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Research on the Exploration of Methods to
Produce Chlorates and Perchlorates by Means
Other Than Electrolytic

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Ralph Robert
By direction of
Chief of Naval Research"

INTERIM RESEARCH REPORT

for

Office of Naval Research

CONTRACT NONR 682 (OO)

May 31, 1952

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MATHIESON CHEMICAL CORPORATION
BALTIMORE, MARYLAND

Research on the Exploration of Methods to Produce Chlorates
and Perchlorates by Means Other Than Electrolytic

INTERIM REPORT FOR PERIOD DEC. 1, 1951 TO MAY 31, 1952

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OFFICE OF NAVAL RESEARCH

MATHIESON CHEMICAL CORPORATION

Inorganic Chemical Research Division

Niagara Falls, N. Y.

J. F. Haller - Supervisor

T. H. Dexter - Author

J. M. Naughton - Co-author

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Research on the Exploration of Methods to Produce
Chlorates and Perchlorates by Means other Than Electrolytic

I. OBJECTIVE

This project was undertaken to investigate chemical methods for producing a) chlorates and b) perchlorates. Only electrolytic methods are commercial today, but methods which do not require platinum and preferably no electricity are needed for a war-time economy.

II. SUMMARY

A. PREPARATION OF CHLORATES

1. A complete survey of all known processes for making chlorates in quantity by chemical means show that the chlorination of an alkali is by far the best general procedure.
2. A cost estimate of the Liebig Process is included in the "Supplement" to this report.
3. No additional experimental work beyond that already in Mathieson's files has been performed or is planned on chlorate production.

B. PREPARATION OF PERCHLORATES

1. A survey of modern production practice shows that all commercial perchlorates are produced electrolytically.
2. No chemical process known today can approach economic competition with electrolysis in perchlorate production.
3. The following chemical oxidants were examined to determine their potentialities to convert chlorine compounds to perchlorates:
 $KO_2, H_2O_2, O_3, O_2, Cl_2, KClO_3, K_2S_2O_8$
4. No perchlorate was produced by the action of KO_2, H_2O_2, O_3, O_2 (2300psig) or Cl_2 on the various chlorine compounds studied in our laboratory.
5. Both $K_2S_2O_8$ and $KClO_3$ will produce perchlorates by action on chlorates. However, $K_2S_2O_8$ is produced exclusively with platinum anodes and $KClO_3$ is being developed primarily by another laboratory.
6. Of the oxidants considered to date (except for $KClO_3$), lead dioxide appears the most promising for oxidizing chlorates to perchlorates.
7. Future studies will cover lead dioxide, sodium bismuthate, and chlorine oxides as potential oxidants.

III INTRODUCTION

The work covered by this investigation falls into two major parts: 1) the non-electrolytic preparation of chlorates, and 2) the non-electrolytic preparation of perchlorates. The first part is an evaluation of data from existing literature, because published literature of industrial processes and private reports of Mathieson are extensive on this topic.

The second part is a laboratory study of novel ideas, supplemented by numerous references to existing literature, covering the most promising oxidants for producing perchlorates from compounds of chlorine.

IV. PREPARATION OF CHLORATES

A. SURVEY OF CHEMICAL PROCESSES

1. General Economic Review

Although the electrolytic process (electrolysis of brine) is used by all United States manufacturers of chlorates, there have been opinions that the chemical process could be less costly, at least in some countries. Shah of India (6), in discussing the advantages of the chemical process (chlorination of an alkali), lists the major features:

"The chemical process is rapidly replacing the electrolytic process owing to its use of surplus by-product chlorine. Other advantages of the chemical process are: (a) The consumption of electrodes is minimized since the chlorate reaction takes place outside the cell. (b) A valuable product, caustic soda is recovered. (c) The production of chlorine compounds can be regulated to suit market demands."

Several Russian workers (5,7,8) wrote that the chemical method is more efficient and more economical than the electrolytic method. Additional evidences of this opinion are the numerous investigations by Russian scientists for studying and improving the chemical method during the period 1929 - 1937 (9,10,13,14,24,35,37,44,45,46,52,57, 59, 62,65,77,81,82).

One reason for the favorable economic outlook of the chemical method in these foreign countries is the low cost of labor. Estimates (1) show that approximately twice the labor is required to produce sodium chlorate by the chemical method as by the electrolytic method. (Estimate of labor by MacMullin and Hampel (4) which indicates 30 man hours/ton electrolytic NaClO_3 but only 6 man hours/ton chemical KClO_3 appears to be a decimal misprint for chemical KClO_3). More likely 60 man hours per ton of chemical KClO_3 would be required. High labor costs have apparently defeated the chemical process in the United States.

The following review will show that most of the conceivable chemical processes for chlorate production have been tested. The best chemical process is still essentially the Liebig process; it is useful today only in regions where electrical power is limited or costly.

2. Chlorate Processes Using Lime

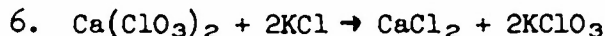
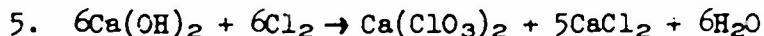
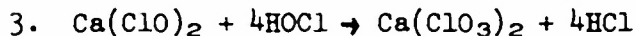
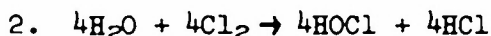
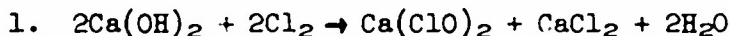
As early as 1813 potassium chlorate was prepared chemically by Gay-Lussac (16). He treated potassium hydroxide with chlorine until the crystals of potassium chlorate precipitated. In 1828 Liebig proposed a valuable modification. He suggested that milk-of-lime,

instead of costly potassium hydroxide, be treated with chlorine until calcium chlorate had formed. The latter, when treated with potassium chloride, would produce crystals of potassium chlorate while calcium chloride remained in the discarded mother liquor. With minor modifications this method was adopted and has maintained its basic superiority over a number of rivals. It was surpassed only by the electrolytic process, beginning about 1900.

There are now two major processes for the chemical production of chlorates in which lime is the initially chlorinated base. The first process (Liebig) produces potassium chlorate; the second process (Pechiney) produces sodium chlorate. Pechiney modified both processes, but was particularly credited with using sodium sulfate to form sodium chlorate from the calcium chlorate - calcium chloride liquor.

The Liebig process is described further in this report in connection with the cost estimate (See Section B). Complete details for operating both lime-chlorate processes are described by Lunge (28,29,30), Jurisch (25), and Partington (39). These descriptions cover the better techniques at the turn of the century. Important recent works are those of Dorph (12), Robson (42), Shah (43), Shcherbakov (44), Shraibman (46), and Thumm (49).

The chlorination reaction appears to follow the course indicated in the equations below (87,88,89). The mechanism may be different in acid and basic media (90).



For a detailed comparison of the actual costs of the Liebig process Dr. Hunter of our engineering department made the cost estimate reported in the supplement to this report.

3. Chlorate Processes Using Magnesia

In 1883 E. K. Muspratt (60) obtained patents for a new chlorate process. This process utilized magnesia instead of lime, a principle proposed by Weldon (64). While the general technique of chlorinating magnesia-

water slurry, removing $MgCl_2$ by evaporation, and adding KCl to form $KClO_3$ was similar to the lime process, the magnesia process was faster, the yield of $KClO_3$ was greater, and the liquor volume was smaller. In addition, the by-product $MgCl_2$ was salable to cotton-sizers. Sodium chlorate was produced readily by treating the $Mg(ClO_3)_2$ liquor with Na_2CO_3 .

There were several important disadvantages however, to the magnesia process. The process required carefully calcined magnesia, because the over-burned magnesia is nearly inert to wet chlorine gas. The high cost of this raw material was justified only in those times when $MgCl_2$ could be sold at a good price. In addition, $MgCl_2$ was much more corrosive than $CaCl_2$ to production equipment, and on some occasions dough-like $MgOHCl$ would form, stopping operations completely.

In spite of these difficulties the Muspratt process was operated at least from 1870 to 1912 when a serious explosion occurred (53). Details of the Muspratt process are described by Jurisch.

In 1932-35 Russian workers (56,57,59) showed interest in the magnesia process. Their aim was the utilization of $MgCl_2$ obtained in great quantity from carnallite ($KCl-MgCl_2-NaCl$). They proposed to hydrolyze $MgCl_2$ to MgO and HCl , convert the MgO to $Mg(ClO_3)_2$ with Cl_2 and thence to $KClO_3$ with KCl . The by-product $MgCl_2$ was to be recycled. Morozov (59) made a careful study of variables in the chlorination and crystallization steps. Overall yields of $KClO_3$ as high as 95% were obtained, but there has been no indication that the process was used industrially.

In the present U. S. economy, there is no economic advantage in the magnesia process. The cost of magnesia is at least four times that of lime, and magnesium chloride sells for roughly the same price as calcium chloride.

4. Chlorate Processes Using Soda

The most direct procedure for preparing sodium chlorate would be the chlorination of sodium hydroxide or other simple sodium alkali such as sodium carbonate or sodium bicarbonate. This principle was patented in detail by Hargreaves and Bird (74) in 1894. Their process was a simple counter-current chlorination of sodium carbonate paste which was apparently in actual commercial operation (79).

Davis (71) claimed in 1897 that finely divided dry sodium carbonate could be chlorinated to form $NaClO_3$. This claim is open to question because Cady (67,68) found that some moisture is desirable for the production of chlorine monoxide from sodium carbonate and chlorine gas. (It has also been observed in our laboratories that essentially no heat is evolved when dry chlorine passes over dry sodium

carbonate, and no appreciable reaction occurs.)

Other workers (66,81) studied the chlorination of sodium carbonate; Russian scientists have shown particular interest.

Shraibman (81) made a careful study of the chlorination of Na_2CO_3 , obtaining 98% conversions to NaClO_3 . Except for the high price of Na_2CO_3 compared to CaO , the process would have good promise.

Kashcuk (77) studied the chlorination of both sodium hydroxide and sodium bicarbonate. In each case the yields were inferior to the sodium carbonate process. Likewise Christopherson (70) studied a complete process for chlorinating the sodium bicarbonate slurry produced in the ammonia-soda process. However, the results have never found commercial significance.

In general, the higher cost of soda prevents it from competing with lime in chemical chlorate processes.

5. Chlorate Processes Using Other Bases

At least two other processes for producing chemical chlorate should be noted, not for the economy of the base but for the value of by-products. The first is the zinc oxide process developed by K. J. Bayer (83). Yields are high and the by-product is zinc chloride. The second is the process of Fleming (84,85) in which a borax solution is chlorinated to produce H_3BO_3 and NaClO_3 . The scarcity and high cost of the raw bases eliminate these processes from large volume production.

V. PART II. PREPARATION OF PERCHLORATES

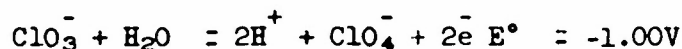
A. SURVEY OF CHEMICAL OXIDANTS

1. General Theoretical Perspective

Perchlorates have the highest ratio of oxygen to chlorine and the highest chlorine oxidation state of any simple chlorine compound. Therefore the problem of preparing perchlorates chemically resolves itself into a search for a compound or combination of compounds which can add oxygen and increase the chlorine oxidation number in a given chlorine compound.

Ideally, every known or conceivable oxidant should be tested. Practically, the search can be limited to relatively few compounds on the basis of oxidizing potential, reactivity and economic availability. The results of such a search by other workers and ourselves are listed and discussed in the following sections.

In modern industry perchlorates are produced by oxidizing chlorates with electric current. This electrical technique is used because a relatively high oxidation potential is necessary to cause the conversion:



While the potential which can be produced electrically is nearly unlimited, the potential which can be produced by a single chemical couple is always small. If the potential of a given couple, written in the form above, does not have a greater negative value than -1.00V, then the oxidized form of the couple cannot oxidize chlorate ion. The oxidized form of the couple is the oxidant.

Among the few chemical oxidants which have been reported to produce perchlorates from chlorine compounds are: hydrogen peroxide (91), barium peroxide (109), potassium persulfate (91), potassium chlorate (94,95,96,106), ozone (91,93), lead dioxide (92,113), and sodium bismuthate (119).

For our study, three more oxidants were added 1) potassium superoxide 2) chlorine, and 3) compressed oxygen. Many more oxidants are possible. For example, Latimer (98) lists 100 couples which are capable, theoretically, of oxidizing chlorates, while the oxidizing agents in most of these oxidizing couples are too costly to be used as direct oxidants, many of them would be suitable as catalytic intermediates.

The potentials of reactions between promising oxidants and chlorate ion are listed in Table 1. The reaction with the highest positive potential should have the greatest power for forming perchlorates. Although the oxidation of chlorate ion to perchlorate ion is used as the example, it should be possible to oxidize other chlorine-containing ions or compounds to perchlorate ion.

It will be noted that reaction potentials provide only a theoretical comparison of oxidants. Cases where theory and practice disagree will become apparent in the following discussion of each type of oxidant.

Table 1REACTION POTENTIALS

<u>Acid Solutions:</u>	<u>E°</u>
1. $\text{HClO} + \text{ClO}_3^- = \text{ClO}_4^- + \text{H}^+ + \text{Cl}^-$	+ 0.49
2. $\text{PbO}_2 + \text{ClO}_3^- + 2\text{H}^+ + \text{SO}_4^{2-} = \text{ClO}_4^- + \text{PbSO}_4 + \text{H}_2\text{O}$	+ 0.69
3. $\text{H}_2\text{O}_2 + \text{ClO}_3^- = \text{ClO}_4^- + \text{H}_2\text{O}$	+ 0.77
4. $\text{S}_2\text{O}_8^{2-} + \text{ClO}_3^- + \text{H}_2\text{O} = \text{ClO}_4^- + 2\text{H}^+ + 2\text{SO}_4^{2-}$	+ 1.05
5. $\text{O}_3 + \text{ClO}_3^- = \text{ClO}_4^- + \text{O}_2$	+ 1.07
6. $\text{F}_2 + \text{ClO}_3^- + \text{H}_2\text{O} = \text{ClO}_4^- + 2\text{H}^+ + 2\text{F}^-$	+ 1.85
<u>Basic Solutions:</u>	
1. $2\text{ClO}_3^- = \text{ClO}_4^- + \text{ClO}_2^-$	+ 0.18
2. $\text{ClO}_2^- + \text{ClO}_3^- = \text{ClO}_4^- + \text{ClO}^-$	+ 0.42
3. $4\text{ClO}_3^- = 3\text{ClO}_4^- + \text{Cl}^-$	+ 0.45
4. $\text{ClO}_2^- + \text{ClO}_3^- = 2\text{ClO}_4^- + \text{Cl}^-$	+ 0.59
5. $\text{ClO}^- + \text{ClO}_3^- = \text{ClO}_4^- + \text{Cl}^-$	+ 0.77
6. $2\text{ClO}_2 + \text{ClO}_3^- + 2\text{OH}^- = \text{ClO}_4^- + \text{ClO}_2^- + \text{H}_2\text{O}$	+ 0.98
7. $\text{O}_3 + \text{ClO}_3^- = \text{ClO}_4^- + \text{O}_2$	+ 1.07

2. Peroxides

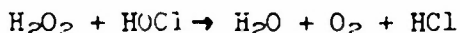
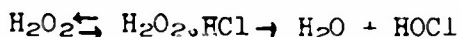
Since hydrogen peroxide shows marked changes in oxidizing potential with change in pH of the reacting medium, discussion of this reagent is best divided into two parts: 1) acid solutions and 2) basic solutions.

In 1860 Lenssen (100) stated that hydrochloric acid is oxidized by hydrogen peroxide to chlorine or hypochlorous acid. This has been confirmed in our laboratories, Table 2. Note that there was no indication from our data that an oxidation state higher than Cl(0) was formed.

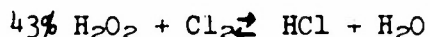
Table 2EXPERIMENTS WITH HYDROGEN PEROXIDE AND CHLORINE COMPOUNDS

<u>Ex. No.</u>	<u>HCl</u>	<u>H₂O₂</u>	<u>Temp.</u>	<u>Contact Time</u>	<u>Results</u>
885C-46	5cc.-12N	5cc.-30%	25°C.	10 min.	Cl ₂ evolved
885C-47	Gas	100cc.-90%	25°C.	1 hr.	a) H ₂ O ₂ dec. spont. after 1/2 hr. b) Cl ₂ evolved c) Ca(ClO) ₂ or Ca(ClO ₂) ₂ formed in CaO ₂ trap.
975C-3	Gas	46cc.-90%	35-50°C.	1/2 hr.	a) Cl ₂ evolved b) Ca(ClO) ₂ and Ca(ClO ₂) ₂ detected in CaO ₂ trap. c) Quantity of CaO ₂ appeared insufficient
975C-10	0.63g. (KClO ₃)	10cc.-90%	150°C.	Boiled to dryness (1/2 hr.)	a) No Cl ₂ evolved b) Recovery of KClO ₃ c) No KClO ₄ formed

As a result of more extensive studies Maass and Hiebert (103) offered the theory that hydrogen peroxide reacts with hydrochloric acid to form hypochlorous acid. The hypochlorous acid then reacts simultaneously with hydrogen peroxide to form hydrochloric acid and with hydrochloric acid to form chlorine.



This theory explains their results (which agree with ours) of treating hydrogen peroxide respectively with Cl_2 and HCl .



It may be concluded that hydrogen peroxide in an acid solution does not oxidize chloride ion effectively above the state $\text{Cl}(0)$, because there is a tendency for H_2O_2 to reduce Cl_2 to Cl^- ion. Because of this latter tendency chlorine gas is not oxidized by H_2O_2 .

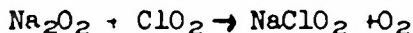
In an acid solution hydrogen peroxide is a reducing agent also to $\text{Cl}(V)$. Bennett and Mack (91) reported that a solution of sodium chlorate and hydrogen peroxide, when acidified with sulfuric acid, produced Cl_2 , ClO_2 , and NaCl . With 30% H_2O_2 the reduction to NaCl was 88%; with 3% H_2O_2 the reduction to NaCl was less. In agreement is a patent by Soule (115,116) who obtained high yields of ClO_2 from chlorates by the action of H_2O_2 and H_2SO_4 .

It is interesting to note that acidified KClO_4 solutions are not reduced perceptibly by 30% H_2O_2 .

In summary, hydrogen peroxide in acidic solutions behaves as a reducing agent to $\text{Cl}(0)$ and $\text{Cl}(V)$ compounds; $\text{Cl}(VII)$ compounds are unaffected.

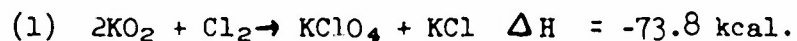
In neutral and basic solutions hydrogen peroxide is even less effective. The work of Bennett and Mack (91) on 1) $\text{NaClO}_3 + 30\% \text{H}_2\text{O}_2$, 2) $\text{NaClO}_3 + \text{Na}_2\text{O}_2 + \text{H}_2\text{O}$, and our own on 3) $\text{KClO}_3 + 90\% \text{H}_2\text{O}_2$ indicates that no reaction occurs between $\text{Cl}(V)$ and H_2O_2 in neutral and basic solutions.

However, in basic solution, $\text{Cl}(V)$ is reduced to $\text{Cl}(III)$. Reyhler (III) found that ClO_2 is reduced by Na_2O_2 :



And the generality is supported further by our work with potassium superoxide.

Potassium superoxide, KO_2 , was studied as a novel approach to perchlorate production. Reactions such as the following were anticipated:



Thermochemistry indicates that all of these reactions should occur spontaneously.

Table 3 lists the variety of conditions which were studied in attempts to achieve the reactions above. In no case was perchlorate formed.

Table 3

EXPERIMENTS WITH POTASSIUM PEROXIDES AND CHLORINE GASES

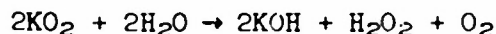
Ex. No.	Potassium Peroxide	Reacting Gas	Condition of Gas	Approx. Temp. °C.	Mole Ratio of KCl/KClO ₃ in Product	Notebook No.	Diluent Gas	Ratio: Diluent G. Reacting G.
8	KO ₂	Cl ₂	Dry	25	18.35	885C	None	-----
9	K ₂ O ₃	Cl ₂	Dry	25	31.40	885C	None	-----
15-2	KO ₂	Cl ₂	Dry	300	708.0	885C	None	-----
15-3	KO ₂	Cl ₂	Damp	25	14.05	885C	None	-----
15-4	KO ₂	Cl ₂	Wet	25	8.83	885C	None	-----
28	KO ₂	Cl ₂	320lb. Cl ₂ Pressure	300	1000	885C	None	-----
31	KO ₂	Cl ₂	Very Dry	-70	∞	885C	Air	100
26	KO ₂	Cl ₂ O	Wet	25	7.86	885C	Air	6.25
4	KO ₂	ClO ₂	Dry (Trace Moisture)	25	4.5 ClO ₂ /ClO ₃	975C	Nitrogen	105
17	K ₂ O ₃	ClO ₂	Wet	25	19.0 ClO ₂ /ClO ₃	885C	Air	20
14	KO ₂	ClO ₂ +CO ₂	Dry	25	No reaction	975C	Nitrogen Carbon dioxide	80
14-1	KO ₂	ClO ₂ +CO ₂	Wet	30	--	975C	Nitrogen Carbon dioxide	4

Note: (1) In the reaction $3K_2O + 3Cl_2 \xrightarrow{H_2O} KClO_3 + 5KCl$ the ratio Cl^-/ClO_3^- is 5. But in the reaction $3KO_2 + 3/2 Cl_2 \rightarrow KCl + 2KClO_3$ the ratio Cl^-/ClO_3^- would be 0.5; therefore, if these reactions occur the ratio Cl^-/ClO_3^- should be less than 5.

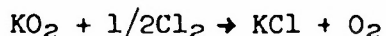
(2) Any perchlorate detected in products was negligible.

The results of Table 3 confirm the conclusion that KO_2 , like other peroxides, is inert or behaves as a reducing agent to chlorine and chlorine oxides. (All runs were made by passing the indicated gas through a loosely-packed charge (approx. 2 g.) of KO_2 (assay 99%).

Experiments 8,9,15 and 28 demonstrate the reduction of $Cl(O)$ to $Cl(-I)$, i.e., Cl_2 to KCl . Simultaneously some $Cl(V)$, i.e., $KClO_3$, was formed. This latter reaction was due, probably, to the hydrolysis of KO_2 by traces of moisture, and subsequent chlorination:



If hydrolysis and chlorination were the only reactions, the KCl/ClO_3 mole ratios: It may be concluded, therefore, that the reduction of chlorine gas by KO_2 follows a reaction such as:



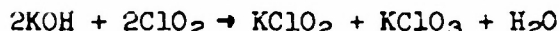
The results of these experiments indicate that the reduction of chlorine by KO_2 be favored by two conditions: 1) decreasing moisture and 2) increasing temperature.

Experiment 26 shows the action of moist chlorine monoxide, Cl_2O , on KO_2 . The chlorine monoxide was prepared by passing chlorine through moist Na_2CO_3 , and, therefore, may have contained chlorine. The $KCl/KClO_3$ ratio of 7.86 is lower than that of any run with Cl_2 , indicating that the following anticipated reaction occurred, in part:



However, since no $KClO_4$ was formed, this reaction was not pursued further.

Experiments 4 and 17 demonstrate the importance of moisture to the reaction of ClO_2 on KO_2 . When the reagents are completely dry, no reaction occurs. When a trace of moisture is present, $KClO_2$ and $KClO_3$ are formed in a higher ratio than would be anticipated for the well-known reaction:



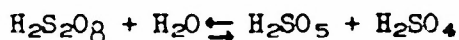
This agrees with Reychler's observation that the alkali peroxides reduce ClO_2 to $KClO_2$. No $KClO_4$ was formed. In Runs 14 and 14-1 no

perchlorate was formed by adding CO_2 to the ClO_2 stream. Besides, no reaction occurred when moisture was absent.

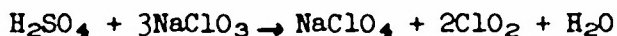
All of these data support the single conclusion that peroxides do not oxidize positive chlorine compounds in either acidic or basic media. It is unlikely, therefore, that hydrogen peroxide or peroxy salts can produce perchlorates by direct oxidation of chlorine compounds.

3. Persulfates

Persulfates are closely allied to peroxides. In an acid solution, persulfates may be considered as sources of hydrogen peroxide because of hydrolysis:



This fact was recognized by Soule (116) who obtained a patent for producing ClO_2 from chlorates by persulfate reduction, in acid solution. This is analogous to his former patent for producing chlorine dioxide from chlorates by H_2O_2 reduction in acid solution. High yields of ClO_2 are obtained in both cases, showing that the reaction is not the simple acid decomposition of chlorates



It is evident that persulfates behave as reducing agents toward chlorates in acid solutions.

The behavior of persulfates toward chlorates in a basic solution is quite different. Bennett and Mack (91) boiled for 30 minutes a mixture of $\text{Na}_2\text{S}_2\text{O}_8$ (10g.) NaClO_3 (1g.), BaO (13g), and H_2O to make 100 cc. A 33.75% conversion of NaClO_3 to NaClO_4 resulted! This is one of the few cases of appreciable oxidation of chlorate by an external oxidant.

Unfortunately, the oxidation of chlorates by an external oxidant is not as sound logistically as the oxidation of chlorates by chlorates themselves, i.e., disproportionation. Persulfate salts, e.g., $\text{K}_2\text{S}_2\text{O}_8$ are produced exclusively with platinum electrodes. In addition, the theoretical cost per available oxygen is greater for $\text{K}_2\text{S}_2\text{O}_8$ than for NaClO_3 , \$24.55 compared to \$1.47 per lb. equivalent of oxidant.

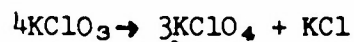
It may be concluded that persulfate salts will oxidize chlorates to perchlorates in basic solution, but such a process would be highly impractical both economically and logistically.

Future plans allow for the study of Caro's acid, H_2SO_5 as an oxidant, because this reagent can be prepared from H_2O_2 and H_2SO_4 . However, in view of the results of both H_2O_2 and $\text{H}_2\text{S}_2\text{O}_8$ discussed above, oxidation of chlorate with Caro's acid is not anticipated.

4. Chlorates

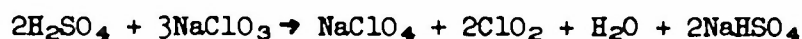
Of all the potential oxidizing agents for producing perchlorates from chlorates, the least expensive oxidants are chlorates themselves. This is particularly true of sodium chlorate, which is produced electrically and sells for 8 1/2 cents/lb.

This cost appears even lower when it is realized that virtually all the oxygen in the chlorate is converted to perchlorate in the thermal disproportionation:



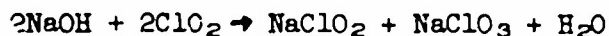
This latter equation is claimed to occur with yields as high as 92% (107). Quick, high temperature appears important. At the present stage of technical development the more expensive KClO_3 converts more readily than NaClO_3 . The maximum yield reported for NaClO_3 is 20% of the above type equation (106). The action of high frequency inductive heating may be of value here.

Beside the thermal conversion of chlorates to perchlorates, there is the acid conversion. Here again all of the oxidizing action comes from the chlorates themselves. An example is:

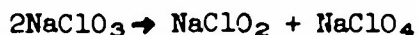


As was shown in the previous sections, the presence of a reducing agent such as H_2O or SO_2 , will cause the formation only of chlorine dioxide without formation of perchlorate. In the absence of a reducing agent, however, the yield of perchlorate may be 100% on the basis of the above equation (95,96), but in the above equation only 33% of the NaClO_3 becomes NaClO_4 .

If the ClO_2 is collected in caustic, partial conversion to chlorate occurs:



The sodium chlorate thus recovered can be recycled. In this manner, 50% of the NaClO_3 becomes NaClO_4 and NaClO_2 is a by-product. In effect the following reaction occurs:

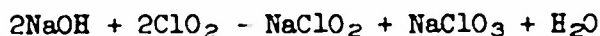


Whereas the by-product NaClO_2 has an appreciable market in the bleaching industry, the acid conversion of chlorates to perchlorates could run in close competition with the thermal conversion.

If NaClO_2 were not marketable it could be converted to NaClO_3 by a) thermal disproportionation (101,102):



or b) chlorination and caustic absorption



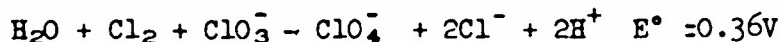
In the latter case, NaClO_2 must be recycled.

Therefore, of the two alternatives the thermal conversion would be the most economical, in the absence of a sufficient market for NaClO_2 .

While both the thermal and acid conversions of chlorates to perchlorates appear good from the economic standpoint, no laboratory study has been made by us, because these phases are being studied under contracts to other laboratories. Also, future studies on these phases are planned except the effect of oxygen under pressure.

5. Chlorine

According to oxidation potentials, chlorine itself should oxidize chlorates to perchlorates in acid solution:



However in actual practice there is no indication that chlorine has ever oxidized a chlorate to perchlorate. The great abundance of data lies in the various processes for the production of chlorate in which an alkali is treated with chlorine, e.g., Liebig process. During this process the solution is initially basic and finally acidic, but no perchlorate formation has been reported under this variety of conditions.

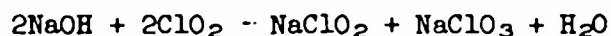
To confirm these negative reports chlorine gas (0.87 g./min.) was passed through a porous plug of 10g. KClO_3 at room temperature for 30 min. No heat of reaction was observed and the sample of KClO_3 did not change in weight. It was concluded that no reaction occurred.

6. Ozone

In a literature report by the Pennsylvania Salt Manufacturing Company (110) the conclusion is drawn that the oxidation of chlorate to perchlorate by ozone may be possible but would be very inefficient. This statement is based on conflicting reports by Fairley (93), Bennett and Mack (91), and Knibbs and Palfreeman (97). Our data (Table 4) confirm the reports that no perchlorate is formed. The positive reports of Bennett and Mack may have been the result of acid disproportionation of chlorates.

Hypochlorites are said to be oxidized in trace amounts to perchlorates (91,93) by ozone. However, our tests (Table 4) indicated that not even a trace of perchlorate was formed.

According to Levi (101,102) chlorites are oxidized by ozone to chlorine dioxide. If the chlorine dioxide is not swept out of the basic solution, it will react with the base and disproportionate to chlorite and chlorate,



Our experiments (Table 4) agree precisely with those of Levi. In this way, chlorites are oxidized indirectly by ozone, via ClO_2 .

It would appear from the above information that ozone has only a weak oxidizing effect on most simple chlorine-containing salts. The only report of appreciable oxidation of a chlorine salt is that of Spies (117) on the production of chlorates by the action of ozone on chlorides.

The maximum oxidation state of chlorine, produced by ozone action, is Cl (VI). Cl_2O_6 is formed by treating chlorine dioxide with ozone. It is apparent that the chlorine oxide gases can be oxidized by ozone higher than chlorine oxygen salts. However, the practical oxidation of any chlorine-oxygen compound to Cl (VII) directly by ozone is to be doubted.

The experiments listed in Table 4 cover attempts to ozonize various solutions of KClO_4 , KClO_3 , NaClO_2 , NaClO , KCl , and Cl_2 . The ozone stream was a mixture of 1% ozone in oxygen. In order to obtain maximum ozone absorption in the aqueous solvent, neutral or basic solutions were used. No perchlorate ion was produced in any run.

Future studies will include the ozonolysis of salts in acidic solutions.

Table 4

EXPERIMENTS WITH OZONE AND CHLORINE COMPOUNDS

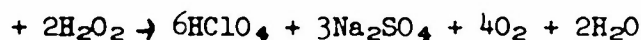
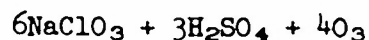
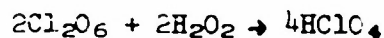
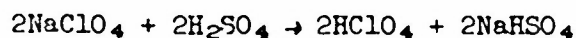
Salt or Gas	Ex. No.	Temp. °C.	Time Hrs.	Quantity Salt Gr	Purity Salt	Solvent	Remarks
Potassium Perchlorate	*37	25	5.0	2.0	c.p.	98 Gr H ₂ O	No reaction
Potassium chlorate	40	25	5.5	5.0	c.p.	100cc. of 1.0 N.NaOH	No reaction
Potassium chlorate	35	25	6.5	7.0	c.p.	93 Gr H ₂ O	No reaction
Sodium chlorite	42B	25	2.0	2.0	Technical 84.7% NaClO ₂	100cc. of 1.0N. NaOH	ClO ₂ liberated, forms NaClO ₃ with more O ₃ in basic medium
Sodium hypochlorite	39	25	7.0	5.08	+HTH + Na ₂ CO ₃	45 Gr H ₂ O	No perchlo- rate detectable
Sodium hypochlorite	38	0.0	25	5.08	HTH + Na ₂ CO ₃	45 Gr H ₂ O	No perchlorate detectable
Potassium chloride	50	25	2.0	2.0	c.p.	100cc. of 1.0N. NaOH	No reaction
Chlorine [‡]	3	25	8.0	5.54	Mathieson chlorine	7.2 Gr H ₂ O	Some HCl formed No perchlorate detectable

* - Approx. 1.2 millimoles O₃/min., diluted with 1.0 liter O₂/min. in each expt.

+ - HTH - Mathieson's high test calcium hypochlorite

‡ - Chlorine mixed with oxygen and water was passed through the ozonizer itself.

There is one proposed process, using ozone, which may have promise for the production of perchloric acid. It was proposed in our laboratory and is part of our program for extended research on perchlorate production. The description is best illustrated by equations:



Cost of raw materials (as lb-moles):

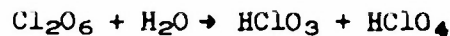
6NaClO ₃	\$52.69
3H ₂ SO ₄	5.30
4O ₃	48.00
2H ₂ O ₂ (90 %)	<u>14.28</u>
	120.27

Value of products (as lb-moles):

6HClO ₄	\$361.62
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From these very approximate cost figures it appears that such a process operating at 100% efficiency could give products worth three times the reactants.

The reaction of Cl₂O₆ + H₂O₂ is the only reaction which has never been performed. If it should be unsuccessful, a good alternative would be the simple hydrolysis of Cl₂O₆ to produce chloric and perchloric acids:



The chloric acid can be recycled by converting it to ClO₂, which would be returned to the ozonolysis step.

At the present stage of technical development, however ozone is not an economic oxidant for producing perchlorates.

7. Oxygen (under pressure)

It was the object of this study to force the formation of perchlorates by treating various chlorine compounds with oxygen at very high pressures. Some compounds, such as ClO_2 , would explode under such treatment, but others, such as KClO_3 or Cl_2 might be expected to form perchlorates.

The heats of formation and free energies of formation listed in Table 5 give an indication of the relative tendencies of several typical compounds to form perchlorates or chlorine oxides. It will be noted that by these criteria the chlorate salts should react spontaneously to form perchlorate salts. On the other hand, chlorine itself would require considerable external activation to react with oxygen to form any oxide.

Note that the presence of water should assist the reaction of chlorine with oxygen, but it is more likely that chloric acid will form instead of perchloric acid. The effect of high pressure should tend to force all of these reactions to the right, but the energy change is probably too great for oxidizing chlorine simply by increasing oxygen pressure. A logical improvement would entail passing an electric discharge through the compressed mixture of chlorine and oxygen.

Table 5

HEATS OF FORMATION

$\text{NaClO}_3(\text{s}) + 1/2 \text{O}_2 \rightarrow \text{NaClO}_4(\text{s})$	$\Delta\text{H} = -6.45 \text{ kcal.}$
$\text{NaClO}_3(\text{aq}) + 1/2 \text{O}_2 \rightarrow \text{NaClO}_4(\text{aq})$	$\Delta\text{H} = -7.91 \text{ kcal.}$
$\text{KClO}_3(\text{s}) + 1/2 \text{O}_2 \rightarrow \text{KClO}_4(\text{s})$	$\Delta\text{H} = -10.10 \text{ kcal.}$
$\text{KClO}_3(\text{aq}) + 1/2 \text{O}_2 \rightarrow \text{KClO}_4(\text{aq})$	$\Delta\text{H} = -7.91 \text{ kcal.}$
$\text{Cl}_2(\text{g}) + \text{O}_2 \rightarrow \text{ClO}_2(\text{g})$	$\Delta\text{H} = +24.7 \text{ kcal.}$
$\text{Cl}_2(\text{g}) + 3/2 \text{O}_2 \rightarrow \text{ClO}_3(\text{g})$	$\Delta\text{H} = +37.0 \text{ kcal.}$
$\text{Cl}_2(\text{g}) + 7/2 \text{O}_2 \rightarrow \text{Cl}_2\text{O}_7(\text{g})$	$\Delta\text{H} = +63.4 \text{ kcal.}$
$1/2 \text{Cl}_2(\text{g}) + 5/4 \text{O}_2 + 1/2 \text{H}_2\text{O}(\text{g}) \rightarrow \text{HClO}_3(\text{aq})$	$\Delta\text{H} = +5.5 \text{ kcal.}$
$1/2 \text{Cl}_2(\text{g}) + 7/4 \text{O}_2 + 1/2 \text{H}_2\text{O}(\text{g}) \rightarrow \text{HClO}_4(\text{aq})$	$\Delta\text{H} = -2.51 \text{ kcal.}$
Free energies of formation	
$\text{NaClO}_3(\text{m.l}) + 1/2 \text{O}_2 \rightarrow \text{NaClO}_4(\text{m.l})$	$\Delta\text{F} = -1.95 \text{ kcal.}$
$\text{KClO}_3(\text{m.l}) + 1/2 \text{O}_2 \rightarrow \text{KClO}_4(\text{m.l})$	$\Delta\text{F} = -1.95 \text{ kcal.}$

Several experiments were performed with pressurized oxygen. These are listed in Table 6 below. In no case was perchlorate ion found in the product.

Table 6

EXPERIMENTS WITH POTASSIUM CHLORATE
AND OXYGEN UNDER PRESSURE

Ex. No.	Reagent	Total Pressure (psig)	Temp. (°C.)	Contact Time (Hrs.)	% KClO ₃ Recovered as	
					KCl	KClO ₃
18	1.4427g. KClO ₃ + 20 cc. H ₂ O	809	25	5	-	98%
19	1.5342g. KClO ₃ (dry)	2200	300	1	0	100%
20	1.4779g. KClO ₃ + 10 cc. H ₂ O	4050	300	1	6.4%	90.9%

No perchlorate ion was detected by nitron precipitation test. Recovery of 98% of KClO₃ should be within experimental accuracy.

8. Lead dioxide

In recent reports from Germany (92, 113) a complete process for the production of perchlorates from chlorates by oxidation with lead dioxide is presented. The yield of perchlorate, based on chlorate, is 91.6%.

The process is simply the reaction of lead dioxide with potassium chlorate in sulfuric acid solution. The product, potassium perchlorate, is separated from the reaction mixture by a series of washings and filtrations. One of the major difficulties is the regeneration of PbO₂ from PbSO₄ before recycling. All regenerations suggested require the separation of PbSO₄ and unreacted lead oxides from the strong acid solution, because the

regenerations are carried out in a basic medium. One hypochlorite and two nitrate processes are suggested.

From the standpoint of simplicity, regeneration by hypochlorite is the most promising. It was formerly discarded because the chlorine required comes generally from electrolytic sources. However, wet Deacon chlorine comes from chemical sources entirely.

No work has been performed to date on this process by our laboratory. However, studies of the regeneration of PbO_2 by hypochlorite, hydrogen peroxide, and ozone have been planned.

9. Other Oxidants

Many other oxidants, which should have the potential to oxidize chlorates or other chlorine compounds to perchlorates, have been suggested and considered. Among these are F_2 , F_2O , ClF_3 , Cl_2 , Cl_2O , Cl_2O_6 , $HOCl$, HNO_3 , HNO_4 , HSO_5Cl , H_2SO_5 , $NaBiO_3$, $KMnO_4$, $K_2Cr_2O_7$ and K_2CrO_4 . In general, all of these compounds are expensive or impractical for application to modern engineering techniques. It is anticipated that many will be reconsidered particularly from the catalytic standpoint, and will therefore, be discussed more thoroughly in our next report.

VI. CONCLUSION

A. PART I. PREPARATION OF CHLORATES

1. A survey of all known processes for producing chlorates chemically and without electricity shows that good chemical methods, by modern standards, have been discovered and used already on a commercial scale. The best of these is the Liebig process for producing KClO_3 . A cost estimate of this process is included in the supplement.

B. PART II. PREPARATION OF PERCHLORATES

1. There is no chemical process to our knowledge which can compete economically with the present electrolytic production of perchlorates. Our efforts to develop such a chemical process have been testing chemical reagents which might oxidize chlorine compounds to perchlorates.
2. The chemical oxidants considered and tested were hydrogen peroxide, potassium superoxide, persulfuric acid, potassium persulfate, potassium chlorate, sodium chlorate, chlorine, ozone, pressurized oxygen, and lead dioxide. In most cases the yield of perchlorate is very low, or none.
3. The least costly of the various processes proposed are those using chlorates, ozone, and lead dioxide as oxidants respectively. Additional studies are planned for the development of each of these oxidants.
4. Many more oxidants are to be considered, but none show promise of producing perchlorates at less than twice the present market price of electrolytic chlorates.
5. There are not enough data at present to build a working pilot plant for perchlorate production by means other than electrolytic.

VII. FUTURE WORK

All future work should be directed toward perchlorate production. Additional studies should include development of the following potential processes, each of which utilizes sodium chlorate or potassium chlorate as a raw material:

1. Acid decomposition of chlorates followed by ozonolysis of evolved ClO_2 to make Cl_2O_6 which is hydrolyzed to perchloric acid. By-products are recycled.
2. Acid oxidation of chlorates by PbO_2 to produce perchlorates with regeneration, and recycling of PbO_2 by one of several techniques.

Further exploratory work on other oxidants particularly NaBiO_3 and Cl_2O should be considered.

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