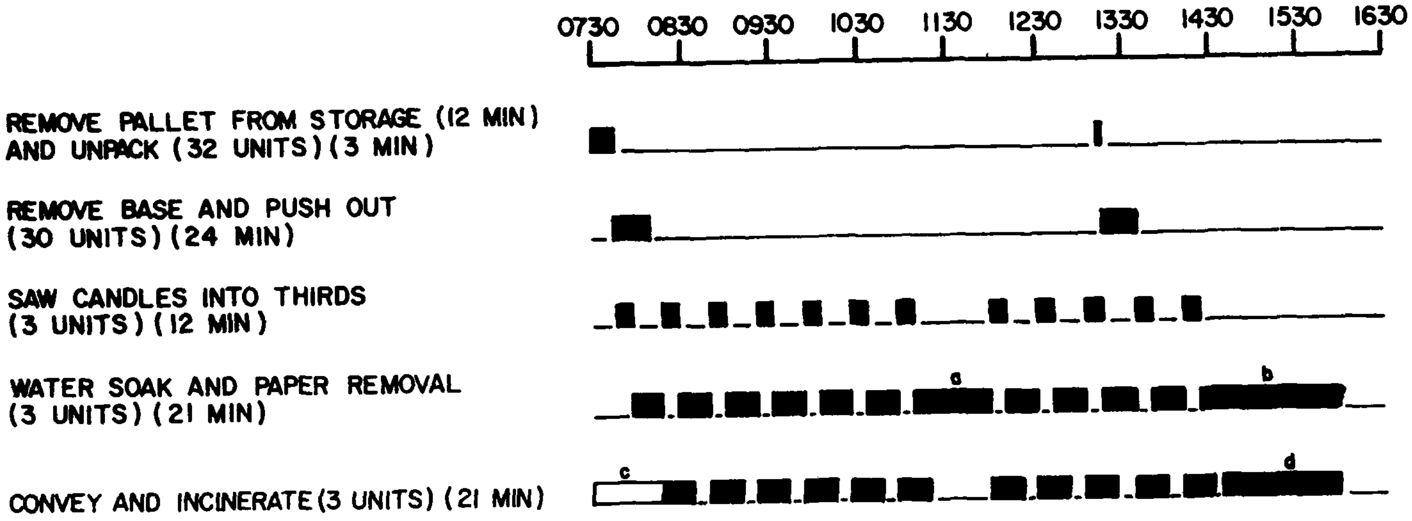
TABLE 10

Average Time and Labor Required to Demilitarize Mk 25 Marine Location Markers

Step No.	Activity	Time-Labor (Man-Min/Unit)	Time Min/Unit	Time Min/Batch
1	Unpalletize, 256 units, 2 men, 2 min.	0.083	0.42	
2	Open box of markers, 8 units, 1 man, 30 sec.	0.062	0.062	
3	Load band saw and remove base, 30 units, 1 man, 18.6 min.	0.622	0.622	
4	Push out, 30 units, 1 man, 5.85 min.	0.195	0.195	
5	Radial arm saw, 3 candles into 3rds*, 30 units, 1 man, 112.8 min.	3.76	3.76	11.28
6	Water soak, 3 units, 20 min.			20.0
7	Remove paper, 3 units, 1 man, 1 min.			1.0
8	Convey, 3 units, 1 man, 1 min.			1.0
9	Incinerate, 3 units, 2 men, 20 min.			20.0

* Step 5 - Time included water fill of the radial arm saw reservoir, loading and sawing three Mk 25 candles, draining the water from the reservoir, and dumping the candle sections into the conveyor feed hopper.

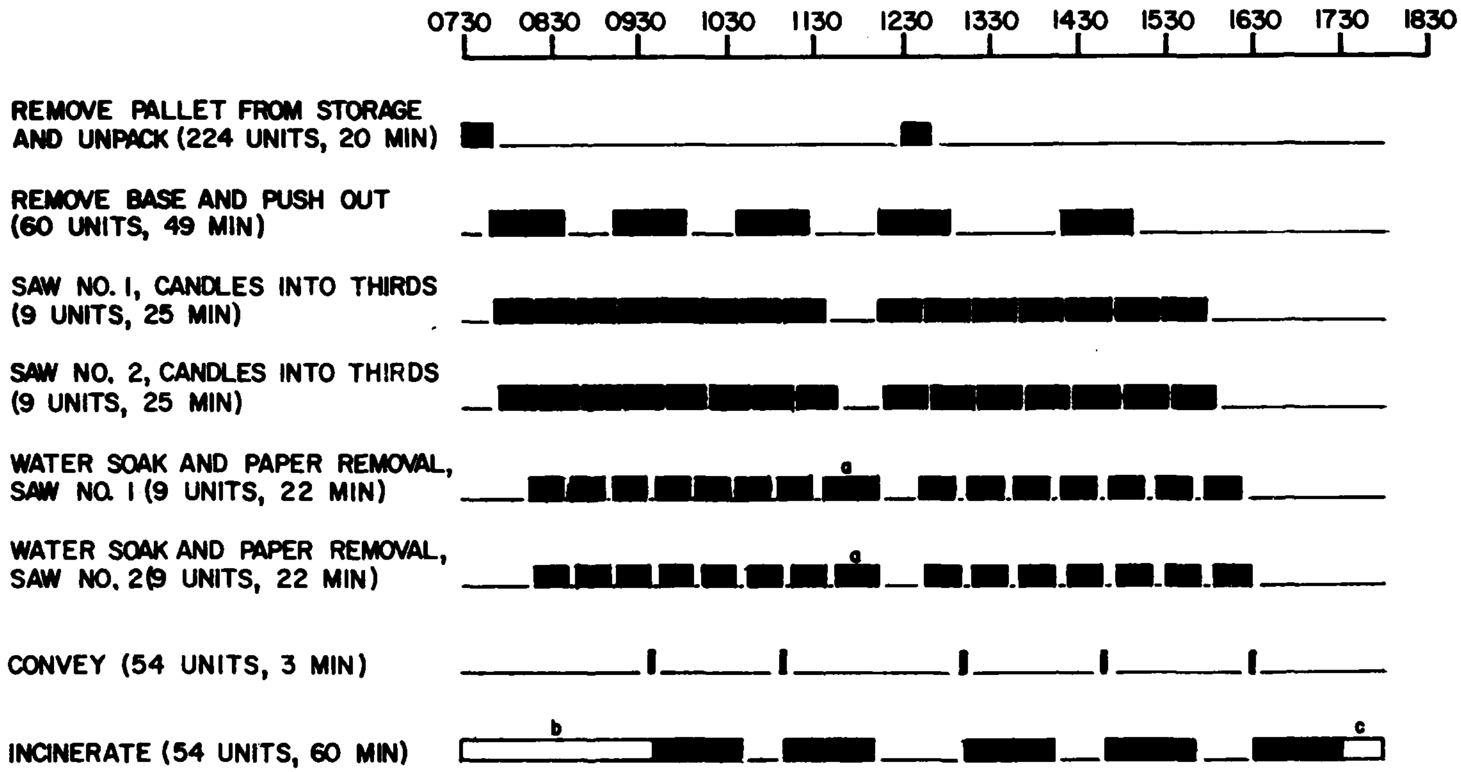
TABLE II. FLOW PLAN FOR PROCESSING 58 LB RED PHOSPHORUS COMP THROUGH EXISTING PILOT PLANT.



a. LONG SOAK PERIOD FOR LUNCH
b. OVERNIGHT SOAK PERIOD TO ALLOW EARLY START ON FOLLOWING DAY
c. INCINERATOR PREHEAT
d. CLEAN UP

NOTE: THIS FLOW PLAN UTILIZES THREE MEN.

TABLE 12. FLOW PLAN FOR PROCESSING 472 LB RED PHOSPHORUS COMP THROUGH SCALED UP PILOT PLANT.



a. LONG SOAK PERIOD FOR LUNCH
b. INCINERATOR PREHEAT
c. CLEAN UP

NOTE: THIS FLOW PLAN WOULD UTILIZE FOUR MEN.

TABLE 13

Economic Analysis for Disposal of Mk 25 Marine Location Markers

The total value of the recovered materials is approximated by the following:

	Pilot Plant 33 Mk 25 MLM (58 lb comp/da)	Production Plant 270 Mk 25 MLM (472 lb comp/da)
Phosphoric acid (agricultural grade)	87 lb = $7.22	714 lb = $59.26
Scrap aluminum	66 lb = $17.16	540 lb = $140.40
Total income	$24.38	$199.66

The total expenses are approximated by the following:

Labor-Operating		
3 men X 8 hr/da X $20.00/hr	$480.00	
4 men X 10hr/da X $20.00/hr		$800.00
Labor-Handling of materials after processing to sale		
1 man X 4 hr X $20.00/hr	$80.00	
1 man X 6 hr X $20.00/hr		$120.00

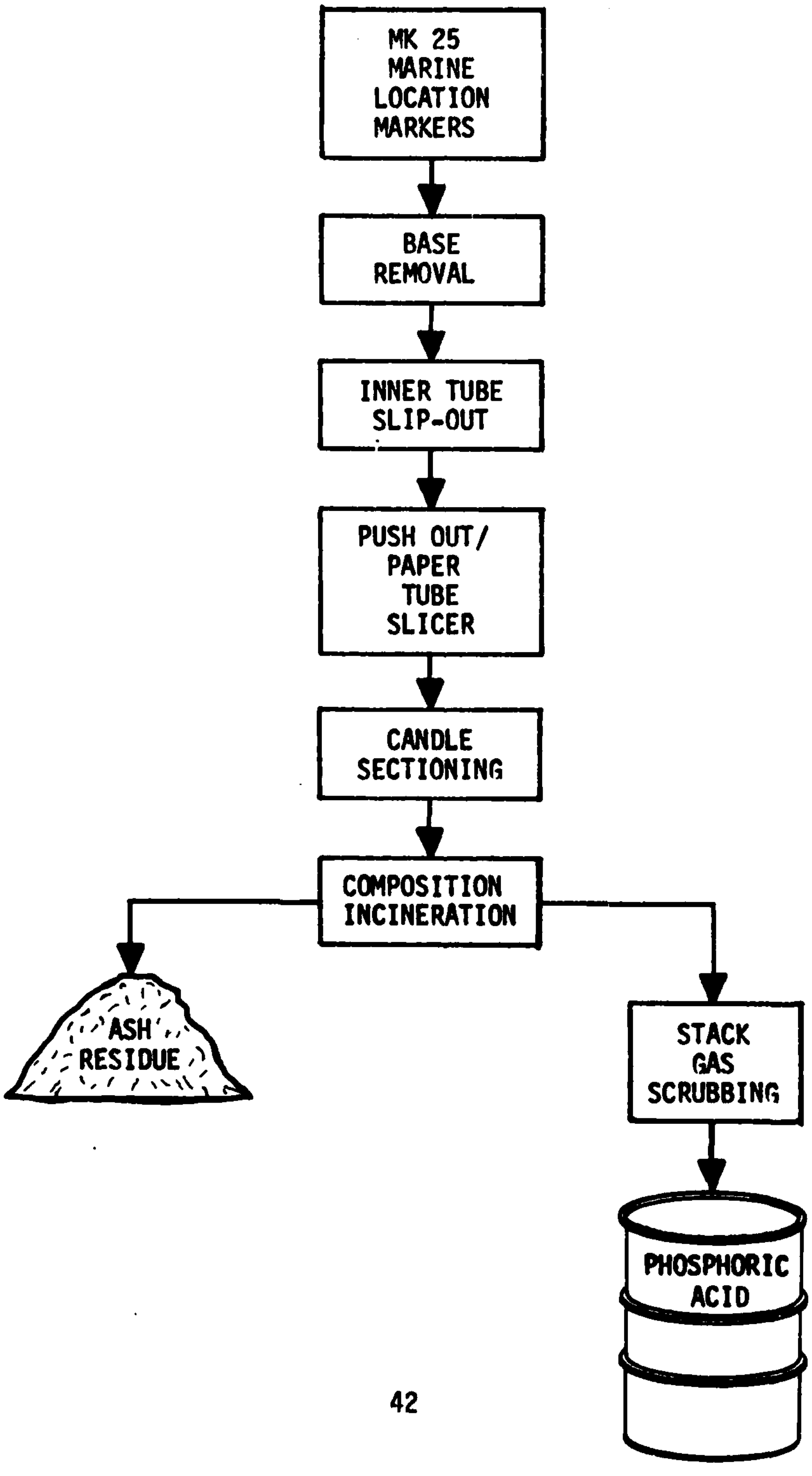
Utilities
Electrical power — These factors are paid from overhead
Water — generated by labor.

Scale-Up

The cost to scale-up ($524.6K) amortized over a ten year period equals $2.25/lb composition processed	________	472 lb = $1062.00
Total expenses	$560.00	$1982.00
Net cost/lb of comp. processed	$9.66	$4.20

FIGURE 1

PROCESS FLOW CHART



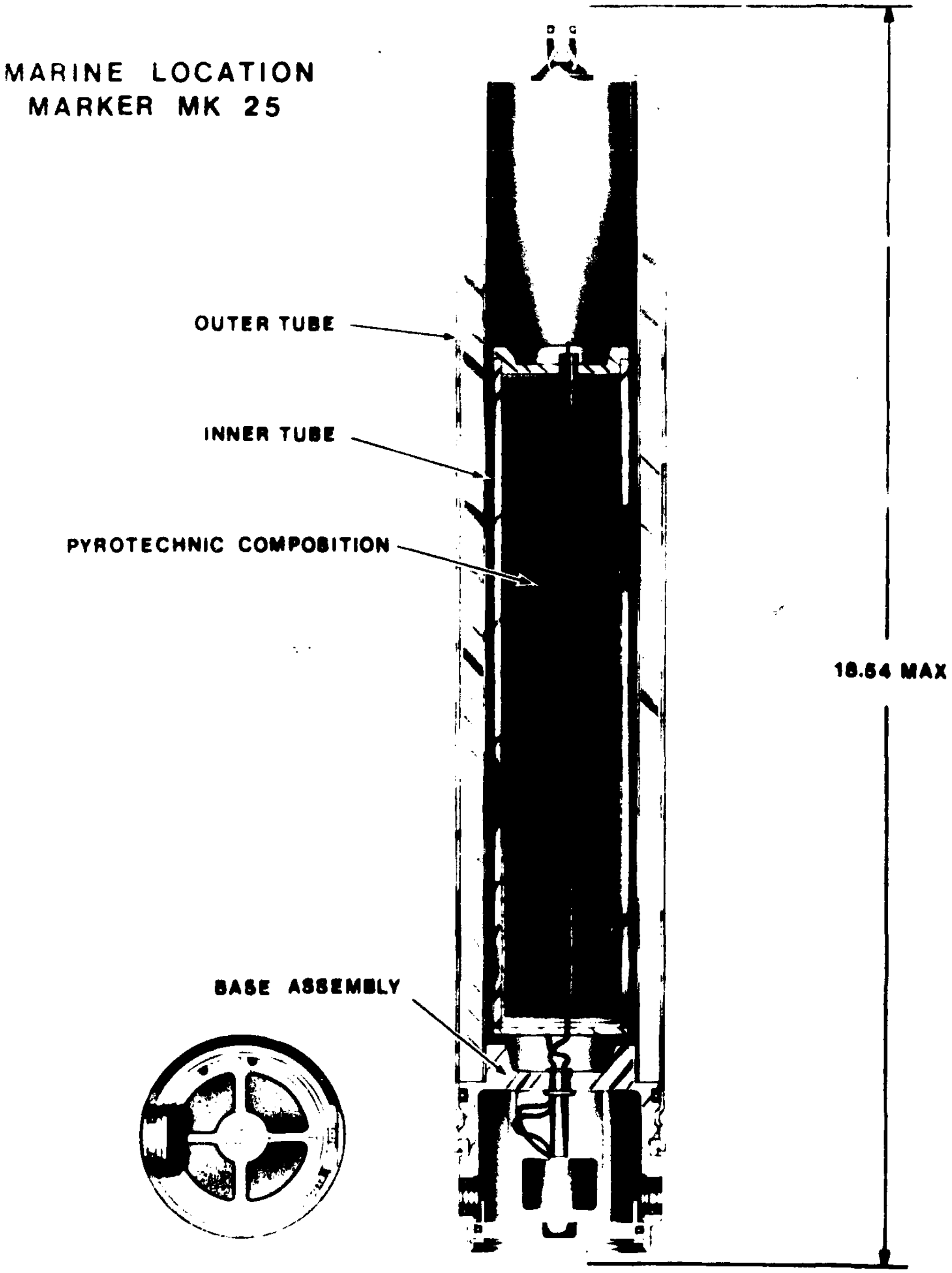


Figure 2 Cutaway view of Mk 25 Marine Location Marker

Figure 3 Operator approaches band saw with a Mk 25 Marine Location Marker

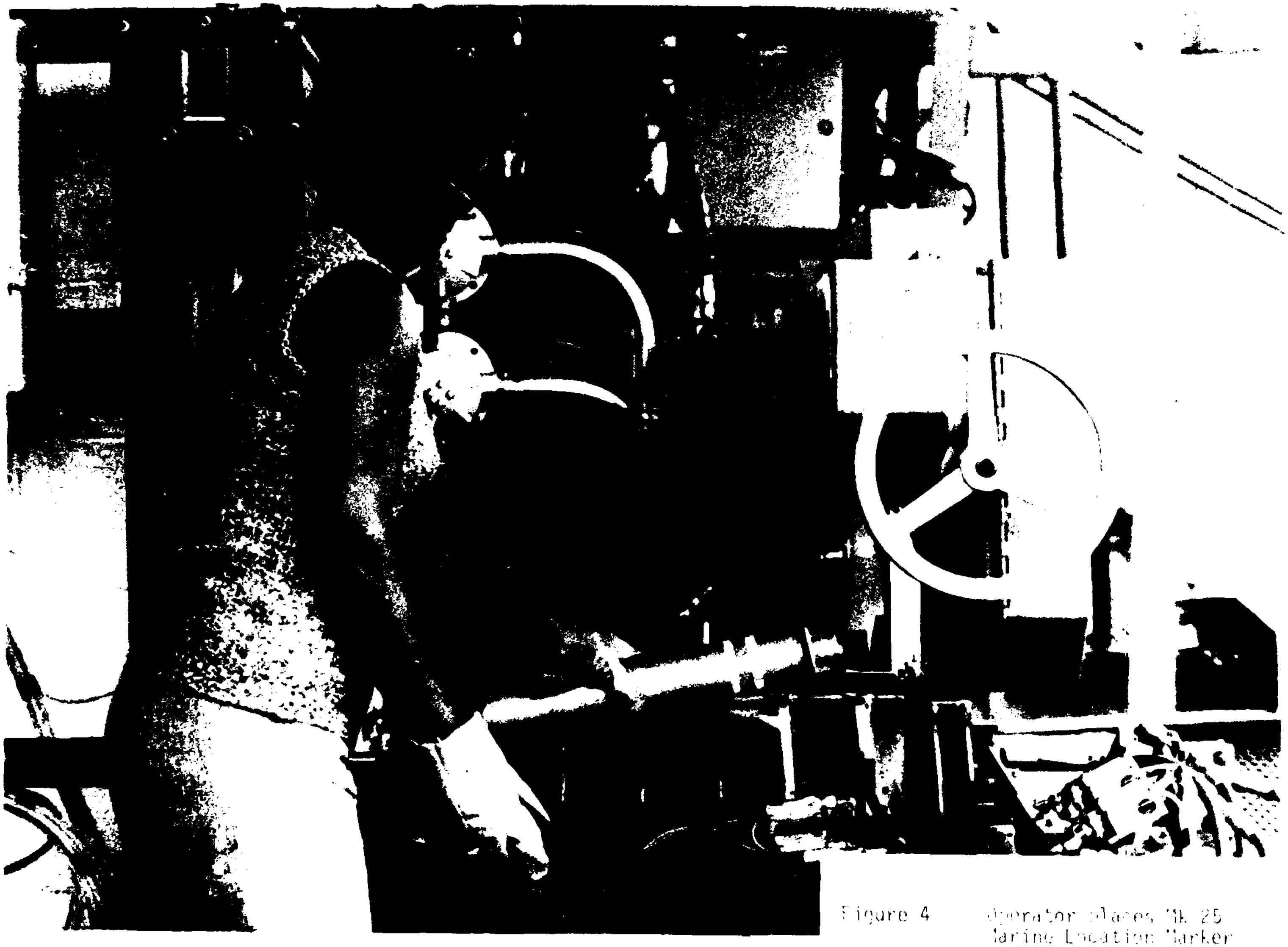


Figure 4 Operator places Mk 25 Marine Location Marker in band saw

Figure 5 Operator places Mk 25 Marine Location Marker in band saw

Figure 6 [illegible] 20 in band saw with base removed

Figure 7 Operator slips inner tube from foam liner and outer tube

Figure 8 Liner tube with pyrotechnic candle is placed in push out fixture

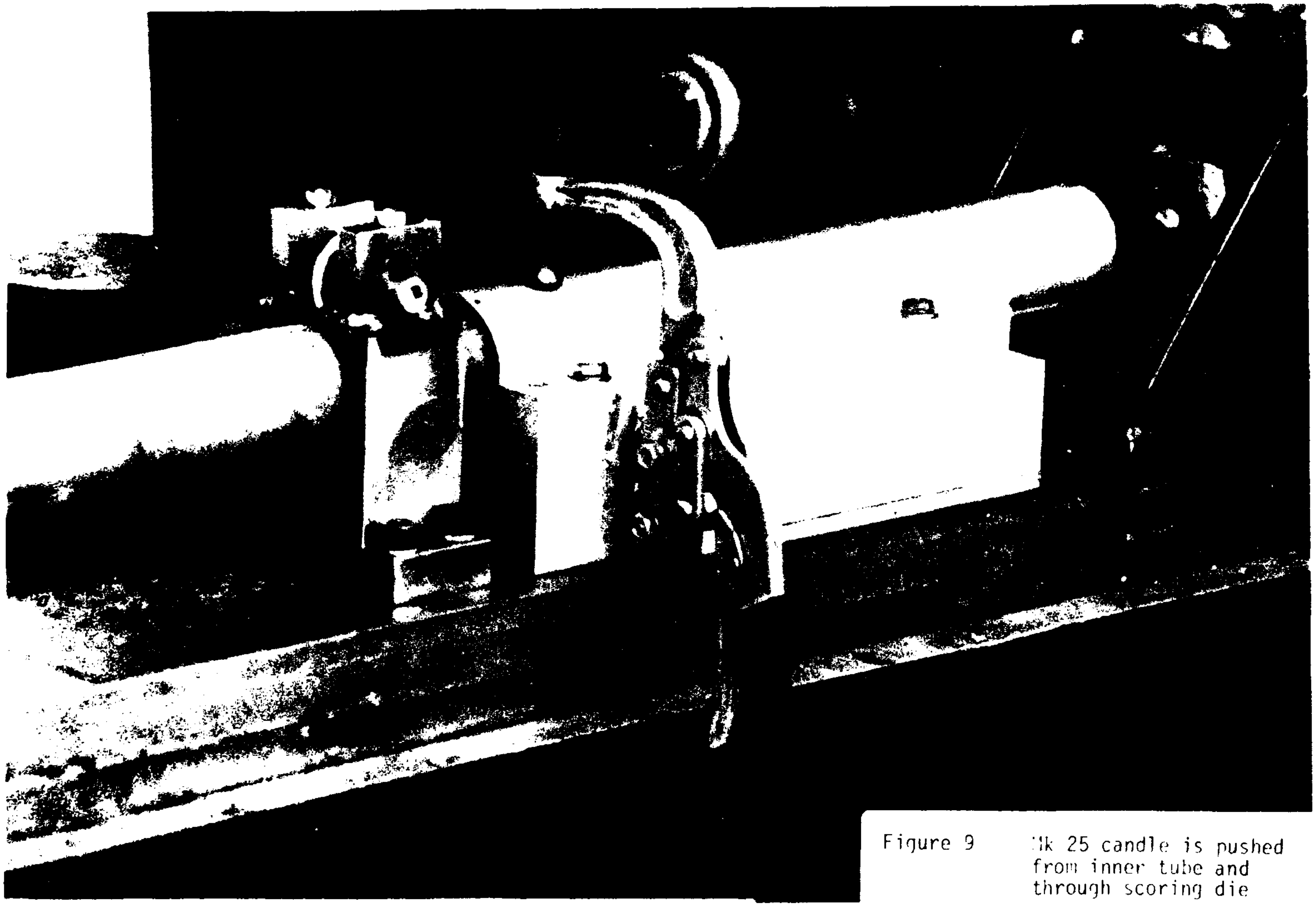


Figure 9 Mk 25 candle is pushed from inner tube and through scoring die

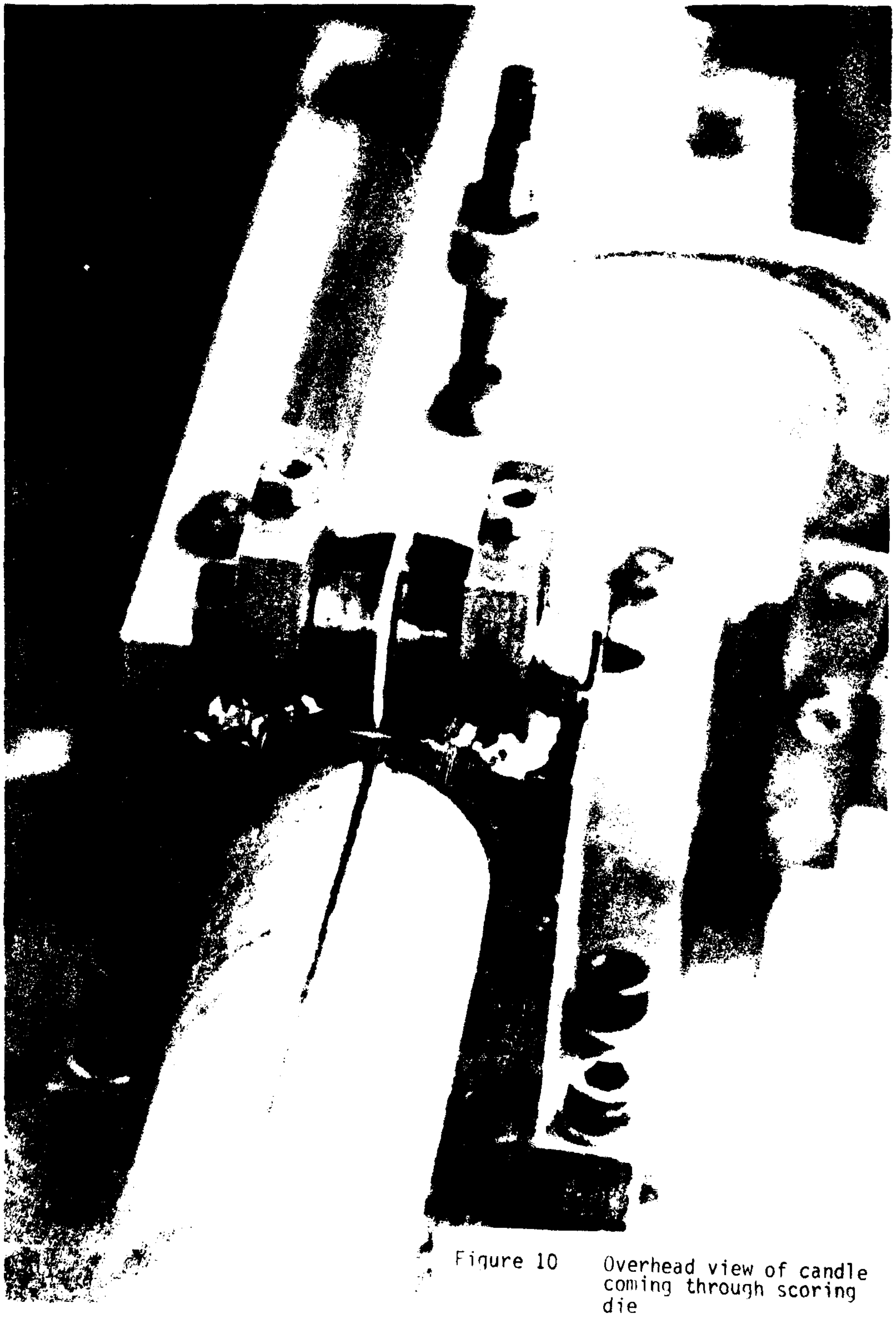


Figure 10 Overhead view of candle coming through scoring die

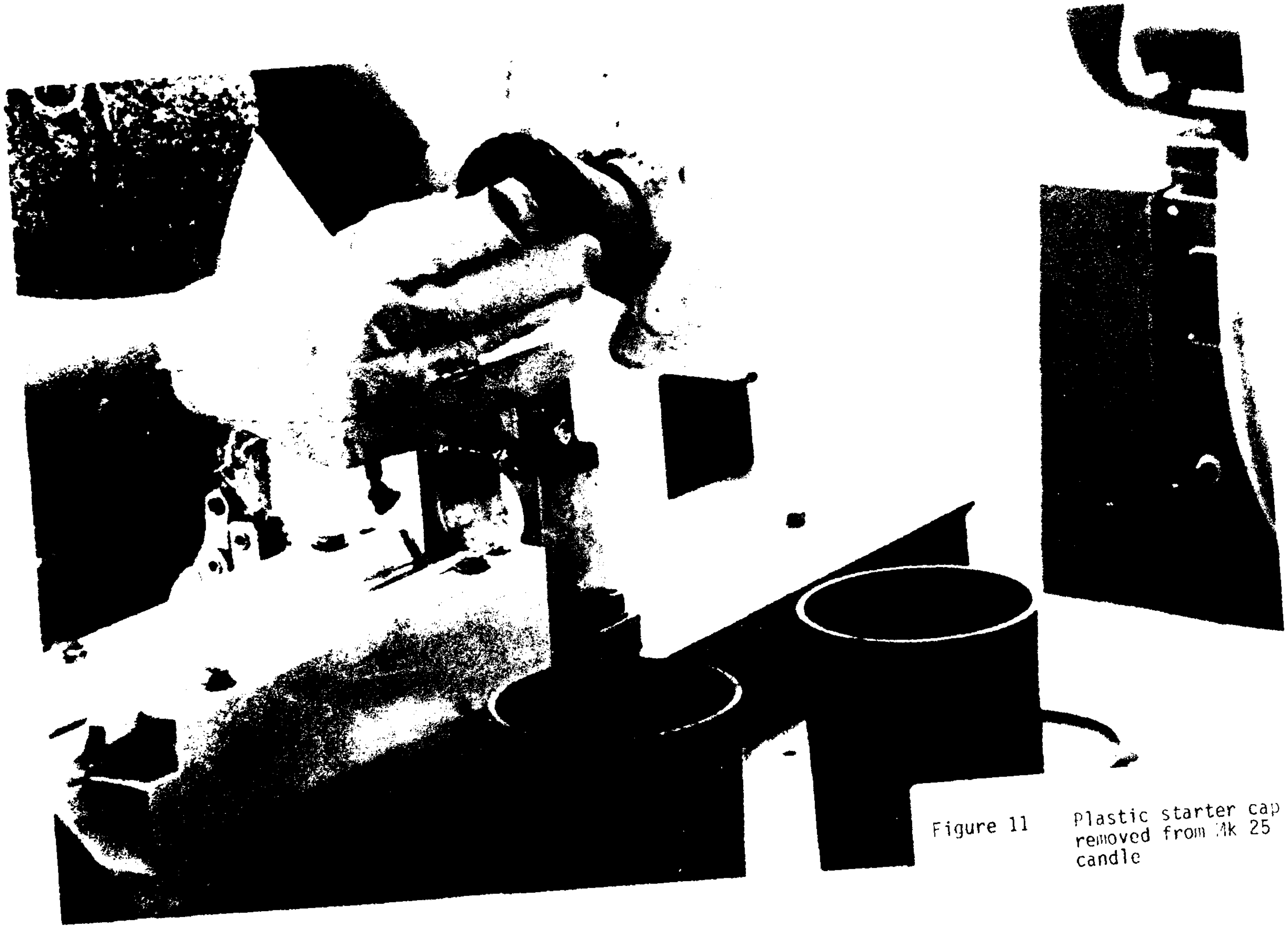


Figure 11 Plastic starter cap removed from Mk 25 candle

Figure 12 Loose ignition composition is poured into conductive containers

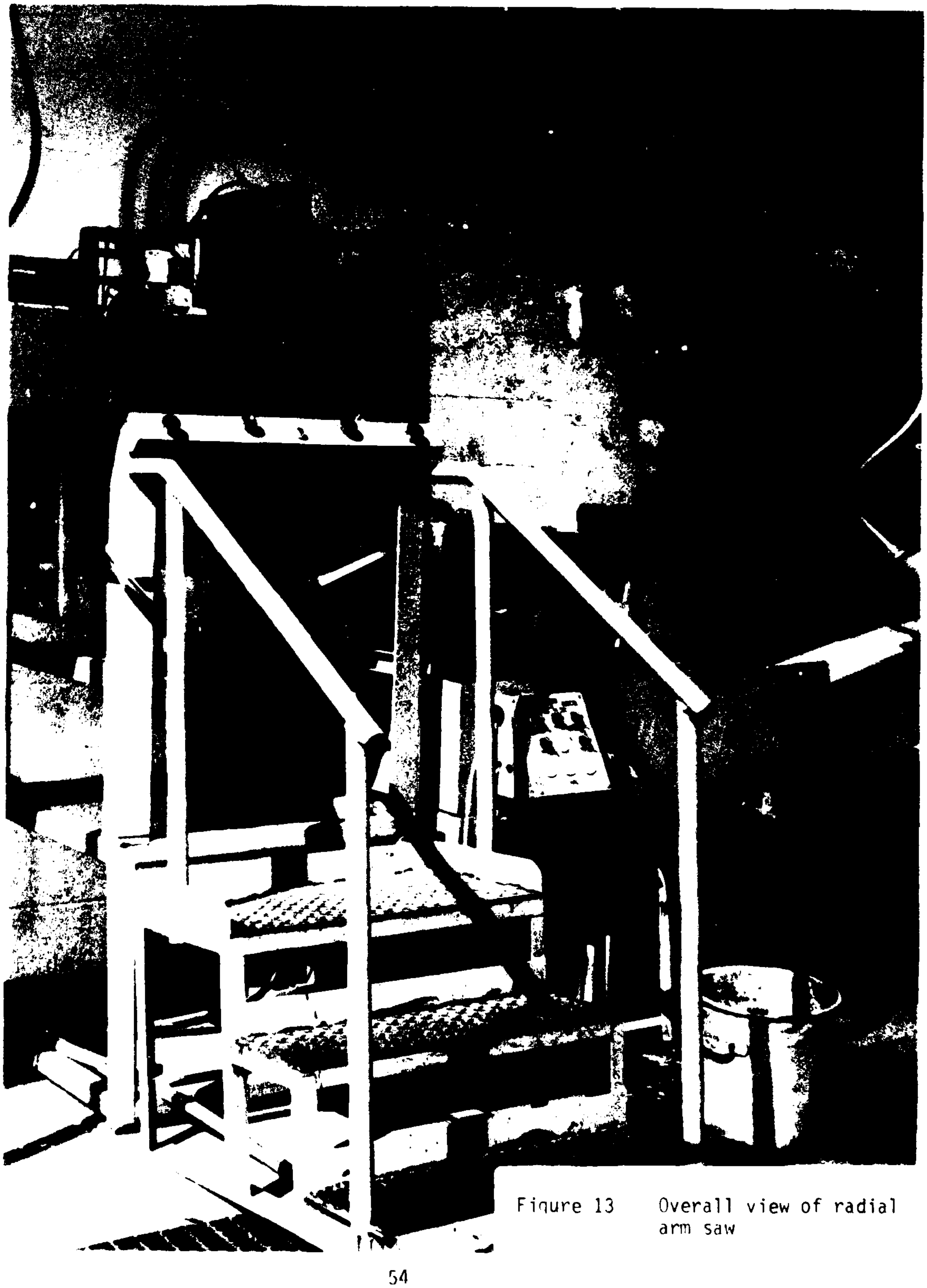


Figure 13 Overall view of radial arm saw

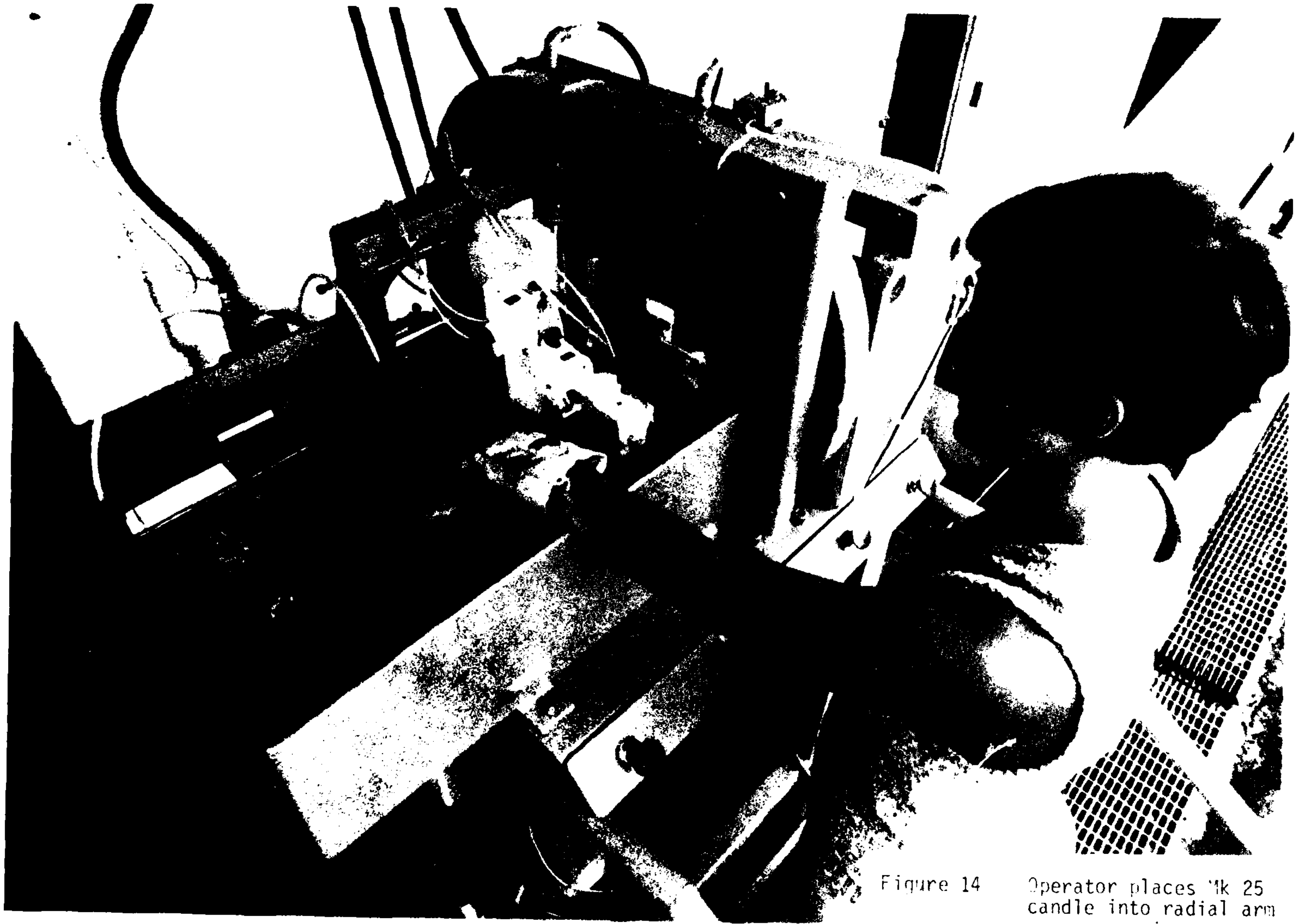


Figure 14 Operator places Mk 25 candle into radial arm saw reservoir

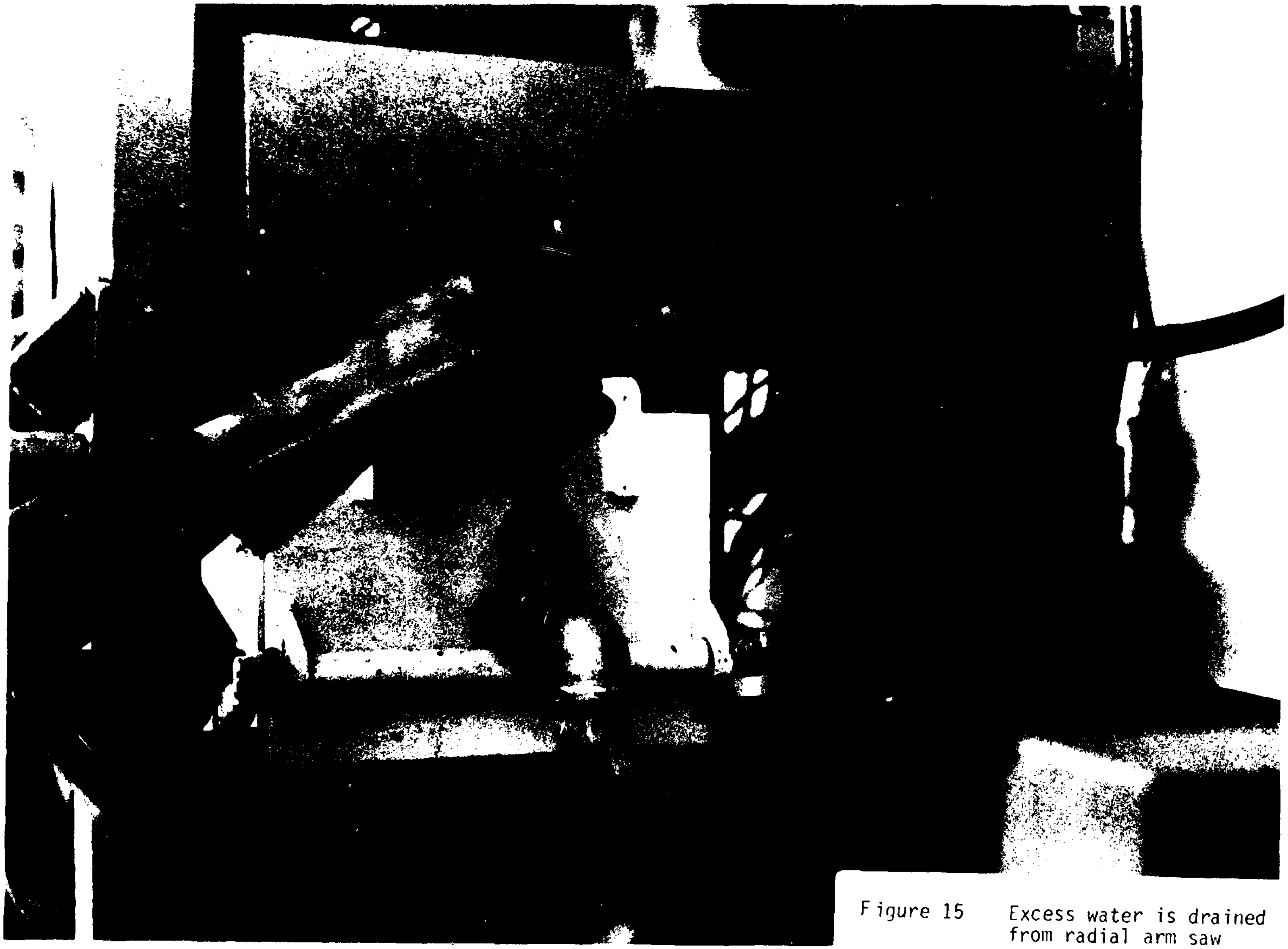


Figure 15 Excess water is drained from radial arm saw reservoir

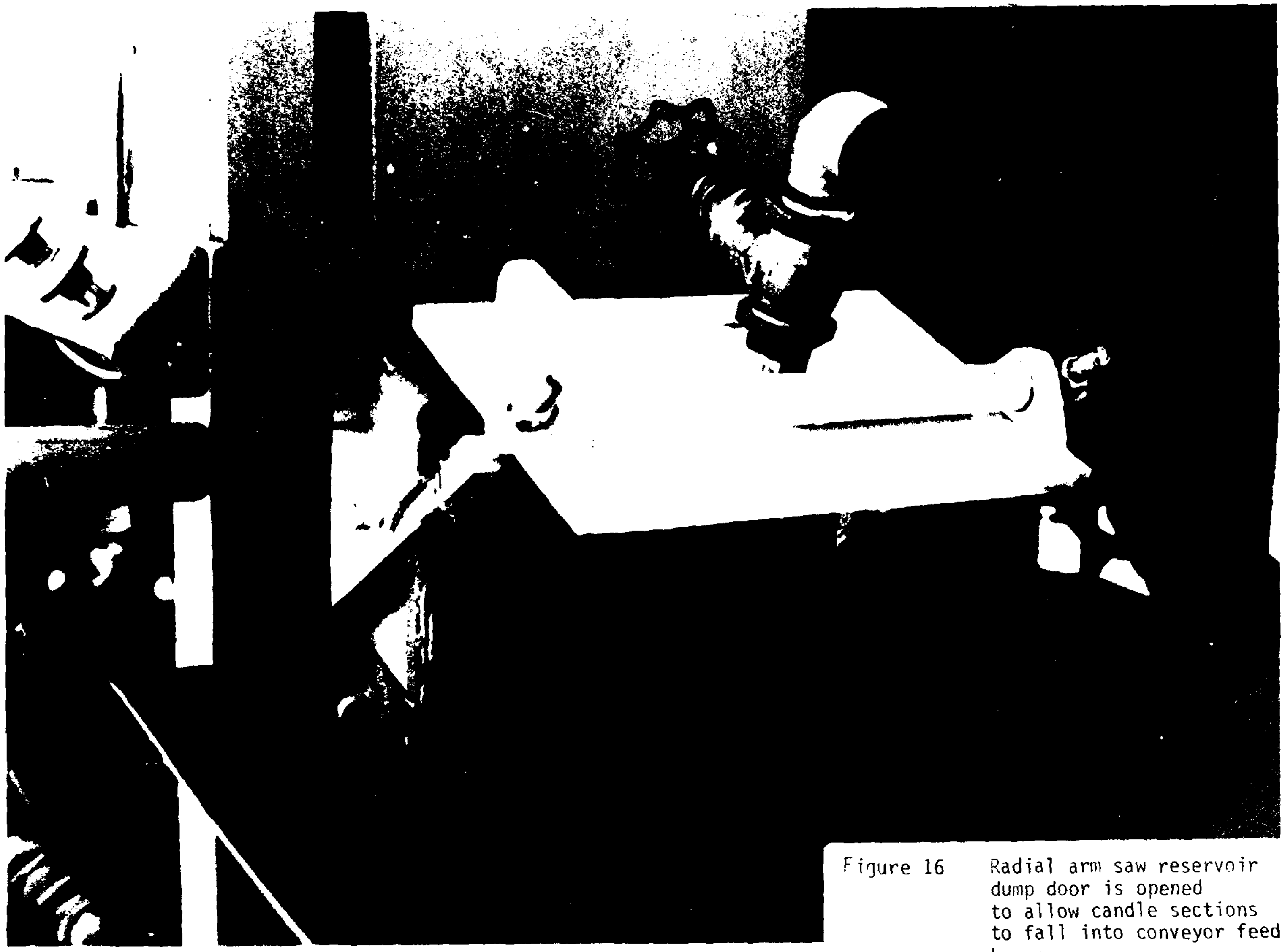


Figure 16 Radial arm saw reservoir dump door is opened to allow candle sections to fall into conveyor feed hopper

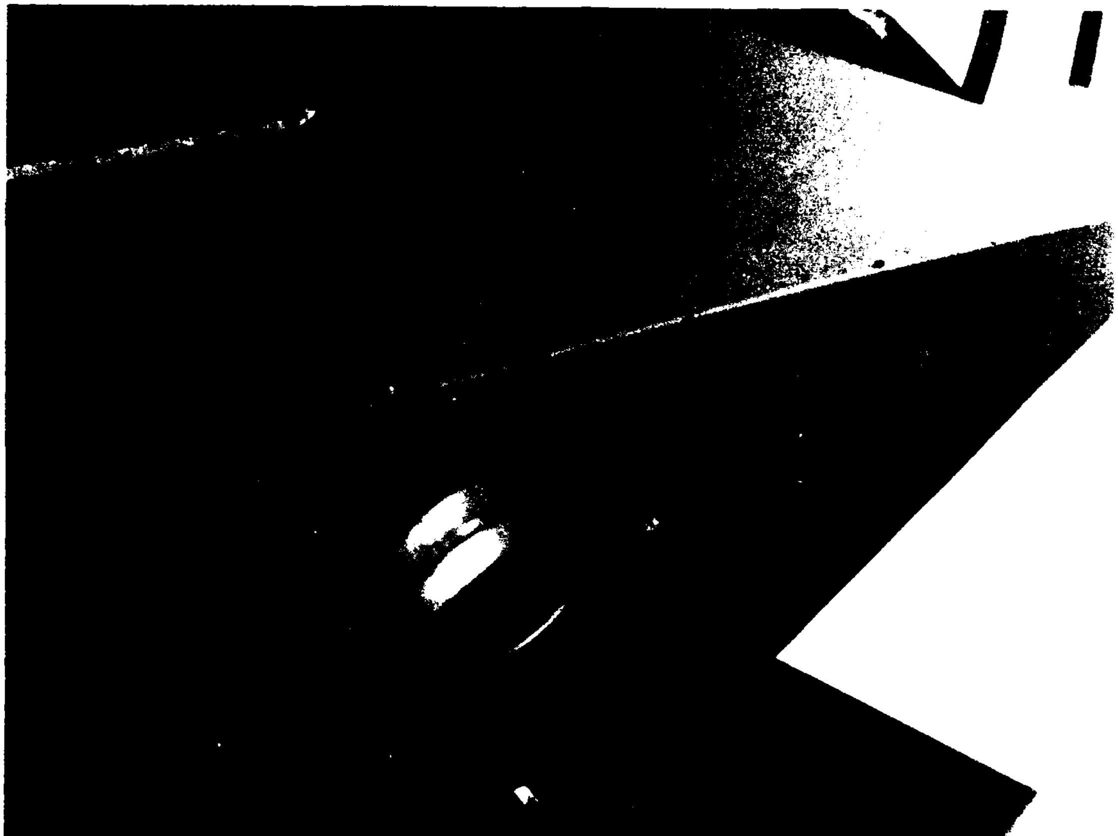


Figure 17 Conveyor feed hopper

Figure 18 After soak period, paper is easily removed from Mk 25 candle sections

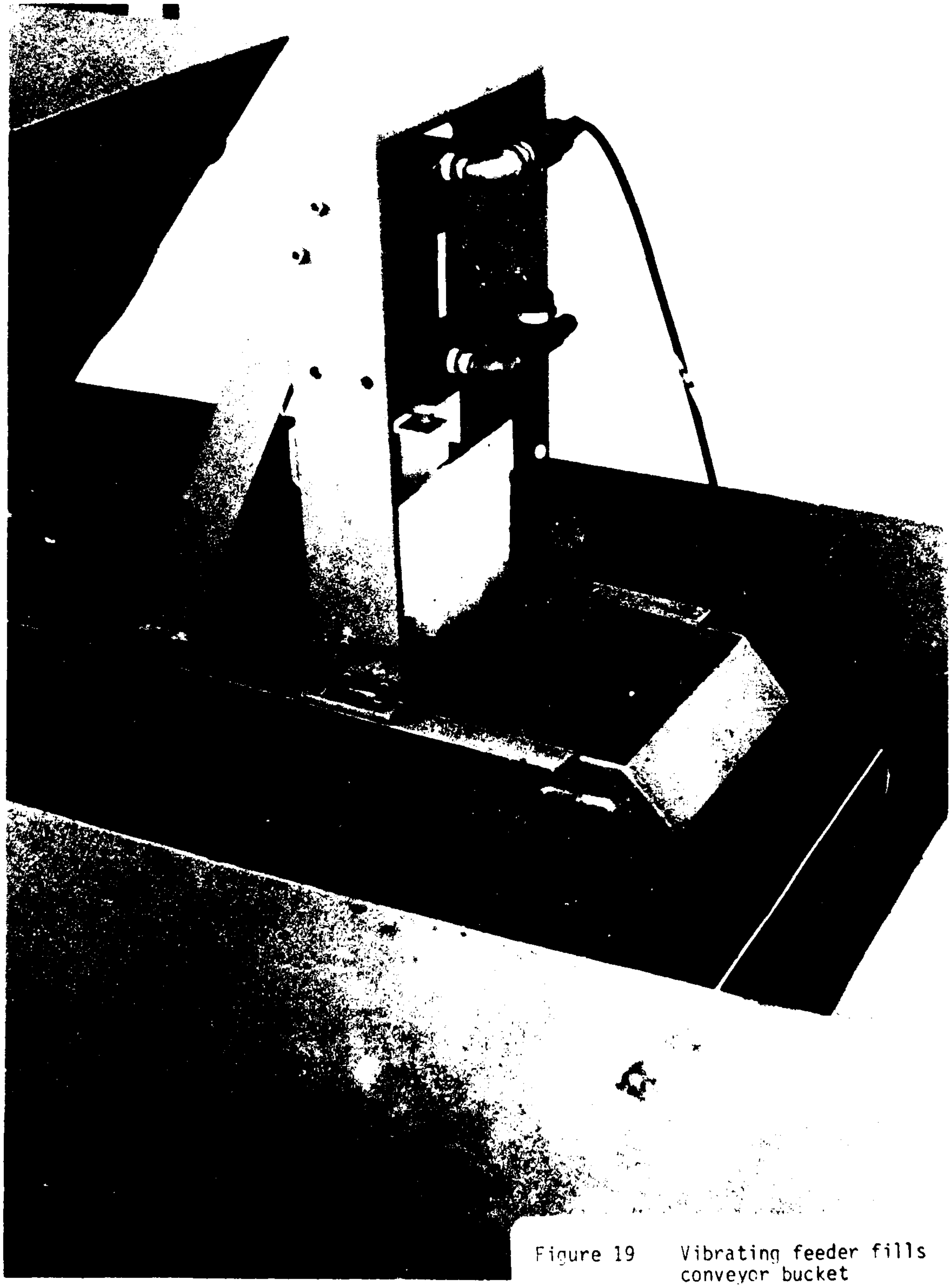


Figure 19 Vibrating feeder fills conveyor bucket

Figure 20 Candle composition is conveyed toward the incinerator

Figure 21 Conveyor bucket dumps into incinerator charge pan

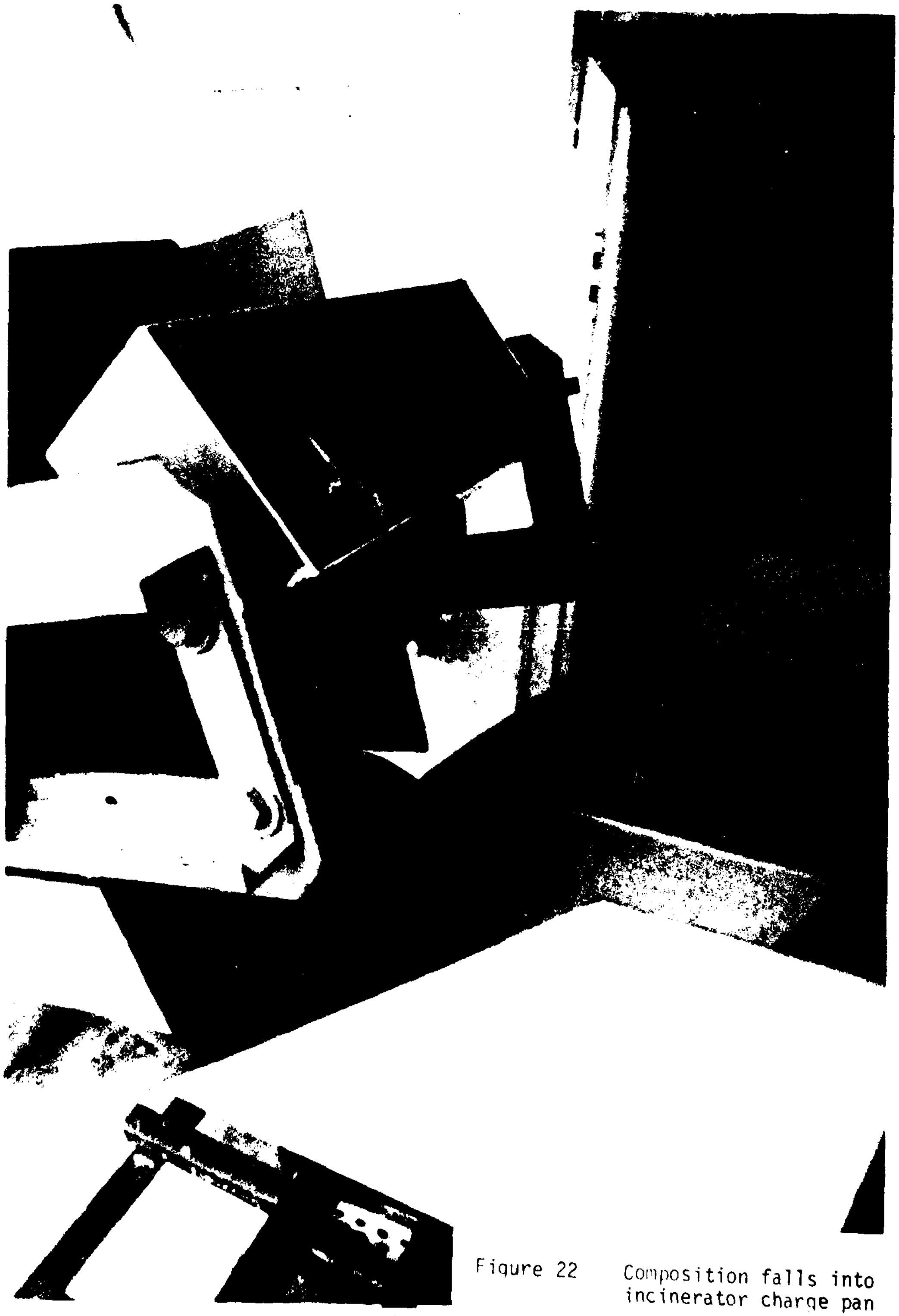


Figure 22 Composition falls into incinerator charge pan

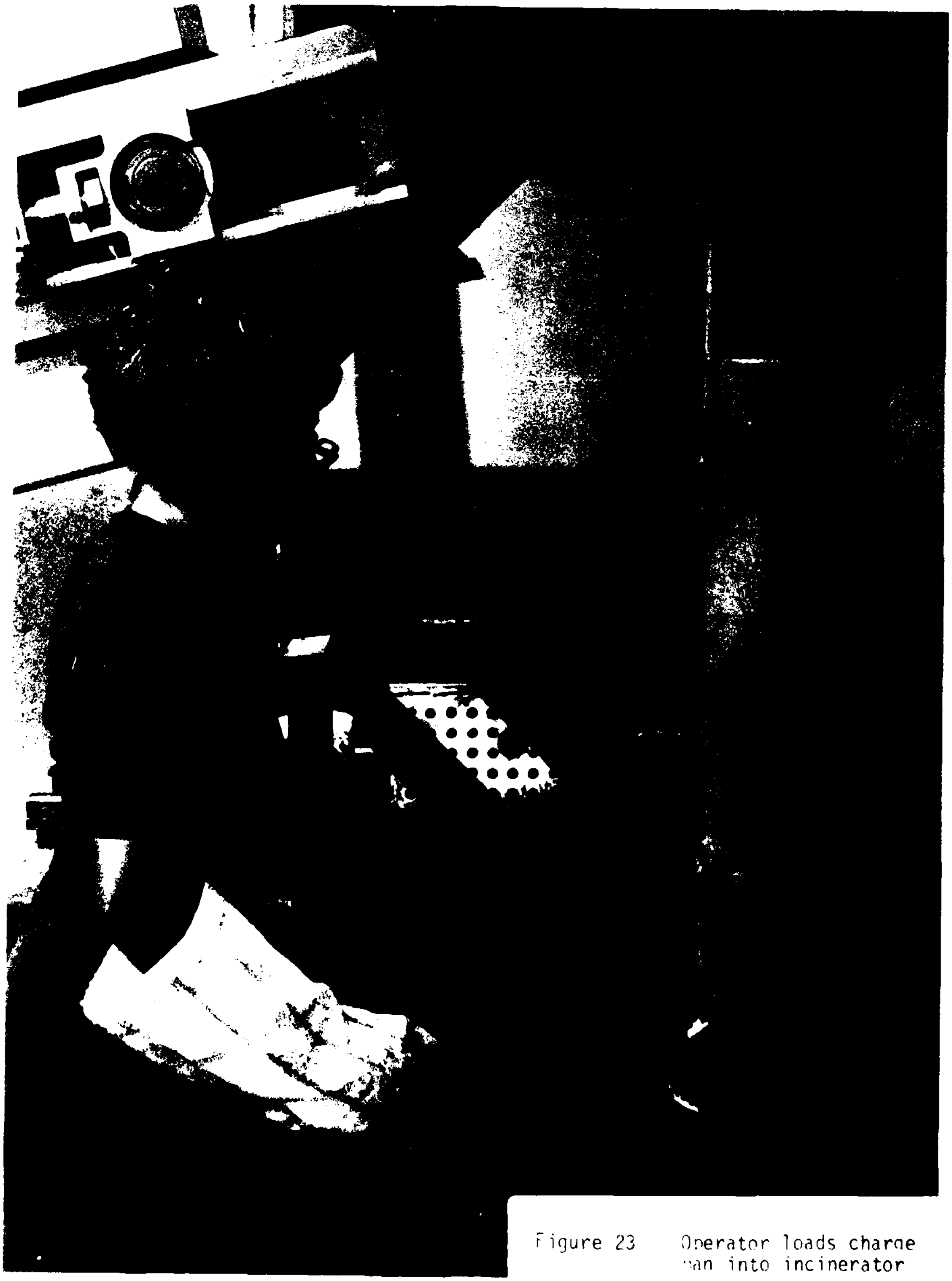


Figure 23 Operator loads charge pan into incinerator

Figure 24 Operator closes incinerator door

Figure 25 Operator turns on burner in first chamber of the incinerator

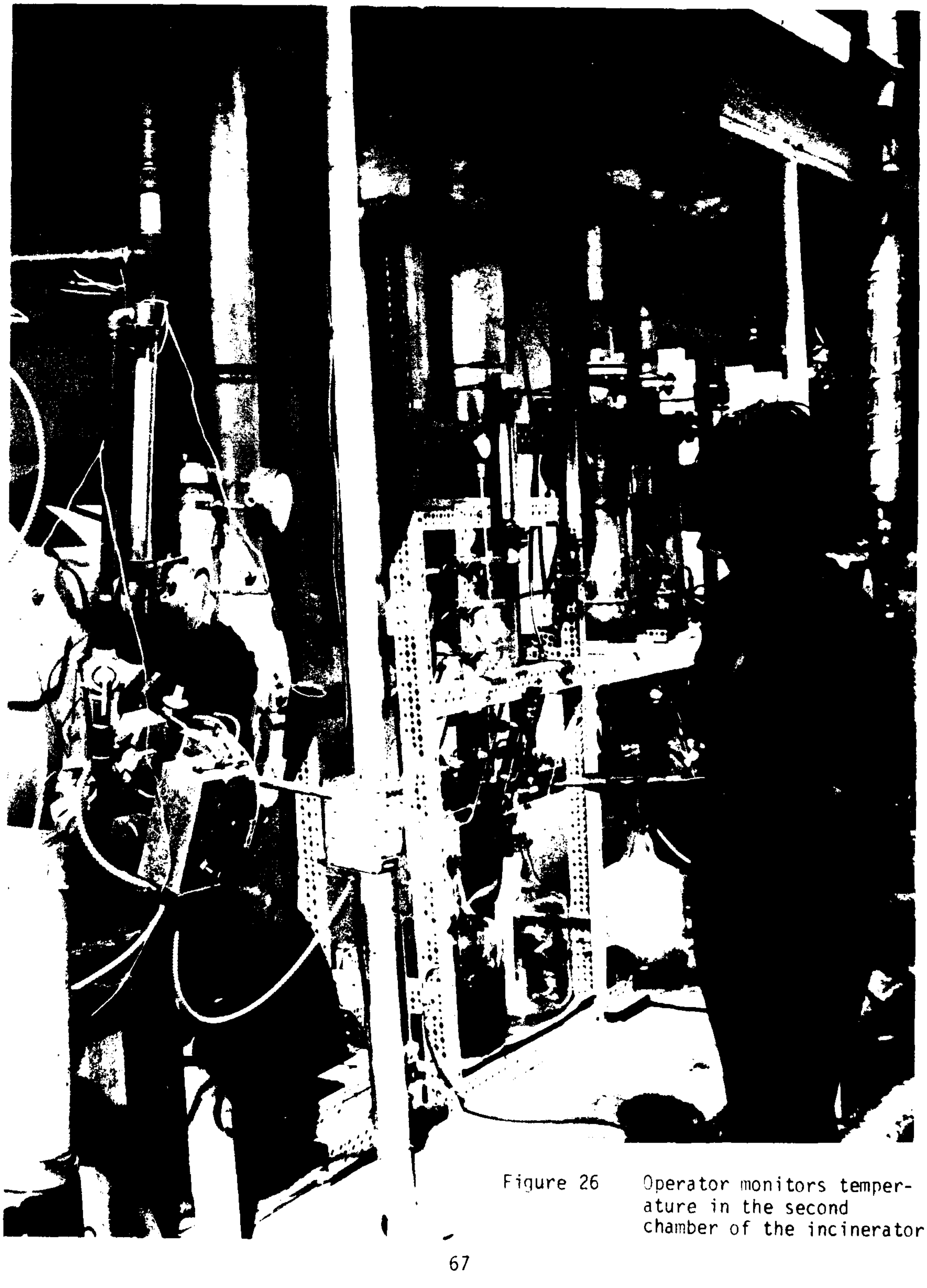


Figure 26 Operator monitors temperature in the second chamber of the incinerator

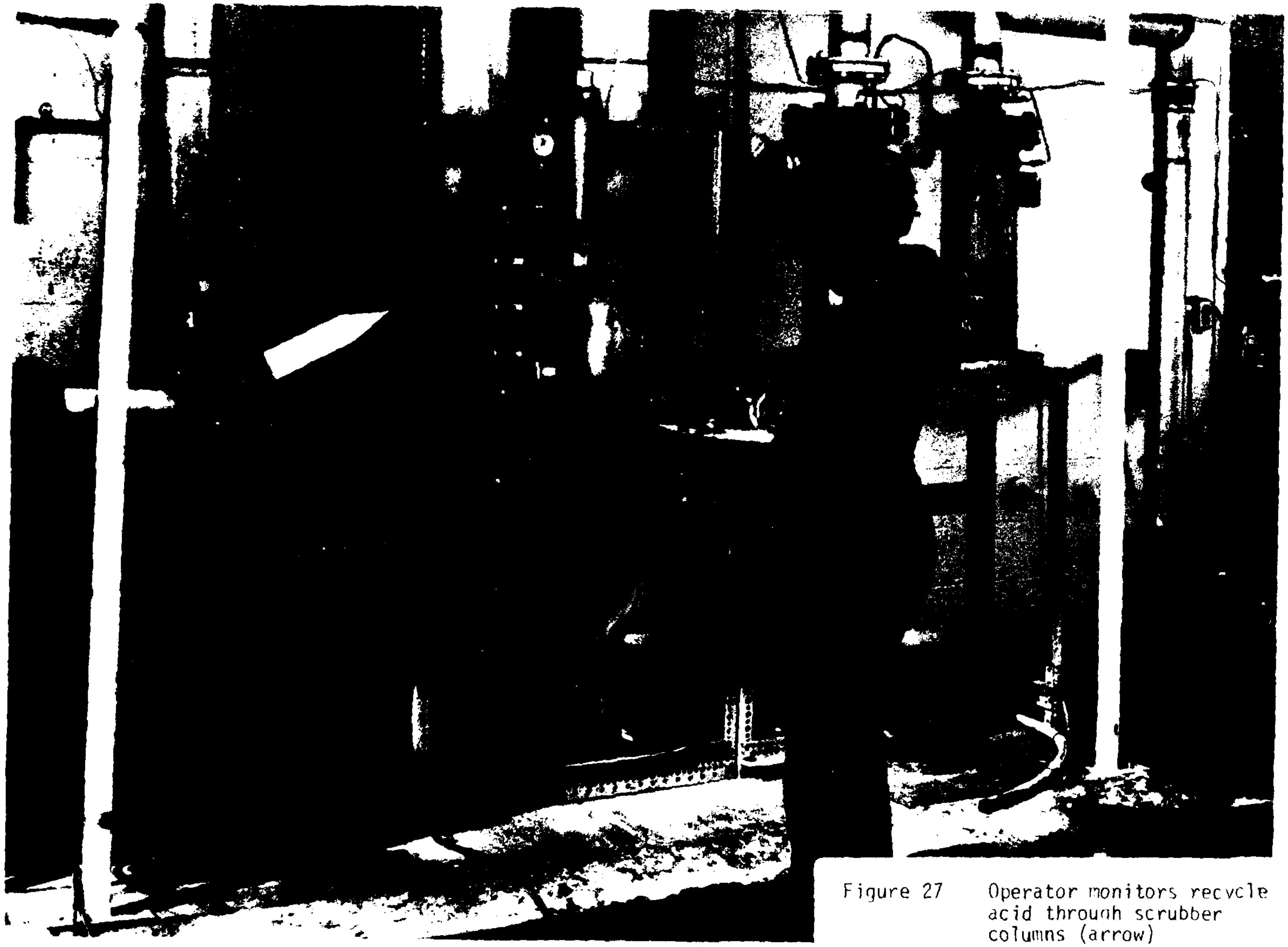


Figure 27 Operator monitors recycle acid through scrubber columns (arrow)

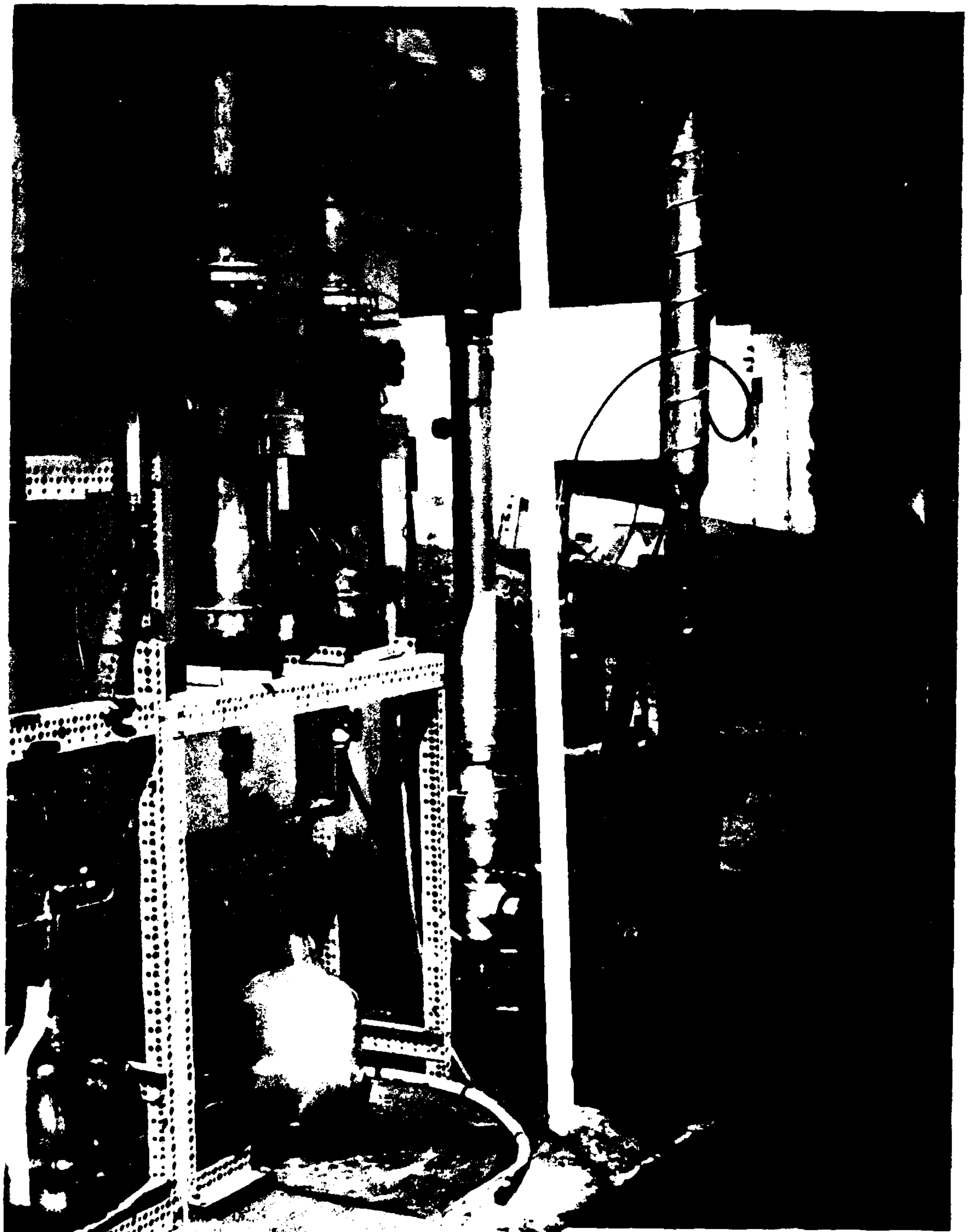


Figure 28 Recycle acid jars under scrubber

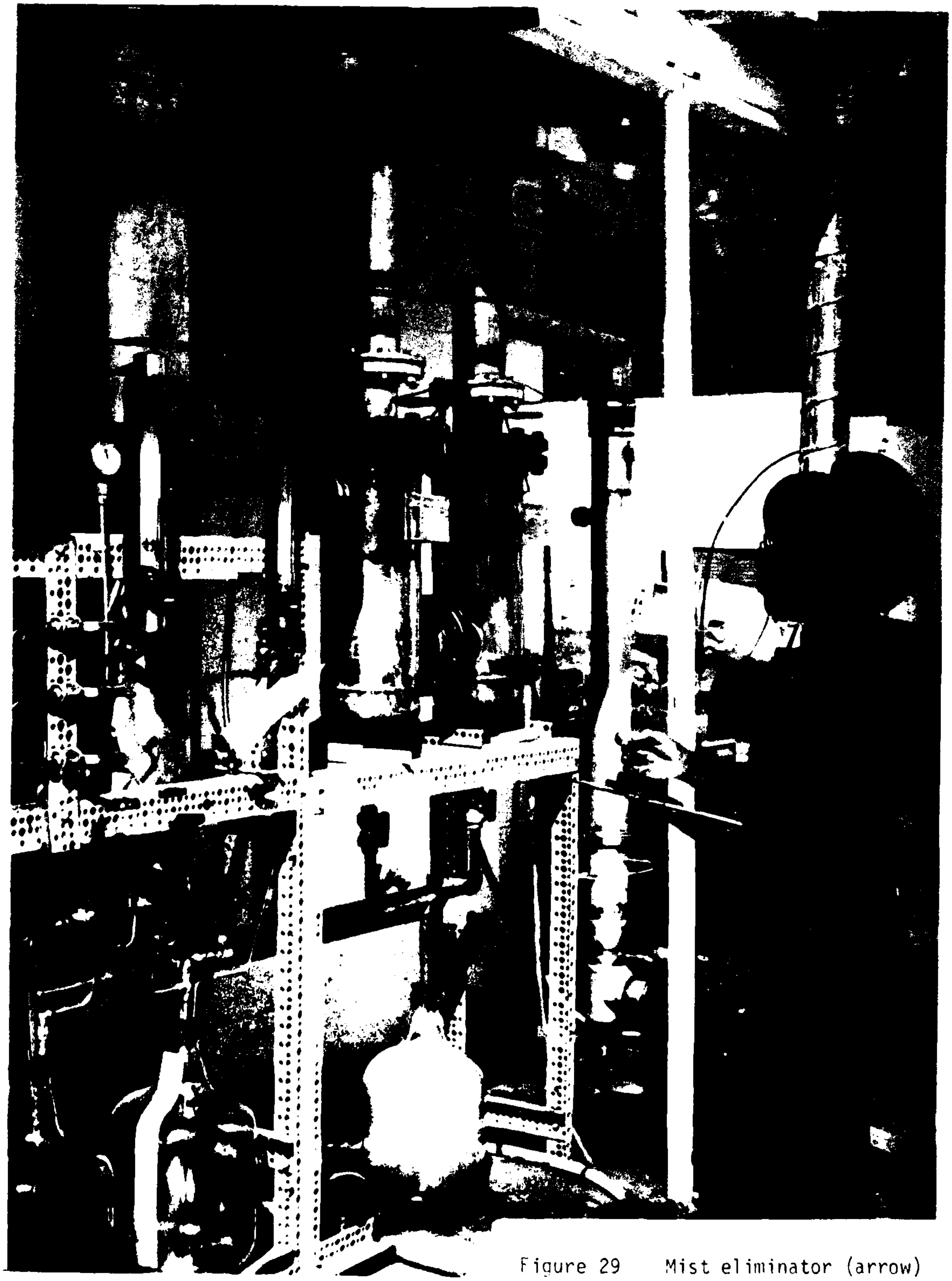


Figure 29 Mist eliminator (arrow)

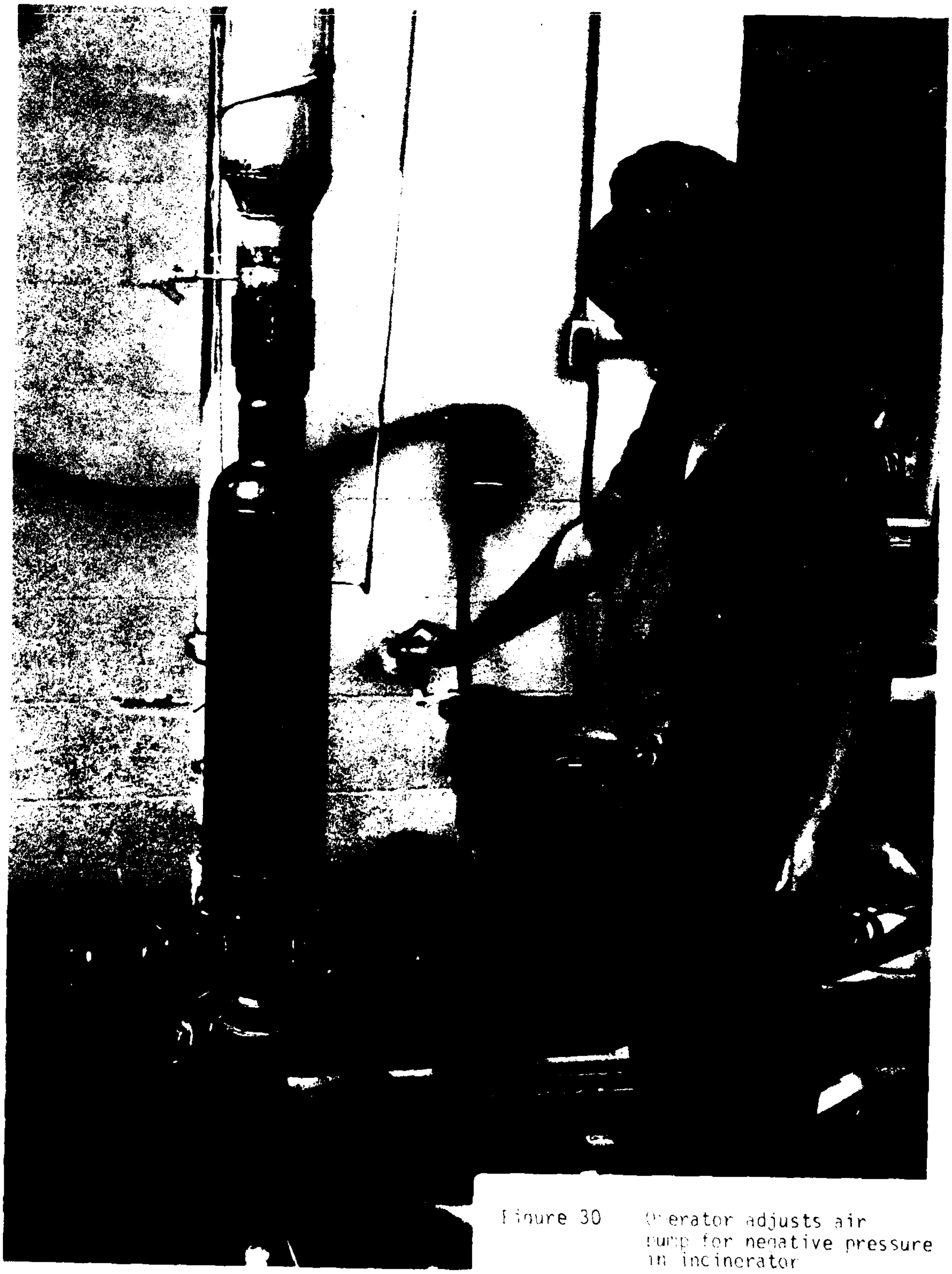


Figure 30 Operator adjusts air pump for negative pressure in incinerator

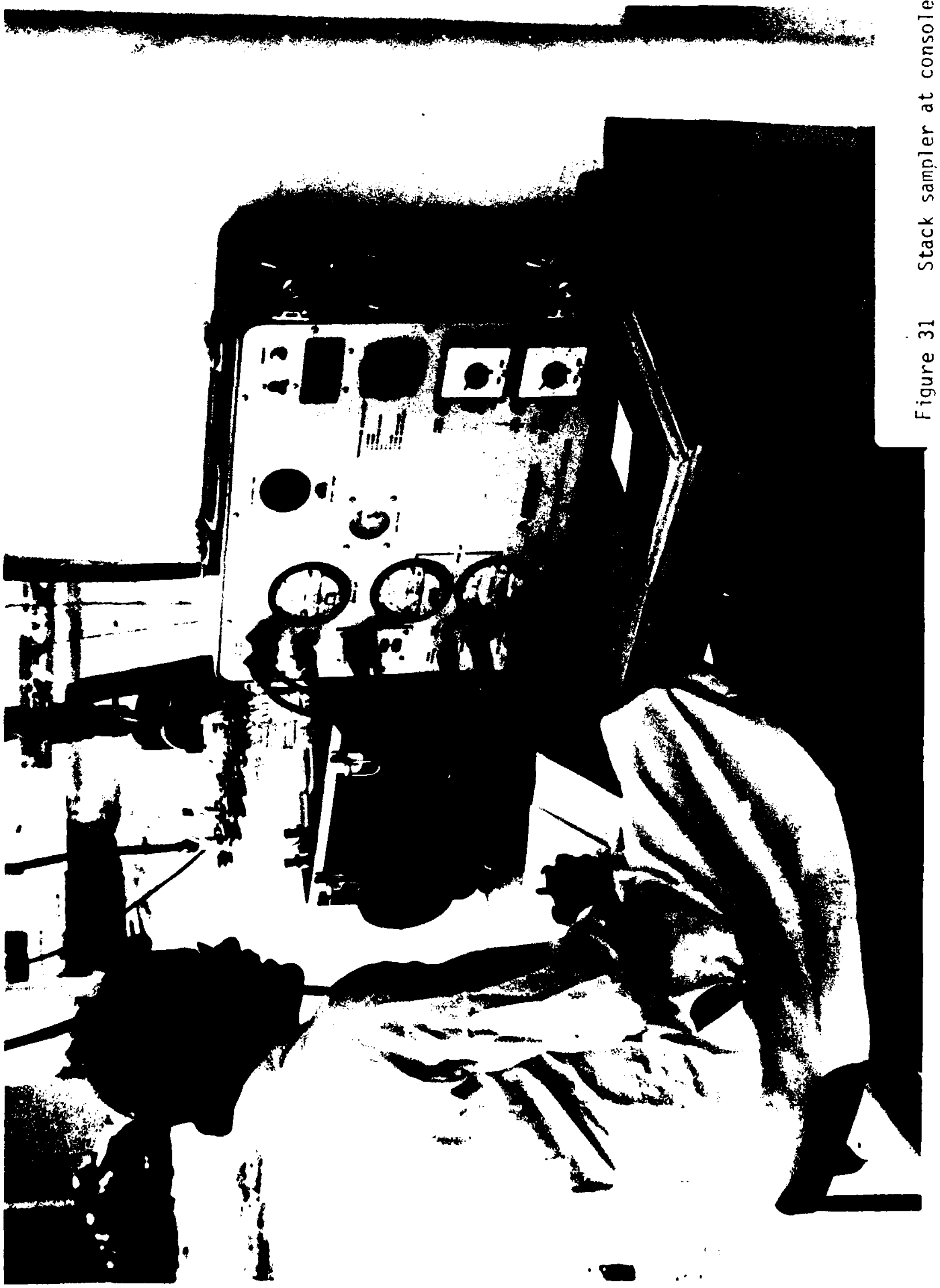


Figure 31 Stack sampler at console

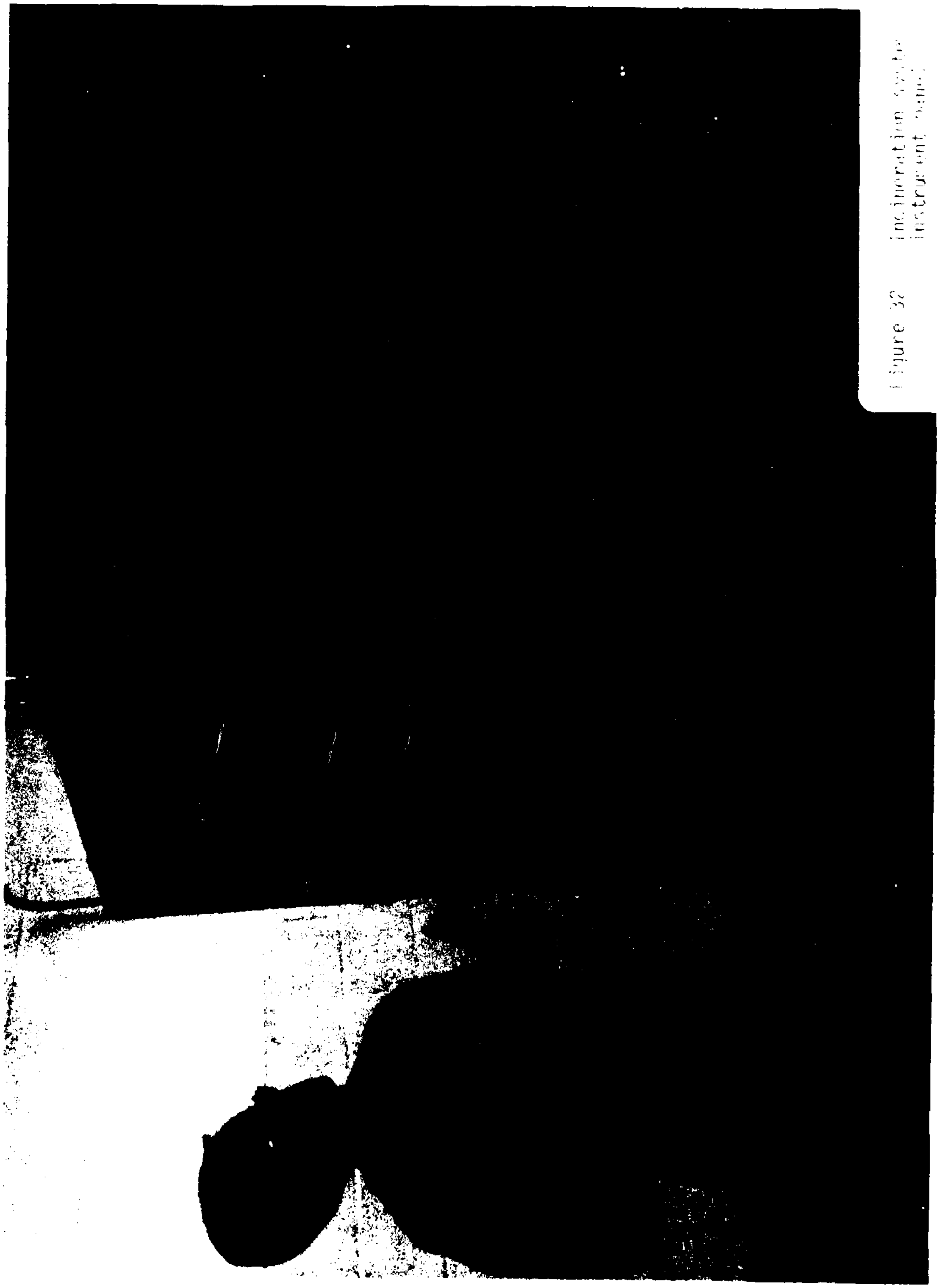


Figure 32 Incineration system instrument panel

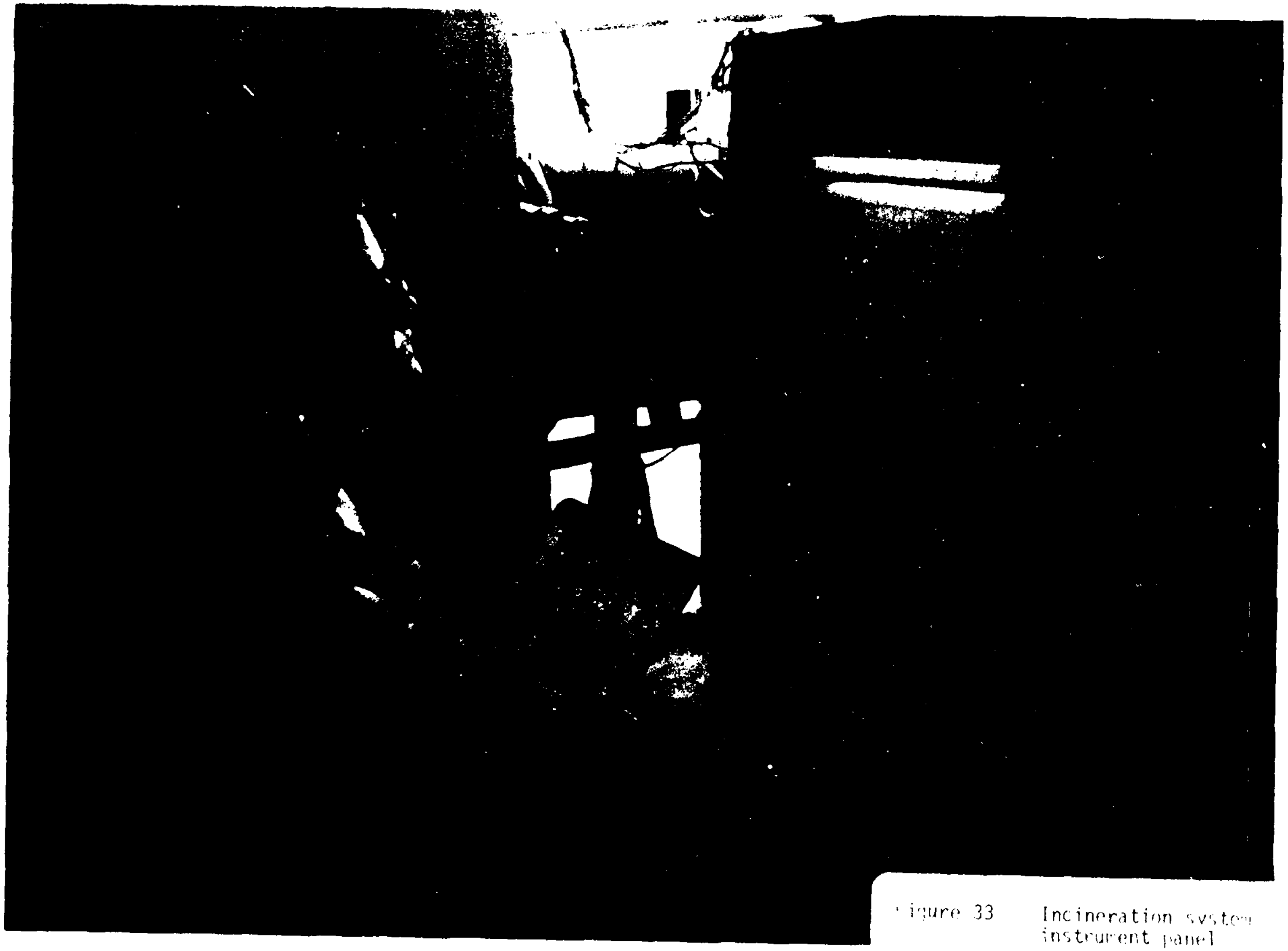


Figure 33 Incineration system instrument panel

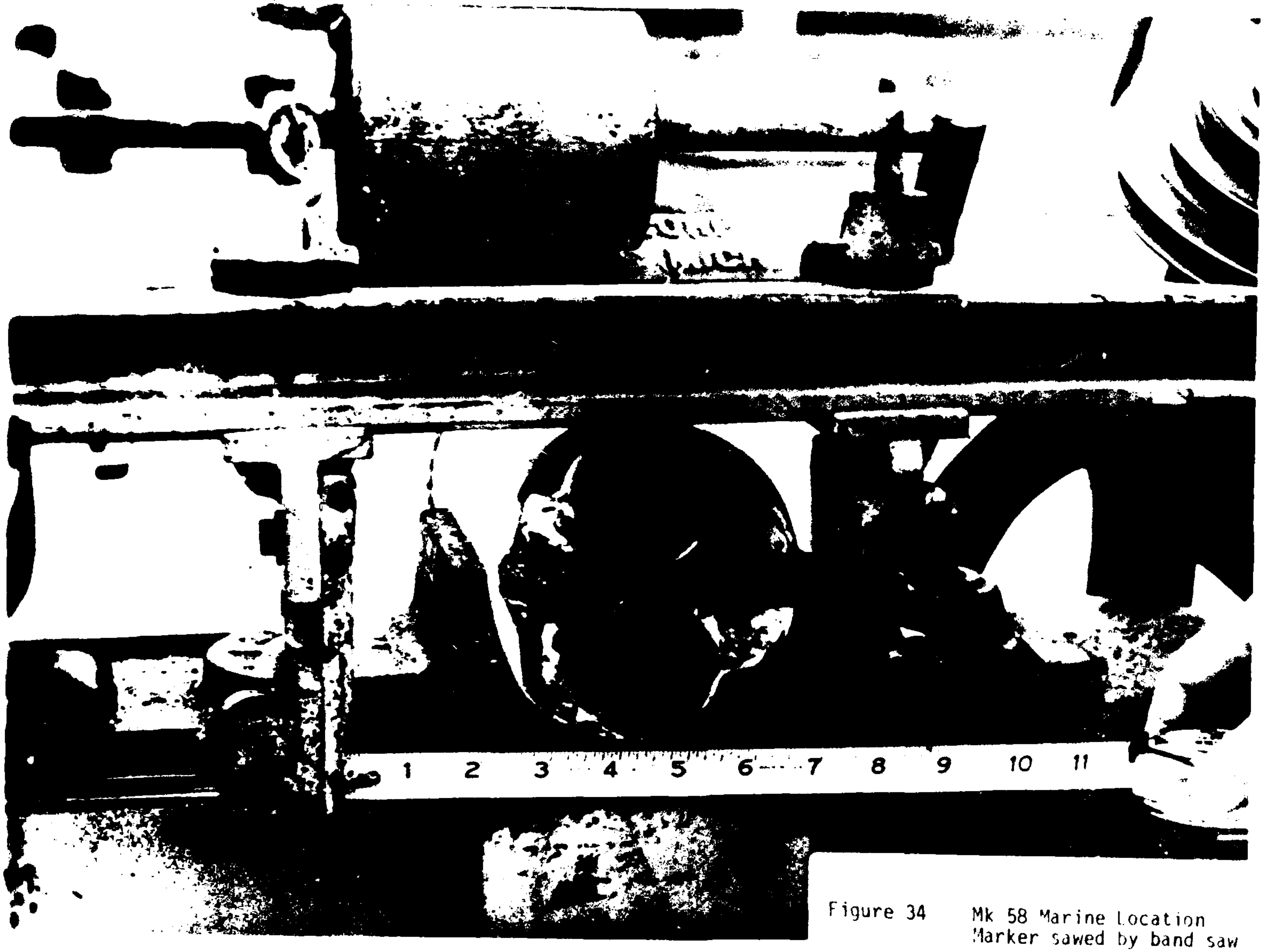


Figure 34 Mk 58 Marine Location Marker sawed by band saw

Figure 35 Mk 6 Aircraft Smoke and Illumination Signal sawed by band saw

Figure 36 Spring is cut from Mk 25 Marine Location Marker

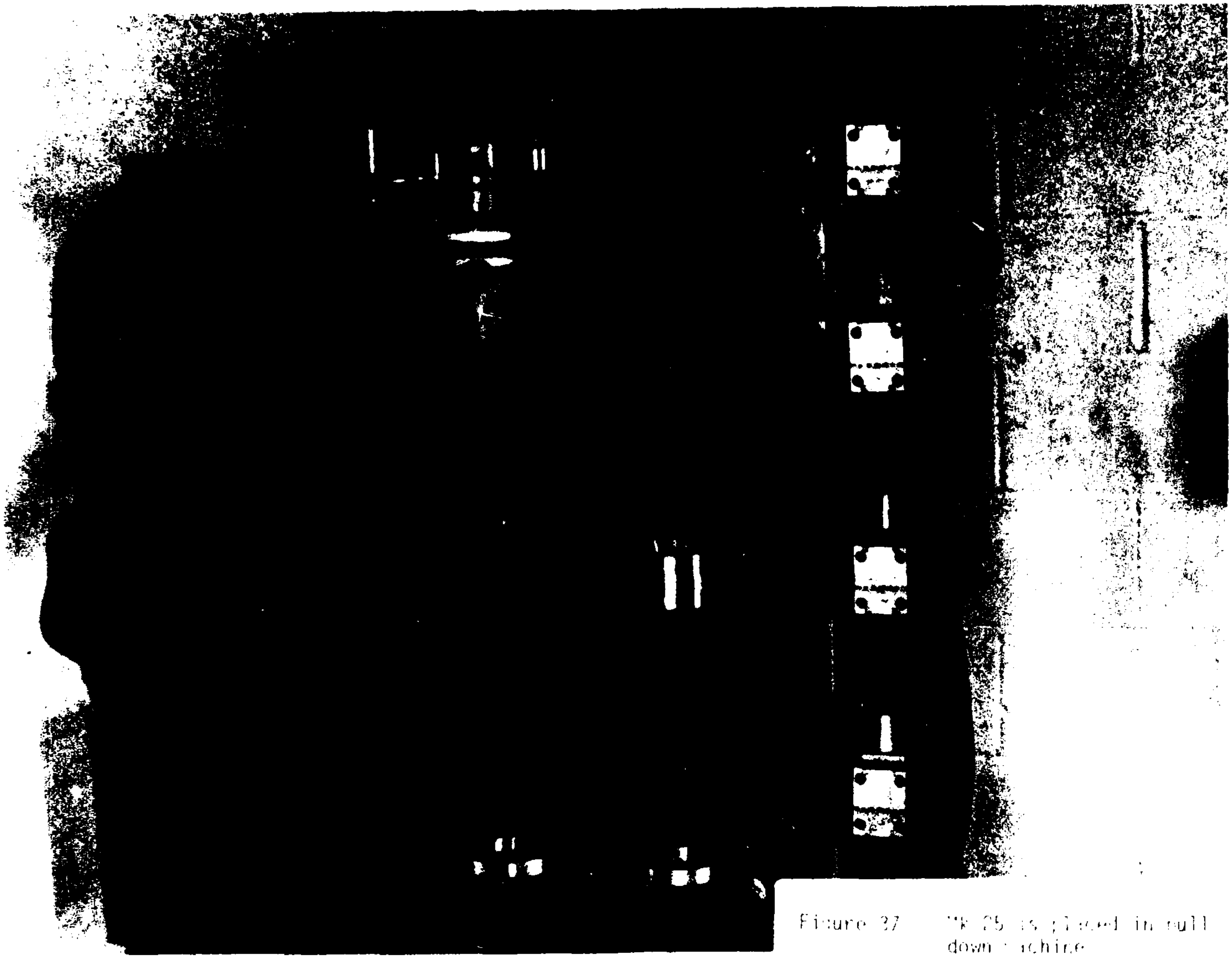


Figure 37   TR 25 is placed in pull down machine

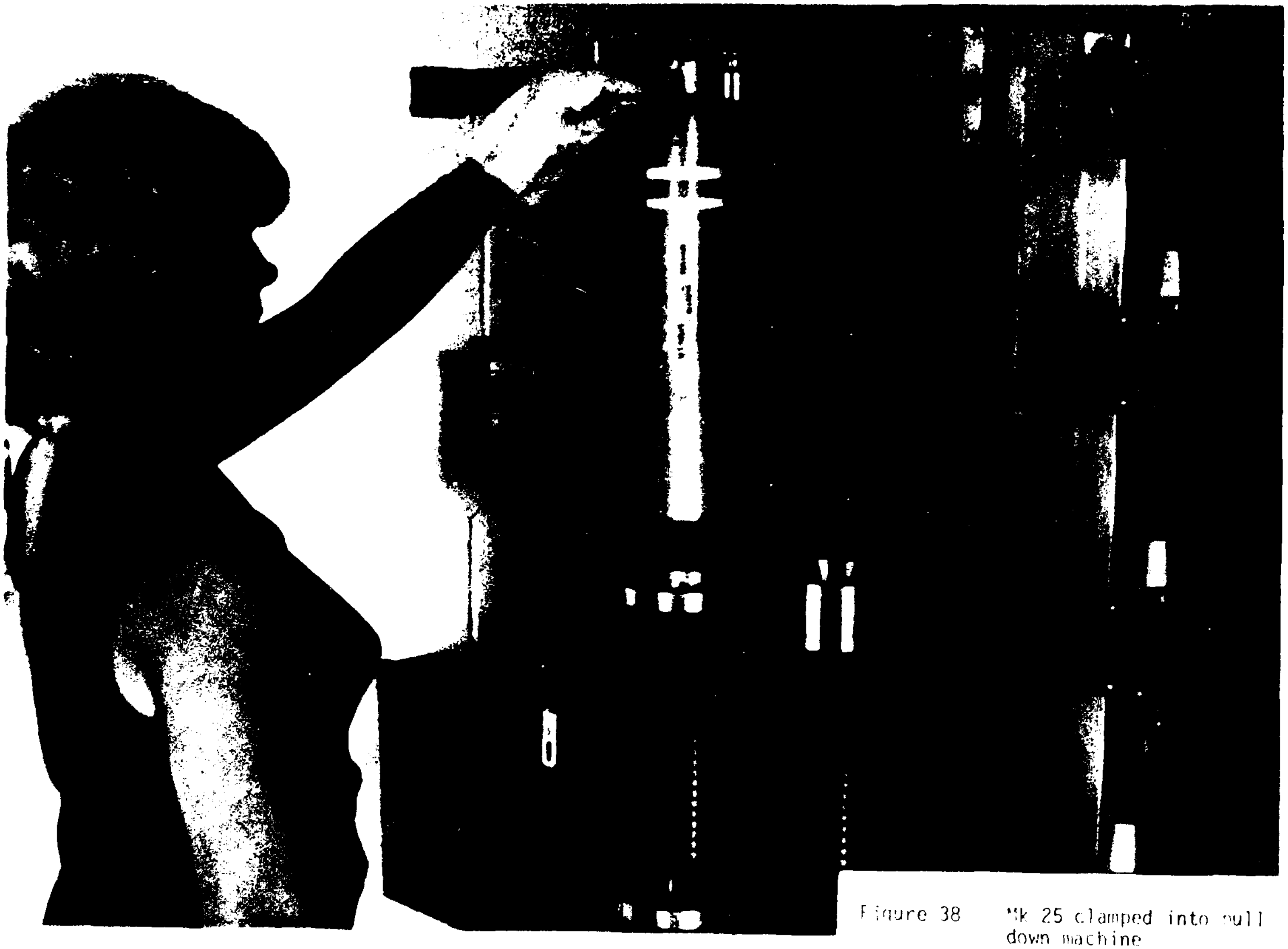


Figure 38   Mk 25 clamped into pull down machine

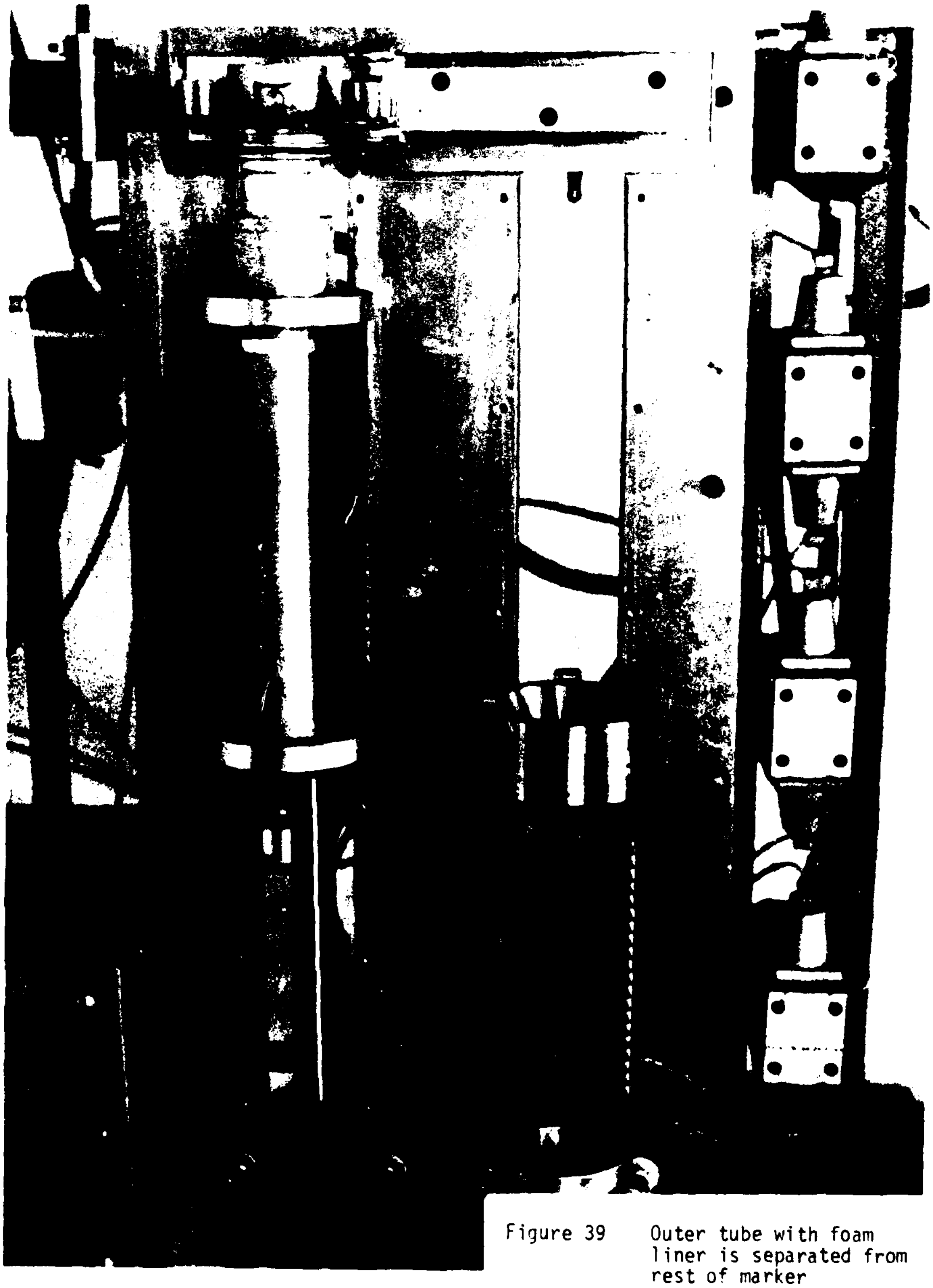


Figure 39 Outer tube with foam liner is separated from rest of marker

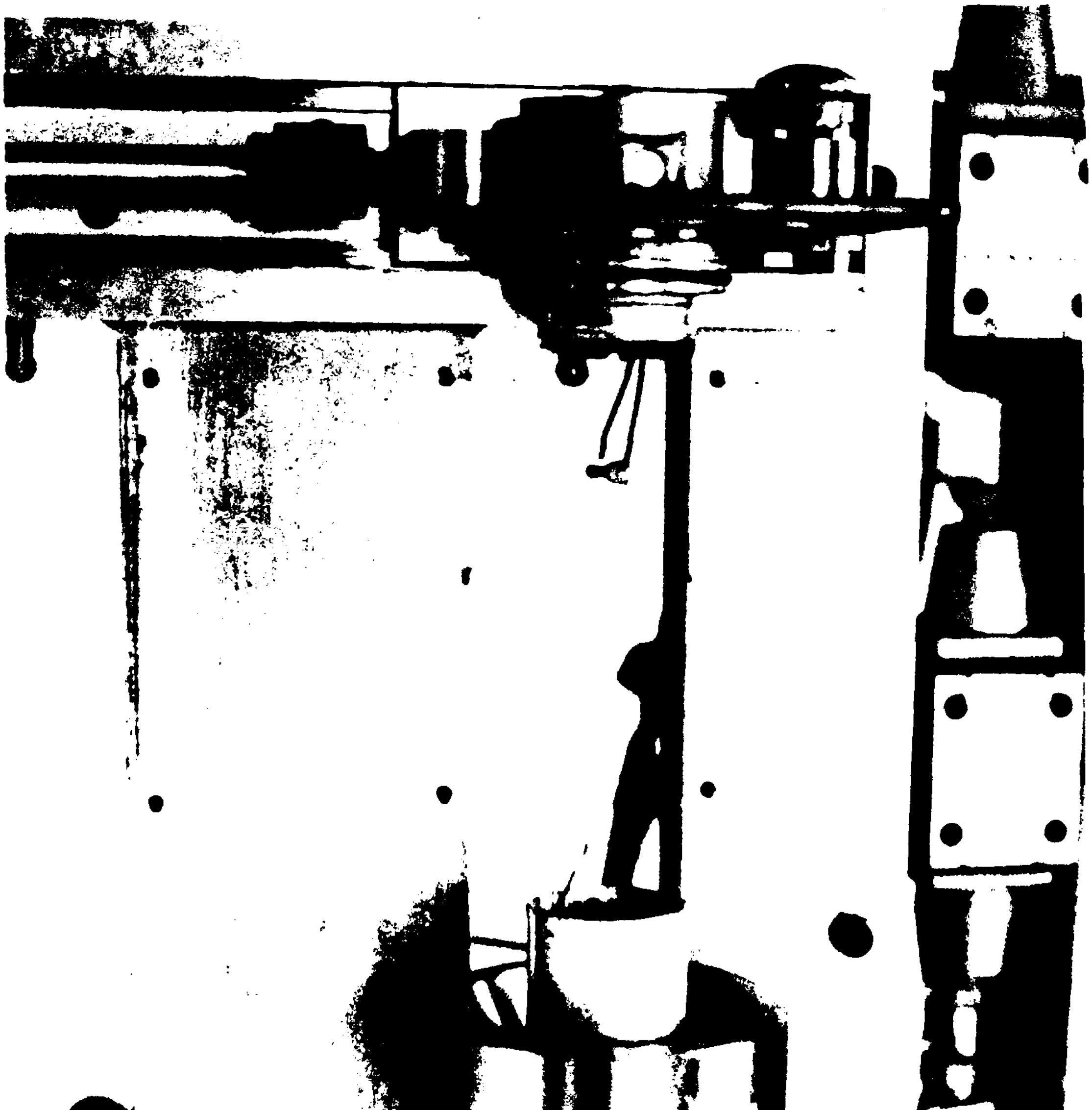


Figure 40 Inner tube of marker is separated from base fuze housing

Figure 41 Decrimper removes crimp prior to candle push out

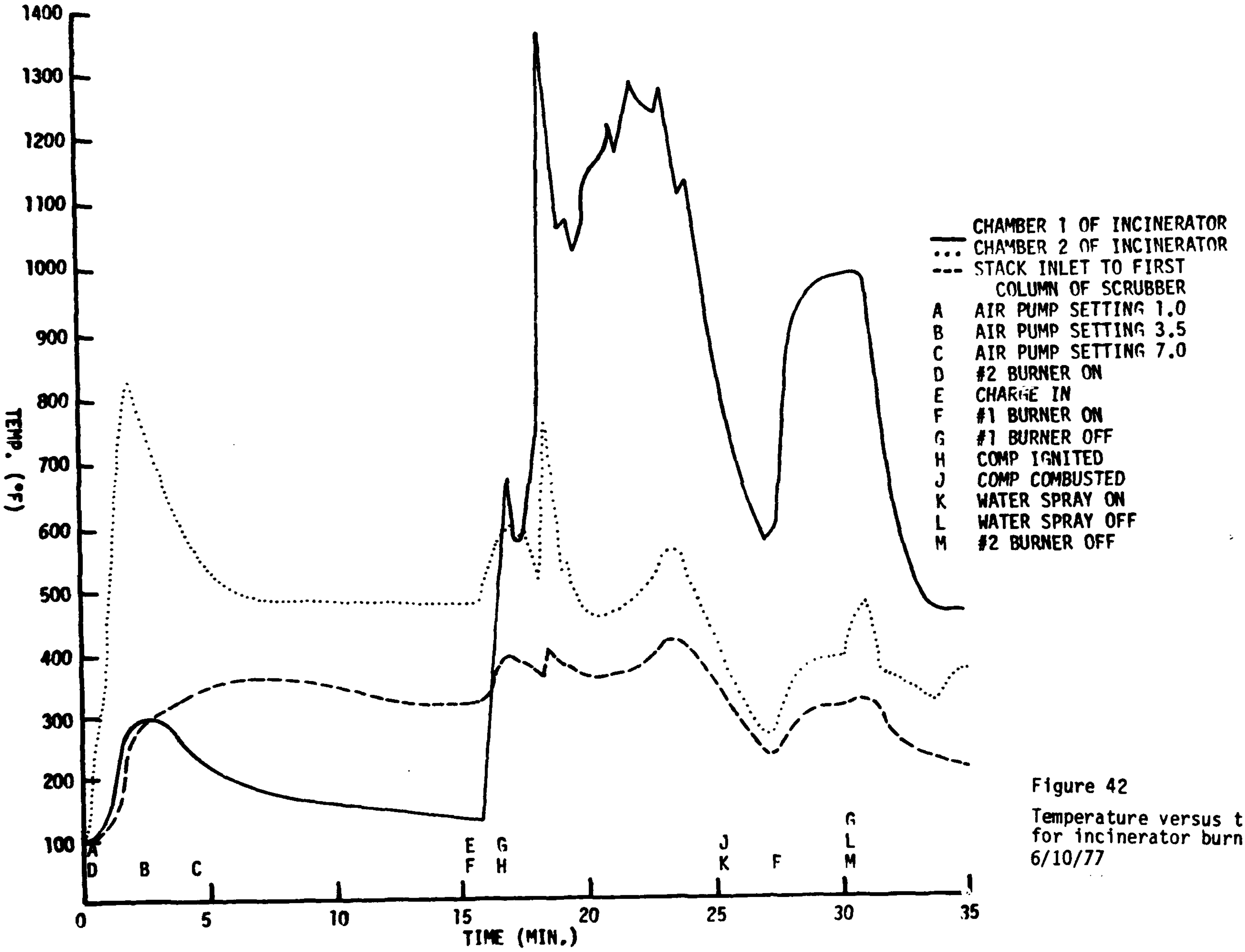


Figure 42

Temperature versus time for incinerator burn 6/10/77

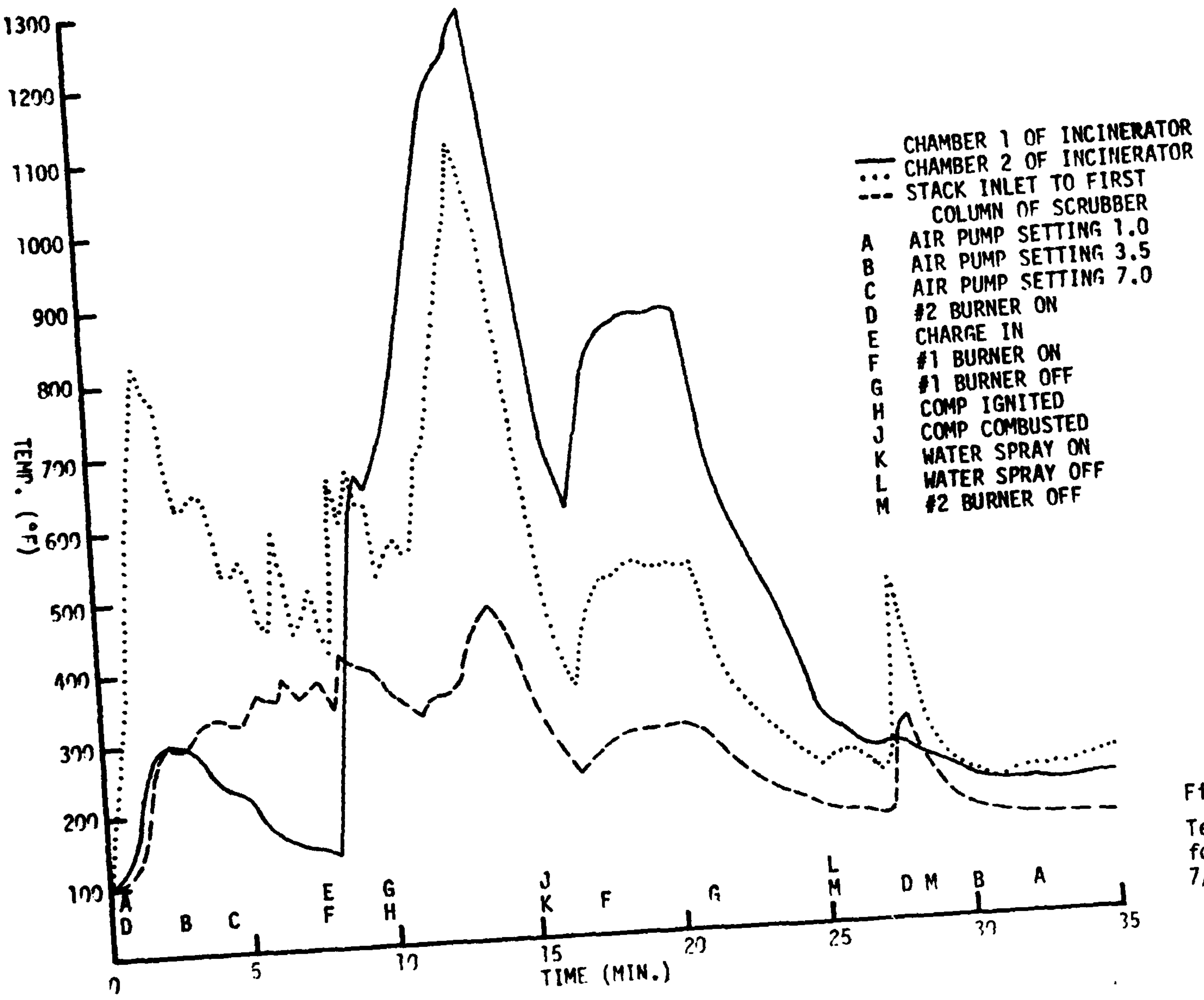


Figure 43

Temperature versus time for incinerator burn 7/13/77

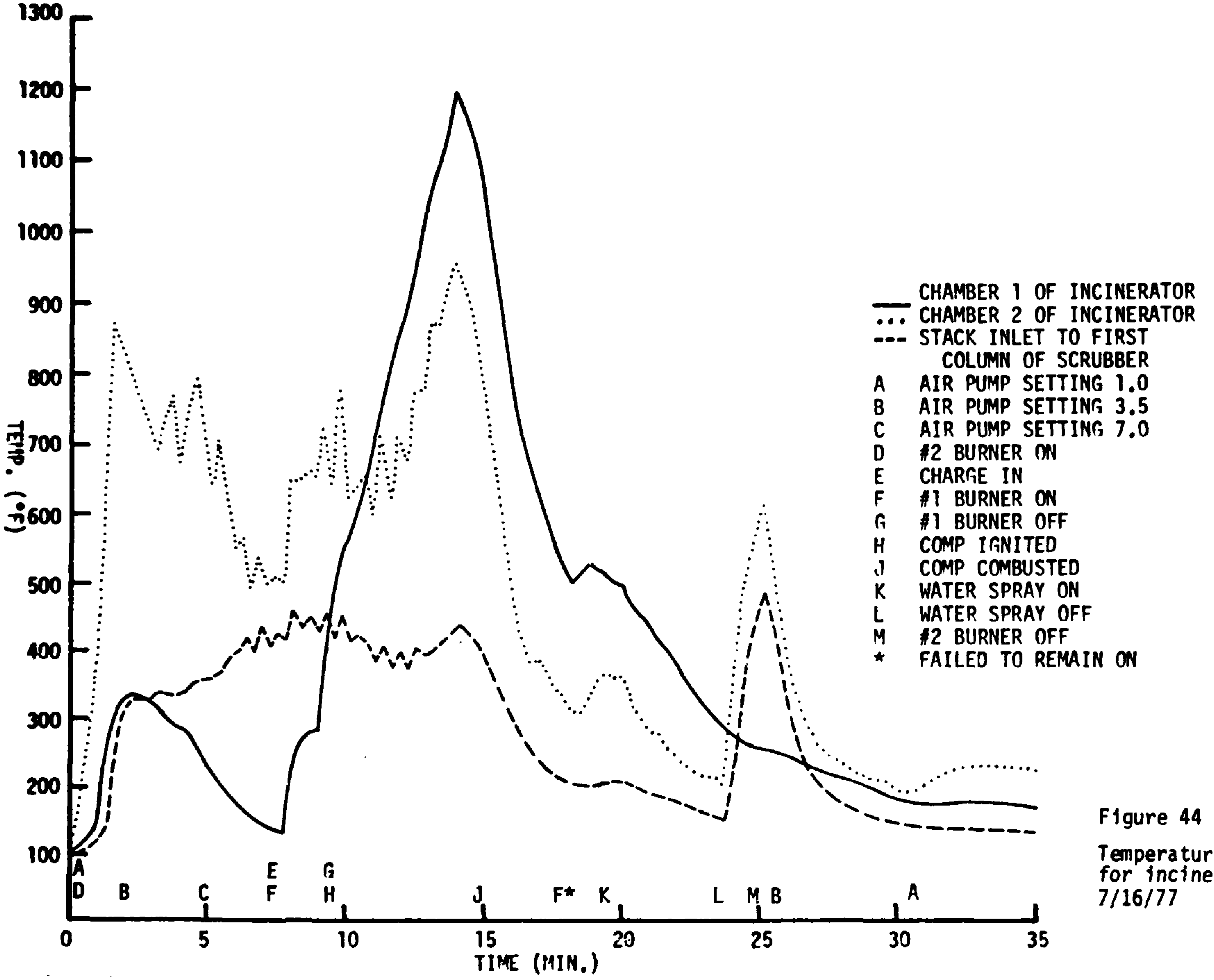


Figure 44

Temperature versus time for incinerator burn 7/16/77

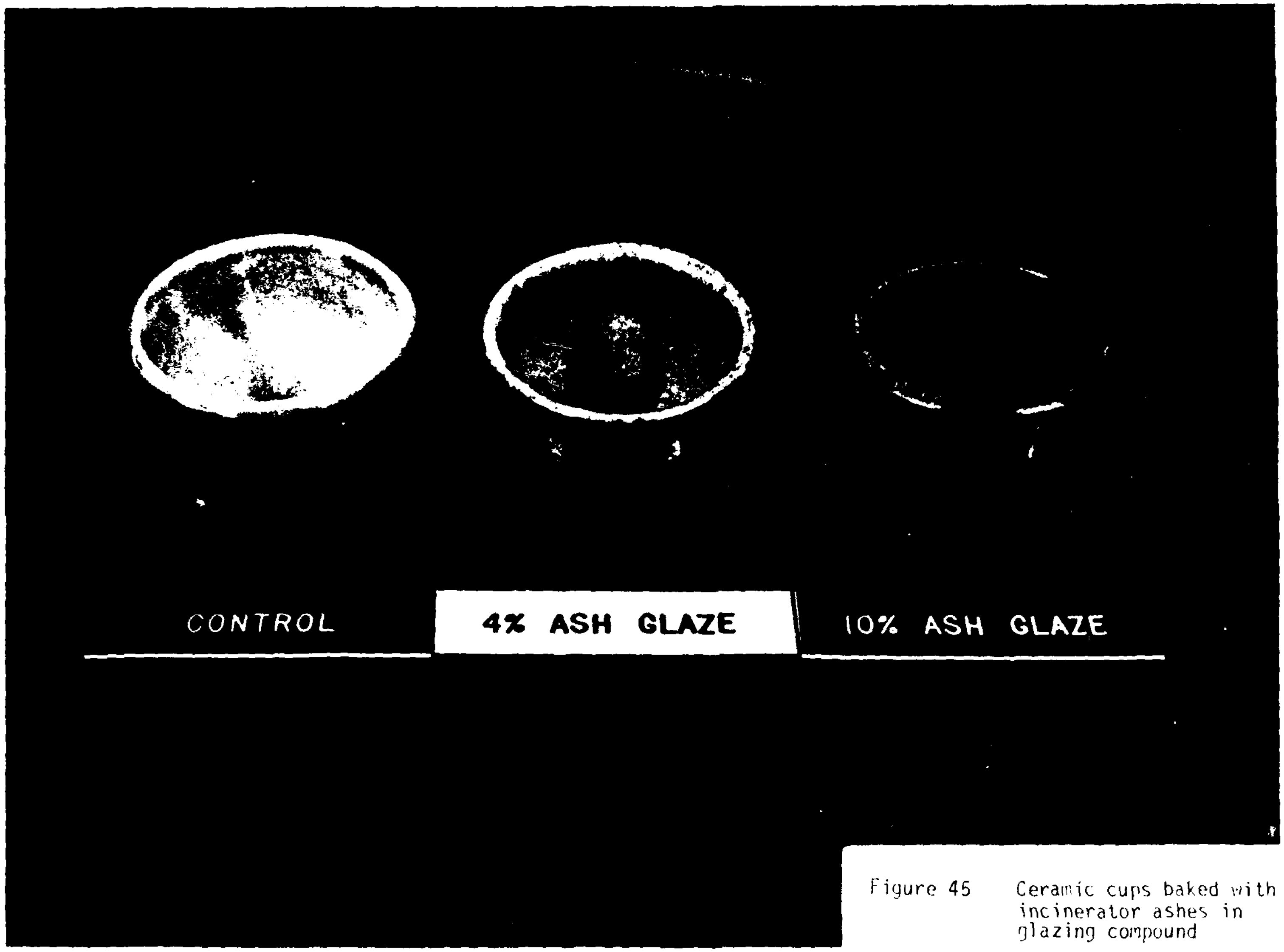


Figure 45 Ceramic cups baked with incinerator ashes in glazing compound

Figure 46 Sea water battery exposed for reclaim in base fuze housing

APPENDIX A

INCINERATION STUDY

MANAGEMENT SUMMARY

Naval Weapons Support Center (NWSC) Crane has developed a process concept for the demilitarization of a pyrotechnic composition used as a location marker (Marine Marker Mk 25). The concept involves combustion of the red phosphorus contained in the pyrotechnic composition to reclaim a phosphoric acid product for fertilizer application. A preliminary evaluation of the process concept was conducted by Battelle-Columbus (Contract No. N00164-75-M-3636) for NWSC Crane in an early study. The results indicated that the overall process concept proposed by NWSC Crane appeared technically sound and feasible.

As part of the overall development efforts by NWSC Crane, Battelle-Columbus was requested to pursue the concept on a pilot plant scale to further examine the technical feasibility of the process concept and to develop design data for a production facility.

A pilot plant capable of processing around 10 pounds of composition/batch was constructed. The plant consisted of incinerator, scrubber, mist eliminator, gas pump, stack, stack gas sampler, and control panel. A total of 39 runs were made for calibration and equipment checkout, incinerator curing, exploratory operations, and test operations.

The results of the operations confirmed that the process concept is technically sound and feasible. The plant was able to be operated in an environmentally acceptable fashion. The combustion residue was chemically stable after water treatment and the stack gas emission for P_2O_5 was below the current Ammunition Procurement and Supply Agency (APSA) standard when the pilot plant is operated at optimal operating condition. The quality of the product acid is considered to be equivalent to an agricultural-grade phosphoric

acid. The acid yield was around 41 percent, based on the total phosphorus in the feed composition without allowing for the recovery of condensed acid from the incinerator and process lines.

A preliminary design of a production facility capable of processing around 100 pounds of composition in a batch operation was made based on information obtained from the pilot plant operations. Using a standard Utility Financing Method, the capital requirement of the production facility was estimated around $620,000 at May, 1977 dollar base. The net annual operating cost was estimated at $150,000. The operating labor (around $63,000 or about 42 percent of the operating cost) and the administration and general overhead (around $49,000 or around 32 percent of the operating cost) are the major cost items in the operating cost. The average incineration cost for the red phosphorus pyrotechnic composition was estimated at $2.03/pound of composition.

Acknowledgement

The authors would like to express their thanks to Mr. James E. Short, Jr., Project Officer of Naval Weapons Support Center (NWSC), and his staff, Messrs. Frank Montgomery and William Weaver for their cooperation, advice, and understanding during the course of this study; Mr. Richard B. Landrigan for his technical advice and assistance during the construction of the pilot plant; Mr. Wilbur Mefferd for his diligence and expertise in the operation and various modifications of the pilot plant, analyses of various samples, and the shipping of the pilot plant; Mr. Harry Nuzum for his assistance in the construction of the pilot plant; Mr. William Baytos for his assistance in stack-gas sampling and analysis; Dr. Eugene Mezey for his assistance in the review of phosphorus chemistry as related to combustion; Messrs. Dan Chase and Robert Iden for their assistance in the analyses of various ash, acid, and gas samples; Dr. James E. Flinn, Mr. S. T. DiNovo, and Dr. Douglas W. Hissong for their constant advice and encouragement during the course of the study.

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List of Figures (Cont'd)

List of Figures (Cont'd)

A PILOT PLANT STUDY OF A PYROTECHNIC COMBUSTION PROCESS

by

P.S.K. Choi and B.C. Kim

INTRODUCTION

Disposal of obsolete or unserviceable conventional ammunition has been performed in the past primarily by deep-water dumping or by open field detonation or burning. These practices are no longer considered acceptable because (1) no salvage value of the constituent component of the ammunition can be realized, (2) considerable cost may be incurred in packaging and transportation for deep-water dumping, and (3) adverse environmental effects may be created from deep-water dumping or from open field detonation or burning.

As part of the current efforts by the Department of Defense in demilitarization of ammunition items, Naval Weapons Support Center (NWSC) Crane has developed a process concept for the disposal of and recovery of a reusable product from a red phosphorus pyrotechnic composition used in Marine Location Marker Mk 25. The concept is based on burning the composition in a closed system and scrubbing the combustion products with water to produce a fertilizer-grade phosphoric acid. A preliminary evaluation of the concept was conducted by Battelle for NWSC Crane(1) (Contract No. N00164-75-M-3636). The result indicated that the overall process concept proposed by NWSC Crane appeared technically sound and feasible for the reclamation of an agricultural-grade phosphoric acid from the red phosphorus composition. Consequently, NWSC Crane decided to pursue the concept on a pilot plant scale to further examine the technical feasibility and to develop design data for a production facility.

The objective of the study was to (1) conduct an experimental study with a pilot plant capable of processing 10 to 12 lb. of red phosphorus composition in a batch operation, (2) determine the effect of various design parameters; and (3) provide preliminary design data for a production facility to handle batch sizes of approximately 100 lb. of red phosphorus composition.

SCOPE OF WORK

The scope of the present study included these tasks:

(1) Construct a pilot plant capable of processing 10 to 12 lb. of red phosphorus composition/batch.

(2) Perform twenty (20) test runs including the shakedown operations.

(3) Perform seventeen (17) additional test runs for further examination of the pilot plant operation.

(4) Prepare preliminary design and/or equipment specifications for a production facility capable of processing 100 lb./batch of red phosphorus composition.

(5) Submit a final report on this study to NWSC Crane, describing the results and data generated in the study.

CONSTRUCTION OF PILOT PLANT

The pilot plant consisted of three major parts; incineration, scrubbing, and mist elimination systems. The artistic drawing of the overall front view of the plant and the actual installation are shown in Figures 1a and 1b, respectively. The detailed installations of various equipment and instruments are schematically depicted in Figure 2. The detailed list of equipment and materials procured for the plant is given in Table 1. The descriptions of the major equipment follows.

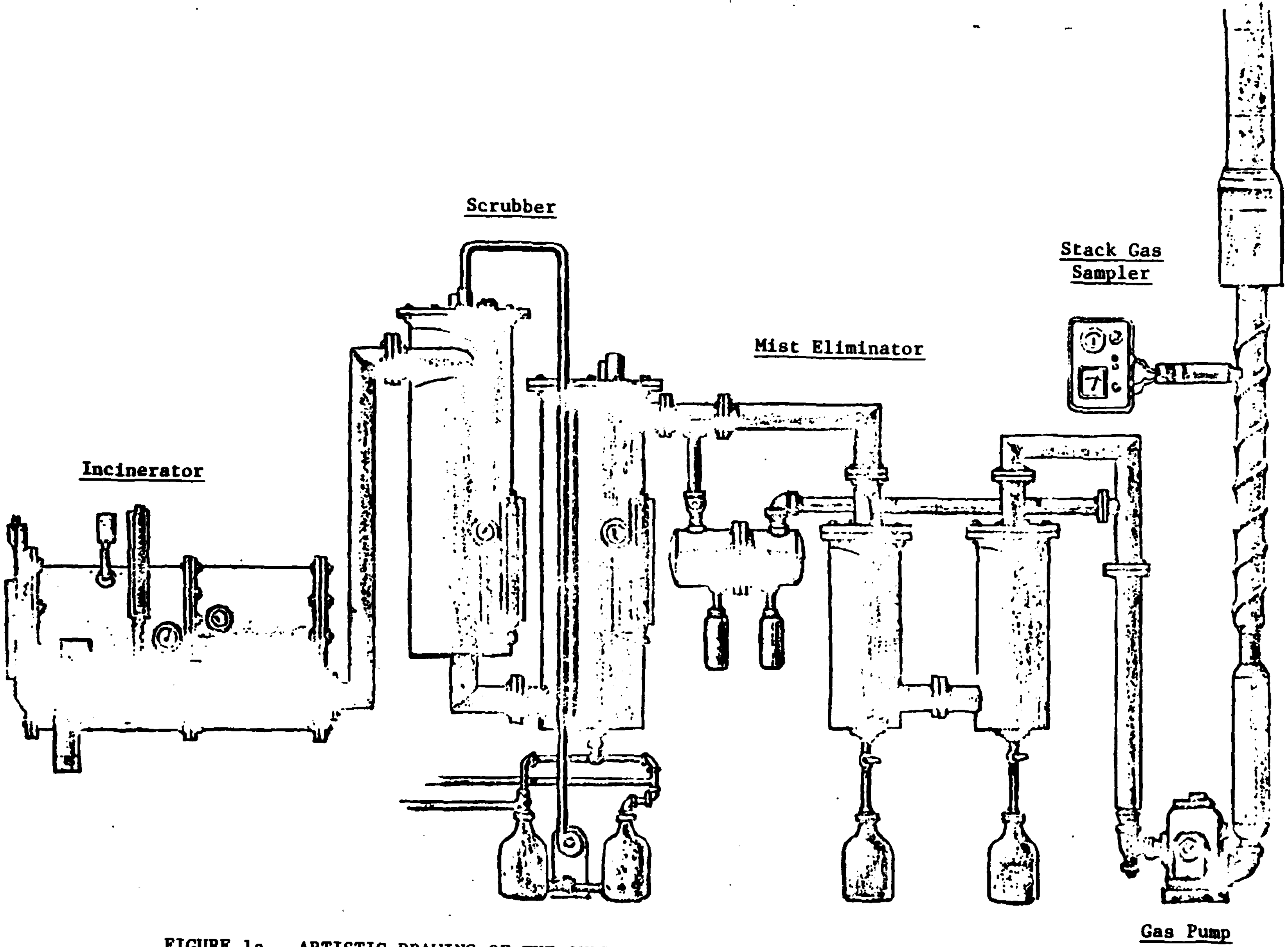


FIGURE 1a. ARTISTIC DRAWING OF THE OVERALL FRONT VIEW OF PYROTECHNIC COMBUSTION PILOT PLANT

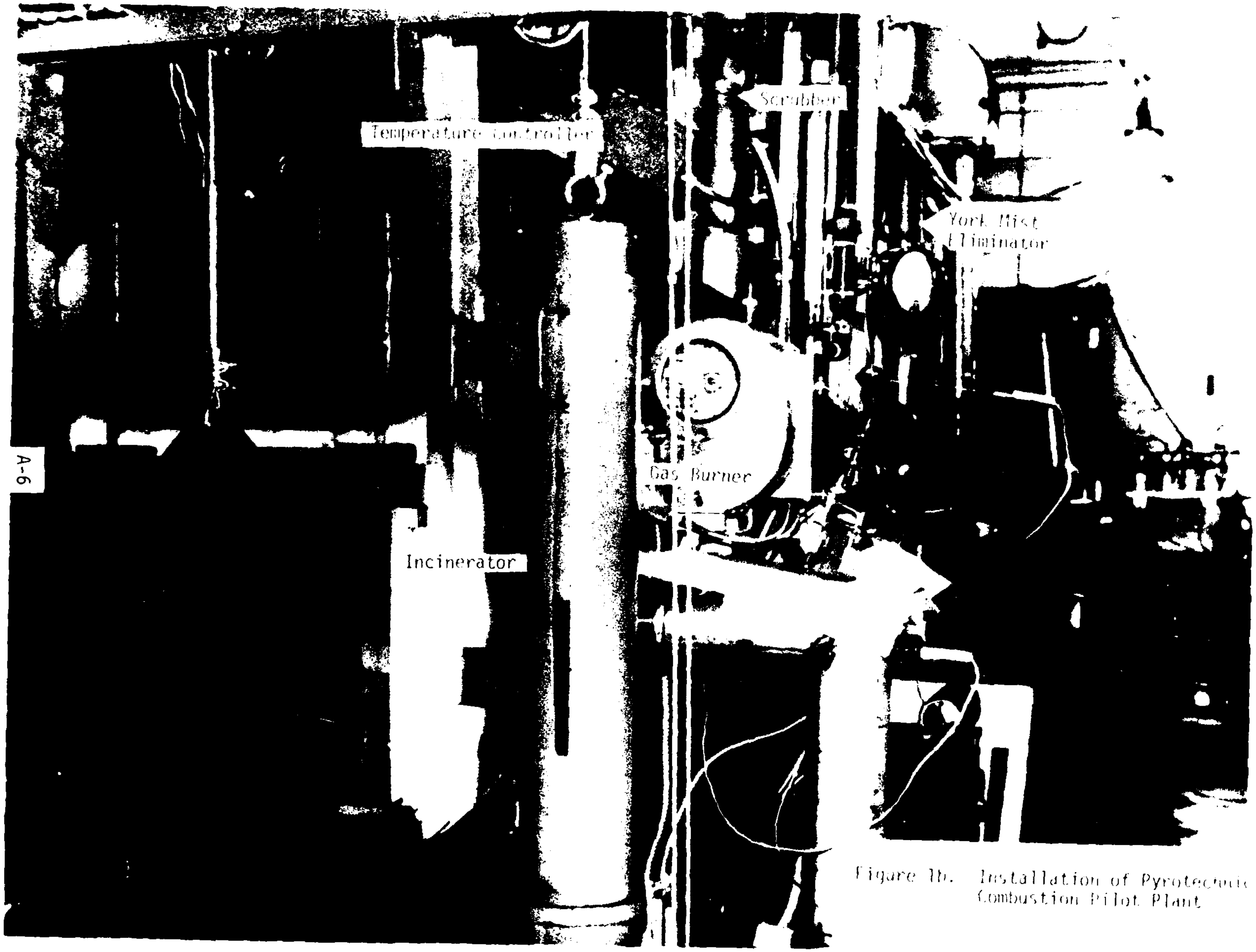
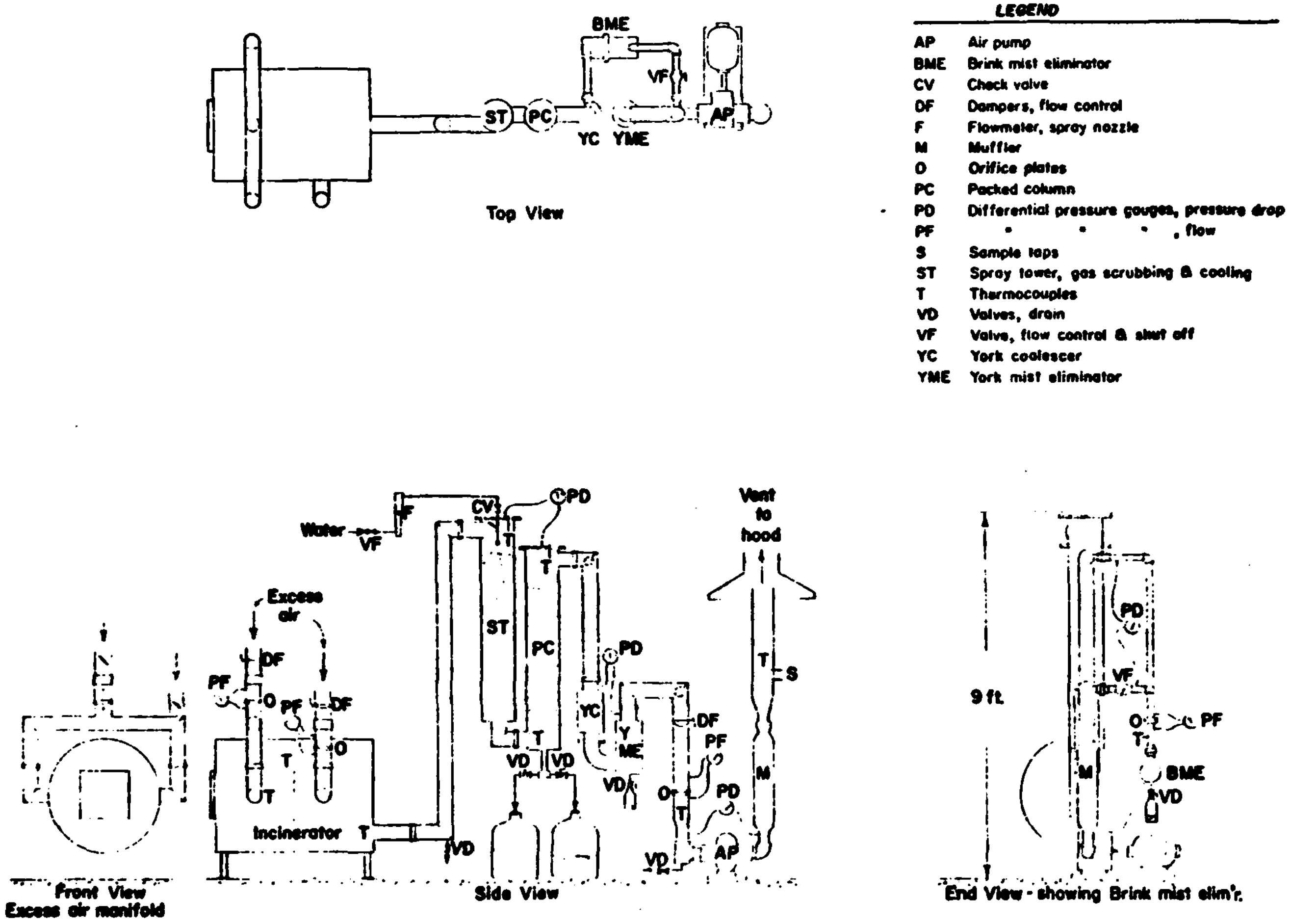


Figure 1b. Installation of Pyrotechnic Combustion Pilot Plant



LEGEND

AP	Air pump
BME	Brink mist eliminator
CV	Check valve
DF	Dampers, flow control
F	Flowmeter, spray nozzle
M	Muffler
O	Orifice plates
PC	Packed column
PD	Differential pressure gauges, pressure drop
PF	" " " , flow
S	Sample taps
ST	Spray tower, gas scrubbing & cooling
T	Thermocouples
VD	Valves, drain
VF	Valve, flow control & shut off
YC	York coalescer
YME	York mist eliminator

FIGURE 2. SCHEMATICS OF INSTALLATIONS OF VARIOUS EQUIPMENT AND INSTRUMENTS IN PYROTECHNIC COMBUSTION PILOT PLANT

TABLE 1. LIST OF EQUIPMENT AND MATERIALS PROCURED

Item	Qty.	Specification	Use	Supplier
Mist Eliminator	1 ea	8" Dia H_3PO_4 Mist Pilot Separator, T-316 S/S for 200 SCFM air at 200 F, EST. ΔP = 40" H_2O	Process stream	York Separators, Inc.
Scrubbing Tower (2 Sections)	1 ea	12" Pipe x 5' Long, Type 316 S/S	Gas scrubbing and cooling	Davis Heliarc Company
Incinerator (2 Sections)	1 ea	12 Ga. T-316 S/S Shell x 34" O.D.	Incineration of Sample Material	Plibrico Sales and Service
Pipe Nipples, STD. I.P.S.	2 ea	1/2" NPT x 2", SCH 40, Type 316 ST. Steel	Scrubber Drain	Williams & Company
Pipe Nipples, STD. I.P.S.	3 ea	1/2" NPT x 3", SCH. 40, Type 316 ST. Steel	Mist Eliminators' drains	Williams & Company
Pipe Nipples, STD. I.P.S.	1 ea	1" NPT x 6", SCH. 40, Type 316 ST. Steel	To brink mist eliminator	Williams & Company
Pipe Nipples, STD. I.P.S.	3 ea	1 1/2" NPT x 3", SCH. 40, Type 316 ST. Steel	To brink mist eliminator (one cut in half)	Williams & Company
Pipe Nipples, STD. I.P.S.	2 ea	1 1/2" NPT x 4", SCH. 40, Type 316 ST. Steel	To brink mist eliminator (one cut in half)	Williams & Company
Pipe Nipples, STD. I.P.S.	2 ea	1 1/2" NPT x 8", SCH. 40, Type 316 ST. Steel	To brink mist eliminator (one cut in half)	Williams & Company
Pipe Nipples, STD. I.P.S.	1 ea	1 1/2" NPT x 10", SCH. 40, Type 316 ST. Steel	To brink mist eliminator (one cut in half)	Williams & Company
Pipe Nipples, STD. I.P.S.	1 ea	1 1/2" NPT x 12", SCH. 40, Type 316 ST. Steel	To brink mist eliminator (one cut in half)	Williams & Company
Pipe Nipples, STD. I.P.S.	3 ea	3" NPT x 4", SCH. 40, Type 316 ST. Steel	To air pump and exhaust duct	Williams & Company
Pipe Tee, Screw, STD. I.P.S.	1 ea	1" NPT x 4", SCH. 40, Type 316 ST. Steel	Scrubber drain	Williams & Company
Pipe Bushings, Screw, STD. I.P.S.	2 ea	1" x 1/2" NPT, SCH. 40, Type 316 ST. Steel	Scrubber drain	Williams & Company
Pipe Elbows, Screw, STD. I.P.S.	3 ea	1 1/2" NPT x 90°, SCH. 40, Type 316 ST. Steel	To brink mist eliminator	Williams & Company
Pipe Unions, Screw, STD. I.P.S.	4 ea	1 1/2" NPT, SCH. 40, Type 316 ST. Steel	To brink mist eliminator	Williams & Company
Pipe Tee, Screw, STD. I.P.S.	1 ea	3" NPT, SCH. 40, Type 316 ST. Steel	To air pump	Williams & Company
Pipe plug, screw, STD. I.P.S.	1 ea	3" NPT, SCH. 40, Type 316 ST. Steel	To air pump	Williams & Company
Pipe flanges, ANSI STD. 150 lb.	2 ea	1 1/2", Weld Neck, SCH. 40, Type 316 ST. Steel	For orifice plate, brink mist eliminator	Williams & Company
Concetric Reducer, STD. I.P.S.	1 ea	4" x 3"-Butt Weld, SCH. 40, Type 316 ST. Steel	To air pump	Williams & Company
Pipe, STD. I.P.S., Welded	20 ft	1 1/2"-Butt Weld, SCH. 40, Type 316 ST. Steel	To brink mist eliminator	Williams & Company
Pipe, STD. I.P.S., Welded	40 ft	4"-Butt Weld, SCH. 10, Type 316 ST. Steel	Process lines	Williams & Company
Tube, Welded	200 ft	1/4" O.D. x .035 Wall, SCH. 10. Type 316 ST. Steel	Pressure meas. lines to panel	Williams & Company
Tube, Seamless	20 ft	1/4" O.D. x .065 Wall, SCH. 10, Type 316 ST. Steel	Pressure and sample tads, T.C. Wells	Williams & Company
Tube, Seamless	20 ft	3/8" O.D. x .065 Wall, SCH. 10, Type 316 ST. Steel	Water line to spray nozzle	Williams & Company
Valve, Screw Ends ("Apollo")	2 ea	1/2" Ball, SCH. 10, Type 316 ST. Steel	Scrubber drain manifold	Mutual Manufacturing
Valve, Screw Ends ("Apollo")	1 ea	1 1/2" Ball, SCH. 10, Type 316 ST. Steel	Brink flow control and shut off	Mutual Manufacturing
Valves, Needle ("Celanese")	20 ea	1/4" FNPT, Califrated Needle (CN-1), PVC	Pressure Line Shut off-Gauge Protection	Pipe Valves, Inc.
Valves, Ball ("Celanese")	3 ea	1/2" FNPT, True Union (TR-4), CPVC	Mist eliminators' drains	Pipe Valves, Inc.
Hose Adapters, No. 62006	30 ea	1/4" MNPT x 1/4" I.D. Hose, Straight, Hi-Den Polyeth.	Pressure Meas. Lines - Panel Board	U.S. Plastic Corp.
Hose Adapters, No. 62030	40 ea	1/8" MNPT x 14" I.D. Hose, 90° EL, Hi-Den Polyeth.	Pressure Meas. Lines - Panel Board	U.S. Plastic Corp.
Tube Unions, ("Swagelok")	32 ea	No. 55-400-6, 1/4", 90° EL, T-316 S/S	Pressure lines connectors	Scoito Valve & Fitting Company
Male Connectors, ("Swagelok")	12 ea	No. SS-200-1-2, 1/8" MNPT x 1/8" Tube, T-316 S/S	Thermocouple fittings	Socito Valve & Fitting Company
Male Connectors, ("Swagelok")	2 ea	No. SS-600-1-8, 1/2" MNPT x 3/8" Tube, T-316 S/S	Water line to tower	Socito Valve & Fitting Company
Male Connectors, ("Swagelok")	2 ea	No. SS-810-1-8, 1/2" MNPT x 1/2" Tube, T-316 S/S	Scrubber drain manifold	Socito Valve & Fitting Company

TABLE 1. (Continued)

Item	Qty.	Specification	Use	Supplier
Female connectors ("Swagelok")	3 ea	No. SS-600-7-2, 1/8" FNPT x 3/8" Tube, T-316 S/S	Water line to spray nozzles	Scioto Valve and Fitting Company
Checkvalves, ("Nupro")	3 ea	No. SS-6C-1, 3/8" Tube x 1 lb, T-316 S/S	Water line to spary nozzles	Scioto Valve and Fitting Company
Flanges ("Janitrol")	28 ea	No. F29C71-1-5.141, Type 321 ST. Steel	Process line duct connections	Janitrol Aero Div. of Midland Ross Corp.
Clamps, ("Janitrol")	14 ea	No. F38C37 STD. Quick-couple, CRES	Process line duct connections	Janitrol Aero Div. of Midland Ross Corp.
Flanges, ("Janitrol")	4 ea	No. F72C13-1-5.141, Type 321 ST. Steel	Process line duct connections	Janitrol Aero Div. of Midland Ross Corp.
Clamp, ("Janitrol")	1 ea	No. F55C45 STD. Quick-couple, CRES	Process line duct connections	Janitrol Aero Div. of Midland Ross Corp.
Nozzle, Full-Jet	3 ea	1/8 GG3.5 STD. Quick-couple, Type 316 ST. Steel	Spray Tower	Spraying System Co.
Line Strainer	1 ea	1/2 RW-100, Brass w/100 mesh S/S Screen	Water line to rotameter	Spraying System Co.
Dampers, 4" Nom.	3 ea	Type 1E-1 STD. Volume Damper, 16 GA., T-316 ST. Steel	Flow control, excess air and total	United Sheet Metal Div. of United McGill Corp.
Reducer, Concentric	1 ea	Type R-1, 5" x 3 1/2", 20 GA, Type 316 St. Steel	Pump Exhaust Line	United Sheet Metal Div. of United McGill Corp.
Exhaust Duct	28-1/2 ft	Spiral Uni-Seal Round, 5" Dia., 22 GA, T-316 S/S	Pump Exhaust Line	United Sheet Metal Div. of United McGill Corp.
Duct Sealer Compound	1 ea	1 qt. Tube - Butyl Styrene Base	Pump Exhaust Line	United Sheet Metal Div. of United McGill Corp.
Differential Pressure Gauges	5 ea	No. 2006, 0-6" Water, Cast Aluminum	Pressure Drop Meas. Incl. Flow	Dwyer Instruments, Inc.
Differential Pressure Gauges	1 ea	No. 2020, 0-20" Water, Cast Aluminum	Pressure Drop Meas. Incl. Flow	Dwyer Instruments, Inc.
Differential Pressure Gauges	1 ea	No. 2060, 0-60" Water, Cast Aluminum	Pressure Drop Meas. Incl. Flow	Dwyer Instruments, Inc.
Differential Pressure Gauges	1 ea	No. 2080, 0-80" Water, Cast Aluminum	Pressure Drop Meas. Incl. Flow	Dwyer Instruments, Inc.
Differential Pressure Gauges	1 ea	No. 2150, 0-150" Water, Cast Aluminum	Pressure Drop Meas. Incl. Flow	Dwyer Instruments, Inc.
Column Packing, Ceramic	2 cu ft	1/2" Intalox, Body 704 White Procelain	Gas scrubbing	Norton Chemical
Bottle, Solution, KIMAX	2 ea	Cat. No. 16144-065, (Kimble #14950), 5 Gal. Cap.	Scrubber Liquor	VWR Scientific
Drying Tubes, 8" Long	2 pk of 12 each	Cat. No. 26625-004 (Nalge #6201-0080), 8" Long	Gauge Protection	VWR Scientific
Ball Valves, "Appolo"	2 ea	No. 76-102-01, 3/8" FNPT, Type 316 S/S	Acid Recycle System	Mutual Manufacturing and Supply Company
Rotameter	1 ea	No. 10A3565-1-45-S, Fischer & Porter, Brass	Burner Gas (~ 2.73 SCFM)	F&P Company
Rotameter	1 ea	No. 10A3565-1-48-S, Fischer & Porter, Brass	Burner Gas (~ 5.5 SCFM)	F&P Company
Rotameter	1 ea	No. 10A3565-1-46-S, Fischer & Porter, Brass	Scrubber Water (0.67 GPM)	F&P Company
Rotameter	1 ea	No. 10A3665, Fischer & Porter, Brass, S/S	Acid Recycle (~ 1.0 GPM)	F&P Company
Pressure Gage	1 ea	No. 63-3212, 0-100 psig, 2 1/2" DIAL, Type S/S	Acid Recycle Line	Matheson Co., Inc.
Drying Tubes	2 pkg (12 pkg)	No. 26625-004 (Nalge #6201-0030), Polypropylene	Gauge Protection	VWR Scientific
Bottles, Kimax	2 ea	No. 16144-065 (Kimble #14950), 5 gal	Acid Recycle System (Scrub, Liquor)	VWR Scientific
Belt, Abrasive	1 nest (10)	4 x 36 inch, 100 Grit, 3-M-ite Resinite Cloth	Shop Replacement	Ross Willoughby Co.
Orifice Plates	3 ea	60 percent Area Hole, Type 316 S/S	Gas Flow Measurement	Davis Heliarc Co.
Orifice Plates	1 ea	1.704" Hole, Type 316 S/S	Gas Flow Measurement	Davis Heliarc Co.
Orifice Plates	1 ea	2.130" Hole, Type 316 S/S	Gas Flow Measurement	Davis Heliarc Co.
Orifice Plates	1 ea	2.556" Hole, Type 316 S/S	Gas Flow Measurement	Davis Heliarc Co.
Female Connector, Swagelok	2 ea	SS-600-7-2, 3/8T x 1/8 FNPT, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Female Connector, Swagelok	1 ea	SS-600-7-4, 3/8 T x 1/4 FNPT, T 316 S/S	Acid Recycle System	Scoito Valce & Fitting Company

TABLE 1. (Continued)

Item	Qty.	Specification	Use	Supplier
Male Connector, Swagelok	1 ea	SS-400-1-4, 1/4 T x 1/4 MNPT, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Male Connector, Swagelok	3 ea	SS-600-1-4, 3/8 T x 1/4 MNPT, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Male Connector, Swagelok	6 ea	SS-600-1-6, 3/8 T x 3/8 MNPT, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Male Connector, Swagelok	3 ea	SS-600-1-8, 3/8 T x 1/2 MNPT, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Union Tee, Swagelok	7 ea	SS-600-3/8 T, Type 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Union Tee, Swagelok	4 ea	SS-600-6, 3/8 T, Type 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Reducing Union	2 ea	SS-810-6-6, 1/2 T, 3/8 T, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Male Adapter	1 ea	SS-601-A-4, 1/4 MNPT T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Front Ferrules	4 ea	T813-1, 1/2 T, Teflon	Acid Recycle System	Scioto Valve & Fitting Company
Ferrules, Front and Back	1 arbor/ 10 ea	SS-400 Sets-10, 1/4 T, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Ferrules, Front and Back	1 arbor/ 10 ea	SS-600 Sets 10, 3/8 T, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Filter, in-line NUPRO	1 ea	SS-6F-60, 60 μ, 3/8 T x 1/4 FNPT, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Adj, Relief Valce, NUPRO	1 ea	SS-4CA4-50-150 PSI, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Regulating Valve, Whitey	2 ea	SS-6LRS6, Union Bonnet w/3/8T, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Ball Valve, Whitey	2 ea	SS-4X6, 3 way w/3/8T, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company
Ball Valve, Whitey	1 ea	SS-43F4, 1/4 FNPT, T 316 S/S	Acid Recycle System	Scioto Valve & Fitting Company

Incinerator

The front and side views of a two-combustion chamber incinerator which was employed in the pilot plant are shown in Figures 3 and 4, respectively. The detailed design drawings are given in Appendix AA of this report. The important features of the incinerator include:

(1) The incinerator is divided into two combustion chambers; a primary chamber for the combustion of the red phosphorus composition and a secondary chamber as an afterburner.

(2) Each chamber includes a gas burner with temperature controller, and combustion air ports.

(3) The primary chamber has a charging door which allows loading of feed material to and unloading of combustion residue from the chamber.

(4) The red phosphorus composition is charged in a charge pan (also called an ash pan) which is mounted on a rail.

(5) The overall dimensions of the furnace are 64 inches long x 38-3/16 inches wide x 50-3/4 inches high from the floor to the top of the charging door counter balance assembly.

(6) The incinerator housing shell is stainless steel 316 (12 gage). All reinforcing steel and furnace support framing is mild structural steel.

(7) The shell is 34 inches in diameter and lined with 1 inch thick mono-block to the steel, and 3 inches thick Plicast Tuffmix® to the mono-block. The dividing wall between combustion chambers is 4 inches thick of Plicast Tuff-Lite®.

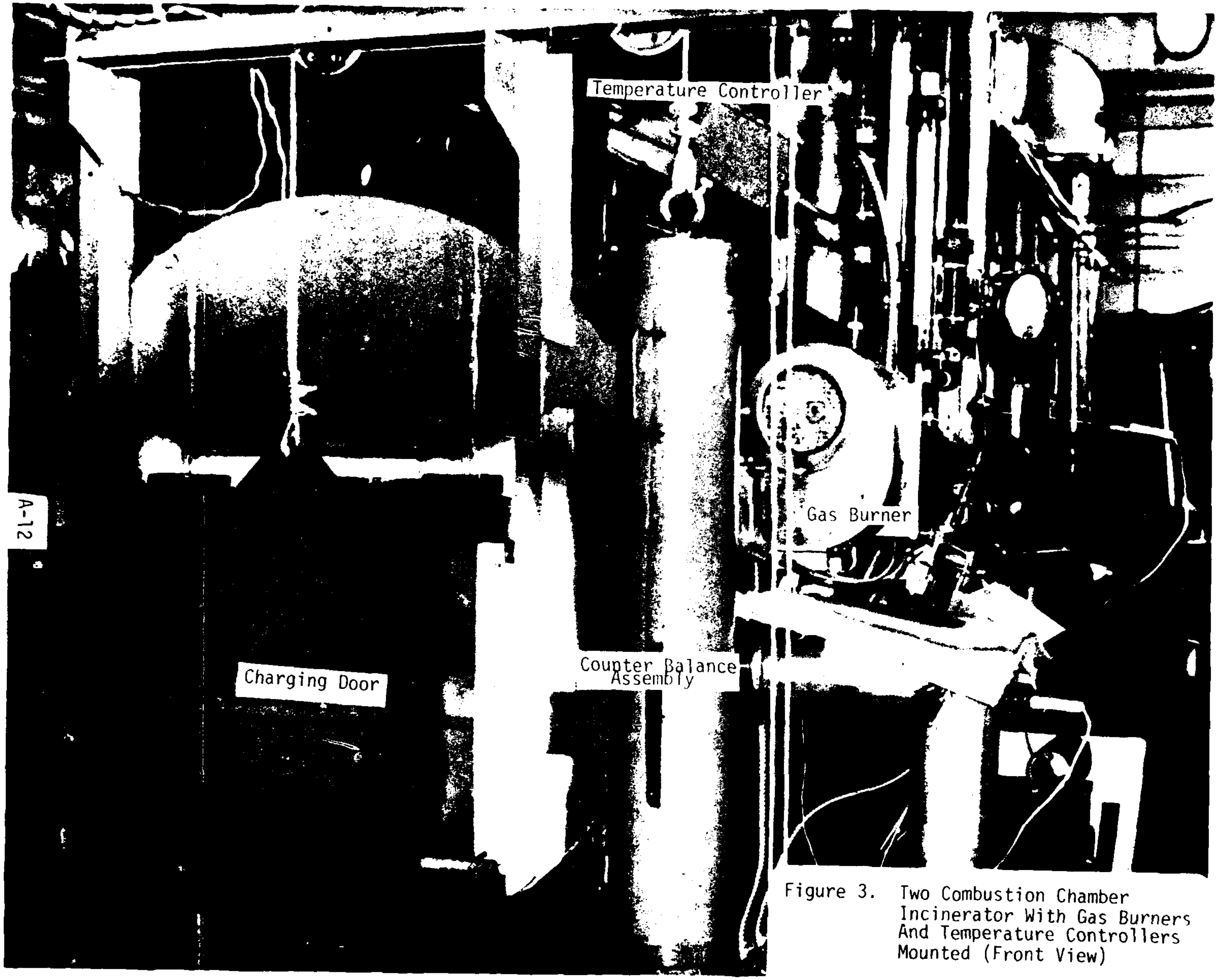


Figure 3. Two Combustion Chamber Incinerator With Gas Burners And Temperature Controllers Mounted (Front View)

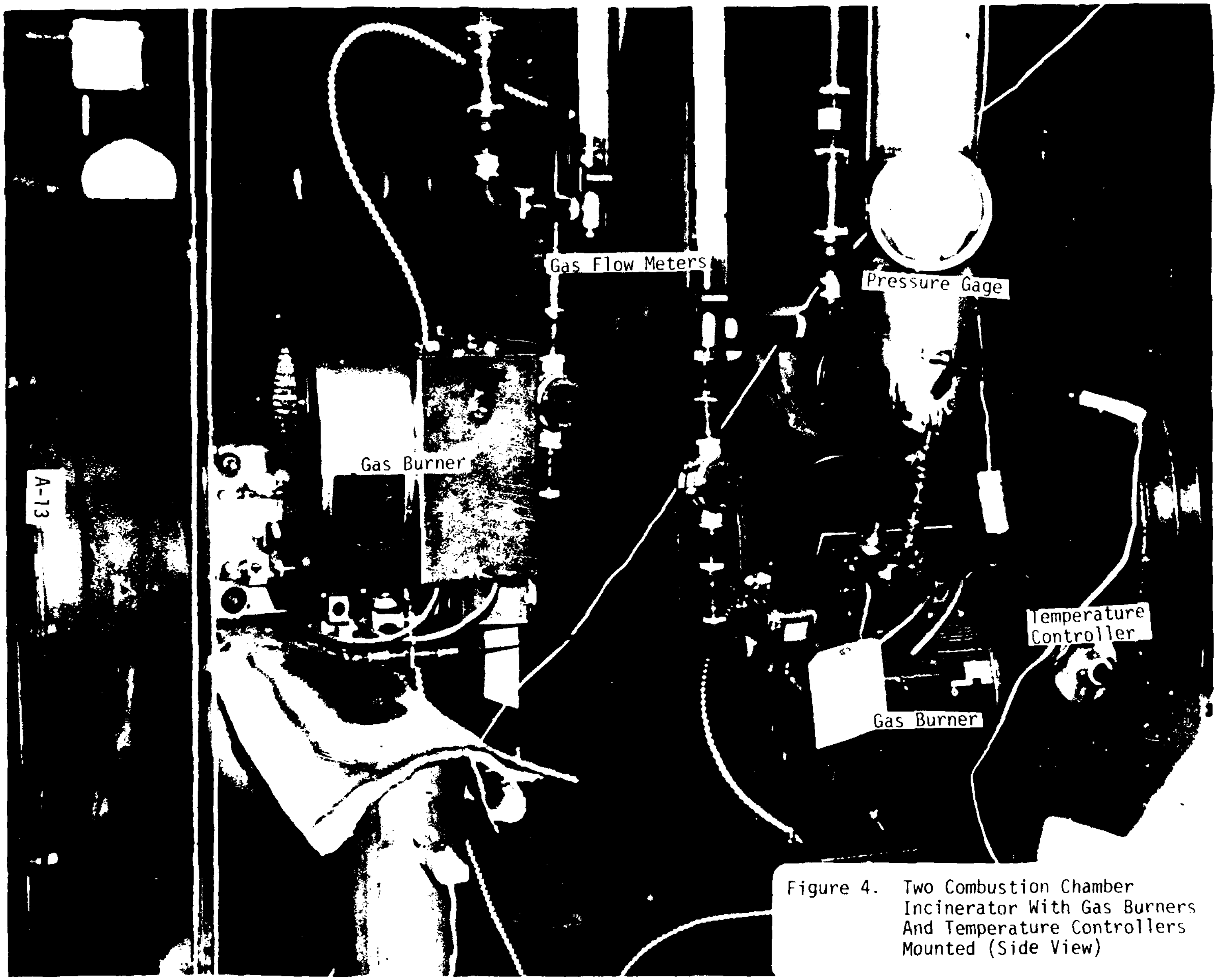


Figure 4. Two Combustion Chamber Incinerator With Gas Burners And Temperature Controllers Mounted (Side View)

Burners With Temperature Controllers

Two burners with temperature controllers were installed to the incinerator, one in each of the two combustion chambers. The burner in the primary combustion chamber (Chamber 1) ignites the red phosphorus composition and the burner in the second combustion chamber (Chamber 2) preheats the chamber and maintains the temperature of the chamber high enough for complete combustion of unburned phosphorus vapor from Chamber 1. The two burner systems are identical with the specifications as follows:

(1) The burners were obtained from Mid-Continent Metal Products Co. in Chicago, Illinois. The brand name is Incinomite "J" Series, Model No. J-40-DS.

(2) The gas is ignited by a direct main flame spark ignition.

(3) The burner has the maximum and minimum heating capacities of 400,000 Btu/hr and 50,000 Btu/hr, respectively, using natural gas. The maximum gas pressure is 15 inches of water and the desired pressure is 5 inches of water.

(4) The electrical supply is 120 volts, 60 Hz, 1 phase.

(5) The temperature controllers were obtained from Burling Instrument Co. in Chatham, New Jersey. The temperature range is from 0 to 2,000°F.

The photograph of the burner without controller is shown in Figure 5 and the installation of the burner with the controller is shown in Figures 3 and 4.

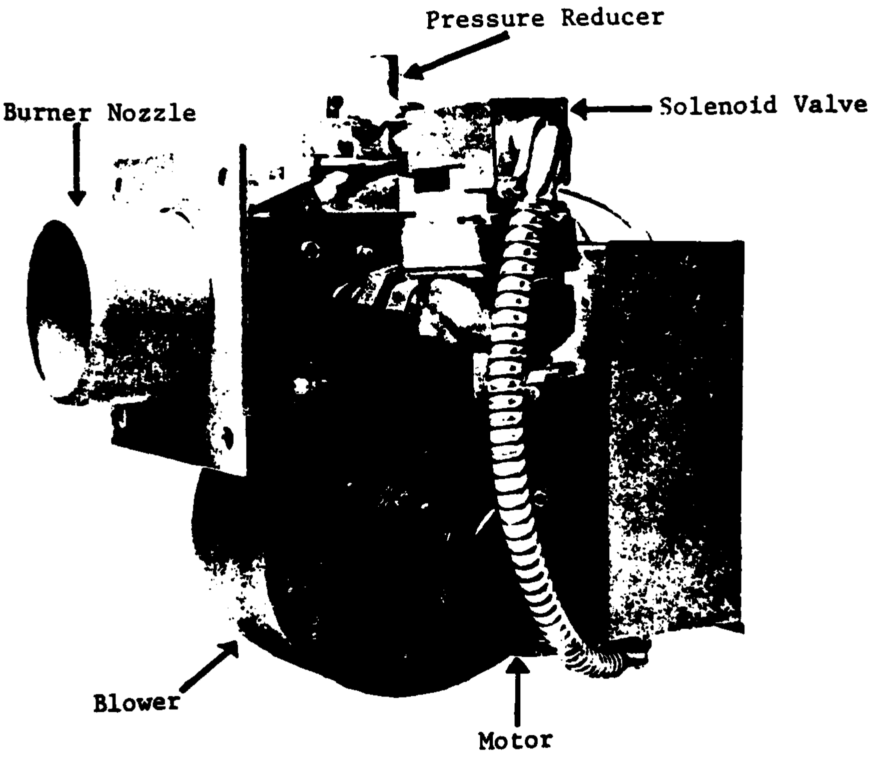


FIGURE 5. INCINOMITE® "J" SERIES GAS BURNER

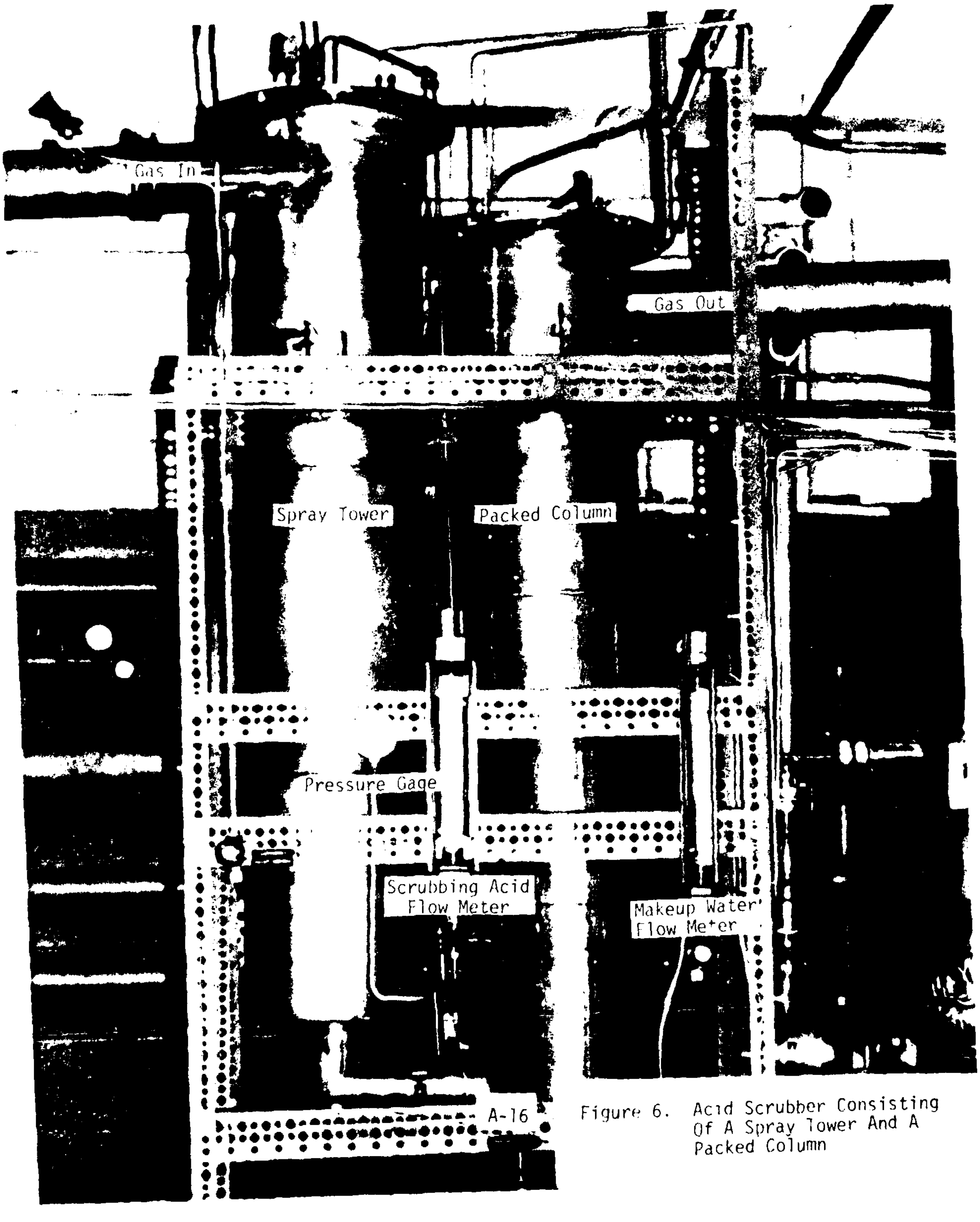


Figure 6. Acid Scrubber Consisting Of A Spray Tower And A Packed Column

Scrubber

A scrubber consisted of a spray tower and packed column (see Figure 6). A scrubbing acid was sprayed at the top of the spray tower to cool off the incoming combustion product gas from the incinerator and to remove P_4O_{10} from the gas. The packed column provides additional contact area and collects air-borne acid mists. The design features of the scrubber are as follows:

(1) The scrubbers are made of stainless steel 316, 7 gage sheet. Both columns are 5 feet high and 11.46 inches in outside diameter (O.D.).

(2) The incoming gas is introduced at the top of the spray tower tangentially to provide an efficient mixing with the scrubbing acid.

(3) The Fulljet® nozzles made of stainless 316 supplied by Spraying Systems Co. in Cleveland, Ohio, were installed for spraying acid.

(4) The spray tower was partly (2 ft. high) filled with 1 inch Intalox® saddle ceramic packings supplied by Norton Chemical Process Products Co. in Akron, Ohio.

(5) The packed column (the second column) was filled with 2 inch Intalox® saddle ceramic packings.

The detailed design drawings are given in Appendix AB of this report.

Mist Eliminator

A type "P" mist eliminator (ME) supplied by York Separators, Inc. was employed in the pilot plant. The unit has the following features:

(1) The unit consists of two stages; a coalescing stage and a mist eliminating stage. The coalescer element is made of stainless steel 316 fibers, and the mist eliminator element is made of Teflon® fibers. The shells are made of stainless steel 316.

(2) The two stages are connected in series to form a "U" shape with drain pipes at the bottom.

(3) The size of cylindrical shells is 8-5/8 inches in outside diameter and 26 inches in height. The overall dimension of the unit is 3 feet high and approximately 3 feet wide.

(4) A spray nozzle was installed on top of the coalescer element to keep the element from plugging.

(5) The design capacity of the unit is 200 scfm at the atmospheric pressure. The maximum allowable gas temperature is 200°F.

The detailed design drawings are given in Appendix AC and the installation in the pilot plant are shown in Figure 7.

A Brink ME furnished by NWSC Crane was installed in parallel with the York ME to compare the performances of the mist eliminators. The specifications of the Brink ME are:

(1) Design flow rate: 46.6 acfm.

(2) Pressure drop at design flow rate: 7 to 9 inches of water.

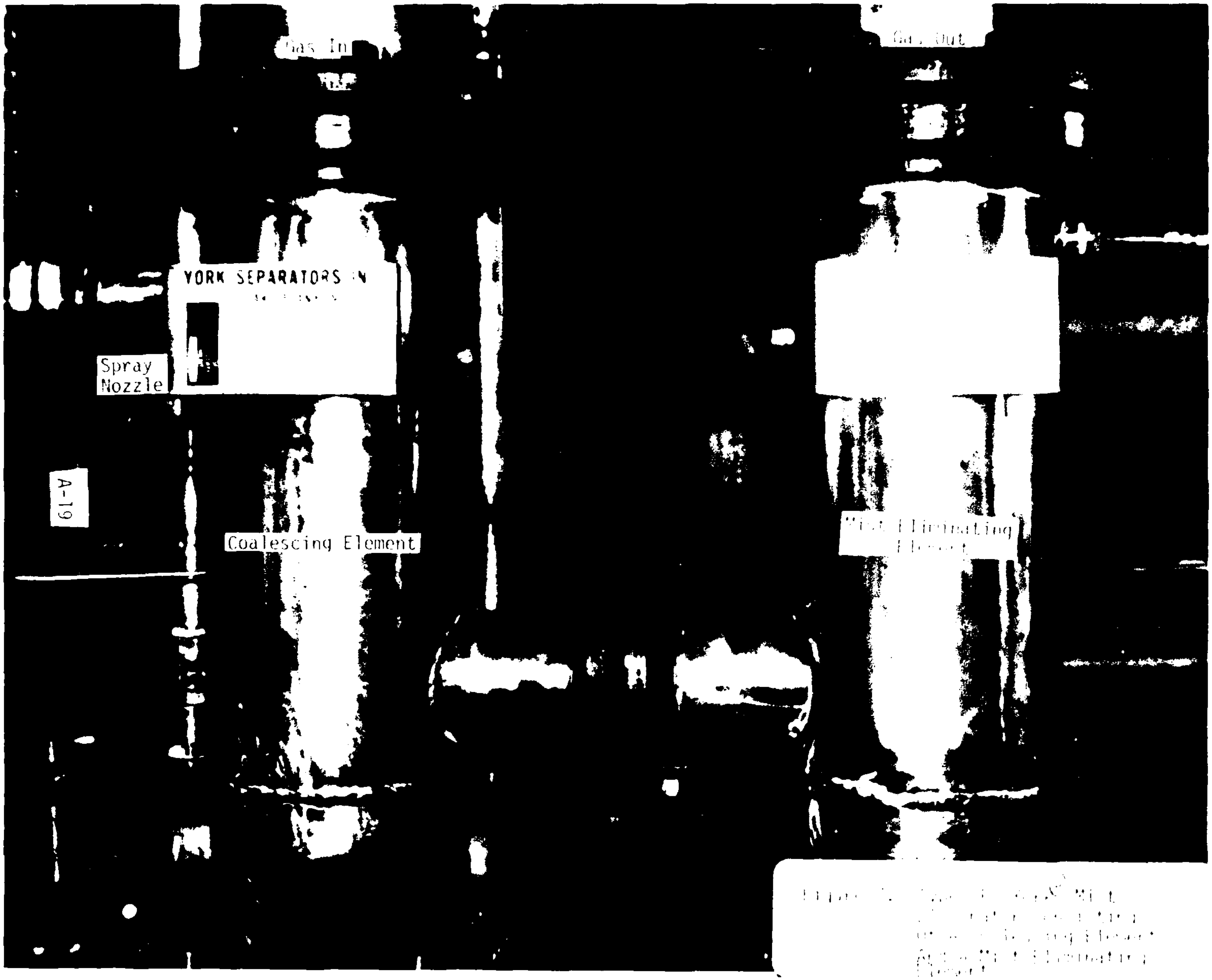


Figure [illegible]
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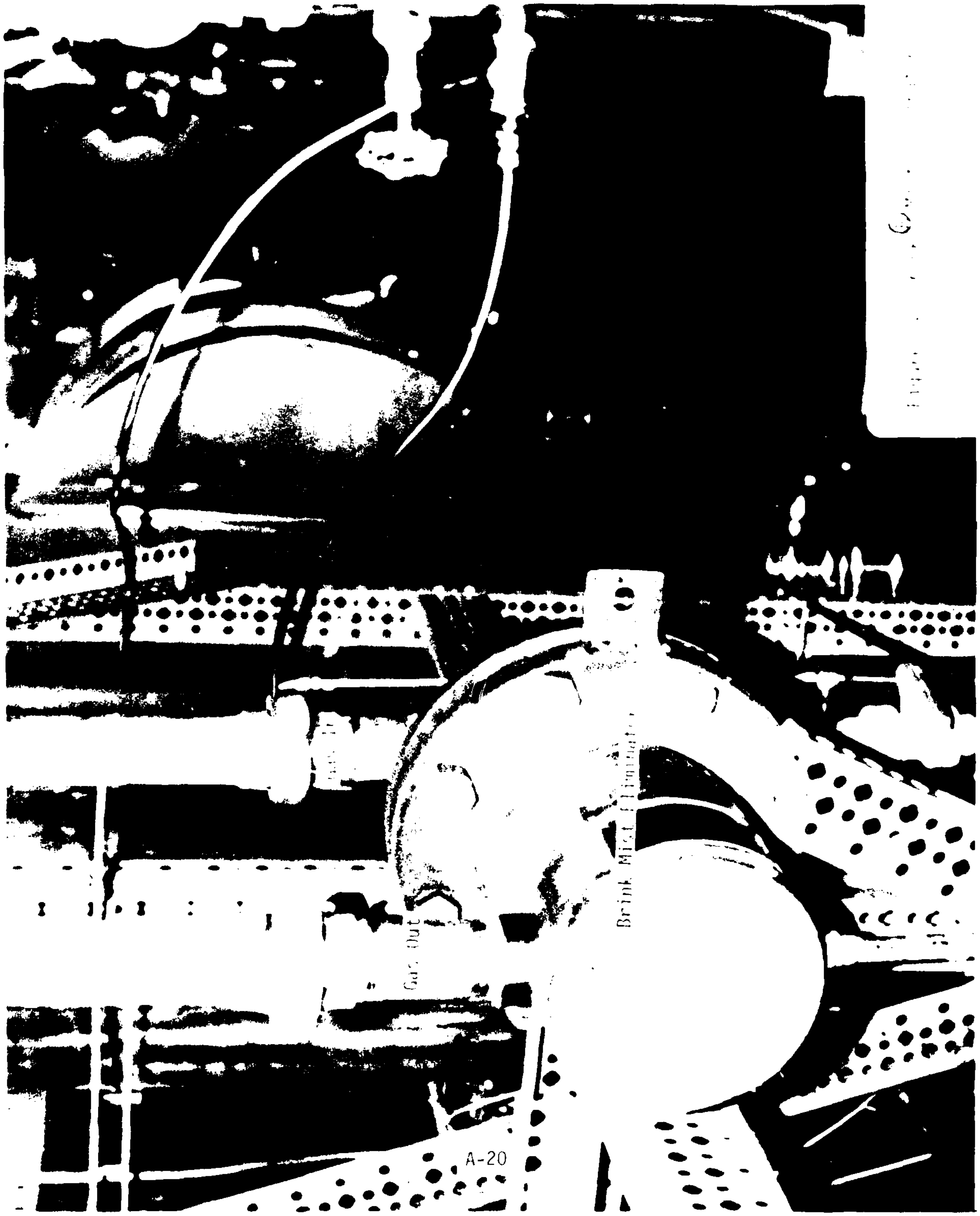
[illegible] Coalescing Element
and Mist Eliminating
Element



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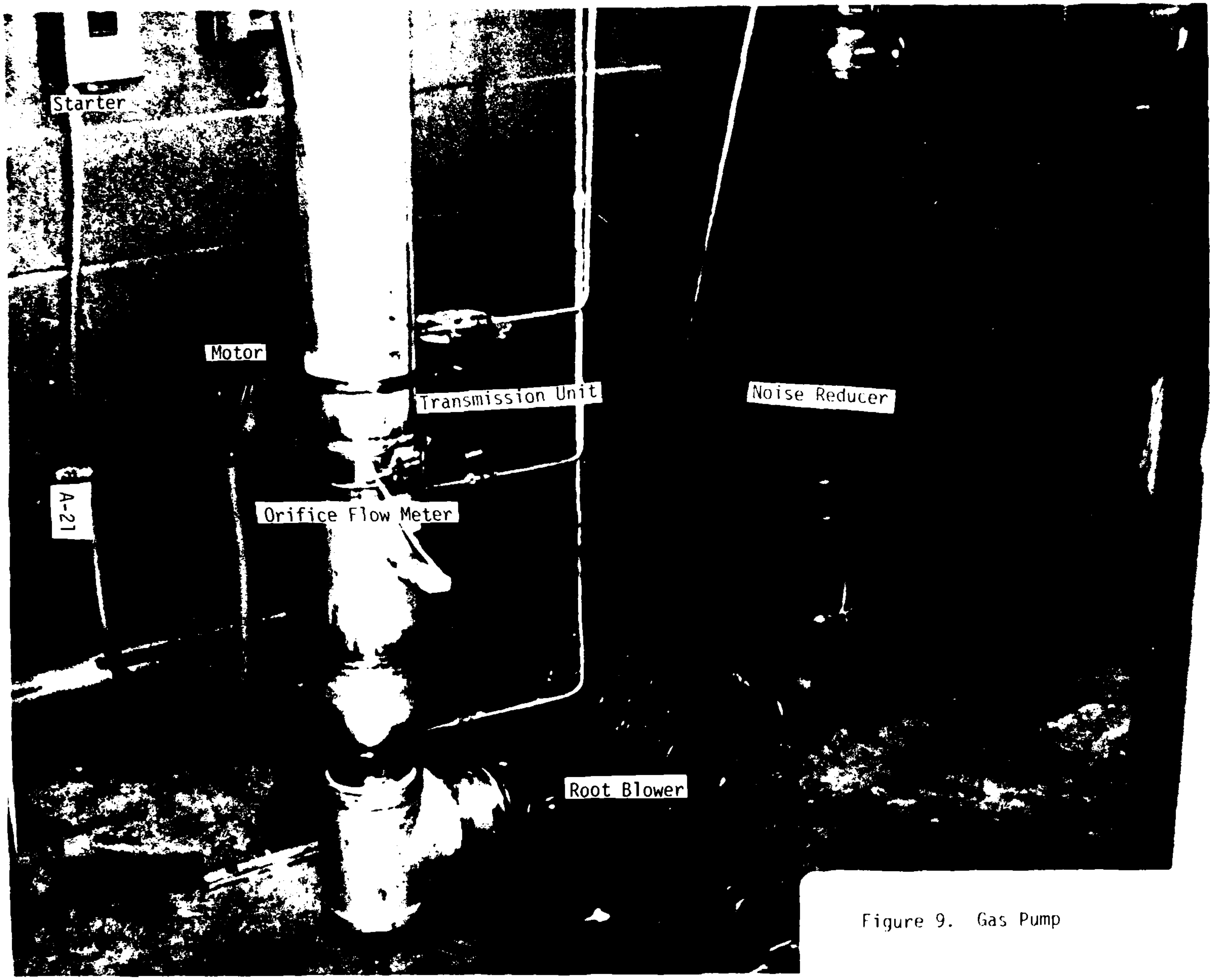


Figure 9. Gas Pump

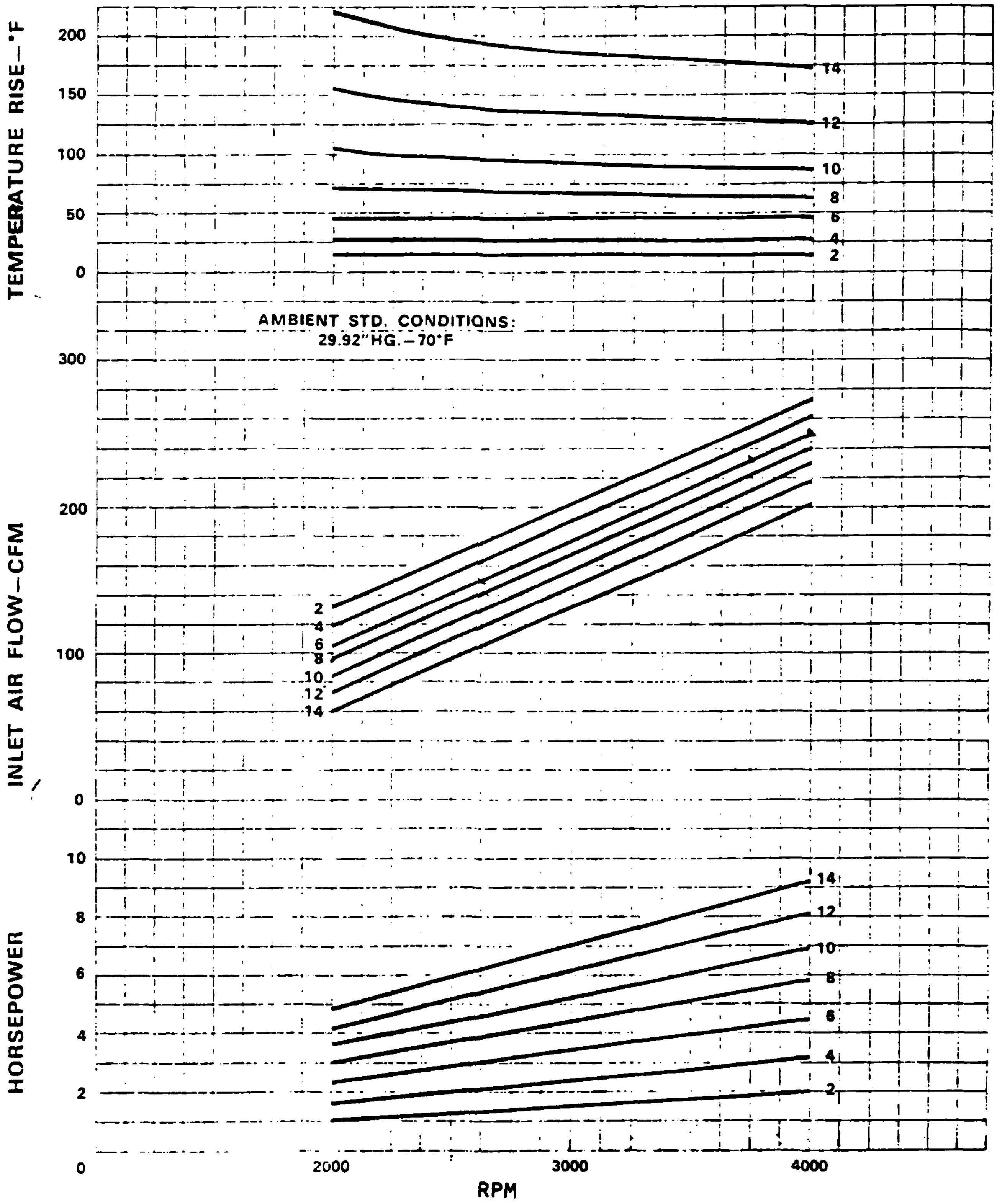


FIGURE 10. VACUUM PERFORMANCE OF SCHWITZER ^{R} MODEL 3006 GAS PUMP

(3) Size: 6 inches in outside diameter and 16 inches long.

(4) Construction material: stainless steel 316L.

(5) Mist Eliminator Element: Teflon®.

The detailed design drawings are given in Appendix AD and the installation in the pilot plant is shown in Figure 8.

Gas Pump

NWSC Crane supplied a gas pump with a motor and transmission unit as Government Furnished Material (GFM). The specifications of the unit are as follows:

(1) Type: Schwitzer Gas Pump (Root Blower).

(2) Model Number: M 3006.

(3) Supplier: Schwitzer Division, Wallace-Murray Corporation, Elwood, Indiana.

(4) Speed: Maximum, 4,000 rpm.

(5) Flow rate: 60 to 275 acfm.

(6) Maximum power: 8 to 9 hp.

Motor and Transmission Unit

(1) Supplier: Louis Allis, Milwaukee, Wisconsin.

(2) Model Number: AJ 58m 10-182 T (S 4736-042 ZR01).

(3) Power of Motor: 3 hp.

(4) Speed Variation of Transmission Unit: 4:1 ratio (658 to 2630 rpm).

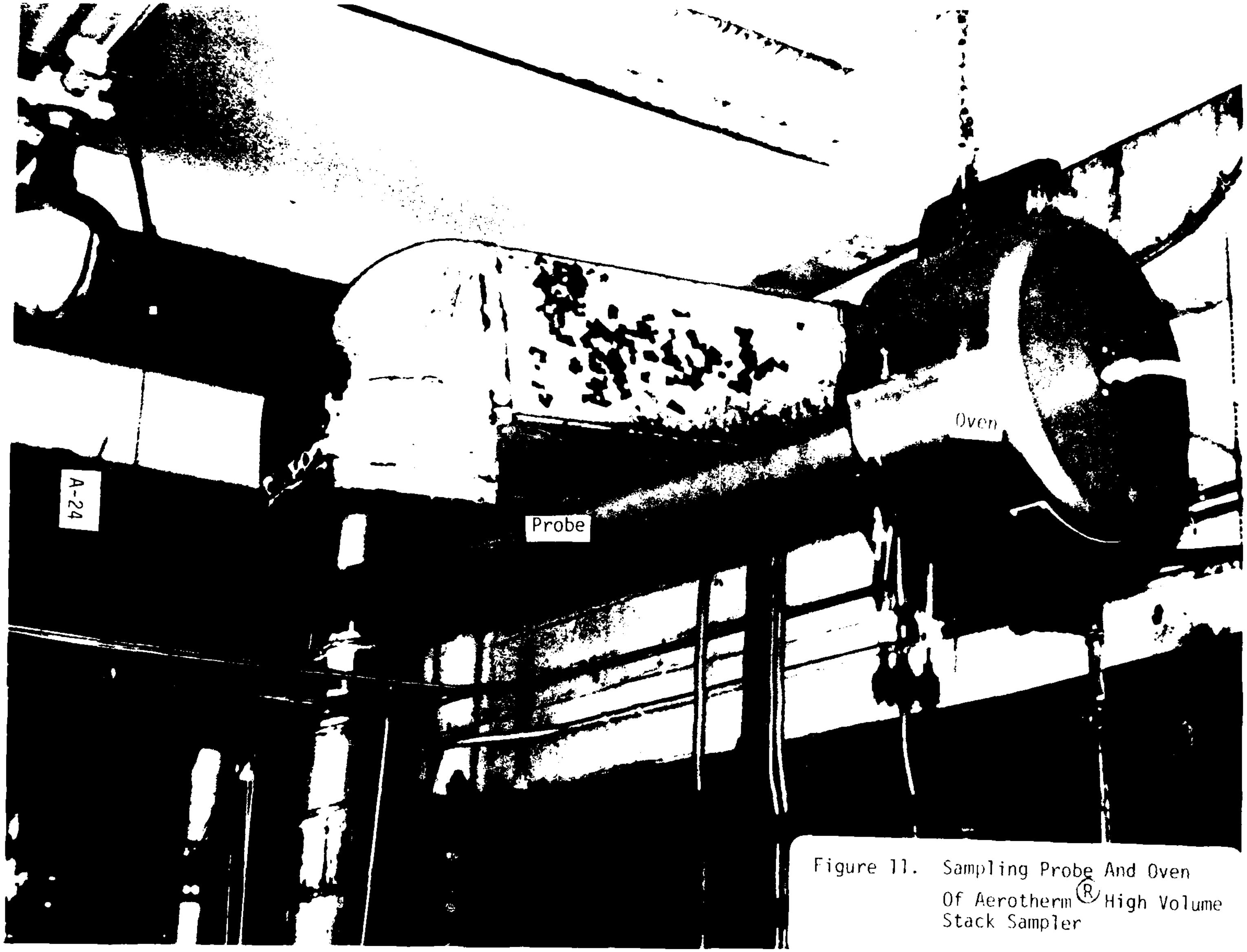


Figure 11. Sampling Probe And Oven Of Aerotherm® High Volume Stack Sampler

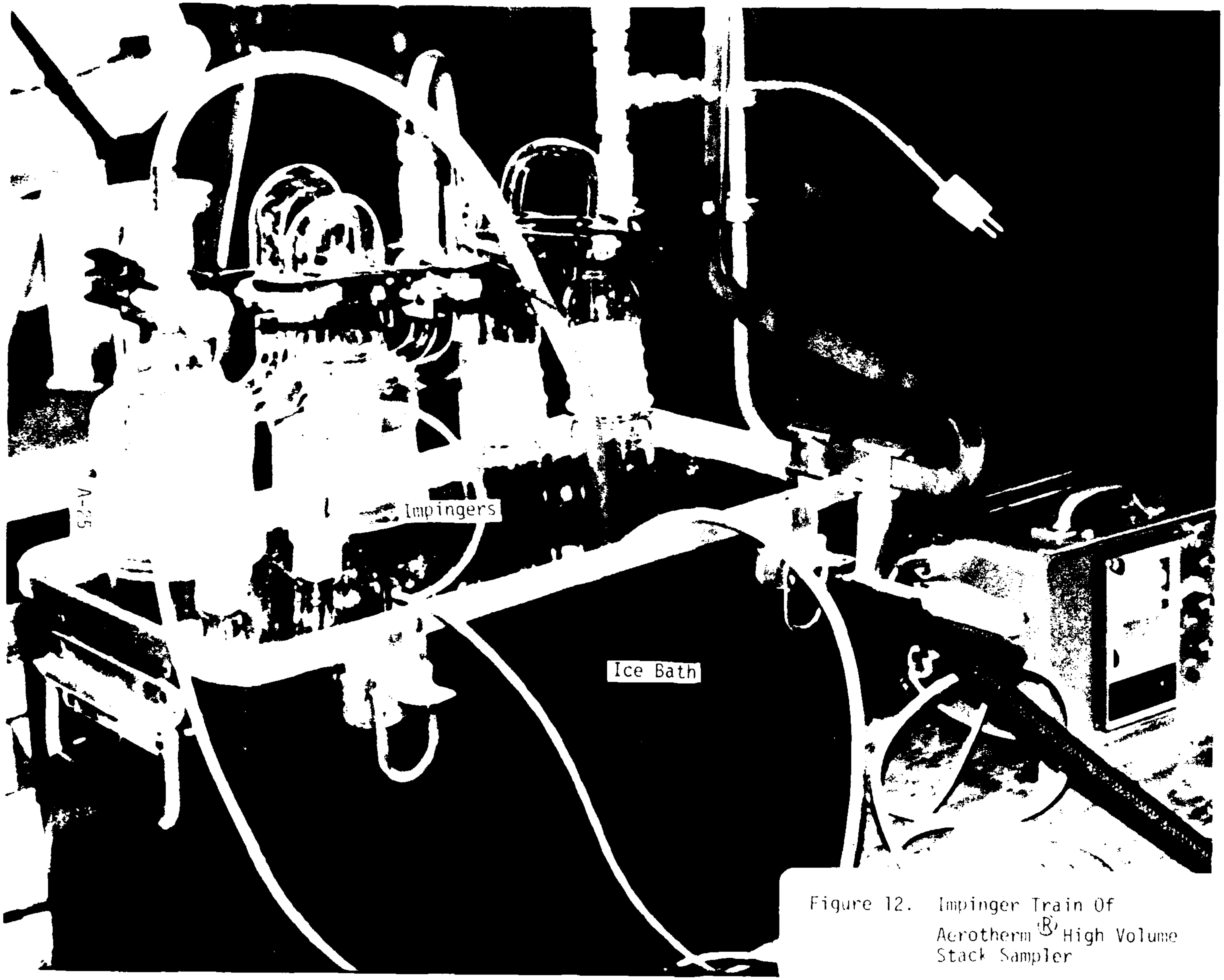


Figure 12. Impinger Train Of Aerotherm® High Volume Stack Sampler

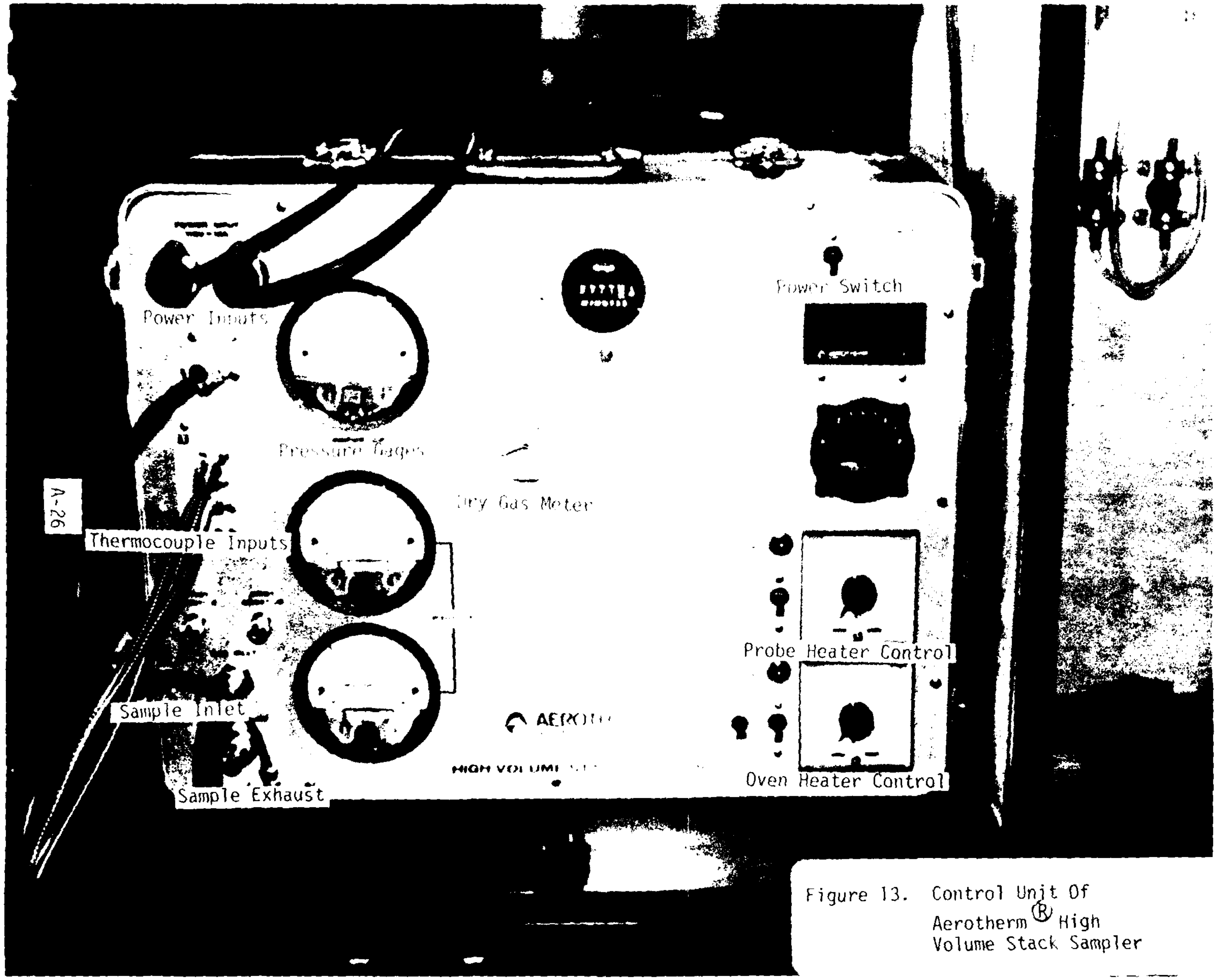


Figure 13. Control Unit Of Aerotherm® High Volume Stack Sampler

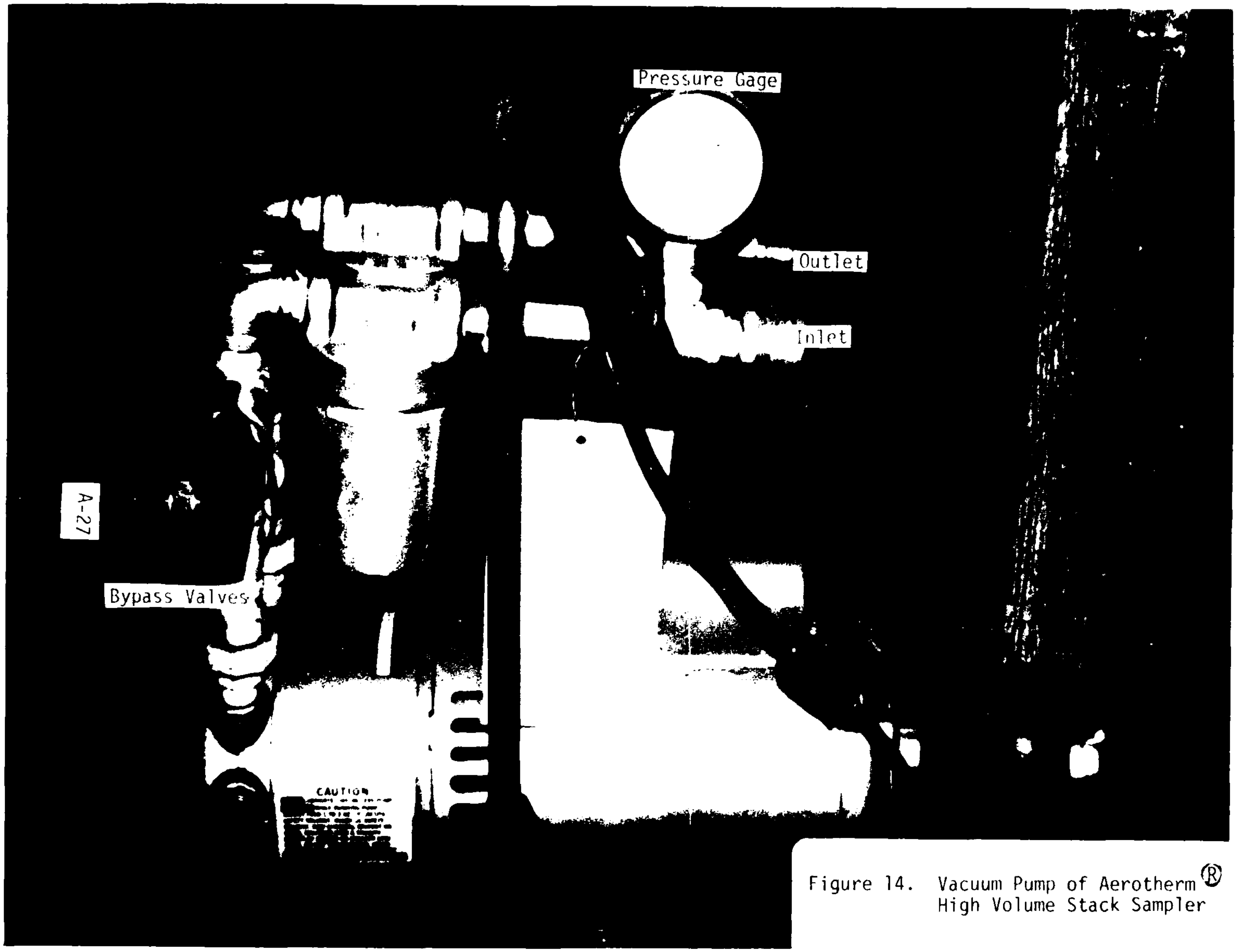


Figure 14. Vacuum Pump of Aerotherm® High Volume Stack Sampler

(5) Power: 220 and 440 volts converted to 110 and 220 volts.

The installation of the unit in the pilot plant is shown in Figure 9 and the performance chart of the pump supplied by the manufacturer is shown in Figure 10.

Stack Gas Sampler

An Aerotherm® high volume sampler was furnished by NWSC Crane for use in this program. The sampler consists of five major parts: probe, oven, impinger train, control unit, and vacuum pump. The photographs of the components are shown in Figures 11 through 14. The high volume sampling system is based on the principles of the Environmental Protection Agency's (EPA's) Method 5 for stack gas sampling. Method 5 is more accurate and reliable than EPA's Method 6 (low volume sampling) for stack gas sampling, since the Method 5 includes a filter and an oven in addition to impingers for more efficient collection of pollutants and the relative significance of possible errors would be minimum due to the high volume sampling.

The important features of the sampling system include:

(1) The oven contains a filter and supports the probe. The maximum operating temperature is 500°F.

(2) The oven and filter are constructed of stainless steel. The filter has a standard 142 mm diameter.

(3) The probe can be mounted on the oven and can be rotated through 360 degrees. The sampling tube is constructed of stainless steel and is equipped with a fiberglass insulated strip heater.

(4) The probe can withstand temperatures up to 550°F.

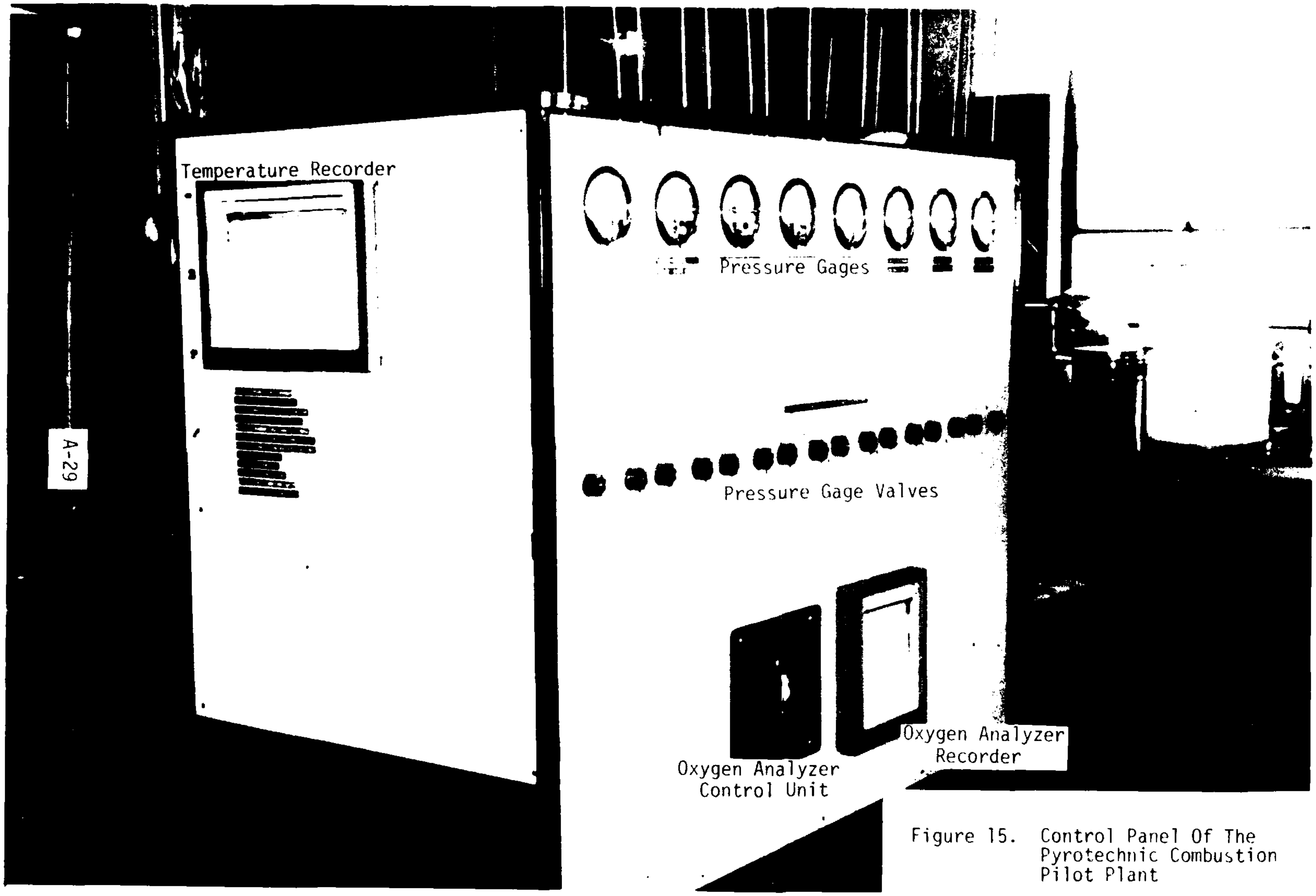


Figure 15. Control Panel Of The Pyrotechnic Combustion Pilot Plant

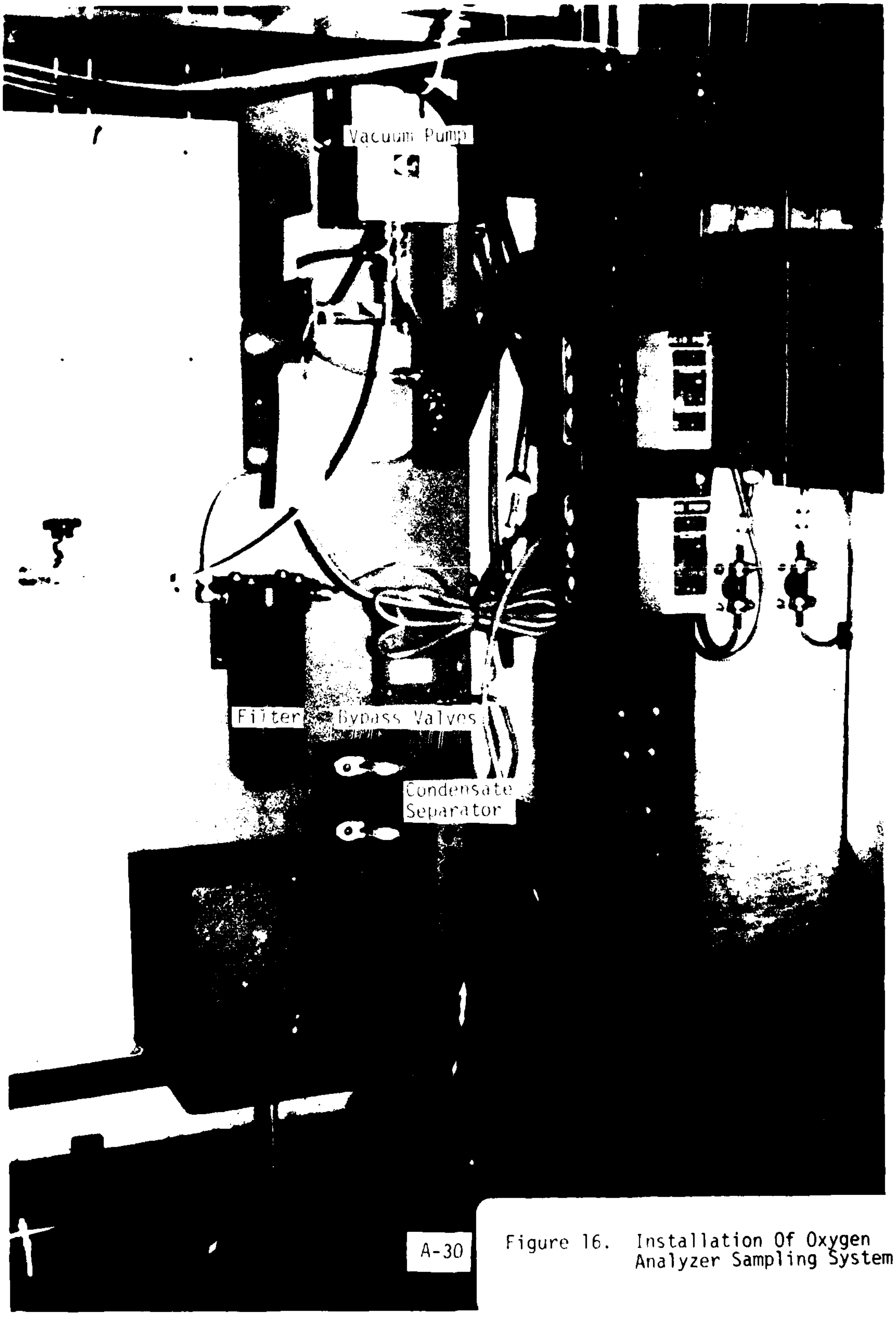


Figure 16. Installation Of Oxygen Analyzer Sampling System

(5) The impinger train has several functions, including cooling the sampled gas to a temperature level safe for the pump and gas meter, condensing to determine water concentration, collection of fine particles, and chemical analysis.

(6) A thermocouple is mounted on the cap of the last impinger for monitoring outgoing gas temperature.

(7) A pump is placed to circulate water in the ice bath for more efficient heat transfer.

(8) The fiberglass carrying case also serves as ice bath.

(9) The sampling rates can be up to 6 cfm.

(10) Circuit breakers are installed instead of fuses in the control unit.

(11) Separate power lines are installed for heaters and pumps to assure obtainability of required power.

Control Panel

The control panel for the pilot plant was constructed as shown in Figure 15. The panel includes switches, a temperature recorder, pressure gages, flow meters, an oxygen analyzer sampling system, an oxygen analyzer, and an oxygen analyzer recorder. The major instruments in the panel are described in more detail below:

(1) Temperature Recorder:

Supplier:	Leeds and Northrup.
Model:	24 Point Speedomax W Strip Chart Recorder.

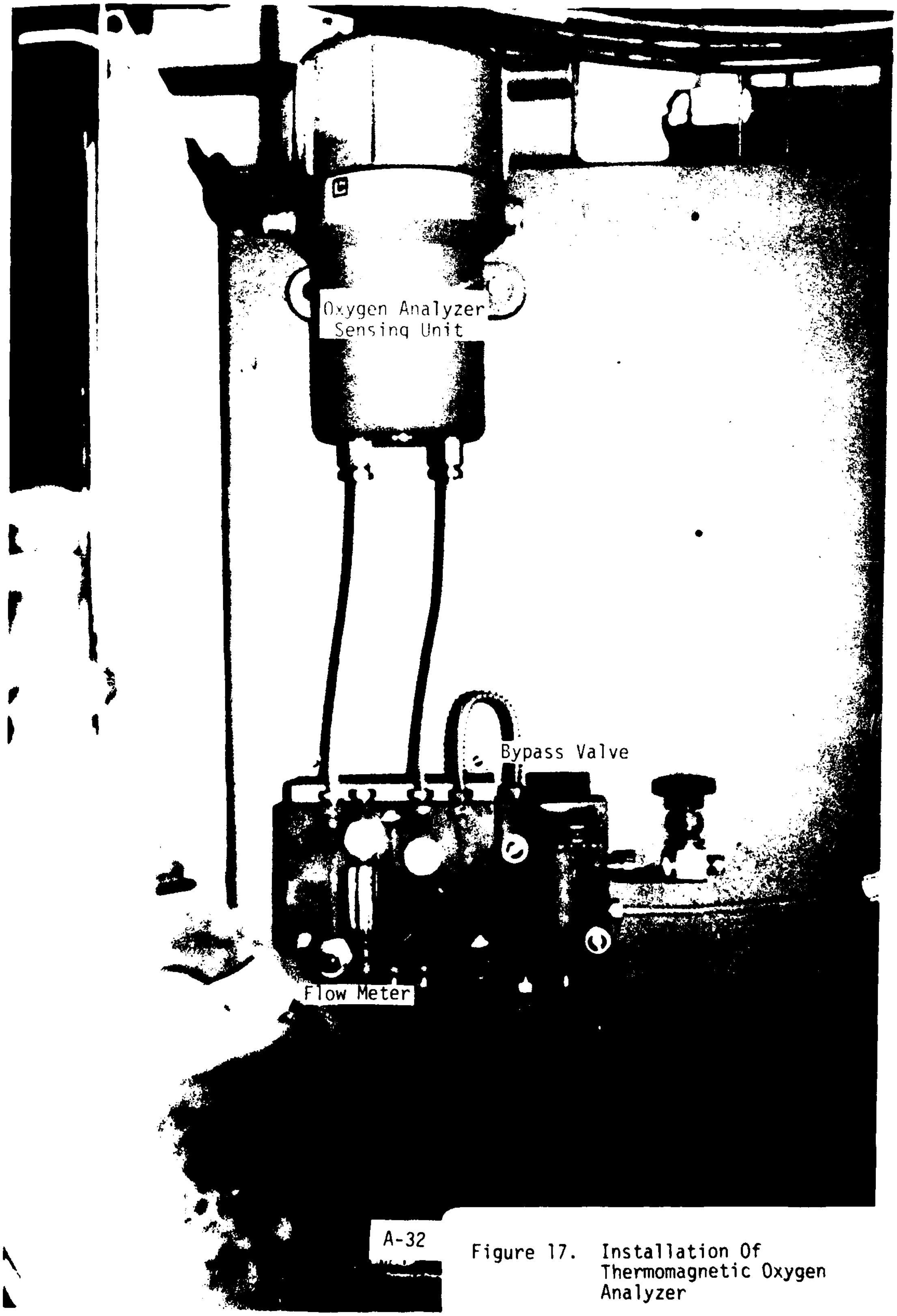


Figure 17. Installation Of Thermomagnetic Oxygen Analyzer

Ranges: 0 to 2,000°F.
Calibrated Chart Width: 9-7/8 inches.
Power: 120 volts, 60 Hz.
Chart Speed: 4 or 12 inches/hr.
Time per Point: 3 seconds.

(2) Sampling System for Oxygen Analyzer (see Figure 16):

Supplier: Leeds and Northrup.
Model: Modular System, Catalog No. 7872-0-1-0.
Accessory Items: Coarse Filter, Fine Filter, Water Repellant Filter, Condensate Separator, Pump (Bellows type), Pump Bypass Valve.
Power: 120 volts, 60 Hz, 2.6 amp.
Ambient Condition: Temperature 32 to 120°F, indoor use only.
Flow Rate: 0 to 5 scfh.

(3) Oxygen Analyzer (see Figure 17):

Supplier: Leeds and Northrup.
Model: Catalog No. 7863, Thermomagnetic.
Power: 115 volts, 50/60 Hz.
Output Signal: 0 to 10 millivolts DC.
Range: 0 to 20% O_2.

(4) Oxygen Analyzer Recorder:

Supplier: Leeds and Northrup.
Model: Single Point Speedomax H Strip Chart Recorder.
Input: 0 to 10 millivolts from No. 7863 O_2 analyzer.

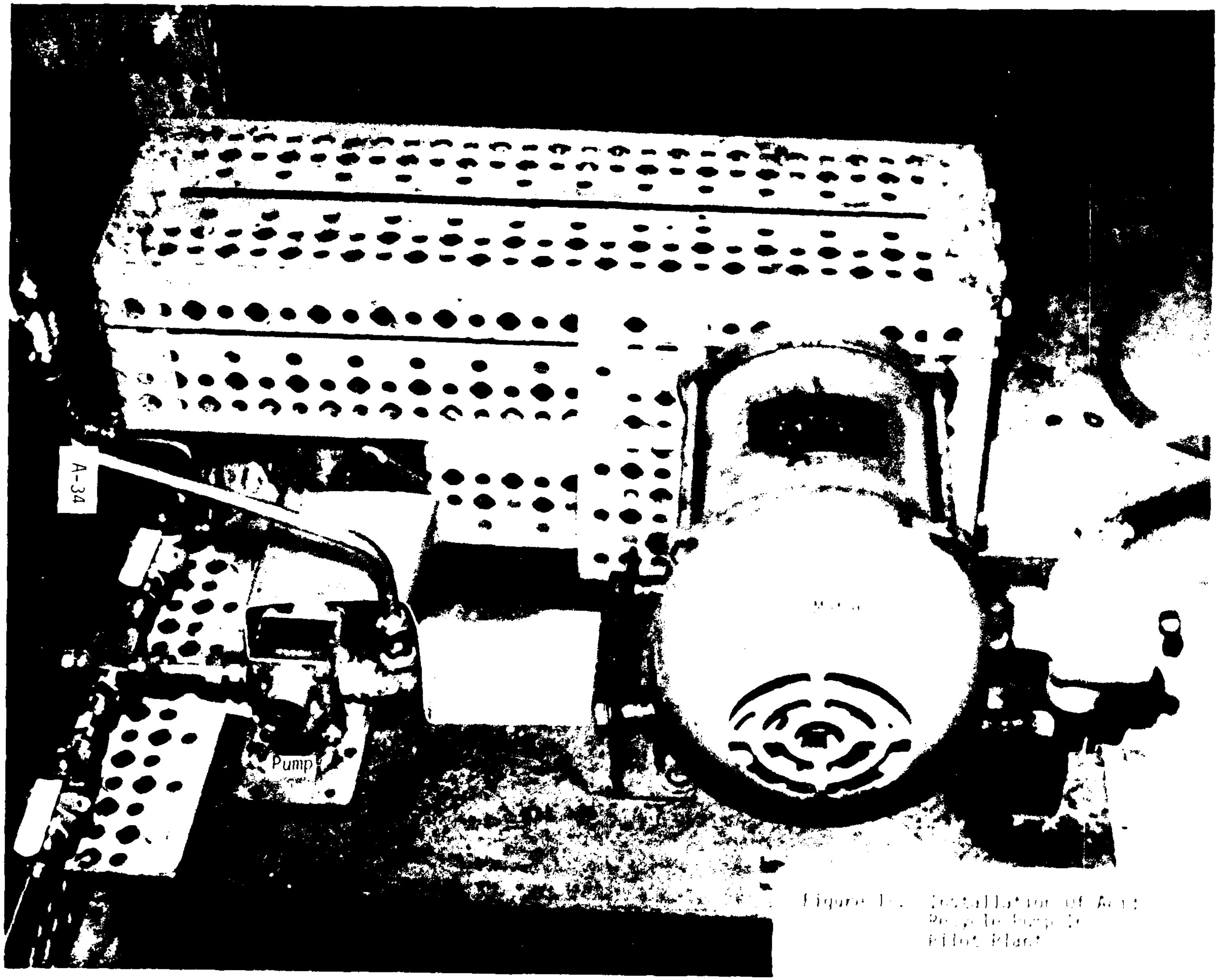


Figure I-[illegible]. Installation of Acid Recycle Pump in Pilot Plant

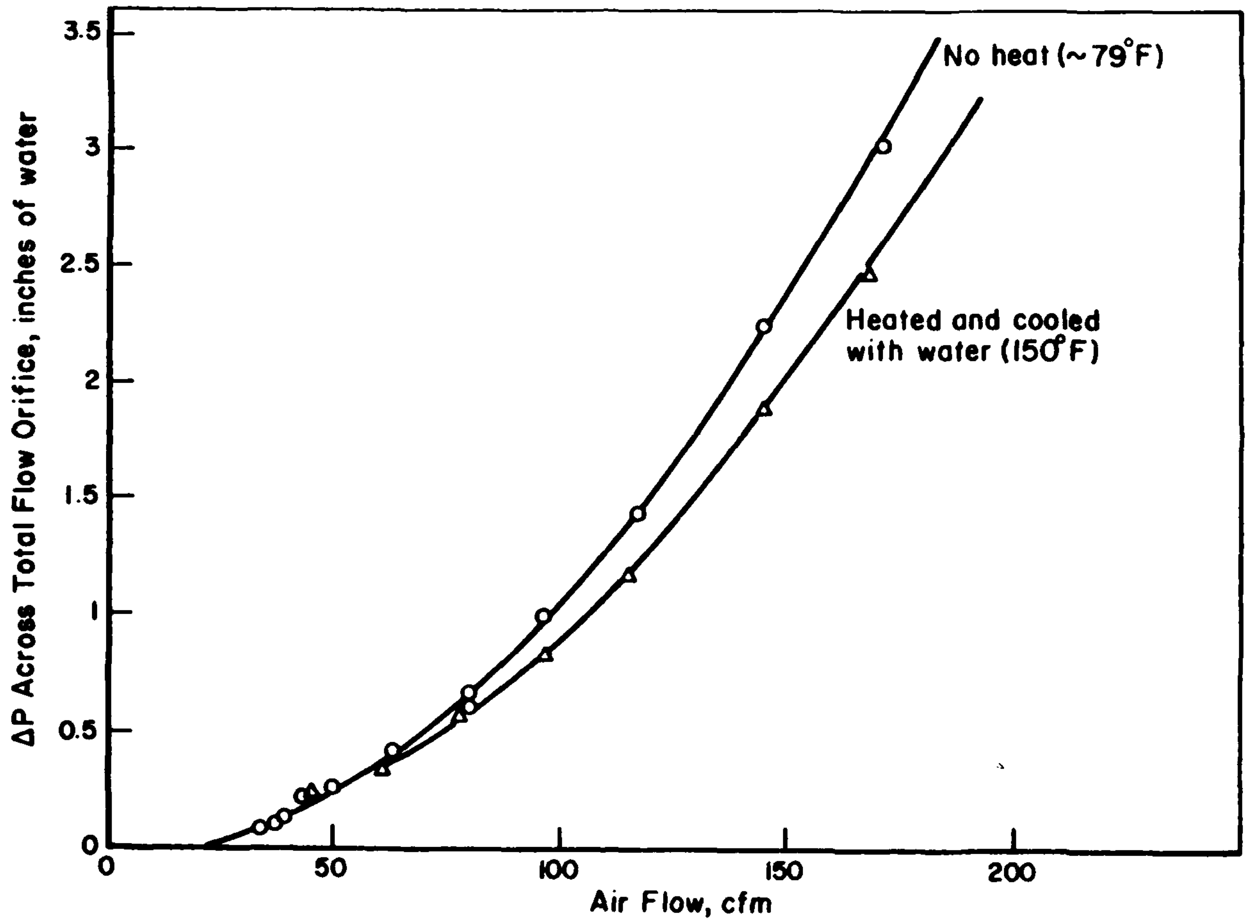


FIGURE 19. CALIBRATION OF ORIFICE FLOW METER FOR TOTAL GAS FLOW INSTALLED PRIOR TO GAS PUMP

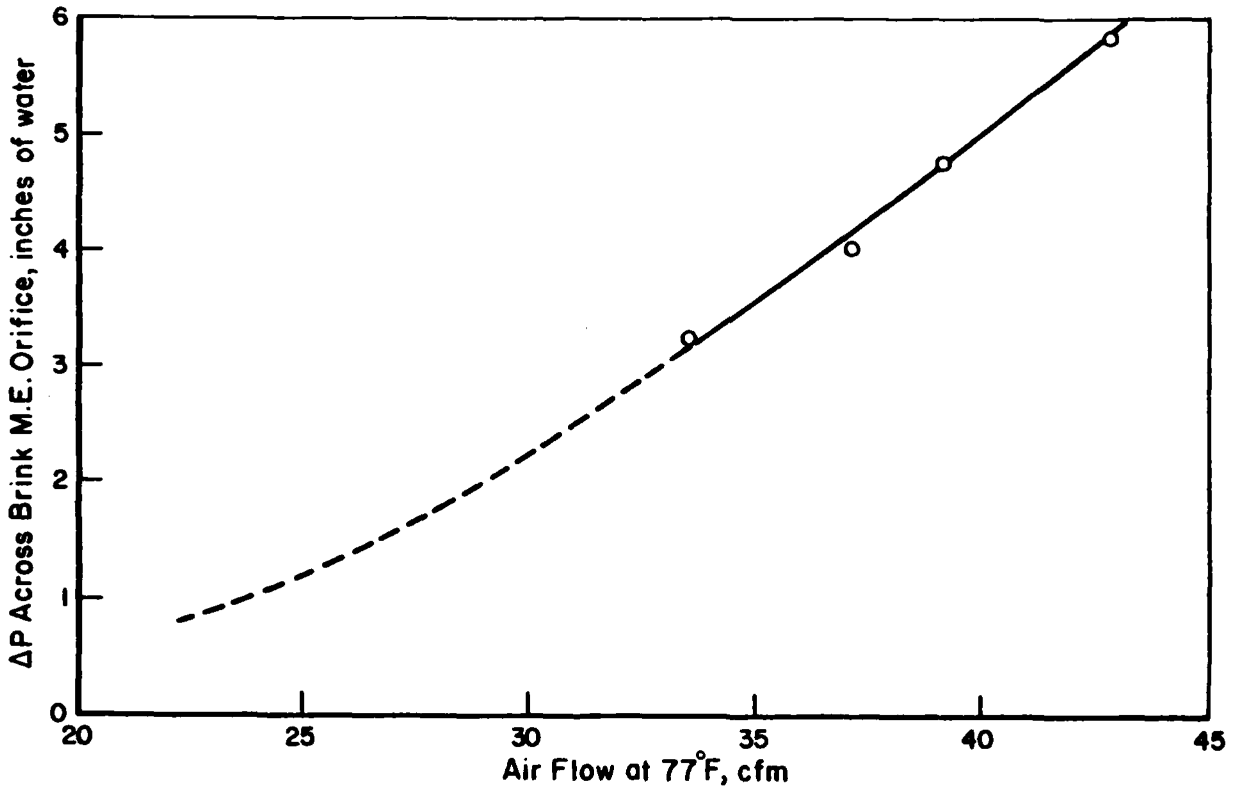
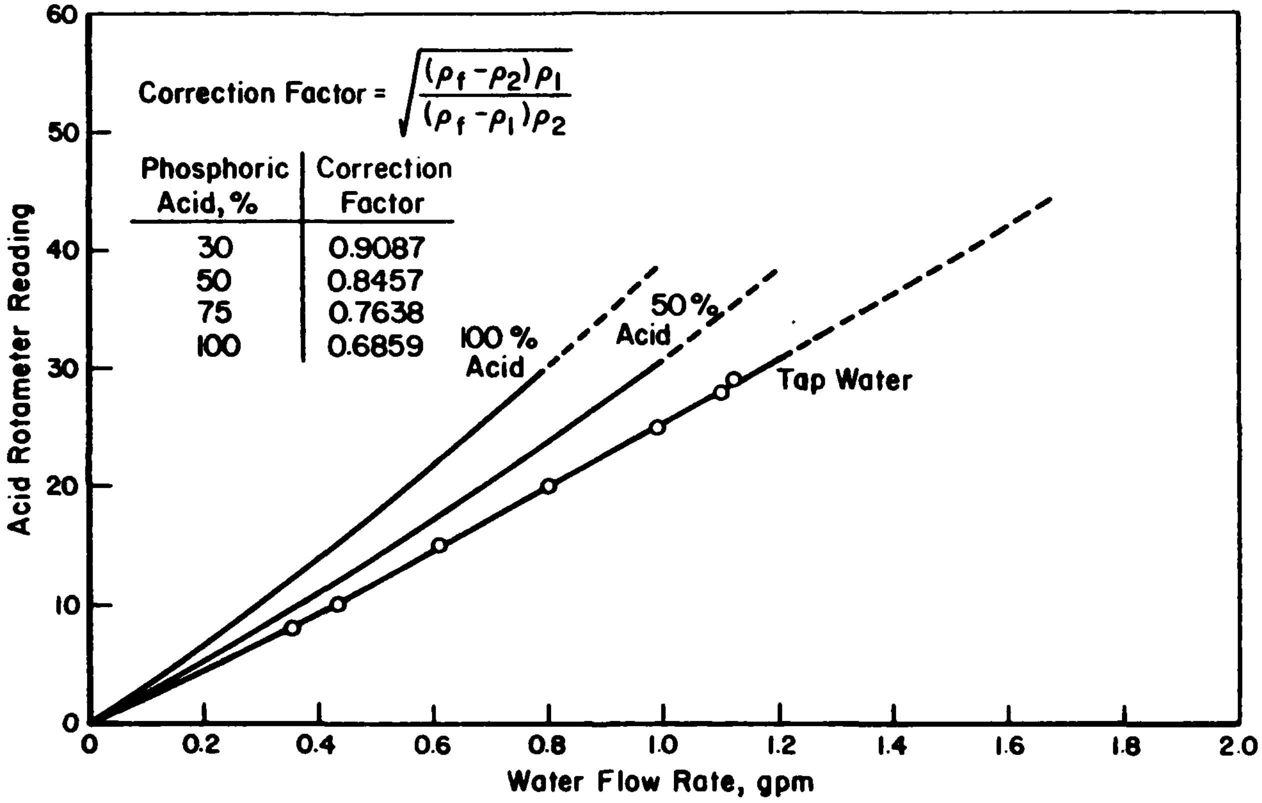


FIGURE 20. CALIBRATION OF BRINK MIST ELIMINATOR ORIFICE FLOW METER



$$\text{Correction Factor} = \sqrt{\frac{(\rho_f - \rho_2)\rho_1}{(\rho_f - \rho_1)\rho_2}}$$

Phosphoric Acid, %	Correction Factor
30	0.9087
50	0.8457
75	0.7638
100	0.6859

FIGURE 21. CALIBRATION OF ACID ROTAMETER FOR PHOSPHORIC ACID

Calibrated Chart Width: 6 inches.
Range: 0 to 20 percent oxygen.
Chart Speed: 4 inches/hr.
Power: 120 volts, 60 Hz.

Acid Receiving Vessels

Three five-gallon jars were employed; two for receiving acid from the scrubber columns and one for collecting acid from the York mist eliminator. A portion of the acid collected from the scrubbers is recycled to the spray tower for scrubbing P_4O_{10} and cooling of combustion product gas. Make-up water is introduced into the scrubber acid receiving jars.

Acid Recycle Pump

An Eco Gearchem® pump was employed to recycle acid within the scrubber system. The pump has the following specifications:

(1) Supplier: Eco Pump Corporation, South Plainfield, New Jersey.

(2) Model: G4-ACT-KKT, Mechanical Seal Eco Gearchem Pump.

(3) Maximum Speed: 1750 rpm.

(4) Capacity: Up to 3 gpm.

(5) Pressure Range: Up to 100 psi.

(6) Temperature Range: -200 to 450°F.

(7) Viscosity Range: Up to 10,000 cps.

(8) Construction Material: Stainless Steel 316 Housing and Plastic Gears.

(9) Motor Horse Power: 1/3 hp.

The installation of the pump is shown in Figure 18.

SHAKEDOWN OPERATION OF PILOT PLANT

A series of shakedown operations were made for calibration and checkout of equipment, for curing of incinerator refractory lining, and for exploration of combustion characteristics of the wet pyrotechnic composition.

Calibration and Checkout of Equipment

A series of blank runs were made for calibration and checkout of equipment. An orifice flow meter for the total gas flow installed prior to the gas pump was calibrated using a turbine gas meter supplied by Grove Manufacturing Company (Model No. Turbo 4-inch T-18) and the results are shown in Figure 19. An orifice flow meter installed to measure the gas flow rate to the Brink mist eliminator was also calibrated and the results are shown in Figure 20. An acid rotameter to measure the flow rate of phosphoric acid scrubbing solution to the spray tower was calibrated and the results are shown in Figure 21.

Various equipment was checked out during the shakedown period, including rewiring of the gas burners.

The operation of the gas burners was very sensitive to the pressure of the gas line and the ratio of gas to combustion air.

The thermocouple sheath of the Burling temperature controllers was made of Inconel which was found unsatisfactory under the corrosive environment of phosphoric acid. The Inconel sheath was replaced with stainless steel 316 sheath and the controller characteristics were recalibrated.

The combustion chambers could not be maintained at a vacuum condition due to excessive leakages from the excess-air supply ports and other openings around the furnace. The excess-air ports were disconnected and plugged off. Other leaks were sealed. A vacuum up to 4/10-inch of water was obtained in the furnace after the modifications.

The locations of thermocouples were rearranged to avoid direct flame from the burner.

The cooling of hot combustion gas in the spray tower was not adequate. The gas temperature leaving the tower was up to 500°F when the inlet temperature was about 1500°F. Two feet of packing was installed to increase the contact area between the gas and the sprayed water. The gas temperature could be controlled under 210°F for the same inlet condition after the modification.

A spray nozzle was added to the second scrubber tower on top of the packings. This could provide additional cooling, if necessary.

With packings installed in the spray tower and the packed column, the scrubber system tended to flood at a high acid spraying rate. The sizes of packings in each column were adjusted to minimize flooding, and the safe operating range of acid spraying rate was determined.

A spray nozzle was added to the York mist eliminator to provide additional cooling and scrubbing for emergency use only. Thermocouples were added to the inlet and outlet of the mist eliminator.

The desired pressure drop could not be obtained across the York® mist eliminator (ME) with the original element because the element baffle was overdesigned compared with the capacity of the gas pump. The original element was replaced with a new set to increase the pressure drop.

The exhaust line of Brink mist eliminator was relocated to control the gas flow rate through the mist eliminator by the damper in the main process line.

A sampling port was installed in the main exhaust duct for easy sampling.

Operation of temperature recorder, oxygen analyzer sampling system, oxygen analyzer, and oxygen analyzer recorder, and Aerotherm® high volume sampling system was checked out during this shakedown operation period, and necessary adjustments, calibrations, and repairs were made. In addition, all process lines were checked out to repair leaks.

Curing of Incinerator Refractory Lining

The molded fresh refractory lining of the incinerator was cured with heat at a high temperature for the evaporation of the free and bound waters in the lining material and for the bonding of the liner. It was conducted according to the following procedures recommended by the incinerator supplier:

(1) Using Burner No. 1 (burner in the primary combustion chamber) only, bake the lining at 150 to 200°F until water is completely evaporated.

(2) Raise the temperature at a rate of 100°F/hr to 600°F.

(3) Hold at 600°F for 4 hours.

(4) Raise the temperature at a rate of 100°F/hr to 1500°F.

(5) Hold at 1500°F for 4 hours.

(6) Shut off the burner.

The supplier estimated time requirement for the curing was 24 hours. The actual time spent for curing was 46 hours.

Exploratory Runs

Three exploratory runs were made for checking out the combustion characteristics of the pyrotechnic composition in the pilot plant. The metal cases of Marine Location Marker, Mk 25, had been removed and the cylindrical-shape element, which is the pyrotechnic composition wrapped with paperboard, had been cut into small pieces (1 to 5 inches long) and stored under water. Some pieces included a plastic cap containing a detonator, powder and ignition wires. The following observations were made during the exploratory operations:

(1) With Burner No. 1 at the upper position, the time to the ignition of the composition was excessive, ranging 30 to 90 minutes. It is attributed to the facts (a) that the burner flame could not contact with the composition at the position and thus could not cause a local hot spot at the surface of the composition for ignition, (b) that the ignition temperation was obtained only by raising the temperature of the chamber which took a considerable time span, and (c) that the composition was wet and wrapped with paperboard and thus it took more time to raise the temperature of the composition.

(2) After soaked in water, the composition burned less violently compared with the dry composition as observed in the previous study. (1)

(3) The color of the scrubbing acid (around 50 percent by weight) became dark green after burning two batches of the composition. Extraction of chromium and nickel from the scrubber construction material (stainless steel 316) by the acid at high temperatures (usually greater than 800°F at the inlet of the scrubber) was suspected. The chromium and nickel concentrations were measured at 310 ppm each.

(4) The gas pump was frozen due to corrosion because it was not made of stainless steel. To minimize the corrosion, the gas pump was cleaned and lubricated after each day of operations.

TEST OPERATIONS OF PILOT PLANT

Startup Procedures

The following startup procedures were used in the operation of the pilot plant:

(1) Turn on exhaust hood blower.

(2) Turn on temperature recorder.

(3) Turn on gas pump (Note: always start and shut off at the minimum speed).

(4) Set gas pump at a low speed during preheating (3.5 on the speed indicator dial).

(5) Open acid recycle valve one full turn.

(6) Open inlet valve to acid pump.

(7) Turn on acid pump.

(8) Set acid recycle flow rate at 0.6 to 1.3 gpm.

(9) Open incinerator door.

(10) Turn on burner/blower main power switch.

(11) Open gas valve for Burner No. 2.

(12) Light Burner No. 2.

(13) Close incinerator door.

(14) Adjust burner air dampers to maintain a vacuum of 0.2 inches of water inside the combustion chambers.

(15) Turn on make-up water to maintain constant acid level.

(16) Turn on stack gas sample pump for oxygen analysis.

(17) Check gas sample flow rate.

(18) Turn on oxygen analyzer recorder and make calibrations and adjustments as required.

(19) Preheat Chamber No. 2 up to temperatures in the range of 900°F to 1000°F.

(20) Increase gas pump speed to 6.5 on the speed indicator dial.

(21) Continue preheating until the temperature of Chamber No. 2 comes up to 900°F.

(22) Adjust scrubbing acid flow rate and make-up water flow rate as needed.

(23) Charge the pyrotechnic composition into Chamber No. 1.

(24) With incinerator door left open, open gas valve for Burner No. 1.

(25) Light Burner No. 1 to start burning.

(26) Close incinerator door.

(27) Set temperatures for Chamber No. 1 at 600°F.

Shutdown Procedure

The following shutdown procedures were used in the pilot plant operation:

(1) Turn off burner/blower switch for both burners.

(2) Turn off natural gas.

(3) Turn off burner/blower main power switch.

(4) After approximately five minutes, turn off make-up water.

(5) After sufficient cooling of furnace (at around 500°F or below), turn off acid recycle pump.

(6) Turn off oxygen analyzer recorder.

(7) Turn off oxygen analyzer sampling pump.

(8) Turn off gas pump.

(9) Turn off temperature recorder.

Sample Analyses

Analysis of Phosphoric Acid Concentration

Various liquid samples such as scrubbing acid and acid collected from mist eliminators were analyzed for phosphoric acid concentration to determine operating characteristics of the scrubber and mist eliminators and the acid yield of the process. The following procedures were used:

(1) The sample is diluted to a concentration in the range of 0.01 normal (N) to 0.5 N of phosphoric acid.

(2) Take 20 ml of the diluted sample.

(3) Add a few drops of methyl orange. The pH range is 3.1 to 4.4. The ionization constants of weak phosphoric acid at 25°C are 7.52×10^{-3}, 6.23×10^{-8}, 4.8×10^{-13} for the first, second, and third ionizations, respectively(3).

(4) Titrate with standardized NaOH solution with concentration range between 0.01 N and 0.5 N.

(5) Compute the concentration using the equations:

$$A = \frac{(97.999)}{(1{,}000)} \cdot V \cdot C$$

$$B = \frac{S}{R}$$

$$D = B - \frac{A}{d}$$

$$E = D + A$$

$$\text{Phosphoric Acid Concentration (\% by weight)} = \frac{100A}{E}$$

where V = volume of standard NaOH solution used, ml

C = concentration of standard NaOH solution, normal

S = volume of diluted sample, ml
R = dilution ratio
d = density of 100 percent phosphoric acid, 1.864 g/cm^3

Experiments for Determination of Elemental Phosphorus

In order to ensure the complete combustion of red phosphorus in the pyrotechnic composition during the incineration, it was necessary to analyze the combustion residue for any remaining elemental red phosphorus. A literature search revealed very little information on the determination of elemental phosphorus. Only two references (5,6) were found which seemed promising. Both methods are based on the same general principle, an oxidation-reduction reaction between elemental phosphorus and an oxidizing agent. A sample containing elemental phosphorus is reacted with a measured excess of the oxidizing agent, the unreacted portion of the oxidizing agent is measured by titration, and the amount of elemental phosphorus which has been oxidized can be calculated.

Exploratory experiments were conducted using ceric sulfate based on the method described in the references (5,6). The reaction went well with pure red phosphorus; recoveries of standards were somewhat high, but not too unreasonable. However when the actual samples were treated with the ceric sulfate-sulfuric acid solution, bubbles appeared and excessive amounts of ceric sulfate were consumed. Some unoxidized metal might be present in the ash which caused hydrogen to be formed when treated with the acidic solution. The hydrogen might reduce ceric sulfate and make the system inoperable.

A treatment of the sample with a reducing acid such as dilute H_2SO_4, prior to the reaction with the ceric sulfate-sulfuric acid would eliminate this problem. However, any elemental phosphorus present must be insoluble in the dilute sulfuric acid to make this approach feasible. When approximately 15 mg of elemental phosphorus was treated as described, only about half of it was recovered, indicating that some of the elemental phosphorus had been dissolved and oxidized by the initial treatment with dilute H_2SO_4.

In order to avoid interferences from other compounds on the determination of elemental phosphorus in the combustion residue, attempts were made to separate the elemental phosphorus from the remaining compounds prior to its determination. A series of tests were made to find an organic solvent which would dissolve elemental phosphorus. The tests consisted of placing 100 mg of elemental phosphorus in each of a series of beakers and adding 50 ml of an individual organic solvent to each beaker. The beakers containing the elemental phosphorus and solvent were then allowed to stand at room temperature with frequent stirring for about six hours.

The list of solvents used was as follows:

benzene
carbon disulfide
chloroform
methyl alcohol
methyl alcohol + NaOH
ethyl alcohol
ethyl alcohol + NaOH
carbon tetrachloride.

No appreciable solubility was noted in any of the solvent systems.

Analysis of Total Phosphorus in Combustion Residue

In order to take a material balance for phosphorus, the combustion residues were analyzed for total phosphorus. The method used for this determination is a standard technique and specific details of the method may be found in reference (4).

Sample Preparation. The samples were mixed, quartered, and a portion was ground to -60 mesh to provide analytical samples. A 0.2 gram portion of each sample was weighed and placed in 250 ml beakers, 50 ml of water and 10 ml of concentrated HNO_3 were added, and the samples were digested on the hot plate at near boiling temperature for 10-15 minutes. These solutions were then filtered, washed with hot water, and the filter paper and residue were ignited at 600°C in platinum crucibles. The ignited residues were treated with 3 ml HNO_3, 2 ml HF, and 2-3 drops of H_2SO_4, then evaporated to dryness and fused with 1 gram of sodium bisulfate. The fused residues were then added to the filtrates to complete the total solution of samples.

Determination. After oxidation of the sample solutions with $KMnO_4$, the phosphorus was precipitated as phosphomolybdic acid by the addition of an acid molybdate reagent. These precipitates were filtered on filter paper, washed with 5% NH_4NO_3 solution, and then dissolved through the paper into clean beakers with 65% NH_4OH solution. The filter papers were washed thoroughly with hot water, dilute HCl, and finally again with the 65% NH_4OH solution.

About 0.5 ml of citric acid was added to each filtrate, the solutions were made slightly acidic with HCl, and then 5 ml of concentrated NH_4OH for each 100 ml of solution was added. The phosphorus was then precipitated as magnesium phosphate by the addition of magnesia mixture (an ammoniacal solution of $MgCl_2 \cdot 6H_2O$ and NH_4Cl) to each solution. The solutions were stirred, allowed to settle, and filtered on filter paper. The precipitates were washed well with a 1:20 NH_4OH solution, transferred to weighed platinum crucibles, and placed in a muffle furnace at 700°C. After the paper had been burned off, the temperature was raised to 900°C for about 1/2 hour, then to 1100°C for an hour. The crucibles were then removed, cooled, and weighed, the gain in weight being $Mg_2P_2O_7$. The phosphorus content of the samples was then calculated as follows:

$$\text{Total phosphorus, \% by weight} = \frac{\text{wt of } Mg_2P_2O_7 \times 0.27185 \times 100}{0.200}$$

Determination of Metals in Phosphoric Acid Solutions

Standardization. The standard solutions were prepared containing Cr, Mg, Mn, Ni, and Zn in suitable concentrations to cover the range of each metal. A blank was also included. These solutions were aspirated into the flame of a Perkins-Elmer® 305B atomic absorption spectrometer. Calibration curves were drawn for each element by plotting absorbance versus concentration.

Analysis. Measured aliquots of the sample solutions were diluted until the concentration of the metal being determined was in range. These diluted sample solutions were then aspirated under the same conditions used for the standard solutions and the absorbance of each solution was recorded. The concentration of each metal in the diluted sample solutions was obtained by referring to the appropriate calibration curve. The concentration of each metal in the original sample was calculated by applying the appropriate dilution factor.

Analysis of P_2O_5 Emmision from Stack

The Aerotherm® high volume sampling system and an EPA's Method 5 sampling system were used to determine concentrations of P_2O_5 in gas streams. The procedures for sampling of stack gas and determination of the concentration are described below:

(1) Prior to stack gas sampling, the train is washed with distilled water and rinsed with analytical-grade acetone.

(2) Load filter holder with a tared 142 mm (in diameter) glass fiber filter (for Aerotherm system).

(3) Fill Number 1 and 2 impingers with 500 ml of distilled water. Number 3 impinger is left empty. Number 4 impinger is filled with 200 grams of silica gel (8 to 16 mesh).

(4) The sample train is assembled and checked out for leaks.

(5) Heat probe and oven containing filter to 250°F.

(6) The impingers are chilled in an ice-water bath.

(7) The heated probe and oven assembly is inserted into the stack.

(8) Collect stack gas sample during combustion period.

(9) Remove the probe and oven assembly from stack and allow to cool to room temperature before disassembly.

(10) Remove filter from the holder and weigh.

(11) The probe and nozzle are washed with distilled water. The wash water is recovered quantitatively.

(12) The impinger water volumes are measured for moisture determination and acid content.

(13) The silica gel in the fourth impinger is weighed for absorbed moisture. This weight gain plus moisture condensed in impingers 1, 2 and 3 are combined for total moisture content of the stack gas sampled.

(14) The glass fiber filter is divided into equal halfs. One half of the filter is used for acid content. The acid collected on the filter is leached in a certain amount of distilled water for titration. The other half was secured for possible further analysis.

(15) The probe and nozzle wash is titrated with a standard base (0.01 to 0.5 N NaOH) using methyl orange for end point.

(16) The impinger water is titrated with a standard base.

(17) The gas volume sampled is corrected at the standard condition, i.e., 70°F and 1 atm.

(18) Combine the results of titrations for probe-nozzle wash, filter leachate, and impinger water for total phosphoric acid content.

(19) Convert the total phosphoric acid to the equivalent P_2O_5.

(20) The total P_2O_5 in gas sample is divided by the total volume of gas sampled to obtain P_2O_5 emission in the stack gas in terms of mg of P_2O_5/scf of stack gas.

Correlation Between Weights of Dry and Wet Compositions

In various operations of the pilot plant, the feed material charged to the incinerator was different in condition; that is, sometimes it was dry with or without detonator intact; sometimes, it was wet with or without paperboard wrapped around the cylindrical surface. In order to take a phosphorus balance for each batch operation, it was necessary to correlate the feed material in the various conditions to that in a standard condition, that is, dry without wrapping paperboard and detonator, for which the nominal composition is known. Weights of feed material were measured at various conditions and the results are given in Table 2.

Characteristics of Pyrotechnic (Red Phosphorus) Composition

The pyrotechnic composition consists mainly of red phosphorus and pyrolusite (MnO_2) and lesser quantities of magnesium metal (Mg), zinc oxide (ZnO), and an organic binder. Nominal composition of the material is shown in Table 3.(1) Pyrolusite is a naturally occurring mineral containing mostly manganese dioxide. Typical analyses of pyrolusite are shown in Table 4.(2) Exothermic heat of combustion for the composition was estimated at 6,520 Btu/lb. of composition at 77°F in the earlier Battelle's study.(1) According to the laboratory-scale experimental study(1), the dry pyrotechnic composition was ignited at temperatures as low as 500°F.

Pyrotechnic Combustion Test Runs

A series of combustion experiments were made during the course of the study to determine the optimum operating condition for the pilot plant and to obtain design data for a large-scale production facility. The optimum operating condition would satisfy the following conditions:

(1) The cycle time for the batch operation, which consists of time periods for feeding of red phosphorus composition to the incinerator, combustion of the material, and discharging of the combustion residue from the

incinerator, should be minimum to increase the rate of the processing.

(2) Elemental phosphorus in the composition must be incinerated completely to produce either P_4O_{10} or phosphate. Unstable and incomplete combustion products such as metal phosphides in the combustion residue, should be converted in the incinerator prior to the disposal.

(3) The pressure in both combustion chambers must be maintained at a vacuum to prevent the escape of toxic fumes such as phosphorus vapor, P_4O_{10}, and/or phosphine out of the chambers.

(4) The temperature of the combustion product gas from the second combustion chamber must be maintained between 500°F and 1,400°F. Below the lower limit unburned phosphorus may exist in the flue gas due to incomplete combustion. Above the upper limit, the existing gas pump may not provide adequate pumping capacity for safe operation due to excess water vapor generated during gas scrubbing.

(5) The emission of acid must be controlled below 1 mg of P_2O_5/scf according to the Ammunition Procurement and Supply Agency (APSA) standard.

(6) The by-product phosphoric acid should be equivalent in quality to an agricultural-grade phosphoric acid for fertilizer.

TABLE 2. CORRELATION BETWEEN WEIGHTS OF DRY AND WET COMPOSITIONS

Feed Condition	Weight lb.	Ratio of W6/Wi
Dry with paperboard and detonator	W_1 = 1.957	0.8636
Dry with paperboard and without detonator	W_2 = 1.931	0.8752
Wet with paperboard and detonator	W_3 = 2.322	0.7278
Wet with paperboard and without detonator	W_4 = 2.291	0.7377
Wet without paperboard and without detonator	W_5 = 1.857	0.9100
Dry without paperboard and without detonator	W_6 = 1.690	1.0000

TABLE 3. NOMINAL COMPOSITION OF PYROTECHNIC COMPOSITION (Marine Location Marker Mk 25)

Constituent	Percent by Weight
Red phosphorus	53
Pyrolusite	34
Mg	7
ZnO	3
Organic Binder	3
TOTAL	100

TABLE 4. TYPICAL ANALYSES OF PYROLUSITE(3)

	Percent by Weight				
	Samples				
Constituent	1	2	3	4	Average(a)
MnO_2	98.72	96.43	94.30	94.53	96.00
MnO	-----	1.67	2.25	1.07	1.25
Fe_2O_3	0.09	0.35	0.22	-----	0.20
Al_2O_3			0.14	-----	
BaO	-----	-----	0.33	0.95	0.32
CaO	-----	0.25	0.08	0.30	0.16
MgO	-----	0.05	-----	0.05	0.03
SiO_2	-----	-----	0.64	-----	0.16
P_2O_5	-----	trace	0.52	0.10	0.16
H_2O	0.91	0.35	1.75	1.70	1.18
Rem.	0.23	0.90	-----	1.60	0.68
TOTAL	99.95	100.00	100.23	100.30	100.14

(a) Average of four analyses.

Typical Test Run

In a typical batch operation, the second combustion chamber is preheated with the gas pump, acid pump, and all other instruments turned on at the present operating conditions. When the temperature of the second chamber comes up to 900°F or higher and maintains a steady state condition at the temperature, a batch of red phosphorus composition is charged into the first chamber and the burner in the first chamber is lit for ignition. As combustion progresses, the temperature of the first chamber rises and reaches the set-point of the controller. The burner is automatically turned off and the combustion becomes self-sustained. The combustion product gas passes through the second chamber where unburned red phosphorus vapor, if any, is completely incinerated.

The combustion product gas from the second chamber is introduced to the scrubber system. In the spray tower, the hot gas contacts with sprayed phosphoric acid and is cooled by evaporating water in the acid. At the same time, P_4O_{10} in the gas stream is hydrated to form phosphoric acid. The gas stream containing acid mist passes through the packed column and larger droplets of the mist are collected by the column. The remaining fine acid mist is removed in the York®ME.

Results of Test Runs

The total of 39 test runs were made in addition to the incinerator curing operation as follows:

Calibration and Equipment Checkout:	3 runs
Incinerator Curing:	46 hours continuous operation
Exploratory Operations:	3 runs
Test Operations:	14 runs
Additional Test Operations:	19 runs
Total:	39 runs

The operating conditions and the results are given in Table 5 for the exploratory runs, test runs, and additional test runs. The analyses of the results and the performance of the pilot plant are discussed in the following section.

TABLE 5. PILOT PLANT TEST OPERATIONS

Operation of Pilot Plant	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
Date	3/19/76	3/22/76	3/26/76	3/29/76	3/30/76	4/5/76
Operating Condition						
Position of Burner 1(a)	upper	upper	upper	upper	upper	lower
Charge Pan Opening						
Lid	100% open	closed	50% open	closed	closed	100% open
Side wall	closed	closed	100% open	100% open	100% open	100% open
Preheating Temperature, °F						
Chamber 1	500	500	600	600	580	80
Chamber 2	1,000	1,040	1,100	1,040	1,070	800
Load, lb	~3(wet, w/paper)	~3(wet, w/paper)	~3(wet, w/paper)	9(wet, w/paper)	6.56(wet, w/paper)	5.25(wet, w/paper)
Combustion						
Preheating Period, min	158	70	101	106	62	92
Time to Ignition, min	75	93	30	57	51	8
Combustion Period, min	7	152	15	40	30	34
Maximum Temperature, °F						
Chamber 1 (Inside Charge Pan)	1,000(b) (NM(c))	870(b) (NM)	NM(1,420)	650(1,610)	1,400(1,540)	800(1,700)
Chamber 2	1,100	1,250	1,120	1,100	1,150	1,000
Pressure in Both Chambers, inch of water vacuum	0.2	0.2	0.2	0.2	0.2	0.2
Recycle Acid for Gas Scrubbing						
Initial Conc., % by wt.	NM	46.74	45.59	50.31	63.34	45.90
Initial Volume, gal	NM	NM	NM	5.02	3.41	5.37
Final Conc., % by wt.	46.74	45.59	40.08	63.34	45.90	41.69
Final Volume, gal	NM	NM	NM	3.44	5.61	5.91
Mist Elimination						
York Mist Elimination (ME) Drain						
Column 1: Volume, gal	NM	NM	NM	0.75	0.351	0.288
Conc., % by wt.	11.66	17.28	NM	40.95	61.27	63.49
Column 2: Volume, gal	NM	NM	NM	0.402	0.173	0.159
Conc., % by wt.	1.02	0.85	NM	5.34	6.80	7.11
Brink Mist Eliminator (ME) Drain						
Column 1: Volume, gal	NE(d)	NE	NE	NE	NE	NE
Conc., % by wt.	NE	NE	NE	NE	NE	NE
Column 2: Volume, gal	NE	NE	NE	NE	NE	NE
Conc., % by wt.	NE	NE	NE	NE	NE	NE
Stack Gas						
Flow Rate, acfm	154	156	153	156	156	160
Temperature, °F	150	155	160	155	160	160
Minimum Oxygen Content, % by vol.	20.6	20.8	20.6	~21.0	~21.0	18.5
Acid Emission, mg P_2O_5/acf	NM	NM	NM	27.0	28.9	NM
Combustion Residue						
Quantity, lb	NM(0.53)(e)	NM(1.59)(e)	NM(1.59)(e)	NM(4.76)(e)	NM(3.47)(e)	2.69
Total Phosphorus, % by wt.	NM(20.0)(f)	NM(20.0)(f)	NM(20.0)(f)	20.3	21.5	NM(19.0)(f)
Remarks	Shakedown operation	Shakedown operation	Shakedown operation	Both burners were off most of the combustion period; White smoke in York ME drain jars; Second column of scrubber empty.	Dark sediment in first York ME drain jar; Second column of scrubber empty.	Combustion self-sustained with burner 1 off; Acid accumulated inside chambers; Dark colored foam in recycle acid jar; Dark sediment in York ME drain jars.

TABLE 5. PILOT PLANT TEST OPERATIONS (Continued)

Operation of Pilot Plant	Run 10	Run 11	Run 12	Run 13	Run 14
Date	4/8/76	4/12/76	4/13/76	4/14/76	4/15/76
Operating Condition					
Position of Burner 1[(a)]	lower	lower	lower	lower	lower
Charge Pan Opening					
Lid	100% open	100% open	100% open	100% open	closed
Side wall	100% open	100% open	100% open	100% open	100% open
Preheating Temperature, °F					
Chamber 1	80	80	80	90	100
Chamber 2	770	600	800	800	800
Load, lb	5.56(wet, w/paper)	5.69(wet, w/paper)	5.25(wet, w/paper)	10.06(wet, w/paper)	10.31(wet, w/paper, detonator, plastic caps, and wire)
Combustion					
Preheating Period, min	91	113	97	89	95
Time to Ignition, min	10	1	11	10	8
Combustion Period, min	26	28	33	54	75
Maximum Temperature, °F					
Chamber 1 (Inside Charge Pan)	820(1,510)	680(1,610)	1,070(1,530)	1,150(1,520)	1,250(1,470)
Chamber 2	1,070	830	1,100	1,180	1,040
Pressure in Both Chambers, inch of water vacuum	0.2	0.2	0.2	0.2	0.2
Recycle Acid for Gas Scrubbing					
Initial Conc., % by wt.	41.69	44.58	41.09	44.60	43.85
Initial Volume, gal	5.37	5.05	5.02	4.98	5.28
Final Conc., % by wt.	42.71	41.09	44.60	43.85	41.90
Final Volume, gal	5.36	5.05	5.02	5.60	5.28
Mist Elimination					
York Mist Elimination (ME) Drain					
Column 1: Volume, gal	0.481	0.481	0.365	0.510	0.367
Conc., % by wt.	37.07	55.27	51.58	62.11	72.96
Column 2: Volume, gal	0.280	0.206	0.254	0.217	0.172
Conc., % by wt.	6.19	8.77	7.41	12.09	11.35
Brink Mist Eliminator (ME) Drain					
Column 1: Volume, gal	NE	NE	NE	NE	NE
Conc., % by wt.	NE	NE	NE	NE	NE
Column 2: Volume, gal	NE	NE	NE	NE	NE
Conc., % by wt.	NE	NE	NE	NE	NE
Stack Gas					
Flow Rate, acfm	157	157	157	160	160
Temperature, °F	155	150	160	160	180
Minimum Oxygen Content, % by vol.	20.0	21.0	20.4	19.5	21.0
Acid Emission, mg P_2O_5/acf	9.5	NM	NM	NM	NM
Combustion Residue					
Quantity, lb	2.69	2.88	2.56	5.94	5.56
Total Phosphorus, % by wt.	19.2	18.9	NM(19.0)[(f)]	NM(19.0)[(f)]	15.5
Remarks	Second column of scrubber filled with 2 inch packing; Less dark sediment in York ME drain jars.	Greenish dark sediment in first column of York ME; Combustion residue sintered; Warm ash reacted with water; Combustion not sustained.	New charge pan used; Combustion not sustained; Red-hot ash reacted with water producing gases other than steam.	Combustion not sustained; Scrubber flooded.	White smoke in recycle acid jar. York #2 plugged completely by carbon soot; Gas pump overloaded, combustion completed with gas pump off. Ash remained red-hot with Burner 1 on; Cooled ash reacted with water for more than 15 min; Scrubber flooded; Dark sediment in York ME drain jars; Dark colored sludges in recycle acid.

TABLE 5. PILOT PLANT TEST OPERATIONS (Continued)

Operation of Pilot Plant	Run 15	Run 16	Run 17	Run 18	Run 19
Date	4/23/76	4/26/76	4/27/76	4/28/76	4/29/76
Operating Condition					
Position of Burner 1[a]	lower	lower	lower	lower	lower
Charge Pan Opening					
Lid	100% open	100% open	closed	closed	100% open
Side wall	100% open	100% open	100% open	50% open	50% open
Preheating Temperature, °F					
Chamber 1	90	70	80	80	80
Chamber 2	820	820	820	800	820
Load, lb	10.13(wet, w/paper)	8.25(wet, w/paper)	10.00(wet, w/paper)	10.88(wet, w/paper)	10.63(wet, w/paper)
Combustion					
Preheating Period, min	93	72	62	65	72
Time to Ignition, min	13	5	5	6	2
Combustion Period, min	48	47	25	27	33
Maximum Temperature, °F					
Chamber 1 (Inside Charge Pan)	1,230(1,470)	790(1,500)	720(1,590)	1,050 (1,620)	1,000 (1,820)
Chamber 2	1,160	1,090	970	960	1,020
Pressure in Both Chambers, inch of water vacuum	0.2	0.2	0.2	0.2	0.2
Recycle Acid for Gas Scrubbing					
Initial Conc., % by wt.	52.05	52.98	51.86	53.45	54.28
Initial Volume, gal	5.19	5.15	5.43	5.39	5.36
Final Conc., % by wt.	52.98	51.86	53.45	54.28	49.57
Final Volume, gal	5.19	5.47	5.43	5.39	6.68
Mist Elimination					
York Mist Elimination (ME) Drain					
Column 1: Volume, gal	0.417	0.317	0.433	0.452	0.399
Conc., % by wt.	63.75	64.87	66.14	65.59	72.17
Column 2: Volume, gal	0.161	0.127	0.137	0.172	0.092
Conc., % by wt.	4.19	3.50	5.97	4.07	7.23
Brink Mist Eliminator (ME) Drain					
Column 1: Volume, gal	NE	NE	NE	NE	NE
Conc., % by wt.	NE	NE	NE	NE	NE
Column 2: Volume, gal	NE	NE	NE	NE	NE
Conc., % by wt.	NE	NE	NE	NE	NE
Stack Gas					
Flow Rate, acfm	160	150	160	160	160
Temperature, °F	160	160	155	155	165
Minimum Oxygen Content, % by vol.	20.8	20.0	~21.0	~21.0	20.4
Acid Emission, mg P_2O_5/scf	NM	NM	NM	NM	NM
Combustion Residue					
Quantity, lb	5.25	4.19	5.38	5.94	5.38
Total Phosphorus, % by wt.	18.8	NM(19.0)(f)	19.6	18.7	19.3
Remarks	Dark sediment in first column of York ME drain jar; Cooled ash not reactive, but odorous; Combustion not sustained.	Combustion went out once; Dark sediment in York ME drain jars.	Combustion sustained; Newly supplied composition burned; Considerable amount of dark sediment in recycle acid; A portion of ash looked green; White smoke appears from charge pan walls during washing with water.	Combustion self-sustained; Burner 1 remained on for 10 min after ignition; New batch of composition burned; Dark sediment in York ME drain jar.	Combustion self-sustained, New composition used, Dark sediment in York ME drain jar; Cooled ash odorous when contacted with water.

TABLE 5. PILOT PLANT TEST OPERATIONS (Continued)

Operation of Pilot Plant	Run 20	Run A-1	Run A-2	Run A-3	Run A-4
Date	5/11/76	5/13/76	6/15/76	6/16/76	6/21/76
Operating Condition					
Position of Burner 1$^{(a)}$	lower	lower	lower	lower	lower
Charge Pan Opening					
Lid	100% open	100% open	100% open	closed	100% open
Side wall	50% open	50% open	50% open	50% open	50% open
Preheating Temperature, °F					
Chamber 1	80	90	90	90	85
Chamber 2	870	910	880	840	900
Load, lb	20.06(wet, w/paper)	16.75(wet, w/o paper)	10.25(wet, w/o paper)	9.44(wet, w/o paper)	11.75(dry, w/paper)
Combustion					
Preheating Period, min	88	81	83	67	44
Time to Ignition, min	2	1	1	1	1
Combustion Period, min	85	15	13	16	13
Maximum Temperature, °F					
Chamber 1 (Inside Charge Pan)	1,140(1,690)	1,580(1,640)	1,420(1,710)	1,470(1,610)	1,420(1,690)
Chamber 2	1,200	1,570	1,340	1,620	1,670
Pressure in Both Chambers, inch of water vacuum	0.2	0.2	0.25	0.2	0.3
Recycle Acid for Gas Scrubbing					
Initial Conc., % by wt.	50.34	54.28	61.44	64.55	0.064
Initial Volume, gal	5.02	4.87	4.72	4.47	5.11
Final Conc., % by wt.	54.28	62.04	64.55	57.98	9.34
Final Volume, gal	4.91	4.57	4.51	5.16	4.76
Mist Elimination					
York Mist Elimination (ME) Drain					
Column 1: Volume, gal	3.424	1.144	0.642	0.576	0.655
Conc., % by wt.	20.54	57.32	52.13	61.86	25.24
Column 2: Volume, gal	0.375	0.225	0.193	0.156	0.182
Conc., % by wt.	4.45	14.53	7.46	8.17	4.17
Brink Mist Eliminator (ME) Drain					
Column 1: Volume, gal	NE	NE	0.079	0.087	0.085
Conc., % by wt.	NE	NE	13.46	9.84	12.61
Column 2: Volume, gal	NE	NE	0.082	0.122	0.066
Conc., % by wt.	NE	NE	29.11	30.08	17.00
Stack Gas					
Flow Rate, acfm	160	145	148	145	140
Temperature, °F	155	160	155	155	160
Minimum Oxygen Content, % by vol.	17.0	13.7	18.1	20.0	15.8
Acid Emission, mg P_2O_5/scf	52.16(2.6)$^{(g)}$	10.23(3.5)$^{(g)}$	5.77	1.5	99.5
Combustion Residue					
Quantity, lb	10.38	NM(9.87)$^{(e)}$	6.06	5.56	6.81
Total Phosphorus, % by wt.	19.3	19.7	19.3	19.8	19.6
Remarks	Combustion not sustained; York ME sprayer was on and off manually to clean the plugged York ME element.	More clear York ME drain without black particles; Sustained combustion; A portion of ash sintered; Ash odorous when contacted with water; New element for York ME.	Spray tower packing (1/2 inch) replaced with 1-inch packing; Second column of scrubber filled with 2-inch packing; Spraying in the second column caused flooding; Ash color more grey than black; Brink ME tested; Cooled ash inert with water.	Combustion self-sustained; Ash mostly grey; cooled ash inert with water; Brink ME tested.	Both ME plugged at middle of combustion; forcing use of emergency bypass route, Red deposits on furnace walls; White smoke in recycle acid jar and ME drain jars; Sparkling and smoking from furnace walls; Recycle acid somewhat dark and red; White deposit in gas pump generating white smoke when flushed with water; Stack gas sampling system filter plugged; Agitation of recycle acid generated white smoke; Cooled ash looked dark and reactive with water

TABLE 5. PILOT PLANT TEST OPERATIONS (Continued)

Operation of Pilot Plant	Run A-5	Run A-6	Run A-7	Run A-8	Run A-9
Date	6/25/76	6/28/76	6/29/76	8/10/76	8/12/76
Operating Condition					
Position of Burner 1[a]	lower	lower	lower	lower	lower
Charge Pan Opening					
Lid	100% open	100% open	closed	100% open	100% open
Side wall	50% open	50% open	50% open	50% open	50% open
Preheating Temperature, °F					
Chamber 1	90	90	100	90	90
Chamber 2	900	880	900	900	800
Load, lb	10.06(wet, w/o paper)	9.31(dry[h] w/paper)	9.50(dry[h] w/paper)	10.19(wet, w/o paper)	10.38(wet, w/o paper)
Combustion					
Preheating Period, min	59	63	63	65	55
Time to Ignition, min	1	4	2	2	2
Combustion Period, min	13	22	14	13	15
Maximum Temperature, °F					
Chamber 1 (Inside Charge Pan)	1,510(1,530)	1,360(1,670)	1,370(1,650)	1,280(1,690)	1,290(1,730)
Chamber 2	1,450	1,580	1,570	1,200	1,080
Pressure in Both Chambers, inch of water vacuum	0.25	0.25	0.3	0.3	0.3
Recycle Acid for Gas Scrubbing					
Initial Conc., % by wt.	0	0	58.37	50.43	0.012
Initial Volume, gal	4.76	4.76	5.16	4.81	4.76
Final Conc., % by wt.	6.68	6.19	57.68	56.44	10.92
Final Volume, gal	5.08	5.02	5.67	4.58	3.70
Mist Elimination					
York Mist Elimination (ME) Drain					
Column 1: Volume, gal	0.933	3.841	0.708	0.645	0.822
Conc., % by wt.	33.06	9.97	21.08	40.19	35.71
Column 2: Volume, gal	0.222	0.254	0.140	0.188	0.225
Conc., % by wt.	5.26	4.79	3.69	4.95	6.53
Brink Mist Eliminator (ME) Drain					
Column 1: Volume, gal	NE	NE	NE	0.079	0.106
Conc., % by wt.	NE	NE	NE	2.90	6.71
Column 2: Volume, gal	NE	NE	NE	0.116	0.172
Conc., % by wt.	NE	NE	NE	17.00	18.79
Stack Gas					
Flow Rate, acfm	130	137	137	142	141
Temperature, °F	155	150	155	155	150
Minimum Oxygen Content, % by vol.	~21.0	11.6	10.7	15.6	16.8
Acid Emission, mg P_2O_5/scf	0.32	25.7	3.2	0.6	0.5
Combustion Residue					
Quantity, lb	5.81	5.25	5.38	5.88	6.94
Total Phosphorus, % by wt.	19.1	21.6	21.6	19.2	19.5
Remarks	Ash reacted with water resulting in gas generation.	Combustion self-sustained; Black particle caused York ME plugged, forcing the ME sprayer on for cleaning; red sediment in recycle, acid jar and York ME drain jars; White smoke in the jars; After combustion, sparkling and smoking from furnace walls; White smoke from acids when agitated.	Combustion self-sustained; York ME plugged and ME sprayer on for cleaning; Particles collected from recycle acid ignited spontaneously when dried and produced white smoke; Sparkling and smoking from furnace walls; Warm ash reacted with water to generate gas.	Combustion self-sustained; Gelman glass fiber filter used instead of MSA filter; Brink ME tested.	Combustion self-sustained; Gelman filter used hereafter; Brink ME tested.

TABLE 5. PILOT PLANT TEST OPERATIONS (Continued)

Operation of Pilot Plant	Run A-10	Run A-11	Run A-12	Run A-13	Run A-14
Date	8/16/76	8/18/76	8/19/76	8/23/76	8/24/76
Operating Condition					
Position of Burner 1[(a)]	lower	lower	lower	lower	lower
Charge Pan Opening					
Lid	100% open	100% open	100% open	100% open	100% open
Side wall	50% open	50% open	50% open	50% open	50% open
Preheating Temperature, °F					
Chamber 1	80	80	90	100	100
Chamber 2	800	740	790	780	760
Load, lb	10.06(wet, w/o paper)	10.00(wet, w/o paper)	20.00(wet, w/o paper)	5.00(wet, w/o paper)	10.00(wet, w/o paper)
Combustion					
Preheating Period, min	58	59	44	82	62
Time to Ignition, min	2	2	1	2	1
Combustion Period, min	14	14	17	12	16
Maximum Temperature, °F					
Chamber 1 (Inside Charge Pan)	1,600(1,430)	1,610(1,680)	1,520(1,620)	1,080(1,700)	1,460(1,770)
Chamber 2	1,250	1,130	1,800	980	1,150
Pressure in Both Chambers, inch of water vacuum	0.25	0.2	0.3	0.3	0.3
Recycle Acid for Gas Scrubbing					
Initial Conc., % by wt.	52.98	0.004	55.00	50.82	51.77
Initial Volume, gal	4.79	4.76	4.76	4.76	4.76
Final Conc., % by wt.	55.09	6.19	62.93	51.77	61.28
Final Volume, gal	4.76	4.49	4.97	5.48	3.60
Mist Elimination					
York Mist Elimination (ME) Drain					
Column 1: Volume, gal	0.660	1.165	1.059	0.705	0.774
Conc., % by wt.	48.5	4.186	48.30	41.12	59.15
Column 2: Volume, gal	0.188	0.232	0.164	0.151	0.161
Conc., % by wt.	5.85	7.32	9.28	6.68	10.39
Brink Mist Eliminator (ME) Drain					
Column 1: Volume, gal	0.090	NE	NE	NE	NE
Conc., % by wt.	5.44	NE	NE	NE	NE
Column 2: Volume, gal.	0.145	NE	NE	NE	NE
Conc., % by wt.	19.20	NE	NE	NE	NE
Stack Gas					
Flow Rate, acfm	141	133	130	134	134
Temperature, °F	150	150	165	150	150
Minimum Oxygen Content, % by vol.	15.5	16.8	11.1	16.0	12.0
Acid Emission, mg P_2O_5/acf	0.9(3.6)(1)	0.4	2.4	0.2	0.4
Combustion Residue					
Quantity, lb.	5.88	5.75	11.75	2.81	5.75
Total Phosphorus, % by wt.	19.6	19.5	20.2	19.5	19.4
Remarks	Clean Recycle acid; Warm ash reactive with water.	Emptied charge pan ignited spontaneously when contacted with flushing water producing small flames and blue smoke.	Furnace exhaust line red-hot; York ME drain became dark; York ME plugged and sprayer applied for cleaning; Warm ash was very reactive with water; violent burning.	After overnight, ash became inert with water.	Ash very reactive with water.

TABLE 5. PILOT PLANT TEST OPERATIONS (Concluded)

Operation of Pilot Plant	Run A-15	Run A-16	Run A-17	Run A-18	Run A-19
Date	8/25/76	8/27/76	8/30/76	9/8/76	9/9/76
Operating Condition					
Position of Burner 1[(a)]	lower	lower	lower	lower	lower
Charge Pan Opening					
Lid	100% open	100% open	100% open	100% open	100% open
Side wall	50% open	50% open	50% open	50% open	50% open
Preheating Temperature, °F					
Chamber 1	120	90	80	90	90
Chamber 2	760	790	850	790	780
Load, lb	10.00(wet, w/o paper)	10.00(wet, w/o paper)	10.00(wet, w/o paper)	10.00(wet, w/o paper)	10.00(wet, w/o paper)
Combustion					
Preheating Period, min	50	48	45	70	39
Time to Ignition, min	2	2	1	1	1
Combustion Period, min	12	15	13	13	20
Maximum Temperature, °F					
Chamber 1 (Inside Charge Pan)	1,600(1,660)	1,530(1,600)	1,560(1,520)	1,660(1,200)	1,620(1,650)
Chamber 2	1,220	1,110	1,330	1,280	1,320
Pressure in Both Chambers, inch of water vacuum	0.3	0.25	0.28	0.25	0.25
Recycle Acid for Gas Scrubbing					
Initial Conc., % by wt.	48.69	53.26	52.52	2.10	5.28
Initial Volume, gal	4.76	4.72	4.76	4.76	4.76
Final Conc., % by wt.	53.26	59.50	49.28	7.63	9.67
Final Volume, gal	4.76	4.12	4.04	3.86	3.70
Mist Elimination					
York Mist Elimination (ME) Drain					
Column 1: Volume, gal	0.716	1.170	0.518	1.06	0.962
Column 1: Conc., % by wt.	64.39	43.13	37.71	36.95	38.40
Column 2: Volume, gal	0.116	0.119	0.129	0.262	0.198
Column 2: Conc., % by wt.	13.45	13.10	4.95	5.63	6.92
Brink Mist Eliminator (ME) Drain					
Column 1: Volume, gal	NE	NE	NE	NE	NE
Column 1: Conc., % by wt.	NE	NE	NE	NE	NE
Column 2: Volume, gal.	NE	NE	NE	NE	NE
Column 2: Conc., % by wt.	NE	NE	NE	NE	NE
Stack Gas					
Flow Rate, acfm	129	129	142	125	129
Temperature, °F	160	160	170	155	160
Minimum Oxygen Content, % by vol.	10.7	12.0	3.2	6.7	13.2
Acid Emission, mg P_2O_5/scf	1.3	1.0	62.1	NM	NM
Combustion Residue					
Quantity, lb.	5.81	5.81	5.81	5.75	5.50
Total Phosphorus, % by wt.	19.6	19.2	19.8	18.6	20.4
Remarks	Ash reacted with water to produce gas which ignited violently with yellowish-orange flame; Movie was made on this test run; Nuclepore polycarbonate filter used in stack gas sampling system.	Nuclepore filter used in stack gas sampling system; Gas resulting from warm ash - water reaction collected under water.	Scrubber flooded due to pluggage; Gas pump overloaded due to increased pressure drop; Warm ash reacted with water to produce gas which ignited spontaneously; Scale on first column walls of scrubber; Leakage from several flanges; Gelman filter used.	Hot ash reacted with water and the resulting gas was collected for analysis.	Hot ash reacted with water and the resulting gas was collected for analysis; White smoke in recycle acid jar; Wet ash used in the analysis.

FOOTNOTES FOR TABLE 5

(a) With the burner at the upper position, the flame was not impinged into the charge pan and vice versa.

(b) The temperature was measured near an outside wall of the charge pan opposite to the burner side.

(c) Not measured.

(d) Not employed.

(e) The value was not measured but estimated based on the data on the ratio of load to combustion residue from other test runs.

(f) The value was not measured but assumed based on the data from the other test runs.

(g) The value indicates P_2O_5 concentration in stack gas during the preheating period.

(h) The flare candles were intact with wrapping paper but soaked in water for five minutes before burning.

(i) The value in the parenthesis indicates the stack gas emission measured by EPA Method 5 sampling system for the identical stack gas.

ANALYSIS OF PILOT PLANT PERFORMANCE

Based on the data described in the preceding section, the performance, and operational and maintenance problems of the pilot plant are discussed in this section.

Operating Characteristics of Incinerator

Burner Position in Chamber Number 1

As given in Table 5, time to the ignition of red phosphorus composition after Burner Number 1 was lighted ranged from 30 to 93 minutes (average, 61 minutes) with the burner at an upper position where the flame of the burner could not make contact with the composition. With a relocation of the burner to a lower position where the flame of the burner could contact the composition, the time to the ignition was shortened, ranging from 1 to 13 minutes (average, 6 minutes) for wet composition with paperboard on and 1 to 2 minutes (average, 1.4 minutes) for wet composition without paperboard on, respectively. With the burner at the upper position, the flame of the burner could not cause a local hot spot at the surface of the composition for ignition. The ignition occurred when the temperature of the combustion chamber was raised to the ignition point. Since it is desirable to shorten the time to ignition in order to increase the turnover of the pilot plant, the burner should be operated at the lower position.

Combustion Characteristics of Wet and Dry Compositions

Combustion of dry composition is more violent than that of wet composition. During the incineration of dry composition, burned and unburned compositions were splattered and carried over with the combustion product gas. This caused pluggings at the York ME and the emergency bypass route was forced to be used. Red deposits were found on the incinerator walls and spontaneous sparkling and smoking took place on the wall after the combustion was over. Dark and red particles were collected at the scrubber and when the particles were dried, they ignited spontaneously with white smoke. During the operation, the scrubbing acid and acid collected at the York ME generated white smoke. Even after overnight, the acids evolved white smoke when agitated.

Combustion of wet composition is less violent than that of dry composition. However, when the wet composition was charged into the incinerator with the wrapping paperboard around it, in many instances, the combustion could not be sustained. It was because ignitions of separate pieces of compositions could not always be sustained from the combustion of other pieces of compositions in the charge pan. Burner Number 1 had to be relighted. In addition, the York ME was plugged frequently when the composition was incinerated with the paperboard. This may be because the carbon soot resulting from the paperboard was carried over with the combustion product gas and deposited on the ME element.

Eleven plastic caps containing detonator and copper wires were incinerated along with wet composition. The combustion resulted in a black smoke and the York ME was plugged quickly, causing failure of the gas pump due to overloading.

The ideal condition of the red phosphorus composition for charging to the incinerator has been "wet without wrapping paperboard". Under the feed condition, the combustion was self-sustained after the initial ignition, the combustion behavior was less violent, and the system upsets such as generation of white smoke from the product acid and pluggages of the scrubber and the York ME were minimized.

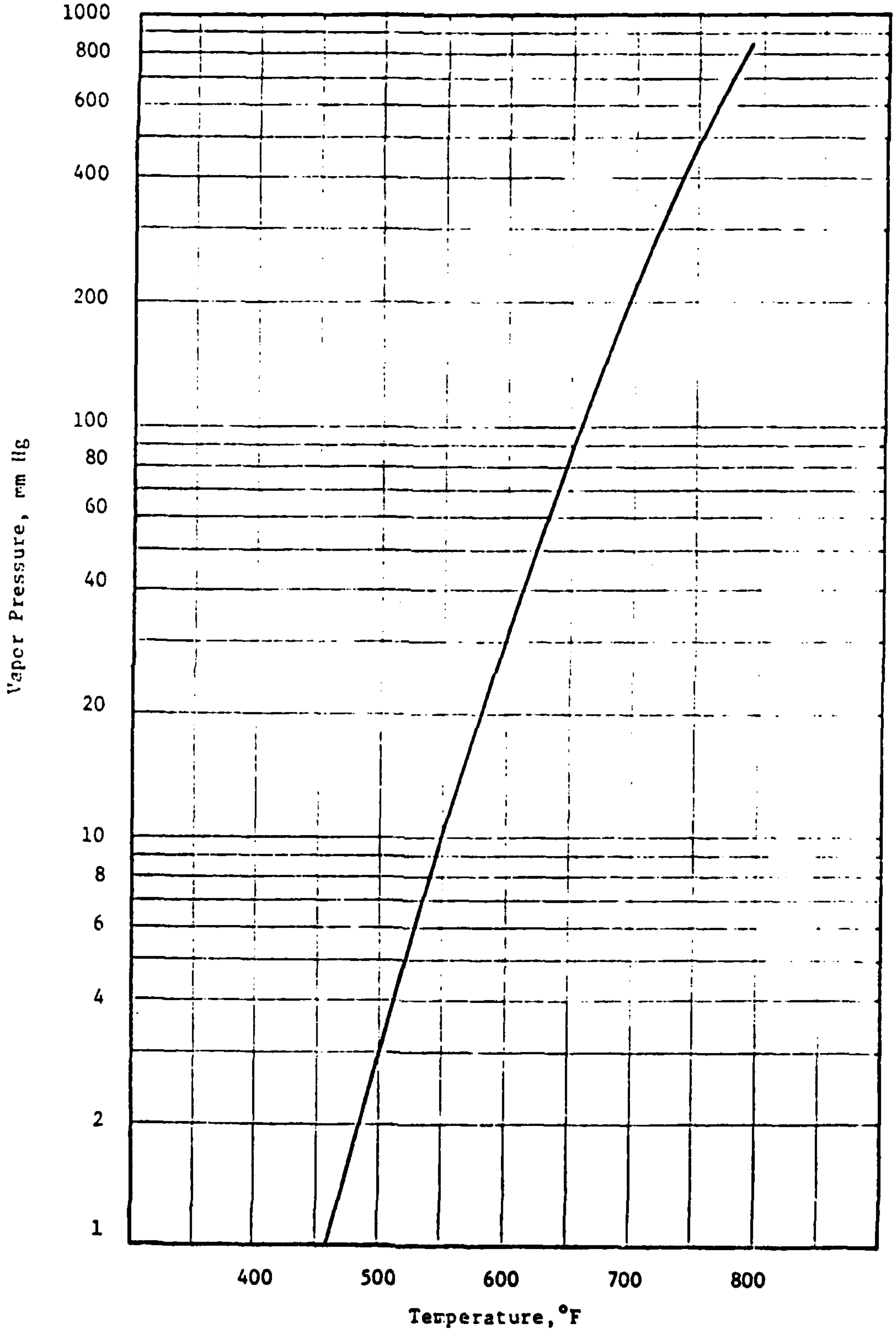


FIGURE 22. VAPOR PRESSURE OF RED PHOSPHORUS (7)

The rate of combustion of red phosphorus may be controlled by adjusting the supply of oxygen available for the reaction. With sufficient oxygen available, the rate of combustion depends on the vapor pressure of red phosphorus, which is a function of temperature as shown in Figure 22. The heat generated in the exothermic reaction of red phosphorus vapor and oxygen increases the temperature of the composition which in turn increases the vapor pressure of red phosphorus and temperature. It was observed in the pilot plant operations that at the peak of combustion, unburned red phosphorus vapor was carried with the combustion product gas into the second chamber where it completed the combustion. Both combustion chambers were able to be maintained at a vacuum pressure (in a range of 0.2 to 0.3 inches of water vacuum) throughout the pilot plant operations.

The effect of charge rate of the composition at a constant combustion air supply per period of combustion in the batch operation is given in Table 6 and plotted in Figure 23. The effect on the maximum temperature of the combustion product gas from Chamber 2 is given in Table 6 and plotted in Figure 24. Since the maximum temperatures of gas in the charge pan and Chamber 1 (see Table 6) were maintained at a relatively constant temperature with respect to variations in charge rate, the combustion rate can be considered as being controlled by the supply of oxygen to the charge pan and Chamber 1. Unburned red phosphorus vapor in the gas stream from Chamber 1 must be incinerated in Chamber 2 as observed in Run Number A-12.

Typical temperature profile of combustion product gas within the incinerator with respect to operating time is shown in Figure 25 and the oxygen concentrations of the combustion product gas at the stack are shown in Figure 26.

Analysis of Combustion of Red Phosphorus Composition

Gaseous combustion products from the auto ignition of the composition without an auxiliary fuel were calculated using the following assumptions:

(1) MnO_2 decomposed to MnO.

(2) Mg oxidized to MgO.

(3) H_2O in pryolusite liberated during combustion.

(4) Composition of the organic binder assumed at 87 percent carbon and 13 percent hydrogen, which is typical for Number 2 fuel oil.

(5) Combustion air is at 70°F and 50 percent relative humidity.

(6) Free water in wet composition is approximately 9 percent by weight.

The gaseous and solid combustion products estimated on the above basis is given in Tables 7 and 8, respectively.

Excess combustion air used in the pilot plant operations can be estimated by using the following relationship:

$$x \text{ (\% by volume)} = \frac{92.8\ (O_2)}{24.09 - 1.1471(O_2)}$$

where (O_2) indicates oxygen content (percent by volume) in stack gas at the room temperature (60°F) and x indicates excess combustion air. The above equation was plotted in Figure 27.

TABLE 6. EFFECTS OF CHARGE RATE ON COMBUSTION PERIOD AND MAXIMUM TEMPERATURE OF COMBUSTION PRODUCT GAS IN PILOT PLANT OPERATIONS

Run No.	Charge lb.	Combustion Period, (min)	Maximum Temperature, °F		
			Chamber 1	Charge Pan	Chamber 2
A-1	16.75	15	1,580	1,640	1,570
A-5	10.06	13	1,510	1,530	1,450
A-8	10.19	13	1,280	1,690	1,200
A-9	10.38	15	1,290	1,730	1,080
A-10	10.06	14	1,600	1,430	1,250
A-11	10	14	1,610	1,680	1,130
A-12	20	17	1,520	1,620	1,800
A-13	5	12	1,080	1,700	980
A-14	10.00	16	1,460	1,770	1,150
A-15	10.00	12	1,600	1,660	1,220
A-16	10.00	15	1,530	1,600	1,110

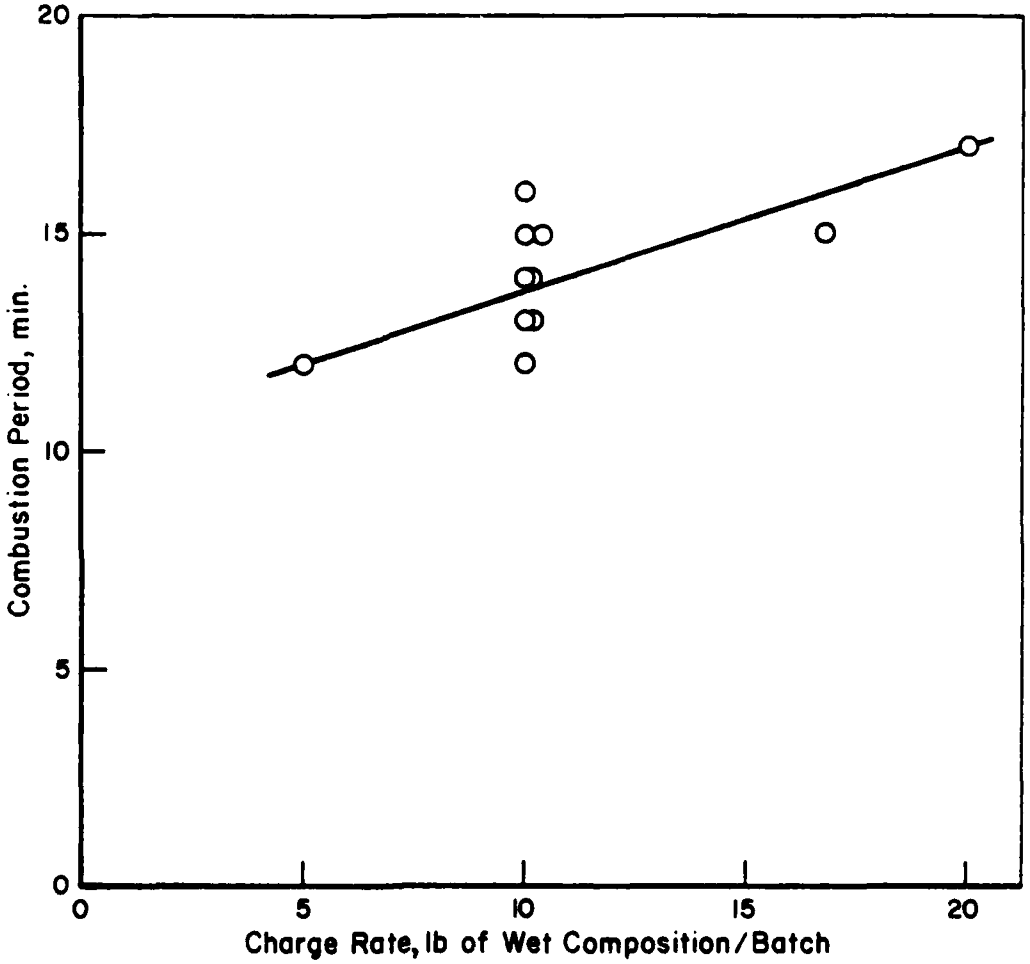


FIGURE 23. EFFECT OF CHARGE RATE ON COMBUSTION PERIOD IN PILOT PLANT OPERATION

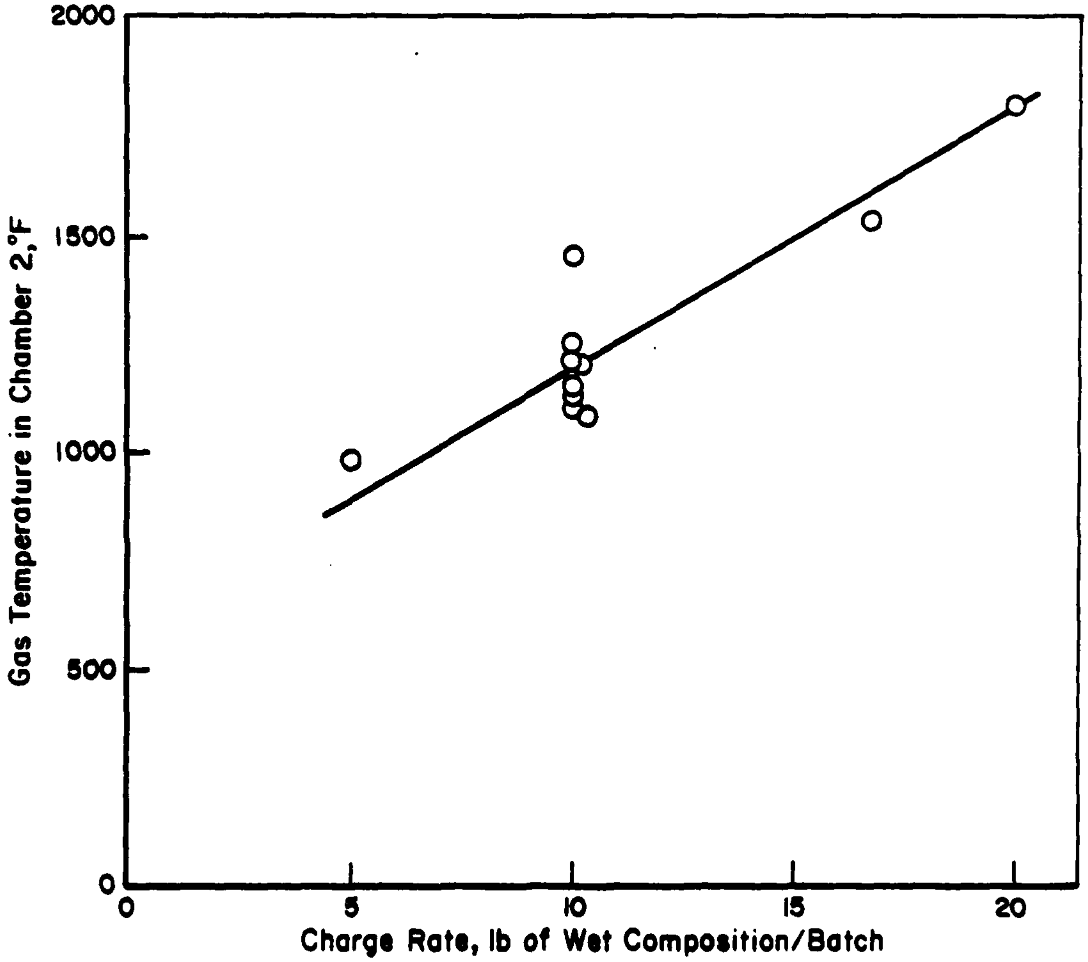


FIGURE 24. EFFECT OF CHARGE RATE ON MAXIMUM TEMPERATURE OF COMBUSTION PRODUCT GAS FROM CHAMBER 2

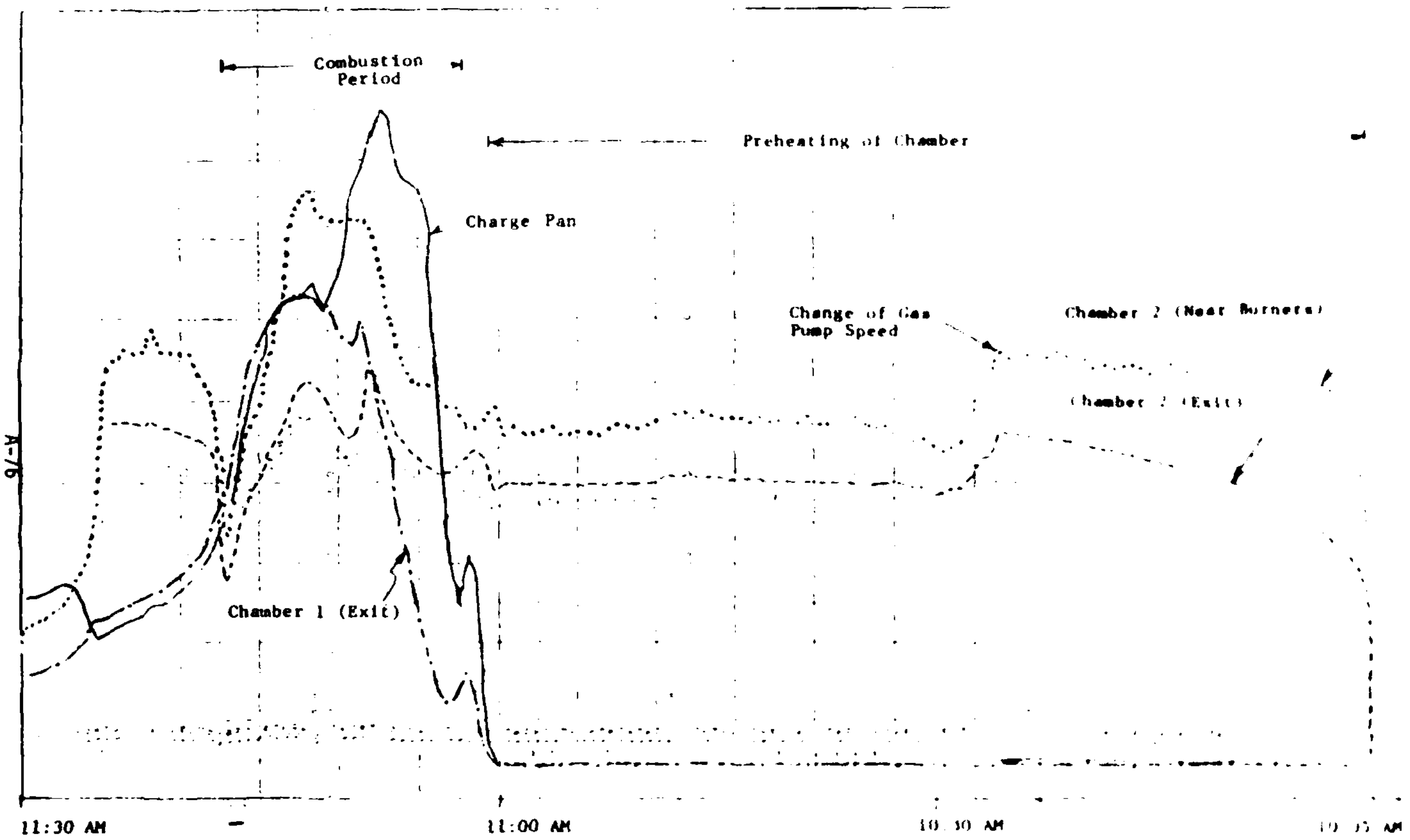


FIGURE 25. TYPICAL TEMPERATURE PROFILE OF COMBUSTION PRODUCT GAS WITHIN INCINERATOR
(Run A-9, August 12, 1976)

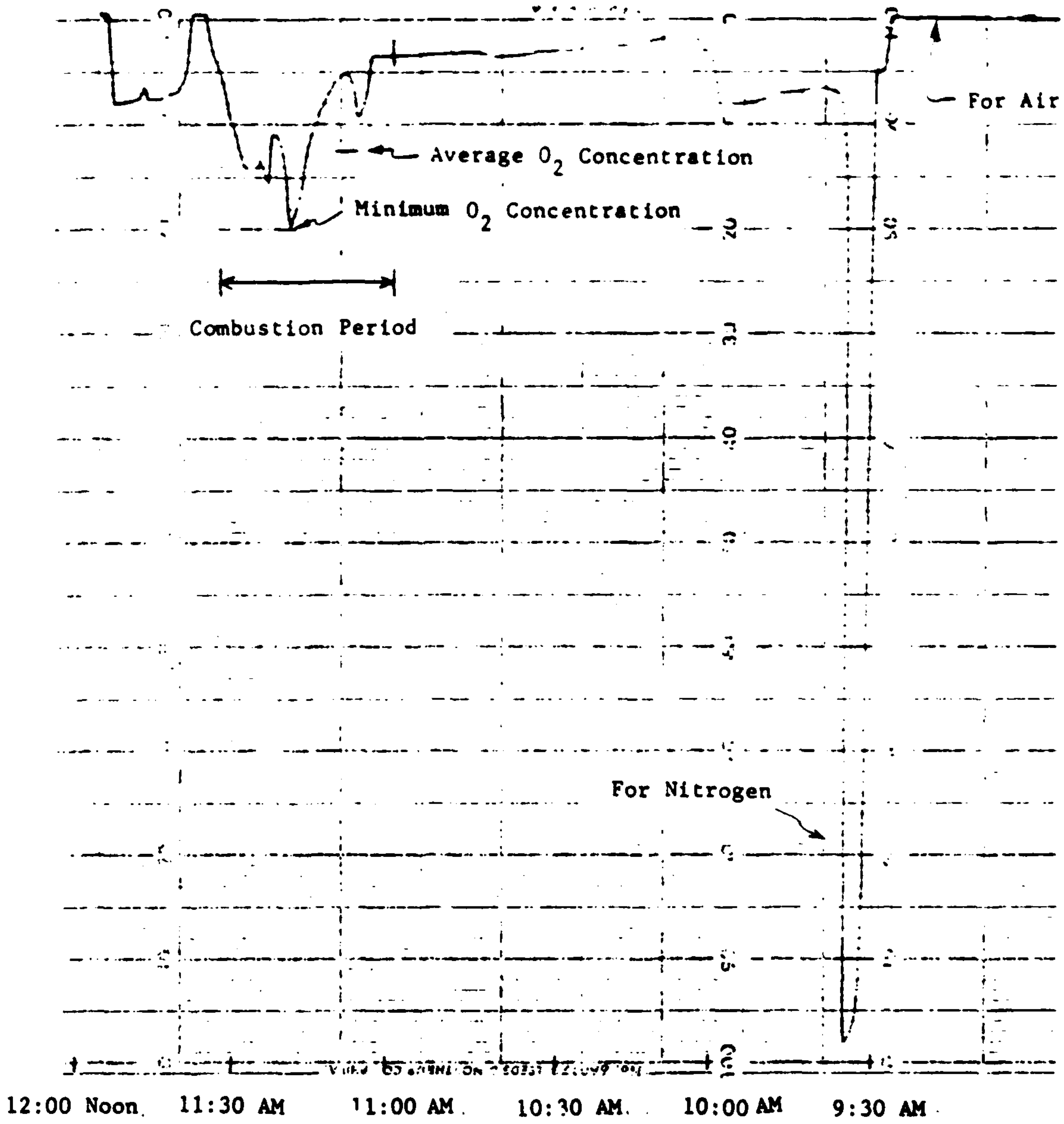


FIGURE 26. OXYGEN CONCENTRATION OF COMBUSTION PRODUCT GAS AT STACK (Run A-9, August 12, 1976)

TABLE 7. GASEOUS PRODUCTS FROM COMBUSTION OF PYROTECHNIC COMPOSITION

Constituent	lb.-moles/lb. of Composition
P_4O_{10}	0.0043
CO_2	0.0022
O_2	0.000241x(a)
N_2	0.09062 + 0.000906x
H_2O	0.00910 + 0.000014x
TOTAL	0.10622 + 0.001161x

(a) x = excess air, percent

TABLE 8. COMBUSTION RESIDUE (ASH) FROM COMBUSTION OF PYROTECHNIC (RED PHOSPHORUS) COMPOSITION (DRY BASIS)

Constituent	lb./lb. of Composition
MnO	0.2660
MgO	0.1161
ZnO	0.03
Phosphorus Compounds(a)	0.2283
Others from Pyrolusite(b)	0.0096
TOTAL	0.65

(a) A part of the original phosphorus was assumed to remain in the residue as various forms of chemical compounds such as metal phosphates and/or metal phosphides.

(b) These include all the materials in pyrolusite other than MnO_2 and water.

Relationships between adiabatic flame temperature and excess combustion air were derived for (1) combustion of the red phosphorus composition alone and (2) combustion of the red phosphorus composition in the charge pan. The following assumptions were made in the derivations:

(1) Weight of the charge pan is 23.1 lb.

(2) Specific heat of stainless steel 316 is 0.12 Btu/lb.-°F in the temperature range of interest.

(3) Free water content of wet red phosphorus composition is 9 percent by weight.

(4) Heat of evaporation of water is 1000 Btu/lb. in the temperature range of interest.

(5) Metal canister and wrapping paperboard are removed from the red phosphorus composition prior to combustion.

(6) Specific heat of the combustion residue is 2.1 Btu/lb.-°F in the temperature range of interest.

(7) Specific heat of the combustion product gas is 7.5 Btu/lb.-mole-°F in the temperature range of interest.

(8) Heat of combustion of the red phosphorus composition is 6,520 Btu/lb. of composition.

For the combustion of the red phosphorus composition alone, the adiabatic flame temperature can be expressed as:

$$T_a = \frac{60.97x + 6,490}{0.871x + 0.980}$$

where T_a is the adiabatic flame temperature and x stands for excess combustion air by percent. For the combustion in the charge pan, the adiabatic flame temperature can be expressed as:

$$T_a = \frac{60.97Wx + 6,490W + 194}{0.871Wx + 0.98W + 2.77}$$

where W indicates the weight of dry red phosphorus composition charged into the incinerator. The above relationships are plotted in Figure 28. For comparison, the maximum temperatures of the combustion product gas obtained from the pilot plant operations are shown in the same figure and in Table 9. The estimated adiabatic flame temperatures are not in good agreement with the maximum temperatures of the combustion product gas in pilot plant operations. This may be attributed to the facts:

(1) Chamber 1 was not preheated and thus a large portion of the heat generated in the combustion must be used in heating the chamber.

(2) Half of the total combustion air was supplied to Chamber 2 and thus at the peak of the combustion, oxygen must be insufficient in the charge pan and Chamber 1. Unburned phosphorus vapor would be incinerated in Chamber 2 where the temperature was maintained at least a preset point (i.e., 800°F or higher) by using an auxiliary fuel (i.e., gas burner).

(3) In actual pilot plant operation, an adiabatic condition cannot be maintained in the incinerator due to heat loss through the walls.

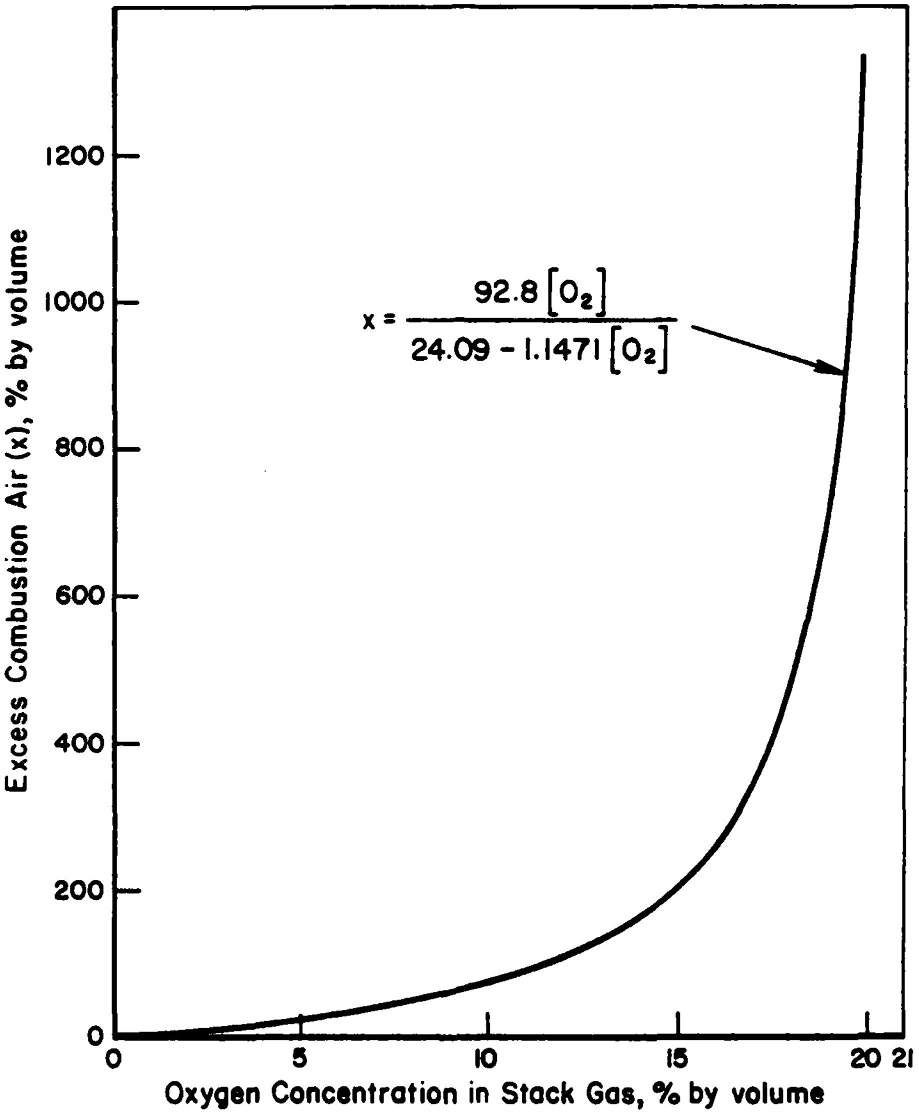


FIGURE 27. EXCESS COMBUSTION AIR AS A FUNCTION OF OXYGEN CONCENTRATION IN STACK GAS

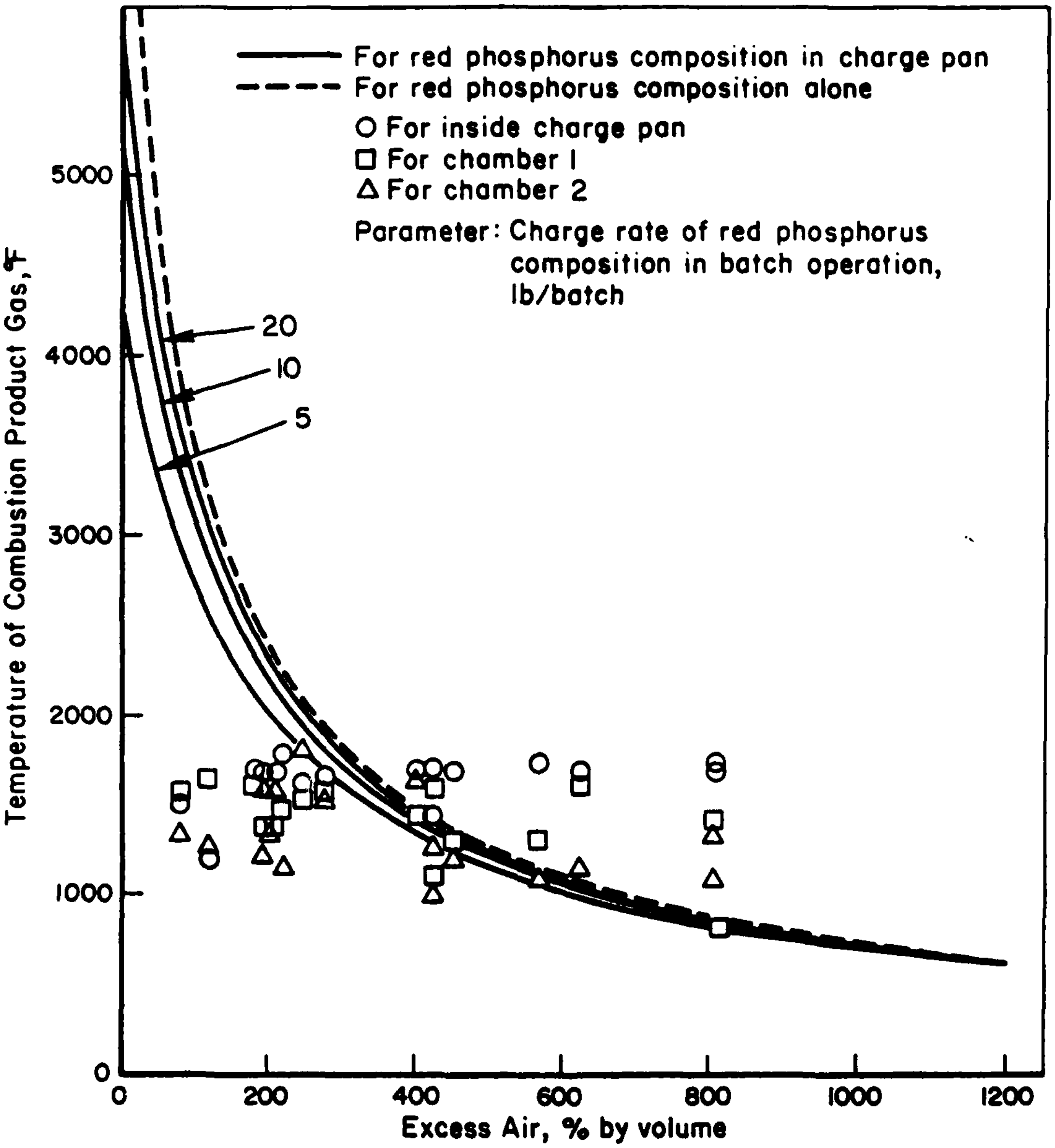


FIGURE 28. ESTIMATED ADIABATIC FLAME TEMPERATURE OF RED PHOSPHORUS COMPOSITION AND MAXIMUM TEMPERATURES OF COMBUSTION PRODUCT GAS AS A FUNCTION OF AVERAGE EXCESS COMBUSTION AIR

TABLE 9. MAXIMUM TEMPERATURES OF COMBUSTION PRODUCT GAS AND EXCESS COMBUSTION AIR IN PILOT PLANT OPERATION

Run No.	Weight of Dry Composition, lb	Oxygen Concentration in Combustion Product Gas, %		Excess Combustion Air, %		Temperature, °F		
		Minimum	Average	Minimum	Average	Charge Pan	Chamber 1	Chamber 2
9	3.87	17.17	18.50	598	813	1,700	800	1,000
A-1	15.24	13.7	16.28	152	279	1,640	1,580	1,570
A-2	9.33	18.1	19.11	505	818	1,710	1,420	1,340
A-8	9.27	15.6	17.85	234	458	1,690	1,280	1,200
A-9	9.45	16.8	18.38	324	567	1,730	1,290	1,080
A-10	9.16	15.5	17.64	228	425	1,430	1,600	1,250
A-11	9.10	16.8	18.59	324	624	1,680	1,610	1,130
A-12	18.20	11.1	15.76	91	243	1,620	1,520	1,800
A-13	4.55	16.0	17.64	259	425	1,700	1,080	980
A-14	9.10	12.0	15.34	108	219	1,770	1,460	1,150
A-15	9.10	10.7	14.61	84	185	1,660	1,600	1,220
A-16	9.10	12.0	15.02	108	203	1,600	1,530	1,110
A-17	9.10	3.2	10.51	15	81	1,520	1,560	1,330
A-18	9.10	6.7	12.50	38	119	1,200	1,660	1,280
A-19	9.10	13.2	15.76	137	243	1,650	1,620	1,320

Chemistry of Potential Problem Areas Associated with Combustion of Red Phosphorus Composition

The following observations were noted in at least one experiment during the course of the pilot plant study.

- Generation of white smoke (combustion) wh [illegible] earing P_2O_5 from cooled combustion chamber wall [illegible] ot plant operation.

- Recovered scrubber fluid smokes when solution is shaken after standing overnight.

- Release of spontaneously combustible gas from fresh ash quenched in water versus no release from ash which had been exposed to ambient air overnight and then quenched with water.

An attempt was made to describe the chemistry probably taking place during and after combustion that might explain such observations.

Generation of Smoke During Clean-Up. During the runs, the thermal history of the walls of the primary combustion chamber were not recorded. However, the thermal history measured elsewhere suggests that the walls of the primary combustion chamber are only at 100 to 150°F (38 to 66°C) when the phosphorus charge was placed into the chamber and then ignited by means of the burner. Under such conditions, the burning red phosphorus provides sufficient heat to vaporize some of the phosphorus which could condense as white phosphorus on the walls. Because of the low levels of air in the chamber during this period, the white phosphorus is not consumed. As the temperature and oxygen levels increase in the chamber during the course of a run and the oxidation of the phosphorus vapor is more complete, P_4O_{10} also condenses on the walls of the chamber (sublimation temperature 347°C or 653°F). This coating of P_4O_{10} would protect the unreacted phosphorus on the chamber walls from contact with air even at more elevated temperatures and also reduce the rate of diffusion of condensed phosphorus back into the chamber at higher wall temperatures. Under such conditions, a small amount of white phosphorus would be expected to remain unreacted on the walls after cool-down. This would explain the observation of smoke formation as the walls are scraped to remove the material coated on the walls after standing overnight. The smoke formation more than likely is attributed to the burning of the freshly exposed phosphorus. The likelihood of the source of smoke being the oxidation of P_4O_6 or P_4O_8 occluded in the P_4O_{10} is less but cannot be ruled out because of the uncertainty of the wall temperature (P_4O_6: melting point 23.8°C (75°F), boiling point 173°C (343°F)).

The problem might be alleviated by preheating the chamber to at least near the boiling point of white phosphorus (i.e., near 287°C (549°F)). It also may not be a problem when a continuous mode of charging is developed.

Scrubber Solution Fuming. Because of the high temperature and excess of air that exist in the second chamber, it is anticipated that all of the phosphorus vapor generated in the first chamber is oxidized to P_4O_{10} before it leaves the incinerator and P_4O_{10} in the combustion product gas would be absorbed in the scrubbers. However, when dry composition was burned, white smoke was generated from the recirculating scrubbing acid. On such occasions, the smoke would disappear on standing overnight, but by shaking or recirculating the scrubber solutions, the air space would be filled with white smoke.

For such behavior to exist, some phosphorus must be present as a lower oxide or elemental phosphorus dissolved in the aqueous phase. White phosphorus is soluble in water to the extent of 33 ppm at room temperature. The solubility in phosphoric acid may be different. Unreacted phosphorus might end up being transported through the combustion chambers during periods when the amount of oxygen is closer to stoichiometric.

The existence of oxides of phosphorus lower than P_4O_6 or P_4O_8 have been ruled out in the literature. However, both these oxides will form during the combustion of elemental phosphorus during slow oxidation due to a limited supply of oxygen (along with the conversion of part of the white phosphorus to the red form). When these oxides react with hot water, phosphine formation can occur which in turn could be oxidized to form the smoke observed. A determination of trivalent phosphorus (as H_3PO_3) in the acid value recovered (in those cases where smoke formed when the scrubber fluid was shaken) was not performed. Therefore, this possibility may still exist.

Under steady-state operation when the oxygen and phosphorus are being utilized completely, such behavior would not be anticipated. Therefore, this problem may not exist in a continuous operation when careful control of combustion is possible.

Release of Spontaneously Ignitable Gas from Water-Quenched Ash. In the primary combustion chamber, the red phosphorus composition attains temperatures sufficiently high enough to vaporize red phosphorus. The pan containing the phosphorus charge underwent temperature excursions up to 1600°F (870°C) during the combustion cycle. If the unburned phosphorus mass attains a temperature of 800 to 1000°F (427 to 540°C), then reaction of the phosphorus with the MnO_2, ZnO, and Mg to form the respective phosphides can occur (8,9,10,11).

$$3\text{Mg} + 2\text{P}_{(\text{red})}\left(\text{or P}_{(\text{vapor})}\right) \xrightarrow{500^\circ\text{C}} \text{Mg}_3\text{P}_2(\text{s})$$

$$\text{ZnO} + \text{P}_{(\text{red})}\left(\text{or P}_{(\text{vapor})}\right) \xrightarrow{\text{glowing}} \text{Zn}_3\text{P}_2(\text{ZnP}_2 \text{ and } \text{Zn}_3(\text{PO}_4)_2)$$

$$\text{MnO}_2 + \text{P}_{(\text{red})} \xrightarrow{\text{heat}} \text{Mn}_3\text{P},\ \text{Mn}_2\text{P},\ \text{MnP}\ (\text{Mn}_3(\text{PO}_4)_2)$$

On those occasions when the ash was quenched shortly after an experiment, a spontaneously combustible gas was released. Analysis of the trapped gas showed it to be principally phosphine (see Table 10 for the composition). Its behavior on exposure to air suggests that diphosphine is an impurity which causes the ignition. Of the phosphides that might form, both Mg_3P_2 and Zn_3P_2 (and ZnP_2) hydrolyze readily in water to produce phosphine (and some diphosphine). They are also unstable in moist air. The transition metal phosphides such as MnP, Mn_2P, and Mn_3P are usually not attacked by water but may be attacked by hot mineral acids to form phosphine-diphosphine mixtures. The presence of any residual P_4O_{10} or acid phosphate in the ash can form the acid to hydrolyze these types of phosphides. The presence of acid also helps the hydrolysis of Zn_3P_2 and Mg_3P_2.

Prolonged exposure to moist air will reduce the phosphide concentration to low levels. However, if the rapid cooling of the ash is needed, it might best be treated with sprayed water or steam, followed by combustion of the phosphine-diphosphine mixture released.

TABLE 10. COMPOSITION OF OFF-GAS FROM ASH-WATER REACTION

Compound	Percent by Volume		
	Run A-17[(a)]	Run A-18[(a)]	Run A-19[(a)]
CO_2	0.5	0.12	0.02
A	0.5	0.23	0.25
PH_3	57.0	81.10	79.00
N_2	34.0	14.60	16.10
H_2	8.0	3.97	4.59
O_2	< 1.	< 1.	< 1.
TOTAL	100.0	100.02	99.96

(a) The reaction container was initially filled with water.

Analysis of Scrubber Performance

The hot combustion product gas from the incinerator was cooled due to heat loss from the process line between the incinerator and scrubber. The maximum temperature at the inlet of the scrubber is usually less than 1,100°F. The scrubber consisting of a spray tower and packed column was able to cool the gas to temperatures less than 200°F. Insufficient cooling occasionally resulted from pluggages in the acid pump or flooding in one of the columns. The pluggages in the acid pump were caused by fly ash collected by the scrubber and circulated with the acid or packing debris. Flooding in the spray tower was often caused by high spraying rates and/or pluggages in the packings due to fly ash collected by the scrubber. Flooding in the packed column was due to smaller packings installed at the early stage of the pilot plant study.

The cooling of hot combustion gas in the scrubber was achieved mainly by evaporation of water in the scrubbing acid. In order to analyze the performance of the scrubber quantitatively, the following assumptions were made:

(1) Excess combustion air for the combustion of red phosphorus composition is 300 percent.

(2) The combustion product gas is cooled from the adiabatic flame temperature of 1,729°F (based on 300 percent excess combustion air) to 1,053°F over the process line between the incinerator and the scrubber.

(3) Cooling of hot combustion gas in the scrubber can be achieved by evaporation of water in the scrubbing acid. (Possible maximum deviation from the assumption would be less than 5 percent.)

(4) Time required for combustion of 10 lb. of red phosphorus composition is 15 minutes and the rate of combustion over the period is uniform.

(5) Phosphorus remained in ash after combustion is 0.043 lb.-mole/10 lb. of dry composition and phosphorus recovered as the condensed acid in the process line between the incinerator and the scrubber is 0.06 lb.-moles/10 lb. of dry composition.

(6) Exothermic heat ($-\Delta H_3$) generated from absorption of P_4O_{10} in water to form phosphoric acid is 1,560 Btu/lb. of phosphorus.

Based on the assumptions, the following information can be derived. Combustion product gas at the inlet of the spray tower (G) = 0.295 lb.-moles/min.

Heat to be removed in the scrubber (Q) = $G\ c_p\ (1{,}053 - T_s) + (-\Delta H_s)\ (F_p)$

Water to be evaporated in the scrubber (q_w) = $\frac{Q}{\Delta H_v}$

where c_p = specific heat of the combustion product gas, 7.5 Btu/lb.-mole-°F

T_s = temperature of scrubbed gas at the exit of the scrubber, °F

F_p = mass flow rate of phosphorus in P_4O_{10} to be scrubbed, 0.1405 lb. of P/min

ΔH_v = heat of vaporization of water at scrubber operating temperature, Btu/lb. of water.

Evaporation of water at the scrubber increases the vapor pressure of water in the gas stream. The vapor pressure should be close to the equilibrium pressure of the acid leaving the scrubber. The vapor pressure of phosphoric acid as a function of temperature and concentration is shown in Figures 29 and 30, and the density of the phosphoric acid at various concentrations is shown in Figure 31.

Heat balances were taken around the scrubber operating at various temperatures and the results are shown in Table 11 and Figure 32.

Material balances were made for phosphorus around the scrubber based on the following assumptions:

(1) Operating temperature of the scrubber is 180°F.

(2) Phosphorus recovered as phosphoric acid in the scrubber is 0.068 lb.-moles/10 lb. of dry composition.

(3) Concentration of product acid from the scrubber is 60 percent by weight.

(4) Acid mist carryover from the scrubber is 620 mg of P_2O_5/scf of gas on dry basis. The acid is 60 percent by weight.

The resulting relationship is:

$$q_{sa} = \frac{155.4}{60 - C_{sa}}$$

where q_{sa} = phosphoric acid flow rate for scrubbing, lb./min

C_{sa} = concentration of the scrubbing acid, % by weight.

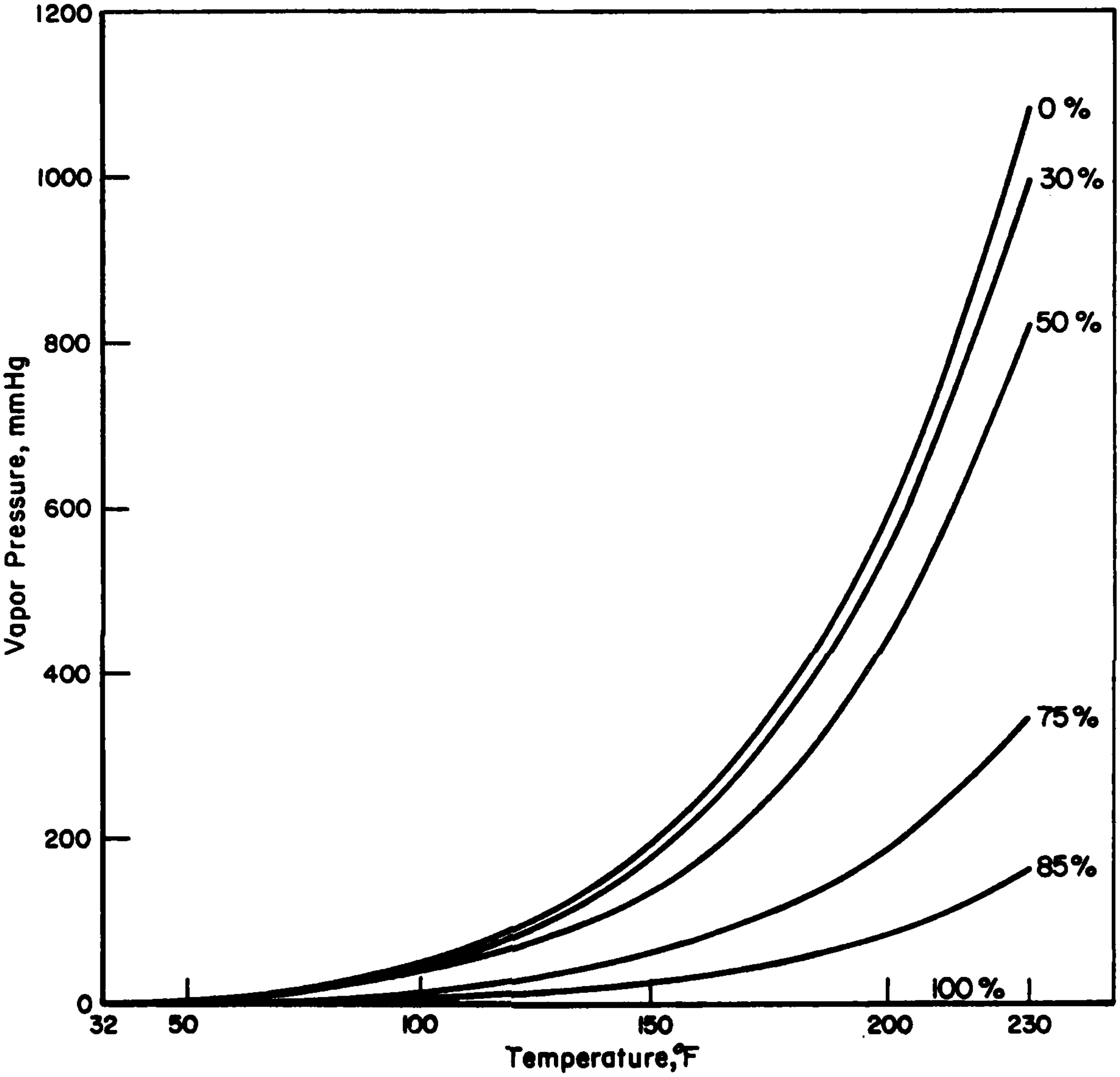


FIGURE 29. VAPOR PRESSURE OF H_3PO_4 SOLUTION AS A FUNCTION OF TEMPERATURE(12)

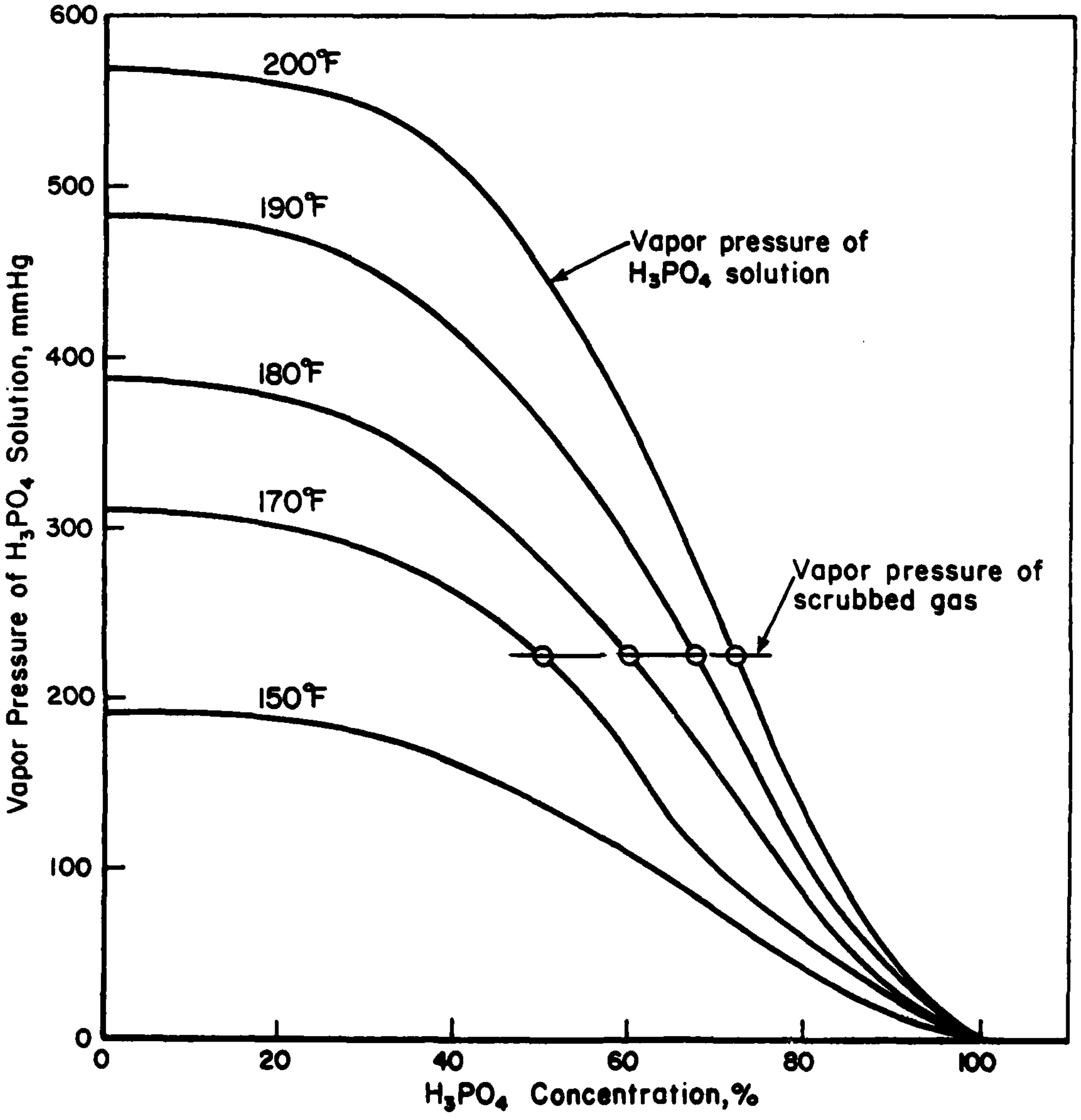


FIGURE 30. VAPOR PRESSURES OF H_3PO_4 SOLUTIONS AT VARIOUS TEMPERATURES AND SCRUBBED GAS(12)

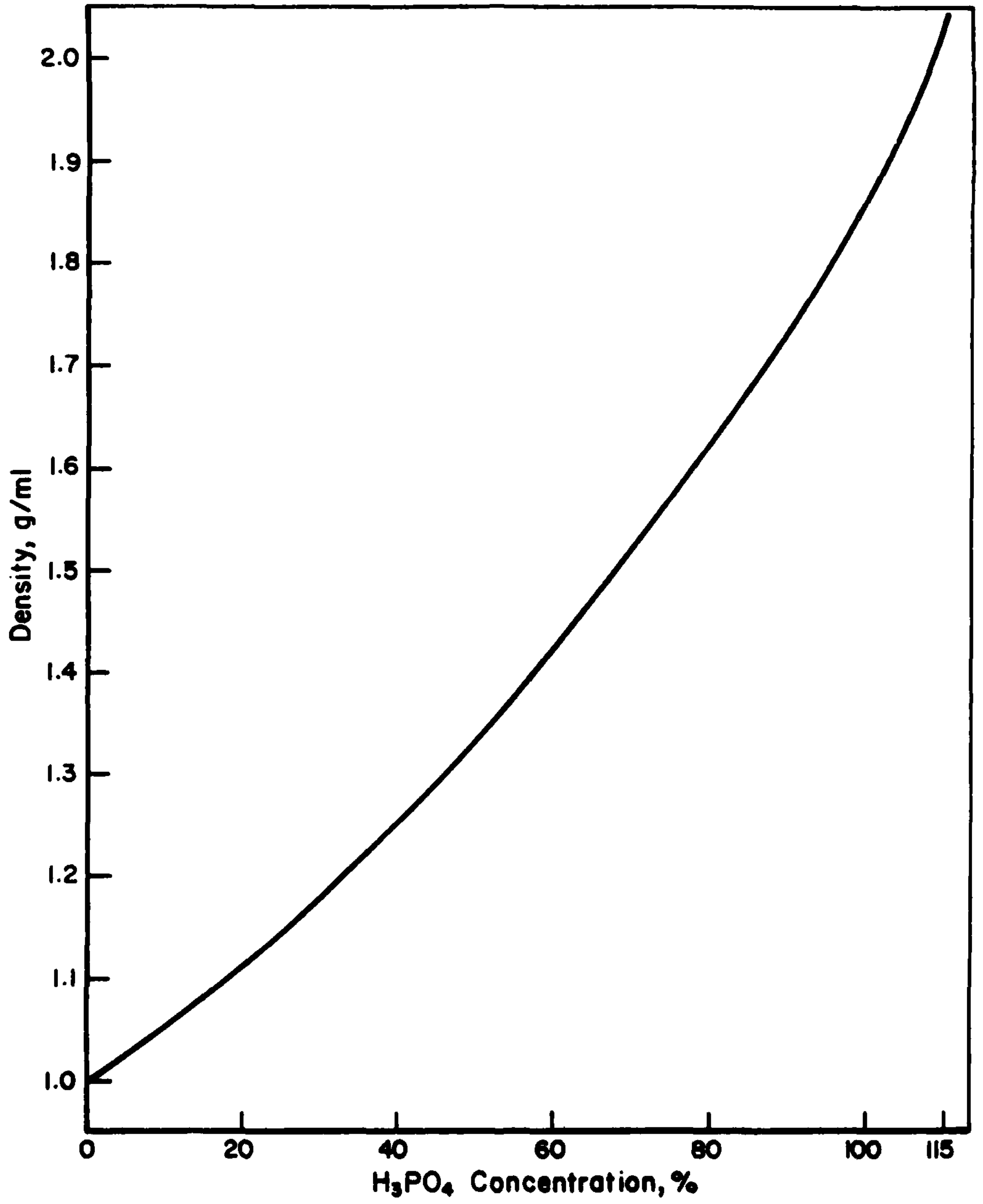


FIGURE 31. DENSITY OF PHOSPHORIC ACID AT VARIOUS CONCENTRATIONS(12)

TABLE 11. HEAT BALANCE AROUND SCRUBBER AT VARIOUS OPERATING TEMPERATURES

Item	Scrubber Operating Temperature, °F 170	180	190	200
Heat to be removed for cooling of gas (Q), Btu/min	2,173	2,151	2,128	2,106
Heat of vaporization (ΔH_v), Btu/lb.	996.1	990.2	984.1	977.8
Water to be evaporated (q_w), lb./min	2.182	2.172	2.162	2.154
Total water vapor output, lb.-moles/min	0.124	0.124	0.123	0.123
Total gas output, lb.-moles/min	0.416	0.416	0.415	0.415
Vapor pressure in outgoing gas stream, mm Hg	227	227	225	225
Equilibrium acid concentration from Figure 30, % by weight	50	60	67	72

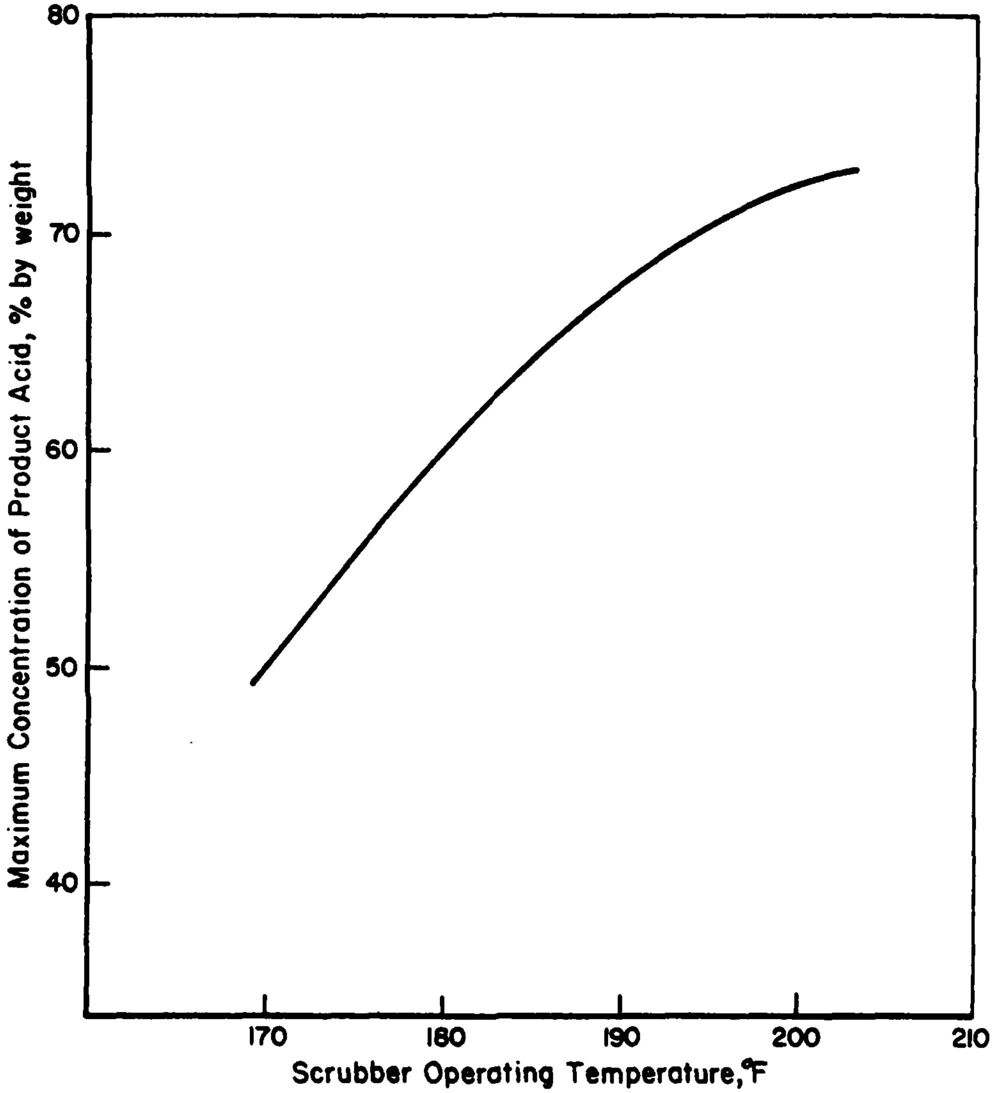


FIGURE 32. MAXIMUM CONCENTRATION OF PRODUCT ACID AS A FUNCTION OF SCRUBBER OPERATING TEMPERATURE BASED ON HEAT BALANCE

The relationship is plotted in Figure 33.

Another phosphorus balance was taken around the scrubber based on the use of 50 percent acid for scrubbing at the same operating temperature. The resulting equation is:

$$C_{pa} = \frac{50q_{sa} + 44.43}{q_{sa} - 1.85}$$

where C_{pa} = concentration of the product acid from scrubber, percent by weight

q_{sa} = flow rate of 50 percent scrubbing acid, lb./min

The relationship is plotted in Figure 34.

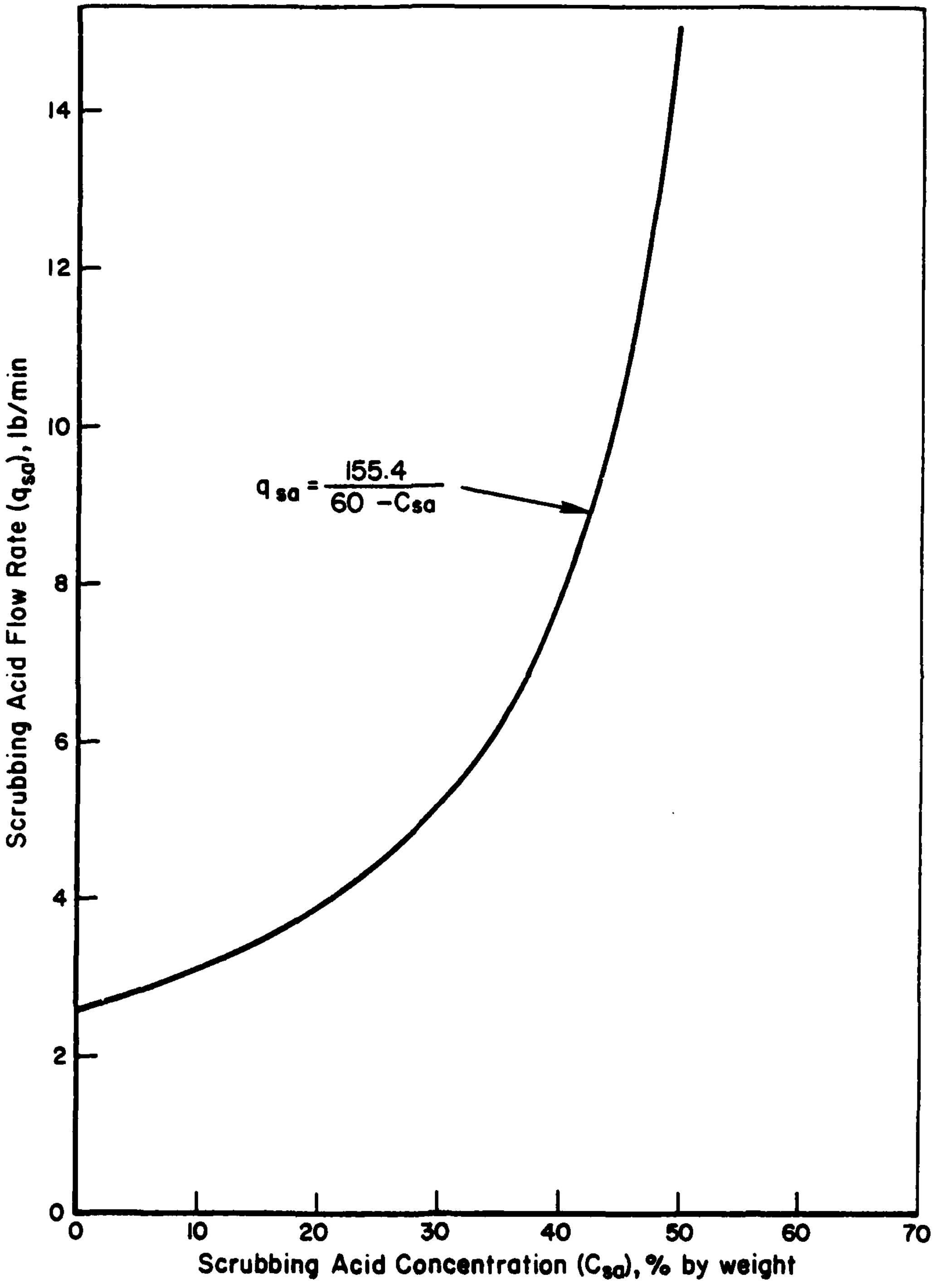


FIGURE 33. SCRUBBER ACID FLOW RATE AS A FUNCTION OF ACID CONCENTRATION TO PRODUCE 60% PRODUCT ACID

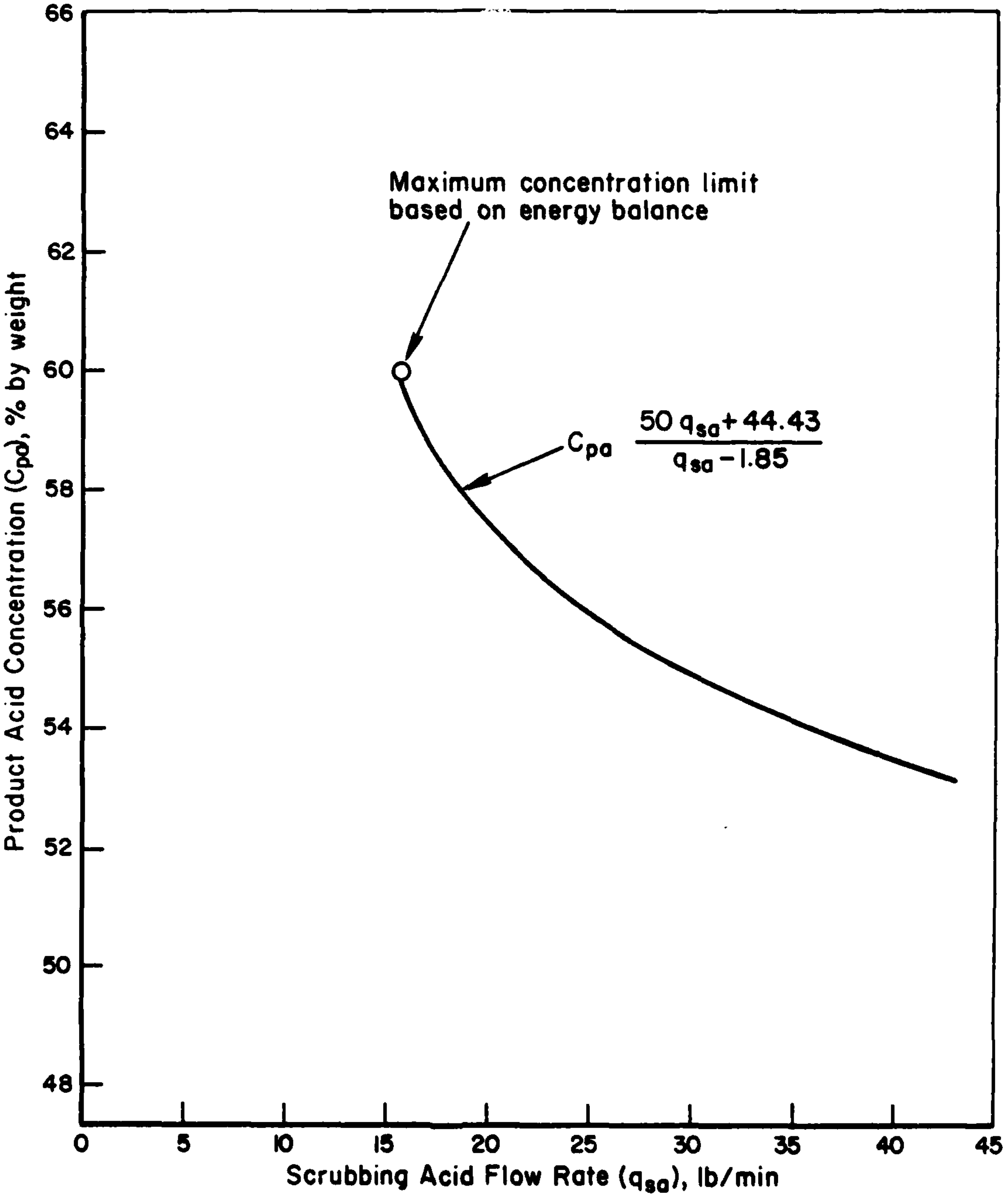


FIGURE 34. PRODUCT ACID CONCENTRATION AS A FUNCTION OF SCRUBBING ACID FLOW RATE AT THE CONCENTRATION OF 50% BY WEIGHT

Performance of Mist Eliminators

Twenty-one stack gas samples have been analyzed for the acid emission from the pilot plant using the Aerotherm high volume sampling system (EPA's Method 5 Sampling System). In addition, ten more samples were taken using the EPA's Method 6 sampling system, which uses impingers to examine the acid mist load to the York and the Brink mist eliminators of the pilot plant and the mist removal efficiency of the Brink mist eliminator. The results are summarized in Table 12.

The efficiency of the York mist eliminator was claimed at 99.9 percent for phosphoric acid at a pressure drop of 40 inches of water by the supplier. The actual efficiency of the mist eliminator in the pilot plant operations was measured at 91.6, 95.35, 95.66 and 98.47 percent with a pressure drop of 10 to 18 inches of water by the Aerotherm sampling system using the MSA filter. The emission from the mist eliminator ranged between 9.5 and 52.16 mg of P_2O_5/scf. The efficiency was increased to 98.35 to 99.95 percent with the median value of 99.49 percent when the pressure drop across the unit increased to 38 to 50 inches of water. The emission ranged between 0.32 and 10.23 mg of P_2O_5/scf. When the Gelman filters were employed in the Aerotherm sampling system, the efficiency of the York mist eliminator was measured at 99.61 to 99.97 percent with the median value of 99.95 percent. The emission from the York mist eliminator ranged 0.2 to 2.5 mg of P_2O_5/scf (mean 0.4 mg of P_2O_5/scf and average 0.79 mg of P_2O_5/scf).

The accuracy of EPA Method 5 sampling system for phosphoric acid analysis is greatly dependent on the pore size of the filter employed in the sampler. The Gelman fiber glass filter recommended for use with the Aerotherm sampling system by the supplier is not

TABLE 12. PERFORMANCE OF YORK AND BRINK MIST ELIMINATORS

Item	Test Run Number											
	7	8	10	20	A1	A2	A3	A4	A5	A6	A7	A8
<u>York Mist Eliminator</u>												
Flow Rate, scfm	130	132	133	136	123	108	107	120	112	119	118	105
Temperature, °F	165	165	165	165	165	155	155	160	155	150	155	155
Pressure Drop, in. of water	18	18	18	10	45	35	47	42	45	40	55	41
Inlet Gas												
Conc., mg of P_2O_5/scf	--	--	--	--	--	472.1	852.9	--	--	--	--	621.3
Sampling Method	--	--	--	--	--	M6(e)	M6	--	--	--	--	M6
Outlet Gas												
Conc., mg of P_2O_5/scf	27.0	28.9	9.5	52.2	10.23	6.8	1.5	99.5	0.3	25.7	3.2	0.3
Sampling Method	M5(a)	M5	M5	M5	M5	M5	M5	M5	M5	M5	M5	M5
Type of filter	MSA(b)	MSA	MSA	MSA	MSA	MSA	MSA	MSA	MSA	MSA	MSA	G(f)
Phosphorus Collected, lb.	1.081	0.847	0.626	2.117	2.513	1.235	1.393	0.521	1.011	1.100	0.455	1.019
Phosphorus Emitted, lb.	0.190	0.152	0.044	0.611	0.052	0.015	0.004	0.201	7×10^{-4}	0.085	0.008	5.6×10^{-4}
Removal Efficiency, %												
Based on P_2O_5 Conc.(c)	95.66	95.35	98.47	91.61	98.35	98.57	99.83	83.99	99.95	95.86	99.49	99.95
Based on P balance(d)	85.05	84.95	93.57	77.63	97.97	98.80	99.75	72.14	99.90	92.82	98.27	98.27
<u>Brink Mist Eliminator</u>												
Flow Rate, scfm	--	--	--	--	--	20	18	--	--	--	--	17
Temperature, °F	--	--	--	--	--	160	200	--	--	--	--	160
Pressure Drop, in. of water	--	--	--	--	--	34	46	--	--	--	--	43
Inlet Gas												
Conc., mg of P_2O_5/scf	--	--	--	--	--	472.1	852.9	--	--	--	--	621.3
Sampling Method	--	--	--	--	--	M6	M6	--	--	--	--	M6
Outlet Gas												
Conc., mg of P_2O_5/scf	--	--	--	--	--	0.6	1.7	--	--	--	--	2.4
Sampling Method	--	--	--	--	--	M6	M6	--	--	--	--	M6
Phosphorus Collected, lb.	--	--	--	--	--	0.104	0.138	--	--	--	--	0.063
Phosphorus Emitted, lb.	--	--	--	--	--	2.5×10^{-4}	6.8×10^{-4}	--	--	--	--	7.8×10^{-4}
Removal Efficiency, %												
Based on P_2O_5 Conc.	--	--	--	--	--	99.87	99.80	--	--	--	--	99.61
Based on P balance	--	--	--	--	--	99.76	99.51	--	--	--	--	98.77

TABLE 12. PERFORMANCE OF YORK AND BRINK MIST ELIMINATORS (Continued)

Item	A9	A10	A11	A12	A13	A14	A15	A16	A17
<u>York Mist Eliminator</u>									
Flow Rate, scfm	106	123	116	110	116	116	110	110	119
Temperature, °F	150	150	150	165	150	150	160	160	170
Pressure Drop, in. of water	41	46	39	50	49	48	51	51	47
Inlet Gas									
Conc., mg of P_2O_5/scf	621.5	903.0	--	--	--	--	--	--	--
Sampling Method	M6	M6	--	--	--	--	--	--	--
Outlet Gas									
Conc., mg of P_2O_5/scf	0.2	0.87 (3.6)(g)	0.4	2.4	0.2	0.4	1.3	1.0	62.1
Sampling Method	M5	M5 (M6)	M5	M5	M5	M5	M5	M5	M5
Type of filter	G	G (-)	G	G	G	G	NP(h)	NP	G
Phosphorus Collected, lb.	0.987	1.240	1.677	1.823	0.997	1.771	1.829	1.744	0.651
Phosphorus Emitted, lb.	4.4×10^{-4}	0.0021 (0.0085)	9×10^{-4}	0.006	5×10^{-4}	0.001	0.002	0.002	0.125
Removal Efficiency, %									
Based on P_2O_5 Conc.(c)	99.97	99.90 (99.60)	99.94	99.61	99.97	99.94	99.79	99.84	90.01
Based on P balance(d)	99.95	99.96 (99.32)	99.95	99.70	99.95	99.94	99.87	99.88	83.86
<u>Brink Mist Eliminator</u>									
Flow Rate, scfm	17	--	--	--	--	--	--	--	--
Temperature, °F	150	--	--	--	--	--	--	--	--
Pressure Drop, in. of water	42	--	--	--	--	--	--	--	--
Inlet Gas									
Conc., mg of P_2O_5/scf	621.5	--	--	--	--	--	--	--	--
Sampling Method	M6	--	--	--	--	--	--	--	--
Outlet Gas									
Conc., mg of P_2O_5/scf	2.2	--	--	--	--	--	--	--	--
Sampling Method	M6	--	--	--	--	--	--	--	--
Phosphorus Collected, lb.	0.114	--	--	--	--	--	--	--	--
Phosphorus Emitted, lb.	7.5×10^{-4}	--	--	--	--	--	--	--	--
Removal Efficiency, %									
Based on P_2O_5 Conc.	99.65	--	--	--	--	--	--	--	--
Based on P balance	99.35	--	--	--	--	--	--	--	--

FOOTNOTES FOR TABLE 12

(a) M5 indicates the EPA Method 5 sampling system which employs a filter prior to impingers.

(b) MSA indicates a glass fiber filter supplied by Mine Safety Appliance. The filter has a collection efficiency of 99.999% on particles of 1/3 $_{\mu}$m or larger in diameter.

(c) The values were obtained by dividing the P_2O_5 concentration of outlet gas by that of inlet gas to the mist eliminators. When the measured concentrations were not available for inlet gas, the median value of the five samples collected, i.e., 621.5 mg of P_2O_5/scf was used in the computations.

(d) The values were obtained by dividing the total phosphorus emission by the sum of the total phosphorus collection in the mist eliminator and the total phosphorus emission from the mist eliminator.

(e) M6 indicates the EPA Method 6 sampling system which employs impingers only.

(f) G indicates a glass fiber filter supplied by Gelman Instrument Company. This filter was recommended for use in the EPA Method 6 sampling system by Aerotherm Acurex Corporation, the supplier of the sampling system.

(g) The values in parentheses indicate the corresponding information obtained by the EPA Method 6 sampling system.

(h) NP indicates a polycarbonate membrane filter supplied by Nuclepore Corporation. The maximum pore size of the filter is 0.4 $_{\mu}$m.

considered adequate for the analysis of phosphoric acid mist emission since the pore size of the filter (between 0.2 and 10 microns) is relatively large as compared with the size of the acid mist (the size of the acid mist ranges from 0.4 to 2.6 microns with a mass median diameter of 1.6 microns). The Mine Safety Appliance (MSA) fiber glass filter used in the earlier test runs is considered better than the Gelman filter because of the small pore size (the collection efficiency of the MSA filter is 99.99 percent on particles of 1/3 micron or larger in diameter).

The acid mist load to the York or Brink mist eliminator was measured at 470 to 910 mg of P_2O_5/scf by an EPA Method 6 sampling system. The median value of the five samples collected is 621.5 mg of P_2O_5/scf.

The efficiency of the Brink mist eliminator was claimed at 99.5 percent for particles larger than 3 microns at a pressure drop of 8 to 12 inches of water. The actual efficiency was measured at 99.61 to 99.87 percent with a pressure drop of 38 to 50 inches of water by EPA Method 6 sampling system. The median value is 99.65 or 99.80 percent. The measured acid emission from the mist eliminator ranges from 0.6 to 2.42 mg of P_2O_5/scf.

The performance of the York mist eliminator as a function of pressure drop is graphically shown in Figure 35 and 36, based on phosphorus balance and P_2O_5 concentration in stack gas stream, respectively. A similar plotting is shown in Figure 37 for the Brink mist eliminator.

Currently, U.S. Environmental Protection Agency has not established any emission standard for P_2O_5 for commercial phosphoric acid plants. However, the Ammunition Procurement and Supply Agency (APSA) standards for air emissions set the limit of acidity emissions at 50 mg/NM^3, which corresponds to 1.4 mg of H_3PO_4/scf or 1.0 mg of P_2O_5/scf(13).

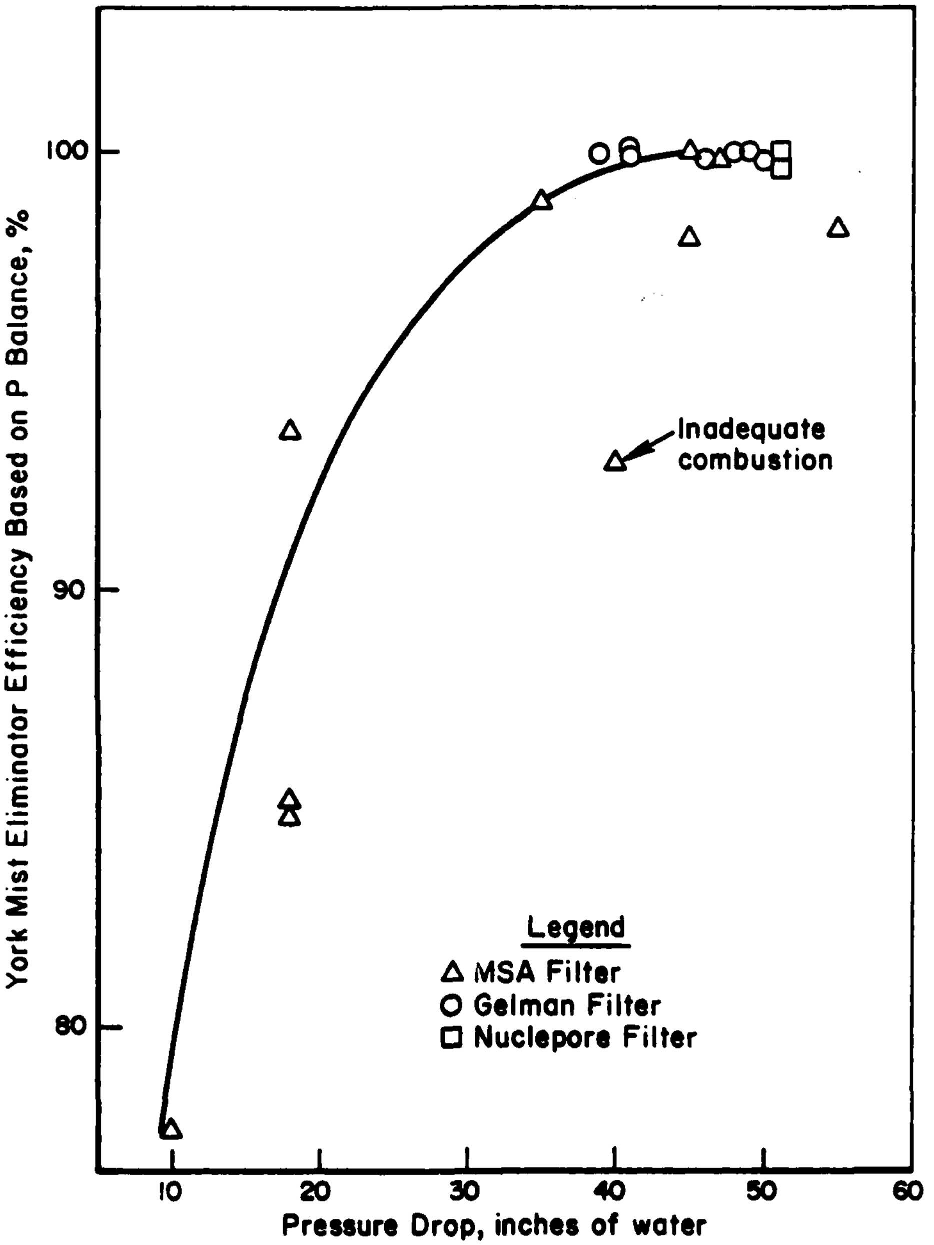


FIGURE 35. YORK MIST ELIMINATOR EFFICIENCY BASED ON PHOSPHORUS BALANCE AS A FUNCTION OF PRESSURE DROP

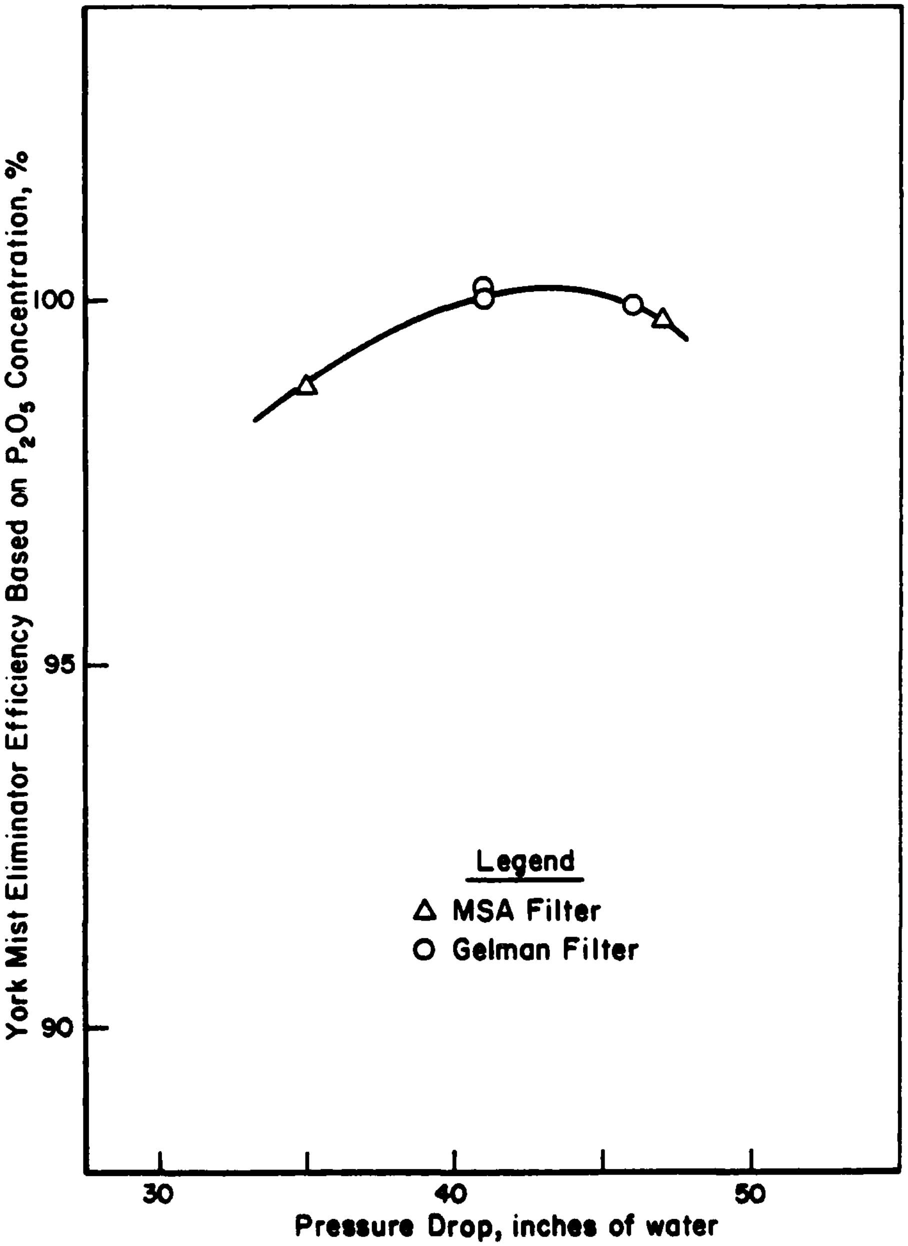


FIGURE 36. YORK MIST ELIMINATOR EFFICIENCY BASED ON P_2O_5 CONCENTRATION AS A FUNCTION OF PRESSURE DROP

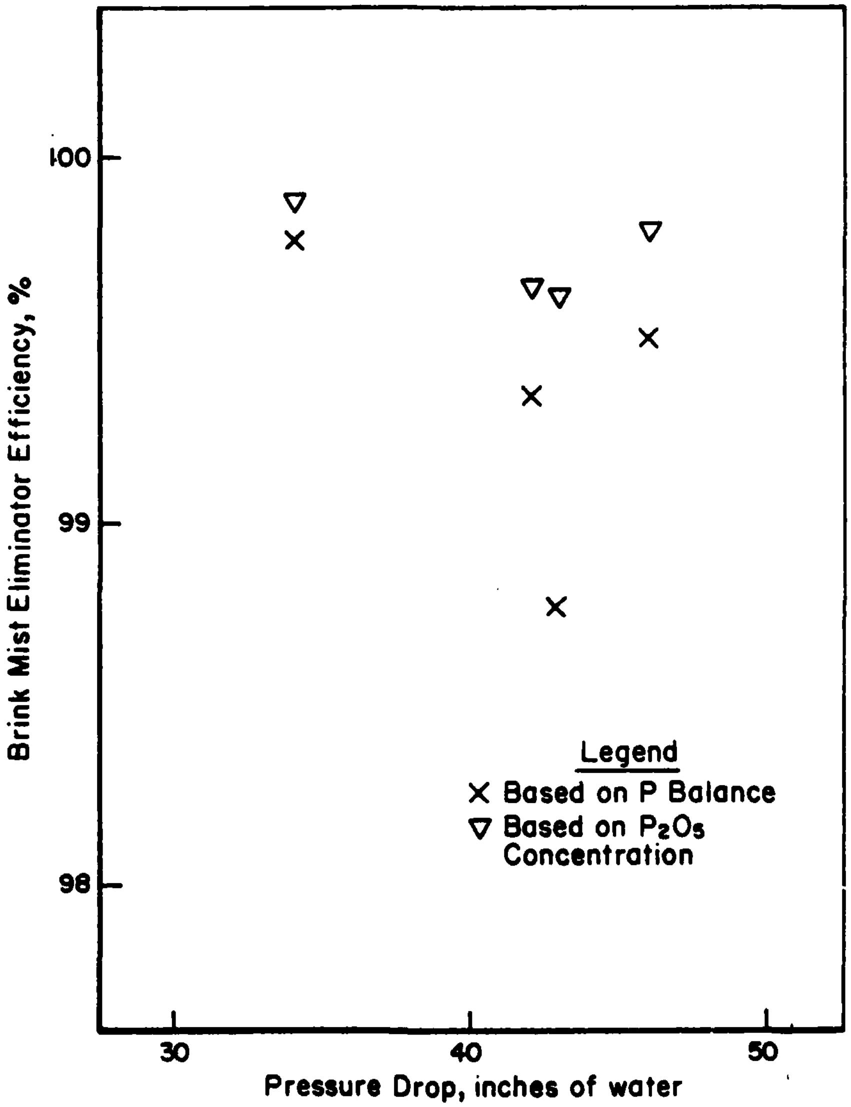


FIGURE 37. BRINK MIST ELIMINATOR EFFICIENCY VS. PRESSURE DROP

Acid Yield

In order to examine the overall operation of the pyrotechnic combustion pilot plant, material and heat balances were made throughout the entire process flow. The layout of the pilot plant is shown in Figure 38 and the results of the material and heat balances are given in Table 13. While recovery of acids condensed in the incinerator and the process line between the incinerator and the scrubber can be recovered as a usable acid, the acid yield of the process, which is defined as the ratio of phosphorus recovered as acid and lost through the stack to phosphorus in feed composition, can be estimated at around 40 to 75 percent based on phosphorus balance for the overall plant.

Phosphorus balances were made using the actual pilot plant operation data and the results are given in Table 14. The acid yield ranged from 22 to 60 percent with the mean value of 41.2 percent and the average value of 40.7 percent. Phosphorus lost through the stack as acid mist could be maintained at less than 0.05 percent of the feed with an adequate operation of the mist eliminator. Total phosphorus remaining with the combustion residue (ash) ranged between 21.3 and 29.2 percent of the feed. Phosphorus which was not recovered in any form of sample during the pilot plant operations ranged from 10.8 to 50.5 percent of the feed with the mean value of 35 percent.

Concentrations of the product acid from the scrubber depends on the initial concentration, the spraying rate, and the makeup water flow rate. Concentrations of the product acid from the mist eliminator depends on the concentration of the scrubbing acid and the amount of water sprayed over the element from the built-in nozzle. Without spraying water, the concentration of the product acid collected at the mist eliminator is often higher than that collected at the scrubber (see Table 5 for the concentrations of the product

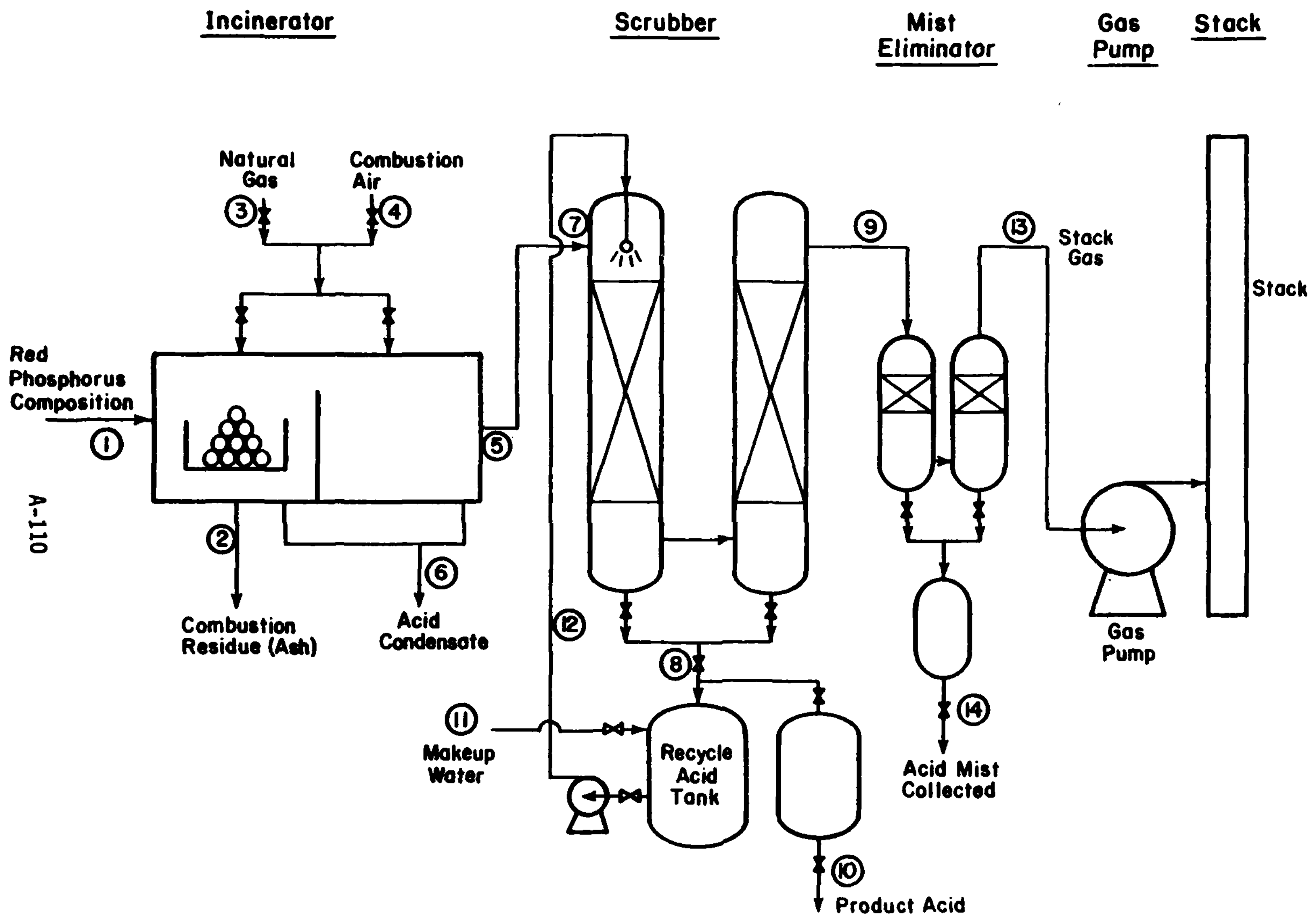


FIGURE 38. LAYOUT OF PYROTECHNIC COMBUSTION PILOT PLANT FOR MATERIAL AND HEAT BALANCES

TABLE 13. STREAM COMPOSITIONS OF PYROTECHNIC COMBUSTION PROCESSES FOR RED PHOSPHORUS COMPOSITION

Load: 10 lb Composition/Batch, Processing Period: 15 min/Batch

Stream Number	1	2	3[f]	4	5[i]	6	7	8	9	10	11	12	13	14
Temperature, °F	70	70	70	70	1,729	70	1,053[j]	180	180	180	70	180	160	160
Pressure, atm	1	1	1	1	1	1	1	1	1	1	1	1	50 inch vacuum	50 inch vacuum
Gas Composition, Mole Percent														
P_4O_{10}			--	--	0.58		0.58		0				0	
[illegible]			0.8	--	0.50		0.50		0.35				0.35	
[illegible]			3.2	79.0	81.83		81.83		58.20				58.20	
[illegible]			--	21.0	16.32		16.32		11.61				11.61	
CH_4			96.0	--	0		0		0				0	
H_2O			--	--	0.97		0.97		29.83				29.83	
Others			--	--	0		0		Acid Mist[k]				Acid Mist[l]	
Total			100.0	100.0	100.0		100.0		99.99				99.99	
Liquid Composition, Weight Percent														
H_3PO_4						100.0		60.0		60.0	0.0	50.0		60.0
H_2O						0.0		40.0		40.0	100.0	50.0		40.0
Total						100.0		100.0		100.0	100.0	100.0		100.0
Solid Composition, Weight Percent (dry basis)														
Red Phosphorus	53.0	0.0												
Pyrolusite	34.0	0.0												
Mg	7.0	0.0												
ZnO	3.0	4.6												
Organic Binder	3.0	0.0												
Phosphorus Compounds	0.0	35.1[a]												
MnO	0.0	40.9[b]												
MgO	0.0	17.9[c]												
Others	0.0	1.5[d]												
Total	100.0	100.0												
Total Flow Rate														
Gas, lb-mole/min			6.5×10^{-3}[g]	0.242	0.295		0.295		0.415				0.415	
acfm			2.5[g]	88.5	471.		326		194				167	
Liquid, gpm						0.025		1.120		0.032	0.311	1.399		0.0561
lb/min						0.392		13.331		0.381	2.59	15.54		0.359
Solid, lb/min	0.667[h]	0.433[e]												

FOOTNOTES FOR TABLE 13

(a) The value was obtained based on the balance of weight. The total phosphorus in the ash was estimated at about 20 percent.

(b) MnO_2 in the pyrolusite was assumed to be converted to MnO during combustion.

(c) Elemental magnesium in the red phosphorus composition was assumed to be converted to MgO during combustion.

(d) The others include materials in the pyrolusite other than MnO_2 and water.

(e) The value was assumed based on the pilot plant test data. That is, about 65 percent of the weight of the dry red phosphorus composition feed remained as the weight of the combustion residue.

(f) Natural gas is used only for preheating of the incinerator and ignition of the feed material.

(g) This represents natural gas burning rate during preheating period. The value should be double during the ignition period because both burners operate.

(h) This represents solid mass flow rate on dry basis. In the actual operation, the feed is stored in water and the water content of the feed is approximately 9 percent by weight.

(i) Excess combustion air was assumed at 300 percent.

(j) This represents the average maximum temperature of the combustion product gas at the inlet of the scrubber based on 15 pilot plant experimental data. The decrease in temperature is due to heat loss from the process line.

FOOTNOTES FOR TABLE 13 (Continued)

(k) The gas stream leaving the scrubber contains 620 mg of P_2O_5/scf on dry basis equivalent to 0.359 lb. of 60 percent phosphoric acid per minute.

(l) After the mist eliminator, the gas contains 0.62 mg of P_2O_5/scf on dry basis.

TABLE 14. PHOSPHORUS BALANCE IN PYROTECHNIC COMBUSTION PILOT PLANT

Item	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
P in Feed, lb	0.39	1.17	1.17	3.52	2.57	2.05	2.17	2.23	2.05	3.93	4.03	3.96	3.23	3.91	4.25	4.16	7.84
P Recovered as Acid,																	
Weight, lb	NA$^{(b)}$	NA	NA	0.58	1.39	0.52	0.85	0.19	1.46	2.04	0.73	1.29	1.10	1.58	1.48	2.22	2.84
Percentage of feed, %	NA	NA	NA	16.5	54.1	25.4	39.2	8.5	71.2	51.9	18.1	32.6	34.1	40.4	34.8	53.4	36.2
P Lost through Stack,																	
Weight, lb	NA	NA	NA	0.19	0.15	NA	0.043	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.61
Percentage of feed, %	NA	NA	NA	5.4	5.9	NA	2.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	7.8
P in Combustion Residue,																	
Weight, lb	0.11	0.32	0.32	0.97	0.75	0.51	0.52	0.54	0.49	1.13	0.86	0.99	0.80	1.07	1.11	1.04	2.00
Percentage of feed, %	28.2	27.4	27.4	27.6	29.2	24.9	24.0	24.2	23.9	28.8	21.3	25.0	24.8	27.4	26.1	25.0	25.5
Balance of P																	
Weight, lb	NA	NA	NA	1.78	0.28	NA	0.76	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.39
Percentage of feed, %	NA	NA	NA	50.5	10.8	NA	34.8	NA	NA	NA	NA	NA	NA	NA	NA	NA	30.5
Acid Yield$^{(a)}$, %	NA	NA	NA	21.9	60.0	NA	41.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	44.0

Item	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10	A-11	A-12	A-13	A-14	A-15	A-16	A-17	A-13	A-19
P in Feed, lb	8.08	4.94	4.55	5.45	4.85	4.29	4.40	4.91	5.01	4.85	4.82	9.65	2.41	4.82	4.82	4.82	4.82	4.82	4.82
P Recovered as Acid,																			
Weight, lb	3.80	1.64	1.42	1.81	1.94	1.95	1.19	2.06	2.23	1.67	2.43	4.30	2.53	1.35	2.86	1.87	-1.33	1.85	1.56
Percentage of feed, %	47.0	33.1	31.3	33.1	40.0	45.5	27.0	42.0	44.5	34.4	50.4	44.6	105.0	28.0	59.3	38.8	-27.2	38.4	32.4
P Lost through Stack,																			
Weight, lb	0.052	0.016	0.004	0.201	0.001	0.085	0.008	0.001	0.001	0.002	0.001	0.006	0.001	0.001	0.002	0.002	0.125	NA	NA
Percentage of feed, %	0.6	0.3	0.1	3.7	0.02	2.0	0.2	0.02	0.02	0.04	0.02	0.06	0.04	0.02	0.04	0.04	2.6	NA	NA
P in Combustion Residue,																			
Weight, lb	1.94	1.17	1.1[illegible]	1.33	1.11	1.13	1.16	1.13	1.35	1.15	1.12	2.37	0.55	1.12	1.14	1.12	1.15	1.07	1.12
Percentage of feed, %	24.0	23.7	24.[illegible]	24.4	22.9	26.3	26.4	23.0	26.9	23.7	23.2	24.6	22.8	23.2	23.7	23.2	23.9	22.2	23.2
Balance of P																			
Weight, lb	2.29	2.12	2.02	2.11	1.80	1.12	2.04	1.72	1.43	2.03	1.27	2.96	-0.67	2.35	0.82	1.83	4.85	NA	NA
Percentage of feed, %	28.4	42.9	44.4	38.8	37.1	26.2	46.4	35.0	28.6	41.9	26.4	30.7	-27.8	48.8	17.0	38.0	100.7	NA	NA
Acid Yield$^{(a)}$, %	47.6	33.4	31.4	36.8	40.0	47.5	27.2	42.0	44.5	34.4	50.4	44.7	105.0$^{(c)}$	28.0	59.3	38.8	-24.6$^{(d)}$	NA	NA

FOOTNOTES FOR TABLE 14

(a) The value is obtained by the summation of P recovered as acid and P lost through stack.

(b) Not available.

(c) The reason for the high acid yield is not apparent.

(d) During the pilot plant operation, the scrubber was flooded and the gas pump failed due to overloading. Leakages of acid were noticed from various flanges.

acids). This may indicate that a portion of hydrated P_4O_{10} in a form of mist, which is high in concentration, escaped the scrubber and was collected at the mist eliminator or that gaseous P_4O_{10} which had not been hydrated in the scrubber was scrubbed in the mist eliminator. A meaningful correlation could not be made using the actual operating data between the final concentration of the product acid from the scrubber and the initial concentration or the scrubber operating temperature. This is mainly because (1) the spraying rate of scrubbing acid was often adjusted to prevent flooding in the column, (2) the makeup water flow rate could not be fixed at a constant value and was adjusted from time to time as desired, and (3) the operating temperature of the scrubber could not be contolled at a constant point since the temperature of the incoming combustion product gas was changing with respect to time in the batch operation.

From the viewpoint of the concentration, the product acid can be considered as an agricultural grade for fertilizer manufacture (two categories in agricultural grade; 52-54 percent and 70 percent). The product acid from the scrubber contained solid particles or sludges, either fly ash, packing debris, or carbon soots. Fly ash from the incinerator and carbon soot originated from the combustion of wrapping paperboard and/or from the combustion of auxiliary fuel (natural gas) during oxygen deficient period.

The acid has a dark and green appearance, similar to agricultural grade phosphoric acid manufactured by the wet process. Preliminary analyses of the sample indicated that impurities such as Mg, Mn, Zn, Cr, and Ni were contained in the acid. Mg, Mn, and Zn originated from the feed composition, and Cr and Ni would be extracted from the walls of the scrubber made of stainless steel 316. Manganese and magnesium in small concentrations are desirable as micronutrients in a fertilizer. There is no published specification on the maximum allowable concentrations of Mn, Mg, Zn, Ni and Cr for fertilizer applications(14). However, fertilizer containing heavy metals in high concentrations may not be acceptable from an environmental standpoint based on stream water or drinking water quality standards.

Possible Utilization of Combustion Residue

The combustion residue (ash) of the red phosphorus composition contained oxides of manganese, magnesium, zinc, and chemical compounds of phosphorus. The content of phosphorus in the ash measured as total phosphorus ranged between 15 to 22 percent by weight with the average value of 19.5 percent according to 31 samples analyzed. Fresh batch of ash contains metal phosphides such as Mg_3P_2, Zn_3P_2, MnP, and Mn_3P_2. The phosphides are unstable and react with moisture in ambient air to generate phosphine which is toxic with a tolerance limit of 0.3 ppm in air. A treatment of the ash with water in the primary combustion chamber with the Chamber 2 burner on is effective in converting phosphides into inert materials in the ash.

A nominal composition of the treated ash was estimated as given in Table 15 based on the following assumptions:

(1) MnO_2 is decomposed to MnO.

(2) Mg is oxidized to MgO.

(3) H_2O in pyrolusite is liberated during combustion.

(4) Weight of ash is approximately 65 percent of weight of feed composition.

Utilization of the ash as a ceramic clay was not tested in this study, and thus the possibility is unknown. The utilization as an ore for manganese recovery would be possible. The United States imports about 98 percent of the total manganese used. A good quality ore contains 35 to 50 percent manganese and a low quality ore contains 10 to 35 percent manganese by weight. The combustion residue would be rich in manganese as indicated in Table 15, equivalent to a good quality ore. The absence of lead in the ash would be an advantage in the ferrous and non-ferrous alloy applications.

TABLE 15. ESTIMATED COMPOSITION OF COMBUSTION RESIDUE OF PYROTECHNIC COMPOSITION (Basis: 100 lb. Dry Composition)

Pyrotechnic Composition		Combustion Residue (Dry Basis)		
Component	Weight, lb.	Component	Weight, l.b	Percent
ZnO	3.0	ZnO	3.0	4.6
Pyrolusite	34.0	MnO	26.6	40.9
Mg	7.0	MgO	11.6	17.9
Red Phosphorus	53.0	Phosphorus Compounds (a)	22.83	35.1
Organic Binder	3.0	Others from Pyrolusite (b)	0.96	1.5
TOTAL	100.0	TOTAL	64.99	100.0

(a) This value was estimated based on the balance of weight. The total phosphorus in ash was estimated at about 20 percent.

(b) This includes materials in the pyrolusite other than MnO_2, MnO, and water.

Operational and Maintenance Problems

Various operational and maintenance problems were experienced in the pilot plant operations. Such problems both experienced and anticipated in the future operation are discussed in this section.

Control of Combustion Rate. Observations of the pilot plant operations indicated that the combustion of the pyrotechnic composition progressed very rapidly after the ignition as shown in the typical temperature curve (Figure 25). However, at a temperature of 1,600 to 1,700°F, the combustion rate was controlled by the supply of oxygen to the combustion chamber. In the design of the incinerator of a batch production facility, considerations should be given to the control of the combustion rate by controlling the oxygen supply. A three-chamber incinerator would be more desirable than a two-chamber incinerator in providing an adequate control of the combustion rate and a complete combustion of phosphorus vapor.

Preheating of Primary Combustion Chamber. In this study, the primary combustion chamber (Chamber 1) was not preheated to prevent possible flashback during loading of the composition into the incinerator. Condensation of phosphorus vapor and P_4O_{10} on the cold chamber walls was suspected at the early stage of the combustion, which resulted in spontaneous ignitions on the walls after completion of the combustion generating sparks and smoke. It is recommended that the primary chamber be preheated at 500°F prior to burning. It is not expected that the flashback would occur at the temperature since the feed composition is wet.

Erosion of Incinerator Liner. It was observed during the pilot plant operations that walls of the combustion chamber were coated with viscous P_4O_{10} condensate and the condensate was accumulated at the bottoms. After more than 1 year of operation, a slight erosion of the liner (Plicast Tuff-Mix® supplied by Plibrco Company, Chicago, Illinois) was noticed. The major components of the liner are alumina (42 percent) and silica (39 percent) which could react with strong phosphoric acid. However, the problem is not considered significant. The accumulation of the condensed acid at the bottom of the chambers may be prevented by installing drain lines to an acid receiving container.

Ignition of Burner. Some difficulties were experienced with lighting of the burner by electrical spark. The ignition system was sensitive to gas pressure and air-gas ratio. It was also necessary to clean the spark electrodes periodically.

Corrosion Problems. A failure of spraying system was noticed in an operation from readings of temperature change and pressure drops in the scrubbing acid line. One of the two spraying lines positioned at the gas inlet to the scrubber was corroded. A thermocouple well installed nearby was also corroded. The well was made of stainless steel 304 and both spraying lines were made of stainless steel 316. The corroded line was nearer to the gas inlet than the other and was covered with solid deposit. From the observations of the corroded tubes, it is conceivable that stainless steel 304 is not adequate as the construction material for the system while stainless steel 316 is marginally acceptable. Barber(15) indicated that the scrubber constructed of stainless steel 316 in a phosphoric acid manufactured from elemental phosphorus should not be allowed to exceed 225°F in order to prevent excessive corrosion of the stainless steel. He suggested installations of cooling jackets around process lines and the scrubber. Another reference(16) indicated that stainless steel 316 would be acceptable at a moderately high temperature up to 160 - 180°F. From the experience of the pilot plant operations, stainless steel 316 is satisfactory for handling strong and weak phosphoric acid at temperatures probably lower than 250°F. Even at temperatures higher than this temperature such as in the process line between the incinerator and the scrubber, the material has been satisfactory for 18 months of operation, revealing no significant indication of corrosion other than the corrosion in a spraying line and a minor solid deposit and slight sign of corrosion at the inlet of the scrubber. However, installations of cooling jackets around the process line and the spray tower (the first column of the scrubber) would minimize possibility of corrosion in the system.

Another sign of corrosion was noticed at the gas pump. For a fixed motor speed and pressure drop, the capacity of gas pumping has been reduced constantly during the operation of the pilot plant. The pump was constructed of carbon steel and thus has been subject to phosphoric acid corrosion. Without cleaning with water, drying with compressed air, and lubrication with oil after each day of operation, the pump would have been corroded rapidly. A gas pump constructed of stainless steel 316 is recommended for a production facility.

Acid Pump Failure. The acid pump used for circulation of acid for scrubbing was made of stainless steel 316 except for the gears which were made of Teflon®. When relatively large particles had a chance to get into the pump, they caused the pump to jam. Consequently, the keyway slot in the Teflon® gear was stripped and the pump failed.

Flooding in Scrubber Columns. Floodings in the spray tower occured in the following occasions:

(1) The rate of acid spraying is unnecessarily high.

(2) The bed is plugged by fly ash in combustion product gas particularly when dry red phosphorus composition is increased, or plastic caps or wrapping paperboard are included in the feed composition.

(3) Drain line of the scrubber is plugged by fly ash or packing debris.

Floodings in the packed column which was operated in a countercurrent fashion occurred when the size of packing was too small for high superficial gas velocity in the column.

Since the temperature of combustion product gas varied with respect to time in the batch combustion process, the flow rate of the scrubbing acid in the spray tower should be adjusted accordingly. Similarly, makeup water flow rate was to be adjusted. To prevent floodings in the second column, the small size packing was replaced with a large one.

When the spray tower was plugged by fly ash, it was cleaned by flushing water through the column with the gas pump on. When the drain line of the scrubber was plugged, it was cleaned by taking apart and cleaning the lines.

Generation of Smoke from Acid. As previously discussed, when combustion was taking place under oxygen-deficient conditions due to plugging in the scrubber of mist eliminator, or violent combustion of dry pyrotechnic composition, various operational problems arose. One of them is the generation of white smoke from the acid when agitated. To prevent the problem, the combustion should be under control and the secondary combustion chamber should always be maintained under oxygen-rich conditions. The pyrotechnic composition should be charged at the wet condition.

Pluggages in York Mist Eliminator. The pluggages were caused by carbon soot resulting from incomplete combustion of wrapping paperboard and plastic caps when incinerated with the composition, or incomplete combustion of auxiliary fuel during oxygen-deficient period, of fly ash not collected by the scrubber. Occasional water spraying over the mist eliminator element during the operation of the pilot plant was helpful in clearing the pluggings. When additional cleaning was necessary, methanol was sprayed over the element with the gas pump on at the maximum speed.

In order to prevent the gas pump failure due to pluggages in the mist eliminators, a bypass route was installed around the mist eliminators for emergency use only.

DESIGN OF PRODUCTION FACILITY

Data Base

A preliminary design of a production facility capable of handling around 100 lbs. of pyrotechnic composition in a batch operation was conducted. The basis of the design study was as follows:

(1) Feed rate of pyrotechnic composition is 100 lb./batch.

(2) Time required for initial preparation on each operating day including preheating of incinerator is 120 minutes.

(3) Time required for combustion of 100 lbs. of the composition is 40 minutes.

(4) Time required for ash treatment is 10 minutes.

(5) Time required for loading of the feed and unloading of combustion residue is 10 minutes.

(6) Daily cleaning at the end of operation requires 60 minutes.

(7) The production facility is operated at 1 shift/day and 5 batch operations/shift (8 hours/shift).

(8) Plant operating schedule was assumed at 250 days/year.

A layout of the pyrotechnic combustion production facility is shown in Figure 39. Based on the flow diagram shown in the figure, heat and material balances were made and the results are given in Table 16. The results were used in sizing the equipment of the production facility.

Description of Sizing of Equipment

An artistic drawing of the production facility is shown in Figure 40. Discussions on individual components of the plant follow:

Incinerator

An incinerator with the following features would be adequate for the production facility.

(1) The incinerator should be divided into three combustion chambers; one for the primary combustion of the red phosphorus composition and the others as afterburners. The rate of combustion will be controlled in the primary chamber by adjusting oxygen supply.

(2) The primary chamber should have an access for loading of feed material (red phosphorus composition) and unloading of combustion residue (ash). A charge pan mounted on a rail would be adequate.

(3) Each combustion chamber should include a burner capable of preheating the chamber and igniting the composition at the startup of each batch operation. A gas or oil burner would be appropriate.

(4) Each combustion chamber should have a drain to remove condensed phosphoric acid out of the combustion chambers.

(5) The primary combustion chamber would have a water spray system for ash treatment at the end of each batch operation.

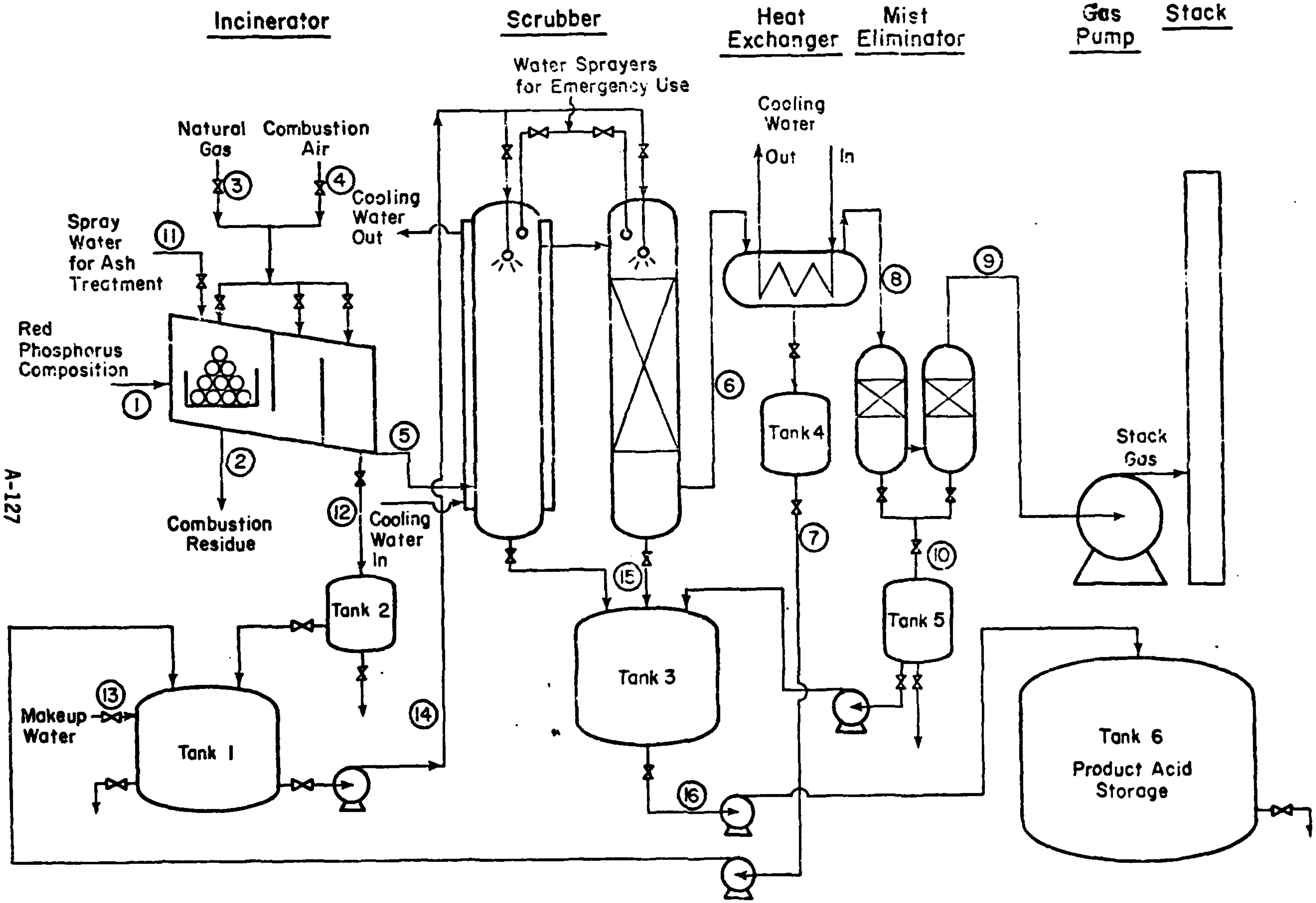


FIGURE 39. LAYOUT OF PYROTECHNIC COMBUSTION PRODUCTION FACILITY FOR MATERIAL AND HEAT BALANCES

TABLE 16. STREAM COMPOSITIONS OF PYROTECHNIC COMBUSTION PROCESS IN PRODUCTION FACILITY

Basis: 1 shift/day, 5 Batch Operations/Shift, 100 lb composition/Batch, 40 min of combustion/Batch

Stream Number	1	2(b)	3(d)	4	5(g)	6	7(i)	8	9	10	11	12	13	14	15	16
Temperature, °F	70	70	70	70	1,729	191	250	150	150	150	60	180	60	104	191	174
Pressure, atm	1	1	1	1	0.2" of water vacuum	5" of water vacuum	5" of water vacuum	7" of water vacuum	50" of water vacuum	50" of water vacuum	40 psig	0.2" of water vacuum	40 psig	40 psig	5" of water vacuum	1
Gas Composition, mole percent																
P_4O_{10}			--	—	0.38	0.0		0.0	0.0							
CO_2			0.8	—	0.50	0.30		0.38	0.38							
N_2			3.2	79.0	81.83	49.65		61.88	61.68							
O_2			—	21.0	16.32	9.90		12.34	12.34							
CH_4			96.0	—	0.0	0.0		0.0	0.0							
H_2O			—	—	0.97	40.15		25.40	25.40							
Others			—	—	0.0	Acid Mist(h)		Acid Mist(h)	Acid Mist(e)							
TOTAL			100.0	100.0	100.0	100.00		100.00								
Liquid Composition, weight percent																
H_3PO_4							5.0(j)			60.0	0	40.0	0	6.0	60.0	60.0
H_2O							95.0			40.0	100.0	60.0	100.0	94.0	40.0	40.0
TOTAL							100.0			100.0	100.0	100.0	100.0	100.0	100.0	100.0
Solid Composition, weight percent (dry basis)																
Red phosphorus	53.0	0.0														
Pyrolusite	34.0	—														
MnO_2	32.64	—														
MnO	0.42	—														
K_2O	0.40	—														
Others	0.54	—														
Phosphorus compounds		35.1														
Mg	7.0	0.0														
ZnO	3.0	4.6														
Organic binder	3.0	0.0														
MnO	0.	40.9														
MgO	0.	17.9														
Others	0.	1.5														
TOTAL	100.0	100.0														
Total Flow Rate																
Gas, scfm			25(e)	351(f)	1,770	878		663(k)	743							
Liquid, gpd							160.0			12.84	44.4	30.0	186	379	50.7	[illegible]
gpm							0.40			0.046	0.89	0.15	0.032	1.85	0.256	[illegible]
lb/min							6.77			0.764(m)	7.4(n)	1.571(o)	0.27(p)	16.11(q)	1.02(r)	1.984(s)
Solid, lb/day	500.(a)	325(e)														

FOOTNOTES FOR TABLE 16

(a) This indicates the flare feed rate on dry basis. In the actual operation the flare is treated under water and the water content in the feed was measured to be approximately 9 percent by weight.

(b) The composition of ash was assumed to be the same as that described in Table 13.

(c) The value was assumed based on the pilot plant test data. That is, about 65 percent of the weight of the dry red phosphorus composition remained as the weight of the combustion residue.

(d) Natural gas is consumed only for preheating of the incinerator and ignition of the flare.

(e) This represents the natural gas burning rate during preheating and combustion periods in the second combustion chamber. The natural gas burning rate in the first combustion chamber would be around 10 acfm during the ignition period (i.e., around 3 minutes) in each batch operation.

(f) Theoretical oxygen requirement = 0.241 lb.-moles/10 lb. of composition. Excess air was assumed at 300 percent. Combustion time = 40 minutes. The gas pump would be on for 7 hours a day.

(g) The composition of the combustion product gas is the same as that described in Table 13. The combustion duration for 100 lb. of flare material was assumed at 40 minutes. A total of 5 batch operations would be made in a day.

(h) The gas stream leaving the scrubber contains 620 mg of P_2O_5/scf on dry basis equivalent to 1.328 lb. of 60 percent phosphoric acid per minute.

FOOTNOTES FOR TABLE 16 (Continued)

(i) A heat exchanger made of 1/2" gage 18 stainless steel tube was assumed to cool the gas stream from 191°F to 150°F. The overall heat transfer coefficient for the system was approximated at 83 Btu/hr-ft^2-°F. The heat transfer area required would be around 65 ft^2.

(j) The condensate was assumed to be 5 percent phosphoric acid.

(k) The gas stream leaving the heat exchanger contains 357 mg of P_2O_5/scf on dry basis equivalent to 0.765 lb. of 60 percent phosphoric acid per minute.

(l) The total gas flow is 58.58 lb.-moles/min.

(m) The efficiency of the York mist eliminator was assumed at 99.9 percent. After the mist eliminator, the stack gas contains 0.36 mg of P_2O_5/scf.

(n) Water evaporated during ash treatment was assumed at 2.4 gal. per batch operation. The treated ash would contain water at 20 percent by weight. The condensed acid from the incinerator will be diluted with the sprayed water to be a 40 percent acid. Approximately 15 percent of the phosphorus in feed was assumed to be recovered as acid from the incinerator. The ash will be treated for 10 minutes at the end of each operation.

(o) Approximately 15 percent of the phosphorus in feed was assumed to be recovered as 40 percent acid from the incinerator.

(p) This was obtained from a water balance around the acid recycle tank.

(q) The value was obtained from heat and material balances.

FOOTNOTES FOR TABLE 13 (Continued)

(r) The value was obtained under the assumption that the acid from the scrubber system would be 60 percent in concentration.

(s) This is the summation of streams 10 and 15.

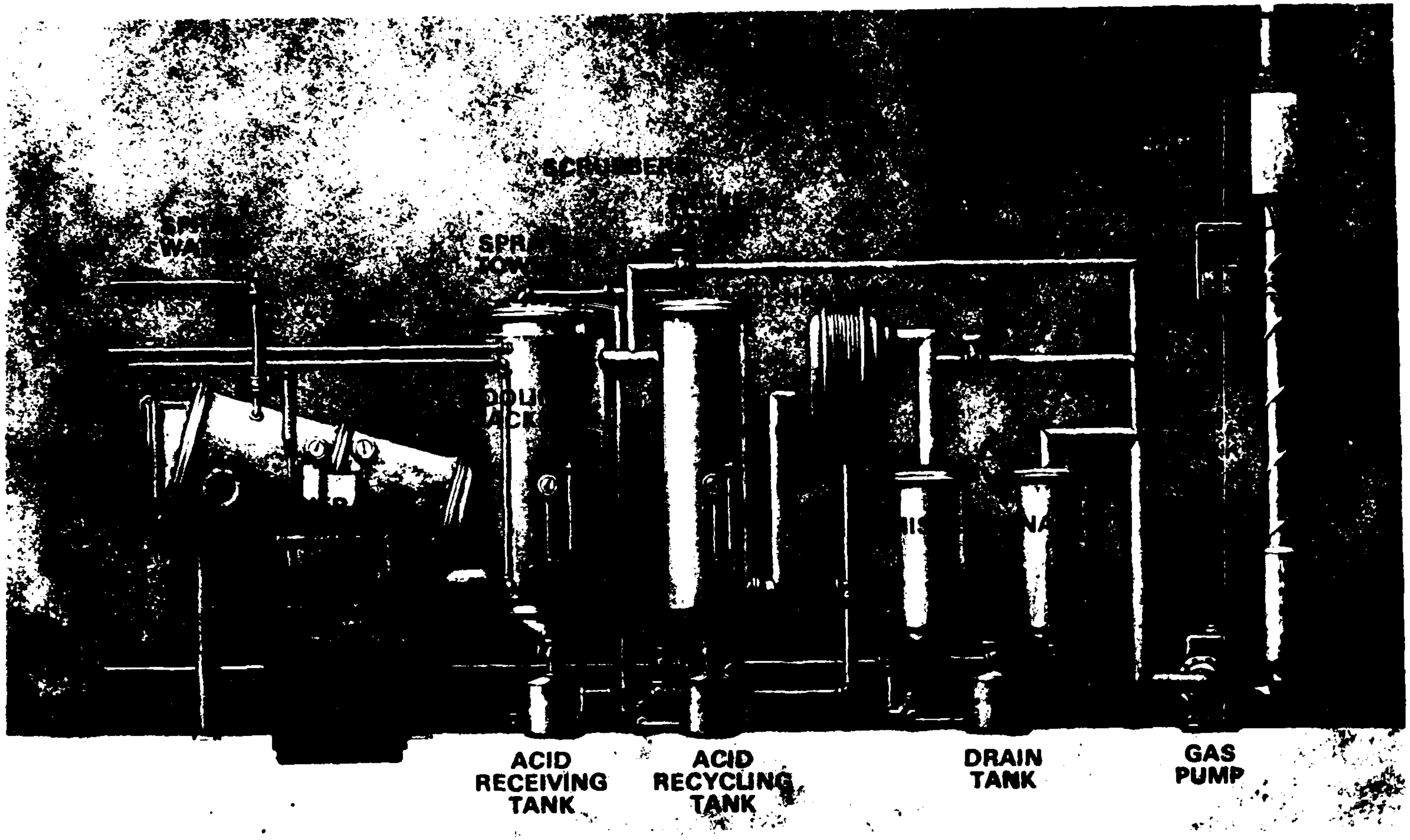


FIGURE 40. ARTISTIC DRAWING OF PYROTECHNIC COMBUSTION PRODUCTION FACILITY

(6) Based on the assumption that the incinerator in the production facility would have the same residence time as the incineration in the pilot plant, i.e., 1.49 seconds based on gas flow, the required volume of the incinerator would be 43.85 ft^3. (Cylindrical with inside diameter of 3 ft and total length of about 6 ft 3 inches). It should be lined with a refractory material resistant to phosphoric acid. The housing shell should be made of stainless steel 316.

Burners with Controller and Blower

Three burners with controller and blowers are needed for each combustion chamber. The burner should be able to burn 25 cfm of natural gas or equivalent amount of oil based on heat input to provide an adequate capability for preheating the combustion chambers.

Scrubber

A scrubber consisting of a spray tower and a packed column should be adequate for the production facility. A cooling jacket would be installed around the spray tower. A concurrent flow pattern would be preferred in the packed column to minimize possible flooding problems. With an assumption that the superficial gas velocities in the spray tower and packed column are 1 ft and 3 ft per second, respectively, the inside diameters of the columns were estimated at 4 ft 4 inches and 2 ft 6 inches, respectively. The heights of the columns were estimated approximately at 7 ft. The columns should be constructed of stainless steel 316.

Heat Exchanger

From the result of heat balance around the heat exchanger (see Table 16), the required heat transfer area was estimated at 65 ft^2.

The type of heat exchanger would be tube and shell with gas on shell side. The cooling tube would be 1/2 inch, gage 18 and tube and shell should be constructed of stainless steel 316. The overall heat transfer coefficient was estimated at 83 Btu/hr-ft^2-$^\circ$F.

Mist Eliminator

A Type "P" York mist eliminator similar to the one used in the pilot plant would be adequate for the production facility. The unit should have a flow capacity of 560 scfm with a pressure drop of 40 to 50 inches of water. A spray nozzle should be installed on top of the coalescing element to provide a means for cleaning the element when plugged. The unit should be constructed of stainless steel 316.

Gas Pump

A root blower with a motor and transmission unit would be adequate. The capacity of the pump would be around 750 acfm or higher at an inlet condition of 50 to 100 inches of water vacuum at 150°F. The pump should be made of stainless steel 316. The power of the motor would be around 10 hp.

Acid Pumps

Four acid pumps (rotary gear type) with a capacity of 3 gpm would be adequate. They should be made of stainless steel 316. The power of the motor would be 1/2 hp.

Acid Tanks

Six tanks made of stainless steel 316 would be necessary in the production facility as shown in Figure 39. The size of each tank is as follows:

Tank 1: 200 gallons.
Tank 2: 50 gallons.
Tank 3: 100 gallons.
Tank 4: 200 gallons.
Tank 5: 50 gallons.
Tank 6: 4,000 gallons (storage tank).

Control Panel

The control panel will include various power switches, valves, pressure gages, flow meters, liquid level controllers, temperature recorder, and oxygen analyzer system (sampling system, analyzer, and recorder).

Capital Requirement and Operating Cost

The capital requirement and annual operating cost were estimated for the production facility with the specifications and sizes as described above. The dollar base for cost estimation was selected as May, 1977. Cost data were obtained from published sources and by contacting equipment suppliers. Raw data were updated to the base year by using the Chemical Engineering Plant Cost Index and modified as needed to conform with specified equipment sizes and operating conditions. Accounting method employed here was the Utility Financing Method(19) with modifications made as needed.

Estimated major equipment cost for the production facility are given in Table 17. The total equipment cost was estimated at $152,100. Based on the total equipment cost, the total capital requirement was estimated at $615,800 as given in Table 18. Note that this cost excluded costs for off-site facilities, land and yard improvement, and utilities such as power, water, sewer, and waste disposal. The net annual operating cost for the production facility was estimated at $150,200 including a credit of $18,900 for by-product acid, as given in Table 19. The major expense items for the net annual operating cost are the direct operating labor ($62,600, 41.7 percent of the operating cost) and the administration and general overhead ($48,700, 32.4 percent of the operating cost).

Disposal cost of obsolete or unserviceable pyrotechnic composition was estimated at $2.03/lb. of composition as given in Table 20. The basis of the estimate was:

(1) Ten-year plant life (currently the total quantity of obsolete or unserviceable pyrotechnic composition was estimated at 500,000 pounds. This will supply feed to the production facility only for four years. However, it was assumed in this study that during the four years of operation, more compositions will be available for feed or that after four years of operation, the plant will handle similar types of pyrotechnic composition with minor modifications as needed).

(2) Ten percent per year straight-line depreciation on total capital requirement excluding working capital.

(3) 75 percent/25 percent debt/equity ratio.

(4) Nine percent/year interest on debt.

(5) 15 percent/year return on equity after tax.

(6) 48 percent Federal Income Tax.

Some of these bases may not be applicable to a specific financing method now being employed by NWSC Crane. Therefore, the disposal cost based on the NWSC Crane's financing method may differ from the estimates in this study.

TABLE 17. ESTIMATED MAJOR EQUIPMENT COST FOR PRODUCTION FACILITY

Base Year: May, 1977

Equipment	Cost, dollars
Incinerator (1)	41,800[a]
Burner and Blower with Controller (3)	14,200[b]
Scrubber (Spray Tower) (1)	14,500[c]
Scrubber (Packed Tower) (1)	6,300[d]
Heat Exchanger (1)	8,100[e]
Mist Eliminator (1)	8,500[f]
Gas Pump (1)	11,500[g]
Acid Pump (4)	2,800[h]
Process Tank (5)	13,500[i]
Acid Storage Tank (1)	15,200[j]
Control Panel and Instruments	15,700[k]
Total Equipment Cost, E	152,100

(a) Cost of an incinerator producing combustion product gas of 471 acfm in 1975 = $15,000.
Combustion product gas to be produced in the production facility incinerator = 1,770 acfm.
Exponent scale-up factor for incinerator (assumed) = 0.7.
CE plant cost index = 182.4 for 1975 and 201.2 for May, 1977.

(b) Cost of a gas burner with a capacity of burning natural gas at 400,000 Btu/hr = $500 in 1975.
Capacity requirement for burners in the production facility = 4,000,000 Btu/hr.
Exponent scale-up factor for burner (assumed) = 0.77.
Cost of a temperature controller (assumed) = $1,500 in May, 1977.

(c) Cost of spray tower with cooling jacket estimated based on Bureau of Mines Cost Manual(17) = $14,500 (May, 1977).

(d) Cost of packed column estimated based on Bureau of Mines Cost Manual (17) = $6,300 (May, 1977).

TABLE 17. (Continued)

(e) This was estimated based on Guthrie(18). Total heat transfer area was assumed at 100 ft^2.

(f) This estimate was obtained from York Separator's, Inc., for a York mist eliminator with a capacity of 560 scfm.

(g) The estimate was based on the size of motor driving pump.
A pump with a 3 hp motor in 1975 = $5,000 (stainless steel).
Horsepower of a gas pump motor in the pilot plant = 10 hp.
Exponent scale-up factor for pump = 0.61 (assumed).

(h) Cost of a pump (stainless steel 316) and motor with a capacity of 3 gpm in 1976 = $700.
CS plant cost index = 192.1 for 1976 and 202.1 for May, 1977.

(i) The costs of acid tanks (stainless steel 316) were estimated based on Bureau of Mines Cost Manual(17).

Tank 1	=	$ 3,600
Tank 2	=	1,800
Tank 3	=	2,700
Tank 4	=	3,600
Tank 5	=	1,800
Total	=	$13,500

(j) The size of storage tank = 4,000 gallons.
Cost of a 4,000 gallon stainless steel based on Bureau of Mines Cost Manual(17) = $15,200.

(k) The cost of control panel was estimated as follows:

Temperature recorder	=	$ 2,500
Pressure gages	=	500
Flow meters	=	2,000
Liquid level controller (6)	=	3,000
Switches	=	1,000
Oxygen analyzer system	=	4,700
Panel frame	=	2,000
Total	=	$15,700

TABLE 18. ESTIMATED CAPITAL REQUIREMENT FOR PRODUCTION FACILITY

Base Year: May, 1977

Item	Cost, 10^3 dollars
Total Equipment Cost, E	152.1
Installation of Purchased Equipment including Labor, Material, Electrical Systems, Piping, etc., 110% E	167.3
Total Direct Cost	319.4
Engineering and Supervision, 40% E	60.8
Construction Expense, 45% E	68.4
Contractor's Fee, 10% E	15.2
Contingency, 40% E	60.8
Total Indirect Cost	205.2
Total Plant Investment (TPI)	524.6[a]
Interest during Construction	23.6[b]
Startup Cost, 20% GAOC[c]	33.8[d]
Working Capital (WKC), 20% GAOC	33.8
Total Capital Requirement (TCR)	615.8

(a) This is the summation of the total direct and indirect costs.

(b) Interest during construction = (TPI) (interest rate) $\left(\frac{\text{construction period}}{2}\right)$

Interest rate = 9% per year (assumed)
Construction period = 1 year (assumed)

(c) Gross annual operating cost.

(d) From Table 19 GAOC was estimated at $169,100.

TABLE 19. ESTIMATED ANNUAL OPERATING COST FOR PRODUCTION FACILITY

Base Year: May, 1977

Item	Cost, 10^3 dollars
Direct Material and Utility Costs	
Gas	7.5(a)
Electricity	0.9(b)
Water	0.4(c)
Total	8.8
Direct Operating Labor (DOL)	62.6(d)
Maintenance Labor, 1.5% TPI	7.9
Maintenance and Operating Supplies, 30% DOL + 1.5% TPI	26.6
Supervision	10.6(e)
Administration and General Overhead	48.7(f)
Solid Waste (ash) Disposal Cost	4.1(g)
Gross Annual Operating Cost (GAOC)	169.1
Credit for By-product Acid	(18.9)(h)
Net Annual Operating Cost (AOC)	150.2

(a) Gas consumption a day (estimated) = 10,000 ft^3.
Cost of gas (estimated) = \$3.00/10 ft^3.
Number of days of plant operation = 250 days/year.

(b) Power consumption a day (estimated) = 35×10^3 kwh.
Cost of power = \$0.025/kwh.

TABLE 19. (Continued)

(c) Process water consumption a day (estimated) = 230 gallons.
Cooling water consumption a day (estimated) = 13,850 gallons.
Cost of water (assumed) = $\$0.5/10^3$ gallon for process water and $\$0.1/10^3$ gallon for cooling water.

(d) Manpower requirement in operation = 2 man hr/hr.
Cost of labor = \$15/man-hr.
Operating time = 2,086 hrs/yr.

(e) This was assumed at 15% of total labor cost.

(f) This was assumed at 60% of total labor cost.

(g) Combustion residue generated = 406 lb. (wet)/day.
Disposal cost (assumed) = \$10/ton of residue.
Plant operation = 250 days/year.

(h) Product acid (60% concentration) generation (estimated) = 757 lb./day.
Price of 60% agricultural-grade phosphoric acid (estimated) = \$200/ton.
Plant operation = 250 days/year.

TABLE 20. ESTIMATED DISPOSAL COST FOR OBSOLETE PYROTECHNIC COMPOSITION
(Marine Marker Mk 25)

Item	Cost, 10^3 dollars
Average Return on Rate Base (RRB)	34.1(a)
Average Annual Depreciation (D)	58.2(b)
Average Federal Income Tax (FIT)	11.2(c)
Net Annual Operating Cost	150.2
Average Annual Revenue Requirement	253.7
Annual Disposal of Pyrotechnic Composition	125×10^3 lb.
Average Disposal Cost (Incineration)	$2.03/lb. of composition

(a) RRB = (0.0525) (TCR+WKC).

(b) D = (0.1) (TCR-WKC).

(c) FIT = (0.01731) (TCR+WKC).

CONCLUSIONS

It was demonstrated successfully on a pilot plant scale that the overall process concept developed by Naval Weapons Support Center (NWSC) Crane is technically sound and feasible for the disposal of the red phosphorus pyrotechnic composition by combustion and the reclamation of a fertilizer-grade phosphoric acid. The pilot plant was able to be operated in a fashion acceptable to the environment. That is, the combustion residue was chemically stable after water treatment and the stack gas emission for P_2O_5 was below the Current Ammunition Procurement and Supply Agency (APSA) standard when the pilot plant operated at the optimal operating condition. The quality of the product acid is equivalent to an agricultural grade phosphoric acid. The contaminations with impurities such as manganese, magnesium, zinc, nickel, and chromium were below an acceptable limit. The acid yield was around 41 percent based on total phosphorus in the feed composition without recovery of condensed acid from the incinerator and process lines.

A preliminary design of a production facility capable of processing around 100 lbs. of composition in a batch operation was made based on information obtained from the pilot plant operations. Using a standard Utility Financing Method, the capital requirement of the production facility was estimated at around $620,000 at May, 1977 dollar base. The net annual cost was estimated at $150,000. The operating labor (around $63,000 or about 42 percent of the operating cost) and the administration and general overhead (around $49,000 or around 32 percent of the operating cost) are the major cost items in the operating cost. The average incineration cost for the red phosphorus pyrotechnic composition was estimated at $2.03/lb. of composition.

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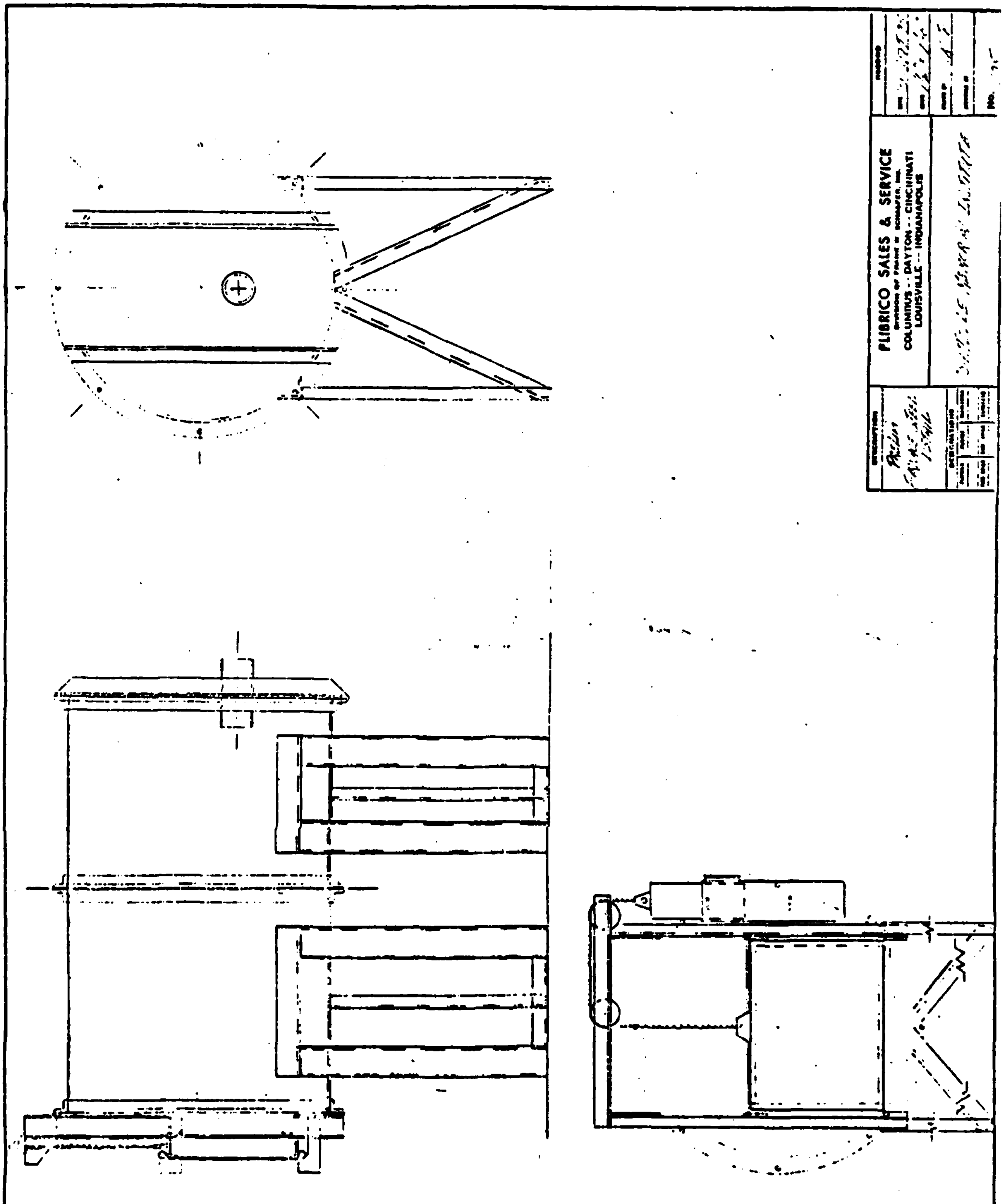
APPENDIX AA

DETAILED DESIGN DRAWINGS OF THE 2-COMBUSTION CHAMBER INCINERATOR

(The figures may not be legible due to a reduction in size of the drawing.)


PLIBRICO SALES & SERVICE
DIVISION OF FRANK W. SCHAEFER, INC.
COLUMBUS -- DAYTON -- CINCINNATI
LOUISVILLE -- INDIANAPOLIS
DESCRIPTION
DESIGNATIONS
No.

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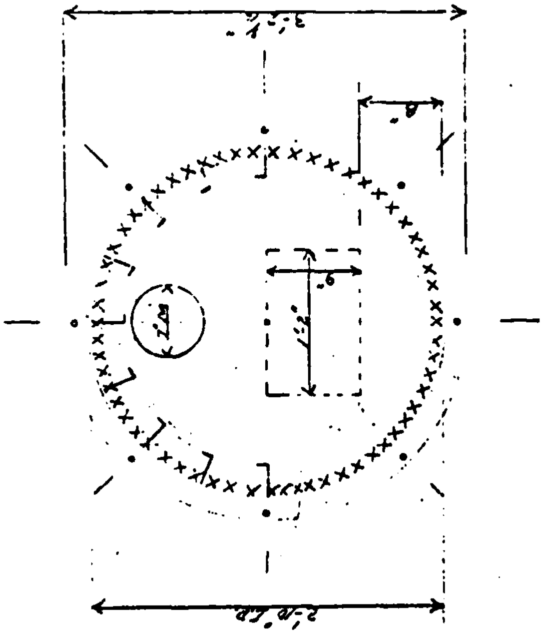

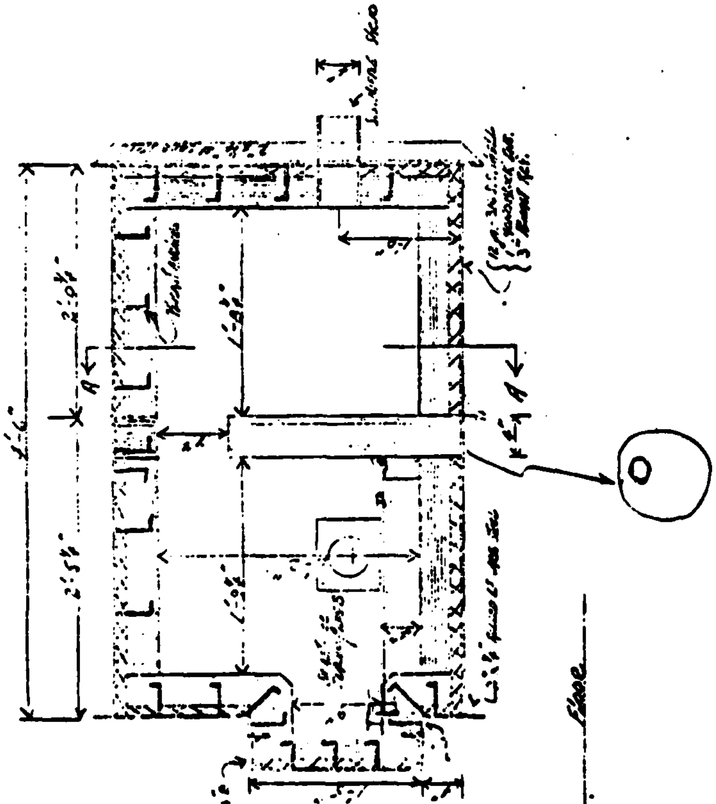

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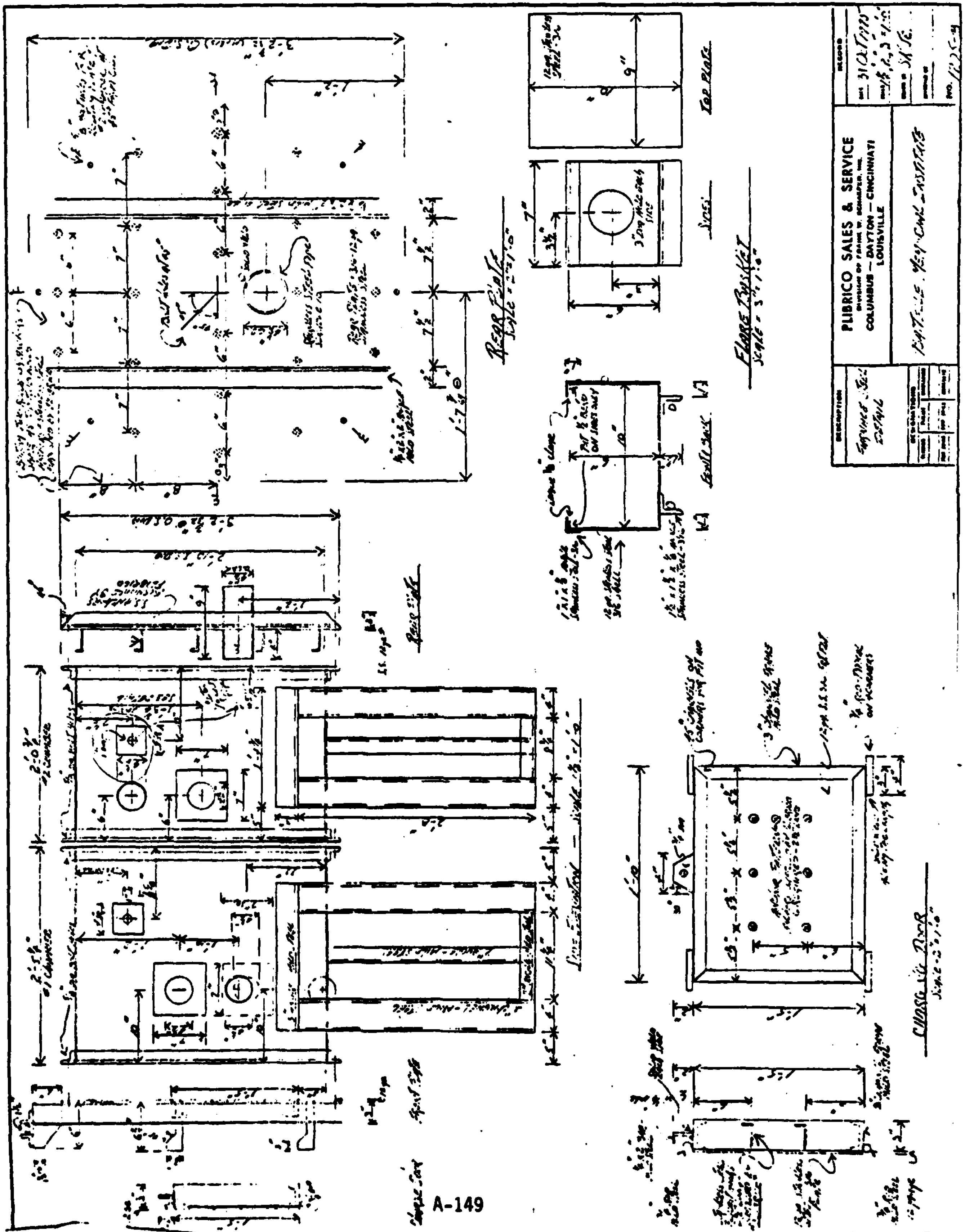
A-148



DESCRIPTION

Furnace Steel Detail

PLIBRICO SALES & SERVICE

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COLUMBUS — DAYTON — CINCINNATI

LOUISVILLE

Battelle Memorial Institute

RECORD

No.

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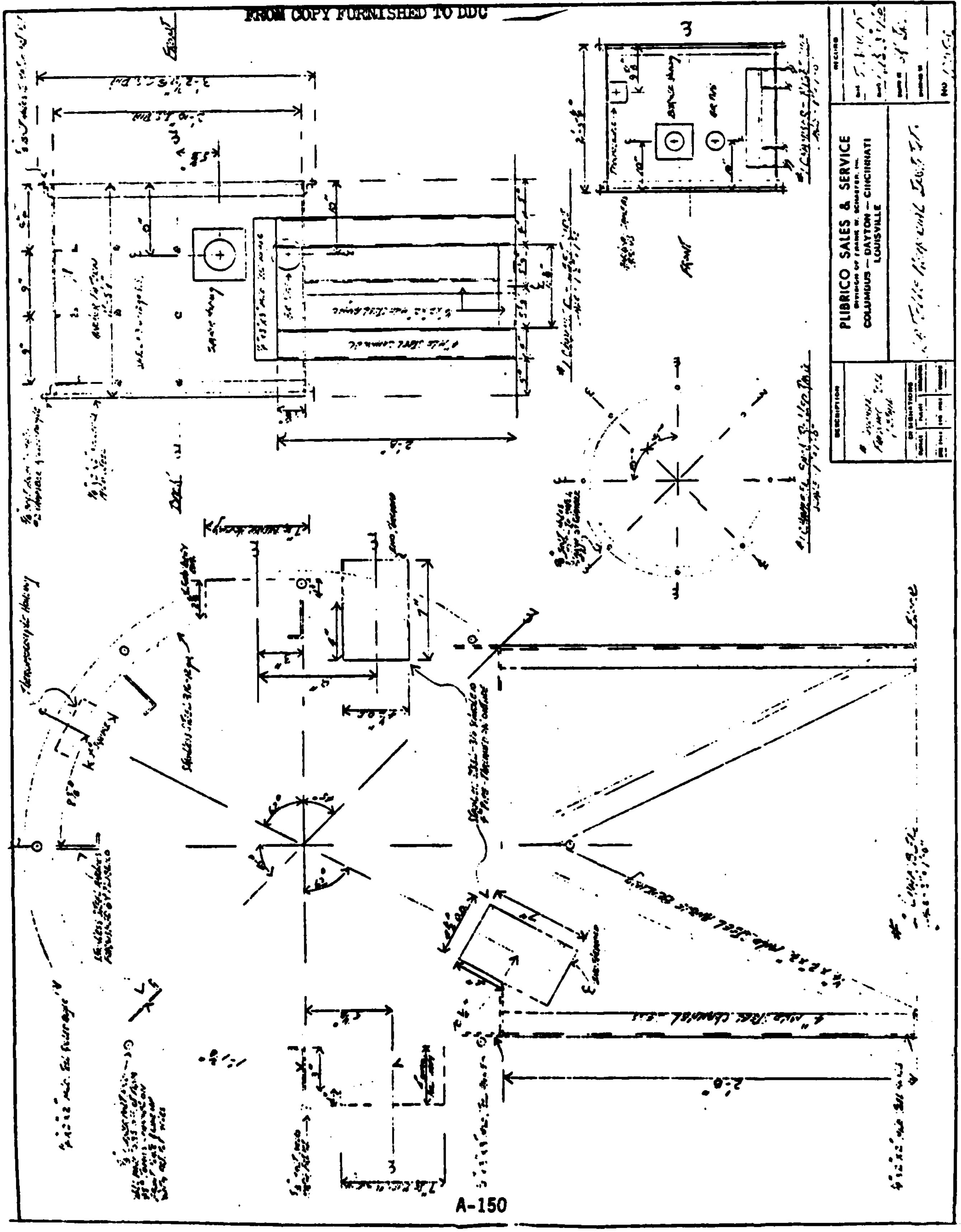

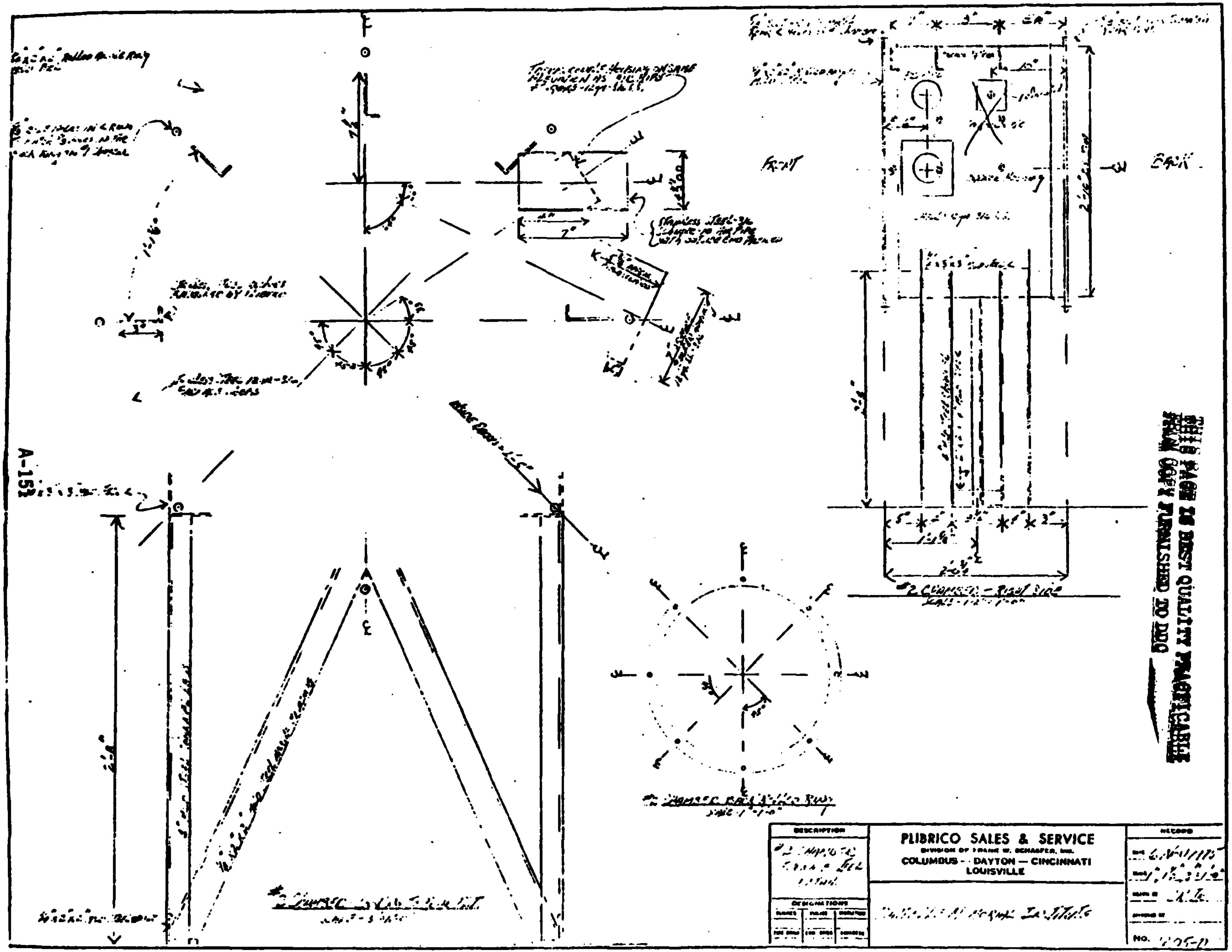

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LOUISVILLE

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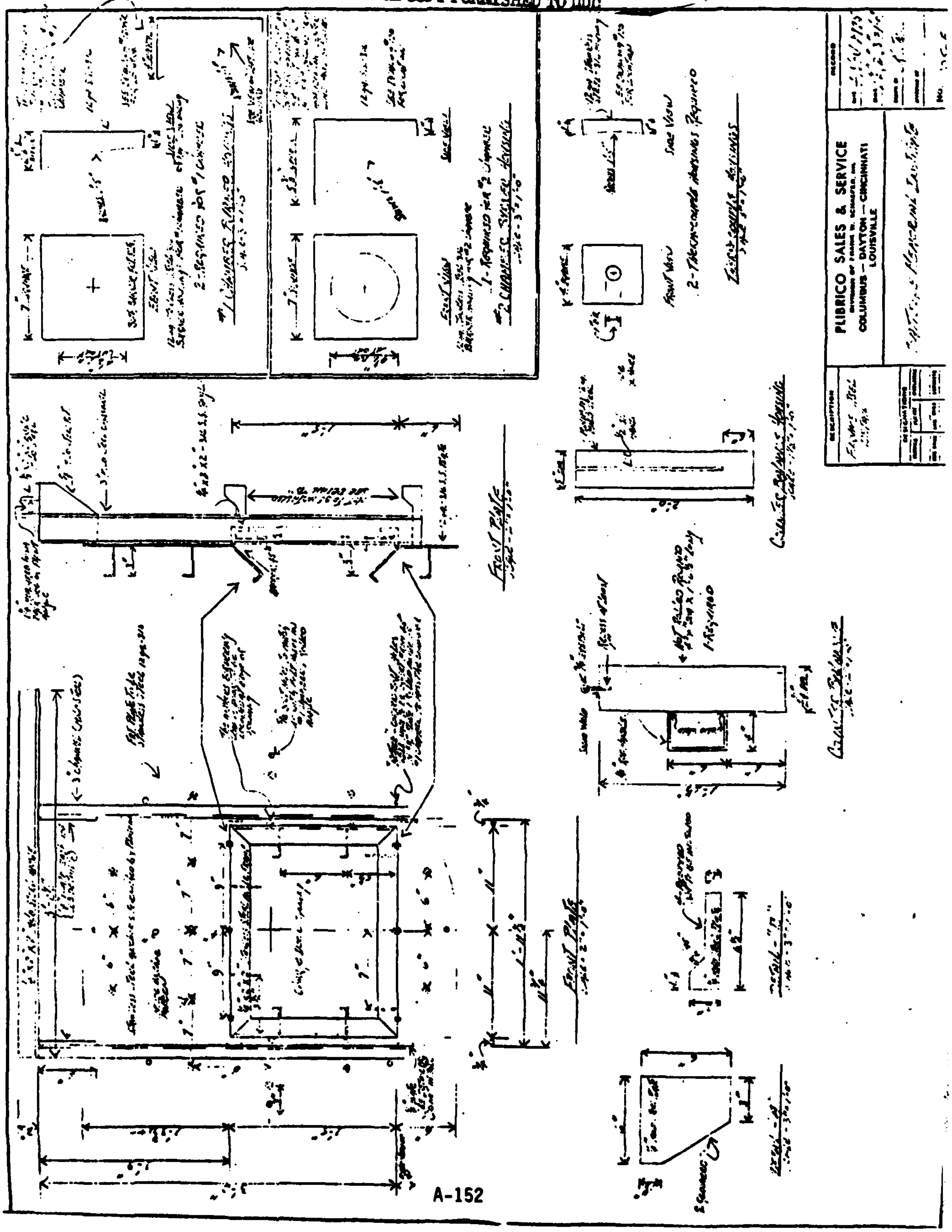

APPENDIX AB

DETAILED DESIGN DRAWINGS OF SCRUBBER

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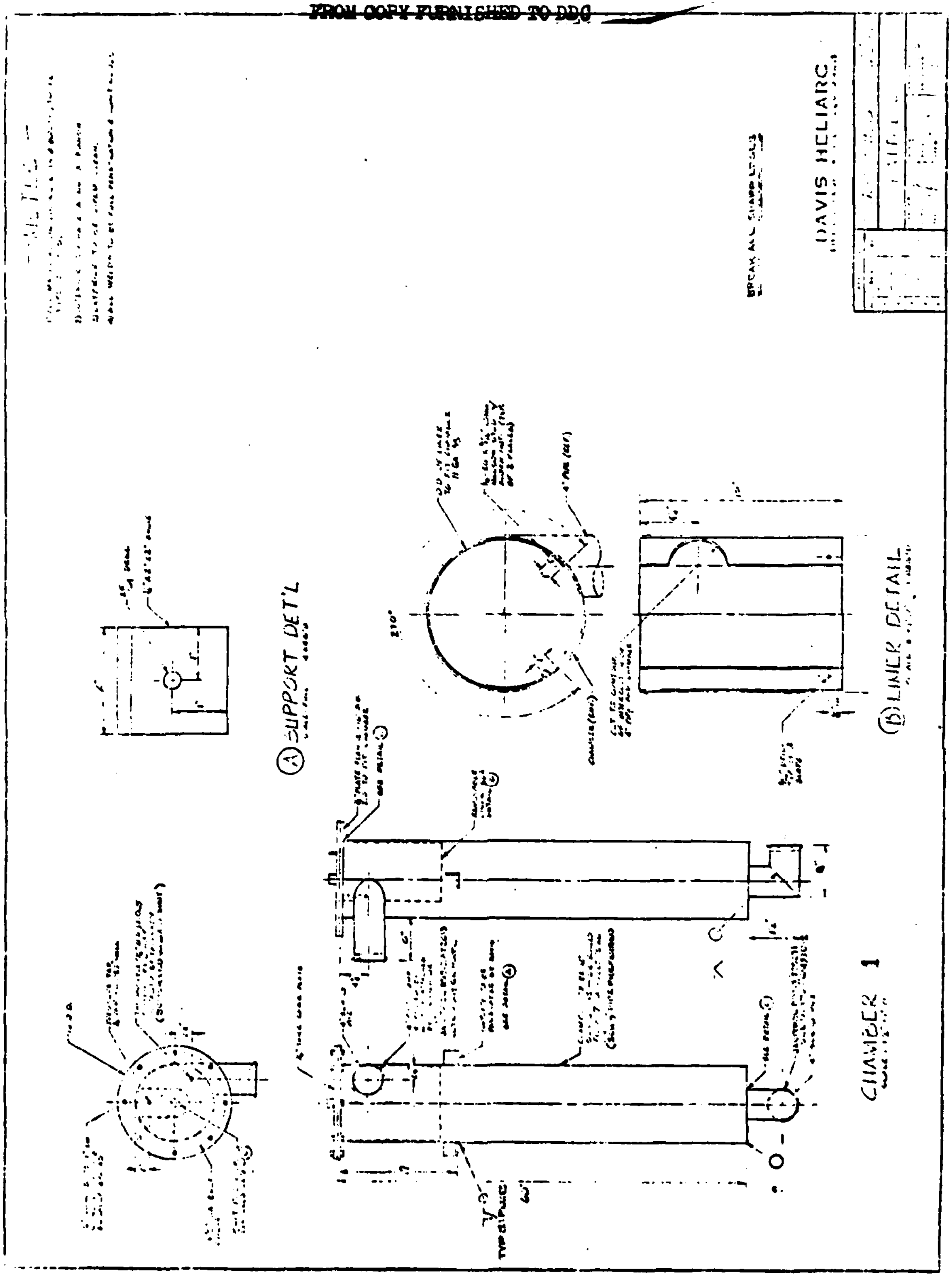
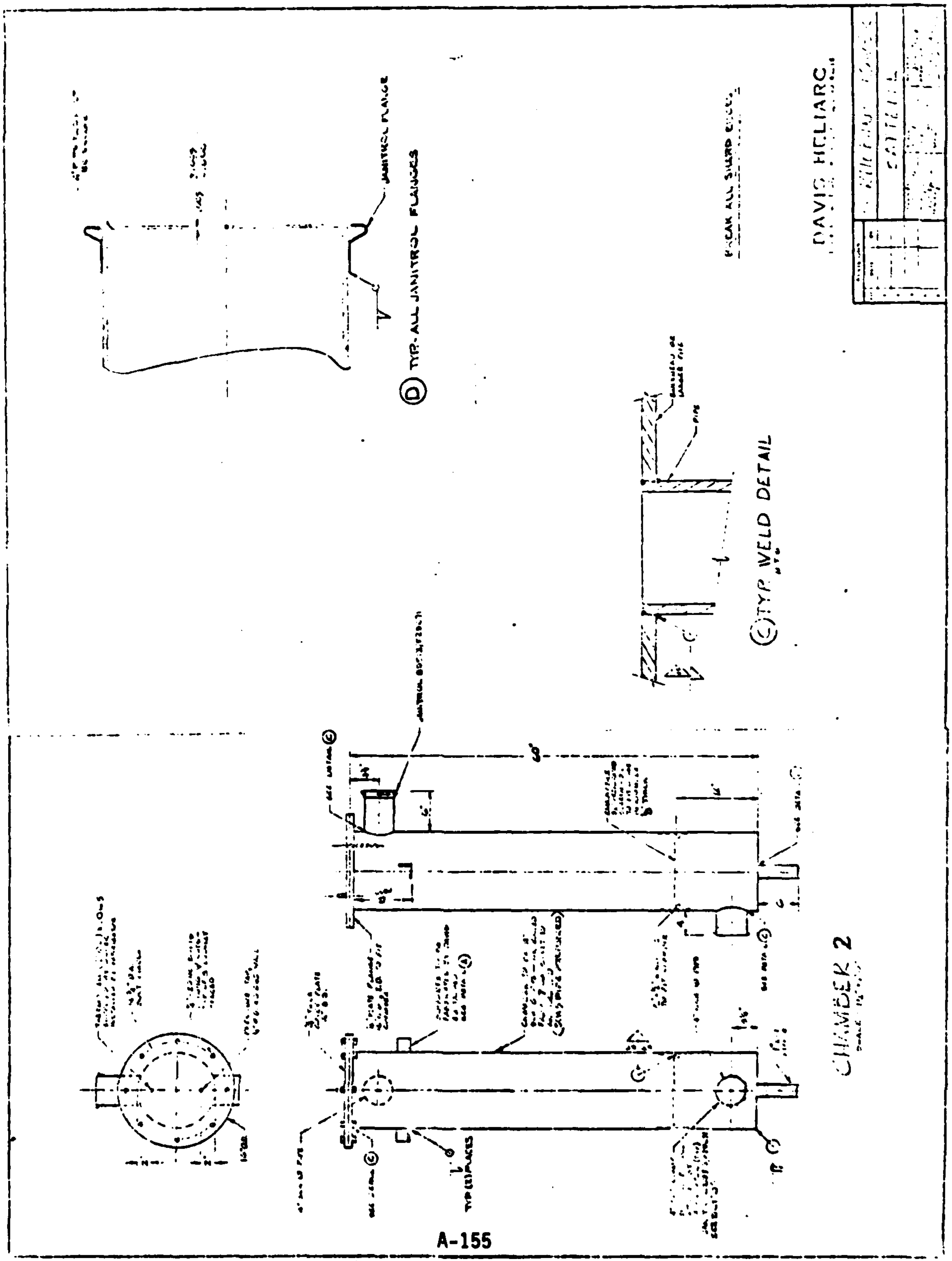
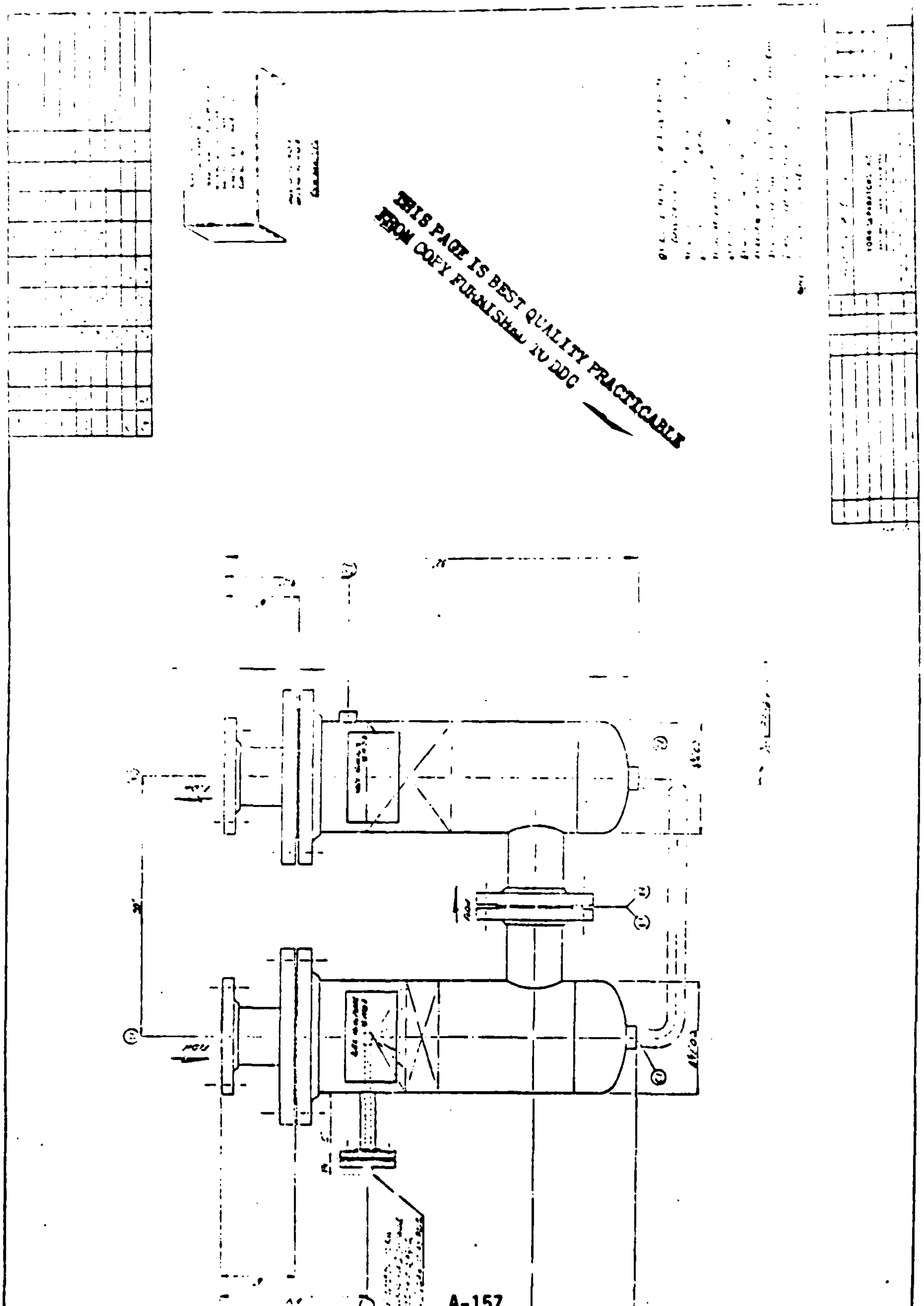

NOTES
DAVIS HELIARC
BREAK ALL SHARP EDGES
Ⓐ SUPPORT DET'L
Ⓑ LINER DETAIL
270°
CHAMBER 1
TYP (2 PLACES)


DAVIS HELIARC
CHAMBER 2
Ⓒ TYP WELD DETAIL
Ⓓ TYP. ALL JANITROL FLANGES
JANITROL FLANGE
BREAK ALL SHARP EDGES

APPENDIX AC

DETAILED DESIGN DRAWINGS OF TYPE "P" YORK® MIST ELIMINATOR

(The figures may not be legible due to a reduction in size of original drawing.)


FLOW
FLOW
30"

APPENDIX AD

DETAILED DESIGN DRAWINGS OF BRINK® MIST ELIMINATOR

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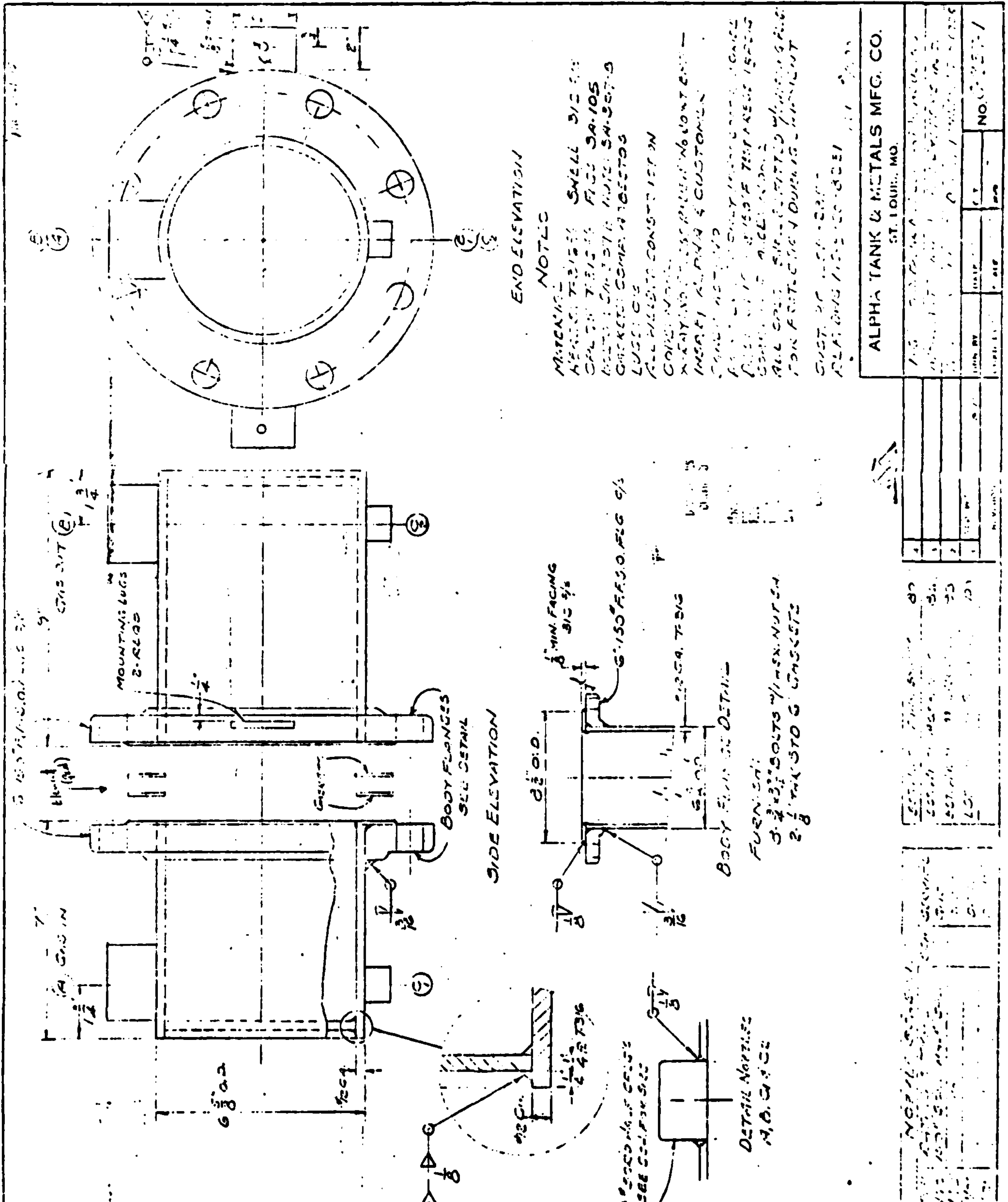
in size of original drawing.)


ALPHA TANK & METALS MFG. CO.
ST. LOUIS, MO.
END ELEVATION
NOTES
SIDE ELEVATION
BODY FLANGES SEE DETAIL
MOUNTING LUGS 2-REQD
BODY FLANGE DETAIL
DETAIL NOZZLES A, B, C & E
FURNISH:
6 5/8 O.D.
1/8 MIN. FACING
6" 150# F.F.S.O. FLG
SHELL
SA-105
150# F.F.S.O. FLGS
TYP

APPENDIX B

MODIFICATIONS TO INCINERATION COMPLEX

APPENDIX B

MODIFICATIONS TO INCINERATION COMPLEX

This report supplements Appendix A and covers the modifications listed below:

Modifications of Pilot Plant

Modifications of the pilot plant as required by Contract Modification No. 5 have been completed as follows:

1. Installation of a sprayer and cleanout drains in both combustion chambers.
2. Installation of a cleanout hole in the second combustion chamber (see Figure 1).
3. Installations of cooling jackets around the process line between the incinerator and the first column of the scrubber and around the first column of the scrubber (see Figures 2 and 3, respectively).
4. Replacement of the existing Janitrol flanges with regular heavy duty (i.e., 150 lb.) stainless steel 316 flanges (12) (see Figures 2 and 3).
5. Installation of a heat exchanger (the second column of the scrubber was modified to install 4 finned tubes).
6. Installation of 2 additional pumps; one for the York mist eliminator drain and the other for the incinerator drain (see Figures 4 and 5, respectively).

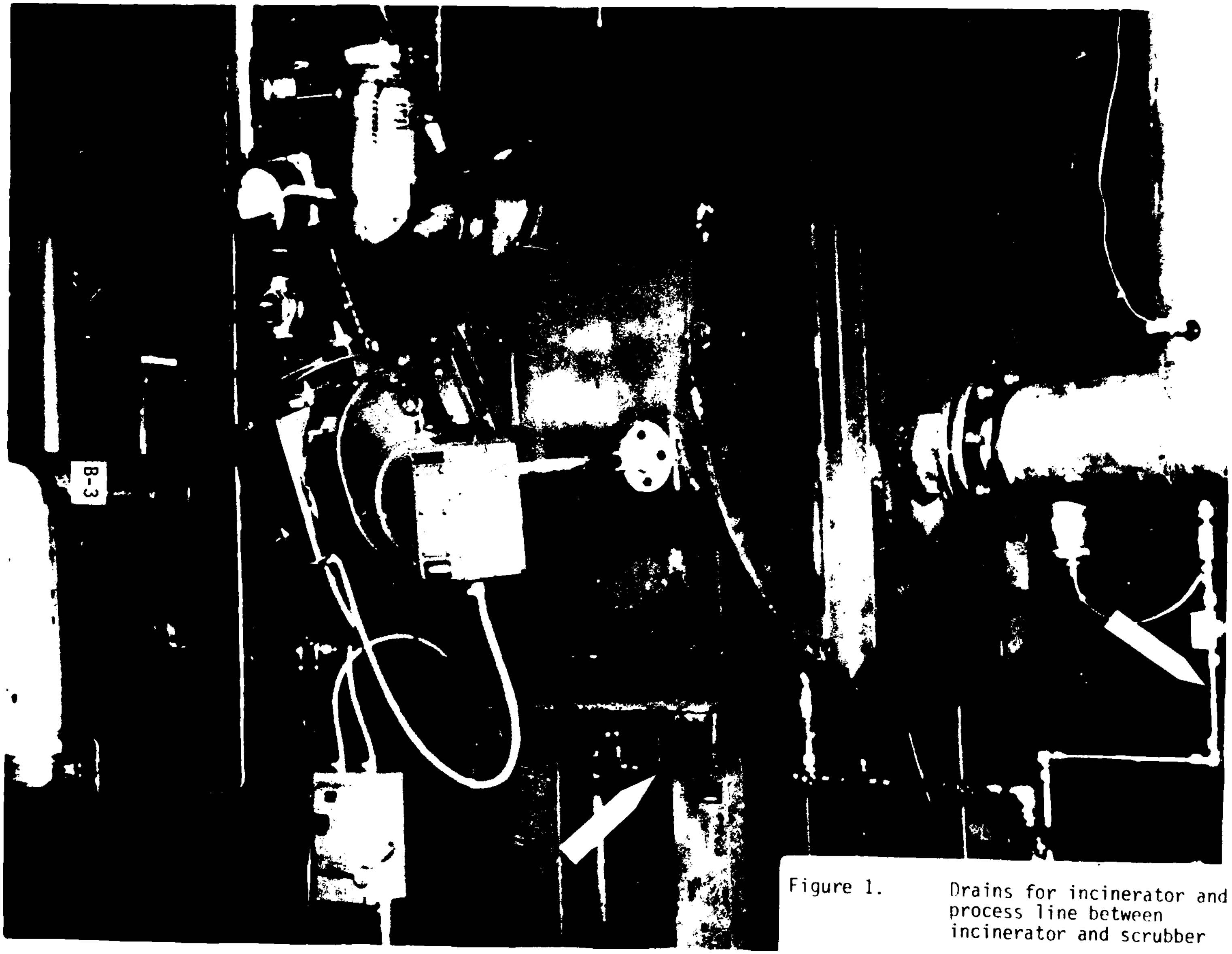


Figure 1. Drains for incinerator and process line between incinerator and scrubber

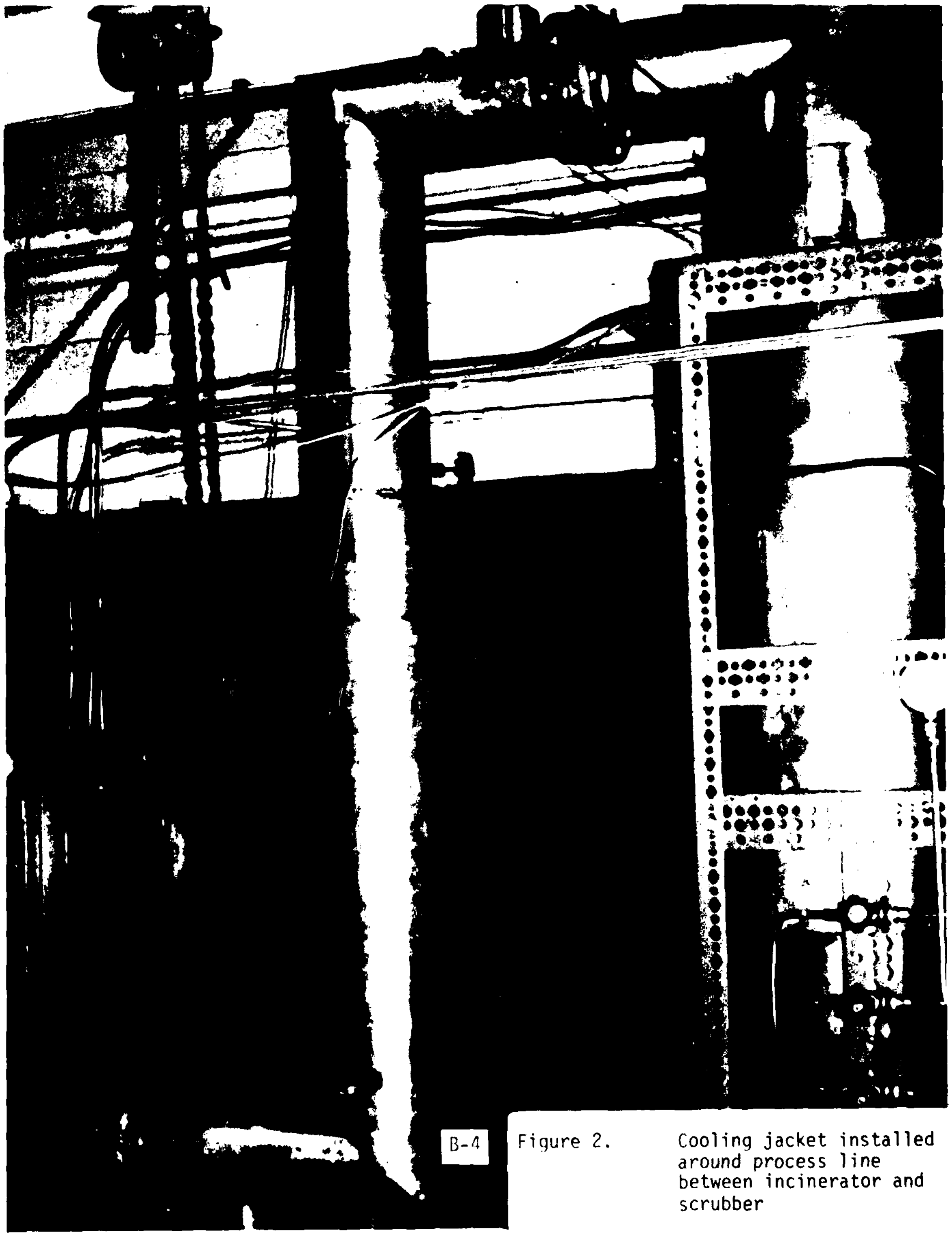


Figure 2. Cooling jacket installed around process line between incinerator and scrubber

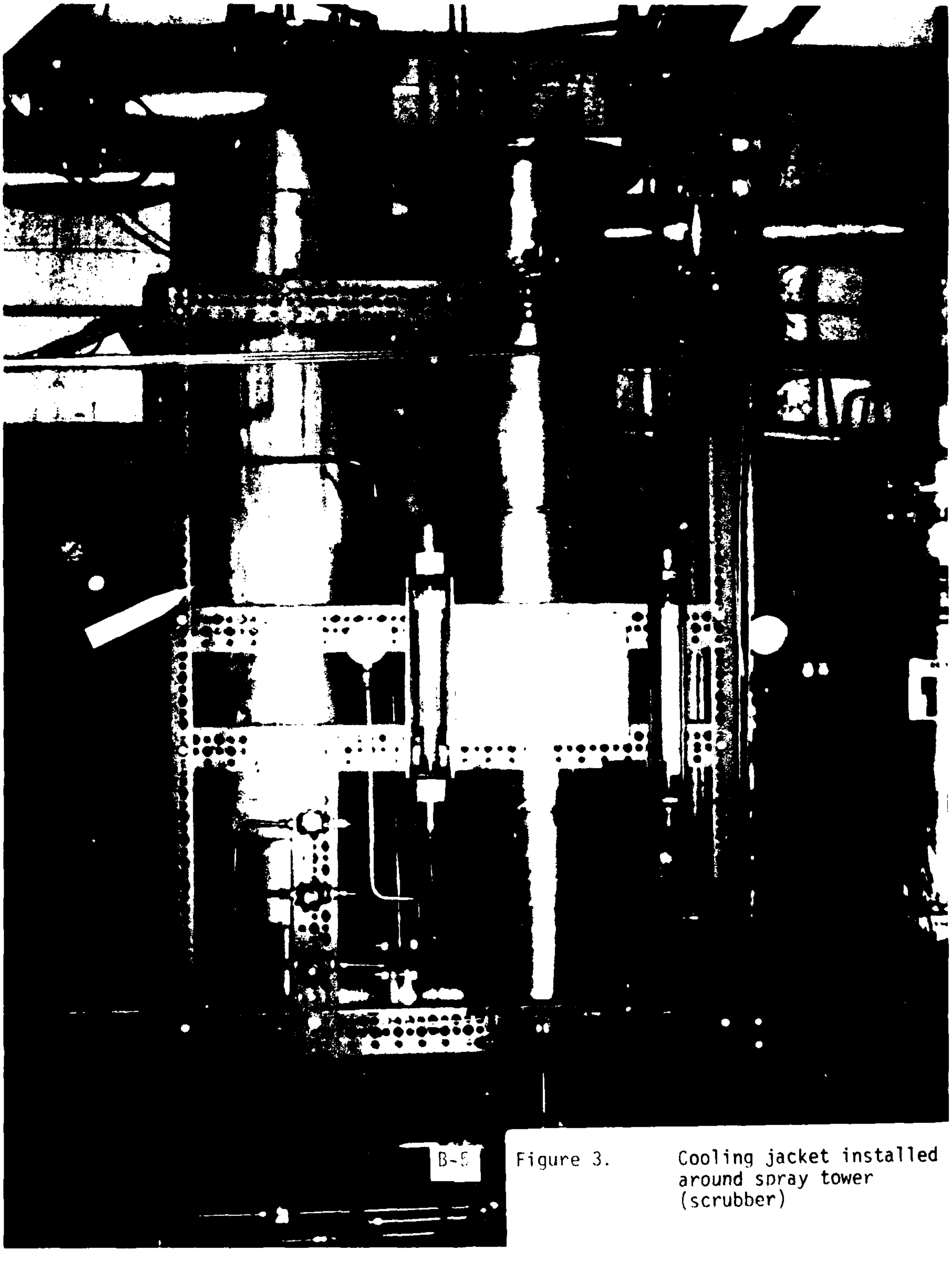


Figure 3. Cooling jacket installed around spray tower (scrubber)

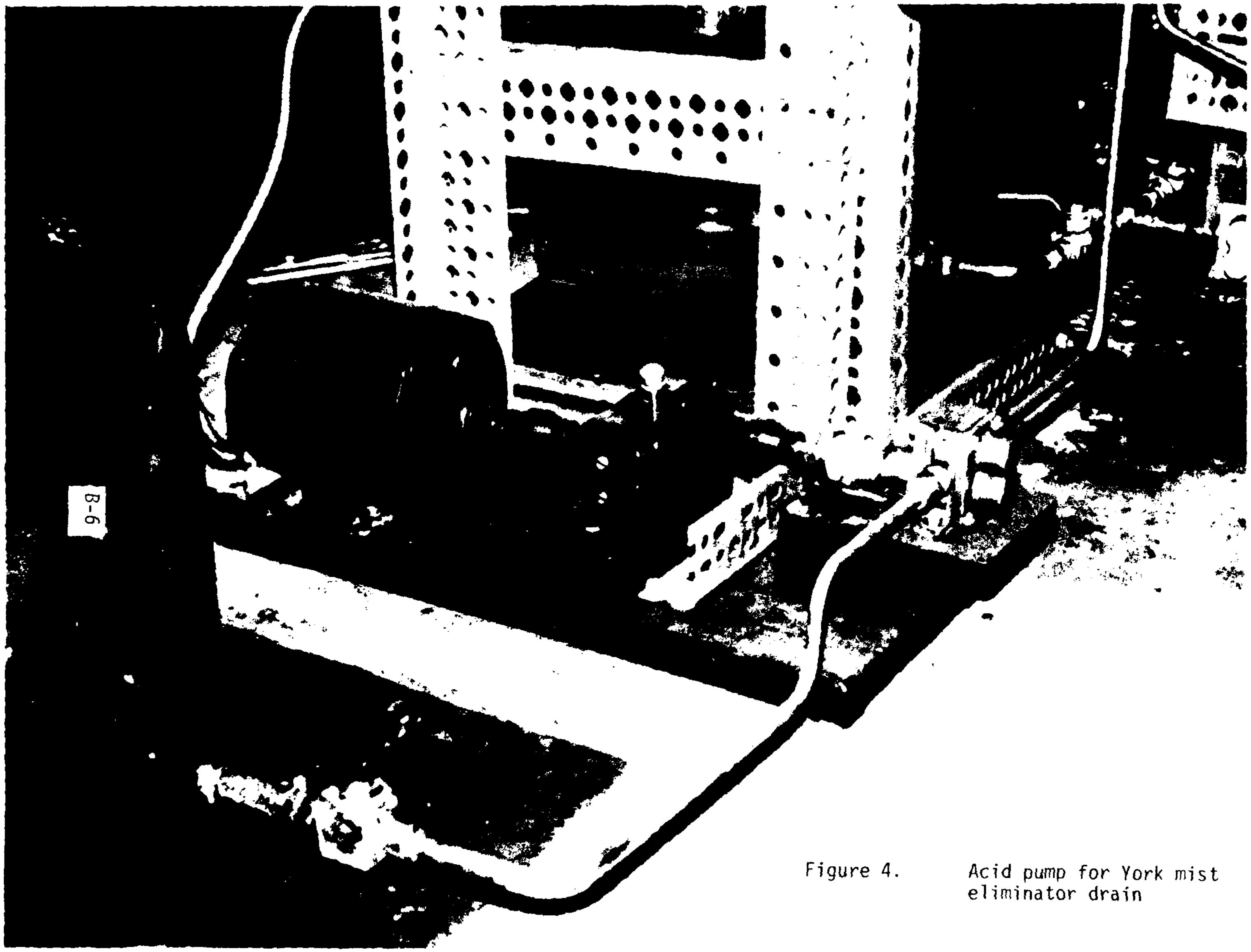


Figure 4. Acid pump for York mist eliminator drain

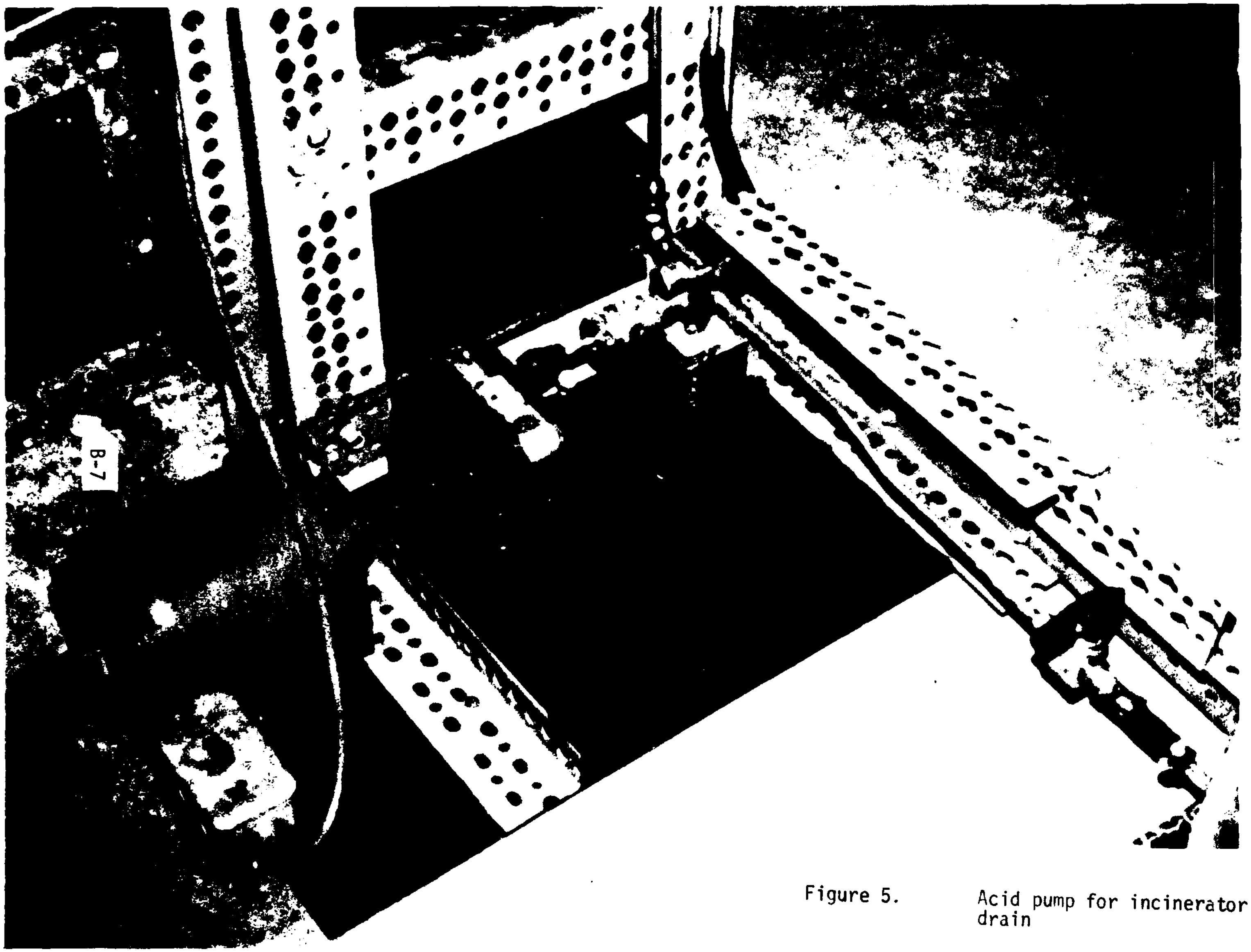


Figure 5. Acid pump for incinerator drain

7. Installation of a 24-point Leeds and Northrup temperature recorder (see Figure 6).

8. Installation of an oxygen analyzer (Leeds and Northrup) (see Figures 6 and 7).

9. Installation of an oxygen analyzer recorder (Leeds and Northrup) (see Figure 6).

10. Installation of a sampling system for oxygen analysis (see Figure 8).

Two (2) checkout runs were made to test newly installed instruments and equipment. Necessary repairs were completed. The installations were inspected by the Project Officer (James E. Short, Jr.) in a project review meeting, held at Battelle-Columbus during the period of March 29-30, 1977.

Analyses of Various Gas, Acid, and Ash Samples

Analyses of various gas, acid, and ash samples were made as required by Contract Modification No. 6. The detailed discussions are given below:

Pilot Plant Operation

The test operations of the pyrotechnic combustion pilot plant after modifications have been completed. A total of seven runs were made: two runs for instrument checkout after plant modifications and five runs for combustion experiments and collection of various gaseous, liquid, and ash samples.

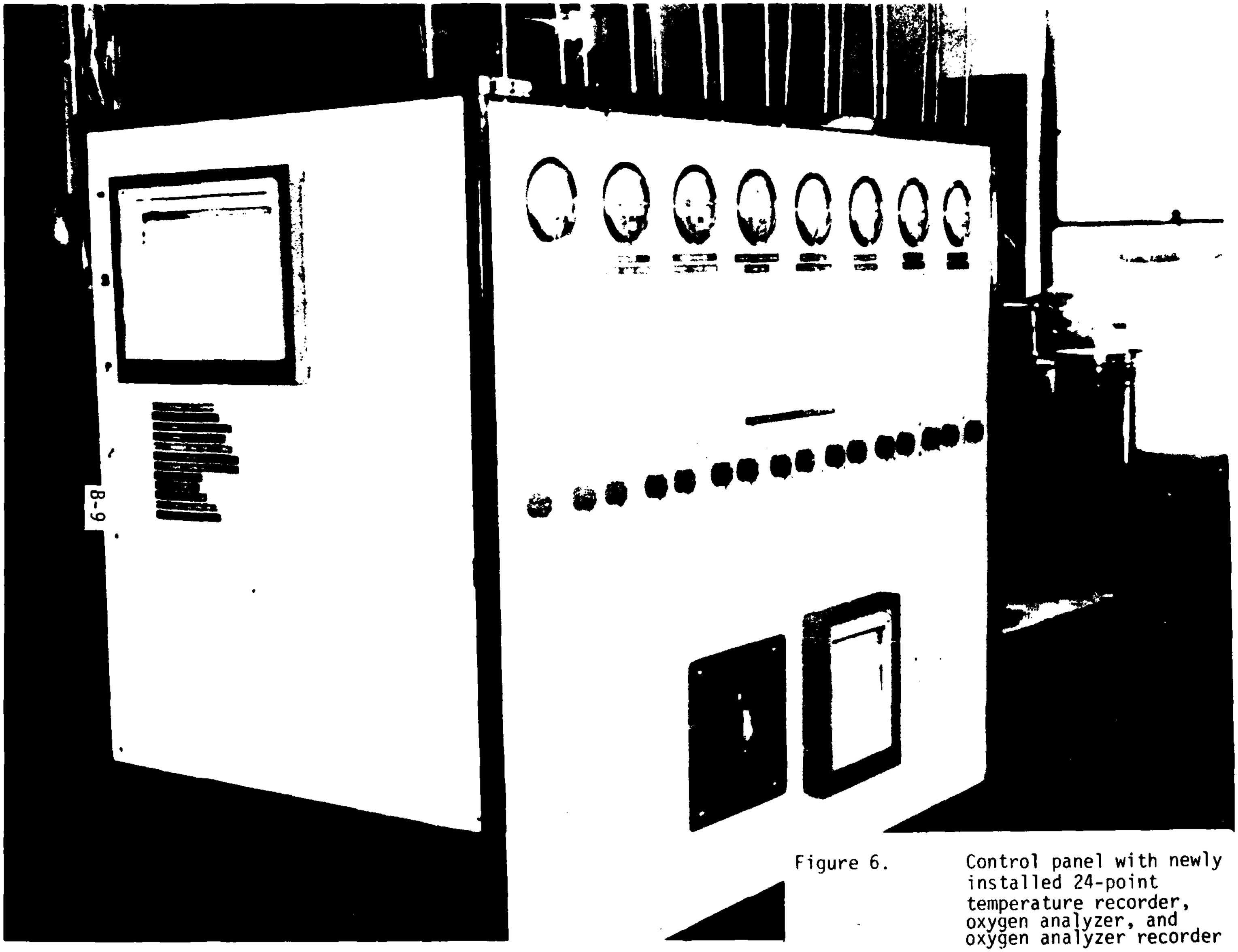


Figure 6. Control panel with newly installed 24-point temperature recorder, oxygen analyzer, and oxygen analyzer recorder

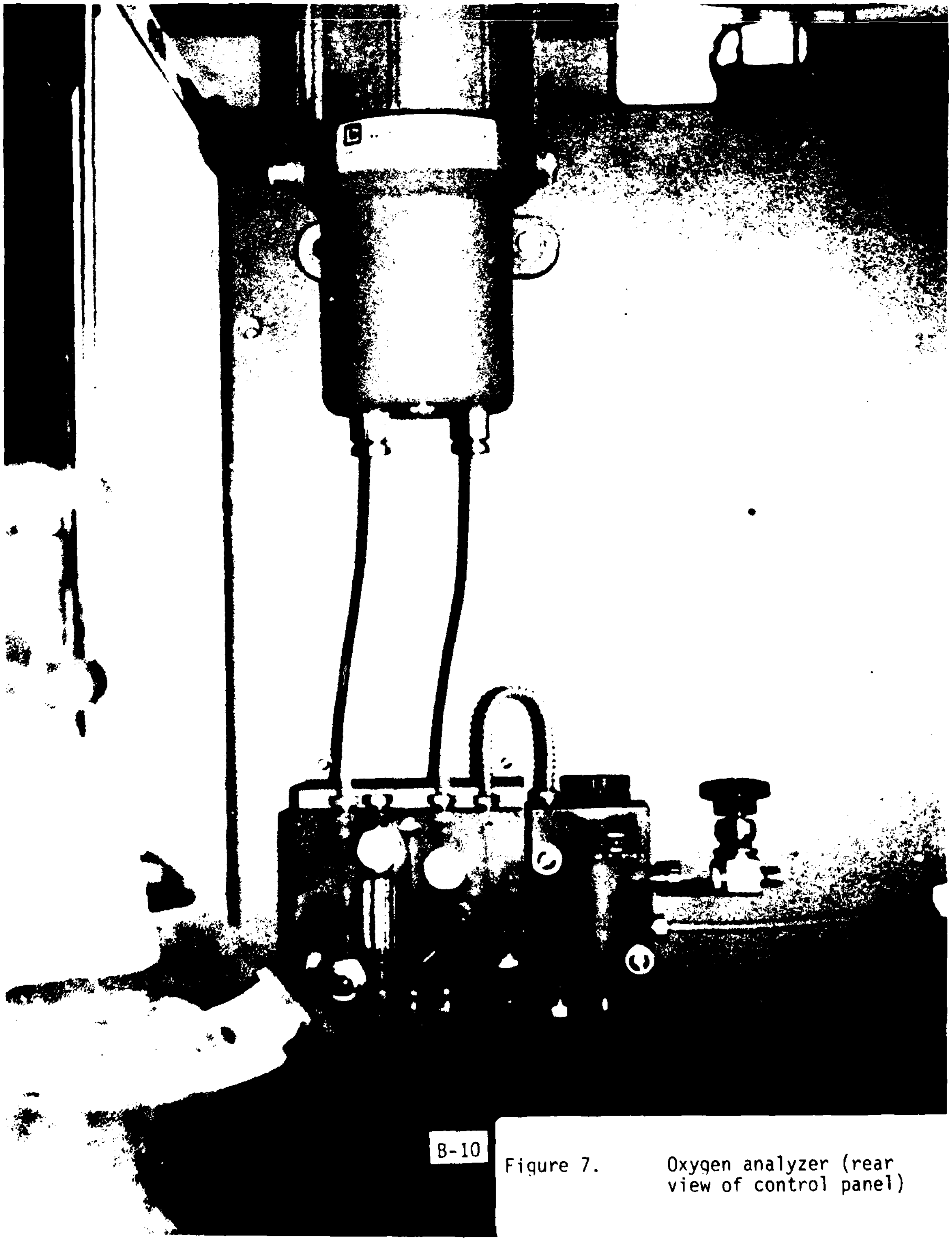


Figure 7. Oxygen analyzer (rear view of control panel)

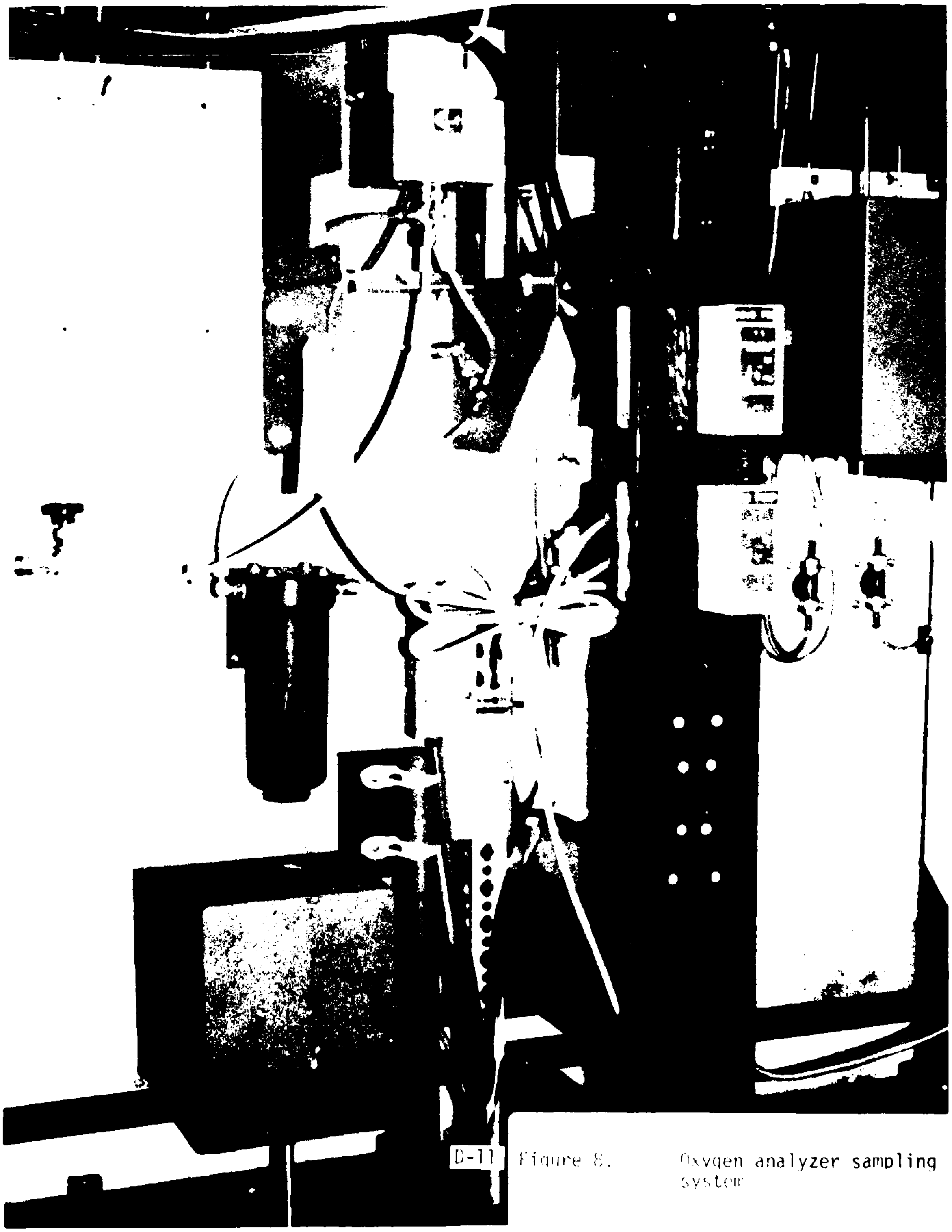


Figure 8. Oxygen analyzer sampling system

TABLE 1. TEST OPERATIONS OF PYROTECHNIC COMBUSTION PILOT PLANT WITH MODIFICATIONS

Operation of Pilot Plant	Run AA-1	Run AA-2	Run AA-3	Run AA-4	Run AA-5	Run AA-6	Run AA-7
Date	3/23/77	3/24/77	3/30/77	4/7/77	4/8/77	4/11	4/19/77
Operating Condition							
Position of Burner 1$^{(a)}$	Lower	Lower	Lower	Lower	Lower	Lower	Lower
Charge Pan Opening Lid	100% open	100% open	100% open	100% open	100% open	100% open	100% open
Side wall	50% open	50% open	50% open	50% open	50% open	50% open	50% open
Preheating Temperature, °F							
Chamber 1	No Preheating	No Preheating	110	120	100	110	—
Chamber 2	No Preheating	No Preheating	960	900	940	920	
Load, lb.	None	None	8.81 (wet, w/o paper)	10.00 (wet, w/o paper)	10.00 (wet, w/o paper)	10.00 (wet, w/o paper)	10.63 (wet, w/o paper)
Combustion							
Preheating Period, min.	—	—	87	90	89	84	33
Time to Ignition, min.	—	—	2	4	1	1	1
Combustion Period, min.	200$^{(a)}$	300$^{(a)}$	12	12	14	15	12
Maximum Temperature, °F							
Chamber 1 (Inside Charge Pan)	950 (1,200)	1,370 (1,630)	1,390 (1,800)	1,240 (1,550)	1,190 (1,740)	1,300 (1,800)	1,400 (1,900)
Chamber 2	1,300	1,500	1,700	1,700	1,720	1,670	1,810
Pressure in Both Chambers, inch of water vacuum	0.2	0.2	0.3	0.3	0.3	0.3	0.3
Recycle Acid for Gas Scrubbing							
Initial Conc., % by wt.	—	—	50.13	47.20	54.00	41.0	50.71
Initial Volume, gal.	—	—	3.69	4.12	3.69	4.49	3.70
Final Conc., % by wt.	—	—	46.90	53.53	40.35	51.0	59.13
Final Volume, gal.	—	—	4.15	3.73	5.60	3.70	2.90
York Mist Elimination (ME) Drain							
Volume, gal.	—	—	0.801	1.004	0.946	1.007	0.882
Conc., % by wt.	—	—	49.64	51.20	54.82	54.82	57.50
Incinerator Drain							
Volume, gal.	—	—	0.258	1.535	0.758	0.824	1.038
Conc., % by wt.	—	—	50.50	7.90	24.67	26.07	21.05
Stack Gas							
Flow Rate, scfm	126	126	140	115	118	123	120
Temperature, °F	120	105	110	120	120	125	130
Minimum Oxygen Content, % by vol.	—	—	—	—	—	—	—
Acid Emission, mg P_2O_5/scf	—	—	—	—	—	—	—
Combustion Residue							
Quantity, lb.	—	—	NM	8.06$^{(b)}$	7.85$^{(b)}$	3.56$^{(d)}$	7.06$^{(d)}$
Total Phosphorus, % by wt.	—	—	18.1 (19.2)$^{(c)}$	18.3 (20.4)$^{(c)}$	17.5 (20.9)$^{(c)}$	NM	NM
Remarks	Check-out test run for newly installed instruments and cooling jackets. Three thermocouples were replaced	The second check-out test run. O_2 analyzer did not work	Water sprayed over the combustion residues reacted with metal phosphide to generate phosphine. The gas ignited spontaneously with no sign of explosion. The treated ash did not react with water. The recycle acid was analyzed for heavy metals.	Stack gas samples were taken for SO_2, PH_3, and NO_x during preheating, combustion, and ash treatment periods.	Stack gas samples were taken for SO_2, PH_3, and NO_x during preheating, combustion, and ash treatment periods. Acid samples were taken for heavy metals analyses.	A gas sample was collected from the ash-water reaction for PH_3 analysis. A recycle acid sample was taken for heavy metal analyses.	A gas sample was collected from the ash-water reaction for PH_3 analysis.

FOOTNOTES FOR TABLE 1

(a) This represents the total operating time after ignition of the gas burners.

(b) This represents the weight of ash after water treatment.

(c) The value in parenthesis represents the total phosphorus on dry basis of the ash sample taken after water treatment. The total P in the ash sample taken after water treatment is higher in concentration than that in the ash sample taken before water treatment probably because the water which becomes acidic after quenching extract magnesium oxide and manganese oxide from the ash resulting in a decrease in the total weight of the ash.

(d) The value represents the weight of ash after water treatment and measured overnight.

TABLE 2. PHOSPHORUS BALANCE IN PYROTECHNIC COMBUSTION PILOT PLANT

Item	Run AA-3	Run AA-4	Run AA-5	Run AA-6	Run AA-7
P in Feed, lb.	4.25	4.82	4.82	4.82	5.13
P Recovered as Acid,					
Weight, lb.	2.06	2.64	2.75	3.22	2.51
% of Feed, %	48.5	54.8	57.1	66.8	48.9
P in Combustion Residue,					
Weight, lb.	0.92(a)	1.01	1.10	1.15(b)	1.45(b)
% of Feed, %	21.6	21.0	22.8	23.9	28.3
Balance of P					
Weight, lb.	1.27	1.17	0.97	0.45	1.17
% of Feed, %	29.9	24.3	20.1	9.3	22.8
Acid Yield %	48.5	54.8	57.1	66.8	48.9

(a) The value was estimated by assuming the ratio of weight of wet ash to weight of wet feed as 0.79.

(b) The value was estimated by assuming the total phosphorus concentration in ash as 20.6 percent by weight.

The newly installed oxygen analyzer was found to be not functioning. The unit was returned to the supplier (Leeds and Northrup) for repair. The cooling jackets installed around the process line between the incinerator and the first column of the scrubber, and around the first column of the scrubber were able to provide an additional cooling of the stack gas by 20 to 40°F. The performance of the ash treatment system was satisfactory, providing an inert ash after treatment with sprayed water. The acid yield was improved from 41 percent to 55 percent in average based on phosphorus in feed. The conditions and results of the test operations are given in Table 1, and the results of phosphorus balance for Runs AA-3 to AA-7 are given in Table 2.

Stack-Gas Emissions

Stack gas was sampled during Runs AA-4 and AA-5 and analyzed for SO_2, NO_x, and PH_3. The results are shown in Table 3. Considering the tolerance limits for the pollutants in air, which are 5 ppm for SO_2 and NO_2 and 0.3 ppm for PH_3, the emissions from the pilot plant are not considered environmentally significant because the concentrations in the ambient air would be much lower than that at the stack due to dilution with air.

Ash-Water Reaction Experiments

The combustion residue generated from the incineration of the flare material should be safe in handling. Since the flare material contains red phosphorus (53 percent) as well as Pyrolusite (34 percent), magnesium (7 percent), and zinc oxide (3 percent), one would expect that metal phosphides such as Mg_3P_2, Zn_3P_2, MnP, Mn_2P, and Mn_3P_2 would be formed in the residue due to a local reducing environment in the middle of the flare pile. The metal phosphides readily react with water to generate phosphine which is toxic with a tolerance limit of 0.3 ppm in air. A series of experiments have been made to examine the emission of phosphine from the combustion residue (ash) and the results are given in Table 4. The findings from the experiment are:

1. The ash became chemically inert to water after remaining in the combustion chamber overnight. The metal phosphides might have reacted with moisture in the air and thus have been converted into more stable metal oxides or hydroxides.
2. The volume of the off-gas generated from the ash-water reaction was measured at 0.59 to 2.06 cm^3/g of ash at atmospheric pressure and room temperature. The phosphine generation was measured at 0.84 to 1.63 mg of PH_3/g of ash. The composition of the reaction off-gas is shown in Table 5.
3. The performance of the ash treatment system, which involves water spraying over the ash in the first combustion chamber, has been satisfactory, resulting in an ash chemically inert to water. No indication of explosion has been noticed during the treatments.

TABLE 3. STACK GAS EMISSIONS OTHER THAN PHOSPHORIC ACID

Pollutants	Run AA-4			Run AA-5		
	Preheating	Combustion	Ash Treatment	Preheating	Combustion	Ash Treatment
SO_2, ppb	<10	31	NM(a)	13	<10	NM
NOx, ppm	<0.4	4.0	NM	<0.4	0.6	NM
PH_3, ppb	<15	<15	130	<15	<15	<15

(a) Not measured.

TABLE 4. OFF-GAS GENERATION FROM ASH-WATER REACTION

Item	Run A-17	Run A-17	Run A-17	Run A-18	Run A-18	Run A-18	Run A-19
Time of Combustion Completion	15:09, 8/30/76	15:09, 8/30/76	15:09, 8/30/76	12:50, 9/8/76	12:50, 9/8/76	12:50, 9/8/76	11:00, 9/9/76
Time of Ash Experiment	15:40, 8/30/76	15:50, 8/30/76	14:00, 8/30/76	13:42, 9/8/76	16:32, 9/8/76	9:00, 9/9/76	13:47, 9/9/76
Ash Used, g	500	400	400	500	500	500	500
Water Used, ml	2,000	2,000	2,000	2,000	2,000	2,000	2,000
Off-gas Collected, cm^3	145	285	175	260	270	?	270
Estimated Loss of Off-gas,$^{(a)}$ cm^3	150	150	150	100	100	0	100
Off-gas Generated, cm^3/g of ash	0.59	1.09	0.81	0.72	0.74	0.014	0.74
Volume of Existing Gas,$^{(b)}$ cm^3	0	0	0	0	0	0	0
PH_3 Conc. in Gas Sample, % by vol.	NM$^{(c)}$	NM	57.0	NM	81.1	NM	79.0
PH_3 Conc. in Off-gas, % by vol.	NM	NM	57.0	NM	81.1	NM	79.0
PH_3 Generated, mg of PH_3/g of ash	NM	NM	0.869	NM	0.862	NM	0.842
Remarks	The off-gas ignited spontaneously when contacted with air without a sign of explosion.	The off-gas ignited spontaneously when contacted with air.	The inside surface of the sample bulb was covered with brown deposits. The deposits were considered to be oxides of phosphorus or elemental phosphorus formed when phosphine reacted with oxygen in the vacuum bulb.			The ash became inert over night. The phosphides in the ash might react with moisture in air.	

TABLE 4. (Continued)

Item	Run A-19	Run AA-4	Run AA-5	Run AA-6	Run AA-5	Run AA-7	Run AA-7	Run AA-7
Time of Combustion Completion	11:00, 9/9/76	11:27, 4/7/77	10:44, 4/8/77	15:40, 4/11/77	15:40, 4/11/77	14:36, 4/19/77	14:36, 4/19/77	14:36, 4/19/77
Time of Ash Experiment	13:57, 9/9/76	13:00, 4/7/77	13:00, 4/8/77	16:00, 4/11/77	15:30, 4/11/77	15:00, 4/19/77	15:30, 4/19/77	15:30, 4/19/77
Ash Used, g	500	500$^{(d)}$	500$^{(d)}$	404	46.1	52	192	223.1
Water Used, ml	2,000	2,000	2,000	65	100	100	220	170
Off-gas Collected, cm^3	340	0	0	490	95	45	115	275
Estimated Loss of Off-gas,$^{(a)}$ cm^3	100	0	0	0	0	0	0	0
Off-gas Generated, cm^3/g of ash	0.88	0	0	1.21	2.06	0.865	0.599	1.233
Volume of Existing Gas,$^{(b)}$ cm^3	0	0	0	995$^{(e)}$	1,169$^{(e)}$	126$^{(e)}$	206$^{(f)}$	191$^{(e)}$
PH_3 Conc. in Gas Sample, % by vol.	NM	0	0	NM	0.05	NM	NM	51.4
PH_3 Conc. in Off-gas, % by vol.	NM	0	0	NM	0.58	NM	NM	87.01
PH_3 Generated, mg of PH_3/g of ash	NM	0	0	NM	0.018	NM	NM	1.628
Remarks		The ash became inert after treatment.	The ash became inert after treatment.				The off-gas ignited spontaneously in the reaction container.	

FOOTNOTES FOR TABLE 4

(a) This is an assumed value.

(b) The reaction container was initially filled with water, air, or nitrogen.

(c) Not measured.

(d) Ash treated with water was used.

(e) The reaction container was initially flushed with nitrogen.

(f) The reaction container was initially filled with air.

TABLE 5. COMPOSITION OF OFF-GAS FROM ASH-WATER REACTION

	Percent by Volume			
Compound	Run A-17[(a)]	Run A-18[(a)]	Run A-19[(a)]	Run AA-7[(b)]
CO_2	0.5	0.12	0.02	0.04
A	0.5	0.23	0.25	0.11
PH_3	57.00	81.10	79.00	51.40
N_2	34.00	14.60	16.10	45.90
H_2	8.00	3.97	4.59	2.58
O_2	<1.	<1.	<1.	<1.
TOTAL	100.0	100.02	99.96	100.03

(a) The reaction container was initially filled with water.

(b) The reaction container was initially flushed with nitrogen.

Trace Metals in Product Phosphoric Acid

In order to examine the possible use in the manufacture of commercial grade fertilizer, the product phosphoric acid was analyzed for the concentrations of various heavy metals, i.e., Mn, Mg, Zn, Cr, and Ni. The results are shown in Table 6. In general, the concentrations in the scrubbing acid increase with respect to the number of runs made with the acid. On the other hand, the heavy metal concentrations in the acid collected by the York mist eliminator are consistent in each of the runs. Manganese, magnesium, and zinc must come from the feed flare and chromium and nickel would be extracted from stainless steel equipment construction material. It should be noted here that the levels of concentrations of Mn, Mg, and Zn in the product acids are not consistent with those in the feed flare. That is, the content of zinc in the feed (i.e., 3 percent by weight) is less than those of magnesium (7 percent by weight) and manganese (more than 30 percent by weight) while the concentration of zinc in the product acids (1,100 to 1,860 ppm for scrubber acid and 5,550 to 5,850 ppm for York mist eliminator drain) is much higher than those of magnesium (41 to 108 ppm for scrubber acid and 220 to 234 for York mist eliminator drain) and manganese (4 to 22 ppm for scrubber acid and 26 ppm for York mist eliminator drain). This may be because the boiling point of zinc (970°C) is lower than those of magnesium (1,107°C) and manganese (2,097°C) and thus, zinc could be more volatile than magnesium and manganese. This hypothesis may also explain why the concentrations of zinc, magnesium, and manganese in the acid collected at the York mist eliminator are higher than those in the scrubber acid.

TABLE 6. ANALYSIS OF TRACE METALS IN PRODUCT PHOSPHORIC ACID

Item	Run 5	Run AA-3	Run AA-5	Run AA-5	Run AA-6	Run AA-6
Source of Acid	Scrubber	Scrubber	Scrubber	York ME	Scrubber	York ME
Number of Batch Operations Made with Acid	2	1	3	-	4	-
Acid Conc., % by weight	45.59	46.90	40.35	54.82	51.0	54.82
Trace Metal Conc., ppm						
Mn	NM	4	13	26	22	26
Mg	NM	41	65	220	108	234
Zn	NM	1,600	1,100	5,850	1,860	5,550
Cr	310	14	66	1	129	1
Ni	310	8	28	2	60	2

APPENDIX C

HAZARD ANALYSIS

PRELIMINARY HAZARD ANALYSIS (PHA)	DEPARTMENT:	REVISION:	COMPILED BY:	CODE:	REVIEWED BY:	C-2
	PROCESS LINE:	REV DATE:				

ITEM NO.	ITEM NOMENCLATURE	OPERATION AND/OR ENERGY SOURCE	UNDESIRED EVENT	* TRIGGERING EVENT	EFFECTS	** PROBA-BILITY	HAZARD CATE-GORY	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS	CONTROLS AND/OR CORRECTIVE ACTIONS USED, OR COMMENTS	**REV. PROBA-
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)

FLOW PROCESS

In this flow process the following operations are performed. A pallet of Mk 25 Marine Location Markers is moved to the depalletizing area where the markers are depalletized. One at a time the markers are placed in the band saw where the base fuze housing is removed from the marker. The inner tube and candle assembly are slipped from the outer tube and foam liner. The inner tube with the candle assembly is placed in the push out fixture where the candle assembly is pushed from the inner tube through a scoring die to cut the paper tube. The igniter cup and first fire are removed to separate storage containers. The candle is placed in the radial arm saw where it is sawed into chunks and allowed to soak under water. The chunks are dumped from the water reservoir, the paper is peeled off, and the composition is placed in a conveyor bucket. The conveyor transports the composition toward the incinerator and dumps into a charge pan. The charge pan is shoved into the incinerator. The composition is burned, converting the red phosphorus to phosphorus pentoxide (P_2O_5), and the stack gases are scrubbed with water to generate phosphoric acid. After combustion, the hot ashes are sprayed with water to generate phosphine which is burned in the incinerator prior to ash removal.

*CAUSE INCLUDES EFFECTS OF HUMAN ERROR, NORMAL AND ABNORMAL ENVIRONMENTS, DESIGN DEFICIENCIES, AND/OR INCOMPATIBILITIES.

**ENTER ONE OF THE FOLLOWING:

LOW	- LOW OR REMOTE PROBABILITY
MEDIUM	- 0.001 TO 0.0001 PROBABILITY
HIGH	- 0.001 OR HIGHER PROBABILITY
UNK	- UNKNOWN PROBABILITY

PRELIMINARY HAZARD ANALYSIS | PROCESS LINE: Red Phosphorus | DEPARTMENT: Applied Sciences | REVISION: 0 | PAGE NUMBER: C-3

ITEM NO. (1)	ITEM NOMENCLATURE (2)	OPERATION AND/OR ENERGY SOURCE (3)	UNDESIRED EVENT (4)	TRIGGERING EVENT (5)	EFFECTS (6)	PROBABILITY (7)	HAZARD CATEGORY (8)	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS (9)	CONTROLS AND OR CORRECTIVE ACTIONS USED, OR COMMENTS (10)	**REV. PROBABILITY (11)
1	Pallet of Mk 25 Marine Location Markers (hereafter called marker or marker component whenever differentiation between the two is not necessary).	Moving pallet of markers from Bldg. storage area to depalletizing area.	Marker initiation or damage.	Pallet of markers struck, dropped or mishandled by MHE.	Marker(s) destroyed, MHE damaged or destroyed, MHE operator injured, building requires clean-up and/or repairs.	med	III	MHE operators be trained in the marker operation and inherent hazards, MHE be maintained regularly to lessen probability of equipment failure, MHE operator inspect MHE for faulty equipment prior to each use, MHE operator inspect pallet of markers for improper palletizing, banding, etc., prior to moving. Markers are packaged and palletized in accordance with OS-8738 and WR 54-54.	Use all actions given in (9).	low
2	Packaging container containing 18 markers.	Depalletizing.	Initiation or destruction of markers.	Packaging container improperly handled during depalletizing.	Markers(s) destroyed, operator injured, building requires clean-up.	low	III	Operator be trained in marker operation & inherent hazards, operator be trained and certified in proper depalletizing methods. Safety department regularly inspect to ensure proper techniques are used.	Use all actions given in (9).	low

PRELIMINARY HAZARD ANALYSIS		PROCESS LINE: Red Phosphorus		DEPARTMENT: Applied Sciences				REVISION: 0	PAGE NUMBER: C-4	
[illegible]	ITEM NOMENCLATURE (2)	OPERATION AND/OR ENERGY SOURCE (3)	UNDESIRED EVENT (4)	TRIGGERING EVENT (5)	EFFECTS (6)	PROBABILITY (7)	HAZARD CATEGORY (8)	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS (9)	CONTROLS [illegible] USED, OR COMMENTS (10)	[illegible]
3	Operator.	Depalletizing.	Operator injured.	a. Dropping packaging container containing markers on self.	a.Disabling injury.	a.med	a.III	a.Operator be certified and trained in proper depalletizing and handling methods. Safety regularly inspect to ensure proper techniques are used.	a.Use all actions given in (9).	a.low
				b. Operator struck by banding.	b.Disabling injury.	b.med	b.III	b.Operator be trained in safe debanding procedures, operator wear PPE, operator use safety band cutters. Safety department regularly inspect to ensure proper techniques are used.	b.Use all actions given in (9).	b.low

PRELIMINARY HAZARD ANALYSIS		PROCESS LINE: Red Phosphorus		DEPARTMENT: Applied Sciences				REVISION: 0	PAGE NUMBER: C-5	
ITEM NO. (1)	ITEM NOMENCLATURE (2)	OPERATION AND/OR ENERGY SOURCE (3)	UNDESIRED EVENT (4)	TRIGGERING EVENT (5)	EFFECTS (6)	PROBA-BILITY (7)	HAZARD CATE-GORY (8)	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS (9)	CONTROLS AND/OR CORRECTIVE ACTIONS USED, OR COMMENTS (10)	[illegible]
4	Individual marker.	Moving marker from packaging container to placing marker in band saw.	Marker initiation or damage.	Improper handling.	Operator injured, marker destroyed, building requires clean-up.	low	III	Operator be trained in marker operation and inherent hazards, operator be trained and certified in proper marker handling methods. Safety department inspect regularly to ensure proper techniques are used.	Use all actions given in (9).	low
5	Operator.	Handling marker from packaging container to placing marker in band saw.	Operator injured.	Operator dropping marker on self.	Disabling injury.	med	III	Controls are remote. Operator be trained and certified in proper marker handling methods, operator wear safety shoes. Safety department regularly inspect to ensure proper techniques are used.	Use all actions given in (9).	low
6	Marker	Placing marker in band saw.	Marker initiation or damage.	Improper installation in band saw.	Marker destroyed, band saw damaged, operator injured, building requires clean-up.	low	III	Controls are remote. Operator be trained and certified in proper marker handling methods, operator wear safety shoes. Safety department regularly inspect to ensure proper techniques are used. Operator be trained in proper use of band saw.	Use all actions given in (9).	low

PRELIMINARY HAZARD ANALYSIS | PROCESS LINE: Red Phosphorus | DEPARTMENT: Applied Sciences | REVISION: 0 | PAGE NUMBER: C-6

ITEM NO.	ITEM NOMENCLATURE	OPERATION AND/OR ENERGY SOURCE	UNDESIRED EVENT	TRIGGERING EVENT	EFFECTS	PROBABILITY	HAZARD CATEGORY	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS	CONTROLS AND/OR CORRECTIVE ACTIONS USED, OR COMMENTS	**REV. PROBABILITY
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
7	Operator.	Installing marker in band saw.	Operator getting hand or fingers cut in band saw.	Hand or fingers in band saw when saw is activated.	Disabling injury.	low	III	Operator be trained in proper use of band saw. Saw is in "off" position for loading and unloading operations. Safety department regularly inspect to ensure proper techniques are used.	Use all actions given in (9).	low
8	Inner tube with candle assembly.	Removal of inner tube with candle assembly from outer tube & foam liner.	Candle initiation.	Static electricity.	Disabling injury.	low	III	Operator wear conductive soled shoes and cotton clothing only. Safety department inspect regularly to ensure proper clothing & techniques are used.	Use all actions given in (9).	low
9	Candle.	Candle push out & paper tube cut.	Candle ignition.	Friction from cutter wheel.	Candle destruction, operator injury, machine damage, building requires clean-up.	low	III	Area around expulsion end of candle shall be kept clear at all times during push out. Recommend push apart operation be further analyzed.	This hazard is to be further analyzed.	

PRELIMINARY HAZARD ANALYSIS | PROCESS LINE: Red Phosphorus | DEPARTMENT: Applied Sciences | REVISION: 0 | PAGE NUMBER: C-7

ITEM NO. (1)	ITEM NOMENCLATURE (2)	OPERATION AND/OR ENERGY SOURCE (3)	UNDESIRED EVENT (4)	TRIGGERING EVENT (5)	EFFECTS (6)	PROBA-BILITY (7)	HAZARD CATE-GORY (8)	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS (9)	CONTROLS AND/OR CORRECTIVE ACTIONS USED, OR COMMENTS (10)	**REV. PROBA-BILITY (11)
10	Candle.	Removal of igniter cup and first fire.	Candle ignition.	Static electricity.	Candle destruction, operator injury.	low	III	Operator wear conductive soled shoes and cotton clothing only. All equipment grounded. Safety department regularly inspect to ensure proper clothing and techniques are used.	Use all actions given in (9).	low
11	Candle.	Sawing candle into chunks.	Candle ignition.	Friction from sawing.	Candle destruction, machine damage.	low	III	Candle under water during sawing operation. Operator starts and stops saw remotely. Operator wears conductive soled shoes and cotton clothing only. All equipment grounded. Safety department regularly inspect to ensure proper clothing and techniques are used.	Use all actions given in (9).	low

PRELIMINARY HAZARD ANALYSIS | PROCESS LINE: Red Phosphorus | DEPARTMENT: Applied Sciences | REVISION: 0 | PAGE NUMBER: C-8

ITEM NO. (1)	ITEM NOMENCLATURE (2)	OPERATION AND/OR ENERGY SOURCE (3)	UNDESIRED EVENT (4)	TRIGGERING EVENT (5)	EFFECTS (6)	PROBABILITY (7)	HAZARD CATEGORY (8)	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS (9)	CONTROLS AND/OR CORRECTIVE ACTIONS USED, OR COMMENTS (10)	**REV. PROBABILITY (11)
12	Composition	Taking wet paper from composition.	Ignition of composition.	Static electricity.	Composition destruction, operator injury, machine damage.	low	III	Composition & paper are wet. Operator wears conductive soled shoes and cotton clothing with water proof gloves. All equipment grounded. Safety department regularly inspect to ensure proper clothing and techniques are used.	Use all actions given in (9).	low
13	Composition	Conveying & dumping into charge pan.	Ignition of composition.	a. Friction between composition & conveyor cover.	a. Composition destruction, machine damage.	a. low	a. II	a. Composition is wet. Operator instructed to not overload conveyor buckets. Safety department regularly inspect to ensure proper techniques are used.	a. Use all actions given in (9).	a. low
				b. Friction between composition & dump chute.	b. Composition destruction, machine damage.	b. low	b. II	b. Composition is wet. Operator instructed to not overload conveyor buckets. Safety department regularly inspect to ensure proper techniques are used.	b. Use all actions given in (9).	b. low

PRELIMINARY HAZARD ANALYSIS			PROCESS LINE: Red Phosphorus		DEPARTMENT: Applied Sciences				REVISION: 0	PAGE NUMBER: C-9
ITEM NO.	ITEM NOMENCLATURE	OPERATION AND/OR ENERGY SOURCE	UNDESIRED EVENT	TRIGGERING EVENT	EFFECTS	PROBA-BILITY	HAZARD CATE-GORY	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS	CONTROLS AND/OR CORRECTIVE ACTIONS USED, OR COMMENTS	**REV. PROBA-BILITY
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
14	Composition.	Feeding composition into incinerator.	Premature ignition of composition.	Composition dry & No. 1 burner on during feeding operation.	Composition destruction, operator injury.	low	III	Composition is wet. Operator shall assure that No. 1 burner is not lit prior to feeding composition into incinerator. Operator wears conductive soled shoes, cotton clothing and fireproof gloves. Safety department regularly inspect to ensure proper clothing & techniques are used.	Use all actions given in (9).	low
15	Ash residue.	Incinerator.	Phosphine (PH_3) generation & leakage from incinerator.	Water contacting hot, partially combusted red phosphorus composition.	Operator injury or death.	low	IV	Water spray in first chamber of incinerator activated for 5 min. after flames from composition have dissipated. Burners in first & second chamber are on to burn any phosphine generated to form phosphorus pentoxide (P_4O_{10}). Operator ensures that the water spray & burners are operated for the prescribed time. Safety department regularly inspects to ensure proper techniques are used.	Use all actions given in (9).	low

PRELIMINARY HAZARD ANALYSIS			PROCESS LINE: Red Phosphorus		DEPARTMENT: Applied Sciences			REVISION: 0		PAGE NUMBER: C-10
ITEM NO.	ITEM NOMENCLATURE	OPERATION AND/OR ENERGY SOURCE	UNDESIRED EVENT	TRIGGERING EVENT	EFFECTS	PROBA-BILITY	HAZARD CATE-GORY	CONTROLS, CORRECTIVE ACTIONS, AND/OR COMMENTS	CONTROLS AND/OR CORRECTIVE ACTIONS USED, OR COMMENTS	**REV. PROBA-BILITY
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
16	Phosphoric acid.	Acid collection & transfer.	Spillage.	Operator error.	Operator injury, machine damage, area requires clean-up.	med	II	Operator wears conductive soled shoes cotton clothing, safety goggles & acid proof gloves for this operation. Should acid contact the body, injury can be avoided by quickly flushing with water. Water required to be available in tub or by garden hose. Safety department regularly inspect to ensure proper clothing & techniques are used.	Use all actions given in (9).	low
17	Incineration.	Incineration complex.	Power failure.	Electrical power outage for any reason.	Gas burners, air pump, instrumentation and all recirculating pumps stop.	low	II	Testing was accomplished under these conditions. The spray nozzle in the first chamber (incinerator) was turned on. The burning composition was cooled and combustion was extinguished.	See (9).	low

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