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

PART I

INTERIM RESEARCH REPORT
for
Office of Naval Research
CONTRACT NONR 682 (OO)

November 30, 1952

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Chief of Naval Research (Code 425)



MATHIESON CHEMICAL CORPORATION

BALTIMORE, MARYLAND

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

INTERIM REPORT FOR PERIOD JUNE 1, 1952 TO NOV. 30, 1952, PART I.

Project NR 352-293/9-14-51

Contract Number NONR 682 (00)

D. J. Jaszka

OFFICE OF NAVAL RESEARCH

MATHIESON CHEMICAL CORPORATION

Inorganic Chemical Research Division

Niagara Falls, N. Y.

STAFF

J. F. Haller - Ass't. Director of Inorganic Research

T. H. Dexter - Supervisor

J. M. Naughton

R. G. Lade

D. J. Jaszka - Author

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

1. OBJECTIVE

The objectives of this study of the lead dioxide process for producing perchlorates were the following:

1. To review and check the results claimed by Ott (1) and Erhardt (2) for the process:
$$\text{PbO}_2 + \text{KClO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{KClO}_4 + \text{H}_2\text{O}$$
2. To reduce the time of the above oxidation step by adjusting concentrations and temperature.
3. To develop an economical method for the regeneration of lead dioxide.
4. To test the feasibility of cyclic operation.
5. To evaluate the chemical specifications of the product.
6. To evaluate the lead dioxide process, as developed, from the cost view point.

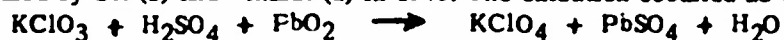
II. SUMMARY

Each of the objectives of this study has been achieved as of below:

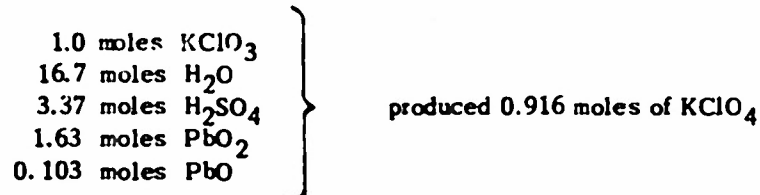
1. The process of Ott (1) and Erhardt (2) to produce potassium perchlorate, KClO_4 , by direct oxidation of potassium chlorate, KClO_3 , with lead dioxide, PbO_2 , was found valid.
2. The duration of the oxidation stage has been reduced by our modifications from 4 hours to 2 hours.
3. A very satisfactory method for regenerating PbO_2 from lead sulphate, PbSO_4 has been developed. Low cost sodium carbonate, Na_2CO_3 and dilute chemical chlorine are the reagents.
4. Cyclic operation of the entire process is satisfactory.
5. The product meets the major specification for KClO_4 . One recrystallization will be necessary to reduce KClO_3 content to specification; lead and sulfate ion content are well within limits.

III. INTRODUCTION

The laboratory-scale production of potassium perchlorate by oxidation of KClO_3 with PbO_2 was studied by Ott (1) and Erhardt (2) in 1943. The oxidation occurred as follows:



To achieve a 91.6% conversion of KClO_3 to KClO_4 Erhardt combined the following reagents with constant mixing for 4 hours at 84°C .

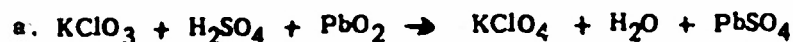


The KClO_4 was extracted from the solid products with hot water; the residual PbSO_4 was regenerated to PbO_2 and recycled. For the latter regeneration step Erhardt suggested three methods, none of which he considered fully satisfactory. The aim of the present research has been (1) to reduce the time of the oxidation reaction and (2) to develop a satisfactory method for regenerating PbO_2 . It will be seen that both of these ends have now been achieved.

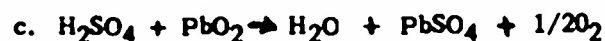
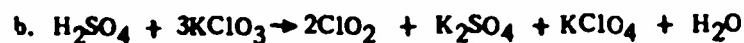
IV. EXPERIMENTAL PREPARATION OF PERCHLORATE FROM CHLORATE WITH PbO₂

A. OXIDATION

KClO₃ can be oxidized to KClO₄ in an acid medium by the oxidizing agent PbO₂.



During the formation of potassium perchlorate there are also two competing reactions.



Since the rates of reaction (a), (b) and (c) are dependent principally on (1) concentration and (2) temperature, these variables were studied and the results are listed in Table I. Table II shows corresponding studies for the preparation of NaClO₄ from NaClO₃.

TABLE I
PRODUCTION OF KClO_4

Exp. No.	Moles of Reagents				Temp $^{\circ}\text{C}$	Time (Min)	%Loss ClO_2	Single Pass Yield of KClO_4
	KClO_3	PbO_2	H_2SO_4	H_2O				
3a	1.0	1.0	1.0	16.6	85	240	—	3.0
2a	1.0	1.6	3.4	16.6	85	240	—	87.5
3b	1.0	1.6	4.4	16.6	85	240	—	91.5
28b	1.0	1.0	2.0	7.3	100	60	1.2	71.4
29a I	1.0	1.0	2.0	8.9	65	60	0	15.0
29b II	1.0	1.0	2.0	8.9	80	60	1.0	42.9
29a III	1.0	1.0	2.0	8.9	100	60	2.0	68.3
29a IV	1.0	1.0	2.0	8.9	115	60	6.3	79.8
29b	1.0	1.0	2.0	8.9	102	30	1.4	50.7
30a	1.0	1.0	2.0	5.9	100	60	4.4	78.3
32a	1.0	1.0	4.0	17.8	125	120	42	87.2

Although oxidation of NaClO_3 was not studied extensively, exploratory experiments, Table 2, show analogous behavior to the KClO_3 system.

TABLE II
PRODUCTION OF NaClO_4

Exp. No.	Moles of Reagents				Temp $^{\circ}\text{C}$	Time (Min)	%Loss ClO_2	%Single Pass Yield of NaClO_4
	NaClO_3	PbO_2	H_2SO_4	H_2O				
17a	1.0	1.6	3.4	16.7	85	240	—	72
16a	1.0	1.6	3.4	8.3	70–130	40	6	94
16b	1.0	1.6	3.4	8.3	65–105	40	7	93

1. Concentration

The concentration of H_2SO_4 affects the rate of all three reactions. When 50–65 weight percent acid is used the reaction (a) proceeds smoothly. However, reaction (b) gives rise to explosion as the concentration approaches 70 weight percent. This is due to the acceleration of reaction (b) evolving more ClO_2 . Increased concentration of H_2SO_4 also increases the reaction (c) between H_2SO_4 and PbO_2 . Hence at a high concentration of acid above approximately 70 weight percent, the oxidizing agent PbO_2 is destroyed. However, an advantage of a

high concentration of acid is the production of greater yields of potassium perchlorate by reaction (a) when the acid concentration is increased from 50 to 70 weight percent. The hazard of explosion of ClO_2 exists. Therefore, the displacement of ClO_2 with N_2 , CO_2 , O_2 or O_3 is necessary to prevent explosion.

The optimum concentration range of H_2SO_4 is 55–65 weight percent where reaction (a) is accelerated but the side reactions (b) and (c) are less pronounced.

2. Temperature

Temperature also affects the rate of reactions (a), (b) and (c). The formation of ClO_2 , reaction (b), is increased slightly but not seriously with an increase in temperature. This effect is shown by plotting the percent conversion of KClO_3 to KClO_4 at various temperatures (Figure I.).

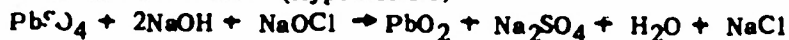
At higher temperatures the efficiency of PbO_2 in reaction (a) is increased (Figure I), the optimum range being 100–115°C. Temperature accelerates reaction (a) greatly resulting in an increase of KClO_4 yield. At 115°C 80% yield of KClO_4 is obtained but only 15% at 65°C (Figure I).

These results show that the optimum temperature is between 100–115°C where the maximum efficiency of PbO_2 is obtained plus a high yield of KClO_4 .

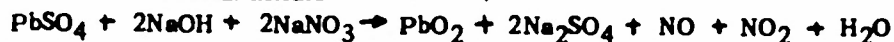
B. REGENERATION

To regenerate the spent residue, PbSO_4 , Erhardt (2) gives three methods. They are as follows:

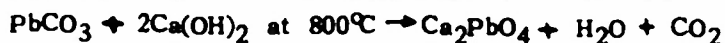
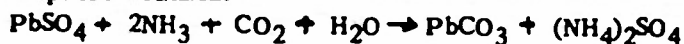
1. Treatment with bleach (Hypochlorite)



2. Fusion with sodium nitrate



3. Stepwise treatment

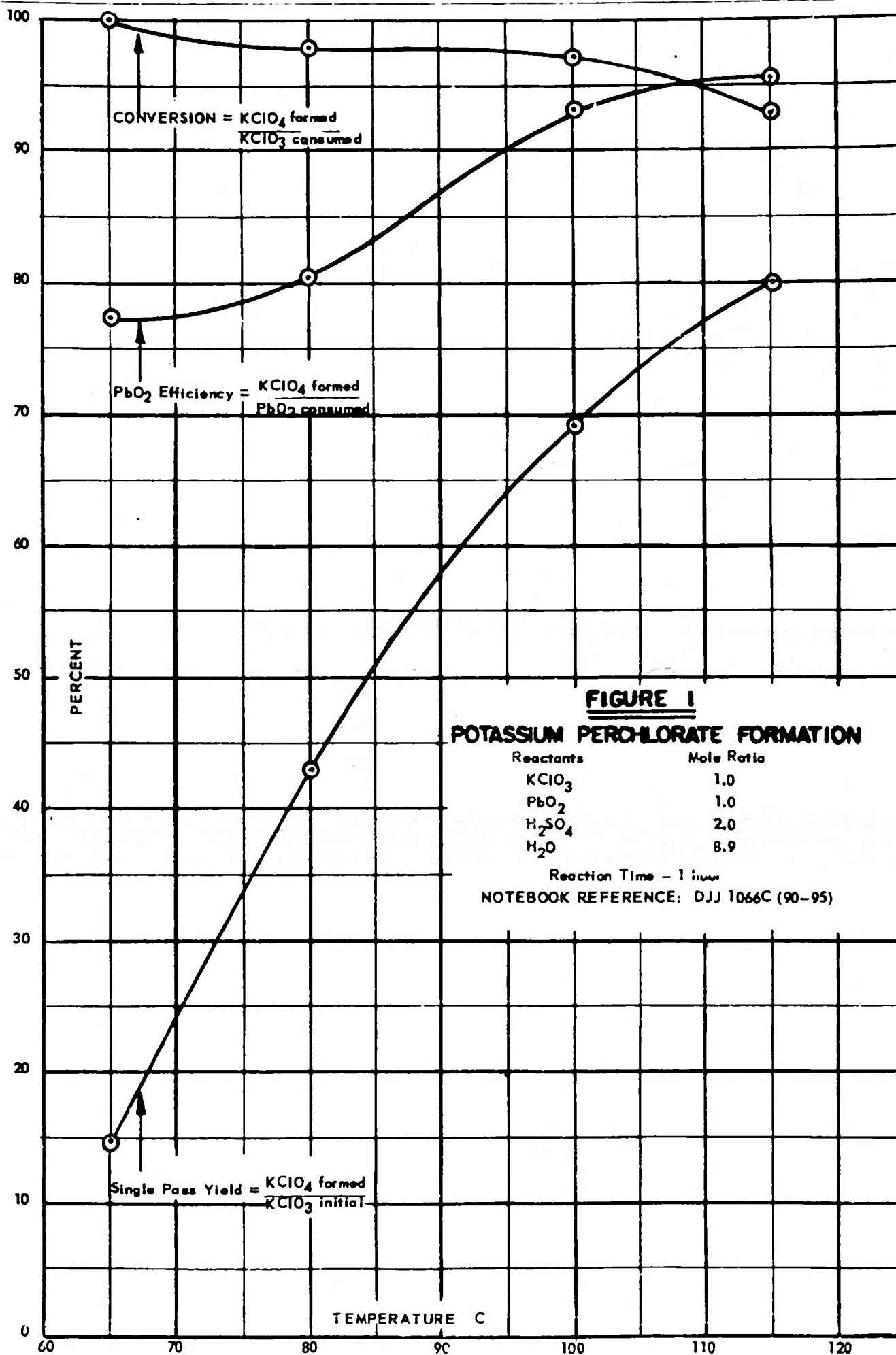


Although Erhardt found (3) most suitable due to continuing market for the by-products and because electricity need not be spent, we have rejected it due to high handling and treating costs. Schlachter (1) also anticipated equipment difficulties for method (3).

We have therefore explored other methods for regenerating the spent residue, PbSO_4 .

The following were considered:

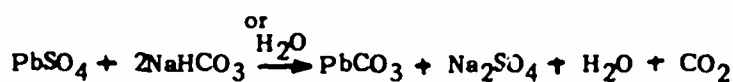
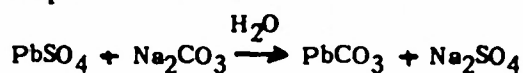
- (4) Fusion of NaClO_3 and PbSO_4 ,
- (5) Chlorination of PbCO_3 produced from PbSO_4 , and
- (6) Ozonolysis of PbCO_3 .



4. A series of experiments was performed to determine if NaClO_3 would easily regenerate PbO_2 from PbSO_4 . It was found that fusion of NaClO_3 and PbSO_4 did produce PbO_2 , but not very effectively, needing a large excess of NaClO_3 and a high temperature (600°C). This method was abandoned since further studies produced a simpler method to convert the spent residue to PbO_2 .
5. The new method is to convert the PbSO_4 to PbCO_3 , by either Na_2CO_3 or NaHCO_3 and then chlorinating the PbCO_3 to produce PbO_2 . F. Aurebach (3) converted PbSO_4 to PbCO_3 by either Na_2CO_3 or NaHCO_3 . It is necessary to have high speed stirring in order to convert the sulfate effectively.

Equations:

Step 1:



Step 2:

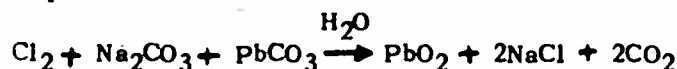


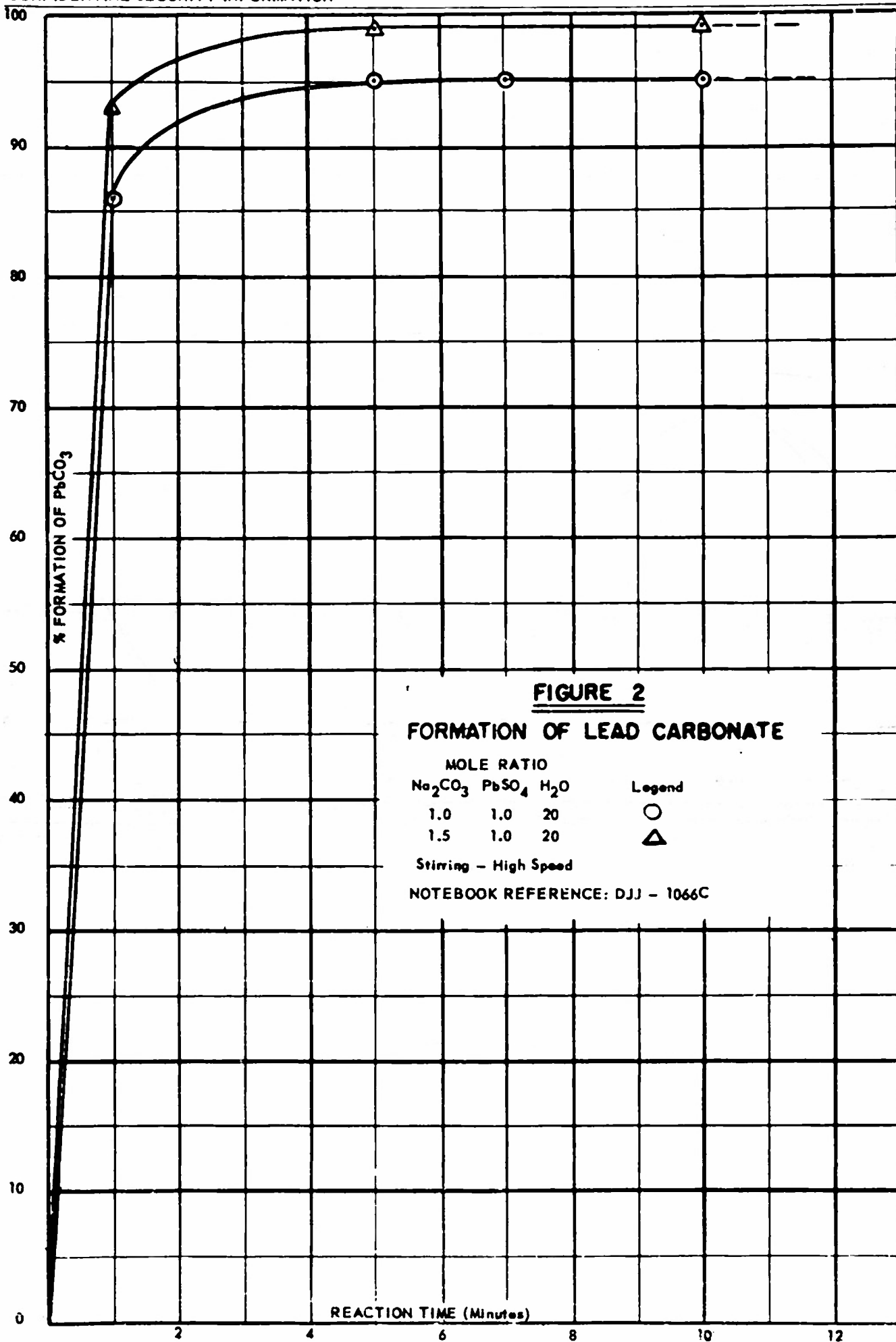
Table III shows that both Na_2CO_3 and NaHCO_3 give excellent conversions.

TABLE III

CONVERSION OF PbSO_4 TO PbCO_3

Exp. No.	Moles of Reactants			Time(Min)	Temp. °C	%PbSO ₄	*Approximate conversion	
	PbSO ₄	Na ₂ CO ₃	H ₂ O				PbSO ₄	PbCO ₃
24c-1	1.0	1.0	40	1	46	18.6	81	
24a-1	1.0	1.0	20	1	46	14.0	86	
24b-1	1.0	1.5	20	1	46	7.5	93	
24a-2	1.0	1.0	20	5	46	5.4	95	
24a-3	1.0	1.0	20	7	46	5.6	95	
24a-4	1.0	1.0	20	10	46	5.95	95	
24a-5	1.0	1.0	20	15	46	6.0	95	
24c-2	1.0	2.0	40	1	46	4.5	95	
24b-2	1.0	1.5	20	5	46	1.3	99	
24c-3	1.0	1.5	20	10	46	0.8	99	
9a-1	1.0	2.0	222	30	29	0	100	
9a-2	1.0	2.0	222	60	29	0	100	
(NaHCO ₃)								
8a-1	1.0	2.0	222	30	29	0	100	
(NaHCO ₃)								
8a-2	1.0	2.0	222	60	29	0	100	

*Conversion is based on PbSO_4 remaining in product and is uncertain to the extent that the average molecular weight of product varied as hydrolysis of PbCO_3 to Pb(OH)_2 occurred. Figure 2 shows that increasing the concentration of Na_2CO_3 increases the rate of formation of PbCO_3 .



Temperature has no pronounced effect on the conversion of PbSO_4 to PbCO_3 but it does tend to increase the formation of the basic carbonate due to hydrolysis of PbCO_3 . F. LeFort (4) found that if the lead salt is hot, an alkali carbonate will precipitate basic lead carbonate $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$; normal lead carbonate is formed only in cold solutions. The equation for the hydrolysis is:



This hydrolysis does not decrease the ultimate yield of PbO_2 since $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ is equally well converted to PbO_2 by chlorine. In the chlorination step 2, PbO_2 is probably formed when NaOCl reacts with PbCO_3 , NaOCl being produced when gaseous chlorine reacts with Na_2CO_3 .

Equations:



Other substitutes for Na_2CO_3 are either NaOH or NaHCO_3 since both yield NaOCl when they react with chlorine. Table IV shows the excellent conversions of PbCO_3 to PbO_2 with 80% efficiency based on chlorine.

TABLE IV

CONVERSION OF PbCO_3 TO PbO_2

Exp. No.	Moles of Reagents				Ph range	Temp °C	Time Min	% PbO_2 Formed
	PbCO_3	Na_2CO_3	Cl_2	H_2O				
13d-1	1.0	1.0	-	195	10.2-6.9	80°	38	77.6
13d-3	1.0	1.2	1.19	195	10.1-7.0	80°	35	98.7
		(NaHCO_3)						
15a-1	1.0	2.4	1.1	195	8.3-6.0	80°	45	97.3
		(NaOH)						
13b	1.0	2.0	-	195	12.2-3.4	80°	50	94.6

It is necessary to control the pH to the extent that it does not fall below 7, otherwise Pb^{+2} ions will be lost in the filtrate.

Equations:

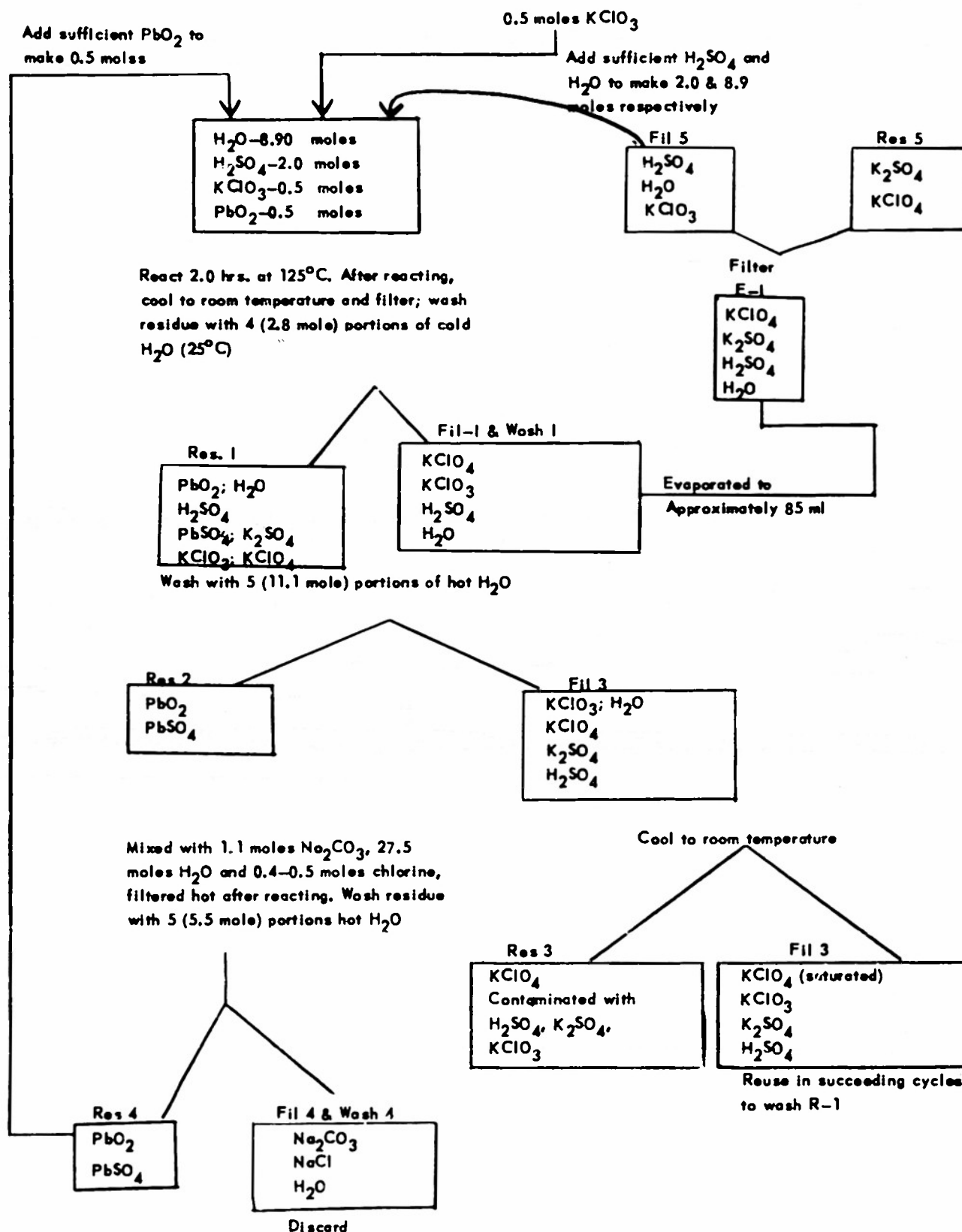


- Qualitative determination showed that ozone is capable of converting PbCO_3 to PbO_2 in dry, aqueous, or acid state but the high cost of ozone makes it uneconomical at present. Sidgwick (5) also states that ozone is capable of oxidizing Pb(OH)_2 to PbO_2 .

• C. CYCLIC OPERATION

• To determine whether both oxidation and regeneration can function together in a cycle without seriously affecting each other, a bench scale pilot plant was operated. The schematic diagram, Figure 3 gives in detail the manner in which the cycle was performed.

FIGURE III
POTASSIUM PERCHLORATE CYCLE



The experimental procedure was as follows employing stock grade chemicals.

A solution consisting of 2.0 moles H_2SO_4 and 8.9 moles H_2O was placed in a one liter reaction flask equipped with a condenser, thermometer and a mechanical stirrer. The flask was heated by means of an oil bath at 100°C . Then 0.5 moles KClO_3 and 0.5 moles PbO_2 were thoroughly mixed and added slowly to the stirred H_2SO_4 - H_2O solution. Since the reaction is exothermic its temperature rose to approximately 125°C ; additional external heat was supplied from the oil bath to bring it up to 125°C and maintain it there during the reaction time. After the 2 hour reaction time had elapsed the reaction flask was removed from the oil bath and allowed to cool to room temperature where it was filtered through a medium porous glass filter. The spent residue (R-1) on the filter was washed four times with 2.8 mole portions of cold water (25°C) to remove most of the adhering H_2SO_4 from the residue. The filtrate (F-1) and washings (W-1) were combined and evaporated to a volume of approximately 85-100 ml. to prepare them for recycling. The residue (R-1) on the filter was then washed five times with 11.1 mole portions of hot water (90° - 100°C) to remove all the KClO_4 from the residue (R-1). The solution (F-3) was cooled to room temperature (25 - 30°C) where crystallization occurred. The KClO_4 crystals (R-3) were separated from the mother liquor by filtration.

The spent residue (approximately 0.5 moles PbSO_4) was removed from the filter and mixed with 1.1 moles Na_2CO_3 and 27.5 moles H_2O in a one liter reaction flask equipped with a high speed stirrer, thermometer and a porous glass gas diffuser. This mixture was also heated by an oil bath at 80 - 90°C for 0.5 hours stirring violently throughout the reaction time. Then this mixture was chlorinated with 0.4-0.5 moles of chlorine at the rate of 1g. Cl_2 /minute. After sufficient chlorine had been added the mixture was filtered hot on a medium porous glass filter and the residue was washed five times with 5.5 mole portions of hot H_2O (95 - 100°C) to remove Na_2CO_3 , Na_2SO_4 and NaCl from the PbO_2 - PbSO_4 residue (R-4) which was recycled repeatedly.

To prepare the materials which are recycled in the reactions, first the evaporated solution (E-1) was filtered to remove any small amounts of KClO_4 and K_2SO_4 crystals which had formed. Then the solution (F-5) which contained about 1-1.4 moles H_2SO_4 and 0.4-0.6 moles H_2O was increased to its original concentration by the addition of H_2SO_4 and H_2O remembering not to include the H_2O present in the wet PbO_2 residue (R-4). Also due to the inability to remove all of the PbO_2 (R-4) from the filter addition of enough PbO_2 to make 0.5 moles was necessary. To test the various compositions small samples were removed during the cycle.

The reactions in the second cycle were carried out in the same manner as in the first utilizing the recycled materials. On this and succeeding cycles the mother liquor (F-3), saturated with KClO_4 at room temperature, was used to wash residue (R-2). This technique enables more KClO_4 to crystallize out of the mother liquor. The hot mother liquor (90° - 100°C) was divided into 4 equal parts to wash the residue (R-2) containing PbO_2 , PbSO_4 and KClO_4 . It was also necessary to wash residue (R-2) with 2 additional 2.8 mole portions of hot water after washing with the mother liquor to remove the KClO_4 completely. These operations were continued until 5 cycles were completed.

Table 5 gives the results of various operations in the cycle.

TABLE V
POTASSIUM PERCHLORATE CYCLE

<u>Charge (Moles)</u>	<u>Oxidation</u>				
	<u>CYCLE</u>				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
KClO ₄ Recycled	0	.01	.01	.01	.02
KClO ₃ Recycled	0	.03	.02	.02	.04
KClO ₃ Added	0.50	.50	.50	.50	.50
H ₂ SO ₄ Recycled	0	1.27	1.28	1.40	1.04
H ₂ SO ₄ Added	2.0	0.78	0.77	0.60	0.96
H ₂ O Recycled	0	2.68	1.67	0.45	1.63
H ₂ O Added	8.9	6.25	7.27	6.99	7.30
PbO ₂ Recycled	0	0.45	0.46	0.42	0.50
PbO ₂ Added	0.5	0.05	0.04	0.07	0
Yield (Moles) KClO ₄	0.28	0.37	0.44	0.40	0.40
Percentage Yield (Product)					
Based on KClO ₃	56%	70%	84%	77%	74%
Based on PbO ₂	56%	74%	88%	82%	80%
<u>Charge (Moles)</u>	<u>Regeneration</u>				
PbSO ₄	0.48	0.47	0.44	0.54	0.52
PbO ₂ (Unreacted)	0.01	0.05	0.03	0.03	0.03
Na ₂ CO ₃	1.10	1.10	1.10	1.10	1.10
Cl ₂	0.41	0.47	0.38	0.54	0.38
Yield (Moles)					
PbO ₂	0.44	0.41	0.39	0.47	0.42
PbSO ₄					
Percentage Yield					
Based on PbSO ₄	92%	87%	89%	87%	81%
Based on Cl ₂	107%	87%	103%	87%	110%

In the oxidation step of cycle 5 the KClO_4 yields have approached static conditions, 74% based on KClO_3 and 80% based on PbO_2 ; hence additional cycles would give corresponding results. To obtain the greatest efficiency from the KClO_3 , conditions should be such that all KClO_3 reacts in the oxidation step since any unreacted KClO_3 is immediately destroyed when evaporating the H_2SO_4 solution, the reactivity being due to the concentrating of acid. As a result, the by-products ClO_2 and K_2SO_4 are formed and the latter contaminates the end product. This situation can be easily remedied by concentrating the filtrate and washing (F-1 and W-1) with sulfur trioxide thereby greatly decreasing the reaction between H_2SO_4 and KClO_3 which is accelerated at temperatures above 70°C .

The regeneration of PbSO_4 to PbO_2 gave an 87% average yield based on PbSO_4 and a 99% average chlorine efficiency. Note that this efficiency is much superior to those reported for batch runs in Table IV. Careful metering of chlorine is of necessity not only to avoid waste of chlorine but also to maintain the pH above 7 to prevent formation of PbCl_2 . The only loss of lead encountered was of mechanical nature, none resulting through chemical reactions.

The product KClO_4 obtained in the cycles was more than 99% pure, the maximum contaminants being H_2SO_4 —0.27%, Pb ion 0.01%, Cl^- ion 0.01% KClO_3 —0.37%, and K_2SO_4 —0.01%. A simple recrystallization would easily remove these impurities, if warranted, to meet specifications.

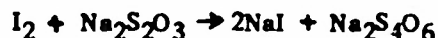
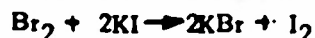
D. ANALYTICAL PROCEDURES

1. Lead Dioxide and Lead Sulfate

a. Lead Dioxide — by potassium iodide

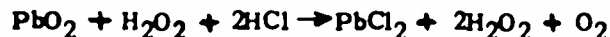
The PbO_2 was quantitatively tested by treating it with NaBr , HCl and KI to liberate free iodine which was titrated with standard thiosulfate. Presence of other substances that oxidize, e.g. ClO_3^- ion, will affect the results since they too liberate iodine.

Equations:



b. Lead dioxide — by hydrogen peroxide

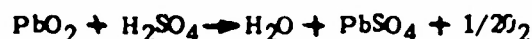
An alternative method is to treat the sample with dilute HCl and a known excess of H_2O_2 . After reacting, the excess H_2O_2 is titrated with standard KMnO_4 solution. Again all other oxidants must be absent.



c. Lead Sulfate

In a mixture of PbO_2 and PbSO_4 the PbSO_4 can be analyzed by converting the mixture entirely to PbSO_4 with concentrated H_2SO_4 . Then using either of the methods cited for analysis of PbO_2 , the difference between the total PbSO_4 and the PbSO_4 equivalent to the PbO_2 analyzed, will give the amount of PbSO_4 contained in the original mixture.

Equation:

2. Chlorate and Perchlorate

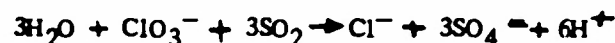
a. Chlorate

The method of analysis for chlorate is identical to the PbO_2 method (1-a) where now the ClO_3^- ion liberates iodine.

b. Perchlorates by Titanium Trichloride

The method described by Von Eugen Spitalsky and S. Jofa (6) has been modified slightly for use in this work. This method was tested in our laboratory and found to give quite consistent results within the limits of accuracy of $\pm 1\%$.

Other oxidizing agents such as chlorate, chlorite, hypochlorite and nitrate which are also reduced by TiCl_3 must be removed completely from the sample being analyzed. The removal of chlorate, chlorite and hypochlorite may be accomplished easily by reduction with sulfur dioxide according to the equation:



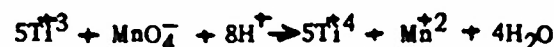
The presence of nitrate ions or nitric acid necessitates the use of a different analytical method, which will be mentioned later.

Since titanous solutions are readily oxidized by air, care must be taken to protect them from contact with air by using an inert atmosphere such as carbon dioxide.

Procedure: After all oxidants other than ClO_4^- have been removed, the sample solution (in a 500 ml Erlenmeyer flask) is acidified with 50 ml of 10% H_2SO_4 , and air excluded from contact with the solution by the addition of dry ice. A measured amount of TiCl_3 solution (previously standardized against potassium dichromate or potassium permanganate) is added. The flask is stoppered with a two hole rubber stopper, containing a tube for the delivery of CO_2 into the flask. The flask is placed on a low temperature hot plate for 1-1.5 hours, to permit complete reduction of perchlorate ion according to the equation:



After heating for the required period of time, the flask is removed from the hot plate and cooled in an ice bath. The stopper is removed and rinsed with water, which has previously been boiled to remove dissolved air and cooled with CO₂ bubbling through it. A piece of dry ice is added to the flask, and the excess TiCl₃ in the sample solution is titrated with standard KMnO₄ solution:



The end point may be taken as the first permanent pink coloration imparted to the solution by a drop of KMnO₄; or an oxidation reduction indicator such as diphenylbenzidine may be utilized, 3 drops of a 1% solution in conc. H₂SO₄ being sufficient.

c. Perchlorate by Thermal Decomposition

For samples containing a mixture of nitrate, chlorate and perchlorate, an aliquot of the sample is treated first with SO₂ which reduces chlorate to chloride. The chloride is then determined gravimetrically and calculated to chlorate. The perchlorate is determined by thermal decomposition of another aliquot and subsequent gravimetric determination of the total chloride. The perchlorate is then calculated from the difference in the two chloride results.

V. CONCLUSION

Economical investigation of the various conditions to produce KClO₄ and the methods to regenerate the PbSO₄ residue show that the following processes are most favorable.

a. Potassium perchlorate is formed from potassium chlorate by PbO₂ in an acid medium utilizing the following conditions:

1. Reagent mole ratio H₂SO₄: PbO₂: KClO₃: H₂O = 4: 1: 1: 17.8.
2. Reaction time - 2 hours
3. Temperature - 107-125°C
4. Yield of KClO₄ - 85%

b. The spent residue PbSO₄ is regenerated to PbO₂ by chlorination of PbCO₃ produced by direct action of Na₂CO₃ and PbSO₄. The conditions for the carbonation reaction are:

1. Reagent mole ratio - PbSO₄: Na₂CO₃: H₂O = 1: 1.1: 20
2. Temperature - 80-90°C (not critical)
3. Time (minutes) - 1.
4. Mixing - high speed
5. Chemical Yield Re: PbSO₄ - 95%

c. The PbCO_3 is then converted to PbO_2 by chlorination.

1. Reagent mole ratio - $\text{PbCO}_3 : \text{Na}_2\text{CO}_3 : \text{Cl}_2 : \text{H}_2\text{C} = 1 : 1.2 : 1.2 : 20$
2. Temperature 80°C
3. Chemical yield Re: PbCO_3 - 98%
4. Chemical yield Re: Cl_2 - 99%

The three reactions (a) oxidation, (b) carbonation and (c) chlorination are combined to produce a continuous process. Consult section on "Cyclic Operation" for the detailed description of the process.

Similar high yields are obtained using sodium chlorate to produce sodium perchlorate. In this case crystallization techniques must be modified to suit the high solubility of NaClO_3 and NaClO_4 .

VI. FUTURE WORK

If a detailed cost estimate becomes desirable for producing KClO_4 the following studies should be made:

1. Phase diagrams of the system $\text{KClO}_4 - \text{KClO}_3 - \text{KHSO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$
2. Filtration rates for all separations.
3. Pilot plant operation

Similar studies should be made also for the analogous sodium perchlorate process.

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