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PENNSYLVANIA SALT MANUFACTURING COMPANY

FIRST QUARTERLY RESEARCH REPORT

1953

PROJECT NR 352-304/2-1-52

CONTRACT NONR-807(00)

Sodium Perchlorate: Research Leading Toward the Development of Selected Methods to Produce Sodium Perchlorate Without the Use of Platinum

by

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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

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) The use of lead dioxide coated anodes

(3) The disproportionation of sodium chlorate in acid solution

SUMMARY

1. This report covers the work done during the months of January, February and March, 1953, under Contract NONR-807(00) which calls for research on selected methods as recommended by Project NR 352-304/2-1-52, to produce sodium perchlorate without the use of platinum.

Silicon-Silicon Carbide

2. To date, no satisfactory silicon-silicon carbide composition has been found for use as anode material in the chlorate-perchlorate cell.

3. Most of the Carborundum Company anode samples have shown the spalling or polarization characteristic found before, and a few samples exhibited rapid erosion as reported in Project NR 352-304/2-1-52.

4. The extruded Durhy #2 composition quenched in molten lead and the 90% silicon-10% silicon carbide composition, previously reported as promising (Project NR 352-304/2-1-52), were investigated further and were found unsatisfactory after a few hours of operation.

5. The following calcined materials impregnated with silicon; untempered Masonite board, Homasote and Compreg, were found to operate at a low voltage and to make perchlorate at a fair current efficiency. However, after a few hours of operation these specimens slowly polarized.

6. Certain of the non-eroding silicon-silicon carbide compositions show promise as base materials for massive lead dioxide plates.

Lead Dioxide

7. Massive lead dioxide electrodes have been successfully electroformed from a lead nitrate plating bath in shapes and sizes suitable for use in the chlorate-perchlorate cell.

8. Tantalum has been the most satisfactory base material used to date for the electrodeposition of lead dioxide, since it is not eroded by chlorate-perchlorate cell electrolyte, which is able to seep through pores of even massive lead dioxide.

9. Metals such as nickel, Monel, copper and iron, when used as bases for lead dioxide deposits, are rapidly eroded in the chlorate-perchlorate cell.

10. Synthetic magnetite, silicon and Durhy materials had shown some promise as lead dioxide base materials in previous preliminary tests.

11. Massive lead dioxide anodes have been tested in the chlorate-perchlorate cell at 3 to 10 amperes for periods of up to 27 days with no failures and little or no erosion.

12. Massive lead dioxide anodes at a current density of 0.1 amp/cm^2 operated at a current efficiency of 50 percent in the sodium chlorate concentration range of 600 to 100 g./l. At 0.2 amp./cm^2, the current efficiency rose to from 65 to 70 percent.

13. Use of the tantalum base as current carrier to the lead dioxide in the chlorate-perchlorate cell resulted in anode heating with even moderate currents.

14. The use of metal pressure plates and clamps as current contacts against the lead dioxide proved inadequate in preventing heating in the contact area.

15. The most satisfactory current contact consisted of massive lead dioxide plated over a base assembly composed of nickel wire wound around or otherwise attached to the upper end of tantalum rod, plate or screen. The free ends of the nickel wire then served to carry the current into the lead dioxide in the chlorate-perchlorate cell. The upper end of the lead dioxide anode containing the nickel wire is above the sodium chlorate electrolyte. (See No. 8).

16. Anodized lead tubing was rapidly eroded in the chlorate-perchlorate cell.

<u>Miscellaneous Anode Materials</u>

17. The following anode materials were found to be satisfactory in the work done in 1951 and 1952: tantalum carbide containing 17% platinum by weight; the mineral plattnerite, and naturally occurring massive lead dioxide; and platinum-plated tantalum sheet.

18. Samples of bearing materials (carbon impregnated with various metals), silicon ferrite, impervious graphite, natural graphite, gold and silver were found to erode rapidly.

19. Manganite ($Mn_2O_3 \cdot H_2O$) showed very little erosion.

20. A nickel ferrite boule showed no appreciable erosion, but conversion of chlorate to perchlorate was very low.

21. Polished plate glass samples with a conductive film on one side failed rapidly.

22. Of three different samples of tin oxide blocks, one showed no appreciable erosion with operation at about 50% current efficiency.

23. Samples of conducting glasses and refractories either eroded or operated at a very high cell voltage.

24. Samples of pressed and fired mixtures of lead dioxide and magnetite showed considerable mechanical disintegration.

25. Several thousand minerals were tested for electrical conductivity. A few of the more conductive ones have been selected for testing, and when these tests have been evaluated, a critical selection will be made from the original list of conducting minerals.

Disproportionation of Sodium Chlorate in Strong Acid

This phase of the project is to be covered in a separate final report.

CONCLUSIONS

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

2. All silicon-silicon carbide compositions tested to date are unsatisfactory as anode materials.

3. Massive lead dioxide generates perchlorate at high current efficiency and with very little erosion.

4. Considerable progress has been made in overcoming the greatest deterrent to the use of lead dioxide electrodes, which is the lack of a good electrical contact between the lead dioxide and the current lead of the chlorate-perchlorate cell.

5. More work is necessary on the current contact problem before massive lead dioxide can be used in commercial size cells.

RECOMMENDATIONS

It is recommended that:

1. Testing of silicon-silicon carbide compositions as anode materials be curtailed.
2. Increased emphasis be placed on developing the massive lead dioxide anode.
3. Testing of miscellaneous anode materials continue.

LABORATORY STUDY

I. Electrochemical Oxidation of Sodium Chlorate

A. Silicon-Silicon Carbide Mixtures as Anodes

1. Method of Preparation

The anode materials submitted to Pennsalt for testing by the Research and Development Division of the Carborundum Company consisted primarily of compositions of silicon and silicon carbide. These compositions have been given the trademark name "Durhy" by the Carborundum Company. Two general methods of forming these materials were followed:

(a) Cold pressing a mixture of silicon and silicon carbide followed by sintering in a protective atmosphere. Variations in these compositions were made by changing the silicon-silicon carbide ratio and also by combining addition agents in the mix before pressing. This product is designated Durhy #1.

(b) Impregnation of a carbonaceous body with silicon metal by placing the body into a bath of superheated molten silicon metal. The silicon metal impregnated the carbonaceous body and reacted with it to form silicon carbide, resulting in a body whose components are silicon carbide, silicon and some free carbon. This material is called Durhy #2. Variations in compositions in the Durhy material were made by additives to the silicon metal and by forming carbon bodies from different materials by carbonization.

Some anodes were treated thermally, chemically and physically to produce variations in surface and internal structures (1)

2. Summary of Previous Work Done Under 1951 Project NR 352-263/2-19-51 and 1952 Project NR 352-304/2-1-52.

In 1951 screening tests and the operation of a 10 ampere cell showed that Durhy #2 (silicon-silicon carbide mixtures) produced perchlorate with little or no normal surface erosion; however this material was always seriously damaged by cracking and shattering upon electrolysis. This effect was particularly noticeable at the top level of the electrolyte. With Durhy #1, polarization of the anode rapidly occurred.

In 1952, 52 samples representing 24 different kinds of materials were obtained from Carborundum Company under the Pennsalt-Carborundum contract agreement. After testing as anodes in the chlorate-perchlorate cell, most of these samples again showed the spalling or polarization characteristic found before, and a few samples exhibited rapid erosion. However, an extruded Durhy #2 composition quenched in molten lead, and a 90% silicon-10% silicon carbide composition showed sufficient promise to be investigated further

(See Work Done in 1953). Up to the end of 1952 no satisfactory silicon-silicon carbide composition for use as anode in the chlorate-perchlorate cell had been found.

3. Work Done in 1953

During the period from January 1st to March 31st, about 200 samples representing about 80 different kinds of materials were received from the Carborundum Company and tested in a small beaker-type chlorate-perchlorate cell.

In summary, it was found that these materials showed considerable improvement over those tested previously in that certain types polarized far less rapidly than before, and others operated at low cell voltage, making perchlorate for a considerable length of time before exploding or spalling. The promising materials found were: calcined, untempered Masonite, calcined Homasote and calcined Compreg, all impregnated with silicon.

The Durhy #2 quenched in molten lead has been eliminated from further consideration (See Work Done in 1952), since the residual lead content was shown to account for its early quiet operation. After the lead is eroded away, the quenched electrodes behave like unquenched Durhy #2. No further work is contemplated with these lead quenched Durhy #2 compositions because of their exploding and spalling characteristic after their lead content has been removed.

To date no entirely satisfactory silicon-silicon carbide composition has been found for use as anode material in the chlorate-perchlorate cell.

The detailed tests of silicon-silicon carbide materials (*) for 1952 and 1953 are shown in the following tables according to the different categories given by the Carborundum Company:

No.	Category
1	Cold pressed and sintered Si-SiC series
2	Silicon alloy impregnation
3	Variations in carbon bases
4	Heating and quenching treatments
5	Surface treatments, chemical and physical, and atmospheres
6	Impregnants (other than silicon) and coatings
7	Cast silicon
8	Variations in physical dimensions
9	Coated graphite or carbon
10	Miscellaneous

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These anode materials were tested in small beaker type cells (400 ml) each equipped with a glass cooling coil. By circulating tap water through the glass cooling coil, the sodium chlorate electrolyte (600g/1) was kept at a temperature of about 12°C. Two stainless steel cathodes were used, being held in place by a Plexiglas cell lid. Whenever possible, four to six cells were operated in series.

(*) Each sample was numbered consecutively with the category number as a prefix.

Category No. 1 - Cold Pressed and Sintered Si-Si C Series

The silicon-silicon carbide compositions fired in an atmosphere of carbon monoxide either gave very little erosion or no erosion at all and no spalling. A few very small explosions were observed with some samples. Similar compositions fired in a helium atmosphere behaved like the carbon monoxide treated compositions with very little erosion and no explosions. The cell voltage seemed to increase about three times faster with the helium treated compositions than with the carbon monoxide treated ones (See Figure 1). Thus it appears that the carbon monoxide has a beneficial effect.

However, the high specific resistivity and polarization characteristic of these materials eliminates them from consideration.

The beta silicon carbide, silicon and carbon mixture (No. 1-33) and the silicon, silicon carbide and manganese dioxide mixture (No. 1-31) eroded very rapidly (Table I).

Category No. 2 - Silicon Alloy Impregnation

All the anode samples in this group exploded, causing early and complete failure of the anode (see Table II).

Category No. 3 - Variations in Carbon Bases

Of this group, samples of calcined untempered Masonite board, impregnated with silicon (No. 3-7) behaved well, operating with no explosions and no erosion at about 30% current efficiency. However, there was a gradual increase in cell voltage.

The following calcined materials impregnated with silicon behaved as follows: Wood doweling, no noticeable erosion, rapid polarization; bamboo, erosion with one sample finally breaking off at electrolyte level, about 60% current efficiency; Homasote, slow polarization, a few explosions blew off some particles of anode material; manila rope, slow polarization, failed by breaking off at electrolyte level; sash cord, slow polarization, erosion; Compreg, no erosion, cracked at electrolyte level; mailing tube, erosion observed; and hardwood charcoal, explosions and heavy erosion noted.

All of the porous carbon and graphite samples impregnated with silicon eroded rapidly with no cell explosions.

The Durhy material made by siliconizing a carbon body formed by extruding a mixture of wheat flour and carbon powder showed severe spalling. Also the Durhy material made by siliconizing a carbon body formed by casting polarized and showed slight spalling (see Table III).

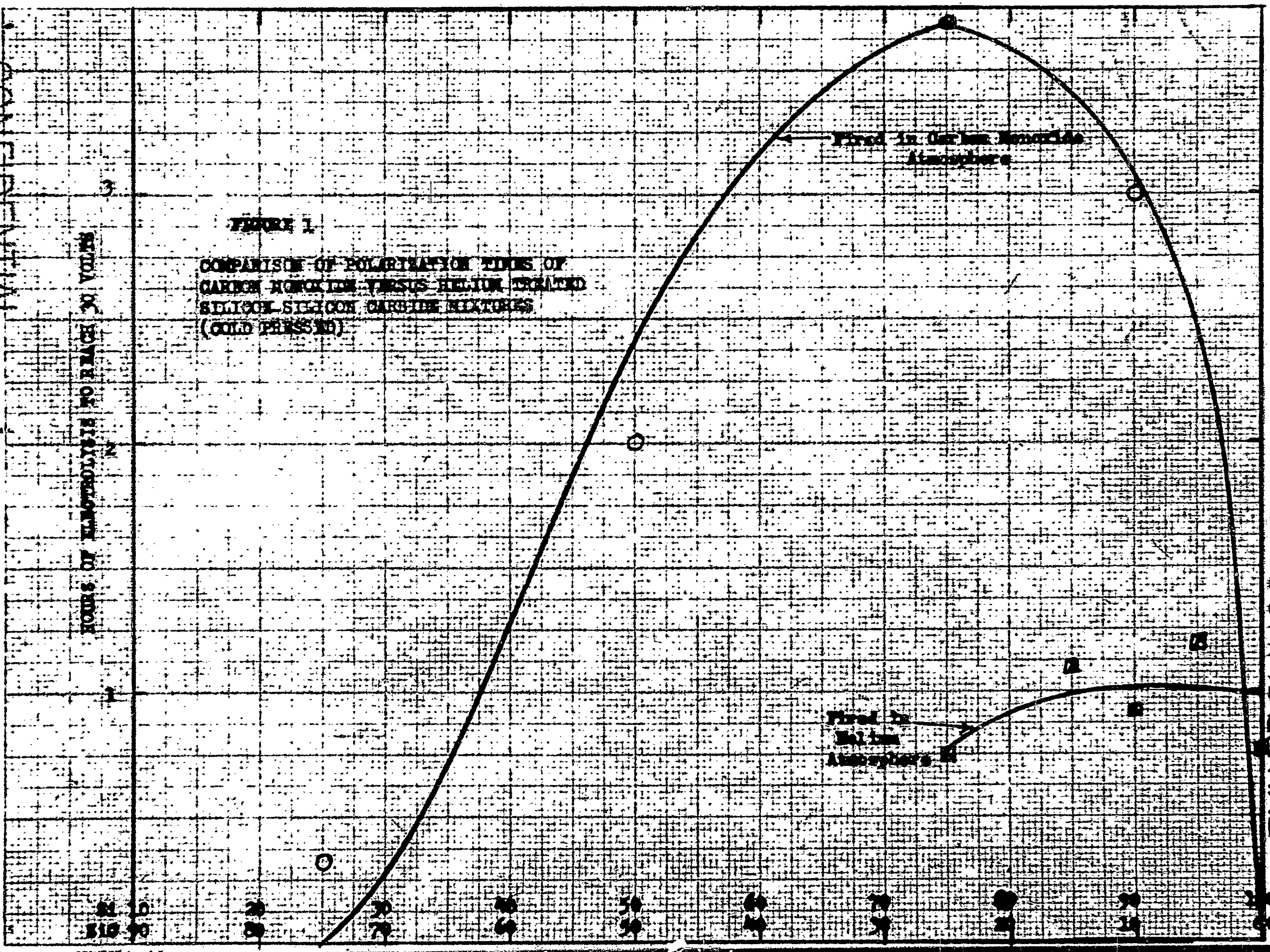

FIGURE 1

COMPARISON OF POLARIZATION TIMES OF
CARBON MONOXIDE VERSUS HELIUM TREATED
SILICON-SILICON CARBIDE MIXTURES
(COLD PRESSED)

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TABLE I
COLD PRESSED AND SINTERED Si - SiC SERIES
CATEGORY NO. 1

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Fired 2 hrs. at 1350°C. in atmosphere of carbon monoxide:-							
100% Silicon (200 MXD)	1-17	543,000	1.95	100	6.6-28	11-27	No noticeable attack on anode at end of 9.5 hrs. electrolysis. Increase in cell voltage from 6.6 - 28 v during this period.
100% Silicon (200 MXD)	1-19	1,178,000	4	200	24-36	- -	Cell operation stopped after 6 min. because of high cell voltage.
100% Silicon	1-25	- -	4	200	20-35	12	No erosion. Increase in cell voltage from 20-35 v in 18 min. Operation stopped because of high cell voltage.
50% silicon (200 MXD); 50% silicon (30 grit)	1-18	295,000	2.2	100	6.3-24.0	11-15	No appreciable erosion over 4 hr. period. Cell voltage increased from 6.3v to 24.0 v during this time.
50% Si (200 MXD) 50% Si (30 grit)	1-24	135,800	4	200	- -	- -	Sample became red hot at portion above electrolyte after about 1 minute of operation.
95% Si (200 MXD) 5% SiC (100 grit)	1-26	756,000	3.7(47min) 1.8(12hrs 32 min)	200 100	11-31.5	12-20	Stopped when cell voltage reached 31.5 volts after 13.3 hours of operation. No explosions and no erosion.
90% Si (200 MXD) 10% SiC (100 grit)	1-27	574,000	3.7(53min) 1.8(12hrs 32 min)	200 100	11-30	12-20	Stopped when cell voltage reached 30 v after 13.5 hrs. operation. A few very small explosions caused small pieces to come from anode surface.

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TABLE I (continued) (1)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x10^{-6}	Average cell Current (amperes)	Anode Current Density (approx) ma/sq cm	Average cell Voltage	Cell Temp °C	Effect on Anode
90% Si (200 MXD) 10% SiC (100 grit)	1-16	476,000	2.0	100	7-27.5	11	Very little erosion at surface level of electrolyte. Increase in cell voltage from 7 to 27.5 volts over 4.5 hour period.
90% Si (200 MXD) 10% SiC (100 grit)	1-23	690,000	4	200	14-35	14-30	Small amount of erosion at electrolyte surface. Cell voltage increased from 14 to 35 volts in 3.75 hours. No explosions.
85% Si (200 MXD) 15% SiC (100 grit)	1-28	705,000	3.7(53min) 1.8(8 hrs 10 min)	200 100	11-32	12-20	Stopped when cell voltage reached 32v after 9 hrs. Few very small explosions caused small pieces to come from anode surface.
80% Si (200 MXD) 20% SiC (100 grit)	1-29	378,000	3.7(53min) 1.8(2 hrs 55 min)	200 100	14-35	12-25	Operation of cell stopped when cell voltage reached 35v with anode current density of 100 ma/sq.cm. after 3.8 hrs. A few very small explosions caused small pieces to come from anode surface.
75% silicon (200 MXD) 25% SiC (100 grit)	1-15	595,00	2.2	100	8.0-19.5	11-15	No appreciable erosion over 4 hr. period. Contact heated up which finally caused plastic cell cover to catch fire.
75% Si(200 MXD) 25% SiC (100 SGM)	1-20	753,000	4	200	18-35	14-46	Small amount of erosion at electrolyte surface. Cell voltage increased from 18 - 35 v in 4 hours. No explosions
75% Si 25% SiC (100 SGM)	1-30	- -	4	200	12-30	12	No appreciable erosion, Slight attack at electrolyte level. Increase in cell voltage from 12-30v in 3.5 hrs. Faint Explosions from cell.
50% Si (200 MXD 50% SiC (100 grit)	1-14	810,000	2.0	100	9-25	11	Anode ran hot with very slight erosion at surface level of electrolyte. Increase of cell voltage from 9v to 25v over 6 hour period of electrolysis.

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TABLE I (continued) (2)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. $x10^{-6}$	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C	Effect on Anode
50% Si (200 MXD) 50% SiC (100 SGM)	1-21	575,000	4	200	16-38	16	Cell voltage increased from 16 to 38 v in 2.5 hours. Anode lead became very hot. No erosion and no explosions.
25% Si (200 MXD) 75% SiC (100 grit)	1-13	893,000	2.0	100	11-27	11	No appreciable erosion over one hour period but cell voltage increased from 11 v to 27 v.
25% Si (200 MXD) 75% SiC (100 SMG)	1-22	654,000	4	200	16-35	16-30	Cell voltage increased from 16 to 35 volts in 20 minutes. Anode current lead became very hot. No erosion and no explosions.
Sintered at 1350°C for 2 hours in a helium atmosphere:- 100% silicon (200 MXD)	1-5	27,800	2.0	100	7-40	11-12	Very little erosion. Slow polarization (increase in cell voltage from 7-40 v over 5 hour period.
100% silicon (200 MXD)	1-7	879,000	4	200	15-36	26-36	No erosion. Increase in cell voltage from 15-36 v in 0.75 hr. Several cracks in portion of anode immersed in electrolyte at end of test.
50% silicon (200 MXD) 50% silicon (30 grit)	1-6	242,000	1.95	100	5.8-50	11	Increase in cell voltage from 5.8-50 v over 3 hrs. No noticeable erosion.
95% Si (200 MXD) 5% SiC (100 SGM)	1-8	80,400	4	200	8.0-35.0	36-30	No explosions and no erosion. Increase in cell voltage from 8.0-35.0v in one hour.
90% Si - 10% SiC	1-4	- -	4	200	14-20	18-43	Electrolyte drawn up within anode by wick action and reacts with anode clamp. Anode clamp area becomes hot. No appreciable attack on anode in 2 hours.
90% Si (200 MXD) 10% SiC (100 SGM)	1-9	90,500	4	200	9.0-39.0	20-43	No explosions and no erosion. Increase in cell voltage from 9.0-39.0v in one hour. When washed with tap water after run, anode mechanically disintegrated into layers.

TABLE I (continued) (3)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
85% Si (200 MXD) 15% SiC (100 SGM)	1-10	110,500	4	200	7.8-26.0	20-43	No explosions. Increase in cell voltage from 7.8 - 26 v in one hour. Mechanical disintegration of anode in layers. Electrolyte black.
80% Si (200 MXD) 20% SiC (100 grit)	1-11	60,500	1.8	100	4-35	12	No explosions and no erosion. Cell operation stopped when cell voltage reached 35v after 3.5 hours.
75% Si - 25% SiC	1-3	- -	4.6	200	23-26	35-30	Anode becomes hot at current lead clamp. Electrolyte drawn up within anode by wick action and attacks anode clamp.
75% Si (200 MXD) 24% SiC (100 SGM)	1-12	226,000	4	200	7.8-36.0	2-33	No noticeable erosion. Increase in cell voltage from 7.8 - 26.0 v in 0.83 hr. No explosions.
50% Si - 50% SiC	1-2	- -	4	200	26-35	25-30	Anode becomes hot at current lead clamp; electrolyte drawn up within anode by wick action & attack anode clamp.
25% Si - 27% SiC	1-1	- -	0.2	25	25	18	Surface erosion advanced after only 5 min. electrolysis. Electrode soaking for one hour before current was applied.
Cold pressed and sintered at 1350°C. for 2 hours in purified CO:- 72% Si (200 MXD) 8% SiC(100 grit SGM) 20% MnO2	1-21	164,000	2.64	125	5.2-30	-	Appreciable erosion particularly at electrolyte level. The outer walls came off in sheets, leaving the immersed area very rough with large pin holes. Increase in cell voltage from 5.2v to 30v after 8.75 hours operation.
80% Beta silicon carbide 14% Silicon (200 MXD) 6% Carbon, cold pressed and sintered at 1350°C for 2 hours in purified CO atmosphere.	1-33	178,000	2	98	4.7-7.0	12	Extremely heavy erosion, particularly at electrolyte level; bottom portion dropped off after 22 minutes of operation. No explosions.

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TABLE II
SILICON ALLOY IMPREGNATION
CATEGORY NO. 2

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Description of Anode Material	Sample No.	Specific Resistivity ohm-cm 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Cast stock impregnated with purified silicon	2-1	32,400	1.95	100	4.6-8.6	11	Exploding anode which finally blew in two. Very slight erosion noticed over 1.3 hr. period.
Cast stock impregnated with low calcium silicon	2-2	26,800	0.8-2.0	100	4.6-20.0	11	Exploding anode. Anode slightly attacked by explosions with some erosion material present in electrolyte.
Cast stock impregnated with low aluminum silicon	2-3	45,100	1.95	100	4.6-18.0	11	Crackling anode with finally a very loud explosion blowing anode sample in half. Some noticeable erosion.
Extruded stock impregnated with silicon containing:							
3% sodium chlorate	2-4	4,070	4	200	5.2-8.4	15-16	Exploding anode. About 1/4 of anode eroded away in 3 hrs. Electrolyte black.
5% sodium chlorate	2-5	4,490	4	200	5.6-9.6	15-16	Exploding anode. About 3/8 of anode eroded away in 3 hrs. Electrolyte black.
10% sodium chlorate	2-6	6,780	4	200	5.4-7.8	15-16	Exploding anode. About 1/2 of anode eroded away in 3 hrs. Electrolyte black.
20% sodium chlorate	2-7	4,530	4	200	5.5-7.8	15-16	Exploding anode. About 1/2 of anode eroded away in 3 hrs. Electrolyte black.
3% lead	2-8	5,430	4	200	5.6-12.0	15-16	Exploding anode; broke beaker after 1 hr. operation. Fainlly anode blew off 3/4" below electrolyte level. Electrolyte black.
5% lead	2-9	4,110	4	200	5.4-8.2	15-16	Exploding anode. About 3/8 of anode eroded away in 3 hrs. Electrolyte black.
10% lead	2-10	5,430	4	200	5.6-8.0	12	Exploding anode. About 1/2 of anode eroded away in 2.75 hrs. Electrolyte black.

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TABLE II (continued)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C	Effect on Anode
20% lead	2-11	3,810	4	200	5.6-9.1	12	Exploding anode. About 1/2 of anode eroded away in 2 hrs; an explosion broke cell beaker at end of period. Electrolyte black. With this, cell voltage immediately dropped and then gradually increased.
Extruded stock impregnated with silicon containing 5% lead dioxide	2-12	3,770	2	100	3.8-6.6	12	Appreciable anode erosion; anode exploded, finally breaking sample in half just below electrolyte level; electrolyte black from anode erosion.
Extruded stock impregnated with silicon containing 20% lead dioxide	2-13	3,570	2	100	3.9-7.3	12	Same as sample above (No. 2-12) with final failure caused by a loud explosion which broke anode in half.
Extruded stock impregnated with silicon containing 5% tungsten	2-14	3,570	2	96	4.0-6.8	12	Same as sample above (no. 2-12) with final failure caused by a loud explosion which broke anode in half
Extruded stock impregnated with silicon containing 20% tungsten	2-15	2,310	2	105	3.8-8.1	12	Same as sample above (no. 2-12) with final failure caused by a loud explosion which broke anode inhalf.
Extruded stock impregnated with silicon containing 5% $MoSi_2$	2-16	2,930	2	98	3.8-7.8	12	Appreciable anode erosion but with only one final explosion which broke anode inhalf after 3 hours.
Extruded stock impregnated with silicon containing 20% $MoSi_2$	2-17	2,310	2	100	3.9-8.0	12	Appreciable anode erosion; final explosion shattered glass cell and anode sample.

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TABLE III
VARIATIONS IN CARBON BASES
CATEGORY NO. 3

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	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.	3-1	- -	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	3-2		0.8-8	200	7-19	5-12	Blarized; slight spalling
			0.6-2.8	200	16-19	16-19	Polarized
Silicon impregnated National Carbon porous carbon #20	3-3	- -	4.5	200	6.5	15	Rapid erosion of anode, - electrolyte becomes black in 1/2 hour
Silicon impregnated National Carbon porous carbon #30	3-4	- -	4	200	6	21	Rapid erosion of anode, - electrolyte turns black with suspension of fine carbon in 1/2 hour.
Silicon impregnated National Carbon porous carbon #50	3-5	- -	4.6	200	6.4	16	Rapid erosion of anode, - electrolyte becomes black in 1/2 hour.
Silicon impregnated National Carbon porous carbon #60	3-6	- -	4.5	200	7	15	Rapid erosion of anode; electrolyte turns black in 1/2 hour.
Calcined untempered Masonite board, impregnated with silicon	3-7	1,980	2.0	100	5-19	14	No erosion, slow increase in cell voltage from 5-19 v over 6.5 hr. perio
Calcined untempered Masonite impregnated with silicon	3-7	26,000	1.8-2.1	180-186	5.5-23	12-20	Operated 27 hrs. without failure, 30% current efficiency at 16 hrs. No appreciable erosion seen.
Calcined untempered Masonite impregnated with silicon	3-7	22,500	3.0	222	6-21	12	No erosion and no explosions. Ran for 10 hrs. with the voltage going from 6v - 21v. Subsequent treatment with 50% HF did not help.

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TABLE III (continued) (1)

escription of Anode aterial	Sample No.	Specific Resistivity ohm-cm x 10-6	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
ational Carbon porous raphite impregnated with ilicon in the following rades:-		8,940	4	200	5-18	15-30	All of the silicon impregnated porous graphite samples eroded rapidly with no cell explosions. Grade 10 eroded the worst with erosion decreasing from Grade 10 to Grade 60
Grade 10	3-8						
Grade 20	3-9	3,560	4	200	5-11.0	15-16	See above
Grade 30	3-10	4,850	4	200	5.2-6.4	15-16.5	See Above
Grade40	3-11	5,120	4	200	5.2-6.1	15-16.5	See above
Grade 50	3-12	5,560	4	200	5.0-5.6	15-16	See above
Grade 60	3-13	6,580	4	200	5.0-5.6	15-16	See above
alcined wood doweling mpregnated with silicon	3-15	19,500	1.8	180	20-44	12	Increase in cell voltage from 20-44 v over 1 hr. period. No noticeable erosion. White film over all of immersed area.
alcined bamboo impregnated with silicon	3-16	23,300	1.8-2.1	205-211	5-10	12	After 18 hrs. operation small shreds of bamboo in bottom of cell. Finally broke off at electrolyte level after 27 hrs. operation. Showed erosion over most of area. About 60% current efficiency
Calcined bamboo impregnated with silicon	3-16	30,900	2.1	152	2.0-18	12	Operated 27.8 hrs. with gradual increase in cell voltage from 5-18v Erosion, with several small holes appearing at the end of period.

TABLE III (continued) (2)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Calcined Homasote impregnated with silicon	3-14	24,600	1.8	111	18-30.3	12	Cell operation stopped when cell voltage reached 30.3v after 9.5 hrs. operation. A few explosions blew off some particles of anode material. No attack at electrolyte level.
Calcined manila rope impregnated with silicon	3-17	30,300	3.0	155	2.0-18.0	12	This sample did not explode or erode. Increase of cell voltage from 5v - 18v over 8 hr. period of electrolysis. Sample failed by breaking off at electrolyte level.
Calcined sash cord impregnated with silicon	3-18	1,600	0.72	200	5.0-30.0	12	This sample showed signs of erosion all through the electrolysis. Some crackling plus shreds of anode flaking off was noted. Increase in cell voltage from 5v - 30 over 3 hr. period of electrolysis.
Calcined Compreg impregnated with silicon	3-19	33,900	3.0-3.7	121-150	6.4-11	12	After 11 hrs. of electrolysis, the sample cracked at electrolyte level while out of cell overnight. Small chunks were off anode after the 11 hrs. No erosion was noted.
Calcined mailing tube, impregnated with silicon.	3-20	- -	3.0	199	10-32	12	All of immersed area showed signs of eroding. About 6 holes were on the bottom half of sample, from electrolysis. Increase in cell voltage from 10v-32v over 1 hour of electrolysis.
Calcined hardwood charcoal impregnated with silicon	3-21	78,000	2.64	165	13.0-30.5	12	After 0.75 hrs. operation, small explosions started with resulting anode erosion coloring electrolyte black. Cell operated 13 hrs. with increase of cell voltage from 13.0 to 30.5v. Very heavy erosion during last 7.5 hrs.

Category No. 4 - Heating and Quenching Treatments

As may be seen from Table IV, all the samples of Durhy #2 given heating or quenching treatments operated with explosions, either causing chunks of anode material to fall off or causing the anode sample to blow apart, except the extruded Durhy #2 quenched in molten lead from 1350°C. (No. 4-6).

This lead quenched Durhy #2 behaved favorably, operating at low cell voltage for 14.5 hours with some erosion of the lead from the sample as evidenced by the muddy color of the electrolyte. At the end of this period there was an explosion, blowing off one large piece of anode. When the lead was removed from the sample by soaking in 35% nitric acid for 3 days, it behaved like Durhy #2 with frequent explosions. Thus it seems that the lead content of the original sample was responsible for the favorable behavior of this lead quenched Durhy #2 (see Table IV).

Category No. 5 - Surface Treatments, Chemical and Physical, and Atmospheres

Durhy #2 samples treated by an aqueous HF-HNO_3 mixture, by an aqueous HF solution and by a caustic solution showed rapid surface erosion and spalling. No explosions were observed.

Globar heating sections, treated by aqueous HF and by nitric acid eroded appreciably particularly at the electrolyte level with the samples finally breaking off at this point.

Extruded Durhy #2 tumbled in SiC grain and also in Al_2O_3 grain operated with severe spalling and numerous explosions in the cell.

Decarbonized Durhy #2 polarized as did a sample of Durhy surface-smoothed with a diamond wheel. The latter sample also showed slight spalling (see Table V).

Category No. 6 - Impregnants (other than silicon) and Coatings

The Globar heating sections impregnated with furfural (No. 6-1), with linseed oil (No. 6-3), with silicone water repellant (No. 6-5) and with paraffin (No. 6-7) operated at too high a cell voltage to be considered practical.

The Durhy #2 samples impregnated with linseed oil (No. 6-4), with silicone water repellant (No. 6-6) and with paraffin (No. 6-8) operated quietly at first in contrast to their usual behavior but after a few hours the customary spalling and explosions were again evident.

A Globar heating element, coated with platinum (No. 6-2) operated with the cell voltage increasing rapidly after one hour of electrolysis and with a slight erosion of anode surface (see Table VI).

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TABLE IV
HEATING AND QUENCHING TREATMENTS
CATEGORY NO. 4

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Durhy - made by siliconizing a carbon rod formed by extruding; annealed at 1350°C. for 8 hours	4-1	- -	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 sample No. 4-1 except annealed at 1350°C for 16 hours.	4-2	- -	3.3-5	200	6-9	17-20	Anode shattered into 3 large pieces.
			0.5-5	200	6-10	2-8	Anode shattered into 2 large pieces.
Durhy - same as sample No. 4-1 except annealed at 1350°C for 24 hours.	4-3	- -	3-5	200	5-9	14-17	Anode shattered into 3 large pieces.
			2.5-5	200	6-8	2-5	Anode shattered into 3 large pieces.
Durhy #2 (extruded) cooled from 1350°C to room temp. at 80° per hour	4-4	- -	4	200	10-18	20	Some explosions with spalling of anode surface within one hour.
Durhy #2 (extruded) quenched in H_2O from 1350°C.	4-5	- -	4	200	9-11	20	Several explosions within 1/2 hour resulting in shattering anode into several pieces.
Durhy #2 (extruded) quenched in molten lead from 1350°C.	4-6	- -	4	200	6	20	Very slight erosion - electrolyte turned brown gray. No spalling observed. Small amount of ppt. in electrolyte after 5 hrs. of electrolysis.
Extruded Durhy #2, quenched in molten lead from 1350°C.	4-6	17,800	2.6,3.0, 3.24	177,200, 205	4.8-14.0	12	After 14.5 hrs. electrolysis with cell voltage increasing from 4.8-7.0v and with some erosion of the lead from the sample as evidenced by the muddy color of the electrolyte, one large piece of anode was blown off. Sample was then soaked in 35% HNO_3 for 3 days and after 15 min. of operation in cell, there was a small explosion. Then soaked in H_2O for 24 hrs. and tried in cell again with frequent explosions, finally causing anode to break in half at electrolyte level. (See sample No. 4-11)

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TABLE IV (continued)

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Effect on Anode
Durhy #2, heated at 1600°C in an Induction Furnace for 2 hours.	4-7	- -	4.5	200	5.5-20	17-32	Surface spalling with explosions begins after 2-1/2 hrs. electrolysis. Voltage rises to 14v in same period.
Durhy #2, extruded stock, heated at 1600°C. for 5 hrs. in an oil fired kiln.	4-8	21,800	2.0	100	4.8-7.2	11-44	Exploding anode with chunks of anode being eroded off. After 3 hrs. anode blew apart a little below electrolyte surface with 1 large explosion breaking beaker containing electrolyte.
Durhy #2, extruded stock, fast (high temp) impregnation	4-9	3,460	2.0	100	4.6-12.0	11-14	Erosion, turning water-white electrolyte gray. After 2.5 hrs. anode blew apart above electrolyte surface with one large explosions.
Durhy #2, extruded stock, slow (low temp) impregnation	4-10	6,080	2.0	100	4.6-7.0	14	Frequent explosions with loose anode material being suspended in electrolyte After 6 hrs. anode blew apart and broke beaker.
Cast Durhy #2, quenched in molten lead from 1350°C.	4-11	128,000	3.24	213	5.8-15.0	12	Exploding anode with small chunks of anode material falling off. Increase in cell voltage from 5.8-15.0 v in about 1 hr. Explosions finally blew sample in half after about 1 hr. of operation. Second sample behaved similarly.
Extruded Durhy #2, quenched in molten sodium nitrate from 1350°C.	4-12	41,800	3.24	184	12.0	12	Exploding anode. Anode blew off slightly below electrolyte level after 10 min operation. Second stage behaved similarly.

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TABLE V
SURFACE TREATMENTS, CHEMICAL AND PHYSICAL, AND ATMOSPHERES
CATEGORY NO. 5

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x10^{-6}	Average Cell Current (amperes) *	Anode Current Density (approx.) ma/sq.cm.	Avarage Cell Voltage	Cell Temp °C.	Effect on Anode
Durhy - made by siliconizing a carbon body formed by casting; surface smoothed by grinding on a diamond wheel	5-1		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 #2 put through a decarbonizing treatment - 50% reduction in free carbon	5-2		0.5-1.3	200	13.4-28	26	Polarized
			1.0-2.8	200	10.0-27.6	26-28	Polarized
Durhy #2 (extruded) tumbled in SiC grain for 50 hours	5-3		4	200	6-10	19-26	Severe spalling with numerous explosions in cell.
Durhy #2 (extruded tumbled in Al_2O_3 grain for 50 hours	5-4		4	200	5-11	20	Severe spalling within one hour resulting in shattering anode into several pieces.
Durhy #2, treated in HF + HNO_3 + H_2O solution	5-5		4.5	200	5.1-9.2	20	Rapid surface erosion and spalling; no explosions noted.
Durhy #2, treated in HF + H_2O solution.	5-6		4.5	200	5.1-7.6	17	Severe spalling of surface with numerous explosions after 2 hrs electrolysis. There was also a moderate normal surface erosion.
Durhy #2, treated in NaOH solution.	5-7		4.5	200	5.2-8.4	20	Rapid surface erosion and spalling; no explosions noted.
"Globar" heating section treated in H_2O and HNO_3	5-8	136,000	2.64	200	6.6-36	12	Increase in cell voltage from 6.6 - 36 v after 1 hr. operation. Appreciable erosion particularly at electrolyte level with sample finally breaking off at this point.
"Globar" heating section treated in HF and H_2O	5-9	124,000	2.64	200	6.0-34	12	Appreciable erosion particularly at electrolyte level with sample finally breaking off at this point. Increase in cell voltage from 6.0-34v after 1 hour operation.

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TABLE VI
IMPREGNANTS (OTHER THAN SILICON) AND COATINGS
CATEGORY NO. 6

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Globar Heating Element Furfural impregnated, treated with HCl, then calcined at 900°C.	6-1	--	0.5	25	28	17	Anode resistance is too high. A powdery substance separates from anode and floats on electrolyte surface.
Globar heating element, coated with Pt. by heating in H_2PtCl_6 solution	6-2	--	4.5	200	10-24	15	Voltage rises rapidly after 1 hr electrolysis; slight erosion of surface; anode is hot at current contact.
Globar heating section impregnated with linseed oil	6-3	9,350	2.2	100	60	21-29	Shut off after 1/2 min operation because of high cell voltage required.
Durhy #2(extruded) impregnated with linseed oil.	6-4	4,320	2.3	100	6.3-9.0	12-14	After 2.25 hr. anode had a thick sticky covering, probably linseed oil. At 3.25 hrs exploding anode broke cell beaker. At 4.14 hrs exploding anode broke new cell beaker. Evidence of spalling on anode sample.
Globar heating section impregnated with silicone water repellant #DC 1107	6-5	37,400	2	100	70	17.5	Anode became very hot after 2 min. operation. Shut off because of high voltage required to operate cell.
Durhy #2(extruded) impregnated with silicone water repellant #DC 1107	6-6	4,190	2.3	100	6.4-20	12-14	Exploding anode after 2.5 hrs quiet operation. After 7.75 hrs, evidence of severe spalling of anode. Cell voltage decreased after exploding anode blew chunks of material off.
Globar heating section impregnated with paraffin	6-7	18,700	2.2	100	30-34	21-47	Ran 12 min. Smoking anode lead contact. Shut off because of high cell voltage required.
Durhy #2(extruded) impregnated with paraffin	6-8	4,280	2.3	100	4.7-13.0	12-14	Exploding anode after 2.5 hrs quiet operation finally breaking cell beaker and cooling coil at 3.25 hrs. Anode also broke in half.

Category No. 7 - Cast Silicon

A cast silicon metal rod (No. 7-1) polarized almost immediately. A rod of cast silicon metal that had been melted in a helium atmosphere (No. 7-2) behaved similarly, showing no erosion but polarizing rather rapidly (see Table VII).

Category No. 8 - Variations in Physical Dimensions

A sample of three thicknesses of Masonite, welded together by impregnation with silicon (No. 8-2) failed because the individual layers separated (see Table VII).

Category No. 9 - Coated Graphite or Carbon

Graphite rods coated with silicon carbide crystals (No. 9-1) eroded through the SiC coating, and then there was severe erosion of the graphite (see Table VII).

Category No. 10 - Miscellaneous

In this group, the carbonized Masonite (No. 10-2), the non-porous graphite heated in molten silicon (No. 10-4), and the Refrax materials (No. 10-5 and 10-6) eroded. The cold pressed silicon carbide recrystallized in helium (No. 10-3) and the Durhy No. 1 rods with no free carbon (No. 10-1) showed no appreciable erosion but operated at increasingly high cell voltage (see Table VIII).

B. Lead Dioxide, Including Massive Plates

1. Summary of Previous Work Done Under 1951 Project NR 352-263/2-19-51 and 1952 Project NR 352-304/2-1-52

In 1951 lead dioxide plating was attempted from the following baths: lead nitrate, lead nitrate and aluminum nitrate, lead acetate, and alkaline lead tartrate. No satisfactory adherent deposit of lead dioxide could be made on steel from a lead nitrate bath. Several baths based on lead acetate proved unsatisfactory for plating on steel, Monel, nickel or tantalum sheet. Addition of gelatine to the plating baths did not seem beneficial at the low current densities used. An alkaline lead tartrate plating bath was developed to give adherent deposits of lead dioxide on the above base metals. A few screening tests of lead dioxide plated electrodes were carried out in a small beaker chlorate-perchlorate cell without conclusive results.

In 1952 it was shown that anodes of electrodeposited lead dioxide on base materials such as Monel, nickel and steel, which are themselves easily eroded in the chlorate-perchlorate cell, are not practical, since the base material is rapidly disintegrated as soon as the continuity of the lead dioxide is broken, even at a pinpoint. Brief attempts to prepare a pure electrodeposited lead dioxide anode by depositing a heavy coat of lead dioxide on copper and steel and then dissolving away the base metal with nitric

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TABLE VII
CAST SILICON
CATEGORY NO. 7

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Cast silicon metal rod	7-1	- -	0.2-2	200	Greater than 20	3-5	Polarized almost immediately
Rod cast silicon metal, melted in helium atmosphere	7-2	2,600	2.64	147	26-70.0	12-30	No erosion. Increase in cell voltage from 26 to 70 after 1.5 hours of operation.
	VARIATIONS IN PHYSICAL DIMENSIONS - CATEGORY NO. 8						
3 thicknesses of Masonite welded together by impregnating with silicon	8-2	17,850	1.8	113	4.4-19	12-15	After 6.3 hrs operation, individual layers of masonite began falling off and cell began exploding. After 9.8 hrs. operation sample had completely broken off at electrolyte level.
	COATED GRAPHITE OR CARBON - CATEGORY NO. 9						
Graphite rods coated with silicon carbide crystals.	9-1	- -	2.9-3	200	6.8-9.4	24-25	Eroded through SiC coating; graphite severely eroded.
		- -	2.8-2.9	200	5.4-14	25.27	Severe erosion of graphite; electrolyte black.

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TABLE VIII
MISCELLANEOUS
CATEGORY NO. 10.

Description of Anode Material	Sample No.	Specific Resistivity ohm-cm. x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp °C.	Effect on Anode
Durhy #1 rodes; no free carbon in these rods.	10-1	- - -	0.2-1	200	20-22	6-9	All samples rapidly polarized in 10-15 min. No appreciable erosion.
Carbonized Masonite	10-2	47,200	2.5	200	9.5-14.0	- -	Eroded particularly at electrolyte surface, finally breaking apart at that place.
Cold pressed silicon carbide recrystallized in helium	10-3	2,200,000	3.7	178	20-30	12	No appreciable erosion. Heavy smoke from anode. Increase in cell voltage from 20v - 30v over 5 min period of electrolysis. No explosions observed during this time.
Non-porous graphite received from Pennsalt, heated in molten silicon	10-4	1,280	3.0	194	4.6-9.0	12	Very rapid erosion of sample. Electrolyte black with suspension of anode material after 34 min operation. Increase in cell voltage from 4.6v - 9.0 v over 3.5 hrs. electrolysis. Anode failed by complete erosion of all immersed area.
Refrax 10, Si_3N_4 bonded silicon carbide heated to 1900°C. to decompose the Si_3N_4.	10-5	255,000	2	95	5.0-15.0	12	Extremely heavy erosion, particularly at electrolyte level; bottom of sample dropped off after 1 hr operation. No explosions.
Refrax 20, Si_3N_4 bonded silicon carbide heated to 1900°C to decompose the Si_3N_4.	10-6	417,000	2	100	7.4-32.0	12	Extremely heavy erosion, particularly at electrolyte level; bottom portion dropped off after 1-1/3 hrs operation. No explosions.

and hydrochloric acids respectively were unsuccessful due to simultaneous attack on the lead dioxide.

Several baths were developed for plating lead dioxide on a tantalum base. Normally, tantalum immediately polarizes anodically in most electrolytes, including that of the chlorate-perchlorate cell. The baths from which the highest quality lead dioxide deposits on tantalum could be obtained were an alkaline lead tartrate (#7M), lead nitrate (#LN-2) and lead perchlorate (#LP-1). The life of lead dioxide plated tantalum anodes in the chlorate-perchlorate cell varied widely and erratically. In most cases, the anodes failed due to the lead dioxide falling loose rather than smoothly eroding. The maximum chlorate-perchlorate cell life of these lead dioxide coatings, which varied in thickness from 0.002 to 0.008 inches, was eight days.

Lead dioxide was readily plated on Durhy #2 base (see Section I-A-1) and on a synthetic magnetite base. A preliminary testing of these plated anodes in the chlorate-perchlorate cell gave sufficient promise to warrant further study. Deposition of lead dioxide on Durhy #1 base (Section I-A-1) could not be satisfactorily accomplished.

A smooth, adherent electrodeposit of lead dioxide on cast silicon was easily obtained, and the electrode operated smoothly in the chlorate-perchlorate cell until the silicon shattered as the continuity of the thin lead dioxide deposit was broken.

Plattnerite, a rare, naturally occurring massive lead dioxide, operated smoothly as anode in the chlorate-perchlorate cell at a low voltage without shattering and with very little erosion.

2. Work Done in 1953

Continued plating and testing of relatively thin lead dioxide coatings (about 0.01 inch maximum thickness), on tantalum produced the same erratic results as noted in 1952. One electrode ran for 12.2 days in the chlorate-perchlorate cell at a current density of 0.1 amp./cm.^{2}, with an efficiency of 48.9 percent. A number of other electrodes plated in the same manner operated for as short a time as a few hours before failure by tantalum polarization and a breaking apart of the lead dioxide coating.

a. Plating Massive Lead Dioxide

In view of the promising results obtained in a preliminary test of a naturally occurring massive lead dioxide as anode in the chlorate-perchlorate cell, effort was concentrated on electroplating lead dioxide in massive forms on various base metals. Table IX shows in detail the plating conditions for these massive electrodes including types of base materials and thicknesses and weights of deposits. First efforts were directed toward plating the lead dioxide on only one side of a flat base metal by blanking off the edges and back with an inert material such as Plexiglas. It was hoped to strip away the base metal backing to produce a pure massive lead dioxide anode. After plating electrodes 191A to D (Table IX), the deposition of lead dioxide on only one side of a base metal was abandoned due to the brittleness of the lead dioxide and the failure of the blanking jig; the lead dioxide grew in large nodules along the base metal edge around the sides of the jig and also through sealed jig joints.

Heavy electrodeposits of lead dioxide were readily made on tantalum rod without any nodular growth or treeing in the LN-2 bath at current densities of 20-30 amps./ft.^{2} and a temperature of 70°C. Massive lead dioxide deposits were also made on flat rectangular sections of Monel screen and tantalum sheet, gauze and screen. In these cases there was some nodular growth at the edges which could be cut away on a diamond-edged circular saw or ground down on an abrasive wheel. Tantalum screen of sufficient weight to remain rigid and flat in the plating bath is now considered the most satisfactory lead dioxide plating base because of its inertness in the chlorate-perchlorate cell and the interlocking afforded to the lead dioxide through the screen holes.

During the plating operations it was found that the addition of 0.5 g./l. of copper nitrate, $Cu(NO_3)_2 \cdot 3H_2O$, to the LN-2 bath was sufficient to prevent plating of lead on the graphite cathodes. The addition of 0.5 to 0.75 g./l. of gelatin to the LN-2 bath had a pronounced effect in reducing the graininess of the lead dioxide. However, the massive deposit had a much lower fracturing strength as compared to that plated from a gelatin-free bath. Extended experience has confirmed the observation that the efficiency of lead dioxide plating from any of several baths is practically 100 percent with a freshly prepared or replenished bath. Litharge, PbO, has been used to replenish the LN-2 plating baths after each plating. To date, no attempt has been made to maintain the initial pH (3.5-4) of the lead nitrate bath during plating, so that the pH dropped to 0.5 or lower, and some nitric acid was lost from the hot bath by fuming. Thus, in replenishing the removed PbO_2 with an equivalent amount of PbO it was necessary to add some nitric acid to dissolve all of the PbO. The composition of the LN-2 bath is given in Table X. When plating on a flat base, at constant current, the area and thus the current density did not change appreciably. However, when plating on tantalum rod, it was necessary to increase the current in finite steps to maintain approximately constant current density.

X-ray diffraction and spectrographic analyses were made of portions of several of the massive lead dioxide deposits, and the results are detailed in Table XI. In all cases the deposit was identified as PbO_2, with lead as the only major spectrographic constituent. The minor constituents were not especially significant, but it was noted that nickel appeared when the deposit was made on Monel screen or on tantalum rod with a nickel wire coiled about the upper end. Also, copper appeared when the plating bath contained 0.5 g./l. or more of copper nitrate (see Section I.-B.-3).

TABLE IX

MASSIVE LEAD DIOXIDE ELECTRODES

Electrode No.	No.	Plating Bath				Current Density Amps/SAFT	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
		$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Gelatin g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 Per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Foot of Surface
191A	LN-2	- -	- -	69-73	Approx. 3.5	20	1/4"x6" copper foil (0.008" thick) cemented with DeKhotinsky cement to glass backing plate	Failed to obtain massive Plate as copper strip immersed in plating bath had almost completely eroded away.	19	75	- -	- -	- -	- -
191B	LN-2	Copper from previous erosion of copper strip present in bath	- -	65-70	Less Than 1	20	1/4"x6" tantalum (0.012" thick) cemented with DeKhotinsky cement to glass backing plate	Hard, dense, smooth deposit extending over sides of glass plate. Large knobs formed at bottom, and side edges are thicker than main surface	165		Approx. 100 grams	3-1/2"High 3/4" wide- 1/4" Ave. Thickness	- -	- -
191C	LN-2	5.6	- -	60-70	Approx. 3.5	20	Platinum plated tantalum sheet with back and sides faced with plexiglass. 1" x4" of platinum plated tantalum immersed in plating bath.	Trees formed on plate which were removed daily from plate. Final plate had many nodules. This plate was not tested in cell as it cracked in half while machining.	142		332 grams Not incl. 247 gms. of trees which were removed.	- -	- -	- -
191D	LN-2	Small amount introduced from copper cathode	- -	58-63	Approx. 3.5	20	Monel sheet (0.05" thick) with back and sides faced with plexigless. 5-3/4" x 1-1/16" of monel immersed in plating bath.	Monel sheet completely dissolved at surface level of plating bath. This plate was not tested in cell as it cracked in half when removed from Plexiglas jig.	89		204 grams	- -	- -	- -
193	LN-2	- -	- -	72-76	Approx. 3.5	20	Tantalum rod 1/4" D. with 6-7/8" immersed in plating bath	Dark gray deposit with granular or crystalline surface very similar to the abrasive surface of #1 emery cloth.	42	13	120 grams	6-7/8"long 7/16" O.D.- 3/32"thick	2325	5.13

TABLE XI. cont.

Electrode No.	No.	Plating Bath				Current Density Amps/SAFT	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
		$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Gelatin g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Feet of Surface
194	LX-2	5.6	- -	56-78	3.9	20	Monel screen with 6" x 3/4" area immersed in plating bath.	Heavy nodular growth along bottom and side edges. Deposit is hard. Monel screen partially dissolved at bath level.	73	30	278 grams	6-1/2"long- 1-1/8"wide- 3/16"thick	2760	6.04
195	LX-2	0.5		70-72	Approx. 3.5	20	Tantalum rod 1/4"D.x7-1/4" long. #20 nickel wire coiled at top end before plating for electrical contact with electrodeposited PbO_2 in chlorate-perchlorate cell.	Similar in appearance to electrode No. 193; no lead plated on cathodes; copper plated on cathodes for 6-10 hours, then redissolves. Voltage drops as copper redissolves.	49	-	132 grams	7-3/8"long- 7/16" O.D.- 3/32"thick	2390	5.27
196	LX-2	Small amts. of nickel and copper from soln. of Monel sht. (Electrode No.191D) and copper cathode.	- -	60-70	4.6	20	50 mesh surgical tantalum gauze(0.003" wire) folded over to prevent sharp edges with 18 B&S nickel wire between folds as current lead. Nickel wire 1-1/2" below plating bath level. 1"x7" area of gauze in plating bath.	Heavy nodular growth as electrode No. 194 and granular surface as for #193.	117	45	788 grams	7-1/2"high- 1-11/16"wide 1/4" thick	4490	9.90
197	LX-2	0.5	0.5	71-72	Approx. 3.5	20	Same as for Electrode #195	Gelatin has pronounced effect in reducing graininess of deposit, which however, is of much lower strength; cracked on normal handling.	45	15	161 grams	7-1/4"high- 15/32"O.D.- 7/64"thick	- -	- -
198	LX-2	0.5	0.5	70-75	3.7	60	Same as for electrode #195	Surface is dull with nodular growths on lower end. Deposit is stronger than #197. Intentionally broken for examination.	21	45	280 grams	7-1/4"high- 7/16"O.D.- 3/16"thick	- -	- -

TABLE IX. cont.

Electrode No.	No.	Plating Bath				Current Density Amps/ SQFT	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
		$Cu(NO_3)_2 \cdot 3H_2O$ g/l	Gelatin g/l	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Foot of Surface
199	IX-2	0.2	0.75	65-73	Approx. 3.5	30	1"x8" Tantalum sheet with #18 B&S nickel wire current leads threaded through holes in top portion of tantalum.	Plate blistered during early period of plating, finally plating over blisters. Intentionally broken for examination.	18		261 grams	- -	- -	- -
200	IX-2	0.2	0.75	65-69	Approx. 1	20-25	Same as for electrode #199	No treeing. Edges only slightly larger than middle of plate. Knobs present at bottom corners and at nickel wire leads. Few cracks on edges at beginning of plating period where PbO_2 had pulled away from tantalum. Most of cracks covered over at end of plating period.	112	30	1400 grams	8-1/2" high 1-7/8" wide 5/8" thick	6690	14.7
201	IX-2	0.5	- -	71-73	1.1	20	Same as for #195 except double nickel wire current lead.	Similar in appearance to #193; some copper plated on cathodes, but less than at initial pH of 3.5	51	30	236 grams	7-1/4" high 9/16" O.D. 5/32" thick	3685	8.13
202	IX-2	0.5	0.5	70-73	3.2	120	Same as for #195 & #201	Deposit had a dull sooty appearance. Heavy nodules on lower end and smaller nodules over entire surface which is very rough. Broken intentionally for examination.	5	55	142 grams	- -	- -	- -
203	IX-2	0.5	- -	70-72	0.6	30	Same as for #195 & #201	Similar in appearance to #193 No copper deposition on cathodes during PbO_2 plating.	28	30	133 grams	7-1/8" high 7/16" O.D. 3/32" thick	2490	5.62

TABLE II, cont.

Electrode No.	No.	Plating Bath				Current Density Amps/ SAFT	Description of Base Material	Description of Plated Electrode	Plating Time		Physical Characteristics of Plated Electrodes			
		$Cu(NO_3)_2 \cdot H_2O$ g/1	Gelatin g/1	Temp. °C.	Initial pH				Hours	Min.	Weight of Plate	Dimensions	Gms. PbO_2 per Sq. Ft. of Surface	Lbs. PbO_2 Per Square Foot of Surface
204A	LX-2	0.5	0.75	61-73	0.5	20	3"x12" Tantalum screen (0.025" wire) with 1/4" nickel tubing and 18 B&S nickel wire current leads	Plating failed because 1/4" nickel tubing current leads eroded away. Lead dioxide plated well on nickel current leads but not on tantalum in area between nickel tubing current leads. Intentionally broken.	49	30	950 grams	- -	- -	- -
204B	LX-2	0.5	0.75	64.69	Less than 0.5	20	3"x12" Tantalum screen (0.025" wire) with 20 B&S nickel wire current leads.	Poor plate on tantalum around nickel wire current leads. Heavier plate on bottom portion. Some knobs present on bottom and sides.	119	18	2927 grams	8" long-4-1/8" wide		

TABLE X

LEAD DIOXIDE PLATING BATH

Name - Acid Lead Nitrate

Formula - LN-2

Lead Nitrate Concentration - 350 grams per liter pH - 3.7

Preparation:

269 mls. of 69.9% nitric acid (266.5 gms. HNO_3)
1000 mls. distilled water
472 gms. lead oxide, PbO

Add the lead oxide slowly to the diluted nitric acid with stirring. Dilute to 2 liters, and heat to 75°C. with stirring. Allow to cool and let stand for twelve hours. Filter through sintered glass.

TABLE XI

X-RAY DIFFRACTION AND SPECTROGRAPHIC ANALYSES OF MASSIVE LEAD DIOXIDE DEPOSITS

Plate No.	L.N.B. Reference	XRD Analysis	Spectrographic Analysis	
			Major	Minor
1910	1365:94-97	PbO_2	Pb	Al, Mg, Cu, Fe
193	1367:102	PbO_2	Pb	Mn, Ca, Mg
194	1367:111,2	PbO_2	Pb	Ni, Cu, Mg, Ca
197	1367:139-41	PbO_2	Pb	Ca, Cu, Ni, Al, Mg
198	1365:175	PbO_2	Pb	Ni
199	1365:175	PbO_2	Pb	Al, Ag, Fe, Bi, Te

b. Testing Massive Lead Dioxide Electrodes

A number of changes were made in the procedure for testing the above massive lead dioxide anodes in the chlorate-perchlorate cell as compared to that followed with thin electrodeposits of lead dioxide in 1952. The cells were cooled by partial immersion directly into a refrigerated bath instead of circulating coolant through small area coils, immersed in the cells. Cell currents were maintained constant as before by means of electronic controllers. Glass was substituted for stainless steel stirring rods on the motor stirrers because of poor electrical shielding from the motor. It was found unnecessary to provide any surface protection for the massive lead dioxide anodes such as a Silicone grease coatings or Tygon sleeves at the liquid-air interface, which had been used to prolong the cell life of thin lead dioxide electrodeposits.

Table XII lists the current efficiencies obtained with massive lead dioxide anodes in the chlorate-perchlorate cell. The electrolysis was carried out batchwise at 3 to 10 amperes in cells containing 1.0 to 1.2 liters of a 600 to 630 g./l. sodium chlorate solution. The degree of conversion of chlorate to perchlorate was checked at 24 to 48 hour intervals by volumetric analysis of a small aliquot for oxidizing power by the bromide-iodide-thiosulfate method. In most cases, the electrolysis was continued to reduce the chlorate content below 100 g./l. The product solution was then removed, the cell replenished with fresh sodium chlorate solution, and the testing of the lead dioxide anode in chlorate-perchlorate electrolysis continued. All electrodes except #201 were initially operated several times at an anode current density of 0.1 amp./cm^2, at which value the average current efficiency in the sodium chlorate concentration range of 600 to 100 g./l. was approximately 50 percent. There was a small increase in current efficiency with successive batch electrolyses at 0.1 am./cm^2. When the anode current density of electrode #195 was increased to 0.2 amp./cm^2, the current efficiency in the same chlorate concentration range rose to from 65 to 70 percent. Also, there was a noticeable increase in current efficiency in the early stages of electrolysis of successive batches.

All cells were operated in the acid range by the manual addition of 0.5N perchloric acid when necessary. It was soon found that the acid requirement of cells operating with massive lead dioxide anodes was much less than those previously operated with anodes having a thin (about 0.01 inch or less) deposit of lead dioxide. As seen in Table XII, approximately 20 mls. of 0.5N perchloric acid addition was necessary per batch electrolysis at 0.1 amp./cm^2, but at 0.2 amp./cm^2 no acid addition was necessary, and the cells automatically adjusted themselves to a pH of 1.5-2. Incases where the cell pH was high the cause

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TABLE XII

CURRENT EFFICIENCIES OF MASSIVE LEAD DIOXIDE ANODES IN CHLORATE-PERCHLORATE CELL

CELL TEMPERATURE - 3-10°C.; Continuous Stirring

Elect. No.	Test No.	Anode Current Density A/cm.^{2}	$NaClO_3$ Conc. Range Over Which Current Efficiency Was Calculated		Current Efficiency %	Cell pH		Mls. of 0.5N $HClO_4$ Added gms. of $HClO_4$=0.0502x mls.of 0.5N $HClO_4$		
									Cumulative for Test	
			Initial g/1	Final g/1		Range	Ave.	Each Range	Mls. of 0.5N $HClO_4$	Gms. of $HClO_4$
191	1	0.1	596 561 494 596	561 494 429 429	30.4 61.2 59.2 49.9(overall)	2.4-6 2.7-6.9 6.65-8.5	3.5 3.5 7.5	2.6 0.2 2.9	5.7	0.29
191	2	0.1	632	Not Analyzed		3.9-10.8	9			
193	1	0.1	632	505	45.2	2.6-7.1	6	10.5	10.5	0.53
193	2	0.1	616 515 616	515 427.5 427.5	33.5 69.6 44.1(overall)	3.5-9.0 5.1-6.7	7 6	7.0 4.5	11.5	0.58
193	3	0.1	616 481 227 130.4 71.8 616	481 227 130.4 71.8 43.8 43.8	47.4 61.2 72.0 40.9 26.4 52.8(overall)	1.5-8.6 1.6-7 1.6-1.7 1.5-1.8 2.0	4.5 5 1.6 1.6 2.0	12.0 6.0 0 0 0	18.0	0.90
194	1	0.1	632 263 632	263 109 109	55.6 37.8 48.9(overall)	1.7-6.6 2.5-4.8	3.5 3.5	2.7 0	2.7	0.14
194	2	0.1	616 503 265 616	503 265 124 124	43.9 35.5 37.4 37.8(overall)	2.1-7 1.5-6.7 1.9-4.7	3.5 2.5 2.5	2.0 3.0 0	5.0	0.25
195	1	0.1	616 437 616	437 336 336	59.9 41.6 51.7(overall)	2.4-7.2 2.2-5.2	5 3.5	13.5 2.0	15.5	0.78

CONTINUED

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TABLE XII. cont.

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Elect. No.	Test No.	Anode Current Density A/cm.^{2}	NaClO$_3$ Conc. Range Over Which Current Efficiency Was Calculated		Current Efficiency %	Cell pH		Mls. of 0.5N HClO$_4$ Added gms. of HClO$_4$=0.0502x mls. of 0.5N HClO$_4$		
			Initial g/1	Final g/1		Range	Ave.	Each Range	Cumulative for Test	
									Mls. of 0.5N HClO$_4$	Gms. of HClO$_4$
195	2	0.1	616	448	60.7	1.8-6.9	4	11.5		
			448	206	57.6	1.5-8.2	4.5	8.0		
			206	164.5	31.2	1.5-2.5	1.8	0		
			164.5	128.7	25.0	1.9-2.5	2.1	0		
			128.7	83.3	40.7	2.0	2.0	0	19.5	0.98
			616	83.3	49.1(overall)					
195	3	0.1	616	510	65.7	1.7-6	3	6.0		
			510	335	59.8	1.7-5.8	3	7.0		
			335	168.6	41.8	-	-	0	13.0	0.65
			616	168.6	52.5(overall)					
195	4	0.2	605	402	67.8	1.3-1.6	1.4	0		
			402	193	70.7	1.4-2.1	1.8	0		
			193	59.6	54.5	-		0	0	0
			605	59.6	64.9(overall)					
195	5	0.2	605	381	81.5	1.4-1.7	1.5	0		
			381	189	75.1	1.4-2.0	1.7	0		
			189	63.8	54.2	1.7-2.1	1.9	0	0	0
			605	63.8	71.0(overall)					
195	6	0.2	605	328	91.7	11.0-1.4	3(?)	0		
			328	106.5	77.3	1.4-9.5	3(?)	0		
			106.5	32.3	31.3	9.5-10.1	9.7	0	0	0
			605	32.3	69.4(overall)					
196	1	0.1	616	447	40.9	1.7-9.8	5	12.0		
			447	321	38.5	1.7-8.6	4	6.0		
			321	28	37.5	1.1-7	3	0	18.0	0.90
			616	28	38.6(overall)					
196	2	0.1	616	341	64.9	2.3-10.1	6	10.0		CONTINUED

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TABLE XII, cont.

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Elect. No.	Test No.	Anode Current Density A/cm.^{2}	$NaClO_3$ Conc. Range Over Which Current Efficiency Was Calculated		Current Efficiency %	Cell pH		Mls. of 0.5N $HClO_4$ Added gms. of $HClO_4$=0.0502x mls. of 0.5N $HClO_4$		
									Cumulative for Test	
			Initial g/l	Final g/l		Range	Ave.	Each Range	Mls. of 0.5N $HClO_4$	Gms. of $HClO_4$
196	2	0.1	341 21.3 616	21.3 20.7 20.7	40.3 2.9 48.1(overall)	0.9-9 1	3.5 1	10.0 0	20.0	1.00
196	3	0.1	616 340 163 616	340 163 69 69	58.7 45.3 28.6 46.0(overall)	1.7-10 1.7-9.4 1.5-1.8	5 4 1.7	19.0 9.0 0	28.0	1.40
196	4	0.1	605 349 103.7 605	349 103.7 24.8 24.8	56.9 62.6 25.4 50.3(overall)	1-1.4 0.5-1.4 0.5-0.9	1.2 0.9 0.7	5.0 0 0	5.0	0.25
196	5	0.1	605 290 85.3 605	290 85.3 59.1 59.1	71.6 55.1 46.8 63.2(overall)	10.9-0.9 1.0-1.4 1.0	3(?) 1.2 1.0	0 0 0	0	0
196	6	0.1	605 232 47.2 605	232 47.2 4.4 4.4	85.9 44.9 12.9 50.9(overall)	1.0-1.4 1.4-0.65 0.65-0.8	1.2 1 0.7	0 0 0	0	0
201	1	0.2	605 413 210 605	413 210 96.2 96.2	63.0 70.1 49.1 61.7(overall)	1.3-1.6 1.3-1.6 1.3	1.4 1.4 1.3	0 0 0	0	0

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was found to be failure of the stirring apparatus. On recommencing stirring, the pH dropped to 1.5 within ten minutes.

The appearance of the lead dioxide anodes after testing in the chlorate-perchlorate cells at 0.1 amp./cm^2 was essentially unchanged. There was no localized or serious erosion or cracking of the lead dioxide deposit.

In general, the peaks of the surface lead dioxide crystals lost their metallic luster, and under the microscope a smoothing of the points was apparent. When the anode current density was increased to 0.2 amp./cm^2, the lead dioxide surface initially turned to an orange-brown color from its normal dark gray. This brown coloration gradually disappeared, and there was otherwise no attack on the anode. The electrolyte in all cases remained clear and colorless. Weight losses of lead dioxide anodes on electrolysis in the chlorate-perchlorate cell for periods up to 9 days on a continuous basis were negligible. The changes in weight were generally within the experimental error in weighing, considering the possibility of small weight changes caused by electrolyte or wash water held within the pores of the lead dioxide. As seen in Table XIII, the largest lead dioxide anode weight loss was equivalent to a loss of 51 grams for each ton of sodium perchlorate produced at 50 percent current efficiency.

In view of the concern expressed over possible lead contamination of perchlorate from a cell using a lead dioxide anode, a spectrographic study was made of the product electrolyte. A spectrogram of evaporated electrolyte from a chlorate-perchlorate cell after 28 hours operation at 5.8 amperes with a lead dioxide filled storage battery plate showed no evidence of lead, although there was considerable erosion of lead from the plate. Spectrograms of cathode scum and insoluble cell liquor precipitate, obtained after operating cell #194-1 (see Tables IX and XII) for five days at 5 amperes with an electrodeposited massive lead dioxide anode, showed lead as a minor constituent. The evaporated electrolyte from the same cell revealed no spectrographic trace of lead. Thus, the eroded lead from the anode either plated out on the cathode or formed an insoluble compound.

c. <u>Current Contact to Lead Dioxide</u>

Due to the relatively high contact resistance of lead dioxide, especially to tantalum, which now appears to be most favorable for use as a lead dioxide plating base, the contriving of a workable, non-heating lead dioxide current contact has taken a considerable part of the research effort. Tables XIV and XV list the various methods used to bring current into the massive lead dioxide electrodes. The use of metal pressure plates and clamps against the outside surface of the lead dioxide proved inadequate in preventing heating in the contact area with even moderate currents. Casting of a low melting

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TABLE XIII

WEIGHT LOSSES OF LEAD DIOXIDE ANODES IN CHLORATE-PERCHLORATE CELL

Electrode Number	Number of Times $NaClO_3$ Electrolyte Was Replenished in Cell	Chlorate-Perchlorate Cell Operation Hours	Cell Current Amps.	Current Density A/cm^2	Weight Change Gms.	Grams Wt. Loss per 10,000 amp-hrs.= Production of 25.2 lbs. $NaClO_4$ at 50% Current Efficiency	Grams Wt. Loss per ton $NaClO_4$ Formed at 50% Current Efficiency
193	3	311	3.2	0.1	+ 0.02	None	None
195	3	430	3.2	0.1	- 0.06	0.436	34.6
195	1 after 3 as above	72.8	6.4	0.2	- 0.03	0.643	51.0
196	3	238.8	10	0.1	+ 0.58	None	None

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TABLE XIV

TESTING OF CURRENT LEADS TO MASSIVE LEAD DIOXIDE ANODES IN CHLORATE-PERCHLORATE CELL

Plate No.	Test No.	Description of Current Lead	Observations
191B	1	Universal clip (Mueller Electric Co.) direct to lead dioxide-wrapped with No. 33 electrical tape to protect clip from cell spray	Anode ran warm-clip corroded by electrolyte spray and seepage.
191B	2	Brass plates to lead sheet to lead dioxide, screw to tighten assembly. Assembly covered with wax.	Current lead operated warm. Finally lead dioxide cracked under the brass plate pressure. Evidence of reaction between lead sheet and brass plates and between lead sheet and lead dioxide.
193	1	Sheet copper wrapped around lead dioxide plated on tantalum rod. Sheet copper tightened against lead dioxide with hose clamp. Current lead soldered to sheet copper. Assembly covered with No. 33 electrical tape.	Current lead ran warm. No attack or corrosion.
193	2&3	18 B&S copper wire tightly wound around lead dioxide on tantalum rod. Wood's metal cast around copper wire with ends of copper wire through Wood's metal as external lead.	Operated satisfactorily but there was slight corrosi of Wood's metal by electrolyte spray.
194	1&2	18 B&S nickel wire tightly wound around lead dioxide plated on Monel screen. Wood's metal cast around nickel wire with ends of nickel wire through Wood's metal as external lead.	Operated satisfactorily but there was slight corrosion of Wood's metal by electrolyte spray. Portion of Monel screen below electrolyte level and within lead dioxide was completely eroded away.
195	1 thru 6	20 B&S nickel wire tightly wound around tantalum rod with one end of nickel wire as external current lead. Lead dioxide plate over tantalum and nickel wire.	Operated satisfactorily at slightly lower cell voltage (0.2 to 0.3 volts) than Plate No. 193, Tests 2 and 3.
196	1 thru 6	18 B&S nickel wire between folds of tantalum gauze with four nickel wire external leads-Lead dioxide plated over tantalum and nickel wire. Wood's metal cast at top of plate to hold nickel wire external leads rigid.	Operated satisfactorily.
201	1	20 B&S nickel wire tightly wound around tantalum rod with two ends of nickel wire as external current leads. Lead dioxide plate over tantalum and nickel wire.	Operated satisfactorily.

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TABLE XV

OTHER CURRENT LEADS TO LEAD DIOXIDE ANODES

Electrode No.	Description of Current Lead	Observations
	Lead dioxide on magnetite - current lead (Universal clip)	Anode became hot (about 100°C.) at current contact lead to magnetite
191A	Lead dioxide on copper sheet backed with glass plate	Copper sheet dissolved in acid lead nitrate plating bath (Formula LN-2)
191D	Lead dioxide on Monel sheet	Monel sheet dissolved in acid lead nitrate plating bath (Formula LN-2)
197A	18 B&S copper wire tightly wound around tantalum rod with two ends of copper wire as external current leads Lead dioxide to be plated over tantalum and copper wire.	Copper wire eroded in acid lead nitrate plating bath (Formula LN-2). No lead dioxide deposited.
197B	20 B&S Nickel wire tightly wound around tantalum rod with two ends of nickel wire as external current leads	Lead dioxide plated on nickel and tantalum. Lead dioxide plate protected nickel wire from erosion
1[illegible]	Same as for 197B	Same as for 197B
200	18 B&S nickel wire threaded through holes in top portion of tantalum sheet. 4 wires as external current leads. Lead dioxide plate over tantalum and nickel wire.	To be tested
204A	18 B&S Nickel wire threaded through tantalum screen and twelve strands brought up through two 1/4" nickel tubes slotted 1-1/2" to slide on tantalum screen. Nickel wire and tube to serve as current leads.	Nickel wire and nickel tubing dissolved in acid lead nitrate plating bath (Formula LN-2) at plating bath level.
204B	20 B&S nickel wire threaded through tantalum screen-ten strands to serve as external current leads.	Nickel wire dissolved in acid lead nitrate plating bath (Formula LN-2)

alloy such as Wood's Metal (m.p. 70°C.) around the upper end of a lead dioxide anode, which had already been closely wrapped with copper or nickel wire to serve as current leads proved more satisfactory. This type of contact, however, was somewhat bulky and it was necessary to protect the surface of the metal casting from immersion or spray contact with the chlorate-perchlorate cell electrolyte to prevent serious corrosion.

The most satisfactory current contact developed to date consists of massive lead dioxide plated over a base assembly composed of nickel wire tightly wound around or otherwise attached to the upper end of tantalum rod, plate or screen. The portion of the electrode containing the embedded nickel wire remained above the electrolyte level in the chlorate-perchlorate cell. On the finished electrode, the free ends of the nickel wire served to carry the current into the lead dioxide. Thus, the tantalum served only as a supporting base and current carrier during plating, since it gradually heated up when carrying even moderate currents in the chlorate-perchlorate cell.

When massive lead dioxide was plated over Monel screen (Plate #19¼, Table IX), the Monel served adequately to carry the current into the lead dioxide during operation in the chlorate-perchlorate cell. However, when the electrode was broken open after 11 days' operation at 5 amperes, it was found that the Monel screen base had completely eroded away below the electrolyte level, leaving voids in the lead dioxide. On spectrographic analysis of the precipitate from the above cell liquors, nickel was found to be a major constituent and copper a minor constituent. The current efficiency was lower than with a tantalum base anode.

d. Other Forms of Lead Dioxide Electrodes

Lead storage battery grids were tested as anodes in the chlorate-perchlorate cell. The electrode consisted of an anodized lead battery sheet, that is, compacted lead dioxide in a lead grid which was obtained as a sample from Electric Storage Battery Co., Philadelphia. In operation, the anode portion above the electrolyte level heated to about 80°C. for the first two to three hours and then ran cool. The electrolyte was light brown after 24 hours. The anode failed at 30 hours due to complete erosion of the supporting lead grid at the solution-air interface, and the lead grid throughout the immersed portion of the anode was seriously eroded. A current efficiency of 39 percent was obtained.

In an attempt to produce a lead dioxide coating by means other than normal electroplating, lead tubing was anodized to form a lead dioxide film. The lead tube was first degreased in 5 percent sodium hydroxide solution, pickled in 15 percent nitric acid, and then successively anodized at 25 amps./ft^2 and 25°C. in a 30 g./l. sodium cyanide solution for 6 minutes, and a

75g./l. sodium carbonate solution for one hour. A white coating with brown spots was formed in the cyanide bath. This was converted to a velvety brown coating in the carbonate bath. On testing in the chlorate-perchlorate cell at 0.1 amp/cm^2 more than half of the coating came loose and was dispersed in the cell within five minutes. The lead tube was rapidly attacked, and fuzzy lead was plated on the cathode. The electrolyte turned milky, and its pH rose from 3.3 to 10. The same results were obtained with an initially alkaline electrolyte.

3. Physical Properties of Lead Dioxide

a. Electrical Conductivity of Lead Dioxide

Upton B. Thomas of the Bell Telephone Laboratories (2) measured the electrical conductivity of dense samples of lead dioxide prepared by the electrolysis of lead perchlorate and lead sulfamate. The specific resistance of these dense samples was of the order of 200×10^{-6} ohm-cm. The specific resistance of porous samples prepared from storage battery oxides was 7400×10^{-6} and porous samples prepared from pressed powder was $14,200 \times 10^{-6}$ ohm-cm. (see Table XVI).

Thomas made electrical contacts to the lead dioxide sample by one of three ways:

(1) copper wires were cemented to the PbO_2 with conducting cement

(2) thin strips of silver foil were pressed directly against the specimen; or

(3) against areas on its surface, onto which a thin layer of gold has been evaporated.

W. H. Palmaer (3) measured the electrical properties of lead dioxide made by electrolysis of a dilute lead nitrate solution. He found the specific resistance of lead dioxide to be 92×10^{-6} to 97×10^{-6} ohm-cm. with a positive temperature coefficient of 0.06 percent per degree in the range of 22-84°C.

At Pennsalt, the specific resistance of a massive piece of lead dioxide (5.7 cm. x 2.5 cm. x 0.7 cm.) plated from an acid lead nitrate bath was measured. The original nodular plate was cut with a diamond saw to obtain smooth surfaces. Electrical contact was made at the ends of the dense lead dioxide by first wrapping on copper foil and then tightly wrapping thin copper wire over the foil. This was pressed firmly against the lead dioxide by screw-type hose clamps. Current was passed through the lead dioxide (4 and 8.6 amperes) and the voltage drop across a 2.54 cm. length of lead dioxide was measured by pressing probes leading from a Rubicon potentiometer firmly against the lead dioxide. The copper-lead dioxide contacts were not satisfactory, as evidenced by the fact that the whole assembly became hot. The specific resistivity according to these measurements was from 40 to 50×10^{-6} ohm-cm.

TABLE XVI

SPECIFIC RESISTANCE AT ROOM TEMPERATURE OF VARIOUS SAMPLES OF LEAD DIOXIDE COMPARED WITH OTHER MATERIALS

Description of Sample	Specific Resistance Ohm-cm. x 10^{-6}	
	Porous	Dense
Lead dioxide		
Storage battery positive active material, 46% porosity (2)	7,400	
Pressed powder, 32% porosity (2)	14,200	
Electrolyzed from lead perchlorate (2)		94 to 405
Electrolyzed from lead sulfamate (2)		1,200
Electrolyzed from dilute lead nitrate solution (3)		92 to 97
Electrolyzed from acid lead nitrate bath (Formula LN2) at Pennsalt (4)		40 to 50
Other Materials		
Graphite	800	
Mercury	96	
Bismuth	115	
Platimum	10.5	
Copper	1.69	
Silver	1.62	

Thus lead dioxide has characteristics which more nearly approach those of metals than those of semi-conductors. Its conductivity is much higher than that of most semi-conductors, and decreases with temperature. Dense lead dioxide is more conducting than graphite (800 x 10^{-6} ohm.-cm.) and its specific resistance is about equal to that of the poorly conducting metals such as mercury and bismuth.

b. Specific Gravity

W. H. Palmaer (3) measured the specific gravity of lead dioxide electrolyzed from dilute lead nitrate solution. Its specific gravity at 20°C. was 9.36.

In the present study a massive piece of lead dioxide electrolyzed from the acid lead nitrate bath (Formula LN-2) had a specific gravity of 9.32 at 24°C.

c. Hardness

W. H. Palmaer (3) found that the hardness of electroplated lead dioxide was between 5 and 6 on the Moh scale.

In the present study, the massive lead dioxide plates have been hard (not measured) causing difficulty in machining off nodules formed on thick plates. Such samples given to Carborundum Company were found by them to machine easily in the following manner (5):

(1) grinding with Carborundum Brand - A 36-06-V30 wheel, 8" diameter x 1" wide, and

(2) cutting with a metal bonded diamond wheel - No. 18005, 8" diameter x 0.045" wide (60 grit, 25 concentration).

4. Review of Japanese Literature on Massive Lead Dioxide

An apparently sustained effort on the preparation of lead dioxide electrodes and their application to various electrolytic oxidation processes including the production of sodium perchlorate has been carried on by various Japanese investigators at the Tokyo Institute of Technology for the past 20 years. English translations of three papers and a Japanese patent on this work have recently been received.

The first paper by Kato and Koizumi (6) was published in 1934 and is titled "A New Process for the Preparation of Lead Peroxide Anodes". A 30 percent solution of lead nitrate containing a hydrophil such as gelatin was used for a lead dioxide plating bath, and it was recommended that the bath be operated at 80°C. and an anode current density of 100 amps./$dm.^2$, (929 amps./$ft.^2$). The lead dioxide which was deposited on graphite and nickel was said to be very fine with no pores and was made in flat plates up to 20 by 15 cms. In a discussion of oxygen overvoltage, it was stated that the value for lead dioxide was somewhat higher than platinum and thus it could be used as anode in the electrolysis of sodium chlorate to perchlorate. A 50 percent sodium chlorate solution containing 5 percent sodium dichromate was used as electrolyte. The bath temperature was maintained at 5°C. and the current density at 12 amps./dm.^{2} (111 amps./ft.^{2}), under which conditions the cell voltage was 4.9. A current efficiency of 58 percent was attained with the lead dioxide anode as compared to 81 percent with platinum at the same current density. However, when the current density of the platinum was increased to its normal value of 30 amps./dm.^{2} the same amount of perchlorate was produced in both cases by equal amounts of power.

Kato and co-workers (7) published a paper in 1941 titled "Outline of Semi-industrial Research for the Electrolytic Preparation of Sodium Perchlorate with New Metal-like Lead Peroxide Anodes". They reported the oxygen overvoltage of lead dioxide to be 0.15 volts lower than that of polished platinum in 1-N KOH at 30°C. and a current density of 10-20 amps./dm.^{2} (92.9-185.8 amps./ft.^{2}). Their plating bath composition and operating conditions were very similar to those described above, except that a lower current density, 15-20 amps./dm.^{2} (139-186 amps./ft.^{2}), was used, the cathode was graphite or a rotating copper rod, and the lead dioxide was plated to a thickness of 7 mm. on the inside of a nickel cylinder. This plated cylinder with the provision of a suitable bottom then served as the chlorate-perchlorate cell container. On electrolysis of a 40 percent sodium chlorate solution at an anode current density of 17 amps./dm.^{2} (158 amps./ft.^{2}), and a cell temperature of 26°C., a current efficiency of 44 percent was obtained with an 86 percent conversion of chlorate to perchlorate. A sudden drop in current efficiency at 85 percent conversion was explained as being caused by the reduction of perchlorate at the cathode. The current efficiency was increased to 57 percent with the reaction carried to 99 percent completion when a small piece of platinum (1-2% of area of PbO_2) was placed in the cell connected in parallel with the lead dioxide. The increased current efficiency was attributed to deposition of dissolved platinum on the cathode, thereby lowering the hydrogen overvoltage of the cathode and preventing cathodic reduction of perchlorate.

Direct electrolytic production of sodium perchlorate from sodium chloride in a single electrolysis was also carried out, using the above lead dioxide anode with an overall current efficiency of 49 percent.

During extended electrolysis with the anode consisting of lead dioxide on nickel, the nickel base was oxidized, causing contact resistance between the lead dioxide and nickel to increase, and thus the voltage for electrolysis to rise. In addition, the electrolyte seeped through pinholes in the lead dioxide and dissolved the nickel base, causing electrode failure. It was found possible to separate the lead dioxide from the nickel base by cooling, and obtain a long lived electrode, taking advantage of the greater coefficient of thermal expansion of lead dioxide. Electrical connection was made at the top end of this electrode to a part of the nickel base that had not been removed.

Sugino (8) published an abstract in 1950 of twelve previously published papers on "Preparation, Properties, and Application of the Lead Peroxide Electrode Manufactured by a New Method". His lead dioxide plating bath composition and operating conditions were very similar to those described in the above two papers. A lower anode current density of 6.96 amps./dm.^{2} (64.6 amps./ft.^{2}) was used, no hydrophil addition agent was added to the plating bath, and the lead dioxide could be plated on the inner surface of an "iron" cylinder by using a neutral lead nitrate solution. During electrolysis, the pH and concentration of lead ion were maintained constant by continuously circulating the electrolyte through an external train system consisting of a holding tank, a neutralizing tank in which $Pb(OH)_2$ was kept in suspension by agitation, a filtering bed, and a reheating tank from which the replenished and neutralized electrolyte was returned to the cell. The "iron" cylinder was cut away from the inner electrodeposited lead dioxide cylinder, and the lead dioxide was then cut lengthwise into sixteen rectangular strips 300 mm. x 45 mm. x 8-10 mm. thick. Current contact was made to the lead dioxide by first wrapping silver foil around the upper end, and then tightly clamping an aluminum or brass strip over the silver, the anode lead then being fastened to this clamp.

In an alternate method, the lead dioxide was deposited from neutral lead nitrate at 27-31°C. on the outer surface of a rotating rod which was covered with a paraffin-graphite mixture. A hollow cylinder of lead dioxide was then obtained by melting the paraffin and sliding out the rod. The plating bath for this use was modified by the addition of 10-30 g./l. $Cu(NO_3)_2$ and 60-80 g./l. $NaClO_4$.

The lead dioxide anode was reported to be a good conductor, carrying above 20 amps./dm.^{2} (186 amps./ft.^{2}), and almost perfectly insoluble. On electrolysis of sodium chlorate solution using this lead dioxide anode and 18-8 stainless steel cathode at 20 amps./dm^2 (186 amps./ft.^{2}) and 30°C., a current efficiency of 41% was obtained on a 99.9 percent conversion of chlorate to perchlorate. The addition of 2 g./l. of sodium fluoride was found to increase the current efficiency to 82 percent over the same concentration range. Direct electrolytic production of sodium perchlorate from sodium chloride was similarly carried out, except that during the initial stage of electrolysis from Cl^- to ClO_3^- the cell temperature was maintained at 60-65°C. and a small amount of hydrochloric acid was added from time to time to maintain the electrolyte slightly acidic. When the chlorate formation was almost complete, 2 g./l. sodium fluoride was added to increase the chlorate to perchlorate current efficiency. An overall current efficiency of about 60 percent was obtained. This method for direct electrolytic production of sodium perchlorate is covered by Sugino in a Japanese patent (9) issued in 1946. Potassium chlorate was electrolytically formed from potassium chloride at a current efficiency of 81 percent.

The oxygen overvoltage of the lead dioxide anode was measured in 1N sulfuric acid at 30°C. at various current densities and compared with that of smooth platinum. The values for lead dioxide were found to be somewhat lower than for platinum, for example, 0.16 volts lower at 1 amp./dm.^{2} (9.3 amps./ft.^{2}). On addition of various amounts of hydrofluoric acid, it was found that the overvoltage of lead dioxide increased with the logarithm of the concentration of hydrofluoric acid.

5. Miscellaneous Anode Materials - Screening Tests

a. Summary of Previous Work Done Under 1951 Project NR 352-263/2-19-51 and 1952 Project NR 352-304/2-1-52

Tantalum carbide containing 17% platinum by weight obtained from the Carboloy Department of General Electric Company gave favorable results with repeated tests. Anode loss rates varied from 1 x 10-5 to 20 x 10-5 grams per ampere hour, and current efficiencies as shown by electrolyte analysis have been as high as 70%.

Plattnerite, a rare, naturally occurring massive lead dioxide, operated smoothly as anode in the chlorate-perchlorate cell at a low voltage without shattering and with very slight erosion.

Magnetite anodes showed slight erosion but produced sodium perchlorate at a current efficiency of only about 4 to 5%.

Platinum plated tantalum sheet performed entirely satisfactorily as an anode material.

The mineral ilmenite from Ward's Natural Science Establishment behaved well in screening tests conducted in 1951. No further work has been done on this material since that time.

All other materials which are listed in detail in the reports for 1951 and 1952 proved to be unsatisfactory.

b. Work Done in 1953

Samples of *bearing materials* (carbon impregnated with various metals) from the Carbone Corporation, Boonton, N.J. were tested in the chlorate-perchlorate cell. These samples were RSS Copper, RS Copper, RSS Babbitt, RS Babbitt and RS Silver, with the RSS material being somewhat harder and stronger than the RS material. The specific resistance of these compositions was of the same order of magnitude as that of graphite, but when tested as anodes all eroded rapidly with the RS Silver composition showing the least, but still appreciable, attack (see Table XVII).

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TABLE XVII

MISCELLANEOUS ANODE MATERIALS (BEARING MATERIALS – CARBON IMPREGNATED WITH VARIOUS METALS)

ELECTROLYTE – 600 g/1 $NaClO_3$

Research Notebook Reference	Description of Sample and Source	Specific Resistance x 10^{-6}	Average Cell Current (amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
1364:186	From the Carbone Corp., Boonton, N.J. RSS – Copper	667	1.5	100	3-4	12	Blue-black precipitate in electrolyte and anode sample appreciably eroded
1364:187	RS – Copper	167	1.5	100	4.0	12	Blue-black precipitate in electrolyte and anode sample appreciably eroded
1364:188	RSS Babbitt	855	1.5	100	4.0	12	Brown precipitate in electrolyte and anode sample appreciably eroded
1364:189	RS Babbitt	480	1.5	100	4.0	12	Brown precipitate in electrolyte and anode sample appreciably eroded
1364:190	RS Silver	400	1.5	100	4.0	12	Cloudy electrolyte; anode sample etched; least erosion of all bearing material samples

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Electrical Conductivity Rating of Some Minerals

Several thousand minerals in the University of Pennsylvania's collection were tested for electrical conductivity. The measurements were made by firmly pressing point electrodes on a clean portion of the mineral and measuring the voltage drop caused by a known flow of current. Because of the shapes of the mineral specimens the specific conductance could not be calculated from the measurements made. However, the resulting readings were compared to similar readings made on well-known materials of varying degrees of conductivity. The results were grouped into the following categories: those minerals whose conductivity was similar to that of graphite were rated as excellent, those similar to carbon were rated good, those similar to pyrolusite were rated poor, while those much below this were rated very poor, and those showing no passage of current were classed as non-conductors. It was observed that the conductivity varied greatly in different specimens of the same mineral species. The results are listed in Table XVIII. The naturally occurring metals and metal alloys which are known to be good conductors are not listed in this table.

In order to round out our survey of useful materials for anodes in the perchlorate cell, the following minerals were selected from Table XVIII as being most promising: Hematite, cassiterite, psilomelane, pyrolusite, zincite, and chromite. These minerals will be tested by the standard screening tests when characteristic samples are on hand.

A sample of silicon ferrite from Horizons, Inc. eroded rapidly when tested as an anode in the chlorate-perchlorate cell, as did a sample of impervious graphite from Falls Industries, Solon, Ohio. However, a sample labelled pyrolusite ($MnO_2 + 2\frac{1}{2} H_2O$) obtained from the Pennsylvania State College showed very little erosion. This sample later proved to be manganite ($Mn_2O_3 \cdot H_2O$) by X-ray analysis.

Natural graphite (Rhombohedral, Colombo Mines, Island of Ceylon) from Ward's Natural Science Establishment eroded very rapidly.

A nickel-ferrite boule from the Linde Air Products Company, which was previously reported as a poor conductor (page 25, Second Quarterly Research Report for 1952), was found to have a non-conductive outer layer. After grinding this outer layer off, the inner layers were found to be conductive enough to be tested as an anode in the chlorate-perchlorate cell. There was no appreciable erosion, but conversion of chlorate to perchlorate was very low.

A 24 carat gold rod was attacked as evidenced by a weight loss, the formation of an orange precipitate in the electrolyte and also the formation of a rust-colored film on that portion of the gold rod immersed in the electrolyte.

TABLE XVIII

ELECTRICAL CONDUCTIVITY RATING OF SOME MINERALS*

Conductivity rating: Nonconductor –; very poor conductor +; poor conductor ++; good conductor +++; excellent conductor ++++.

Mineral	Composition	Conductivity Rating
Stibnite	Sb_2S_3	–
Bismuthinite	Bi_2S_3	+++
Kermesite	Sb_2S_2O	+++
Pyrite	FeS_2	++++
Cobaltite	$CoAsS$	+++
Gersdorffite	$NiAsS$	++
Ullmannite	$NiSbS$	+++
Loellingite	$FeAs_2$	+++
Safflorite	$(Co,Fe)As_2$	+++
Rammelsbergite	$NiAs_2$	+++
Marcasite	FeS_2	+++
Arsenopyrite	$FeAsS$	+++
Glaucodote	$(Co,Fe)AsS$	++
Molybdenite	MoS	++
Krennerite	$AuTe_2$	++
Sylvanite	$AgAuTe_2$	++
Skutterudite	$(CoNi)As_3$	++
Smaltite Bismuthian	$(CoNi)As_{3-x}$	++
Chloanthite	$(NiCo)As_{3-x}$	++
Pyrargyrite	Ag_3SbS_3	++
Proustite	Ag_3AsS_3	++
Xanthoconite	$AgAsS_3$	++
Wittichenite	Cu_3BiS_3	+++
Tetrahedrite	$(CuFe)_{12}\ Sb_4S_{13}$	++
Pyrochroite	$Mn(OH)_2$	–
Manganite – pseudo Calcite	$Mn_2O_3 \cdot H_2O$	+++
Psilomelane	$BaMn_2 \cdot Mn_8O_{16}(OH)_{14}$	++++
Goethite	$Fe_2O_3 \cdot H_2O$	–
Limonite	$Fe_2O_3 \cdot 3H_2O$	–
Magnetite – Isometric N.Y.	$Mn_2O_3 \cdot H_2O$	++++
Cassiterite	SnO_2	+
Pyrolusite	MnO_2	+++
Rutile	TiO_2	–
Braunite	$(MnSi)_2O_3$	–
Valentinite – Canada	Sb_2O_3	++
Arsenolite	As_2O_3	++
Ilmenite	$FeTiO_3$	+
Hematite – Specular	Fe_2O_3	+

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*The conductivity varied greatly in different specimens of the same mineral species.

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TABLE XVIII - Cont.

Hematite - Rhombohedral Michigan	Fe_2O_3	++++
Corundum	Al_2O_3	-
Zincite	ZnO	+
Cuprite - Isometric	Cu_2O	+++
Jamesonite	$2PbS \cdot Sb_2S_3$	-
Cosalite	$Pb_2Bi_2S_5$	++++
Aikinite	$PbCuBiS_3$	++
Bournonite	$PbCuSbS_3$	++
Enargite	Cu_3AsS_4	++++
Famatinite	Cu_3SbS_4	+++
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	+++
Franklinite	$ZnFe_2O_4$	++
Chromite	$FeCr_2O_4$	+
Cerargyrite	$AgCl$	+
Tetradymite	Bi_2Te_2S	+++
Nagyagite	$Pb_5Au(TeSb)_4S_5$	++++
Domeykite	Cu_3As	+++
Algodonite	Cu_6As	+++
Dyscrasite	Ag_3Sb	++++
Argentite	AgS	+++
Hessite	Ag_2Te	++
Berzelianite	Cu_2Se	++
Petzite	Ag_3AuTe_2	+++
Chalcocite	Cu_2S	++++
Stromeyerite	$CuAgS$	+++
Bornite	Cu_5FeS_4	+++
Galena	PbS	++++
Clausthalite	$Pb-CuSe$	++
Altaite	$PbTe$	+++
Sphalerite - Ferriferous	ZnS	++
Metacinnabar	HgS	++++
Tiemannite	$HgSe$	++++
Chalcopyrite	$CuFeS_2$	++++
Stannite	Cu_2FeSnS_4	+++
Pyrrhotite —	$Fe_{1-x}S$	++++
Niccolite	$NiAs$	+++
Millerite	NiS	++++
Pentlandite	$(FeNi)_4S_8$	+++
Cubanite	$CuFe_2S_3$	+++
Covellite	CuS	+++
Sternbergite	$AgFe_2S_3$	-
Cinnabar	HgS	-
Tetrahedrite - Mercurian	$(CuFe)_{12}Sb_4S_{13}$	+++
Siegenite	$(CoNi)_3S_4$	+++
Carrollite	Co_2CuS_4	++

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TABLE XIX

MISCELLANEOUS ANODE MATERIALS

Research Notebook Reference	Description of Sample and Source	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
1400:14	Silicon ferrite from Horizons, Inc.	5.0	294	4.2-5.0	11	Appreciable erosion of anode sample as evidenced by dark red-brown electrolyte
1400:15	Impervious graphite from Falls Industries	5.0	149	5.0-5.3	11	Appreciable erosion of anode sample as evidenced by black electrolyte
1400:16	Manganite from Penn State College	2.0	125	11-12	11	No noticeable erosion
1400:16	Natural graphite from Ward's Natural Science Establishment	10.0	200	6.0	-	Very rapid erosion
1400:57,93	Nickel-ferrite boule from Linde Air Products Co.	1.2	200	7.0-8.6	12	No noticeable erosion but conversion of chlorate to perchlorate was very low
1400:56	Gold Rod	1.0	100	4.0	5	Anode weight loss was 43 mg. per ampere hour; orange precipitate formed in electrolyte and a rust colored film formed on gold rod.
1364:177	Silver Sheet	2.6	200	6.1-19.0	0-2	Electrolyte was maintained alkaline at a pH from 7.5 to 8.5. Silver surface is etched unevenly and also a dark gray smut is formed. Appreciable erosion even after silver sample was first anodically electrolyzed in 1% sodium hydroxide to form a black deposit.

The testing of silver sheet as anode in the mildly alkaline electrolyte (pH = 8.5) in the chlorate-perchlorate cell resulted in rapid and uneven etching of the silver and the formation of a dark gray smut over the anode surface. A high rate of erosion also resulted when the silver was first anodically electrolyzed in 15% sodium hydroxide solution to form a black deposit.

Polished plate glass samples with a conductive film on one side fabricated by Pittsburgh Plate Glass Company failed rapidly. They operated at low current and high voltage with either the conductive film coming off as a cloud, the plate glass cracking at the electrolyte level, or the current lead melting off because of the heat generated.

Tin oxide blocks, also furnished by Pittsburgh Plate Glass Company were more promising, showing: for Sample A123, slight amount of erosion and about 15% current efficiency; Sample B92, contact difficulties were so great that current efficiency could not be obtained; Sample B8, no erosion and about 17% current efficiency; and Sample B53, no appreciable erosion and about 50% current efficiency. Further samples of the Type B53 should be tested (see Table XX).

Samples of conducting glasses and refractories from the Corning Glass Works either eroded or operated at a very high cell voltage, (see Table XXI).

Samples of platinum group metals and their alloys have all been received from Baker & Co., and tests will start shortly.

A pressed and fired mixture of lead dioxide and magnetite was fabricated (*) for testing as anode material. These samples were hard and showed good conductivity. When tested in the chlorate-perchlorate cell, they showed considerable mechanical disintegration.

Additional samples were made by pressing lead dioxide alone or with varying amounts of manganese dioxide or magnetite. Samples were made without binders and with 50% potassium hydroxide and sodium silicate (8% Na_2O, 26% SiO_2) in the range of 0.02 to 0.07 gram per gram of powdered mixture. Firing was done at 300°C. in oxygen or air for periods ranging from 3 to 18.5 hours. The more promising of these samples as shown by conductivity tests and mechanical disintegration tests in sodium chlorate solution (600g./l.) will be prepared in sizes suitable for testing as anodes in the chlorate-perchlorate cell.

(*) A powdered mixture of C.P. lead dioxide powder (75 weight %) and minus 250 mesh magnetite (25 weight %) with a binder of 0.045 parts of 50% potassium hydroxide per part of PbO_2-Fe_3O_4 mixture was pressed at 15,000 pounds per square inch and then fired in air for 6 hours at 300°C. The resulting cylinder (21.9 mm. high x 28.6 mm. O.D.) had a density of about 5.6 grams per cc.

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TABLE XX

PITTSBURGH PLATE GLASS SAMPLES

Research Notebook Reference	Description of Sample	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode
1400:47,61	Tin Oxide Block-Sample A123-NESA on the large unsilvered faces	1.0-2.3	87-200	5.1-9.8	12	Slight amount of pinpoint erosion. Cell operated at about 15% current efficiency
1400:17,71	Tin Oxide Block-Sample B92-NESA on the large unsilvered face	0.96	100	20-44	12	Poor conductor so that good electrical contact could not be obtained
1400:59	Tin Oxide Block-Sample B8- No NESA coating on any face	1.0	200	6.2-14.0	12	No noticeable erosion.Cell operated at about 17% current efficiency
1400:58	Tin Oxide Block-Sample B53-No NESA coating on any face	1.0	115	4.2-7.5	12	No noticeable erosion.Cell operated at about 50% current efficiency
1400:72	Polished Plate Glass-NESA Solution "A" on one face (4 samples)	0.5-1.8	-	60-110	-	All these samples operated at very low current and high voltage with either the conductive film coming off as a cloud,or the plate glass cracking at the electrolyte level, or the current lead melting off because of the heat generated.
1400:72	Polished Plate Glass-NESA Solution "B" used for coating the faces (4 samples)	0.5-1.8	-	60-110	-	

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TABLE XXI

CORNING GLASS WORKS SAMPLES

Research Notebook Reference	Description of Sample	Average Cell Current (Amperes)	Anode Current Density (approx.) ma/sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
1400:48,60	Sample A – Conducting Refractory	2.6	200	7.8–9.0	12	Appreciable erosion giving electrolyte white cloudy appearance. Current efficiency was about 40%.
1400:50	Sample B – Conducting low expansion glass	0.6	–	43	–	Operated at too high cell voltage to be considered practical.
1400:49	Sample C – E.C.Glass Rod	2.6	245	6.0–33	12	Appreciable erosion giving electrolyte a white cloudy appearance.

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1 Dr. W. A. LaLande.

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