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(9) FIRST QUARTERly RESEARCH REPORT. no. 1, Feb-Jun 52,

1952

~~PROJECT-4-00048-60~~

(6) SODIUM PERCHLORATE: Research Leading Toward the Development of Selected Methods to Produce Sodium Perchlorate Without the Use of Platinum.

Project Number (16) NR-352-304/2-1-52

by

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(15) Nonr-507(00)

(11) 18 Jul 52

(12) 26p.

(14) [illegible] 52-6341)

[illegible] (278400)

July 18, 1952

Inorganic Research Dept.
R. and D. Division

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INCORPORATED 1850 [redacted]

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July 30, 1952

Dr. Lewis W. Butz
Office of Naval Research
Washington 25, D. C.

Re: ONR Project No. Nonr-807(00) ✓

Dear Dr. Butz:

With this letter are 4 copies of our first technical report on the subject contract, which covers research on methods of making perchlorates which do not require platinum. This report covers the working period from February through June, 1952.

Right now, the status of this project is about as follows: The acid disproportionation method looks good as a practical procedure which can be engineered to full scale production. We do not yet know how the economics of this method will compare with those of the current electrolytic process, but the procedure does not appear to require any highly critical construction materials. On this method, points remaining to be cleared up include selection of construction materials, and proof that chlorine dioxide which is liberated during the disproportionation, can be effectively absorbed in alkali and electrolysed back to chlorate.

The lead dioxide work appears to be coming to an unfavorable conclusion. Although the life of lead dioxide-coated electrodes has been greatly increased, and some tests have successfully passed 5-1/2 days of operation, the life of the electrode would still have to be increased many fold before large scale use could be contemplated. We are continuing our studies in this direction, but are not optimistic about the successful use of lead dioxide anodes.

We have not yet completed our agreement with Carborundum Corporation, who will assist us in preparing and evaluating various types of silicon-silicon carbide anodes. Some miscellaneous specimens have been received, but these have not shown substantial improvement in the elimination of the unfortunate spalling exhibited by silicon-silicon carbide materials in perchlorate electrolysis.

Of a small number of miscellaneous anode materials received and tested during the current contract, a tantalum carbide containing 17 wt. % of platinum was the only one that gave favorable results. Of course, use of this material could only mitigate the platinum requirement currently experienced, and then only if the material can be made into forms of high surface-to-volume ratio. This latter point is being checked with the manufacturer before any additional recommendations for research can be made.

Our meeting with you the other week indicated that our directions of effort are still in harmony with the requirements of ONR. We intend to continue research on all three phases of this project, with special emphasis on a larger laboratory scale testing of the acid disproportionation method.

Very truly yours,

J. F. Gall

J. F. Gall, Director
Inorganic Research Department
R. and D. Division

JFG/pr

(Distribution list attached)

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SUBJECT

Sodium Perchlorate; Research Leading Toward the Development of Selected Methods to Produce Sodium Perchlorate Without the Use of Platinum (Project Number ~~NR~~ 352-304/2-1-52; Contract Number Nonr - 807 (00)

OBJECT The objective of this research was

To investigate methods for production of sodium perchlorate without the use of platinum; to include, but not necessarily be limited to, the following:

(1) the use of anodes comprising silicon - silicon carbide; (2)
~~(2)~~ the use of lead dioxide coated anodes; and (3)
~~(3)~~ the disproportionation of sodium chlorate in acid solution.

SUMMARY

1. This report covers the work done during the months February through June, 1952, under contract NONR - 809 (00) which calls for research on selected methods as recommended by Project NR 352-263 to produce sodium perchlorate without the use of platinum.

2. Laboratory assistance from the Carborundum Company at Niagara Falls is being sought to make anodes of silicon-silicon carbide mixtures of several compositions and by several procedures, in an attempt to overcome the spalling characteristic of the "Durhy" rod as reported in project NR 352-263. Carborundum Company has submitted several such anodes, in partial fulfillment of this object, none of which have proven satisfactory.

3. Several miscellaneous materials received too late to be included in the previous contract were tested. Only one of those, tantalum carbide with 17 weight percent of platinum from the Carboloy Department of the General Electric Company gave favorable results in preliminary testing.

4. Lead dioxide plated anodes were prepared from several plating baths and on several base materials. All of those on a metal base other than tantalum failed almost immediately, although the deposits appeared sound. Failure was caused by microscopic pinholes in the coat, resulting in rapid local attack on the base material.

5. More durable lead dioxide plates were formed on tantalum and on cast silicon, materials that polarize in the perchlorate cell and are not subject to anodic attack. These anodes ultimately failed either because the lead dioxide was slowly eroded away, or because the plate became loosened from the base and fell off. However, in a few of the runs a substantial amount of current passed before the anode failed.

6. The optimum safe condition for the production of perchlorate by the disproportionation of sodium chlorate in sulfuric acid has been found to be an acid concentration of 70% at 93°C., or 83% acid at 69°C. Yields of 36% conversion of sodium chlorate to perchlorate have been achieved. These yields are close to theory and chlorine dioxide is the major reduced product of the reaction.

7. When perchloric acid is used in place of the sulfuric acid in the disproportionation procedure a 32% conversion of sodium chlorate to perchlorate is obtained with 71% acid at 69°C. This yield compares favorably with the sulfuric acid process.

8. Work has been done to resolve the problems of recovering perchlorate values from the disproportion method. For the sulfuric acid procedure perchloric acid can be separated by vacuum distillation or ammonium and potassium perchlorate can be recovered by a fractional crystallization method. When perchloric acid is used in this process sodium perchlorate can be recovered by direct crystallization.

CONCLUSIONS

1. No anode material has been found to date that works as well as platinum for the production of perchlorates.

2. More extensive experimental work must be done before silicon-silicon carbide anodes can be fully evaluated.

3. Tantalum carbide-platinum composition must be studied further as anode material in the perchlorate cell.

4. The most practical way to form commercial anodes of lead dioxide appears to be by electroplating it on an inert base material.

5. To date, lead dioxide anodes have been found to be eroded at a substantial rate during the electrolysis of chlorate to perchlorate.

6. The reaction for the disproportionation of sodium chlorate in strong oxide is:

$$\underset{(2HClO_4)}{H_2SO_4} + 3NaClO_3 \longrightarrow NaClO_4 + 2ClO_2 + \underset{(2NaClO_4)}{Na_2SO_4} + H_2O$$

When Cl_2 is formed it appears to come from the decomposition of chlorine dioxide and not from sodium chlorate.

7. The above reaction can be controlled and yields close to theory for both sodium perchlorate and chlorine dioxide can be realized, and the recovery of perchlorate as perchloric acid, sodium perchlorate, ammonium or potassium perchlorate is possible.

RECOMMENDATIONS

None this quarter.

LABORATORY STUDY

A. Electrochemical Oxidation of Sodium Chlorate

1. Silicon-Silicon Carbide Mixtures (Carborundum Company)

Laboratory assistance from the Carborundum Company at Niagara Falls, N.Y. has been sought to fabricate anodes of silicon-silicon carbide mixtures of several compositions and by several procedures, in an attempt to overcome the spalling characteristic of the Durhy rod as reported in Project NR 352-263. (See final research report-Investigation of Methods to Produce Sodium Chlorate Without the Use of Platinum - Part II Laboratory Work - Project NR 352-263/2-19-51 Contract No. NONR 372 (00) - Office of Naval Research - by Pennsylvania Salt Manufacturing Co. R&D staff) Of the twelve samples of Durhy material submitted by the Carborundum Company in partial fulfillment of this contract, either anode polarization or spalling of the Durhy rod was observed as reported in last year's work. (see Final Report, loc. cit.) The results of these tests are shown in Table I.

This spalling phenomenon was not observed when Durhy was used as an anode in salt brine electrolysis or as a cathode in the chlorate-perchlorate cell. Also, the spalling phenomenon was not noted when either tap water or sodium chlorate solution was dripped on Durhy rod material heated by a current of 8 amperes. However, when the Durhy material was used as an anode in an electrolytic cell containing pure sodium perchlorate solution, the same spalling phenomenon was observed as in the chlorate-perchlorate cell.

A piece of cast silicon rod polarized almost immediately in the chlorate-perchlorate cell. (See Table I)

A trip to the Carborundum Company will be scheduled in the near future to discuss new preparation of silicon-silicon carbide compositions.

2. Lead Dioxide Coated Anodes

The equipment used for the anodic electroplating of lead dioxide in the work on Project NR 352-263-2/19/51, underwent some minor changes. The cell body was standardized to a two liter beaker, and the cathodes were changed to two inch wide strips of 1/16 inch thick lead sheet. Three of these lead strips were centered at 120 degree intervals along the inside circumference of the cell, and extended to the bottom of the cell, with a one inch bend along the bottom of the cell to provide good covering power in plating the lower end of the anode rod.

TABLE I

SILICON-SILICON CARBIDE MIXTURES (CARBORUNDUM COMPANY)

Electrolyte: 600g/1 $NaClO_3$; 4g/1 $Na_2Cr_2O_7$° $2H_2O$ (except where noted)

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density(approx.) ma./sq.cm.(1)	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Durhy - made by siliconizing a carbon body formed by extruding a mixture of wheat flour and carbon powder	2.5-5	200	6-9.8	4-15	Severe spalling; end broken off with large pieces in bottom of cell
Durhy - made by siliconizing a carbon body formed by casting	0.8-8	200	7-19	5-12	Polarized; slight spalling
	0.6-2.8	200	16-19	16-19	Polarized
Durhy - same as previous sample except surface has been smoothed by grinding on a diamond wheel.	0.3-9.0	200	10-20	3-7	Polarized; slight spalling
	0.2-9.0	200	6-14	14-18	Polarized; slight spalling
Durhy - made by siliconizing a carbon rod formed by extruding; annealed at 1350°C. for 8 hours.	1.6-5	200	6-9	15-21	Anode shattered at top surface of electrolyte after explosions at cell
	4.8-5	200	7-10	2-8	Anode shattered into two large pieces
Durhy - same as previous sample except sample was annealed at 1350°C. for 16 hours.	3.3-5	200	6-9	17-20	Anode shattered into three large pieces
	0.5-5	200	6-10	2-8	Anode shattered into two large pieces

(1) Anode current density stated is starting current density.

con't. next page

TABLE I - con't.

SILICON-SILICON CARBIDE MIXTURES (CARBORUNDUM COMPANY)

Electrolyte: 600g/1 $NaClO_3$; 4g/1 $Na_2Cr_2O7°$ $2H_2O$ (except where noted)

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.(1)	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Durhy - same as previous sample except sample was annealed at 1350°C. for 24 hours.	3-5	200	5-9	14-17	**Anode shattered into three large pieces**
	2.5-5	200	6-8	2-5	**Anode shattered into three large pieces**
Durhy No. 1 rods; no free carbon in these rods (3 samples tried)	0.2-1	200	20-22	6-9	**All samples rapidly polarized**
Cast silicon metal rod	0.2-2	200	greater than 20	3-5	**Polarized almost immediately (2)**

(1) Anode current density stated is starting current density.
(2) No dichromate used.

The feasibility of using lead as a base metal for the anodic plating of lead dioxide was investigated under various plating conditions. The lead was cast into rods 9/32 inch in diameter in silicone coated glass tubes. Satisfactory lead dioxide deposits could not be obtained due to the simultaneous and rapid anodic erosion of the lead, and scum formation over the anode surface.

The lead dioxide plating of monel rod was continued with different plating baths. Compositions of these baths are given in Table II. From the alkaline tartrate bath #7P, a smooth lustrous black deposit was obtained, and from the acid bath #LP-1, the deposit was gray with a satin finish. In all cases, the monel was rapidly eroded in the perchlorate cell when the continuity of the PbO_2 deposit was broken. This occurred in one to two hours or less when electrolyzing at an anode current density of 0.2 amps./cm^2 (186 amps./$ft.^2$).

It was then decided to plate lead dioxide on base materials such as tantalum, cast silicon, Durhy (silicon carbide), or magnetite which either polarize or do not erode in the perchlorate cell. This was considered more promising than plating on easily eroded metals, or trying to prepare a pure lead dioxide anode as was done by the Japanese (3), because of the comparatively high resistance of lead dioxide alone, as well as the difficulty in making and handling anodes made of pure lead dioxide.

Durhy #1 rod was plated with lead dioxide in a 7M bath. The deposit was bright but not continuous, and was poorly adherent. This plated rod polarized in less than one-half hour in the perchlorate cell. It is suggested that the non-continuity and poor adherence of the lead dioxide may have been due to the extreme roughness of the Durhy #1 surface. A rectangular shaped stick of Durhy #2 with two sides polished has been received from Carborundum Co. and will be plated with lead dioxide for testing in the perchlorate cell in the near future.

A smooth, adherent electrodeposit of lead dioxide on cast silicon rod, was readily obtained. This electrode gave promising results in the perchlorate cell, operating for 111 ampere hours per gram of PbO_2 deposited. As the silicon began to polarize, it shattered. Additional samples of cast silicon will be requested from Carborundum Co. for further tests with lead dioxide deposits from different plating baths.

The major effort on lead dioxide plating was carried out with tantalum rod and sheet, and with tantalum drawn over a copper rod core. As the work progressed, 1/4 inch diameter tantalum rod was used almost exclusively, being in greater supply. Of the highly alkaline tartrate baths 7M, 7N and 7P, the best deposit

TABLE II

Composition of Lead Dioxide Plating Baths

7M pH = ca. 13

50 gms. potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$
25 gms. sodium hydroxide, $NaOH$
48 gms. lead oxide, PbO

Dissolve in one liter of water at 40° - 60°C. Filter when temperature is below 40°C.

7N pH = ca. 13

50 gms. potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$
50 gms. sodium hydroxide, $NaOH$
40 gms. lead oxide, PbO

Dissolve in one liter of water at 40°-60°C. Filter when temperature is below 40°C.

7P pH = ca. 13

50 gms. potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$
10 gms. sodium hydroxide, $NaOH$
40 gms. lead oxide, PbO

Dissolve in one liter of water at 40°-60°C. Filter when temperature is below 40°C.

LP-1 No free $HClO_4$; 4.74% lead; pH = 5.0
108 mls. of 60.3% perchloric acid (100 gms. $HClO_4$)
167 mls. water
111.0 gms. lead oxide, PbO

First prepare 30% $HClO_4$ by diluting the 60% acid with water. Then dissolve the litharge at room temperature. Add sufficient distilled water to make 2 liters. Heat to boiling (102°C.) for 2-3 minutes to dissolve white precipitate. Cool and use.

LP-2 (2.01% free $HClO_4$; 4.69% lead; pH = 0.65)
155 mls. of 60.3% perchloric acid (144 gms. $HClO_4$)
241 mls. water
111.0 gms. lead oxide, PbO

Prepare this bath in the same manner as LP-1, except that it is not necessary to heat after diluting to 2 liters, since no precipitate forms.

TABLE II - con't.

LP-3 (5.14% free $HClO_4$; 4.61% lead; pH = 0.32)
232 mls. of 60.3% perchloric acid (215 grams $HClO_4$)
360 mls. water
111.0 gms. PbO

Prepare this bath in the same manner as LP-2. Dilute to 2 liters.

LP-4 (No free $HClO_4$; excess PbO) 6.98% lead; pH @ 6.1)

108 mls. of 60.3% perchloric acid (100 gms. $HClO_4$)
167 mls. water
167.4 gms. lead oxide, PbO

Prepare this bath in the same manner as LP-1, except it is necessary to boil the solution after dilution to 2 liters for several hours to dissolve all the litharge.

LP-5 (Basic, with excess PbO; 8.99% lead; pH - 7.0)
108 mls. of 60.3% perchloric acid (100 gms. $HClO_4$)
167 mls. water
221 gms. lead oxide, PbO

Prepare this bath in the same manner as LP-4. Dilute to 2 liters.

from the standpoint of smoothness and adherence was obtained from 7M, operating at 55°C. and a current density of 0.7-1.5 amps./ft^2. The highest perchlorate cell life was obtained with a thin (4 gms. PlO_2/ft.^{2} electrode surface) coating from this bath. These alkaline baths were developed from information contained in an expired patent (1).

Another series of lead dioxide plating baths was based on lead perchlorate. These perchlorate baths were formulated from information published by Mathers (2). LP-1 contains stoichiometric equivalents of lead oxide (PbO) and perchloric acid. LP-2 and LP-3 contain increasing excesses of perchloric acid. LP-4 and LP-5 are essentially the LP-1 formula with increasing excesses of lead oxide. In the latter cases, the baths had to be boiled for several hours to dissolve the excess lead oxide. Compositions and pH values of these baths are given in Table II. The character of the deposits from the acid perchlorate baths was entirely different from that obtained from the highly alkaline baths previously mentioned. Baths 7M, 7N, and 7P generally gave a hard, lustrous black deposit, while the deposit from the acid LP baths (LP-1, LP-2, LP-3) was gray with a satiny etched finish. A dull black deposit plated out from the more basic LP-4 and LP-5 baths. The highly alkaline tartrate baths were found to be very sensitive, and it was quite difficult to obtain a perfect, adherent deposit free of blisters, especially when thick coatings were desired. Smooth deposits free of imperfections were easily obtained from the LP-1 and LP-5 perchlorate baths operating at 25°C. LP-2 and LP-3 gave uneven deposits, and deposits from LP-4 developed fine hair cracks on air drying. Almost all lead dioxide plating was carried out at current densities ranging from 0.4 to 1.5 amps.1 ft^2.

The lead dioxide plated tantalum electrodes which were of at least fair quality were tested as anodes in a perchlorate cell operated at 0.2 amps. /cm^2(186 amps./ft^2). As the testing of these electrodes continued, control of the variables in the operation of the perchlorate cell was gradually developed. An attempt at pH control of the electrolyte was begun by small manual additions of 0.1N to 1N hydrochloric acid. It was then found that the pH varied widely within the cell. Therefore, continuous stirring of the electrolyte has been adopted as standard practise. It has also been found more convenient to use platinum coated tantalum sheets for cathodes in place of steel sheets, which corroded and discolored the electrolyte. A refinement added later, was the development of a pH control device for the automatic addition of controlled amounts of acid to the cell at equal intervals to maintain the electrolyte slightly acid, preferably in the range of pH 4 to 6. Cell current has been maintained constant by the use of an electronic controller. Any desired cell temperature can be maintained by immersed cooling coils through which is circulated coolant from an Aminco refrigerator-heater bath. It was found that when the perchlorate cell was operated at 25°-30°C., a considerably larger amount of hydrochloric acid addition was required to maintain the pH on the acid side, than when the cell was cooled to 2°-5°C.

The results of erosion tests of the lead dioxide plated tantalum anodes in the perchlorate cell have not been entirely consistent nor satisfactory to date. However, it is felt that considerable progress has been made in understanding and solving the problems involved in plating and testing of lead dioxide coated electrodes. The most serious problem has been the cracking and breaking loose of supposedly adherent deposits from tantalum and other electrodes which normally polarize anodically after a short period of electrolysis in the perchlorate cell. The cracking of the lead dioxide often occurred very soon after the electrode had been replaced in the perchlorate cell after having been removed at the end of a previous day's run and stored overnight in air or water.

Attempts were made to improve the lead dioxide adherence by various pre-plating treatments of the tantalum. The most satisfactory cleaning cycle was a 3/0 emery cloth and crocus cloth rubbing following by cotton cloth wiping. A hydrofluoric acid dip was definitely harmful, and various other chemical treatments, including hot alkali-silicate detergent solution, nitric acid, cathodic cleaning in phosphoric acid and cathodic cleaning in a sulfuric and hydrochloric acid mixture did not show any beneficial effect.

Another approach which did not improve electrode life, was to plate the tantalum cathodically first with lead for 10-20 minutes at five times the normal current density, and then continue normal anodic lead dioxide plating. Also, as noted above, thin deposits from the highly alkaline tartrate baths were hard, smooth and quite adherent, but heavier deposits blistered. On the other hand, heavy PbO_2 deposits from the perchlorate baths were free of surface imperfections, but possibly less adherent. Therefore a plating cycle was carried out in which the tantalum was first given a thin deposit of lead dioxide in bath #7M, and the plating was then continued in the perchlorate #LP-5 bath. Electrodes prepared in this manner showed, on the average, a somewhat longer life in the perchlorate cell than electrodes plated in either of the baths alone.

A brief summary of the lead dioxide plating and erosion testing done during this period is given in Table III.

It is planned to continue the plating and testing of lead dioxide plated electrodes with special emphasis on increasing the adherence of lead dioxide to the tantalum (or other similar base metal), and decreasing cracking tendency or brittleness of the lead dioxide. Several other lead dioxide plating baths are to be tried, including those based on lead fluoborate and lead fluosilicate. The Japanese work with a lead nitrate bath will be more thoroughly checked than was done in the preliminary work under Project NR 352-263-2/19/51.

TABLE III

SUMMARY OF LEAD DIOXIDE PLATING AND EROSION TESTING

Base Metal	Plating* Bath	Notes on PbO_2 Plating	Notes on Erosion Testing of PbO_2 Plated Metals in Perchlorate Cell
Lead	7M	Unsatisfactory as base metal; would not take a PbO_2 plate	-
Durhy #1	7M	PbO_2 plates at 4.7 amps./ft.^{2} Deposit is bright, but not continuous, and poorly adherent.	Polarizes in 23 minutes ($<$ 1/2 amp-hour.)
Silicon	7M	Smooth, adherent deposit	Rod shattered during electrolysis
Monel	7P	Glossy, black, smooth deposit	Monel is rapidly eroded when continuity of PbO_2 is broken (in 1-2 hours at 4 amps.)
	LP-1	Gray deposit with satin finish	
Tantalum	7M	Lustrous, black, smooth deposit with bath at 55°C. and 0.7-1.5 amps./ft.^{2} Very poor PbO_2 deposit after HF preclean	Highest perchlorate cell life with thin (4 gms./ft.^{2}) deposit from this bath.
	7N	About same quality of deposit as that obtained from bath 7M	Very short life in perchlorate cell.
	7P	Larger number of blisters formed than with 7M or 7N	Slightly longer life than PbO_2 from 7N bath.
	LP-1	Smooth, gray deposit with satin finish	Compares favorably with 7M
	LP-2	Uneven coverage of tantalum by PbO_2	Not tested
	LP-3	Poor, uneven plating	All PbO_2 fell loose before current could be adjusted to steady value.
	LP-4	Deposit develops fine hair cracks on air drying.	Deposit has moderate life; fails by flaking loose from tantalum.
	LP-5	Deposit is dull and black, but smooth and continuous	Electrode failed by portion of PbO_2 falling loose from tantalum.
	7M (flash coat, followed by: LP-5	Deposit is smooth and dark gray black	Average perchlorate cell life somewhat longer than electrodes heavily plated in either #7M or #LP-5 bath alone.

* Bath composition.

3. Miscellaneous Anode Materials

Various samples from the Linde Air Products Co. were tested as anodes in the chlorate-perchlorate cell (See Table IV). All these materials polarized after a relatively short period of operation.

Samples of titanium boride, TiB_2; titanium carbide, TiC; and zirconium boride, ZrB_2; from the American Electro Metal Corporation, all eroded rapidly when used as anodes (Table IV).

A sample of pure silicon metal deposited on a molybdenum core wire from the Foote Mineral Company was found to be too poor a conductor to work as an anode in the chlorate-perchlorate cell.

Favorable results have been obtained with repeated tests on a sample of tantalum carbide containing 17% platinum by weight obtained from the Carboloy Department of General Electric Company. Anode loss rates have varied from $1x10^{-5}$ to $20x10^{-5}$ grams per ampere-hour and current efficiencies as shown by electrolyte analysis have been as high as 70%(Table V).

This sample was prepared by powder metallurgy methods by the Carboloy Co. in the form of a bar 8.3 cm.x 0.7 cm. x 0.6 cm. They state that thin sheets or plates would be quite difficult to fabricate, and would be limited to pieces of relatively small area. Due to inherent hardness and brittleness, the metal cannot be rolled into sheets by conventional methods. Plates of TAC-Pt composition could be brazed to a material such as copper, but methods providing complete enclosure of the base metal would most probably prove difficult and at present are considered impractical by the Carboloy Co. The value of the starting powder materials approximates $280 per pound, of which amount approximately 90% is represented by the market value of the platinum constituent.

Further evaluation study is therefore necessary to determine the practicability of using the 83% TaC, 17% Pt (by weight) composition as anode material in the chlorate-perchlorate cell.

B. Disproportionation of Sodium Chlorate in Acid Solution.

1. Reaction Study

The purpose of this phase of the work was to determine the feasibility of and the optimum conditions for the production of perchlorates by the disproportionation reaction of a chlorate such as sodium chlorate in a concentrated strong acid. The major part of our effort to date has been in reactions with sulfuric acid, although a few preliminary experiments were carried out with perchloric acid.

TABLE IV

MISCELLANEOUS ANODE MATERIALS

Electrolyte: 600g/1 $NaClO_3$; 4g/1 $Na_2Cr_2O_7 \cdot 2H_2O$

Description of Sample and Source	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
Linde Air Products Co.:- Tungsten Carbide, WC-Pure (No Co or other binder)	0.4-2	200	11-23	2	Polarized after about 1-hour.
Tungsten Silicide, 70% W, 30% Si, by wt.	0.1-0.4	200	18-20	2	Polarized
Tungsten Silicide, 75% W, 25% Si, by wt.	0.2-1	200	12-22	2-3	Polarized
Tungsten Silicide, 65% W, 35% Si, by wt.	0.1-1	200	13-20	1	Polarized
Molybdenum Silicide, 50% Mo, 50% Si, by wt	0-0.6	200	10-22	1	Polarized
Molybdenum Silicide, 55% Mo, 45% Si, by wt	0-0.1	200	19-22	0	Polarized
Molybdenum Silicide, 63% Mo, 37% Si, by wt	0.0-0.9	200	15-19	1	Polarized
Molybdenum Tungsten Silicide 30% Mo, 35% W and 35% Si, by wt.	0.0-0.8	200	11-20	0	Polarized
American Electro Metal Corp.:- Titanium Boride, TiB_2	2	200	5-8	1-9	Eroded rapidly
Titanium Carbide, TiC.	2	200	5	2-5	Eroded rapidly
Zirconium Boride, ZrB_2	2	200	5	3-4	Eroded rapidly
Foote Mineral Company:-Silicon Metal deposited on a molybdenum core wire	Poor conductor.	No current would pass when potential of 18 volts was applied.			

TABLE V

Carboloy Sample No. 12

83 weight % TaC
17 weight % Pt.
Electrolyte: 600 g/l $NaClO_3$
4g/l $Na_2Cr_2O_7 \cdot 2H_2O$ (except where noted)
Current Density: 200 ma./sq.cm.

Run No.	Average Cell Current (amperes)	Average Cell Voltage	Cell Temp. °C.	Hours of Electrolysis	Total Ampere Hours	Total Anode Loss In Grams	Anode Loss Rate Grams per ampere-hour	Current Efficiency from Chlorate Loss	Current Efficiency from Perchlorate Formation	Remarks
1	0.2	4.3	15-18	1.2	0.236	0.0019	0.008	-	-	
2	2.6	5.4-6.8	2-5	48	124.8	0.0215	0.00020	65	56	
3	2.5-2.6	5.4-6.6	1-7	75.7	189	0.0056	0.00003	52	58	No dichromate used
4	2.6	5.8-6.4	4-11	47.4	125.7	0.0214	0.0002	55	55	
5	2.6	5.6-6.1	4	47.75	124	0.0015	0.00001	72	70	No dichromate used.

Numerous reactions are possible, depending on reactant concentrations, temperature, etc. between the limits of the two following equations:

$$(1)\ H_2SO_4 + 3NaClO_3 \longrightarrow NaClO_4 + 2ClO_2 + Na_2SO_4 + H_2O$$

$$(2)\ H_2SO_4 + 7NaClO_3 \longrightarrow 5NaClO_4 + Cl_2 + Na_2SO_4 + H_2O$$

It may be expected that the separation of perchlorate from the resulting complex mixture will require considerable research effort.

Sodium chlorate was introduced into the reaction as a concentrated solution, 650 gms./l. This was found to be very satisfactory and much preferable to the use of solid sodium chlorate, which results in violent local reaction. In a series of preliminary experiments, the sulfuric acid was held in an open pyrex vessel, and the sodium chlorate solution was added dropwise. When all the sodium chlorate had been mixed in with the acid, the temperature of the mixture was raised to the desired point (60°-100°C.) and digested for periods of 1/2 to 5 hours. The solution was flushed at all times with nitrogen gas introduced through a fritted glass gas washing tube.

The reaction of 50% sulfuric acid with sodium chlorate solution was too slow and mild. Using 70% sulfuric acid, promising yields were obtained in the temperature range of 70°-100°C. with a 3 hour reaction period. Use of 83% sulfuric acid yielded more perchlorate than 70% acid under approximately the same conditions. The reaction of 96% sulfuric acid with the concentrated sodium chlorate solution tended to be violent and resulted in the immediate precipitation of a considerable amount of solids at or near room temperature. These solids dissolved at about 70°C., but heavy foaming of the reaction mixture occurred at this elevated temperature. Although the yield from one experiment with 96% sulfuric acid was good, it was decided to carry out further work with the 70% and 83% acid.

In order to determine, infurther experiments with sulfuric acid, whether any perchloric acid was being distilled out of the reactor during the heating of the chlorate-acid mixture after they had been mixed at room temperature, and, also, to determine the composition of the reactor vapors, especially in regard to oxidizing power, a closed reaction vessel was used. The reactor vapors were flushed out with nitrogen and absorbed in a train of two 8% sodium hydroxide solutions of 125 mls. each. The reaction mixtures, except as otherwise noted, consisted of 90 mls. of sulfuric acid of given strength and 38.5 mls. of a 650 gms./l. $NaClO_3$ solution (25 gms. $NaClO_3$). For 70% acid this gave an $H_2SO_4/_{NaClO_3}$ weight ratio of 4.1, and for 83% acid, the ratio was 5.3. The following variables were studied with 70% and 83% sulfuric acid: (1) reaction temperature, and (2) ratio of acid to chlorate.

The reactions with 70% acid were carried out at 69° and 93°C. with reaction periods of 3 to 6 hours. At 69°, the conversion of sodium chlorate to the perchlorate fell in the range of 11 to 22% for the above respective reaction times. At 93°C. the yield was about 33%, practically independent of reaction time. The conversion of sodium chlorate to the perchlorate at 69°C. when using 83% sulfuric acid ranged from 29 to 33% for reaction periods of 3 to 6 hours respectively. Attempts to heat a mixture of 83% sulfuric acid and concentrated sodium chlorate solution to 93°C. resulted in moderate explosions at about 78°-80°C. At these temperatures the concentration of yellow chlorine dioxide in the reactor vapor space increased too rapidly to be carried away by any practicable flow of nitrogen.

From analyses of the absorber solutions for oxidizing power and chlorine content, the composition of the reactor vapors was expressed as per cent chlorine and chlorine dioxide. With 70% acid reacted at 69°C., the composition of the reactor vapors could be considered as 100% ClO_2, and when the reaction temperature was raised to 93°C., the ClO_2 content dropped to 24% (76% Cl_2). When reacting 83% sulfuric acid with sodium chlorate solution and heating to 69°C., the ClO_2 content of the absorbed reactor vapors ranged from 88 to 85% (12 to 15% Cl_2) for reaction periods of 3 to 6 hours respectively.

As the ratio of the weight of equivalent 100% H_2SO_4 to the weight of equivalent solid sodium chlorate was increased from 2.6 to 8.1 when reacting 70% acid at 93°C., the conversion of sodium chlorate to the perchlorate rose from 28 to 36%. At the same time the ClO_2 content of the absorbed reactor vapors dropped from 48 to 23% (52 to 77% Cl_2). When reacting 83% acid in the acid-chlorate ratio range of 3.4 to 10.5, from 30 to 35% of the sodium chlorate was converted to perchlorate respectively at 69°C. Under these conditions, the absorbed reactor vapors ranged in composition from 93 to 84% ClO_2 (7 to 16% Cl_2). The reaction period for all experiments in this series was 4.5 hours.

In interpreting the above yields, it should be noted that for a reaction exactly following equation (1) above in which chlorine dioxide is the only oxidizing gas given off, a 33.3% conversion of sodium chlorate to perchlorate represents the maximum possible yield, while for equation (2) where chlorine is the only oxidizing gas given off, a 71.4% conversion represents the maximum possible yield. In most of the above experiments in which the reaction of sulfuric acid and sodium chlorate were carried out, a considerable amount of chlorine dioxide was formed. Thus, the yields might be expected to be closer to the lower value for equation (1). Even in those cases where the reactor gases as absorbed in sodium hydroxide solution are analyzed as having been to a large degree chlorine, it is possible, and even likely that the gases just as they evolved from the reactor solution contained a higher percentage of chlorine dioxide. Brown(4) has found that in the gas phase, chlorine dioxide undergoes thermal decomposition into chlorine and oxygen. This reaction rate rises rapidly with temperature, especially above 60°C. In aqueous solution, chlorine dioxide may undergo catalytic hydrolysis into chloric and hydrochloric acids. If no catalyst is present, the solutions are stable, even at 96.5°C.

Distillation or carry over as mist of perchloric acid from the reactor was found to be negligible at the reaction temperatures used (93°C. max.) Also there was little or no chloride formed in the reaction of sulfuric acid and sodium chlorate.

During the course of these experiments the observation was made that as the mixture of 70% sulfuric acid and concentrated sodium chlorate solution is heated, there is a continuous evolution of strong y yellow vapors until the temperature reaches 90°-93°C., at which point the evolution of the yellow vapors stops sharply. For 83% sulfuric acid, this characteristic temperature is 67-69°C. These then were considered to be the minimum desirable temperatures for carrying out the formation of perchlorate. When the 83% sulfuric acid and chlorate mixture was heated to 75°C. and higher, there was a reappearance and very rapid increase in concentration of the yellow vapors with the mixture exploding at about 80°C. No attempts were made to carry out any experiments with 70% acid above 93°C. These observations apply to the series of experiments in which the reactor vapors were confined and swept through an absorbing train of caustic solutions by nitrogen bubbled through the reactor solution. In a preliminary experiment in which the reactor was completely open to the atmosphere, a similar mixture of chlorate and 83% sulfuric acid could be heated to 102°C. without exploding.

The reaction of 70% and 83% sulfuric acid with sodium chlorate solution was also carried out by slowly adding the sodium chlorate solution to acid already preheated to the reaction temperature rather than mixing at room temperature and then heating. The yield of sodium perchlorate was not appreciably affected by this change in reaction technique. However, the composition of the evolved reactor vapors was radically changed. With 70% sulfuric acid, the chlorine dioxide content dropped from about 24% to 0% (76% to 100% Cl_2), and with 83% sulfuric acid, the chlorine dioxide content dropped from about 88% to 0% (12% to 100% Cl_2). A number of experiments were also carried out in which air was substituted for the nitrogen used in flushing out the reaction vessel. This change had no effect on the yield of perchlorate or the composition of the reactor vapors.

One advantage in using 83% sulfuric acid for carrying out the disproportionation reaction is that considerably less unreacted sodium chlorate remains in the reaction mixture. The presence of an appreciable amount of unreacted sodium chlorate could cause difficulties in the separations for the recovery of perchlorate as discussed in section B2 of this report. At the end of an average reaction period of 4.5 hours, approximately 2% sodium chlorate remains unreacted. In contrast, with 70% sulfuric acid, approximately 15% sodium chlorate remains unreacted after 4.5 hours. This is somewhat counterbalanced by the possibility of the reaction with 83% sulfuric becoming violent in case the reaction temperature is not closely controlled.

It has been established in a few experiments that perchlorates may be made by heating sodium chlorate with perchloric acid. When reacting 60.3% perchloric acid with concentrated (650 g./ 1.) sodium chlorate solution, the mixture must be heated to 93°C. to obtain an appreciable conversion (16%) of the sodium chlorate to perchlorate. With 70.7% perchloric acid, 32% of the sodium chlorate can be converted to perchlorate at 69°C., which practically equals the best yield obtained using sulfuric acid. The reactor vapors in this case were found to be 98% chlorine dioxide. Raising the reaction temperature with 70.7% perchloric acid to 93°C. did not increase the yield of perchlorate. In the above reactions, the initial $HClO_4/_{NaClO_3}$ weight ratio with 60.3% perchloric acid was 3.5 and with 70.7% acid it was 4.5. The batch charge in each case was 94.2 mls. of perchloric acid of the given strength and 38.5 mls. of a 650 g./1. $NaClO_3$ solution (25 gms. $NaClO_3$).

2. Recovery of Perchlorate

The following methods of recovering perchlorate from solutions resulting from the disproportionation of chlorate in strong acid solution are being considered:-

(1) fractional crystallization
(2) precipitation of potassium perchlorate or ammonium perchlorate by the addition of potassium chloride or ammonium chloride.
(3) addition of anhydrous HCl to precipitate sodium ion as sodium chloride, filtering, and heating to drive off excess HCl. Pure perchloric acid should remain when it is used as the strong acid in the disproportionation of chlorate.
(4) same as (3) except vacuum distillation will be necessary to separate perchloric acid from the concentrated sulfuric acid when sulfuric acid is used as the strong acid in the disproportionation of chlorate.
(5) vacuum distillation of perchloric acid from solutions resulting from the disproportionation of chlorate in strong sulfuric acid. Even if this is possible,

> sodium will remain behind in the still residue as sodium acid sulfate. This salt may be removed by cooling the still residue, but some acid values would then be lost.

Method (1) (fractional crystallization) was shown to be impractical since solubility studies indicated that sodium perchlorate was too soluble at 0°C. in sulfuric acid solutions to be crystallized out of solutions of the low perchlorate concentration resulting from the disproportionation of chlorate in concentrated sulfuric acid solution.

Method (2) (precipitation of perchlorates) has shown considerable promise in work to date.

The following method was found to yield about 90% of the perchlorate present in the disproportion reactor solution as ammonium and potassium perchlorate. Up to 45% of the perchlorate can be recovered as the ammonium salt and about 45% as the potassium perchlorate by the following procedure:

> For every mol of sodium perchlorate in the reactor solution add 1.3 mols of ammonium chloride as the dry salt. If all of the solid does not dissolve heat to 60°C. for fifteen minutes, and stir constantly. Cool to 2°C. and filter while cold through a sintered glass funnel using vacuum. The precipitate is removed and slurried with ice water, using about 1/7 of the original solution volume, filter and wash with cold water using 1/80 of the original solution volume. The ice water precipitate is again slurried with about 1/14 of the original solution volume, filtered, washed as before, and vacuum dried. This will yield about 45% of the perchlorate present as ammonium perchlorate, estimated to contain less than 1% of sulfate.
>
> The combined filtrate from the above preparation is warmed to 60°C. and one mol of potassium chloride added for each mol of sodium perchlorate present in the original solution. After fifteen minutes the solution is cooled to 2°C. and filtered and washed as in the ammonium perchlorate precipitation except that all washing and filtering is done at room temperature. This will yield another 45% of the perchlorate as the potassium salt.

Method (3) (addition of anhydrous HCl) has not yet been thoroughly studied. However, preliminary experiments indicate that about 70% of the sodium ion remaining in the filtrates from the ammonium and potassium perchlorate precipitations may be precipitated as sodium chloride from the sulfuric acid solution by saturating it with anhydrous HCl.

Method (4) has not been experimentally studied to date.

Method (5) (vacuum distillation of perchloric acid) has been shown to be practical. By working with a synthetic reactor solution of the following composition:

$NaClO_4 \cdot H_2O$ - 90.2 grams
Na_2SO_4 - 91.0 "
H_2SO_4 (95.5%) - 435 mls.
H_2O - 572 "
Total volume = 1000 mls.

it was found that 95% of the perchlorate could be recovered as perchloric acid by vacuum distillation. In a typical run 250 ml. of the synthetic reactor solution was charged into a standard distillation apparatus. To prevent bumping and the formation of solid hydrates of perchloric acid steam was slowly bled into the boiler through a capillary tube. At a vacuum of between 27 and 27 1/2 inches the first condensate of water was observed between 41°C. and 45°C. vapor temperature. This water cut was removed from the liquid receiver and the still temperature slowly raised. At a pot temperature of 128°C. and a vapor temperature of 92°C., perchloric acid started to distil over and was complete when the pot reached 196°C. and a vapor temperature of 116°C. This cut of 36.5 gm. was found to be 41.6% perchloric acid and 2.9% sulfuric acid. The residue of 206.5 gm. was found to be 95.1% sulfuric acid (based on $SO_4{}^=$ content) with 2% perchloric acid.

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UNCLASSIFIED

EXPERIMENTAL WORK RECORDED IN RESEARCH NOTEBOOKS:

1217:	196 - 200
1258:	1 - 200
1289:	1 - 97

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