UNCLASSIFIED

AD NUMBER

AD003174

CLASSIFICATION CHANGES

TO: **unclassified**

FROM: **confidential**

LIMITATION CHANGES

TO:

Approved for public release, distribution unlimited

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; Jan 1953. Other requests shall be referred to Office of Naval Research, 800 North Quincy Street, Arlington, VA 22217-5660.

AUTHORITY

31 Jan 1965, DoDD 5200.10; ONR ltr, 13 Sep 1977

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD NUMBER

AD003174

CLASSIFICATION CHANGES

TO

confidential

FROM

secret

AUTHORITY

31 Jan 1956, DoDD 5200.9

THIS PAGE IS UNCLASSIFIED

AD-
3174

SECRET

31

Oldbury Electro-Chemical Research Laboratory
31

SECURITY INFORMATION

THERMAL DECOMPOSITION OF ALKALI METAL CHLORATES

Final Report

Research Team:

Robert J. Dearborn,	Research Chemist
Rex A. Schad,	Assistant Chemist

Supervisor:

J. Howard Brown,	Asst. Director of Research

Reports Prepared by:

John J. Pernert	Director of Research

Oldbury Electro-Chemical Company

Research Laboratory

January 30, 1953

RECEIVED
OPNAV
CENTRAL MAIL SECTION
FEB 5 1953
Reg. No. 3790
Copy No. 1-2
Routed to

001280

Office of the Chief of Naval Operations
OP-42

FEB 6 - 1953

SECURITY INFORMATION

53AA-3732

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

Authorization

Contract No. NONR-68100 Project NR 352-299
Office of Naval Research/ Oldbury Electro-Chemical Co.

Subject

Thermal conversion of chlorates to perchlorates, and the preparation of potassium perchlorate and ammonium perchlorate of sufficient purity to meet military and commercial requirements.

Objects

To systematically investigate the thermal decomposition of commercially available chlorates with the objectives of finding optimum conditions for maximum yields and efficiency, finding suitable materials for construction of equipment, and determining the feasibility of the process for manufacturing perchlorates. To find means for converting thermally produced perchlorate into useful salts of adequate purity.

Scope

This investigation was limited in scale of operations to those which could be carried out in the laboratory, and in the use of materials to those which are commercially available. The use of platinum in any significant quantity was specifically avoided, since this is a prime objective of the entire perchlorate program.

Summary

1- Sodium chlorate has been thermally decomposed, or converted, batch-wise, in quantities of 5 grams to 10,000 grams under a great variety of conditions and in several different containers. The highest yields and conversion efficiencies, and the optimum composition of the product, were obtained by melting the salt and maintaining it at carefully controlled temperatures for a relatively long time. The time/temperature schedule was found to be critical. The higher the temperature the shorter was the required time, and the less efficient the conversion process. The size of the batch, and the shape of the reacting mass of chlorate are also important factors. Large masses require a time/temperature schedule different from small ones.

No conditions were found under which sodium chlorate could be converted completely to a perchlorate - chloride mixture. The mixed salt always contains some chlorate, and the molar perchlorate/chlorate ratio appears to approach a constant value of about 7. Products obtained under conditions giving maximum yields and conversion efficiencies contain perchlorate/chlorate in a molar ratio around 5.

There is a critical temperature, its value depending upon various factors such as batch-mass, contact surface, etc., at which any batch of sodium chlorate in the process of conversion may decompose spontaneously, very rapidly and completely, and highly exothermally, into oxygen and sodium chloride, leaving the latter as a red-hot, fused mass. This phenomenon will impose serious limitations upon equipment design, batch size, and procedures in the operation of the process. There is believed to be a critical mass, or mass/area ratio, above which it would not be possible to control this spontaneous decomposition. Its value would, necessarily, depend upon a number of factors, and has not been definitely established for any set of conditions.

2- The thermal conversion of potassium chlorate to mixed perchlorate-chlorate-chloride proceeds in a manner generally similar to that of sodium chlorate, but at somewhat higher temperatures. At comparable conversion rates this temperature is, roughly, 40°C higher. Yields of perchlorate and conversion efficiencies are slightly higher in the case of the potassium salt.

3- When a mixture of sodium chlorate and potassium chloride is converted by heating, the temperature of conversion is approximately the same as for sodium chlorate but yields and conversion efficiencies are slightly higher than those for potassium chlorate. This effect has been attributed to a favorable "catalysis" by potassium chloride, but it seems probable that conversion of sodium chlorate takes place in the normal way and that potassium perchlorate, no doubt formed by metathesis in the melt, decomposes at a lower rate at the conversion temperature than sodium perchlorate. Whatever the mechanism may be the facts are that such mixtures gave conversion efficiencies among the highest so far obtained.

4- Trace impurities adversely affect conversion efficiencies, and this is true, also, of contact of the hot chlorate with the surfaces of most containers. Quartz glass, Vycor, and Pyrex were extensively tested and compared. Quartz and Vycor are about equally inert, but new Pyrex has an adverse effect. After repeated use Pyrex improves, and after about half a dozen runs it has been found approximately equal to quartz. So far as could be determined quartz surfaces have no effect upon the course of the decomposition of heated chlorates.

5- As a practical matter ceramic materials would not be used if suitable metals could be found. The common corrosion resistant alloys were found to catalyze the decomposition strongly, and in an adverse manner. Methods have been found, however, for "passivating" the surfaces of some of these alloys to such an extent that they compare favorably with glass or quartz in inactivity. Quantities of sodium chlorate as large as 10 kilograms (22 lbs.) have been converted in a passivated metal pan.

6- The mixed salts obtained by thermal conversion, under optimum conditions, of sodium chlorate contain approximately 62%

$NaClO_4$, 13% $NaClO_3$, and 25% NaCl. Nearly all of the NaCl may be separated from such a mixture by conventional methods involving solution in, and crystallization from, water but no practical method for separating sodium perchlorate from sodium chlorate, other than destruction of the latter, has been found. An investigation of the system $NaClO_4$ (H_2O) - $NaClO_3$ - NaCl - H_2O was made to confirm and supplement published solubility data.

7- One of the principal perchlorate salts required is ammonium perchlorate. This is usually made by metathesis from commercially pure sodium perchlorate. Efforts to prepare sodium perchlorate in pure form from thermally converted chlorate having failed, it was of interest to determine whether or not the crude mixture could be used. A process has been developed for preparing this salt by metathesis using ammonium chloride. The ammonium perchlorate obtained by operation of the process on a laboratory scale appears to meet commercial and military requirements as to purity.

8- Potassium perchlorate, the other principal salt required, has been made by direct conversion of potassium chlorate, as already noted, and also by metathesis similiarly to ammonium perchlorate. Laboratory data indicate that this salt may be obtained in any desired degree of purity by recrystallization or other known methods.

9- A flow-sheet of a suggested pilot-plant based on the thermal conversion of sodium chlorate has been prepared. The proposed process includes conversion to ammonium perchlorate. The same plant, or a simplified version, could also be used to manufacture potassium perchlorate.

Conclusions

1. Sodium chlorate may be converted by heating under controlled conditions to a mixed salt product containing, typically, $NaClO_4$ - 62%, $NaClO_3$ - 13%, NaCl - 25%. The efficiency of conversion, under optimum conditions, approximates 80%, i. e. 80% of the sodium chlorate which decomposes is regarded as being converted to perchlorate according to the following reaction;

$$4\ NaClO_3 = 3\ NaClO_4 + NaCl$$

The remainder of the decomposed chlorate is, in effect, wasted by conversion to sodium chloride and oxygen:

$$2\ NaClO_3 + 2\ NaCl + 3\ O_2$$

About 12% of the sodium chlorate used remains unchanged in the mixed salt product.

a. The stated reactions are over-simplified. The exact mechanism of the conversion is not known.

b. Maintenance of optimum conditions involves fairly accurate control of temperature and time.

c. Highest yields and conversion efficiencies are obtained at relatively low temperatures and long times.

d. Trace impurities and contact surfaces may, in many cases, catalyze the reactions adversely. No known catalyst improves the conversion.

e. There is a critical temperature above which any batch will spontaneously, and uncontrollably, decompose completely to oxygen and sodium chloride.

f. The actual value of the critical temperature depends upon several factors, of which the mass/area ratio, and the presence of catalysts or catalytic surfaces are known to be important.

g. Recognition of the critical temperature factor is a prime requisite in the design and operation of apparatus for carrying out the thermal conversion of chlorates.

h. Commercial grades of sodium chlorate give substantially the same results as products highly purified by recrystallization or other methods of purification.

2. Potassium chlorate may be converted, thermally, to a mixed salt product containing, typically, $KClO_4$ - 68%, $KClO_3$ - 9%, KCl - 23%. Conversion efficiencies under optimum conditions approximate 83%. As a rule the control of the conversion process has been more difficult than in the case of sodium chlorate.

All conclusions listed under 1., above, are applicable.

3. Sodium chlorate - potassium chloride mixtures, when heated appropriately, produce perchlorate at higher conversion efficiencies than potassium chlorate. The highest conversion efficiency reported, 88.4%, was obtained in this way. Values approximating 86% are typical.

4. Fused quartz and Vycor glass are practically inert, catalytically, when in contact with chlorate under the conditions required for conversion.

a. Most metallic surfaces catalyze the reactions adversely, and cannot be used.

b. Certain alloys may be passivated by special treatment to such an extent that the surfaces are comparable to quartz in catalytic inactivity.

c. Quantities of sodium chlorate at least as large as 10 kilograms (22 lbs.) may be successfully converted in metal pans.

5. The sodium chloride contained in the sodium chlorate conversion product may be almost completely separated by leaching the mixed salt product with water.

a. Sodium perchlorate and sodium chlorate cannot be separated from one another by any known simple method.

6. Ammonium perchlorate may be prepared by metathesis from ammonium chloride and the mixed salt product made by thermal conversion of sodium chlorate.

7. Potassium perchlorate may be prepared by metathesis from potassium chloride in a manner analagous to that used for ammonium perchlorate.

Recommendations

1. The thermal conversion of sodium chlorate should be extended to a scale larger than the 22 lb. batches so far successfully converted.

a. It is believed that larger batches may be successfully converted, especially if the length and breadth of the container are increased without excessive change in the depth of the charge. It is believed that charges of greater depth may be converted, also, but that there is a critical volume/surface ratio near which control will become increasingly difficult. The determination of these factors, experimentally, is essential to the design of the most economical plant.

b. The initial stage of the process, melting and heating the chlorate, requires a positive heat input, and the environment in this stage must, therefore, have a temperature in excess of that of the charge. The reaction is, however, exothermic and the excess heat must be dissipated at the proper rate. It is clear, therefore, that the charge must be moved to a cooling environment immediately after conversion begins. At least two stages or compartments are necessary. It is doubtful whether a simple two-stage process can provide optimum conditions. It is recommended, therefore, that provisions for at least two additional stages, each with thermal controls, be made. This phase of the process deserves extensive study.

c. The critical temperature, at which the reaction becomes uncontrollable, should be determined for several different batch shapes and sizes.

d. To accomplish the extension of the scale, and to provide facilities for the intensive study of the conversion process, it is recommended that a tunnel oven, comprised of several units arranged in series, be designed and constructed.

1. The recommended number of units is four.

2. The units should be identical in size and shape, but may differ in heat input capacity and in other thermal characteristics.

3. The temperature of each unit should be regulated and controlled independently.

4. The temperature range within which points may be selected at will (in the cases of the 2nd, 3rd, and 4th stages) should be 50° to 550°C. The temperature range in the first, (heating) stage should be 450° to 550°C., minimum.

5. The recommended size of each unit is 42" x 42" x 14" deep, all being inside dimensions of the oven cavity.

6. The recommended pan size is 36" x 36" x 8".

7. It is recommended that electrical heating be used, initially, for maximum uniformity and ease of control. Consideration of the possibility of gas heating should be deferred until the conditions for satisfactory operation have been more definitely established. Radically different methods, for example: continuous processes, should be, likewise, deferred until more extensive study of the process has been completed.

8. Ample provision for the escape of gas, in case of uncontrolled decomposition, is recommended.

2. The conversion of potassium chlorate to perchlorate should be, similarly, extended to a larger scale and further investigated. No additional equipment should be required.

3. Further investigation of the conversion of mixed sodium chlorate - potassium chloride, or of mixed sodium and potassium chlorates, should be undertaken only if justified by economic analyses of the proposals in comparison with the simpler and more direct methods.

4. It is recommended that all new suggestions or ideas as to suitable materials of construction be considered and, if economy or technical advance is indicated in any case, promptly investigated.

5. It is recommended that new methods for processing the mixed salt products of thermal conversion be dilligently sought.

6. It is recommended that the conversion of unchanged chlorate in the mixed sodium perchlorate - chlorate solution by the alternative method of electrolysis in the conventional perchlorate cell be checked experimentally. If the results confirm the possibility of operating the thermal conversion process in conjunction with the standard electrolytic process an economic analysis, based upon experimental data, should be made. It is, theoretically, possible to multiply the productive capacity of a unit of platinum anode by four or more.

7. It is recommended that a small pilot-plant, minimum daily capacity - 100 lbs. of ammonium perchlorate, be designed for the manufacture of this salt by metathesis from ammonium chloride and thermally produced sodium perchlorate - chlorate. The crude ammonium perchlorate should be purified by repeated recrystallization.

a. It is recommended that the manufacture of potassium perchlorate, analagously, by metathesis from potassium chloride and the crude sodium perchlorate be investigated in this apparatus and the capacity of the plant determined.

I INTRODUCTION

The detailed data accumulated in the course of work in this project have been recorded and reported in a series of Interim Reports. In this Final Report these are briefly summarized and the most informative and pertinent findings presented as concisely as possible.

The partial conversion of chlorates, especially alkali chlorates, into perchlorates and other products has been long known and extensively investigated. The most important published observations were confirmed, and to some extent extended, by research in the Oldbury Electro-Chemical Company Research Laboratory a decade or more ago.

The present project was undertaken because of prospective large demands for certain perchlorate derivatives. The conventional method of manufacture involves electrolytic oxidation of the chlorate ion at a platinum anode, and relatively large quantities of this metal are required. Although this process is economically sound in spite of the large investment involved it cannot be expanded, indefinitely, because of limited availability of platinum. The primary objective, therefore, was to develop a process which would eliminate the need for any substantial amount of platinum. Costs of production, while obviously important, were regarded as secondary.

The work has, throughout, been directed toward practical goals. A certain amount of fundamental data not available elsewhere has, necessarily, had to be obtained experimentally, but aspects of academic interest, only, have been avoided.

Thermal conversions have been limited to sodium chlorate and potassium chlorate, these being the only chlorates manufactured in large quantities.

No serious attempts have been made to find catalytic substances or additives to improve the yields. Previous experience, as well as most observations recorded in the literature, indicate that all catalysis is adverse.

After having established a standard of reference by the conversion of a large number of small batches of chlorate the process was extended to a larger scale. The largest batch converted was 10 Kg (22 lbs.) of sodium chlorate, this being the practical limit in the apparatus available.

Solubilities in the system: $NaClO_4 - NaClO_3 - NaCl - H_2O$ were determined to confirm and supplement data obtained from the literature.

The utilization of the mixed salt product obtained from thermal conversion is an essential part of the project. Alternative methods have been considered, of which two types appear practical. Both ammonium perchlorate and potassium perchlorate have been prepared by metathesis, and this method deserves consideration although it has aspects which are not particularly attractive, economically. The second alternative involves combining the thermal process with the usual electrolytic, using the sodium perchlorate - chlorate mixture from the former as the cell feed for the latter. The method has not been confirmed by actual trial. As to the separation of the mixed salt products into each of its components no encouraging progress has been made.

II METHODS, APPARATUS, and PROCEDURES

A. Analytical Methods

The analytical methods usually used have been described in detail in the First Interim Report.

1. Gravimetric Determination of Oxygen Loss. This was obtained by weighing the chlorate and the mixed salt product before and after conversion.

2. Volumetric Determination of Chloride in the presence of chlorate and perchlorate was made by titration of the neutral solutions with standard silver nitrate solution adding potassium chromate as the indicator.

3. Volumetric Determination of Chlorate involves reduction of the chlorate by standard ferrous sulfate in dilute sulfuric acid solution, followed by titration of the excess ferrous ion with standard dichromate solution adding diphenyl amine sulfate as the indicator.

4. Gravimetric Determination of Perchlorate depends upon the insolubility of either tetraphenyl phosphonium perchlorate or tetraphenyl arsonium perchlorate in cold aqueous 10% sodium chloride solution, and low solubility in ice-water. The quaternary perchlorate is precipitated metathetically followed by filtration, drying and weighing.

5. Determination of Perchlorate by Difference is applicable in cases where the chloride and/or chlorate of a single metal ion are the sole contaminants.

6. Yield of Perchlorate is calculated on the assumption that all perchlorate formed during conversion is produced by the reaction: $4\ MClO_3 = 3\ MClO_4 + MCl$. This, therefore, represents the "theoretical", or 100% yield. The actual yield is always less, and may be expressed as % of theoretical, or simply Yield - %.

7. Conversion Efficiency is calculated by assuming that all chlorate taken for conversion is (a) converted to perchlorate as in (6), (b) decomposed according to the equation: $2\ MClO_3 = 2\ MCl + 3\ O_2$, or (c) remains unchanged. The ratio of the quantity converted according to (a) to the sum of the quantities involved in (a) and (b) represents conversion efficiency - %. Unchanged chlorate is assumed to be completely recoverable.

B. Apparatus

The various items of special apparatus have been described in detail in the Interim Reports to which reference is made:

1. Chlorate Containers. First, Second, and Fourth Interim Reports.

In the preliminary experiments with five gram batches standard 1" x 7 3/4" test-tubes of Pyrex, Vycor, or fused quartz were used. The preliminary investigation of various metals was carried out by inserting small samples in the test-tubes with the chlorate.

After suitable alloys had been found larger batches of Chlorate were converted in rectangular pans 10" x 4" x 2" deep, 10" x 4" x 4", and 15" x 15" x 4". Methods of "passivating" metal pans are described in the Second and Fourth Interim Reports.

2. Heating Apparatus. First, Second, and Fourth Interim Reports.

The five-gram batches were heated in a fused salt bath composed of lithium chloride, 44.4%, and potassium chloride, 55.6%, contained in a solder melting pot, electrically heated. The fused salt was stirred, and the temperature was controlled automatically. The description and complete specifications of this apparatus are in the First Interim Report.

Larger batches, 250 to 900 grams, were heated in an ordinary laboratory muffle furnace, as described in the Second Interim Report. The thermal characteristics of this furnace were unfavorable and fully automatic control within the desired temperature limits was impossible. Supplementary manual control was necessary to obtain satisfactory results.

The largest batches, 2.5 to 10 Kilograms, were heated in an electrically heated glass-annealing oven, described in the Fourth Interim Report. This oven, internal dimensions 18" x 18" x 15", has built-in automatic controls and fairly good thermal characteristics. By supplementary manual control satisfactory conditions were obtained, empirically, and the results were good.

3. Pan-handling Apparatus. Fourth Interim Report. The hazard of handling heavy pans of molten chlorate was minimized by the use of a hand-operated lift-truck suitably adapted.

C. Procedures

1. Conversion of Alkali Chlorates in Test-Tubes. First Interim Report (Sodium Chlorate), Second Interim Report (Potassium Chlorate), (Sodium Chlorate - Potassium Chloride Mixtures).

Five grams, plus or minus 5%, of the alkali chlorate was accurately weighed into a tared test-tube which was then quickly immersed in the molten salt bath and, after the desired time interval, withdrawn and allowed to cool in a stream of air. The weight loss was determined and the mixed salt product dissolved and analyzed.

Preliminary tests of metals were made by placing samples in the chlorate and proceeding in a similar way.

2. Conversion of Sodium Chlorate in Metal Pans. Second Interim Report (250 g. and 500 g. sodium chlorate in "conditioned" Inconel, Hastelloy, and #316 Stainless Steel). Fourth Interim Report (250 g. to 10,000 g. sodium chlorate in "passivated" Inconel).

Quantities of 900 g. or less were converted in the small pans heated in the muffle furnace. The desired amount of sodium chlorate was weighed into the tared pan, previously "conditioned" or "passivated", and inserted in the pre-heated (480°C) furnace. A glass enclosed thermocouple junction was imbedded in the crystals to measure the temperature of the molten salt during conversion. The sensitive element of the controller was suspended slightly above the pan contents. When the indicating thermocouple showed that the temperature of the molten chlorate was 460° timing of the process was started. At the end of the desired time the thermocouples were raised and the pan removed and quenched. The temperature was kept as nearly constant at the chosen value as possible.

Quantities of 2,500 g. to 10,000 g. were processed similarly in the larger equipment. In this case the pans were inserted and removed by use of the lift-truck. The procedure was otherwise similar except that it was found difficult to control the larger batches if the temperature within the melt reached 475° or higher. At 470°, therefore, the temperature was maintained as nearly constant as possible by turning off the heat and cooling the oven by opening the door periodically as required. During conversion of the largest batches the oven temperature fell, due to the required elimination of heat of conversion, to 430° at the end of the run. The conversion was considered complete when the melt temperature began to decrease rapidly. The pan was then removed and quenched.

3. Sampling of Mixed Salt Product. A significant nonuniformity due to segregation of sodium chloride was noticed, especially in the largest batches. Several large lumps representing cross-sections of the solidified melt were weighed, dissolved and diluted to a definite volume. Appropriate aliquots were taken for analysis.

4. "Conditioning" and "Passivating" of Alloys. Nearly all of the metals, and all of the commercial alloys, tested were found to catalyze the conversion adversely. After repeated contact with successive batches of molten sodium chlorate at conversion temperatures the catalytic activity of the surfaces of some alloys, notably Inconel, Hastelloy C, and #316 Stainless Steel, was found to diminish greatly.

A "passivating" treatment, involving thorough cleaning and pickling of the metals with warm nitric-hydrochloric acids, followed by a treatment with pure nitric acid, was found to produce a surface comparable to quartz in inertness.

"Conditioning" and "Passivating" are described in detail in the Fourth Interim Report.

III RESULTS

A. Conversion of Sodium Chlorate in Five Gram Batches

The results of approximately 200 runs made at ten degree intervals in the temperature range from 490° to 560°C, and at various times from 50 to 3,600 seconds, are tabulated in the First Interim Report. The data include Weight Loss, %, $NaCl$, %, $NaClO_3$, %, $NaClO_4$, %, Yield of $NaClO_4$, %, and Conversion Efficiencies. The most informative of these are shown graphically in this Final Report:

Fig. I	Yields of Sodium Perchlorate at Various Temperatures and Times
Fig. II	Weight Loss Due to Oxygen Evolution at Various Temperatures and Times.
Fig. III	Sodium Chlorate in Mixed Salt Product at Various Temperatures and Times.

The peak of each curve of Fig. I represents the optimum time at the indicated temperature. The compositions of the products at these maxima are of special interest. The results of conversions under approximately optimum conditions of temperature and time are shown in tables:

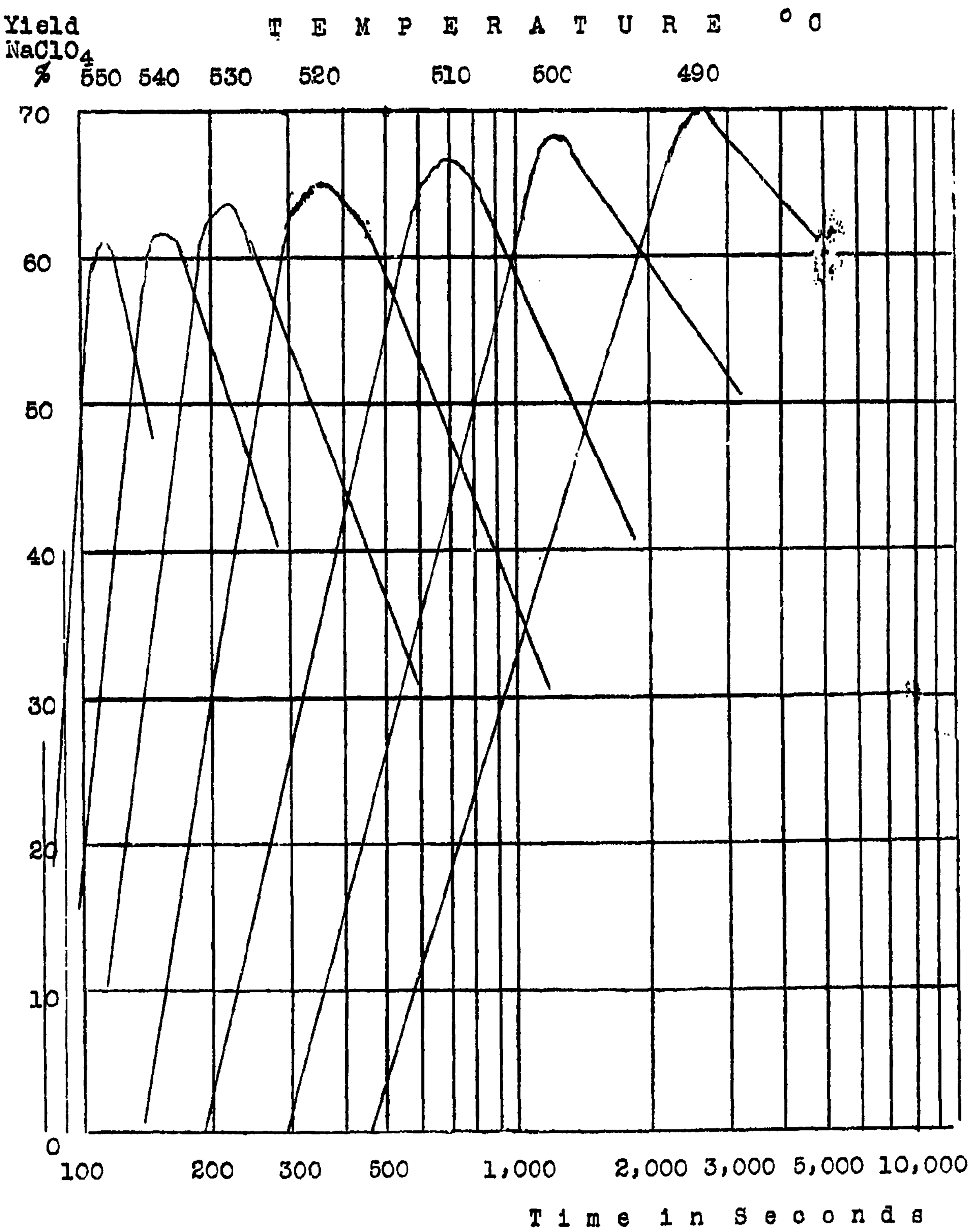
TABLE I	Typical Results at Approximately the Optimum Times at Various Temperatures.
TABLE II	Typical Compositions of the Mixed Salt Products Obtained Under Optimum Conditions.

B. Catalysis by Contact Substances and Impurities

No significant differences were observed when sodium chlorate conversions in Quartz, Vycor or "old" Pyrex test-tubes were compared. Catalysis at such surfaces is, apparently, negligible. When "new" Pyrex tubes were used under similar conditions Conversion Efficiencies were about 5% lower. After being re-used about a dozen times, during which the catalytic activity of the glass gradually diminished, Pyrex compared favorably with quartz in inertness.

Commercial sodium chlorate, as supplied by the Oldbury Electro-Chemical Co., was found to be practically equal to the further purified product. The commercial grade was purified by recrystallization, and also by boiling after acidification with hydrochloric acid (to remove bromate), or by treatment with hydrogen sulfide (to remove heavy metals), prior to recrystallization. The purified product gave, on the average, slightly better results but the improvement (about 1% higher conversion efficiencies) is not considered important or particularly significant.

Fig. I



Yields of Sodium Perchlorate at Various Temperatures and Times

Five Gram Quantities Heated in "Pyrex"

Fig. II

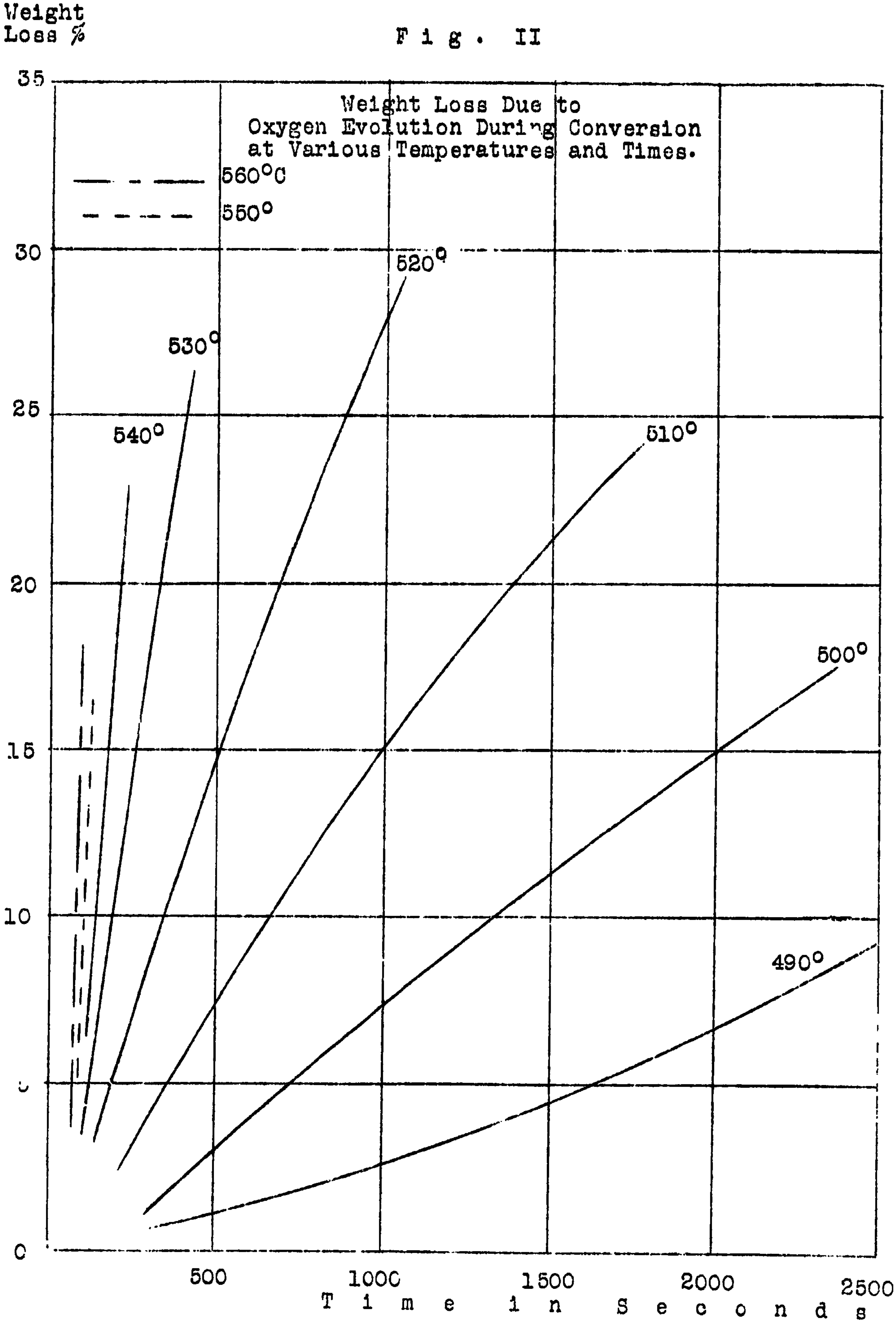

Weight Loss %
Weight Loss Due to Oxygen Evolution During Conversion at Various Temperatures and Times.
560°C
550°
540°
530°
520°
510°
500°
490°
35
30
25
20
15
10
5
0
500
1000
1500
2000
2500
Time in Seconds

Fig. III

Sodium Chlorate in Mixed Salt Product After Conversion of Sodium Chlorate at Various Temperatures and Times

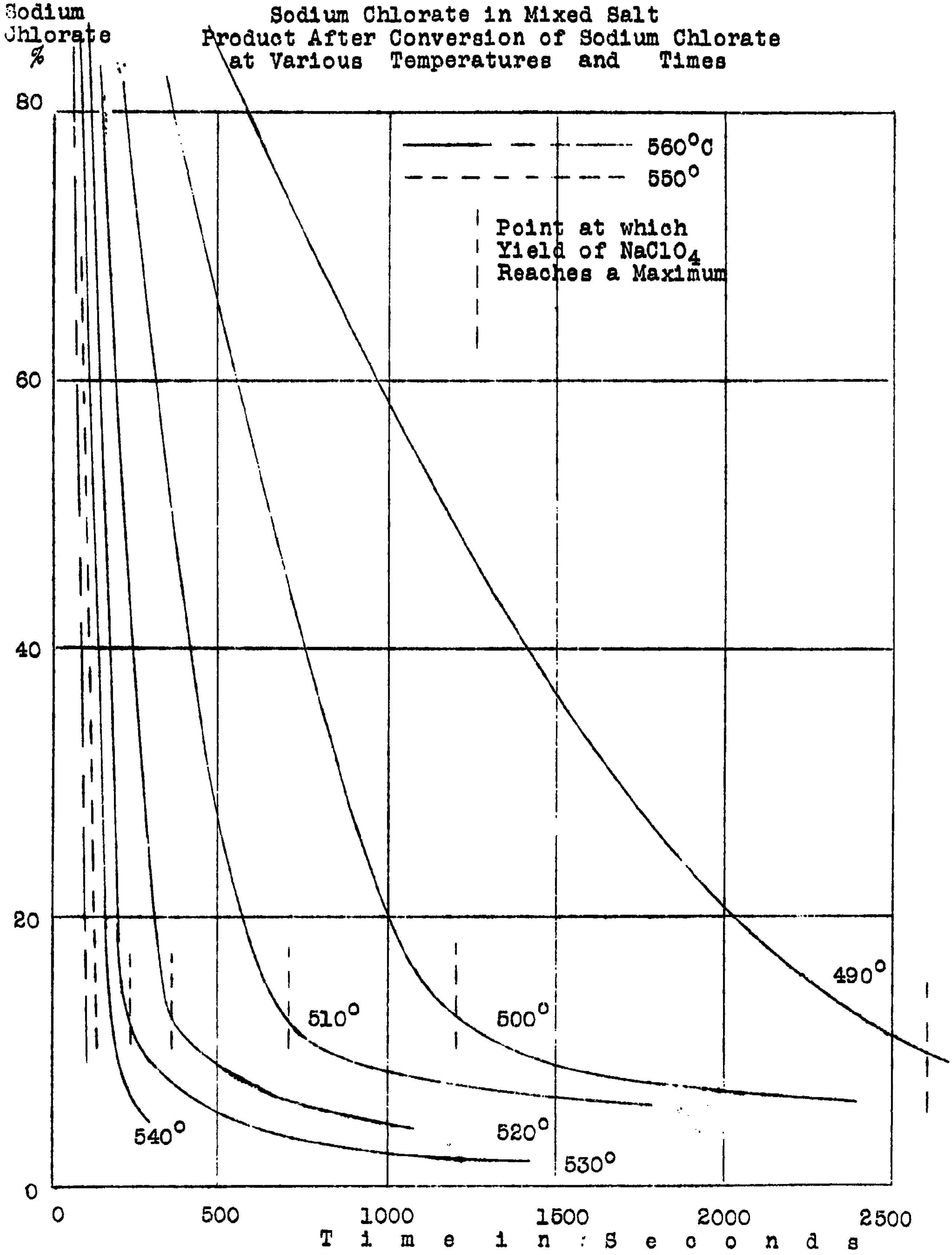


TABLE I

Typical Results at Approximately the Optimum Times at Various Temperatures

Temperature °C	Time in Seconds	Weight Loss %	NaCl %	$NaClO_3$ %	$NaClO_4$ %	$NaClO_4$ Yield %	Conversio Efficienc
560	90	12.8	23.5	12.2	51.5	59.7	68.0
550	110	11.1	21.2	15.9	51.7	60.0	71.3
540	150	12.0	22.4	12.7	53.0	61.4	70.3
530	210	10.7	21.8	12.2	55.2	64.0	72.9
520	375	10.0	20.5	13.8	55.7	64.5	74.8
510	750	10.6	21.4	11.5	56.5	65.4	74.0
500	1200	7.1	20.0	13.3	59.6	69.1	79.7
490	2400	8.6	19.7	12.7	59.0	68.4	78.3

In this table the values for % NaCl, $NaClO_3$, $NaClO_4$, Yield, and Weight Loss are based upon the initial weight of the sodium chlorate. Conversion Efficiencies are calculated from the quantities of sodium chlorate actually destroyed. It is assumed that unchanged chlorate is recoverable for re-use.

TABLE II

Typical Compositions of the Mixed Salt Products Obtained at Approximately the Optimum Times at Various Temperatures

Temperature °C	Time in Seconds	NaCl %	$NaClO_3$ %	$NaClO_4$ %	% of Weight of $NaClO_3$ Heated
560	90	27.0	14.0	59.0	87.2
550	110	23.9	17.9	58.2	88.9
540	150	25.4	14.4	60.2	88.0
530	210	24.4	13.7	61.9	89.3
520	375	22.8	15.3	61.9	90.0
510	750	24.0	12.8	63.2	89.4
500	1200	21.5	14.3	64.2	92.9
490	2400	21.6	13.9	64.5	91.4

The effects of various metals and alloys on the course of the conversion, as well as the resistance of the metals to the hot chlorate, were investigated extensively in the search for suitable materials for use in making containers.

Platinum and Tantalum appear to be inert. Platinum is rejected as a suitable material for obvious reasons. Of the lower cost alloys the most promising were Inconel, Nichrome V, Stainless Steel # 316, and Hastelloy C. These were only slightly catalytic initially, and improved with repeated re-use. Methods of passivating, discovered later, have already been mentioned and described.

Nickel, Monel, Silver, Aluminum Bronze, and the usual ferrous metals are strongly catalytic and, in some cases, also strongly attacked by the molten chlorate.

The results of more than a hundred runs made in testing these various materials are tabulated in the First and Second Interim Reports.

C. Thermal Decomposition of Perchlorates

No conditions have been found under which a perchlorate - chloride mixture, substantially free from chlorate, can be made by thermal treatment of a chlorate. It has been demonstrated that the reaction is reversible, and that sodium perchlorate is partially converted to chlorate under conversion conditions. In one of a series of experiments, fully described in the Second Interim Report, it was found that pure sodium perchlorate heated at 530°C 25 minutes produced a salt mixture not essentially different from that formed by heating sodium chlorate at this temperature 4 minutes:

	Weight Loss %	$NaCl$ %	$NaClO_3$ %	$NaClO_4$ %	ClO_4/ClO_3 Ratio
From $NaClO_3$	14.3	25.0	8.2	52.6	6.5:1
From $NaClO_4$	21.7	19.0	6.0	53.3	9:1

The ration $NaClO_4/NaClO_3$ remained constant at about 9:1 when heating was continued for an hour and more than 96% of the perchlorate had decomposed. It is evident that an equilibrium between these components exists.

D. Conversion of Sodium Chlorate in Metal Pans

A considerable number of batches were made in the course of establishing, by trial and error, the optimum conditions. Each batch size increase required some modification of the conditions and procedure, but it was found comparatively easy to define a set of conditions and repeat the operations with similar results.

Table III of the Second Interim Report gives the results from thirty batches of 250 g. and 500 g. Table I of the Fourth Interim Report gives the results from 29 batches of 250, 500, 750, and 900 g. and Table II of the Fourth from 15 batches to 2.5, 3.75, 5.0, 7.5, and 10 Kilograms.

The results which have the greatest interest and importance are those showing the highest yields and conversion efficiencies, since it may be assumed that, after further experience and process refinement, these may be consistently reached or exceeded.

Table III of this Final Report contains data representing the results from selected batches showing some of the highest yields obtained under several sets of conditions. In some cases the averages of several batches are also shown to indicate the degree of reproducibility.

E. Solubilities in the System: $NaClO_4$-$NaClO_3$-$NaCl$-H_2O

The Third Interim Report, a copy of which is included in the Appendix to this Final Report, is devoted, exclusively, to selected published data and unpublished results of solubility studies made in the Research Laboratory of Oldbury Electro-Chemical Co. This material is presented in the form of tables and graphs.

Index to the Third Interim Report:

Table	Solubilities in the System
I	$NaClO_4$ - H_2O
II	$NaClO_3$ - H_2O
III	$NaCl$ - H_2O
Graph	From data of Tables I, II, and III
IV	$NaClO_4$ - $NaClO_3$ - H_2O
V	$NaClO_4$ - $NaCl$ - H_2O
VI	$NaClO_3$ - $NaCl$ - H_2O
VII	$NaClO_4$ - $NaClO_3$ - $NaCl$ - H_2O
Graph	From data of all Tables at T.=35°C
Graph	" " " " " " 50.8°
Graph	" " " " " " 80°

F. Attempted Separation of $NaClO_4$ - $NaClO_3$ - $NaCl$

Commercial perchlorate derivatives such as the ammonium or potassium salts are required to be essentially free from chlorate and chloride. The utilization of the mixed salt product obtained by thermal conversion of sodium chlorate therefore requires practical methods for separating the components of the mixture in pure states or, alternatively, using the mixture, with or without partial purification, as the raw material for processes especially developed to utilize it.

TABLE III

Conversion of Sodium Chlorate in Metal Pans

at Various Temperatures and Times.

Time in Minutes	Weight Loss %	NaCl %	NaClO$_3$ %	NaClO$_4$ %	NaClO$_4$ Yield %	Conversion Efficiency	
Inconel - 480°C - 250 g. batch							
50	10.0	19.8	15.1	55.1	63.9	75.3	Best of 9
50	10.4	19.2	19.6	50.8	59.4	73.3	Ave. of 9
45	10.6	19.4	19.9	50.1	58.1	72.5	Ave. of 3
50	8.4	16.9	23.3	51.4	59.6	77.7	Best of 5
50	10.9	20.4	20.2	50.6	58.6	71.9	Ave. of 5
Inconel - 480°C - 500 g. batch							
55	10.0	17.1	15.4	57.5	66.6	78.8	Best of 2
47	8.7	17.4	19.4	54.5	63.2	78.4	Single
Inconel - 460-470°C - 750 g. batch							
70	9.9	15.6	17.2	57.3	66.4	80.2	Single
Inconel - 470-480°C - 900 g. batch							
52	10.9	20.7	9.9	58.5	67.8	75.2	Best of 2
47-90	10.0	19.2	15.2	55.6	64.5	76.0	Ave. of 6 Best of 10
Inconel - 455-465°C - 5,000 g. batch							
Net 100	8.1	18.1	16.4	57.3	66.5	79.5	Best of 8 at various Times and Tempera-tures
Inconel - 465-475°C - 5,000 g. batch							
Net 50	7.7	16.2	20.3	55.8	63.7	81.2	
Inconel - 465-472°C - 7,500 g. batch							
Net 55	7.7	17.4	18.9	56.0	64.9	80.1	Best of 2
Inconel - 465-472°C - 10,000 g. batch							
Net 50	8.6	19.2	14.4	57.9	67.1	78.3	Best of 2
Net 50	8.4	19.5	14.9	57.3	66.4	78.0	Ave. of 2
Hastelloy - 480°C - 250 g. batch							
30	12.4	22.6	10.3	54.7	63.4	70.7	Best of 4
Stainless Steel # 316 - 480° - 250 g. batch							
30	10.2	18.9	16.5	54.4	63.0	75.5	Best of 4

Complete separation of the components of the mixed salt product has not been achieved in any practical manner. By leaching with water it has been found possible to dissolve practically all of the perchlorate and chlorate salts leaving a major part of the sodium chloride undissolved. Thus a practical separation of the chloride component is possible. No such success can be claimed for the separation of the perchlorate component from the chlorate.

The Second Interim Report contains detailed descriptions of seven experiments in which attempts were made to separate the three salts by fractional crystallization from a composition representing a typical mixed salt product:

$NaClO_4$ - 62%, $NaClO_3$ - 13%, NaCl - 25%,

When such a mixture was dissolved in water and boiled at atmospheric pressure to a boiling temperature of about 140°C (equivalent to leaching with the minimum quantity of water at 140°) the composition of the dissolved salt mixture (on the dry basis) approximated:

$NaClO_4$ - 82% $NaClO_3$ - 17% NaCl - 1%

Crystallization, by cooling of a hot, saturated solution so obtained, invariably gave a mixture of sodium perchlorate and chlorate containing the two salts in a nearly unchanged ratio. Because of the very high solubility of such a salt mixture it was even difficult to effect a major reduction in the sodium chloride content although, theoretically, the crystals should be uncontaminated with this salt. The mother liquors are syrupy especially when cold.

A minor improvement in the perchlorate/chlorate ratio was achieved by cooling a solution, made as described at 130°, to minus 25°C. Due to the relatively low solubility of sodium chlorate at this sub-zero temperature the $NaClO_4/NaClO_3$ ratio in the crystals was somewhat lower, and that in the mother liquor correspondingly higher, as shown by the analyses below:

Composition (dry basis)

Crystals	$NaClO_4$	- 79.38%	$NaClO_3$	- 20.32	NaCl	- 0.3%
Solution		- 82.98		- 15.07		- 1.95

The results of relatively large scale leaching experiments are fully described in the Fifth Interim Report, a copy of which is a part of the Appendix to this Final Report.

G. Alternative Methods of Utilizing the Mixed Salt

Of several possible alternative methods:

1. Use of non-aqueous solvents
2. Electrolytic oxidation of residual chlorate
3. Chemical oxidation, e. g. by lead dioxide, of the chlorate
4. Partial conversion according to the reaction:

$$3\ HClO_3 = HClO_4 + 2\ ClO_2 + H_2O$$

5. Destruction of the residual chlorate by reduction
6. Development of metathetical procedures using the mixed salt as the raw material

only (2) and (6) appear economically and technologically attractive. Only (6) has been extensively investigated. Both ammonium perchlorate and potassium perchlorate have been prepared by metathesis from solutions of the mixed salt product obtained by thermal conversion of sodium chlorate and ammonium or potassium chloride.

(a) Potassium Perchlorate

Simple solution of the mixed salts, without any preliminary separation of sodium chloride, followed by addition of potassium chloride solution in an amount equivalent to the perchlorate content gave the desired salt, slightly contaminated with chlorate, in yields of nearly 90%. The result was similar when all salts were dissolved, by heating the mixture to boiling and adding sufficient water, followed by cooling to crystallize the potassium perchlorate.

Run No.	$KClO_4$ Yield %	Cl' as NaCl	ClO_3' as $NaClO_3$
1	89.0	0.15	0.34
2	88.0	0.19	0.31
3	88.8	0.08	0.22
4	90.8	0.29	0.49

By recrystallization of the product the chlorate, which is apparently present as a mixed crystal and cannot be removed completely by washing, may be reduced to the extent required.

Further processing of the mother liquors to recover the remaining perchlorate and chlorate values has not been investigated.

(b) Ammonium Perchlorate

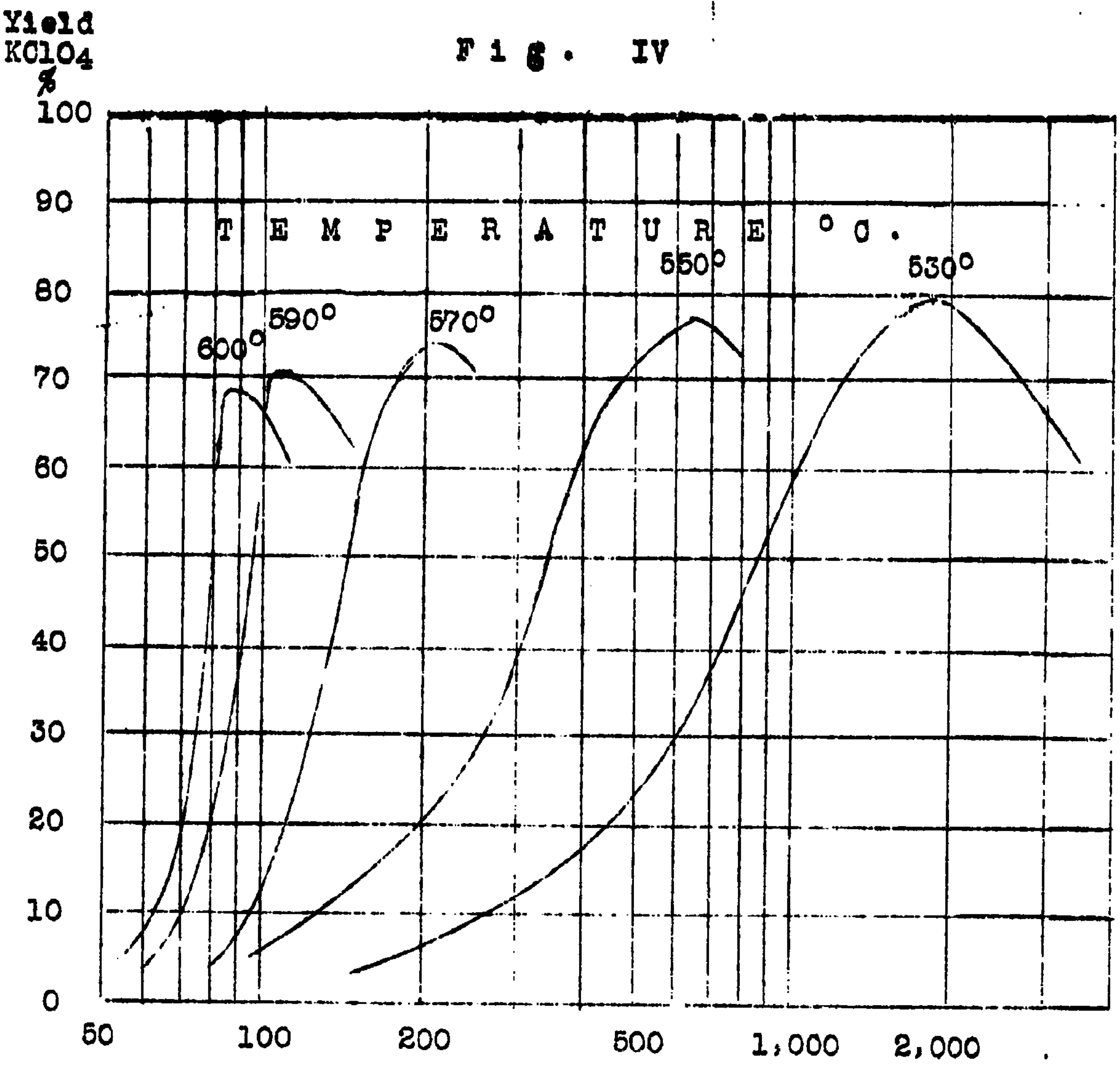
The laboratory work is fully described in the Fifth Interim Report, included in the Appendix, to which reference may be made. This Report also contains a suggested Flow Sheet and Estimated Working Capacities for various items of equipment based on the production of 1,000 lbs. per day of ammonium perchlorate.

H. Conversion of Potassium Chlorate in Five Gram Batches

The Conversion of potassium chlorate to the perchlorate by thermal treatment follows the pattern found with sodium chlorate except that conversion temperatures are considerably higher and yields and conversion efficiencies somewhat greater.

Fig. IV Yields of Potassium Perchlorate at Various Temperatures and Times.

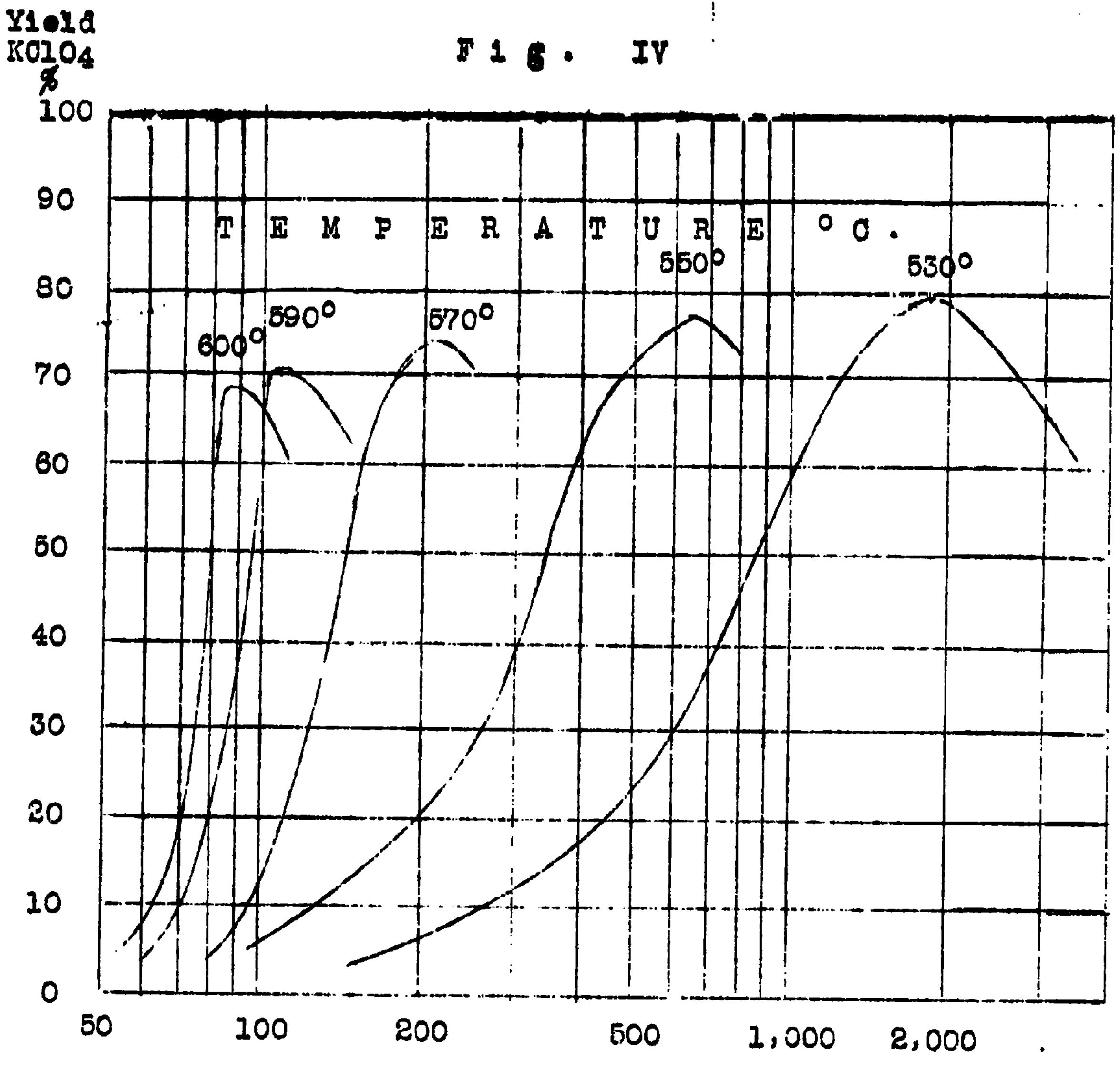
Fig. IV



Yields of Potassium Perchlorate at Various Temperatures and Times

Five Gram Quantities Heated in Pyrex

Fig. IV



Yields of Potassium Perchlorate at Various Temperatures and Times

Five Gram Quantities Heated in Pyrex

TABLE	IV	Typical Results at Approximately the Optimum Time at Various Temperatures.
TABLE	V	Typical Compositions of the Mixed Salt Products Obtained Under Optimum Conditions.

I. Separation of Components of Mixed Salt Product

The separation of the three components, potassium chloride, chlorate, and perchlorate, offers fewer of the difficulties met in the case of the sodium salts because of the very different solubility characteristics. Potassium chloride is relatively soluble and may be extracted by a correspondingly small amount of water. The solubility of potassium perchorate in cold water is low, while that of the chlorate is several fold greater. It is, therefore, possible to effect a nearly complete separation without the use of excessive amounts of water.

Potassium chlorate and perchlorate tend to form mixed crystals. The perchlorate, when crystallized from a solution containing chlorate, is always slightly contaminated by the latter. Purification to any required extent is, however, possible by repeatedly recrystallizing the product. The process has not been fully investigated.

The solubilities of the three salts: potassium chloride, chlorate, and perchlorate, in water are shown, graphically, in Appendix 1.

J. Conversion of Sodium Chlorate - Potassium Chloride Mixtures in Approximately Five Gram Batches

Potassium chloride has been reported to "catalyze" the thermal conversion of sodium chlorate to perchlorate. Whatever the mechanism of the reaction there is no doubt that there is a substantial improvement in yields when mixtures of these salts are appropriately heated. Conversion takes place at the temperatures and times characteristic of sodium chlorate but yields and conversion efficiencies are higher than those for either sodium or potassium chlorate.

TABLE VI shows the results from selected batches typical of those recorded in Table VII of the Second Interim Report. For comparison some of the best results obtained with sodium chlorate alone under similar conditions are included.

This process has been investigated very little. It would not be readily adaptable to the preparation of any salt other than potassium perchlorate, and complications may be readily foreseen in this case because of the relatively complex mixture of salts produced.

TABLE IV

Typical Results at Approximately the Optimum Times at Various Temperatures

Temperature °C	Time in Seconds	Weight Loss %	KCl %	$KClO_3$ %	$KClO_4$ %	$KClO_4$ Yield %	Conversion Efficiency
600	90	9.6	23.7	8.6	58.1	68.6	75.1
590	100	7.5	20.6	14.7	57.1	67.4	79.1
570	210	7.6	22.5	7.9	62.2	74.3	79.6
550	600	6.2	20.3	8.6	65.0	76.7	83.8
530	1800	5.9	20.5	6.2	67.5	79.6	84.9

In this table the values for % KCl, $KClO_3$, $KClO_4$, Yield, and Weight Loss are based upon the initial weight of the potassium chlorate. Conversion Efficiencies are calculated from the quantities of potassium chlorate actually destroyed. It is assumed that unchanged chlorate is recoverable for re-use.

TABLE V

Typical Compositions of the Mixed Salt Products Obtained at Approximately the Optimum Times at Various Temperatures

Temperature °C	Time in Seconds	KCl %	$KClO_3$ %	$KClO_4$ %	% of Weight of $KClO_3$ Heated
600	90	26.2	9.5	64.3	90.4
590	100	22.3	15.9	61.8	92.4
570	210	24.3	8.5	67.2	92.6
550	600	21.6	9.2	69.2	93.9
530	1800	21.8	6.6	71.6	94.2

TABLE VI

Typical Results from Sodium Chlorate - Potassium Chloride Mixtures. Temperature 530°C, Time 210 Sec.

Mixture		Weight Loss %	$NaCl$ %	$NaClO_3$ %	$NaClO_4$ %	Yield $NaClO_4$ %	Conversion Efficiency
KCl %	$NaClO_3$ %						
23	77	7.6	17.4	13.0	62.0	71.9	82.6
29	71	4.9	15.0	21.5	58.6	67.9	86.5
34	66	4.2	14.0	23.3	58.5	67.8	88.4
0	100	10.7	21.8	12.2	55.2	64.0	72.9
0	100	10.7	20.5	15.9	53.0	61.4	73.0
Temperature - 550°					Time - 110 Sec.		
29	71	5.2	14.2	28.6	52.1	60.4	84.6
34	66	4.1	10.0	46.3	39.7	46.0	85.5
0	100	11.1	21.2	15.9	51.7	60.0	71.3

K. Conversion of Potassium Chlorate in Metal Pans

"Passivated" Inconel and Hastelloy pans were found much less inert to potassium chlorate than to the sodium salt under the conditions required for conversion. Further modification of the process was required before satisfactory results were obtainable.

In the initial experiments the molten potassium chlorate quickly attacked the passivated metal, both Inconel and Hastelloy, causing severe pitting and dispersion of the corrosion product throughout the melt. The majority of the batches decomposed uncontrollably, and those which could be kept under control gave very poor yields and conversion efficiencies. The mixed salt products were gray or brown.

Although it is known that the addition of substantial quantities of alkali-metal hydroxides and other alkaline salts has an adverse effect upon the thermal conversion of chlorates to perchlorates the effects of comparatively small amounts was unknown. It was, accordingly, considered worthwhile to investigate the addition of traces of alkaline materials with the hope that corrosion might be prevented, or at least minimized, without greatly diminishing the conversion efficiencies. This modification proved to be successful and led to results comparable to those obtained in the conversion of sodium chlorate.

The use alkaline materials was accomplished in several ways. In some cases potassium hydroxide solution was sprayed over the potassium chlorate prior to melting; recrystallizing the potassium chlorate from a solution containing some potassium hydroxide was equally effective. Simply painting the inside of the pan with solutions of potassium hydroxide, potassium carbonate, or potassium silicate also gave good results.

Potassium chlorate has a strong tendency to "creep" over the edge of the metal pan during conversion. The most effective method found to minimize this involves painting the area above the melt with 20% potassium silicate, followed by drying in air. The most satisfactory runs were made by painting the pan as described, weighing in the potassium chlorate, and spraying the desired quantity of 1% KOH over the chlorate.

Insufficient data has been obtained to warrant conclusions as to the optimum amount of alkali. Corrosion is not entirely prevented. Washing of the pans and removal of traces of oxide formed above the melt level was required. Oxide films formed below the melt level remained firmly attached and the passivity of the surface was retained.

Unlike the mixed salt product from sodium chlorate, which becomes semi-solid during conversion, the product from potassium chlorate remains liquid throughout, although it solidifies very quickly when removed from the oven.

Conversion efficiencies tend to increase slightly with increasing batch size, as in the case of sodium chlorate conversions.

Table VII of this Final Report contains data representing the results from selected batches showing some of the highest yields obtained under several sets of conditions. A total of about thirty batches were made in trying to establish optimum conditions by trial and error.

TABLE VII

Conversion of Potassium Chlorate in Metal Pans at Various Temperatures and Times

Time in Minutes	Weight Loss %	KCl %	$KClO_3$ %	$KClO_4$ %	$KClO_4$ Yield %	Conversion Efficiency	
	Hastelloy - 495-502°C - 500 g. Batch						
100	6.5	20.1	10.3	63.1	74.4	82.9	(a)
	Inconel - 495-504°C - 500 g.						
90	7.4	20.9	12.1	59.6	70.3	80.1	(a)
	Inconel - 495-509°C - 500 g.						
52	7.1	20.9	10.9	61.1	72.1	80.9	(b)
	Inconel - 495-520°C - 5,000 g.						
Net 18	4.3	16.0	26.7	52.9	62.4	85.2	(c)
Net 25	5.1	18.9	14.9	61.1	72.1	84.7	(c)
	Inconel - 480-510°C - 7,500 g.						
Net 45	4.7	17.6	19.0	58.7	59.3	85.6	(c)
	Inconel - 490-505°C - 10,000 g.						
Net 70	5.6	19.3	12.9	62.3	73.5	84.3	(c)
	Inconel - 495-505°C - 10,000 g.						
Net 55	4.7	18.1	16.6	60.7	71.6	85.9	(c)

Notes:

(a) Pan painted with 20% potassium silicate. The $KClO_3$ was recrystallized.

(b) Same as (a) except that $KClO_3$ was not recrystallized.

(c) Sides of pan painted with 20% potassium silicate to minimize creeping. Potassium hydroxide added as a 1% solution in amounts equivalent to 0.02% of the $KClO_3$. The solution was sprayed over the dry salt prior to heating.

IV SUPPLEMENT

Conversion of Sodium Chlorate at Lower Temperatures

Ammonium Perchlorate by Metathesis - Larger Scale Experiments

V APPENDIX

Solubility in Water of Potassium Perchlorate, Chlorate, and Chloride

Summary of Calculations on Energy Requirements

Third Interim Report - Solubilities in the System: $NaClO_4$ - $NaClO_3$ - $NaCl$ - H_2O

Fifth Interim Report -

Extraction of Product from Thermally Decomposed Sodium Chlorate

Ammonium Perchlorate by Metathesis

Solubility in Water of Ammonium Perchlorate

Tentative Process Proposal With Flow-Sheet

Discussion and Conclusions

IV SUPPLEMENT

Conversion of Sodium Chlorate at Lower Temperatures

Previous work has indicated that improved results are obtained when conversions are carried out at lower temperatures, longer times, and in larger quantities. It was decided, therefore, that it would be of interest to extend the work to the practical limits of available equipment.

A further object of the supplementary experiments was to determine whether or not conversions could be satisfactorily made in a constant temperature oven without any provision for cooling to dissipate the heat of reaction. This would, obviously, simplify the process.

The oven and Inconel pan previously described were used. A differential thermo-couple was used to measure the temperature rise within the converting mass, one junction being immersed in the melt while the other was adjacent to the controlling thermo-couple. The differential thermo-couple operated a recorder, and a continuous record of the temperature difference was made throughout the run. The sensitivity of the recorder was so adjusted that a temperature rise of 0.5°C could be easily detected.

The converting chlorate did not foam, and creeping was prevented by painting the upper surfaces of the pan with sodium silicate solution. The practical capacity of the pan was fifty pounds sodium chlorate. This quantity filled the 15 x 15 x 4 inch pan to a level about 3/4 inch below the rim.

Two runs were made using 50 pounds sodium chlorate, the oven temperature being held constant at 420°C, heating time 25 hours and 28 1/2 hours, respectively. One run, using 22 pounds sodium chlorate, was made at 420°C - 20 hours.

A run was made at an oven temperature of 430°, but is not reported because of trouble encountered with the oven controller. Indications are, however, that a 22 pound batch will not get out of control at this temperature.

A 22 pound batch heated in the oven at 450°C became uncontrollable, the temperature within the mass rising from 420° to 480° in the course of an hour. The rise could not be checked by the usual procedure of opening the oven door, and the pan was removed and quenched in water.

The results from the three most successful batches are shown in the Table on the following page.

These results indicate that continuous conversion of sodium chlorate in some form of tunnel-oven may be practical. There is, as yet, no indication that the use of pans as containers may be eliminated.

TABLE

NaClO$_3$ - 22 #, Temperature - 420°C.

Time Hours	Weight Loss %	NaCl %	NaClO$_3$ %	NaClO$_4$ %	NaClO$_4$ Yield %	Conversion Efficiency
20	3.7	9.8	45.7	40.9	47.4	87.3
		NaClO$_3$	- 50 #,	Temperature - 420°C.		
25	5.9	15.9	17.9	60.3	69.8	85.1
		NaClO$_3$	- 50 #,	Temperature - 420°C.		
28 1/2	7.4	18.7	12.4	61.5	71.2	81.3

The temperature within the converting mass in the 22 # batch rose to 425°C, i. e. 5° above the oven temperature. The time required for the cold pan and contents to reach the oven temperature, 420°, was two hours. The net heating time was therefore about 18 hours.

The temperature within the converting mass in both 50# batches remained at oven temperature for nearly 12 1/2 hours. At this Time it was observed that a solid crust was beginning to form over the melt Thereafter the temperature rose above that of the oven. At 12 1/2 hours it was 423°, i. e. 3° above oven temperature. It soon increased to 433°, i. e. 13° above oven temperature, where it remained until the end of the runs.

The time required for the cold pan and contents to reach oven temperature was, in the case of the first 50 # batch, five hours. The net heating time was therefore about 20 hours. In the case of the second 50# batch the preliminary heating time was 3 1/2 hours, and the net time 25 hours.

It will be observed that the optimum time appears much less critical under the conditions described here than at the higher temperatures used previously.

SUPPLEMENT
(continued)

Ammonium Perchlorate by Metathesis - Larger Scale Experiments

The preparation of ammonium perchlorate from ammonium chloride and the solution made by extraction of the mixed salt product from sodium chlorate conversion was extended to a larger scale. The procedures were similar to those described in the Fifth Interim Report (see Appendix) except for minor changes including centrifugation instead of filtration.

Typically, three liters of extraction liquor was treated with sufficient NH_4Cl (added as a hot solution containing 475 grams per 1,000 ml H_2O) to be equivalent to the perchlorate plus 5% excess. The solution was cooled to 0°C and centrifuged. The spun crystals were washed in the centrifuge with 2-400 ml ice-water. Portions of the crystals, filtrate, and washings were analyzed. The results from four batches were similar. Those reported here are typical:

Weight of Moist Crystals	$NaCl$ %	$NaClO_3$ %	NH_4ClO_4 %	Moisture %	Recovery of NH_4ClO_4 %
2,040 g.	1.07	1.47	93.3	5.2	79.3

Volume of Filtrate	$NaCl$ gpl	$NaClO_3$ gpl	NH_4ClO_4 gpl	NH_4Cl gpl
4,820 ml	237	138	94	9
Volume of Wash Sol.				
478 ml	209	61	105	4

Recrystallization of Crude Ammonium Perchlorate

Typically, 2,060 grams crude crystals, containing 1,875 g. NH_4ClO_4, dissolved in 2,300 ml water by heating and subsequent cooling gave 1,715 grams moist crystals after being centrifuged and washed with water.

Weight Moist Crystals	$NaCl$ %	$NaClO_3$ %	NH_4ClO_4%	H_2O %
1,715 g.	0.09	0.19	95.2	4.51

Volume of Filtrate	$NaCl$ gpl	$NaClO_3$ gpl	NH_4ClO_4 gpl
2,180 ml	13.5	14.9	111
Volume Wash Liquor			
265 ml	10.7	8.3	109

Recovery of NH_4ClO_4 on recrystallization was 87%.

Second Recrystallization of Ammonium Perchlorate

Typically, 2,200 g. of once recrystallized ammonium perchlorate was dissolved in 2,500 ml water, dissolved, cooled, centrifuged, and washed, etc.

Weight of Precipitate	$NaCl$ %	$NaClO_3$ %	Moisture %
1,880 g.	0.005	0.033	5.58

Volume of Filtrate	$NaCl$ gpl	$NaClO_3$ gpl	NH_4ClO_4 gpl
2,350 ml	0.85	1.62	121

Reduction of Chlorate in NH_4ClO_4 by Sulfur Dioxide

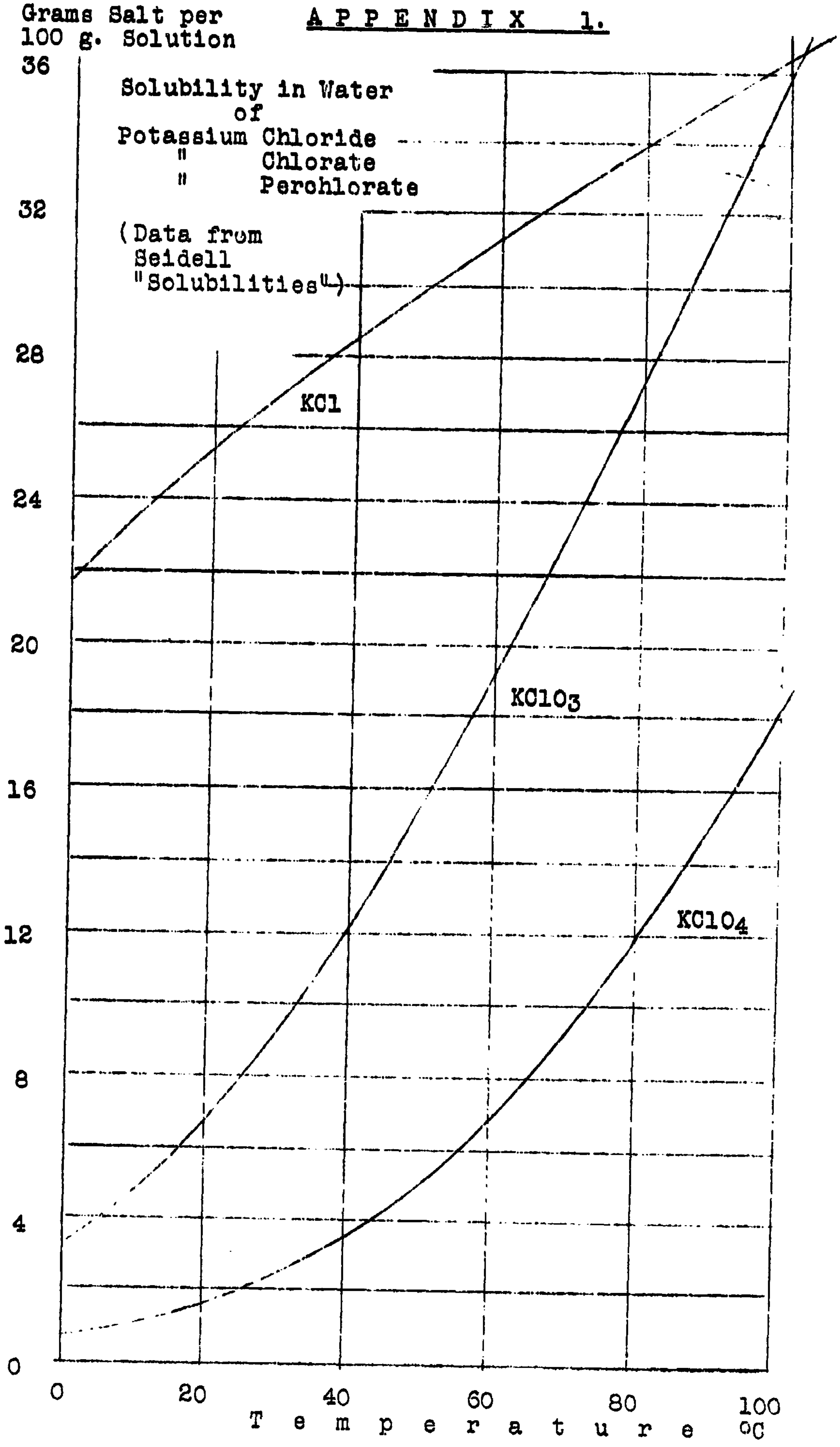
As a possible alternative method crude ammonium perchlorate was dissolved in water, gassed with SO_2 to remove chlorate by reduction, and crystallized. Specifically, 2,140 g. of the crude salt containing 2,000 g. NH_4ClO_4 was dissolved in 3,400 ml water at 75°C, gassed with sulfur dioxide until free of chlorate, neutralized with ammonia, and evaporated to about 3,000 ml. When cooled, centrifuged, washed, etc. the product contained no chlorate, but was contaminated with sulfate:

Weight of Precipitate	$NaCl$ %	$(NH_4)_2SO_4$ %	Moisture %
1,910 g.	0.09	0.20	5.0

Volume of Filtrate	$NaCl$ gpl	$(NH_4)_2SO_4$ gpl	NH_4ClO_4 gpl
1,810	24	68	82
Volume of Wash Liquor			
335 ml	11	26	124

Recover of NH_4ClO_4 - 90.5 %

APPENDIX 1.


Grams Salt per 100 g. Solution
Solubility in Water of Potassium Chloride " Chlorate " Perchlorate
(Data from Seidell "Solubilities")
KCl
KClO3
KClO4
36
32
28
24
20
16
12
8
4
0
0
20
40
60
80
100
Temperature °C

APPENDIX II

Summary of Calculations on Energy Requirements

In the production of sodium perchlorate by the electrolytic process two steps are involved. Sodium chlorate is first produced, and this salt is further oxidized to sodium perchlorate. The use of electrical energy in each step is essential, and no substitution is possible. From data obtained in the large-scale manufacture of both salts the electrochemical energy requirements of these processes have been accurately calculated.

In the production of sodium perchlorate by the thermal process sodium chlorate would be produced at the same cost in KWH per lb. as above. It would be necessary, however, to use about 65% more sodium chlorate per lb. of produced sodium perchlorate in the thermal process than in the electrolytic. By making reasonable assumptions, based upon laboratory results, the electrochemical requirement of this process has been calculated.

Assuming that:

Electrochemical energy, only, is considered.
Thermal conversion of chlorate is at 80% efficiency.
Recovery of materials is equal in both processes.

$$\frac{\text{Electrochemical KWH (Thermal Process)}}{\text{Electorchemical KWH (Electrolytic Process)}} = 1.146$$

In the thermal process it is necessary to use heat to melt and raise the temperature of the sodium chlorate. It may be assumed that it is possible to use either electrical energy or a burning fuel for this purpose. Assuming the use of electrical energy at 50% efficiency, using the best available data on the thermal properties of sodium chlorate and making a reasonable estimate as to the mass of the apparatus to be used, the additional energy requirement has been calculated as KWH per lb. $NaClO_4$:

$$\frac{\text{Total Energy as KWH (Thermal Process)}}{\text{Total Energy as KWH (Electrolytic Process)}} = 1.247$$

Energy used in lighting, heating, motors, and the like. is assumed to be approximately the same in both processes. The advantages, if any, would be with the electrolytic method, since processing of the product from the thermal process will be, unquestionably, more complicated.

SECURITY INFORMATION

Oldbury Electro-Chemical Company
51
Research Laboratory

THERMAL DECOMPOSITION OF ALKALI METAL CHLORATES

Third Interim Report

Oldbury Electro-Chemical Company

Research Laboratory September 30, 1952

INTRODUCTION TO THIRD INTERIM REPORT

In the Second Interim Report it was stated that "The lack of reasonably complete solubility data made it necessary to proceed rather empirically in attempting to separate the components of the salt mixture (obtained by thermal decomposition of sodium chlorate) by fractional crystallization from water."

Solubility determinations have now been made to fill the most important gaps in our knowledge, and to provide the basis for a critical evaluation of the accuracy of published data.

In this Third Interim Report selected published data and/or results from the Research Laboratory of the Oldbury Electro-Chemical Company for the following Systems are recorded:

TABLE I - $NaClO_4$ - H_2O
TABLE II - $NaClO_3$ - H_2O
TABLE III - $NaCl$ - H_2O
TABLE IV - $NaClO_4$ - $NaClO_3$ - H_2O
TABLE V, VA - $NaClO_4$ - $NaCl$ - H_2O
TABLE VI - $NaClO_3$ - $NaCl$ - H_2O
TABLE VII - $NaClO_4$ - $NaClO_3$ - $NaCl$ - H_2O

The data of TABLES I, II, and III have been plotted as a series of curves which follow TABLE III.

The principal points of TABLES IV, V, VI, and VII, for Temperatures 35, 50.8, and 80 degrees C, are plotted as orthographic projections of regular tetrahedra and follow TABLE VII. The lines joining the principal points have very slight curvatures not shown in the drawings.

METHODS:

The methods used in the OEC Research Laboratory in determining solubility values and other data are entirely conventional and require no description. Sodium perchlorate, due to its high solubility, produces rather viscous, syrupy solution and the handling of these requires more than ordinary skill and patience on the part of the researcher, but no new techniques were found necessary.

The study of the curves and data has resulted in no conclusions different from those derived from the empirical study reported in the Second Interim Report.

TABLE I

Solubility of Sodium Perchlorate in Water

Temperature °C.	Grams $NaClO_4$ per 100 grams H_2O	Grams $NaClO_4$ per 100 grams Solution	Grams $NaClO_4$ per Liter	Density	Solid Phase
0	169.3	62.87	1,031	1.640	$NaClO_4$:
10	183.3	64.7	1,070	1.654	H_2O
20	199.9	66.65	1,150	1.673	"
30	219.0	68.65	1,163	1.694	"
40	241.9	70.75	1,215	1.718	"
50	272.4	73.15	1,279	1.749	"
50.8	274.5	73.30	1,288	1.755	$NaClO_4$: H_2O and $NaClO_4$
20	257	72.0	1,265	1.757	$NaClO_4$
30	261	72.3	1,270	1.757	"
40	268	72.8	1,278	1.756	"
50	274	73.3	1,286	1.755	"
60	283	73.9	1,298	1.756	"
70	292	74.5	1,309	1.757	"
80	303	75.2	1,321	1.757	"
90	315	75.9	1,334	1.758	"
100	329	76.7	1,348	1.758	"

The values in this table are derived from those published in Seidell - "Solubilities of Inorganic and Metal Organic Compounds" - 3rd Edition. The figures from 0° to the transition temperature, 50.8°, are regarded as reliable. Two points, 35° and 50.8°, have been checked in the Research Laboratory of the Oldbury Electro-Chemical Company. The figures are less consistent, and the values are regarded as less reliable, for solutions containing $NaClO_4$, anhydrous, as the solid phase, but are adequate for present purposes.

One point, 80°, was checked in the Research Laboratory; the value found was about 1% higher than that given above.

TABLE II

Solubility of Sodium Chlorate in Water

Temperature °C.	g. $NaClO_3$ per 100 g. H_2O	g. $NaClO_3$ per 100 g. Soln.	g. $NaClO_3$ per Liter of Soln.	Density
0	79.6	44.32	615	1.389
10	87.6	46.70	658	1.410
20	95.9	48.95	700	1.430
30	105.3	51.30	744	1.451
40	115.2	53.54	788	1.472
50	126.2	55.8	833	1.493
60	139.2	58.2	881	1.514
70	152.5	60.4	928	1.536
80	167.4	62.6	976	1.559
90	184.9	64.9	1026	1.582
100	204.0	67.1	1076	1.604

The values in this table are derived from those published in "Seidell." The figures of Bell are regarded as most reliable. Their accuracy has been confirmed by results obtained in the OEC Co. Research Laboratory.

TABLE III

Solubility of Sodium Chloride in Water

Temperature °C.	g. NaCl per 100 g. H_2O	g. NaCl per 100 g. solution	g. NaCl per liter solution	Density
0	35.70	26.30	318	1.2090
10	35.80	26.35	317	1.2040
20	35.95	26.45	317	1.2000
30	36.20	26.55	317	1.1955
40	36.45	26.70	318	1.1915
50	36.75	26.85	319	1.1870
60	37.15	27.05	320	1.1830
70	37.60	27.30	322	1.1785
80	38.05	27.55	324	1.1745
90	38.50	27.80	325	1.1705
100	39.05	28.10	327	1.1660

The values in this table are derived from those published in "Seidell"--The figures of Berkeley are regarded as most reliable.

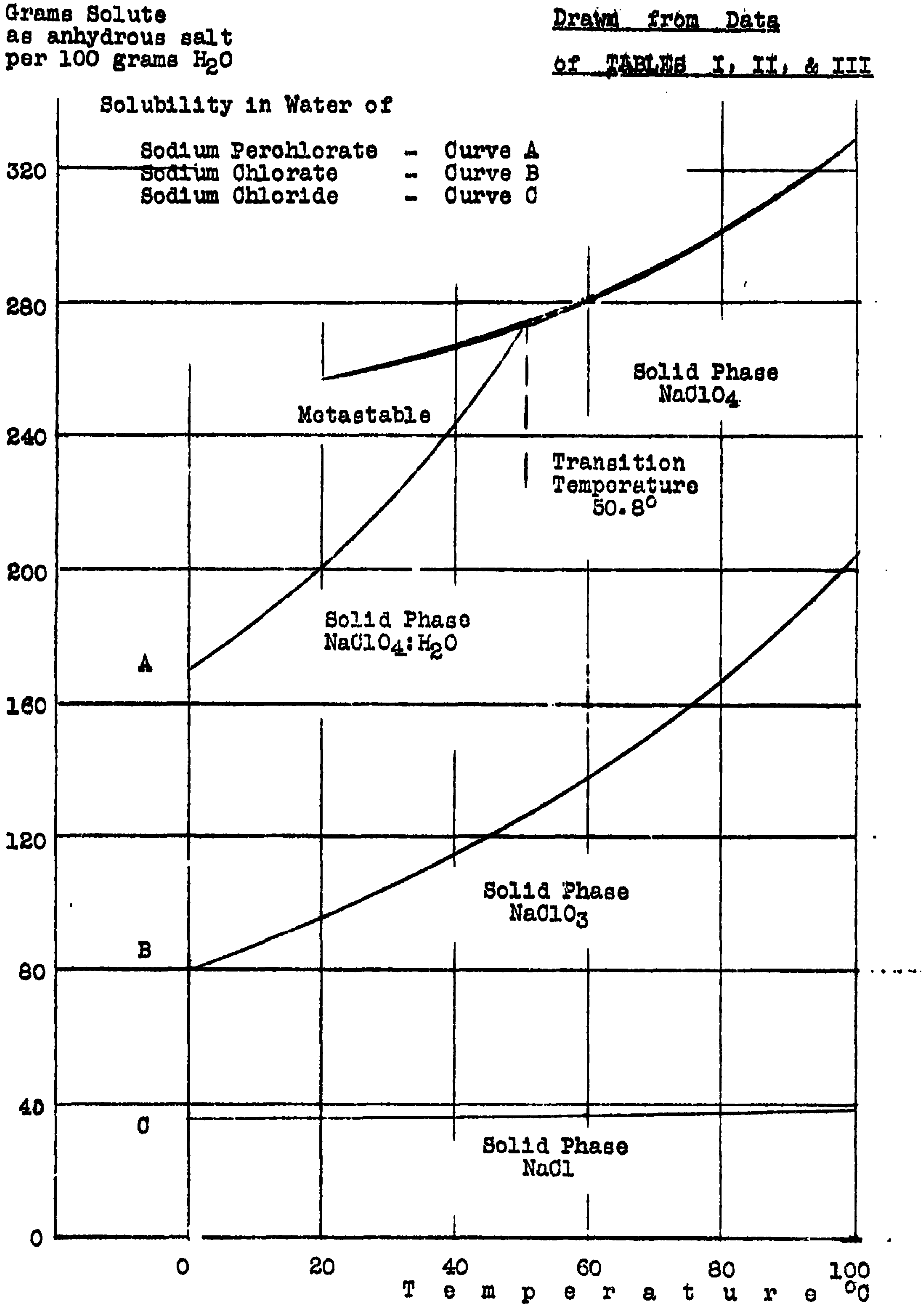

Grams Solute
as anhydrous salt
per 100 grams H_2O
Drawn from Data
of TABLES I, II, & III
Solubility in Water of
Sodium Perchlorate - Curve A
Sodium Chlorate - Curve B
Sodium Chloride - Curve C
320
280
240
200
160
120
80
40
0
Metastable
Solid Phase
$NaClO_4$
Transition
Temperature
50.8°
Solid Phase
$NaClO_4:H_2O$
A
Solid Phase
$NaClO_3$
B
C
Solid Phase
NaCl
0
20
40
60
80
100
Temperature °C

TABLE IV

Equilibrium in the System

$NaClO_4$ — $NaClO_3$ — H_2O

Temperature °C.	g. per 100 g. H_2O $NaClO_4$	g. per 100 g. H_2O $NaClO_3$	g. per 100 g. Solution $NaClO_4$	g. per 100 g. Solution $NaClO_3$	Density	Solid Phase
35	230.0	0	69.7	0	1.704	$NaClO_4$ H_2O
35	229.6	28.74	64.07	8.02	1.744	"
35	229.6	37.39	62.56	10.19	1.755	"
35	231.0	45.52	61.35	12.09	1.769	$NaClO_3$ + "
35	0	109.9	0	52.36	1.457	"
50.8	274.5	0	73.3	0	1.748	$NaClO_4$
50.8	275.6	16.75	70.24	4.27	1.771	"
50.8	272.2	32.05	67.33	7.93	1.787	"
50.8	271.0	58.15	63.15	13.55	1.809	$NaClO_3$ + "
50.8	0	127.2	0	55.98	1.488	"
80	307.3	0	75.45	0	1.768	$NaClO_4$
80	306.1	19.76	71.88	4.64	1.777	"
80	307.2	97.38	60.88	19.30	1.840	$NaClO_3$ + "
80	0	169.8	0	62.93	1.551	"

Results of O E C Research Laboratory.

TABLE V

Equilibrium in the System

$NaClO_4$ - NaCl - H_2O

Temperature °C.	g. per 100 g. H_2O		g. per 100 g. Solution			
	$NaClO_4$	NaCl	$NaCl_4$	NaCl	Density	Solid Phase
35	230.0	0	69.7	0	1.704	$NaClO_4:H_2O$
35	226.7	3.63	68.6	1.10	1.703	NaCl + "
35	0	36.3	0	26.6	1.1935	"
50.8	274.5	0	73.3	0	1.748	$NaClO_4$
50.8	272.7	2.85	72.6	0.76	1.749	NaCl + "
50.8	0	36.8	0	26.9	1.187	"
80	307.3	0	75.45	0	1.758	$NaClO_4$
80	303.8	3.21	74.64	0.79	1.757	NaCl "
80	0	38.05	0	27.55	1.1745	"

Results of OEC Research Laboratory.

TABLE VA

Equilibrium in the System

$NaClO_4$ - NaCl - H_2O

Temperature °C.	g. per 100 g. H_2O		g. per 100 g. Solution			
	$NaClO_4$	NaCl	$NaClO_4$	NaCl	Density	Solid Phase
0	169.3	0	62.87	0	1.640	$NaClO_4:H_2O$
0	158.0	6.7	59.69	2.53	--	NaCl + "
0	125.2	10.21	52.82	4.37	--	"
0	80.1	17.0	40.65	8.63	--	"
0	39.3	25.4	23.86	15.44	--	"
0	0	35.7	0	26.30	1.209	"
25	209.1	0	67.65	0	1.683	$NaClO_4:H_2O$
25	207.7	4.27	66.58	1.37	1.683	NaCl + "
25	0	36.05	0	26.50	1.198	"
50	274	0	73.3	0	1.755	$NaClO_4:H_2O$
50	271	3.03	72.46	0.81	1.749	NaCl + "
50	0	36.75	0	26.85	1.1870	"
75	297	0	74.8	0	1.757	$NaClO_4$
75	296	3.32	74.15	0.83	1.757	NaCl + "
75	0	37.78	0	27.42	1.1765	"
100	329	0	76.75	0	1.758	$NaClO_4$
100	325	3.77	75.79	0.88	1.757	NaCl + "
100	237	4.9	69.32	1.44	1.664	"
100	157	8.1	59.23	3.06	1.532	"
100	83	17.7	41.44	8.81	1.367	"
100	0	39.05	0	28.10	1.1660	"

Derived from values published in "Seidell".

TABLE VI

Equilibrium in the System

NaClO$_3$ - NaCl - N$_2$O

Temperature °C.	g. per 100 g. H$_2$O		g. per 100 g. Solution			
	NaClO$_3$	NaCl	NaClO$_3$	NaCl	Density	Solid Phase
0	79.6	0	44.32	0	1.389	NaClO$_3$
0	33.1	27.3	20.65	17.0	1.350	NaCl+"
0	0	35.7	0	26.3	1.209	NaCl
25	100	0	50.0	0	1.440	NaClO$_3$
25	64.8	22.7	34.6	12.1	1.390	NaCl+"
25	33.3	28.5	20.6	17.6		NaCl
25	0	36.0	0	26.5	1.198	"
35	110	0	52.4	0	1.460	NaClO$_3$
35	85.4	14.6	42.7	7.3	1.429	"
35	77.5	20.2	39.2	10.2	1.420	NaCl+"
35	0	36.3	0	26.6	1.1935	"
35	0	36.3	0	26.6	1.1935	NaCl
50.8	127.5	0	56.0	0	1.495	NaClO$_3$
50.8	98.7	16.8	45.8	7.8	1.461	NaCl+"
50.8	94.0	18.3	44.3	8.6	1.448	NaCl
50.8	68.5	22.0	36.0	11.5	1.387	"
50.8	43.6	26.6	25.6	15.6	1.320	"
50.8	20.7	31.7	13.6	20.8	1.253	"
50.8	0	36.8	0	26.9	1.187	"
70	152.5	0	60.4	0	1.536	NaClO$_3$
70	129.1	14.8	52.9	6.0	1.525	NaCl + "
70	0	37.6	0	27.3	1.178	"
80	169.8	0	62.93	0	1.559	NaClO$_3$
80	148.1	14.1	56.5	5.4	1.535	NaCl+"
80	103.9	18.1	46.8	8.14	1.449	NaCl
80	64.7	23.94	34.3	12.7	1.357	NaCl
80	29.2	31.0	18.2	19.4	1.262	"
80	0	38.05	0	27.55	1.1745	"

Derived from results obtained in Oldbury Electro-Chemical Co. Research Laboratory. Data in Seidell are not regarded as reliable.

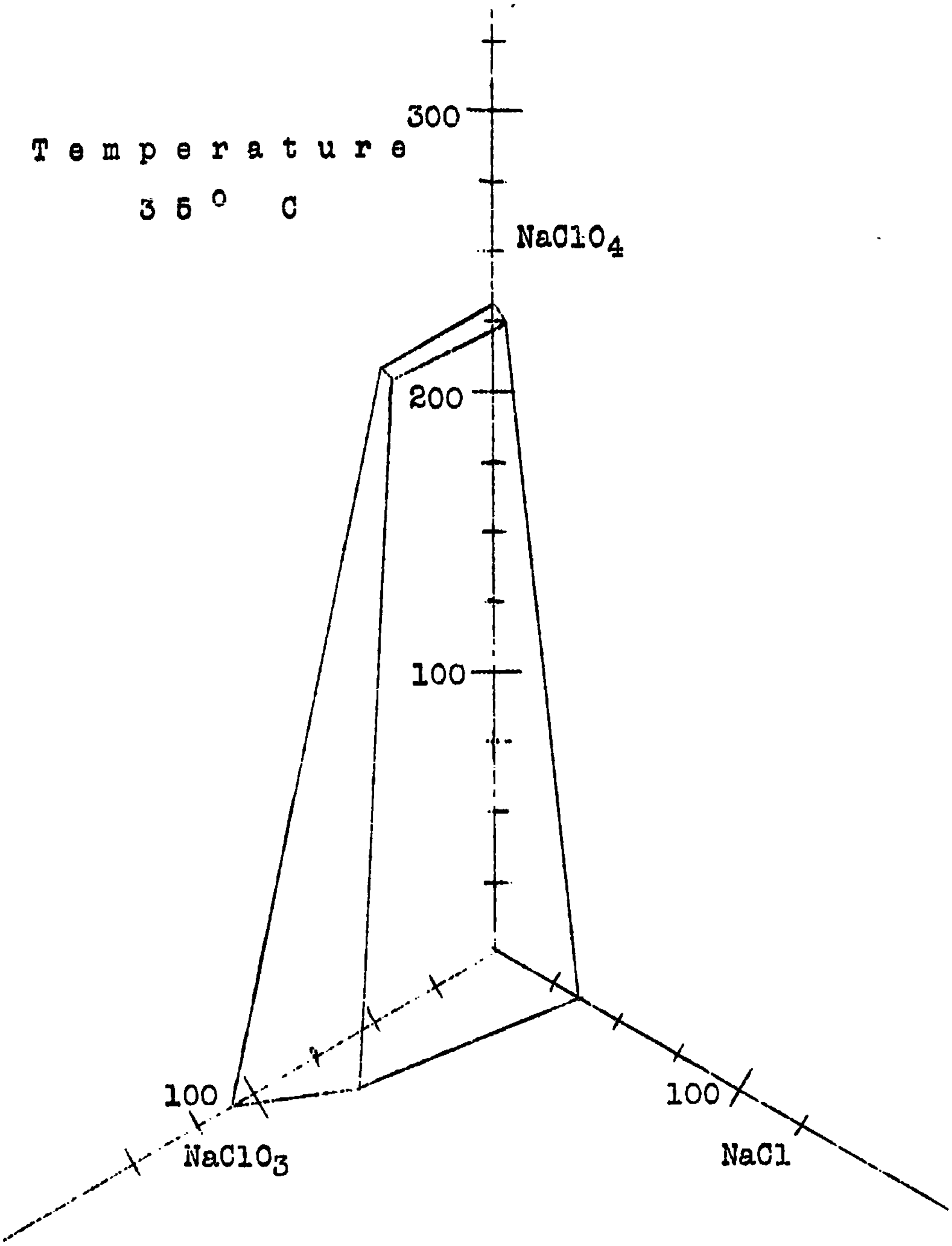
TABLE VII

Equilibrium in the System

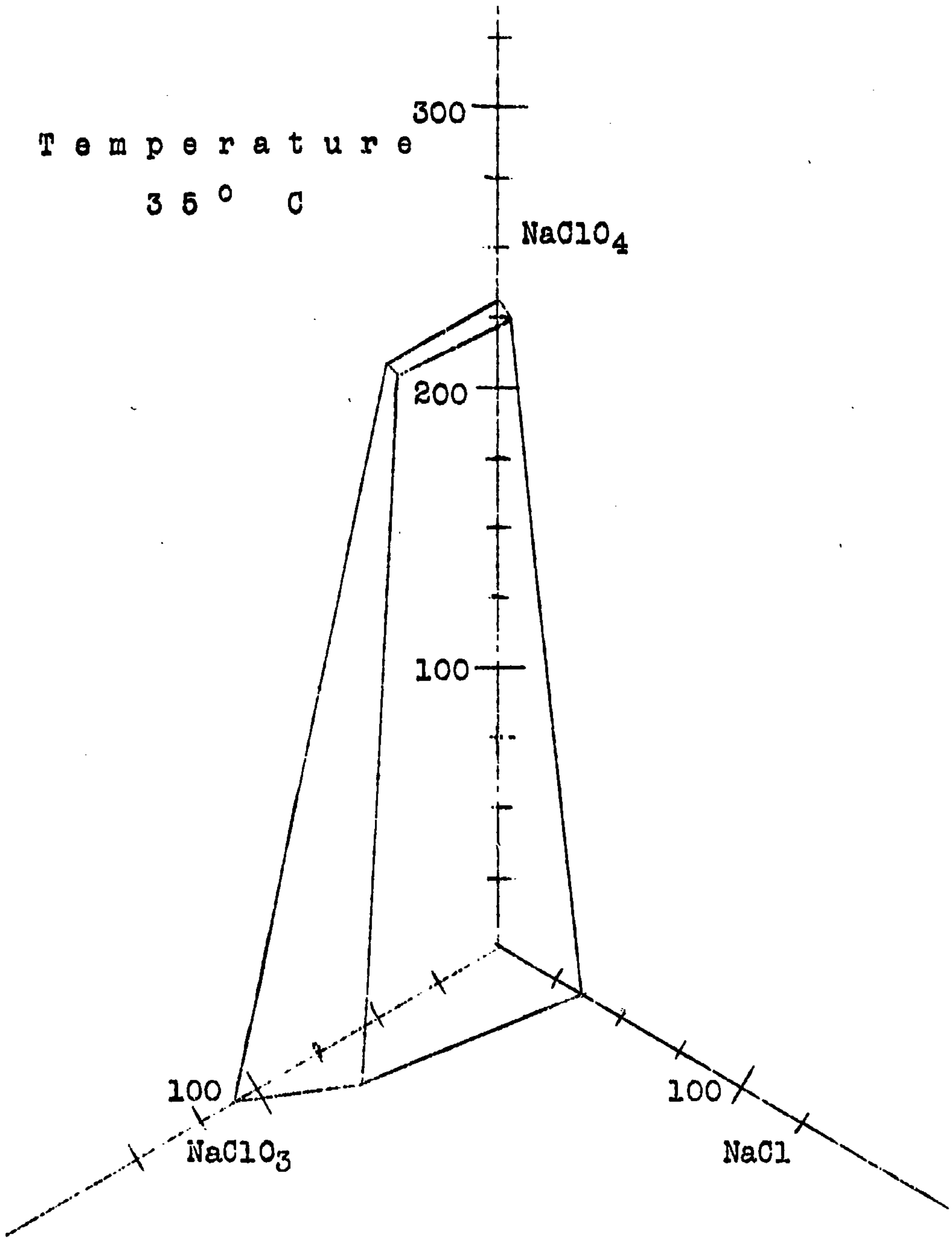
$NaClO_4$ - $NaClO_3$ - $NaCl$ - H_2O

Temp. °C.	g. per 100 g. H_2O			g. per 100 g. Solution			Density	Solid Phase
	$NaClO_4$	$NaClO_3$	$NaCl$	$NaClO_4$	$NaClO_3$	$NaCl$		
35	225.8	15.98	3.35	65.43	4.63	0.97	1.726	$NaClO_4:H_2O$ + $NaCl$
35	226.5	27.85	3.18	63.35	7.79	0.89	1.742	$NaClO_4:H_2O$ + $NaCl$
35	228.9	44.39	2.97	60.83	11.80	0.79	1.766	$NaClO_4:H_2O$ + $NaCl$ + $NaClO_3$
50.8	272.3	17.67	2.83	69.32	4.50	0.72	1.771	$NaClO_4$ + $NaCl$
50.8	270.2	35.68	2.74	66.13	8.73	0.67	1.788	$NaClO_4$ + $NaCl$
50.8	270.0	56.83	2.75	62.85	13.23	0.64	1.807	$NaClO_4$ + $NaCl$ + $NaClO_3$
80	303.8	95.73	3.22	60.43	19.04	0.64	1.840	$NaClO_4$ + $NaCl$ + $NaClO_3$

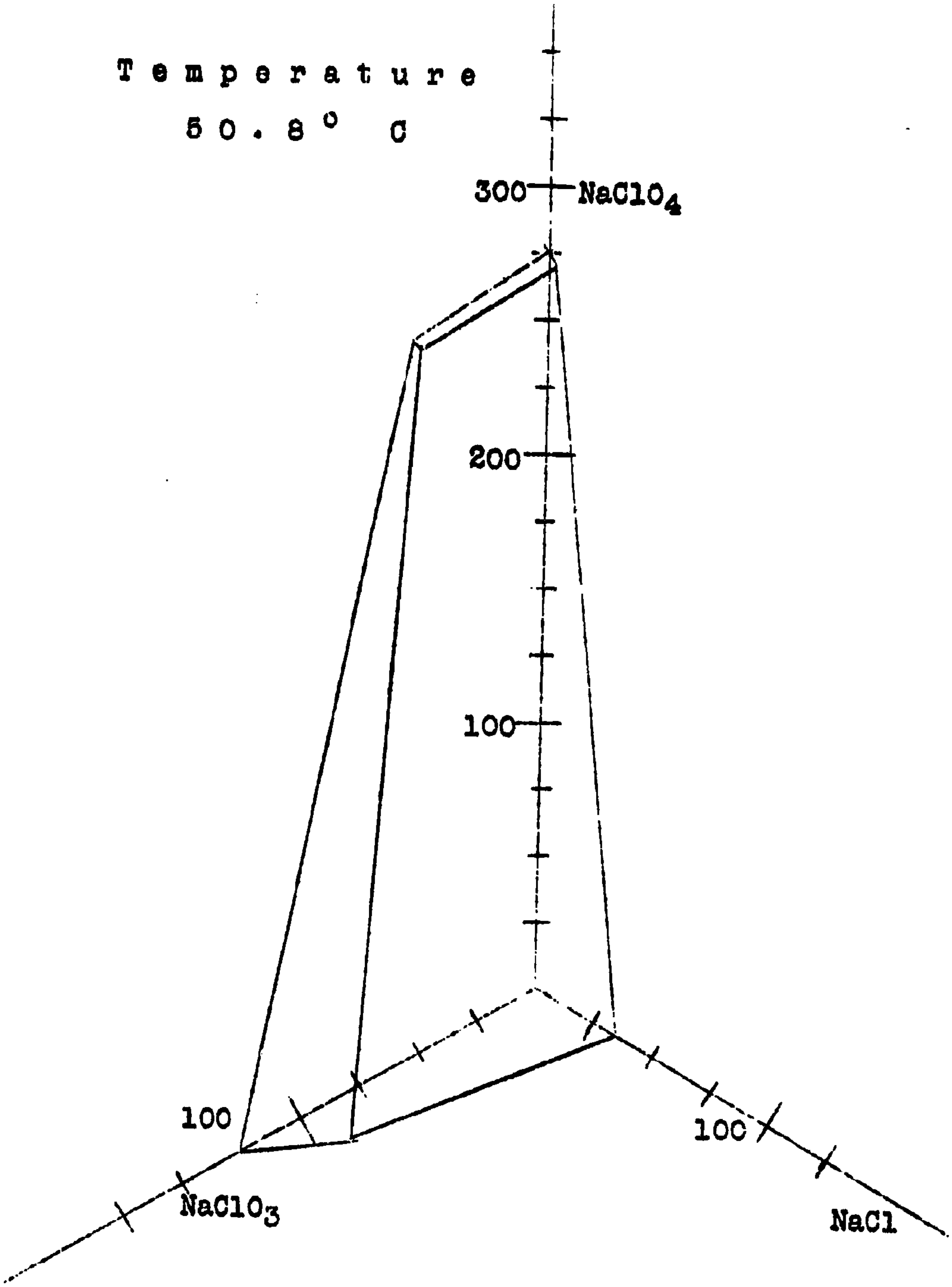
Results of OEC Research Laboratory

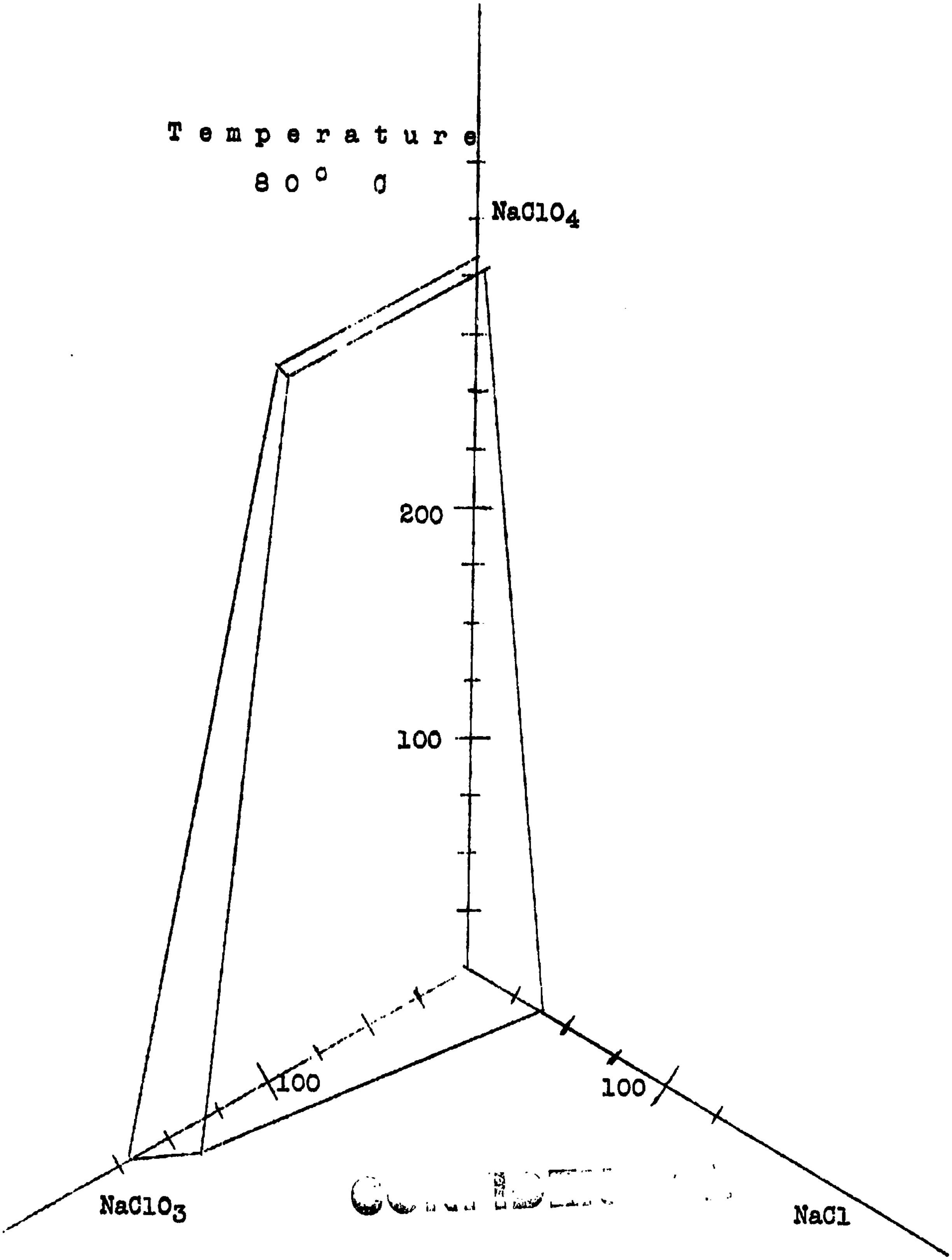


Temperature
35° C
300
200
100
NaClO4
100
NaClO3
100
NaCl



Temperature
35° C
300
NaClO$_4$
200
100
100
NaClO$_3$
100
NaCl


Temperature
50.8° C
300
$NaClO_4$
200
100
100
$NaClO_3$
100
NaCl


Temperature
80° C
NaClO4
200
100
100
100
NaClO3
NaCl

SECURITY INFORMATION

CONFIDENTIAL

51

THERMAL DECOMPOSITION
OF
ALKALI METAL CHLORATES

Fifth
Interim Report

Oldbury Electro-Chemical
Company

Research Laboratory November 14, 1952

CONFIDENTIAL

SECURITY INFORMATION

1. INTRODUCTION TO THE FIFTH INTERIM REPORT

It has been demonstrated (Ref: Second Interim Report, Section V) that salt mixtures simulating those obtained by thermal conversion of sodium chlorate may be extracted with water producing solutions which contain all of the perchlorate and chlorate leaving a solid residue containing a large proportion of the sodium chloride.

In this Fifth Interim Report it is shown that the results obtained by extraction of the actual reaction product are similar to those from synthetic mixtures, and that the recovery of perchlorate/chlorate solutions and solid, nearly pure, sodium chloride is practical and efficient.

* * * * * *

It has been demonstrated (Ref: Second Interim Report, Section VI) that ammonium perchlorate may be prepared by metathesis from concentrated solutions of sodium perchlorate, containing chlorate and chloride, and ammonium chloride.

In this Fifth Interim Report these experiments have been greatly extended in number and scope, and results are reported in greater detail. Solutions used were obtained by actual extraction of thermally decomposed sodium chlorate, and not synthetically.

A rather detailed procedure is suggested, together with a flowsheet, for economic evaluation of the proposed process.

This process is believed to contain elements of novelty which may be patentable. Applications for Patents will be made by Oldbury Electro-Chemical Company when clearance is obtainable by declassification or otherwise.

2. EXTRACTION OF PRODUCT FROM THERMALLY DECOMPOSED $NaClO_3$

Experiment A. In this experiment the principal objective was to prepare a relatively large quantity of the approximately saturated solution of sodium perchlorate/chlorate/chloride as the starting material for further experiments. The behavior of the kibbled product in contact with water was observed.

A 22 liter flask was nearly filled with broken fragments of the product obtained by converting sodium chlorate in an Inconel pan. Sufficient water was added to cover the solid and solution was allowed to proceed at 25°C with only occasional stirring. The density increase was followed by periodic specific gravity determinations. About 72 hours was required to reach a maximum density. The solution was decanted from the residue, which was again extracted with a further quantity of water. The lumps were observed to disintegrate completely leaving a residue of fine salt. The operations were repeated, adding solidified melt or water as required, until 30 liters of solution had been prepared.

ANALYSIS:

Density	1.663	
Total Solids	1.102	grams per liter
Sodium chloride	29.2	" " "
" chlorate	245.0	" " "
" perchlorate		
(by difference)	828.0	" " "
(determined)	835.0	" " "

Experiment B. In this experiment accurately weighed or measured quantities were used and further data accumulated. 4.500 grams of the product from a 10,000 gram conversion run, kibbled to pass a 3/8 inch screen, was weighed into a 4 liter bottle. Two liters of water (including wash water from a previous batch) was added. Extraction proceeded 3 days if at room temperature, or 6 hours, if warmed on a steam bath, with occasional shaking of the bottle. The residual salt was filtered off with suction, removing as much solution as possible, and slurreed with 250 ml hot water. After a second filtration, followed by washing with 125 ml additional water, samples of the concentrated solution, wash solution, and salt were analyzed.

Analytical and Other Data

	Batch	
Concentrated Solution	B	C
Volume in liters	3.300	3.275
Total Solids, g. p. l.	1,118	1,135
NaCl g. p. l.	29.5	29.4
NaCl % of Total Solids	2.6	2.6
$NaClO_3$ g. p. l.	232.0	260.0
$NaClO_3$ % of Total Solids	22.7	22.9
$NaClO_4$ g. p. l.	857	845
$NaClO_4$ % of Total Solids (by difference)	76.7	74.5
Wash Solution		
Volume in liters	0.370	0.425
Total Solids, g. p. l.	218	224
NaCl g. p. l.	65.4	54.6
NaCl % of Total Solids	30.0	24.4
$NaClO_3$ g. p. l.	30.1	35.6
$NaClO_3$ % of Total Solids	13.8	15.9
$NaClO_4$ g. p. l.	122.5	133.8
$NaClO_4$ % of Total Solids (by difference)	56.2	59.7
Salt (dry basis)		
Weight, grams	902	828
NaCl %	96.8	96.0
$NaClO_3$ %	0.36	0.46
$NaClO_4$ %	2.8	3.5

Wash solutions were diluted with water and used in subsequent extractions. Approximately 90% of the NaCl contained in the conversion product was separated as solid. This salt was contaminated by $NaClO_3$, amounting to about 0.4% of the total, and by $NaClO_4$, amounting to approximately 1.0% of the total.

3. AMMONIUM PERCHLORATE BY METATHESIS

It has been demonstrated, in an earlier Report, that substantial yields of ammonium perchlorate are obtainable by mixing ammonium chloride with the sodium perchlorate/chlorate/chloride solution. The solubility of ammonium perchlorate is known to vary with the temperature. It was, therefore, of interest to investigate the effects of temperature on the yields.

A series of metathesis mixtures, all having the same composition, was made and the various batches cooled to different temperatures in the range: -20° to +20°C. Solution obtained as described in Section 2 of this report was mixed with ammonium chloride and sufficient water to prevent precipitation of sodium chloride. The amount of ammonium chloride used was slightly more then one mole per mole of perchlorate:

Components of Metathesis Mixture

Sodium Perchlorate Solution			Composition	
Volume		250 ml		-------
$NaClO_4$	(1.7 moles)	209 g.		-------
$NaClO_3$	(0.58 ")	61.5 g.	(0.58 moles)	61.5 g.
$NaCl$	(0.13 ")	7.5 g.	(1.83 ")	107 g.
H_2O		137		-------
Ammonium Chloride Solution				
NH_4Cl	(1.77 moles)	95 g.	(0.07 ")	4.0 g.
H_2O		200 g.		-------
NH_4ClO_4		---------	(1.70 ")	200 g.
H_2O	(total)	337		337 g.

After cooling the crystal slurry to the desired temperatures the crystals were, in each case, filtered with suction and analyzed without further purification. Analytical results are reported on the dry basis, but the crystals were not actually dried. The results are shown in TABLE I.

Effects of Washing: The crude ammonium perchlorate contained a considerable amount of mother liquor. To determine the extent to which washing with water might be expected to purify the product two batches were slurried with water, 100 ml per batch, cooled to 0°C, and filtered with suction. The extent to which this treatment contributed to the purification of the ammonium perchlorate is indicated by the results shown in TABLE II.

Effects of Water Content of Metathesis Mixture: In a series of experiments similar to those of TABLE I the water content of the mixture was varied in the range 337 g. to 287 g. Processing was similar to that previously described, all solutions being cooled to 0°C before filtration. Results are shown in TABLE III.

Processing of Mother Liquors by Evaporation: The mother liquor separated from the crude ammonium perchlorate obtained by metathesis contains, roughly, 20% of the total ClO_4', 90% of the ClO_3', and 90% of the Cl'. It was anticipated, and experimentally verified, that partial evaporation of the solution would produce a crop of sodium chloride, and that cooling of the concentrated solution would produce a second crop of ammonium perchlorate. The results of these experiments are shown in TABLE IV.

This procedure is not regarded as safe because of the instability of the solutions containing high concentrations of ammonium and chlorate ions. Both the heated solutions and the moist crystals (on standing) became colored greenish-yellow and had a strong odor of chlorine. It is recommended, therefore, that an alternative procedure be considered.

Processing of Mother Liquors by Removal of Ammonia: A safer procedure for recovery of the values contained in the metathesis mother liquors involves treating the solution with sodium hydroxide in an amount equivalent to the ammonium ion, boiling off and recovering the ammonia, and returning the ammonium-free sodium perchlorate chlorate/chloride solution to the cycle at an appropriate point after evaporation to the extent required to avoid the accumulation of an excessive amount of water.

The results of the experimental verification of this procedure are shown in TABLE V.

TABLE I

Ammonium Perchlorate by Metathesis

Effects of Temperature

Temp.	Percentage of Total Anion Found in Precipitate			Composition of Precipitate		
°C	ClO_4' %	ClO_3' %	Cl' %	NH_4ClO_4 %	$NaClO_3$ %	$NaCl$ %
-20	87.1	13.1	18.7	86.4	3.9	9.7
-20	87.7	15.6	21.8	84.6	4.4	10.9
-12	84.8	10.2	11.5	90.4	3.2	6.4
-12	84.3	10.7	10.8	90.5	3.3	6.2
0	80.7	9.1	10.7	90.6	3.0	6.4
0	80.5	8.6	10.0	91.2	2.8	6.0
0	81.7	11.3	12.3	89.0	3.7	7.3
+20	71.2	7.3	10.3	90.4	2.7	6.9
+20	71.8	8.5	11.1	89.5	3.1	7.4

Composition of Each Mixture

	Grams	Moles
NH_4ClO_4	200.0	1.70
$NaClO_3$	61.5	0.58
$NaCl$	107.0	1.83
NH_4Cl	4.0	0.07
H_2O	337	-----

TABLE II

Effects of Washing Upon Crude Ammonium Perchlorate

	Net Wt.	Wt. NaCl	%	Wt. $NaClO_3$	%	Wt. $NaClO_4$	%
Composition of Crude Crystals							
A	476.5 g.	40.9	9.7	16.2	3.9	367.1	86.4
B	501.0 g.	48.4	10.9	19.4	4.4	373.7	84.6
Composition of Washed Crystals							
A	361.0 g.	7.9	2.2	6.6	1.8	349.6	96.0
B	379.5 g.	11.8	3.2	7.9	2.2	355.5	94.6
Composition of Salts in Wash Water (Dry Basis)							
A	-----	31.2	56.3	9.2	16.6	14.9	27.1
B	-----	31.4	54.6	10.1	17.5	16.0	27.9

TABLE III

Ammonium Perchlorate by Metathesis

Effects of Water Content

Total H_2O	Percentage of Total Anion Found in Precipitate			Composition of Precipitate		
Grams	ClO_4' %	ClO_3' %	Cl' %	NH_4ClO_4 %	$NaClO_3$ %	NaCl %
337	81.7	11.3	12.3	89.0	3.7	7.3
312	82.8	12.5	21.0	84.7	3.7	11.6
312	82.7	11.7	20.0	85.4	3.5	11.1
287	84.4	12.8	29.1	81.3	3.6	15.1
287	84.8	12.7	29.6	81.1	3.6	15.3

TABLE IV

Metathesis Followed by Evaporation of Mother Liquor

	Weight (Moist) g.	Composition (Dry basis) NH_4ClO_4 %	$NaClO_3$ %	NaCl %
Crude NH_4ClO_4 by Metathesis				
A	195.9	91.0	3.3	5.7
B	195.3	90.6	3.3	6.1
NaCl by Evaporation of Mother Liquor to 50% of its volume.				
A	80.5	3.3	3.7	93.3
B	88.5	5.2	7.5	86.3
Crude NH_4ClO_4 from cooled evaporated Mother Liquor				
A	25.0	83.2	14.4	2.4
B	23.5	84.1	13.1	2.8
Filtrate from cooled evaporated Mother Liquor				
A	----	20.3	53.3	26.4
B	----	17.5	53.6	28.9

Note: Evaporation of Mother Liquor was accompanied by some decomposition, as indicated by development of yellow color and evolution of chlorine-like fumes.

The crude ammonium perchlorate obtained from the evaporated solution also developed a yellow color when stored moist. The procedure is not recommended.

TABLE V

Recovery of Values by NaOH Treatment of Metathesis Mother Liquor

	Salts in NaOH Treated Solution after removal of NH_3 (Volume - approximately 1.5 liters)	Salts in NaCl Precipitate (after evaporation of solution to thick slurry		Salts in Wash Solution. (100 ml H_2O)		Salts in Final Mother Liquor	
	grams	grams	%	grams	%	grams	%
NaCl	333	294.7	88.0	13.0	3.8	27.4	8.2
$NaClO_3$	202	8.2	4.3	23.1	12.1	160.2	83.6
$NaClO_4$	107	4.5	4.1	12.8	11.7	92.4	84.2

Composition (Dry Basis) of Solid, Wash Solution, and Mother Liquor.

	Solid (NaCl)	Wash Solution	Mother Liquor
NaCl	95.9%	26.6%	13.3%
$NaClO_3$	2.7	47.1	53.7
$NaCl_4$	1.4	26.3	33.0

Note: It will be observed that perchlorate ion has been removed from the solution as ammonium perchlorate, and that chloride is here removed as sodium chloride. Chlorate, however, has accumulated. By reference to the solubility data of the Third Interim Report it will be seen that a salt mixture having the composition of that in the Mother Liquor, above, may be further concentrated, separated, and cooled to produce pure sodium chlorate crystals. Perchlorate, chloride, and chlorate may thus be separated.

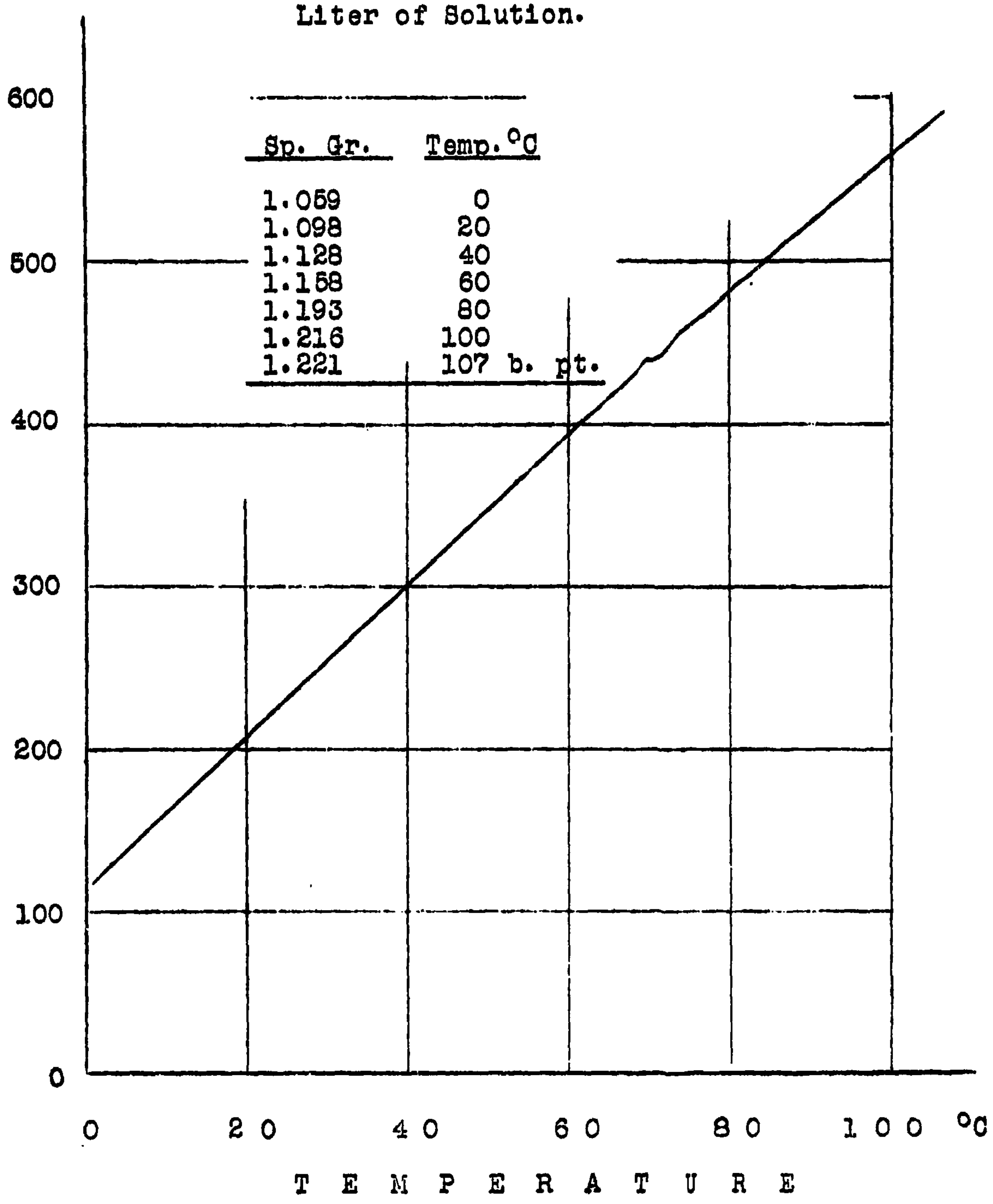
Solubility in Water
of
Ammonium Perchlorate.
(Seidell)

NH_4ClO_4

g. p. l

Grams NH_4ClO_4 per

Liter of Solution.



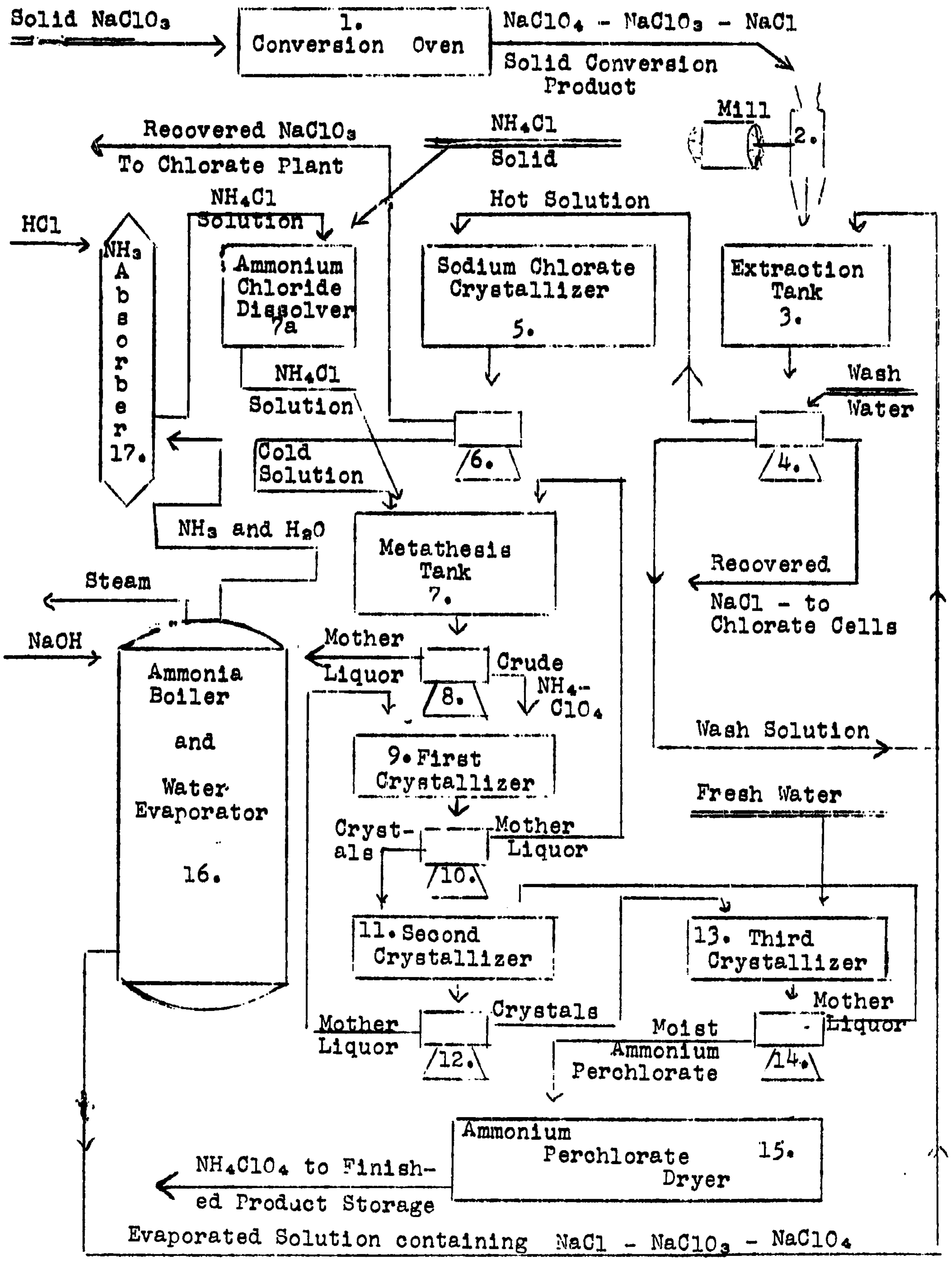
Sp. Gr.	Temp. °C
1.059	0
1.098	20
1.128	40
1.158	60
1.193	80
1.216	100
1.221	107 b. pt.

4. TENTATIVE PROCESS PROPOSAL WITH FLOW SHEET

In drawing the Flow Sheet which indicates the steps in the preparation of ammonium perchlorate, starting with sodium chlorate and ammonium chloride, certain auxiliary items of equipment which would be necessary for actual operation or for efficiency have been omitted for simplicity.

Estimated Working Capacities. The estimates for the working capacities of the various units are calculated on the basis of a production rate of 1,000 lbs. per eight hour day of finished ammonium perchlorate. Production at a higher rate would, usually, require proportionately larger equipment or multiple units.

Data for these estimates were obtained prinicpally from laboratory results, but in part from records of the operation of an ammonium perchlorate plant (based upon the use of ammonium sulfate and sodium perchlorate) designed in this laboratory in 1940 and successfully operated in Canada.


Solid $NaClO_3$
1. Conversion Oven
$NaClO_4$ - $NaClO_3$ - NaCl
Solid Conversion Product
Mill
2.
Recovered $NaClO_3$
To Chlorate Plant
NH_4Cl
Solid
HCl
NH_4Cl Solution
NH_3 Absorber 17.
Ammonium Chloride Dissolver 7a
Hot Solution
Sodium Chlorate Crystallizer 5.
Extraction Tank 3.
NH_4Cl Solution
Wash Water
Cold Solution
6.
4.
NH_3 and H_2O
Metathesis Tank 7.
Recovered NaCl - to Chlorate Cells
Steam
NaOH
Ammonia Boiler and Water Evaporator 16.
Mother Liquor
8.
Crude NH_4-ClO_4
Wash Solution
9. First Crystallizer
Fresh Water
Crystals
Mother Liquor
10.
11. Second Crystallizer
13. Third Crystallizer
Mother Liquor
Crystals
Mother Liquor
12.
Moist Ammonium Perchlorate
14.
Ammonium Perchlorate Dryer 15.
NH_4ClO_4 to Finished Product Storage
Evaporated Solution containing NaCl - $NaClO_3$ - $NaClO_4$

$NaClO_3$ required for conversion (78% efficiency) 1,900#/day
Rate of conversion - 250# per hour
1. Size of Conversion Oven - ?
(ref: Fourth Interim Report, Section 4)

Conversion product to be milled or crushed 1,750#/day
Rate of milling - 4# per minute
2. Size of Mill - ?
May be a standard hammer-mill or a crusher.

Volume solution required to contain 1,085# $NaClO_4$ - 575 liters
Batches to be leached per day - 1
3. Working Capacity of Tank - (approx.) 700 "
This would be an open tank equipped with agitator and steam-coil. Cone-bottom outlet or discharge via pump.

Solid sodium chloride to be centrifuged 5-600#/day
Spinning cycles (maximum) 6
4. Working capacity of Centrifuge (min.) 100#
This would be a standard centrifuge.

Volume of solution to be cooled to recover $NaClO_3$ 575 liters
Working capacity of tank (approx.) 575 "
5. This would be an open tank equipped with agitator and cooling-coil. Cone-bottom outlet or pump discharge.

Solid sodium chlorate to be centrifuged 325#/day
Spinning cycles (maximum) 4
6. Same Centrifuge as 4.

Volume of metathesis liquor and crystals 1,500 liters
Working capacity of tank 1,500 "
7. This would be an open tank equipped with agitator and refrigerated cooling-coil. Cone-bottom outlet or pump discharge.

7a Stirred auxiliary tank for making or storing ammonium chloride solution 750 "

Crude ammonium perchlorate to be centrifuged 1,100#/day
Spinning cycles (maximum) 11
8. Same centrifuge as 4.
TOTAL CYCLES FOR CENTRIFUGE 4, 6, and 8 21

Volume of liquor in each crystallizer 1,500 liters
9., 11., and 13. Working capacity, each 1,500 "
Each batch crystallizer would be equipped with agitator and cooling-coils. Open tanks with cone-bottom outlets or discharge via pumps. The number of crystallizers required is uncertain.

	Crystallized NH_4ClO_4 to be centrifuged (max.)	3,000#/day
	Spinning cycles (maximum)	20
10., 12., 14.	Working capacity of centrifuge 100-150# This would be a standard centrifuge. The same machine would be used for all crystallizers. It would be more efficient to use a larger centrifuge and reduce the number of cycles.	
	Purified NH_4ClO_4 to be dried	1,000#/day
	Drying rate required	125#/hour
15.	Tray Dryer, working capacity 1,000# or Rotary Dryer, minimum working capacity about 150# per hour.	
	Volume of solution to be de-ammoniated (approx.)	2,000 liters
	Working capacity of Ammonia Boiler	2,000 "
16.	Water to be evaporated (approx.)	2,500#/day
	Evaporative capacity (minimum)	400#/hour
	Ammonium chloride to be recovered (approx.)	100#/day
	Working capacity of NH_3 absorber	100#/hour
17.	Heat of neutralization to be dissipated (roughly)	36,000 Kg Cals 144,000 B.T.U.

Chemicals Required per Day

Sodium chlorate	1,900 lbs. (-325=1,575)
Ammonium chloride	460
Caustic Soda (NaOH)	75
Hydrochloric acid (35%)	200

Chemicals Recovered per Day

Sodium chlorate	325 lbs
Sodium chloride	500
Ammonium chloride (recycled)	100

In our process, however, contamination of the ammonium perchlorate necessitates recrystallization, the value of the relatively large amount of chlorate necessitates recovery, and destruction of the chlorate (ignoring its value) would be expensive.

Our process is further complicated by the instability of solutions containing relatively high concentrations of ammonium and chlorate ions. This introduces an element of hazard which cannot be ignored. The steps involving the removal of ammonia from the metathesis mother liquor, admittedly economically unsound, are necessary to minimize the hazard.

The process outlined in this Report is considered workable. With due regard to its economic limitations we recommend consideration of the design of a Pilot-Plant based upon the Tentative Proposals and Flow-Sheet of Section 4.

* * * * *

An alternative process should also be considered: The sodium perchlorate/chlorate/chloride solution of Section 2 could, presumably, be "finished" by the conventional electrolytic process to a sodium perchlorate solution essentially identical to the best present commercial product. This suggestion is based upon the opinion of competent operators of the perchlorate plant of Oldbury Electro-Chemical Company, but has not been verified experimentally. It seems obvious that the output of perchlorate per unit of platinum anode area would be greatly increased, but such a process would not, of course, eliminate the use of this metal. The experimental verification of this procedure, to eliminate the element of speculative uncertainty, would be an appropriate subject for further work.