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INVESTIGATION OF METHODS TO PRODUCE SODIUM PERCHLORATE WITHOUT THE USE OF PLATINUM

PART I - Literature Review

PROJECT - NR 352-263/2-19-51

CONTRACT NUMBER - NONR 372(00)

OFFICE OF NAVAL RESEARCH

PENNSYLVANIA SALT MANUFACTURING COMPANY

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SUBJECT: Sodium Perchlorate, Methods of Producing Without the Use of Platinum.

Office of Naval Research Project NR 352-263/2-19-51: Contract Number NONR 372(00).

OBJECT: An investigation in respect to the determination of a method for producing sodium perchlorate without the use of platinum, to include, but not necessarily to be limited to, the following:

(1) Literature and patent review, both domestic and foreign, on possible substitutes for platinum as anode materials in the production of sodium perchlorate:

(2) Preliminary laboratory experiments with the more promising anode materials:

(3) Literature and patent review, both domestic and foreign, on the thermal decomposition of sodium chlorate for the production of sodium perchlorate; and

(4) Preliminary laboratory experiments to indicate the feasibility of a thermal decomposition method.

SCOPE: The rapid expansion of the production of perchlorates during the last few years and contemplated increases in the demand for perchlorates, together with the decreasing reserves of platinum, the metal now used in the production of sodium perchlorate (the starting material for potassium and ammonium perchlorate), make it desirable at this time to search for methods to produce perchlorates that will require less platinum. Part I of this report bound in this cover, comprises a review of the technical literature, including patents, of all methods reported for the production of perchlorates, and of all apparatus and techniques that might be adapted to such production. Part II of this report, to be bound separately, is a short but critical laboratory study of the methods described in the literature, and of other methods that were suggested during the course of the work.

Every effort was made to make the literature review complete to the end of 1950. The 1951 literature was covered as completely as possible by checking chemical abstracts to date; however, many 1951 foreign references may have been missed.

SUMMARY:

1. The physical, chemical and thermodynamic properties of the common chlorates and perchlorates are reviewed.

2. The historical development of electrolytic perchlorate manufacture is outlined with special reference to the effect of such operating variables as electrolyte concentration, temperature, current density, and pH.

3. The operation of three modern perchlorate plants is described in some detail. Under the conditions employed in modern perchlorate cells, platinum appears to be the only practicable anode material thus far proposed, although extensive work has been done on the development of a substitute.

4. Among the platinum-substitute anode materials which have reportedly been used successfully in small scale perchlorate production are magnetite, lead dioxide, silicon, silicon carbide, and graphite (in a diaphragm cell). Various methods of fabricating magnetite and lead peroxide anodes to improve their mechanical strength, electrical properties, etc., are reviewed.

5. Other "insoluble" anode materials, which have not been tested in perchlorate formation but which have been proposed for use under severe conditions, include lead-antimony-silver alloys, lead-thallium-tin alloys, copper-silicon-iron alloys, ferrosilicon and other silicides, ilmenite, and manganese dioxide.

6. Detailed work on the thermal conversion of chlorate to perchlorate has been limited almost entirely to small-scale studies on potassium chlorate. With this salt, the theoretical maximum yield of about 85 g. $KClO_4$ per 100 g. $KClO_3$ has not been realized because of the concurrent thermal decomposition of $KClO_3$ and $KClO_4$ to KCl and O_2. Sodium chlorate appears to give lower yields than the potassium salt and the alkaline earth and heavy metal perchlorates appear to be entirely unsuitable.

7. Large scale studies of the thermal method are lacking. Since the time-temperature-yield relationship is profoundly influenced by the amount of material involved, it is not possible to evaluate this method as a possible commercial method on the basis of existing knowledge.

8. In most cases, chemical oxidizing agents do not convert chlorate to perchlorate efficiently. Possible exceptions to this generalization are the oxidation of potassium chlorate with lead dioxide and the oxidation of hypochlorites with ozone.

9. The conversion of chlorates to perchlorates by the action of a strong mineral acid, such as sulfuric acid, gives a theoretical yield of 57.4 g. $NaClO_4$ per 100 g. $NaClO_3$ if the chlorite by-product is not worked up. Actual yields may be considerably lower than theoretical.

10. The electrolytic production of perchloric acid from HCl employs platinum anodes. There is no indication that substitute anode materials could be used under the conditions of this electrolysis.

11. The electrolytic oxidation of lithium chloride and alkaline earth chlorides to the corresponding perchlorates has been studied with platinum anodes. Again there is no suggestion as to the possible effectiveness of substitute anode materials.

LITERATURE REVIEW

PERCHLORATES-PROPERTIES AND METHODS OF PREPARATION

A. Introduction

Perchlorates and methods for their preparation had been known and studied for more than 75 years before O. Carlson, in 1895, first began to make these compounds on an industrial scale (140). The commercialization of perchlorates was almost certainly instigated by the discovery of the perchlorate explosives (e.g. "carlsonite"), and Swedish production was soon augmented by plants in France and Germany. Thereafter, world production rose to about 2000 tons per year in 1940.

Prior to World War II, the United States imported a large part of its perchlorate requirements. Only one domestic manufacturer was making perchlorates in 1939 (115), and U.S. production at that time has been estimated at 1000 tons/year (116). The loss of European sources was responsible for the initial expansion of the perchlorate industry in the U.S., and as a result of new military developments, such as rocket propulsion, U.S. production rapidly mounted to about 20,000 tons per year (116). This increased production was made possible by the erection of 4 new plants (3 new manufacturers) during the early 1940's. U.S. producers (86) of potassium perchlorate are reported to include:

G. Frederick Smith Chemical Co., Columbus, Ohio
*Cardox Corporation, Claremore, Okla.
Western Electrochemical Co., Los Angeles, Cal., and Henderson, Nev.
Oldbury Electrochemical Co., Niagara Falls, N.Y.
J. T. Baker Chemical Co., Phillipsburg, N. J.

Apparently, perchlorates are made industrially exclusively by the electrochemical method. In this operation, sodium perchlorate is formed by the anodic oxidation of sodium chlorate. The conditions of the electrolysis are such that platinum has so far been found to be the most suitable anode material and is, in fact, the only anode material used in actual commercial operations described in the literature. However, loss of platinum by electrochemical attack and mechanical disintegration is a significant item in manufacturing costs, and extensive efforts have been made to develop a substitute. The Germans appear to have concentrated on the development of magnetite anodes, and the Japanese on lead peroxide anodes as substitutes for platinum. At the end of the war, however, the Germans were still using platinum anodes in their only perchlorate plant (I. G. Farbenindustrie A.G. at Bitterfeld), although magnetite anodes were used in their chlorate cells (80, 139). The state of the art in Japan has not been revealed.

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* Not listed by ref. (86), but is given by Oil, Paint & Drug Reporter Greenbook, 1950-1951.

The thermal production of perchlorates from chlorates appears never to have been developed commercially, presumably for economic reasons, although a great deal of study has been devoted to the reactions involved.

Other methods of converting chlorates to perchlorates have been investigated, but in considerably less detail.

Sodium perchlorate, the primary electrochemical product, is usually not marketed because its monohydrate, the form in which this compound crystallizes from solution below about 53°C., is hygroscopic and troublesome to handle. The sodium salt is more commonly converted directly into potassium or ammonium perchlorate. These are used (48) in the manufacture of explosive, detonating, flare, matchhead, primer, pyrotechnic, and smoke-producing compositions, as well as in brazing and welding fluxes, chemical heating compositions, and binders for briquetted coal, coke, etc. Miscellaneous analytical, photographic, and pharmaceutical uses also exist.

Specifications for maximum allowable impurities in commercial perchlorates (117) are as follows:

$KClO_4$	
$KClO_3$	0.15%
KCl	0.25
$KBrO_3$	0.04
NaCl	0.20
$CaCl_2$ and $MgCl_2$	0.20
Hypochlorite	none
Metallic elements	0.001
Insolubles	0.10

NH_4ClO_4	
$NaClO_3$	0.15%
NH_4Cl	0.20
$NaBrO_3$	0.04
$(NH_4)_2SO_4$	0.20
Moisture	0.10
Ash (H_2SO_4 treated)	0.25
Metallic elements	0.04
Insolubles	0.10

The potassium salt is quoted at present at 14¢/lb. (carload lots, works), and the ammonium salt at 50¢/lb. (kegs, works). (Oil, Paint and Drug Reporter, July 23, 1951).

B. Properties of Sodium Perchlorate

For ready reference, the properties of sodium and potassium perchlorates and closely related compounds are reviewed at this point because of their bearing on the various processes and operations to be discussed in later sections of this report, and also to provide a basis for the experimental work which forms another part of this project.

1. Physical Properties

In Table I (p. 5) are presented some of the physical properties (50, 74, 75, 109, 117) of sodium perchlorate, together with those of sodium chlorate from which the former is derived, of potassium chlorate, and of potassium and ammonium perchlorates, into which the sodium salt is generally converted.

TABLE I

PHYSICAL PROPERTIES

	$KClO_3$	$NaClO_3$	$NaClO_4$	$KClO_4$	NH_4ClO_4
Formula weight	122.55	106.45	122.45	138.55	117.50
Color	white	white a/	white b/	white	white
Crystalline form, low temp.	monocl.	cubic c/	rhombic d/	rhombic d/	rhombic d/
high temp.	-	-	cubic	cubic	cubic
transition temp., °C.	-	-	308	299-300	240
Specific gravity	2.32	2.490	2.499 (148)	2.520	1.95
Refractive index, n_D^{20}	1.440	1.515	1.4617	1.474	1.482
Melting point, °C.	368 356 (101a)	248 (109) 255 (74) 248-265(87)	474 (57) e/ 482 (21)	610±10 (21) 525-530 f/	decomp. g/
Solubility in water	see Table II and Figure I (pp. 6 , 7)				
Solubility in other solvents	see Table III and Figure II (pp. 8 , 9)				

a/ Anhydrous salt and monohydrate are both hygroscopic.

b/ The monohydrate, which crystallizes from solution below 52.75°C., is hygroscopic; it can be completely dehydrated at 130°C. (30).

c/ Crystals are optically active. An unstable trigonal form is produced when crystallized from a supersaturated solution of the cubic salt or from solution in the presence of $NaClO_4$ or Na_2SO_4.

d/ This dimorphism is exhibited by perchlorates of alkali metals except Li, also by the perchlorates of ammonium, barium, silver, and thallium (142).

e/ Complete decomposition occurs at 460-540°C. in 300 min. (57). Elsewhere it is stated that $NaClO_4$ is stable up to 471°C. (30).

f/ Complete decomposition occurs at 550-580°C. (57); 25% decomposed in 65 min. at 520° and 2.3% in 65 min. at 444.5°C. (138).

g/ Sublimes; begins to decompose in vacuo at 150°C.; deflagrates at 400°C. (117).

TABLE II

SOLUBILITY IN WATER AND DENSITY OF SATURATED SOLUTIONS

(S= grams anhydrous salt/100 grams saturated solution)
(*= saturated solution at the boiling point)

t°C.	$KClO_3$			$NaClO_3$			$NaClO_4$			$KClO_4$			NH_4ClO_4		
	d	S	Ref	d	S	Ref	d	S	Ref.	d	S	Ref	d	S	Ref
0	1.021	3.2	120	-	44.32	8	-	62.64	43	1.0005	0.705	93	1.059	12.39	117
10	-	4.9	120	-	46.70	8	-	-	-	-	-	-	-	-	-
15	1.0363	5.739	71	1.406	47.91	108	1.663	65.57	27,43	1.0076	1.333	71	-	-	-
20	1.0420	6.793	71	-	48.95	8	-	-	-	1.0085	1.647	71	1.098	23.43	117
25	1.0484	7.999	71	-	50.13	8,108	1.683	67.76	27,145	1.0096	2.029	71	-	20.02	43
30	-	9.2	120	-	51.30	8	-	68.71	43	-	-	-	-	-	-
35	-	-	-	-	52.38	8	-	-	-	-	-	-	-	-	-
40	1.073	12.2	120	-	53.54	8	-	70.88	43	1.022	3.60	120	1.128	37.18	117
45	-	-	-	-	54.59	108	-	-	-	-	-	-	-	28.02	43
50	-	15.6	120	-	-	-	1.749	72.31	27,43	1.0181	5.07	93	-	-	-
55	-	-	-	-	-	-	1.756	73.94	27	-	-	-	-	-	-
60	1.115	19.2	120	-	-	-	-	74.3	43	-	-	-	1.158	51.55	117
75	-	-	-	-	61.40	108	1.757	75.0	27,43	1.036	10.36	120	-	39.45	43
80	1.165	27.3	120	-	-	-	-	-	-	-	-	-	1.193	67.76	117
100	1.219	36.0	120	-	67.10	8	1.758	76.75	27	1.0660	15.76	93	1.216	88.25	117
107	-	-	-	-	-	-	-	-	-	-	-	-	1.221	*93.86	117
122	-	-	-	1.654	*74.0	109	-	-	-	-	-	-	-	-	-
143	-	-	-	-	-	-	1.789	79.03	27	-	-	-	-	-	-
200	-	72.0	120	-	-	-	-	-	-	-	52.5	120	-	-	-
280	-	91.0	120	-	-	-	-	-	-	-	-	-	-	-	-

← Solid phase is $NaClO_4 \cdot H_2O$ → (0–50 °C)
← Solid phase is $NaClO_4$ → (55–280 °C)

PENNSYLVANIA SALT MANUFACTURING CO. SUBJECT FIGURE 2

Solubility in Water (from data in Table II)

DATE May 1951

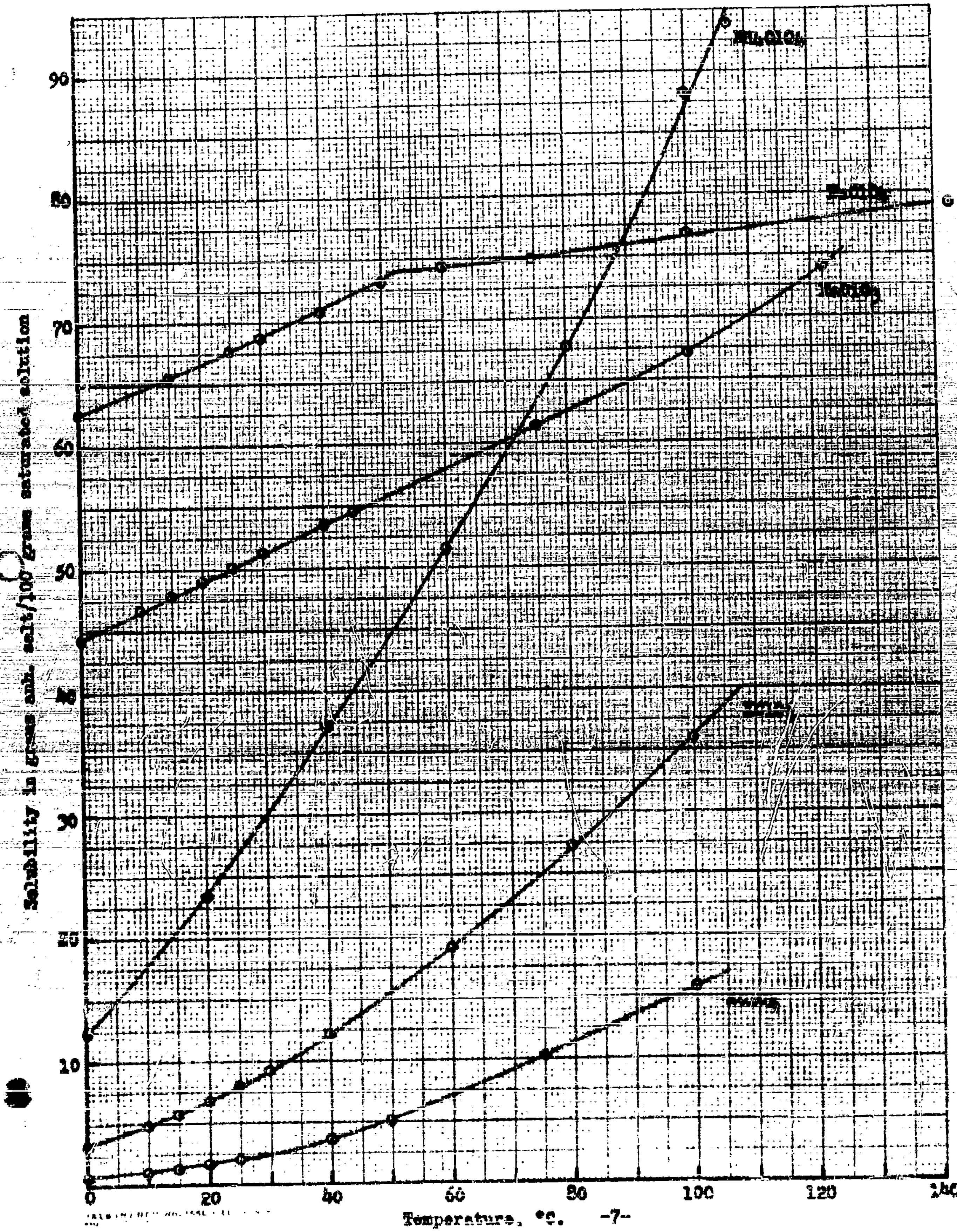


TABLE III

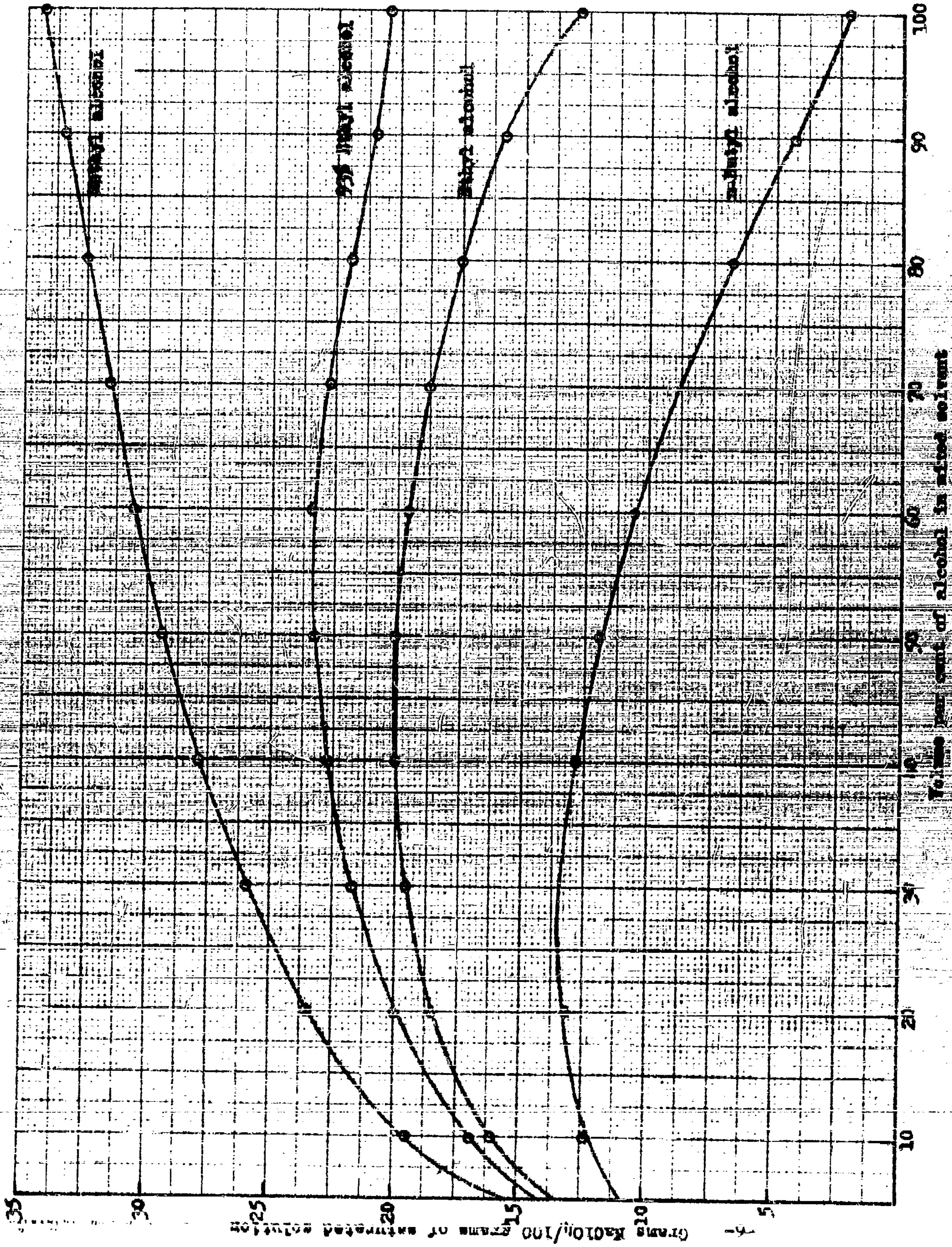
SOLUBILITY IN NON-AQUEOUS SOLVENTS AT 25°C.

	$NaClO_3$	$NaClO_4$		$KClO_4$		NH_4ClO_4	
	Solubility in grams/100 grams of solvent (55)						
Ammonia (120)	-	-		-		137.93	
Ethylenediamine	52.8	30.1		2.81		-	
Monoethanolamine	19.7	90.8		1.36		-	
Ethyleneglycol	16.0	75.5		1.03		-	
Water	106.	209.6		2.07		-	
Sulfur dioxide (120)	-	-		-		0.025 (0°C.)	
	Solubility in grams/100 grams saturated solution (145) (Solution density in parentheses)						
Water	-	67.70	(1.6821	2.02	(1.0096)	19.95	(1.0982)
Methyl alcohol	-	33.93	(1.0561)	0.105	(0.7878)	6.41	(0.8218)
Ethyl alcohol	-	12.82	(0.8685)	0.012	(0.7852)	1.872	(0.7951)
n-Propyl alcohol	-	4.66	(0.8308)	0.010	(0.8011)	0.385	(0.8016)
n-Butyl alcohol	-	1.83	(0.8167)	0.0045	(0.8060)	0.017	(0.8069)
iso-Butyl alcohol	-	0.78	(0.8031)	0.005	(0.7981)	0.127	(0.7988)
Ethyl acetate	-	8.80	(0.9574	0.0015	(0.8945)	0.032	(0.8947)
Acetone	-	34.10	(1.0732)	0.155	(0.7868)	2.21	(0.7997)
Anh. HF (42)	-	-		9.6 ± 2		-	

PENNSYLVANIA SALT MANUFACTURING CO. SUBJECT FIGURE 2

Solubility of $NaClO_4$ in Mixtures of Various Alcohols with Ethyl Acetate (128)

DATE May 1951



In addition to the solubility data given, Cornec and Dickely (27) reported some results on equilibrium in the system $NaClO_4$-$NaCl$-H_2O at 0° to 100°C., and Freeth (43) published results on equilibrium in the system $NaClO_4$-Na_2SO_4-H_2O at 35° and 60°C. Bozorth (15) reported the solubility of $KClO_4$ in aqueous solutions of a number of salts; these values are plotted in Figure 3 (p. 11). Previously, Noyes et al. (94) had determined the solubility of $KClO_4$ in aqueous KCl and K_2SO_4 solutions. Benrath and coworkers (10) studied the system $KClO_4$-KCl-H_2O, including measurements at elevated temperatures (150°-250°C.). Chang and Hsieh (23) found the solubility of $KClO_3$ and $KClO_4$ in heavy water to be 0.935 and 0.947 mole, respectively, per 55.51 moles of D_2O. Calzolari (20) determined the solubilities of potassium, rubidium, and caesium chlorates and perchlorates in the range 0-99°C. Van Valkenberg and McDaniels (141) measured the solubility of sodium and potassium perchlorates in 95 to 99.8% ethyl alcohol at 20°C.; and Seward and Schumb (122) determined the solubility of potassium perchlorate in ethyl alcohol in the presence of other salts.

Kayas (69) studied the separation of $NaClO_4$ and $KClO_4$ using small amounts of radioactive sodium salt. Four recrystallizations from water reduced the amount of sodium to a very low value; ten extractions of the evaporated salt with alcohol was less successful in removing the sodium salt.

Mazzucchelli and Pro (84) measured the densities of aqueous solutions of certain perchlorates and showed that for sodium perchlorate, the apparent volume of the salt increases with increasing concentration and with increasing temperature, in accord with the general rule. In the low concentration range (up to 0.1 molar), Jones (63) found that the densities of aqueous solutions at 25°C. could be expressed by the equations:

$$NaClO_4: \quad d = 0.9971 + 0.0768\, m$$

$$KClO_4: \quad d = 0.9971 + 0.0863\, m$$

Jones (63) also measured the equivalent conductances of sodium and potassium perchlorate in water at 25°C. over the same concentration range.

$$NaClO_4: \quad \Lambda = 117.48 - 87.22\sqrt{c} + 92.6\, c(1-0.2294\sqrt{c})$$

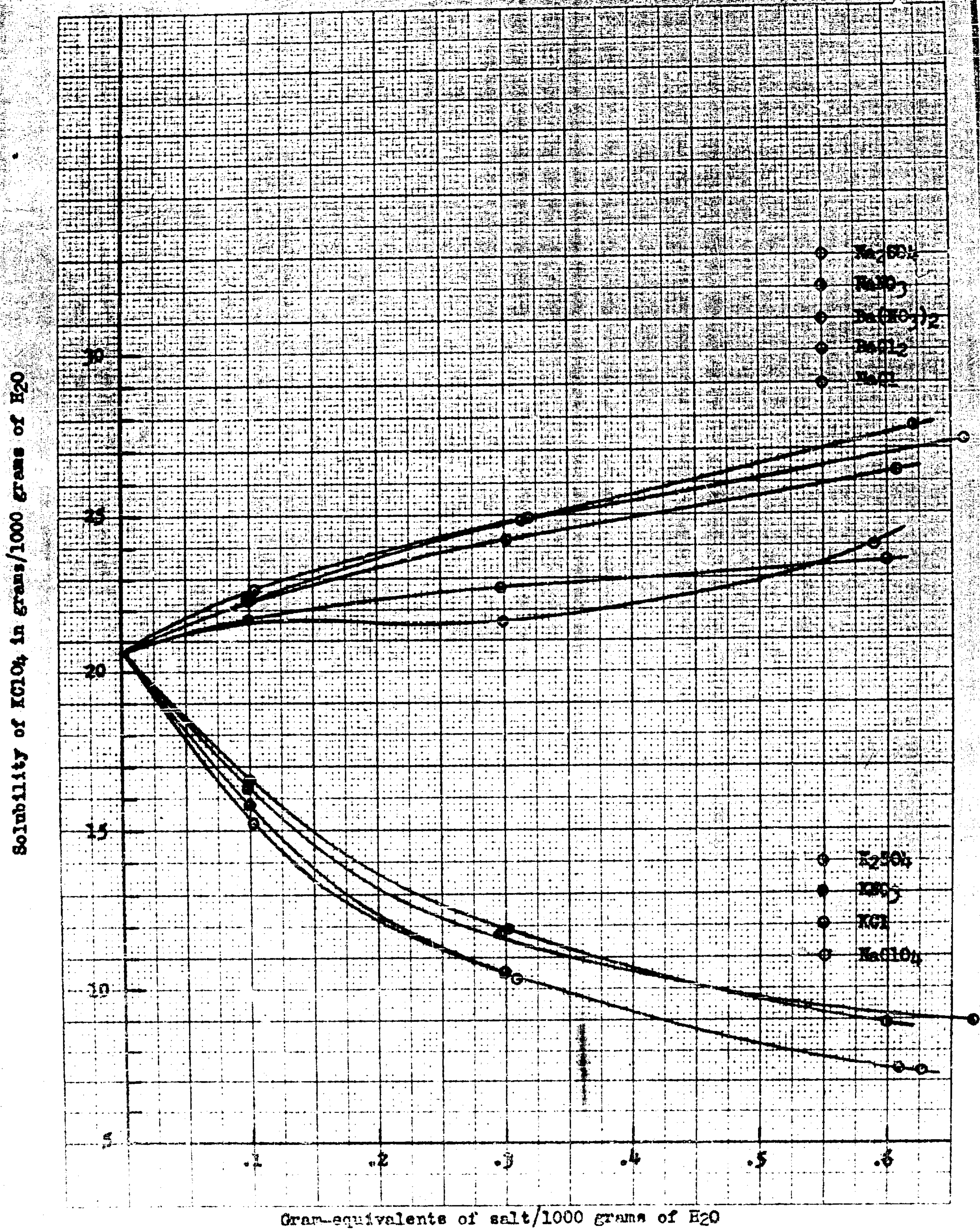
$$KClO_4: \quad \Lambda = 140.04 - 92.57\sqrt{c} + 49.0\, c(1-0.2294\sqrt{c})$$

The limiting conductance of the perchlorate ion, later confirmed by Monk (92), was found to be 67.32. In ethyl alcohol solution, Copley et al. (25) found that the conductance of sodium perchlorate could be calculated from the expression:

$$\Lambda = 52.45 - 233\sqrt{c}$$

PENNSYLVANIA SALT MANUFACTURING CO. SUBJECT FIGURE 3

Solubility of $KClO_4$ in Solutions of Various Salts (15). DATE May 1951



Walden and Ulich (144) made conductivity measurements on dilute aqueous perchlorate solutions at 0°, 18°, and 100°C. Walden and Herm (143) measured the conductivity of sodium perchlorate in anhydrous hydrazine.

Among the miscellaneous physical properties are to be found papers on the structure of the perchlorate ion (16,36,51,118); the freezing points of aqueous solutions of sodium and potassium chlorates and perchlorates up to 1.1 molal (112); the magnetic susceptibilities of a number of perchlorates (98); the dielectric constants of potassium and ammonium perchlorates (79); the coefficients of expansion and densities of potassium chlorate and perchlorate at 19°, -78°, and -195°C. (54); and the compression to 25,000 Kg./cm^2 of a number of perchlorates (17).

2. Chemical Properties

Thermal Decomposition

The thermal decomposition of alkali metal perchlorates yields oxygen and alkali metal chloride; the perchlorates are more stable than the corresponding chlorates, however, and require higher temperatures to effect the decomposition. Marvin and Woolever (82) gave the following decomposition temperatures:

$NaClO_4$	- 480°C.	$LiClO_4$	- 440°C.
$KClO_4$	- 510°C.	$Ca(ClO_4)_2$	- 405°C.

Duval (30) stated that $NaClO_4$ is stable up to 471°C. and begins to decompose at that temperature, decomposition being complete at about 620°C. Carnelly and O'Shea (21) gave 482°C. as the melting point of $NaClO_4$ without stating if any decomposition occurs; Mellor (87) indicates some decomposition at this temperature. Ishikawa and Hagisawa (57) give 474°C. as the melting point of 99.82% pure $NaClO_4$ and say that decomposition begins at about 460°C., with complete decomposition in 300 minutes at 460-540°C. Agreement is thus unsatisfactory and the most that can be taken from the literature is that $NaClO_4$ probably melts somewhere in the range 474-482°C. and that decomposition begins at or slightly below the melting point. The decomposition temperature of $NaClO_4$, however, is apparently well above the melting point of $NaClO_3$, which falls in the range 248-265°C.

Published results on the decomposition temperature of $KClO_4$ show a similar lack of agreement, but it is reasonably certain that this salt does begin to decompose below the reported melting points. McLeod (85) found no evidence of decomposition at 357°C. (boiling mercury). Many reference texts say that $KClO_4$ begins to decompose at 400°C. On the other hand, Scobai (119) reported no detectable decomposition at 411°C., and Franklin and Dingwall (41) found that only 0.3% of the $KClO_4$ was decomposed in 56 hours at 444.6°C. (boiling sulfur). At the same temperature, Tian and Svilovich (136) found 2.3% decomposition in 65 minutes, and

24.9% decomposition in 65 minutes at 520°C. Ishikawa and Hagisawa (57) give 550-580°C. as the range in which complete decomposition occurs. Blau and Weingand (14) obtained their best yields of $KClO_4$ by heating $KClO_3$ for 8 hours (in quartz) at 480°C.; presumably, then, the rate of decomposition of $KClO_4$ in the range 400-480°C. is not high.

Otto and Fry (97) showed that the decomposition of alkali metal perchlorates is unimolecular:

$$KClO_4 \longrightarrow KCl + 2O_2$$

and that, contrary to the reports of earlier investigators (41 and others) no chlorate or chlorine is formed under any conditions of heating. The velocity constant (97) for the decomposition of potassium perchlorate

$$K = \frac{1}{t_2 - t_1} \cdot \log_{10} \frac{a - x_1}{a - x_2}$$

can be calculated at any temperature by means of the equation

$$\log K = 14.0348 - 13245.5/T.$$

Calcium perchlorate on heating yields some oxide (82), the molar ratio of chloride to oxide in the product being about 20:1; other metal perchlorates, when hydrated, yield oxide or hydroxide exclusively:

$$MgClO_4 \cdot 6H_2O \longrightarrow Mg(OH)_2 + 2HClO_4 + 4H_2O$$

The thermal decomposition of the perchlorates is accelerated by a number of substances including the ammonium halides (44), ferric oxide (97), carbonates (56,57), potassium hydroxide (14), copper (14), nickel (14), boron trioxide (14), and nitrites (138). This topic will be discussed in greater detail in Section C.2, page 41.

Oxidation Reactions

Solid perchlorates are powerful oxidizing agents, although they are very much less sensitive to ignition, friction, and percussion in the presence of reducing agents than are the chlorates (117). Thus, potassium perchlorate may be mixed with combustible materials, to make special types of fuel, with comparative safety. Ammonium perchlorate and hydrazine perchlorate are explosive, but the other inorganic perchlorates, according to I.C.C. regulations, may be shipped as "oxidizing agents" in paper or plastic lined steel drums (117).

Stettbacher (129) calculated the heat generated by the combustion of 1 kg. of various incendiary mixtures:

$KClO_4$-Al (dust):	2594 kg.-cal.	$KClO_3$-Al (dust):	2330 kg.-cal.
$KClO_4$-Mg (powder):	2429	$KClO_3$-Mg (powder):	2280
$KClO_4$-P (red):	1477	$KClO_3$-P (red):	1417
$KClO_4$-C (lampblack):	1118	$KClO_3$-C (lampblack):	1083
$KClO_4$-S (rhombic):	705	$KClO_3$-S (rhombic):	672
$NaClO_4$-Al (dust):	2751		

(Iron oxide thermite: 972 kg.-cal.)

Potassium perchlorate is reduced by metallic sodium at 280°C. (6); potassium chlorate, being less stable, is reduced at 100°C. Potassium perchlorate is not reduced by gaseous ammonia below 430°C., whereas the chlorate is reduced below 380°C. (52a).

$$3KClO_3 + 2NH_3 \longrightarrow 2KNO_3 + KCl + Cl_2 + 3H_2O$$

Ammonium perchlorate is reduced by hydrogen at ordinary temperatures (62).

$$2NH_4ClO_4 + 4H_2 \longrightarrow N_2 + Cl_2 + 8H_2O$$

At 400°C., potassium perchlorate reacts with iodides to yield iodate, chlorate, and chloride, with practically no oxygen evolution (44). With warm concentrated sulfuric acid the perchlorates, unlike the chlorates, yield no chlorine dioxide; perchloric acid and potassium sulfate or bisulfate are the products (87,101).

In studying the reaction of perchloric acid with metals, Reedy (106) concluded that the oxidizing power resides in the $HClO_4$ molecule rather than in the ClO_4^- ion. The metal perchlorates are not sufficiently powerful oxidizing agents to react with acidic ferrous solutions, sulfur dioxide, hydrogen peroxide, or with zinc or magnesium in the presence of an acid (47,87). They do not bleach indigo, nor do they react with hot hydrochloric acid (87,101). They will reduce sodium hydrosulfite, but only when the solution is sufficiently alkaline, and heated to the boiling point (7). Potassium perchlorate is reduced by thiosulfate (47), by glucose in the presence of platinum black (47), by ferrous hydroxide in boiling solution (62), and by titanous ion ($TiCl_3$) in strongly acid solution (117).

Electrochemical Reactions

Perchlorates may be reduced cathodically to chlorides under suitable conditions. The electrolysis of concentrated perchlorate solutions at low temperatures yields ozone (117).

3. Thermodynamic Functions

Available thermodynamic and thermochemical data for sodium and potassium chlorates and perchlorates are presented in Tables IV, V, VI, and VII on pages 16, 17, 18, 18.

In addition to the data given in these tables, the literature contains information on the molar heats of hydration and solution of the perchlorates of lithium, sodium, magnesium, calcium and barium (127); on integral heats of solution, differential heats of solution, and the specific heats of $NaClO_3$ and $NaClO_4$ solutions (24); on the integral heats of dilution of $KClO_3$ and $KClO_4$ in great dilutions at 15° and 25°C. (2); and on heats of dilution of $NaClO_4$ in methyl alcohol (61).

C. Manufacture of Sodium Perchlorate

The various methods for the preparation of metal perchlorates may be classified as follows:

1. Electrolysis of an aqueous chlorate solution, in which process the chlorate is oxidized anodically to perchlorate.

2. Thermal decomposition of a chlorate, in which process the chlorate undergoes oxidation-reduction to perchlorate and chloride.

3. Direct chemical oxidation of chlorates to perchlorates by means of such oxidizing agents as persulfates, lead dioxide, ozone, etc.

4. Reaction of a strong mineral acid on a chlorate to produce a perchlorate, a chloride, and chlorine dioxide.

5. Electrolytic production of perchloric acid from hydrochloric acid, followed by neutralization of the acid with the appropriate base.

6. Electrolysis of chloride and hypochlorite solutions.

Of these methods, only the first named has actually been developed on a commercial scale. The literature on all the proposed methods, however, is reviewed in this section of the report.

TABLE IV

HEATS OF FORMATION AND SOLUTION, ENTROPY, AND HEAT CAPACITY AT 25°C.

Compound	State	Heat of Formation ΔH_f kg.-cal./mole	Free Energy of Formation ΔF_f^o kg.-cal./mole	Entropy S^o cal./deg.mole	Heat Capacity C_p^o cal./deg.mole	Heat of Solution ΔH_s kg.-cal./mole
$HClO_3$	Std. aq. m = 1	-23.50 (121)	-	-	-	-
$HClO_4$	liq.	-11.1 (121)	-	-	-	-
	Std. aq. m = 1	-31.41 (121)	-	-	-	-
	aq.	-31.65 (45)	-	-	-	-
$NaClO_3$	cryst.	-85.73 (121)	-	-	23.87 (74)	-
	Std. aq. m = 1	-80.78 (121)	-63.21 (121)	53.4 (121	-	-
	400 aq.	-80.74 (121) -78.34 (12)	-	-	-	-
	∞ dil.	-80.78 (121) -78.23 (12)	-	-	-	5.29 (24)
$KClO_3$	cryst.	-93.50 (121)	-69.29 (121)	34.17 (121)	23.96 (121)	-
	Std. aq. m = 1	-83.54 (121)	-68.09 (121)	63.5 (121)	-	-
	400 aq.	-83.61 (121)	-	-	-	-
	∞ dil.	-83.54 (121)	-	-	-	-
$NaClO_4$	cryst.	-92.18 (121) -93.0 (45) -100.2 (11)	-	-	26.0 (24) 24.1 (121)	-
	Std. aq. m = 1	-88.69 (121)	-65.16 (121)	57.9 (121)	-	-
	400 aq.	-88.76 (121)	-	-	-	3.33 (12)
	∞ dil.	-88.69 (121) -89.5 (45)	-	-	-	3.44 (24) 3.48 (127) 3.51 (5)
$KClO_4$	cryst.	-103.6 (121) -104.4 (45) -112.5 (11)	-72.7 (121)	36.1 (77,121)	26.33 (77,121)	-
	Std. aq. m = 1	-91.45 (121)	-70.04 (121)	63.0 (121)	-	-
	500 aq.	-91.58 (121)	-	-	-	-
	∞ dil.	-91.45 (121) -92.3 (45)	-	-	-	12.1 (11) 12.12 (77)
ClO_3^-	Std. aq. m = 1	-23.50 (121)	-0.62 (121)	39.0 (121)	-	-
ClO_4^-	Std. aq. m = 1	-31.41 (121)	-2.47 (121)	43.2 (121)	-18. (121)	-
NaCl	cryst.	-98.232 (121)	-91.785 (121)	17.30 (121)	11.88 (121)	-
KCl	cryst.	-104.175 (121)	-97.592 (121)	19.76 (121)	12.31 (121)	-

TABLE V

THERMOCHEMICAL RELATIONSHIPS

Eq.	Reaction	ΔH (Heat of Reaction) kg.-cal./mole	Reference
1.	$Cl_2 + 3.5 O_2 \longrightarrow Cl_2O_7$ (gas)	$+63.4 \pm 3$	(45)
2.	Cl_2O_7 (gas) $\longrightarrow Cl_2O_7$ (liq)	-8.3	(45)
3.	Cl_2O_7 (liq) + H_2O (liq) + aq. $\longrightarrow 2HClO_4$ (aq)	-50.0 ± 0.5	(45)
4.	$0.5\ H_2 + 0.5\ Cl_2 + 2\ O_2$ + aq. $\longrightarrow HClO_4$ (aq)	$-31.6_5 \pm 1.7$	(45)
5.	$Na + 0.5\ Cl_2 \longrightarrow NaCl$	-98.232	(121)
6.	$K + 0.5\ Cl_2 \longrightarrow KCl$	-104.175	(121)
7.	$Na + 0.5\ Cl_2 + 1.5\ O_2 \longrightarrow NaClO_3$	-83.73	(121)
8.	$K + 0.5\ Cl_2 + 1.5\ O_2 \longrightarrow KClO_3$	-93.50	(121)
9.	$Na + 0.5\ Cl_2 + 2\ O_2 \longrightarrow NaClO_4$	-92.18	(121)
10.	$K + 0.5\ Cl_2 + 2\ O_2 \longrightarrow KClO_4$	-103.6	(121)
11.	*$NaClO_3$ (solid) $\longrightarrow NaClO_3$ (liq) at 255°C.	5.29	(74)
12.	$NaClO_4$ (solid) $\longrightarrow NaClO_4 \cdot H_2O$ (solid) at 18°C.	-2.015	(127)
13.	$NaClO_3 \longrightarrow NaCl + 1.5\ O_2$	-14.5	(calc. from eqs. 5 & 7)
14.	$KClO_3 \longrightarrow KCl + 1.5\ O_2$	$\begin{cases} -12.1 \pm 0.3 \\ -10.7 \end{cases}$	(52) (calc. from eqs. 6 & 8)
15.	$NaClO_4 \longrightarrow NaCl + 2\ O_2$	$\begin{cases} +3.0 \\ -6.1 \end{cases}$	(11) (calc. from eqs. 5 & 9)
16.	**$KClO_4 \longrightarrow KCl + 2\ O_2$	$\begin{cases} +7.5 \\ -1.73 \pm 0.07 \\ +0.2 \pm 1.7 \\ -0.58 \end{cases}$	(11) (52) (45) (calc. from eqs. 6 & 10)
17.	*** $4\ NaClO_3 \longrightarrow 3\ NaClO_4 + NaCl$	-39.9	(calc. from eqs. 5, 7, & 9)
18.	$4\ KClO_3 \longrightarrow 3\ KClO_4 + KCl$	$\begin{cases} -63. \\ -41.0 \end{cases}$	(11) (calc. from eqs. 6, 8, & 10)

* For this reaction, ΔC_p = 4.9 cal./mole (121)

** For this reaction, ΔF°_{298} = −16.755 kg.-cal. (77)

*** For $4\ ClO_3^- = 3ClO_4^- + Cl^-$, ΔF° = −53.5 kg.-cal (76)

TABLE VI

ACTIVITY COEFFICIENTS

	γ at 25° (64)	log $\gamma\pm$ at the freezing points (112)			
Molality	$NaClO_4$	$NaClO_3$	$NaClO_4$	$KClO_3$	$KClO_4$
0.01	-	0.0433	0.0439	0.0418	0.0492
0.02	-	.0588	.0588	.0583	.0697
0.05	-	.0865	.0857	.0913	-
0.1	-	.1139	.1116	.1277	-
0.2	-	.1482	.1429	.1771	-
0.3	-	.1718	.1640	-	-
0.5	0.667	.2066	.1936	-	-
0.7	-	.2330	.2151	-	-
1.0	.629	.2644	.2393	-	-
2.0	.608	-	-	-	-
4.0	.627	-	-	-	-
6.0	.675	-	-	-	-
6.5	.691	-	-	-	-

TABLE VII

OXIDATION POTENTIALS (76)

$ClO_3^- + H_2O = ClO_4^- + 2\,H^+ + 2e$	$E° = -1.00$
$ClO_3^- + 2\,OH^- = ClO_4^- + H_2O + 2e$	$E° = -0.17$

1. Electrochemical Oxidation of Perchlorates

a. Historical Development of Method

Apparently perchlorate was first produced electrolytically by Stadion, in 1816 (147) - at about this time, or shortly after, this same investigator discovered perchloric acid by reacting sodium chlorate with concentrated sulfuric acid. (Reviewers have occasionally given the credit to Kolbe who published some observations on the process in 1847). Between the discovery of the electrolytic method and the beginning of commercial production in Sweden in 1895, there appears to be little in the literature on the electrolysis of chlorates. In 1898, the first paper of importance appeared; in this publication, Foerster (39) outlined a set of conditions for obtaining high current yields of perchlorate. Many investigators have since contributed improvements to the process. The findings of some of these investigators are presented briefly, in chronological order, in Table VIII (p. 20) to show the evolution of present-day commercial operation. In terms of the several variables that influence the efficiency of the electrolysis, the following developments were significant:

Electrolyte

Potassium chlorate has been generally recognized as unsuitable for large scale operation, although as late as 1919 a German patent (156) was drawn to the electrolysis of a solution of this compound. $KClO_3$ has the disadvantage of limited solubility and of producing a still less soluble perchlorate which may crust the anodes even when the electrolyte is circulated at high velocity (14). Foerster's observation (39) that current yields were lower with $KClO_3$ than with $NaClO_3$ can probably be discounted in view of Winteler's work (147) which showed that at equivalent concentrations the current yields with these two salts are equal. Common practice is to electrolyze the sodium salt, treat the sodium perchlorate with KCl to precipitate potassium perchlorate, and return sodium chloride to the chlorate cells. It has also been suggested (156) that the sodium perchlorate be treated with potassium chlorate to precipitate potassium perchlorate, and return the sodium chlorate to the perchlorate cells. Perchlorate is usually separated from unconverted chlorate by crystallization; other methods to meet special cases have also been devised (161,195, 198).

In the electrolysis of sodium perchlorate, the trend has been towards the use of more concentrated solutions, the optimum concentration apparently being 600-700 grams per liter. (The electrolyte concentration of 0.6 grams per liter given in a Russian review article (111), according to Chemical Abstracts, is probably an error).

In the electrolysis of $KClO_3$, Winteler observed maximum current efficiency at the start of the process. With $NaClO_3$, however, using more concentrated solutions, maximum current efficiency (>95%) was not attained until electrolysis had proceeded for some hours (96,147). The efficiency has been shown by several investigators to remain at a high level until a major part (e.g., 60%) of the chlorate has been oxidized, and then to fall off rapidly, with the result that the over-all or average efficiency may be as low as 85% (1,146). To overcome this, the addition of more $NaClO_3$ to the electrolyte, as the electrolysis progresses, has been suggested (29,194,198).

TABLE VIII

HISTORICAL DEVELOPMENT OF THE ELECTROCHEMICAL

Source/Year (Ref.)	Electrolyte	Anode	Cathode	Temperature
Foerster/1898 (39)	$KClO_3$ - 5% soln. $NaClO_3$ - up to 50% soln. Current yields increased with increasing electrolyte concn.	Pt	No reduction at Pt, Pb, Cu, Zn, or Ni at high C.D. but rapid reduction at Fe and Co.	Low temp. (17-20°C.). Very much better than high temp. (75°C.). Intermediate temps. were not investigated.
Winteler/1898 (147)	$KClO_3$ - saturated soln. $NaClO_3$ - 50% soln. gave about same results as 20% soln. 5% soln. gave lower yields, apparently a minimum concn. exists above which concn. is without effect.	Pt (Platinized Pt is unsuitable)	Pt	Should be below room temp. Poor yields obtained at 50-60°C. No oxidation observed at 100°C. (At boiling point, cathodic reduction occurred).
Lederlin (Pats.)/1902-03 (169,170,171)	Proposes use of dichromate	-	-	-
Oechsli/1903 (96)	Used 4 to 66% $NaClO_3$ solns. States use of $Na_2Cr_2O_7$ (2 g./l.) eliminates cathodic reduction.	Pt (glowed) 3 x 4 cm. sheets. (Platinized Pt gave very much lower yields)	Platinized Pt (one sided sheets) one on either side of anode.	Low temp. gave best results. No perchlorate formed at 80°C.; intermediate temps. not studied.
Allmand/1912 (1) (Reviewing comm. practice).	$NaClO_3$ - 60 to 70% soln.	Smooth Pt High overvoltage said to minimize OH^- discharge	Fe	Under 10°C.
German Pat./1919 (156)	$KClO_3$ solutions	-	-	27°C.
Williams/1920 (146) (Reviewing comm. practice).	$NaClO_3$ - 600 to 700 g./l.	Pt.	Fe	Initially about 30°C. (gradually rises to 45-50°C.). Williams own work showed current eff. does not fall off rapidly up to 60°C. The higher temps. give better current yields: Factor average 3.5; Williams at 42° 3.4; Williams at 59° 3.0
Knibbs et al./1920 (72)	Chlorate solutions show max. conductivity at 550-600 g./l.; perchlorate solns. at 600 g./l. Conductivity falls off above this concn.	-	-	Conductivity increases with temp. Discusses effect of temp. on concn. and discharge of OH^-, Cl^-, ClO^- and on other possible anode reactions.
Bla[illegible] et al./1921 (14[illegible])	$KClO_3$ solutions - 60 g./l.	Pt.	Ni	24-27° Current yield decreased markedly as temp. increased above 20°C. when low C.D. is used (10 amps./dm^2)
Ehrhardt (Pat.)/1932 (194)	$NaClO_3$ - 800 g./l at start $NaClO_3$ is added continuously as electrolysis proceeds, not allowing it to drop below 150 g./l. until $NaClO_4$ is 1000 g./l.	Pt	Fe	40-50°C.
Delavenne/1938 (29)	Solution kept saturated with $NaClO_3$	-		0°C. or lower
[illegible]/193[illegible] (11[illegible])	Current eff. is proportional to chlorate concn.	Pt	-	-

TABLE VIII

...MENT OF THE ELECTROCHEMICAL PERCHLORATE PROCESS

Temperature	Current Density	pH	Voltage	Other Observations
Low temp. (17-20°C.). Very much better than high temp. (75°C.). Intermediate temps were not investigated.	Up to 16.6 amps./dm^2. Obtained up to 98% yield over 22 hrs. in electrolysing a 50% soln. at a C.D. of 8.3 amps./dm^2	Neutral or acid. In alk. solution, oxidation of chlorate occurs only at the beginning.	4.5 v.	Theoretically, 1 amp. should convert 50g. $NaClO_3$ to $NaClO_4$ in 25 hours. O_2 observed toward end of run. Current yields with $KClO_3$ were lower than with $NaClO_3$.
Should be below room temp. Poor yields obtained at 50-60°C. No oxidation observed at 100°C. (At boiling point, cathodic reduction occurred).	Investigated 1,4,8,16 amps./dm^2. Yield increases with increasing C.D.	Neutral	6v with $KClO_3$ 4-4.5v with $NaClO_3$	Current yields with $KClO_3$ are same when equiv. concns. are used. Some reduction occurs if cathode C.D. falls below 2 amps./dm^2. Mechanical agitation is essential.
-	-	Non-alkaline conditions	-	-
Low temp. gave best results. No perchlorate formed at 80°C. Intermediate temps. not studied.	Used 2 to 6 amps./dm^2. If C.D. is high enough, chlorate concn. must fall below a very low value before current yield is appreciably affected.	Increasing alkalinity decreases current yields.	A minimum anode potential is necessary (value not stated).	Amount of O_2 increases as electrolysis continues. Current yield is always a few % lower at start than later in process.
Under 10°C.	8 amps./dm^2	Slightly acid	6.5 - 7 v	Good agitation is needed. Current eff. averages 85% 1 Kg. $NaClO_4$ requires 3.5 KWH.
27°C.	15 amps./dm^2	-	-	-
Initially about 30°C. (gradually rises to 45-50°C.). Williams own work showed current eff. does not fall off rapidly up to 60°C. The higher temps. give better current yields: Factor average 2.5; Williams at 42° 3.4; Williams at 59° 3.0	Initially 45-50 amps./dm^2 (gradually falls to 30 amps./dm^2)	Should not be alkaline, but there is no advantage to acidifying except at higher temps.	Voltage increases as electrolysis proceeds.	O_2 appears only after $NaClO_3$ concn. falls below 10 g./l. Avg. current eff. is 85% or better. During electrolysis NaCl is produced and there is an equilibrium value for each temp. (2.3 g/l @ 31° to 4.7 g./l. at 59°)
Conductivity increases with temp. Discusses effect of temp. on concn. and discharge of OH^-, Cl^-, ClO^- and on other possible anode reactions.	-	Acidity needed to reduce loss of current thru OH^- and Cl^- discharge.	-	Total resistance of perchlorate cell is much higher at end than at beginning of electrolysis although electrolyte resistance may be the same.
20-27° Current yield decreased markedly as temp. increased above 20°C. when low C.D. is used (10 amps./dm^2)	15 amps./dm^2 (anode & cathode) current yield mounted with increase in cathode C.D. while a change in anode C.D. had little effect.	-	7.4-8.5	$KClO_4$ crusts anodes even with high electrolyte velocities.
40-50°C.	36 amps./dm^2	-	-	Current eff. = 93% 1 Kg.$NaClO_4$ requires 3.0 KWH Pt loss = 3 mg./Kg.$KClO_4$
0°C. or lower	High C. D. not essential if special cell is employed (very rapid circulation, pressure, cooling.	-	-	-
	Current eff. is proportional to 1/3 power of C.D.	-	-	-

Temperature

The earlier investigators insisted on low temperatures, preferably below room temperature, for best results. Above 60°C., current yields are low (39,147), and at 80-100°C. there is no perchlorate formation (96,147). Blau and Weingand (14) showed that the current efficiency is markedly reduced by increasing temperature if low current densities (e.g., 10 amps/sq.dm.) are used, but that the effect was much less noticeable at higher current densities (e.g., 15 amps/sq.dm.). At 45-50 amps/sq.dm., Williams (146) found no adverse effect on current efficiency up to 60°C. and, because of the better power yields, preferred to work at the higher temperatures. Present practice is to use temperatures in the range 40-55°. Some cooling is therefore necessary and this is accomplished by using external jackets (199) or internal coils or chambers (1,49) for cooling water, or by using water-cooled cathodes (150,199,202).

Circulation

The need for adequate agitation of the electrolyte was recognized by the earliest investigators and the circulation of electrolyte through the cells became and remained standard practice. Special cells have been designed to improve the agitation (29,150), but in modern cells, simple recirculation of electrolyte apparently suffices.

Acidity of Electrolyte

Almost without exception, the electrolysis of $NaClO_3$ has been carried out in neutral or slightly acid solution. Foerster (39) stated that in alkaline solution, chlorate is oxidized to perchlorate for a short time only, after the start of electrolysis. Lederlin (170), in 1903, was able to secure a patent on the maintenance of non-alkaline conditions in a perchlorate cell. Williams (146) pointed out that there is no advantage to acidifying the electrolyte when operating at low temperatures, but that at higher temperatures (e.g., 40-60°C.) the frequent addition of acid was beneficial. Knibbs and Palfreeman (72) discuss the desirability of keeping the hydroxyl ion concentration low to minimize current losses that would attend the discharge of hydroxyl, chloride, and hypochlorite ions. In present day perchlorate manufacture, apparently only the Cardox Corporation process (49) employs a slightly alkaline electrolyte.

Current Density

It was recognized early in the study of the electrolytic oxidation of chlorate that current yields improved with increasing current density. Higher current densities are said to minimize the adverse effects of operation at higher temperatures (14,146), of the gradual depletion of chlorate in the electrolyte (96), and of competing anode reactions (72), such as

$$ClO_3^- \longrightarrow ClO_3^0 + e$$
$$2\,ClO_3^0 + H_2O \longrightarrow 2\,HClO_3 + O$$

In German industrial production up to 1929, the anode current density was said (140) never to be under 30 amps/sq.dm., with 40-70 amps/sq.dm. the usual range. The corresponding cathode current density was 10-20 amps/sq.dm. The most modern German cells used 30 amps/sq.dm. at the anode (80,139). In England, in 1912, a current density of 8 amps/sq.dm. was employed commercially (1); by 1920, it had been stepped up to an initial 45-50 amps/sq.dm., leveling off to about 30 amps/sq.dm. as the cell resistance increased (146). Modern U.S. cells also operate with a high current density (over 30 amps/sq.dm.).

Winteler (147) showed that some reduction of chlorate occurred if the cathode current density fell below 2 amps/sq.dm., and Blau and Weingand (14) found the current yields mounted with increasing cathode current density. In most commercial cells for which values are given, the cathode current density is smaller* than the anode current density.

Theory of Anodic Oxidation

Oechsli (96) proposed that discharge of the chlorate ion is the primary process, followed by reaction of the discharged radical with water to form chloric acid

$$2\,ClO_3^- + 2\,F + H_2O \longrightarrow 2\,HClO_3 + O \qquad [1]$$

At the high concentration presumably existing at the electrode surface, the chloric acid disproportionates to form perchloric acid and chlorous acid, and the latter reacts with the oxygen liberated in equation 1 to reform chlorate

$$2\,HClO_3 \longrightarrow HClO_4 + HClO_2 \qquad [2]$$

$$HClO_2 + O \longrightarrow HClO_3 \qquad [3]$$

Oechsli argued against chemical oxidation by nascent oxygen from hydroxyl ion discharge, since perchlorate formation takes place less readily in alkaline solution, or oxidation by ozone which appears in the anode gas, since direct treatment of chlorate with 6 vol.-% ozone produced no perchlorate.

Bennett and Mack (9) favored the theory of direct chemical oxidation by active oxygen formed at the anode on the basis of their experiments which indicated that chlorate could be oxidized with persulfuric acid, ozone, hydrogen peroxide, and oxygen in the presence of ultraviolet light. They also argued that perchlorate is formed at the anode at a potential far below that necessary for the continuous discharge of any ion present in the solution.

Knibbs and Palfreeman (72) did not consider Bennett and Mack's proof of direct chemical oxidation by reagents, other than persulfuric acid, sufficiently conclusive to support their theory, nor did Knibbs and Palfreeman believe that the Bennett and Mack theory satisfactorily explained the effect of alkalinity on efficiency. Knibbs and Palfreeman supported Oechsli on the principle of chlorate ion discharge, but proposed a different mechanism, similar to persulfate formation, for the reactions that follow:

$$O_2ClO- + -OClO_2 \longrightarrow O_2Cl\text{-}O\text{-}O\text{-}ClO_2$$

$$O_2Cl\text{-}O\text{-}O\text{-}ClO_2 + H_2O \longrightarrow O_2Cl\text{-}O\text{-}O\text{-}H + O_2ClOH(=HClO_3)$$

$$O_2Cl\text{-}O\text{-}O\text{-}H \longrightarrow O_3ClOH(=HClO_4)$$

b. Modern Commercial Perchlorate Cells

Three modern cells have been described in the literature: the Schumacher cell of Western Electrochemical Co. (114,115,116,199), the Cardox Corporation cell (49), and the I. G. Farben (Bitterfeld) cell 80,139). The characteristics of these cells are summarized in Table IX (p. 24) and the operating conditions employed by these three manufacturers are outlined in Table X (p. 25). The construction of the two U.S. cells is further shown in Figures 4 and 5 (pp. 26, 27). Flow diagrams for the manufacture of chlorate and perchlorate are given in Figures 6, 7, and 8 (pp. 28, 29, 30).

c. Anode Materials

The classic literature on the electrolytic production of perchlorates indicates a unanimous acceptance of platinum as the only suitable anode material. This work, of course, was on so small a scale that economic considerations did not enter the picture. Yet, in spite of the high capital investment involved and the significant replacement costs due to electrochemical attack and mechanical disintegration, platinum is still used in the major perchlorate installations. The search for a platinum substitute, both for perchlorate manufacture and in other electrochemical operations requiring highly resistant electrodes, has proceeded for many years. The fact that none of the materials investigated has been adopted commercially indicates that they are unsatisfactory, compared to platinum, either as to chemical resistance or in their electrical properties. Presumably some of them could be used if our supply of platinum should fail.

Platinum

The thinnest possible platinum sheets consistent with strength and rigidity appear to be mandatory to keep the investment at a minimum. Western Electrochemical used 0.15 mm. (0.006") sheet with no other support than that offered by glass guide rods. I. G. Farben. used 0.05 mm. (0.002") sheet but thickened the upper margin (contact edge) to 0.1 mm. over a depth of 20 mm. and stiffened the edges with 0.75 mm. platinum wire.

TABLE IX

COMMERCIAL ELECTROLYTIC PERCHLORATE PRODUCTION
CELL CHARACTERISTICS

	Western Electrochemical Co. 1st Stage	Western Electrochemical Co. 2nd Stage	Cardox Corporation	I. G. Farben. A.-G. (Bitterfeld)
Raw Material	$NaClO_3$	$NaClO_3$	$NaClO_3$	$NaClO_3$
Product	$NaClO_4$	$NaClO_4$	$NaClO_4$	$NaClO_4$
Cell body				
Material of construction	mild steel	mild steel	sheet steel	steel with acid proof brick and coating
Length x width x height	8'6" x 5" x 2'0"	8'6" x 5" x 2'0"	30" x 16" x 33"	10' x 4' x 6.5'
Capacity, cu. ft.	5.9	5.9	6.7	(194 = (5.5m^3)
Cover	synthetic stone	–	–	–
Anode				
Material of construction	platinum sheet (perforated)	platinum sheet (perforated)	platinum-clad copper rods	platinum sheet
Size	14" x 16" x .006"		0.5" (diam.) x 30" 0.02" of platinum	21.6" x 9.8" x .002"
Number per cell	8		4	16
Loss per ton of product	0.2 troy oz.	0.2 troy oz	–	0.9 troy oz.
Cathode				
Material of construction	mild steel	mild steel	steel tubes	perforated steel plates (one on each side of anode).
Size	cell body	cell body	3" (diam.) x 33" (4 tubes, each drilled with 8-10 1/2" holes	
Anode-cathode spacing	–	–	1.25 in.	1 cm.

TABLE I

COMMERCIAL ELECTROLYTIC PERCHLORATE PRODUCTION OPERATING CONDITIONS

	Western Electrochemical Co. 1st Stage	Western Electrochemical Co. 2nd Stage	Cardox Corporation	I. G. Farben, A.-G. (Bitterfeld)
Raw Material	$NaClO_3$	$NaClO_3 + NaClO_4$		
Product	$NaClO_3 + NaClO_4$	$NaClO_4$		
Charge				
Initial concn. $NaClO_3$, g./l.	600	90-110 (+ 500 g. $NaClO_4$/l.)	650-700	400-500 (more added periodically)
Initial concn. $Na_2Cr_2O_7$, g./l.	5	5	1	3-4
pH	6.1-6.4	–	alk., <10.5 (not regulated)	weakly acid
Product				
Final concn. $NaClO_4$, g./l.	500	580-600	800	1000
Final concn. $NaClO_3$, g./l.	90-110	5	20	50 or less
Platinum loss, troy oz./ton	0.2	0.2		0.9
Operation	Continuous, with recirculation at 2 gal./min. thru cells in parallel	Batch, with recirculation at 2 gal./min.	Batch	Batch (8 days) with recirculation through 5 cells in series
Temperature, °C.	40-45	40-45	45-55	35
Electrical conditions				
Current per cell, amp.	5000	5000	500	12,000
Current density, amp./sq.ft.			480 (52 amp./dm.^{2})	279 (30.0 amp./dm.^{2})
at anode	288 (31.1 amp./dm.^{2})	288 (31.1 amp./dm.^{2})	–	–
at cathode	72 (7.7 amp./dm.^{2})	72 (7.7 amp./dm.^{2})		
Voltage per cell	6.8	6.8	6.2-6.8	6.5
Energy consumed, KWH/lb.	1.5	1.9	1.6	1.84
Energy efficiency, %	14.4	11.4	–	–
Current efficiency, %	90	70	97-97	–
Production	1,200 tons/mo. (Henderson)		2 lb./cell/hr.	83 tons/mo. (5 cells)

FIGURE 4

WESTERN ELECTROCHEMICAL COMPANY

PERCHLORATE CELL

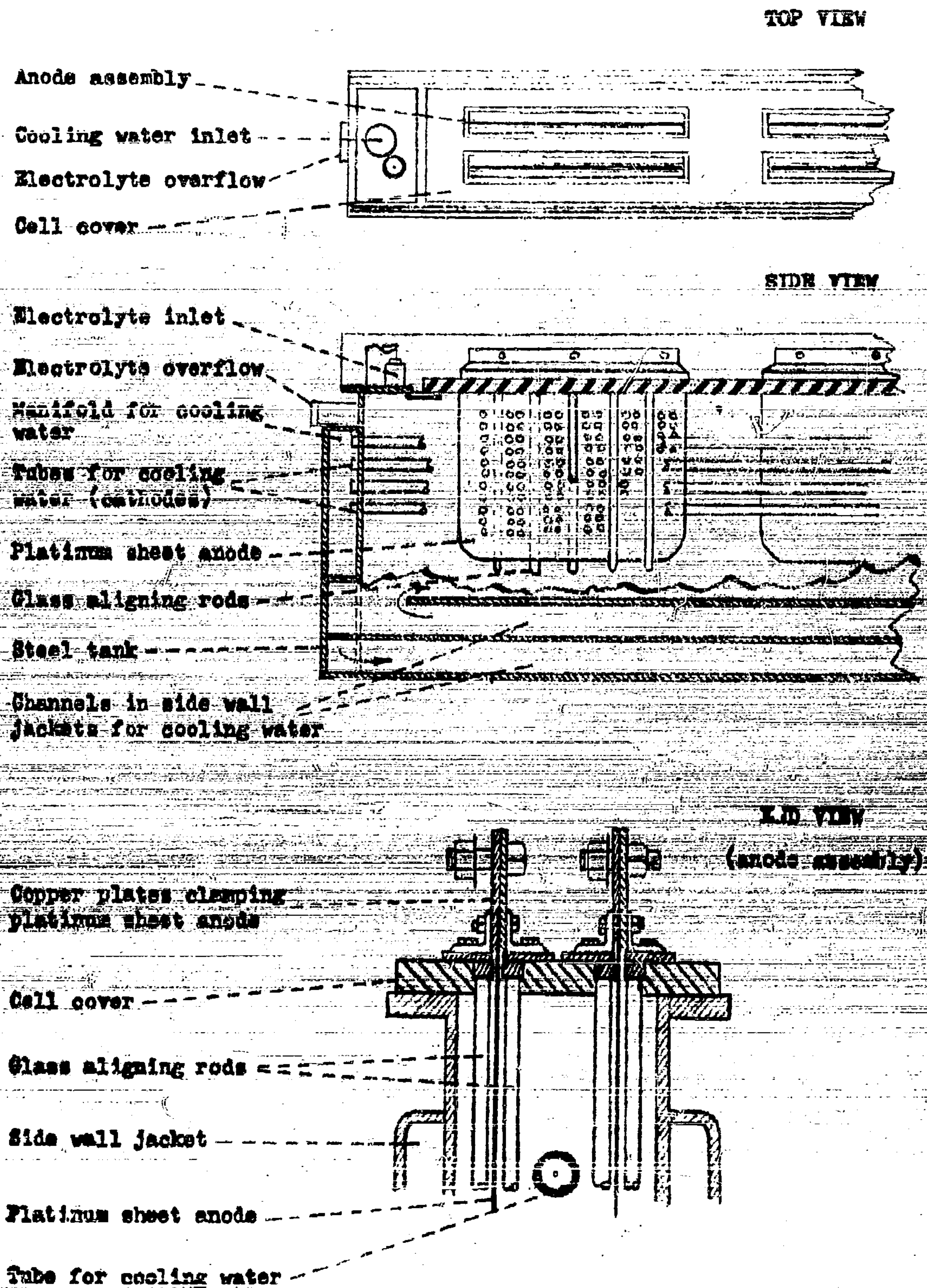


FIGURE 5

CARDOX CORPORATION

PERCHLORATE CELL

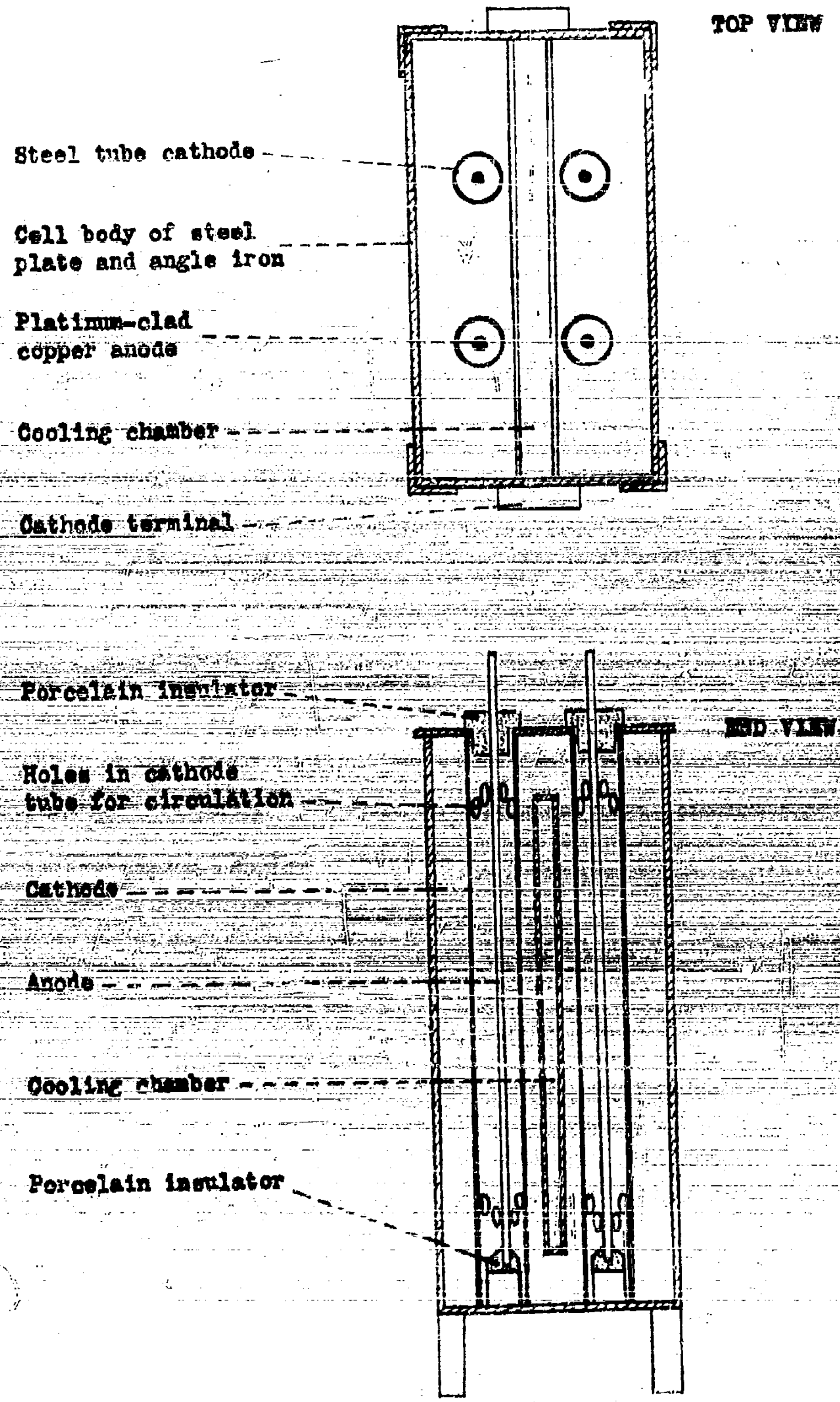


FIGURE 6

WESTERN ELECTROCHEMICAL COMPANY

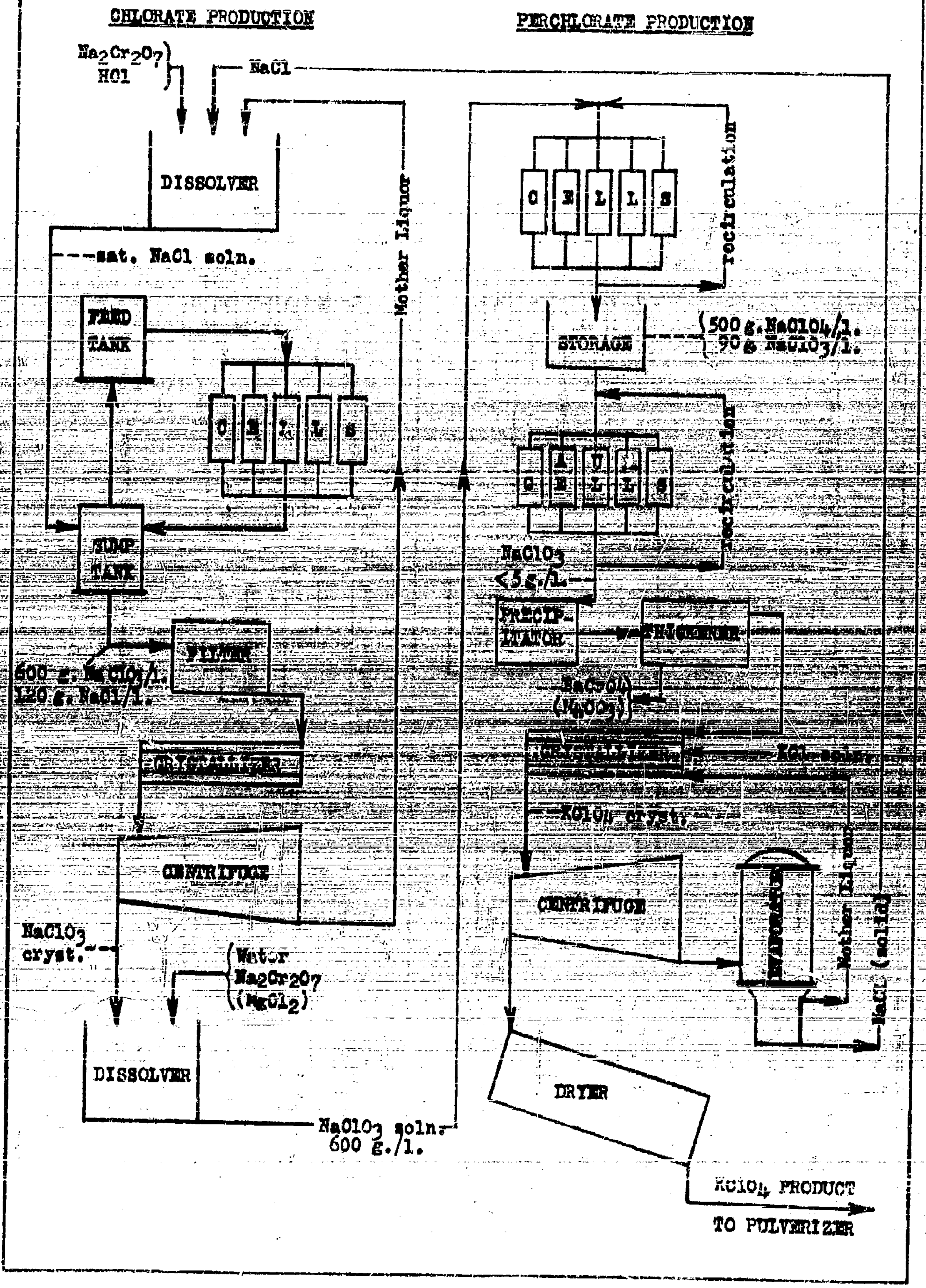


FIGURE 7
CARDOX CORPORATION

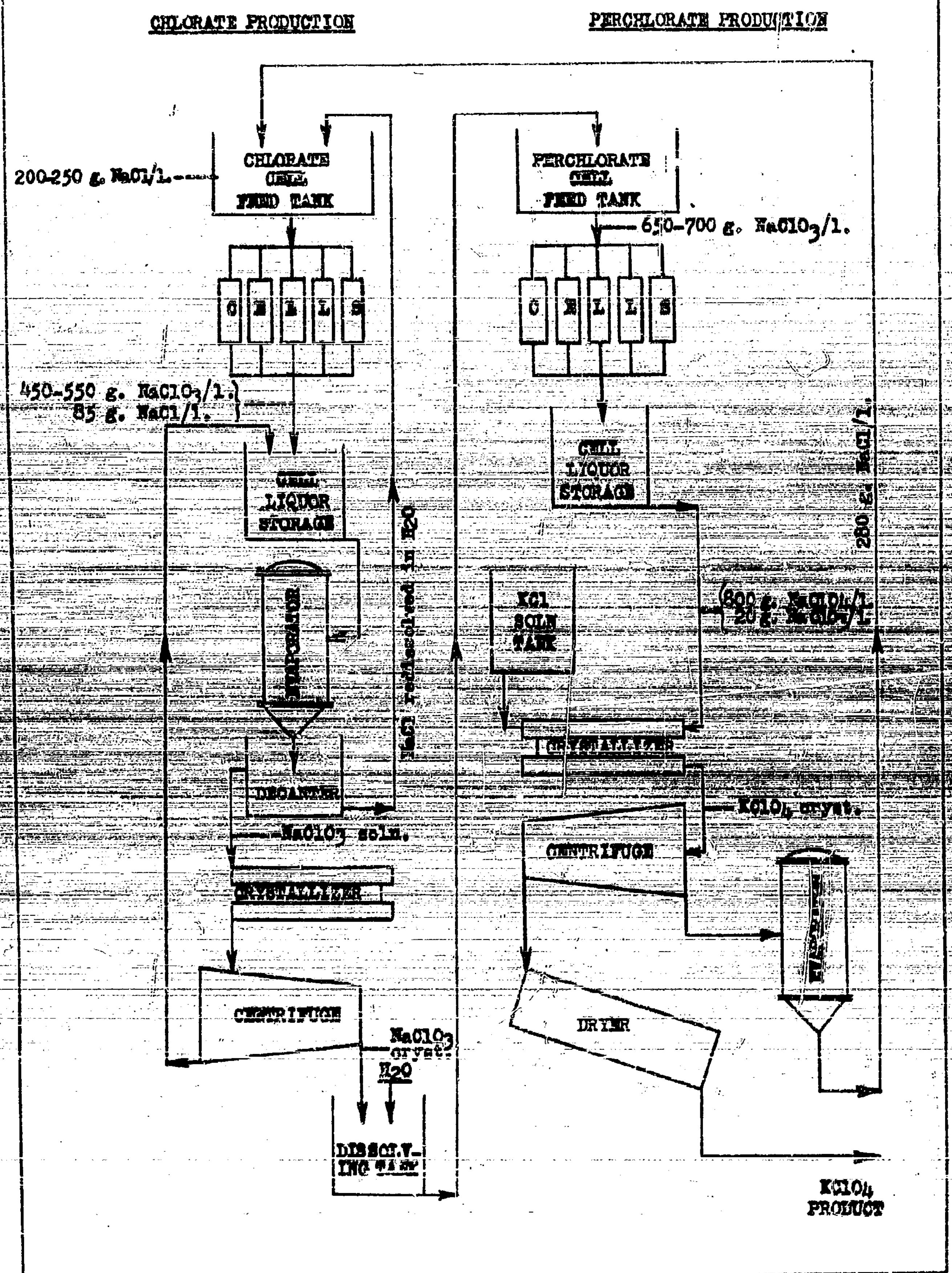
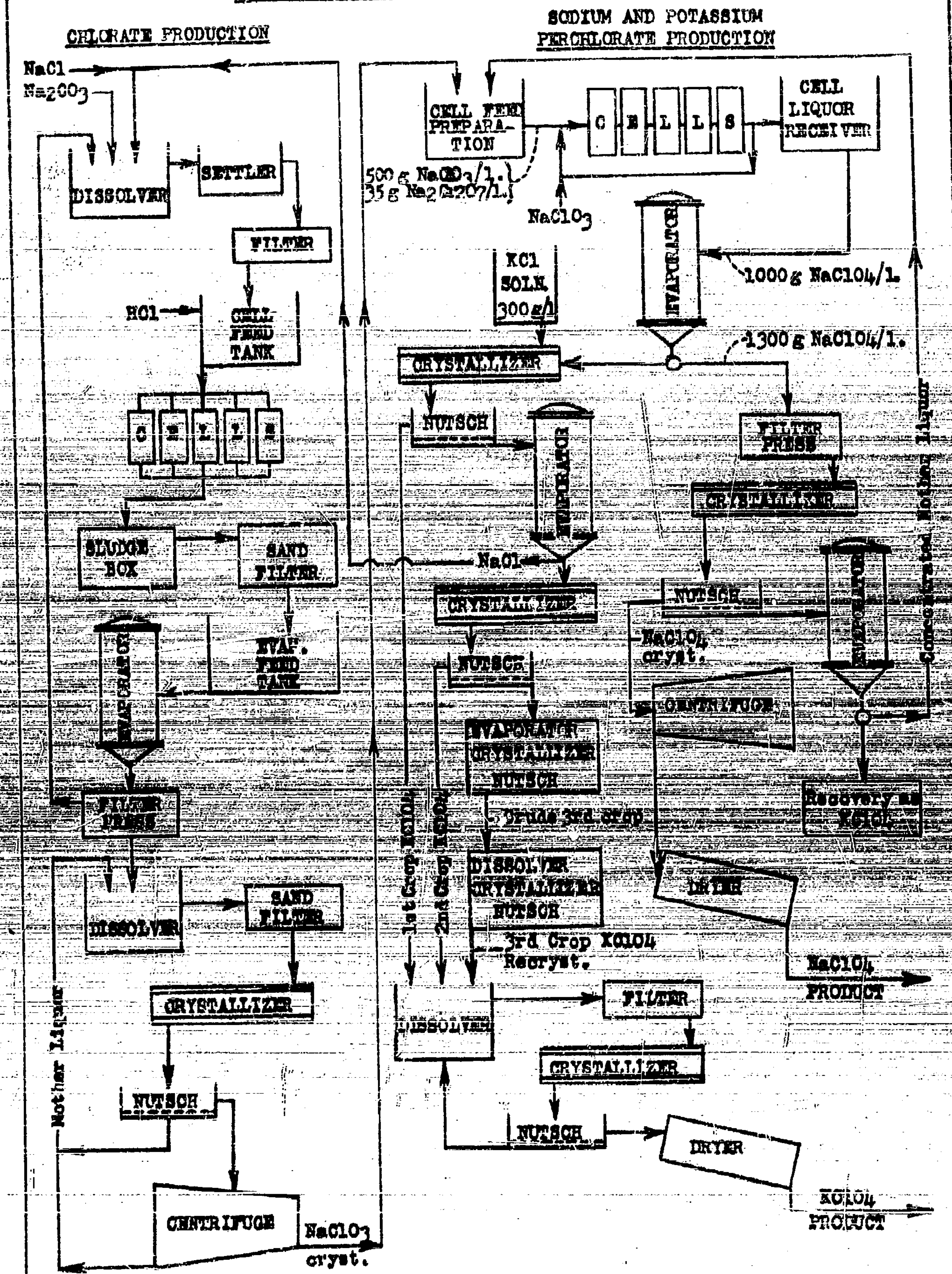


FIGURE 8
I. G. FARBENINDUSTRIE A.-G. (BITTERFELD)



Various methods have been suggested to reduce the bulk of platinum required:

Yamaga and coworkers (149), studying the properties of 9 varieties of platinum and 15 kinds of platinum alloy in the electrochemical oxidation of ammonium sulfate to persulfate, found that platinum alloys containing a small quantity of gold, iridium, rhodium, etc. showed almost the same oxygen overvoltage as pure platinum.

Liebknecht (190) proposed anodes made of thin platinum foil or gauze with reinforcing frames of metallic zinc, for the electrolytic production of perborates and other "per" salts.

Adolph and Dretschger (196) disclosed as anodes, suitable for the production of "per" compounds, a composite structure comprising a core of conducting material (such as a copper rod) covered by a sheath of non-conducting material (such as hard rubber), a platinum tip on which nascent oxygen develops, and a tantalum connection between the core and the platinum tip, extending through the sheath and separating it from the platinum tip so that no nascent oxygen develops in contact with the sheath.

Baum (191) proposed a tantalum base partly coated with platinum by electrolysis, hammering, welding, rolling, etc. as anode for making persulfates.

Cardox Corporation used platinum-clad anodes, as previously described. Such anodes have been criticized as uneconomical since only one face of the layer of platinum is exposed. However, Burman (18) has indicated that clad anodes (copper rods) are available with platinum thicknesses down to 0.002" (0.05 mm.). This thickness of cladding would provide a better surface-weight ratio than either Western Electrochemical's 0.15 mm. sheets or I. G. Farben's reinforced 0.002" sheets.

Other Metals and Alloys

Angel (3) investigated the behavior of tungsten and molybdenum as anode materials. With tungsten anodes in the electrolysis of solutions containing 540-580 g. of $NaClO_3$ per liter, both with or without 3 g. per liter of $Na_2Cr_2O_7$, very little current passed until 70 volts was applied. The tungsten was then strongly attacked, with the formation of WO_3. Molybdenum behaved similarly. When platinum wires were used as leads and partially immersed in the chlorate solution, practically all of the current was carried by the platinum. Howard (53) reported trying all of the common metals and some of the rarer metals as anodes in this process and found they all corroded very rapidly.

Corrosion resistant anodes have also been a problem in the electroprecipitation of copper from acid copper sulfate solutions containing nitric and hydrochloric acids. U.S. Patent 2,305,133 (197) discloses an "insoluble" anode of lead alloyed with 9-18% antimony and 0.5-1.5% silver;

0.2-1.5% arsenic may also be present. Anodes of this type are used by the Chile Exploration Company. British Patent 212,871 (151), also assigned to the Chile Exploration Company, claims that electrodes of the following composition are resistant to anodic disintegration: Cu= 60-65%, Si= 23-27%, Fe= 7-9%, Pb= 1.9-2.5%, Sn= 1-2%. Such electrodes are activated before use, to reduce their operating voltage, by using them for 20-30 hours in a cell containing weak acid copper sulfate solution. Fink and Eldridge (37) report a corrosion resistant alloy of lead containing 10% thallium and 20% tin; this alloy gave a loss of 1.2 lbs./100 lbs. of copper deposited as compared with 65 lbs. for ordinary lead. In a later paper, Fink and Conard (38) describe the electrodeposition of lead-thallium alloys, which are among the most insoluble alloys known, from a perchlorate bath of the two metals. In use, the lead-alloy anodes become coated with a layer of lead dioxide. (See discussion of lead dioxide anodes, below). Electrowinning operations are usually carried out at 11-16 amps/sq.ft., which is considerably below the current density used in perchlorate manufacture. Hence, there is no indication of how these alloys would behave in perchlorate cells. Presumably any value they might have would depend upon the formation of a dense, impermeable lead dioxide coating.

Carbon

Ullmann (140) says that graphite is too strongly attacked to be serviceable in perchlorate production. On the other hand, U.S. Patent 1,279,593 (186) reports that retort carbon, preferably impregnated with molten paraffin, ceresin, or ozokerite to protect it from mechanical disintegration, when used in a diaphragm cell, sustains a loss of only 9% of the weight of perchlorate produced at a current density of 3 to 20 amps/sq.dm., and gives a current efficiency of 50% or greater. Koshunov (73) impregnates graphite anodes (use not stated in the abstract) in coal tar (1.5 to 2 hrs. at 150-180°C.) or pitch (3-5 hrs. at 300-350°C.) or a mixture of either with a bakelite lacquer and heats the impregnated anodes to 300-500°C. to drive out the more volatile compounds.

Sihvonen (123) says that neither perchlorate nor persulfate is formed at a graphite electrode.

Silicon And Silicides

U.S. Patent 1,279,593 (185) mentions the use of silicon anodes for the electrochemical oxidation of chlorates.

For use as electrodes, U.S. Patent 882,169 (176) proposed non-ferruginous compositions of silicon with another substance such as carbon or copper, which other substance is "capable per se of resisting attack by chlorine and chlorous compounds." These electrodes are made by "alloying" the other substance with 10-25% silicon. Russian Patent 69,700 (165) claims the use of silicon carbide or SiC-coated carbon electrodes in place of platinum for the electrolytic production of perchlorates and persulfates. On the other hand, Howard (53) states that carborundum and high-silicon alloys are "valueless" as anode materials in perchlorate formation.

U.S. Patent 546,328 (164) proposes the use of ferrosilicon, containing not less than 10% silicon, as anode material for a variety of electrochemical processes including the electrolytic decomposition of halogen salts. The anode may be cast solid, or applied as a coating on carbon, or incorporated in a plastic substance such as paraffin. U.S. Patent 1,311,096 (189) describes oxidation-resistant anodes of silicon-iron for use in the electrodeposition of metals from acid solution. The composition should contain 12-20% Si (preferably 14-15% Si); if too little silicon is present, there is not sufficient resistance to oxidation and if too much silicon is present, the anodes will be brittle and have a high electrical resistance. There is no indication in either of these patents that ferrosilicon would be suitable for chlorate oxidation. Silicon alloys in general, however, should probably be investigated further because of their inertness.

Magnetite

Considerable attention has been directed toward the development of magnetite anodes for various electrochemical operations. Magnetite is cheap, has a reasonably good mechanical strength, is highly resistant to chemical attack, and, like platinum, is insensitive to OH- discharge (13). It is one of the best electrical conductors among the minerals (28) although its resistance is high compared to the metals (about 850 times that of mercury).

Fabricated magnetite electrodes were used extensively in Chile for the electrolysis of acidic copper sulfate solutions but were found to be very brittle and to require very careful handling (28,137). Magnetite electrodes have also been used in Europe for perborate manufacture, and in this service, they are said to last for 2 to 3 years if properly handled (81). Generally they are useful only at low current densities (2 to 3 amps/dm^2)(81).

Billiter (13) indicates that magnetite electrodes have been used in Germany for the manufacture of chlorine and chlorinated lime. The particular advantage of magnetite over graphite is that a CO_2-free chlorine is obtained. Japanese patents 34,913 (158) and 38,818 (159) disclose fused mixtures of iron oxide and clay as anodes, in place of platinum, for the electrolysis of halogen salts. Elitzur (32) reports the following solubilities for natural magnetite anodes:

NaCl electrolysis 22-118 v., 65°C.: 3-20 g. Fe/KWH

Na_2SO_4 electrolysis 44-103 v., 65°C.: 11-26 g. Fe/KWH

U.S. Patent 568,229 (165) covers the use of a conductive oxide of iron, such as magnetite or "black-slag", as electrode material for making sodium hypochlorite. Such electrodes are claimed to be generally applicable under powerful oxidizing conditions.

MacMullin (80) reports that magnetite electrodes were in use in I. G. Farben's Bitterfeld chlorate plant, where each cell contained 28 steel cathodes and 144 magnetite anodes. Magnetite replaced graphite because consumption of the latter was higher at the high current densities and high temperatures used; graphite, however, gives a lower cell voltage (3.2 v. against 3.6 v. for magnetite). Mantel (81) states that magnetite electrodes give a lower efficiency than platinum in chlorate manufacture. Getz (43a) reports that I. G. Farben representatives claimed U.S. graphite electrodes were better than magnetite for chlorate production but that an equally satisfactory grade of graphite was not available in Germany.

French Patent 704,325 (152) states that magnetite electrodes have not given as good results as platinum or graphite in sodium chlorate manufacture because they produce an appreciably greater proportion of perchlorate as the concentration of chlorate mounts. Ullmann (140) claims that magnetite anodes have not come into commercial use for perchlorate manufacture because they do not reach a high enough anode potential. U.S. Patent 1,271,633 (185) prefers platinum and fused magnetite to graphite as anodes for the electrolytic oxidation of chloric acid to perchloric acid. In this operation, 0.1-1.0N hydrochloric acid is electrolyzed to $HClO_3$ and thence to $HClO_4$ at 50 amps/sq.dm., using temperatures up to 50°C.

Various methods have been suggested for the fabrication of magnetite electrodes. In reviewing these, it will be observed that all procedures are directed to obtaining good mechanical strength and electrical conductivity.

Dean and Davis (28) indicate that magnetite anodes can be made by sintering. In general, however, actual fusion and casting appears to be the preferred procedure. U.S. Patent 568,229 (165), for example, proposes melting magnetite or "black slag" and casting it into the desired shape. ("Black slag", obtained from pig-iron furnaces, is essentially magnetic iron oxide, and analyzes 72.18% Fe, 24.02% O, 1.62% SiO_2, 1.12% Al_2O_3, 1.06% CaO + MgO + P_2O_5 + S). In the melting operation, a suitable flux may be used. In Japanese Patent 34,913 (158), a mixture of 80-90 parts of iron oxide with 20-10 parts of clay (containing Al_2O_3, Fe_2O_3 and small amounts of CaO and MgO) and a small quantity of sodium nitrate is thoroughly melted in an electric furnace and cast in a graphite mold. Thompson and Atchison (137) melted magnetite in a hollow graphite rod which served as one electrode of an electric arc furnace. As powdered magnetite was fed in and melted, the central electrode was withdrawn gradually until the hollow was filled. After cooling, the magnetite rod could be withdrawn. In this way, electrodes measuring 3.8 x 25.4 cm. were produced. U.S. Patent 1,226,121 (184) describes a method of casting hollow magnetite electrodes which comprises melting magnetite in an electric furnace of the direct arc type, pouring the molten magnetite at 1590°C. into a 2-piece, hinged and clamped, gray cast-iron mold heated to about 350°C., allowing the mold to stand undisturbed for about one minute to permit a shell of solid magnetite to form in contact with the mold surface, inverting the mold to eject the magnetite that is still molten, stripping off the mold at 1100-1200°C., and slowly annealing the resulting hollow electrode by burying it in powdered insulating material. Thompson and Atchison (137) found that annealing improved the strength of cast electrodes but caused pitting and loss of crystalline structure. In the discussion following the last-named paper, FitzGerald (FitzGerald Laboratories, Niagara Falls) reported that he had made strong magnetite electrodes measuring 12 x 150 x 300 cm. by fusing the mineral in a radiation arc furnace, casting into molds, and cooling them in an annealing furnace at 700° for 2-3 hours.

Thompson and Atchison (137) found that the strength and anodic resistance to corrosion of their cast electrodes were improved by the addition of about 5% of copper oxide. In U.S. Patent 1,302,959 (188) it is indicated that the addition of 2-3% of alumina to fused magnetite will toughen it and make it more resistant to cracking.

U.S. Patent 800,181 (173) describes a method of producing electrodes which consists in melting technically pure non-magnetic oxide of iron and molding the resulting mass. A later patent to the same inventor (178) explains that when Fe_2O_3 is melted, Fe_3O_4 and FeO are formed. The FeO is objectionable because it causes non-homogeneity and because it is not resistant to chlorine and anodic reactions. To avoid this, additional finely pulverized Fe_2O_3 (or Cr_2O_3 or Mn_2O_3) is added to the melt to react with the FeO formed.

Consideration has also been given to the use of metallic supporting materials to increase the mechanical strength and to improve the conductivity. In German Patent 92,612 (which generally corresponds to U.S. Patent 568,229) an iron plate may be coated with magnetite or "black slag" by casting. U.S. Patent 860,659 (174) discloses electrodes made by melting magnetite over a platinum wire. U.S. Patent 931,919 (173) suggests pouring fused magnetite into a cylindrical mold and, while the mass is still molten, inserting a copper or nickel rod and allowing the magnetite to cool and solidify around the rod. In U.S. Patent 1,302,959 (188), electrodes are made by dipping a core of iron, steel or ferrosilicon into fused magnetite and withdrawing it quickly. Two dips are recommended. If the core is first pickled, the Fe_3O_4 is said to adhere tenaciously; no clean cleavage between the core and the coating was observed. Further strength is obtained by using a perforated core which provides anchorage for the Fe_3O_4 coating. Annealing is recommended to toughen the coating. It is emphasized that the core should be selected to have nearly the same coefficient of thermal expansion as magnetite.

Fedotiew (35) reported the production of insoluble iron oxide electrodes by partially oxidizing 1-cm. diameter rods of commercial (not electrolytic) iron. Best results were obtained with air and steam at 1000-1100°C., under which conditions a smooth continuous surface was obtained. Kameyama and Naka found they could not produce firmly adhering Fe_2O_3 coatings on iron by heating iron rods in an atmosphere of oxygen (66) or by heating iron plates in contact with MnO_2 or MnO_2-SiO_2 mixtures (65).

In Japanese Patent 38,818 (159), a tubular electrode is made of a fused mixture of iron oxide and clay; the inner surface is then plated with copper. After filling the hollow tube with a paste of powdered carbon and coal tar, the electrode is burned in a furnace.

German Patent 193,367 (corresponding to U.S. Patent 931,513) proposes electroplating the inner surface of a hollow cast-magnetite electrode to improve its conductivity. The magnetite electrodes used in the I. G. Farben. chlorate plant (43a,80) were cast as hollow rectangular pipes, 2" x 4.5" in cross section, 48" long, with 1/4" walls. (The lower ends were closed). After annealing, the hollow units were pickled in sulfuric acid and copper plated on the inside, from a copper sulfate bath, to a depth of 1 mm. to provide good electrical distribution. Connection was made by placing copper strips in contact with the inside wall of the anode, at the upper end, before electroplating.

U.S. Patent 568,230 (166) proposes ilmenite ($FeO \cdot TiO_2$) as a substitute for platinum or graphite, stating that it is a dense, impermeable conductor that can be sawed to shape or cast in the presence of 3-4% of a flux, such as silica, lime, or magnesia. U.S. Patent 568,231 (167) claims electrodes made of a magnetite-ilmenite mixture fused together or briquetted with a suitable binder (tar or sugar) and dried and baked.

It appears, then, that magnetite electrodes with reasonably good mechanical strength and electrical properties can be made. The cost of such electrodes should not be prohibitive. It remains to be demonstrated, however, if a magnetite anode can actually be made to withstand the severe conditions existing in perchlorate manufacture.

Lead Dioxide and Manganese Dioxide

Lead dioxide anodes have been proposed for the electrodeposition of zinc (180,181) and copper (181) from acid solutions and gold and silver (168) from cyanide solutions.

Mizuguchi (91) has reported the utility of lead dioxide anodes in the electrolytic oxidation of chromic sulfate to chromic acid. He has proposed that the chromic sulfate is oxidized chemically by surface action and that the lead sulfate which results is reoxidized electrolytically:

$$H_2O + Cr_2(SO_4)_3 + 3\,PbO_2 \underset{\text{electrolytic oxidation}}{\overset{\text{surface action}}{\rightleftharpoons}} 3\,PbSO_4 + H_2Cr_2O_7$$

In support of this mechanism, it is pointed out that the current efficiency is zero with a platinum electrode. Addition of hydrofluoric acid reduces the current efficiency of the PbO_2 electrode in this process, presumably by suppressing the surface reaction.

In the electrolytic oxidation of sulfate to persulfate (95,130), on the other hand, Mizuguchi (90) found that the addition of HF improved the current efficiency by increasing the already high oxygen overvoltage of the PbO_2 anode and by suppressing surface reaction between the PbO_2 and the persulfate formed on its surface. Best results were had when the HF concentration was 5-6 g. per 100 cc. of electrolyte; in that case, Sugino and Yamashita (133) found that the current efficiency of a PbO_2 anode approached that of a platinum electrode.

In 1923, Howard (53) stated that lead dioxide and manganese dioxide anodes are decomposed very quickly under the conditions prevailing in the chlorate-perchlorate cell. In 1934, Angel and Mellquist (4) reported that lead dioxide anodes could be used for perchlorate production and that the current efficiency increased with increasing anode current density to a maximum of 79.2% at a current density of 20 amps/dm.^{2}, and a temperature of 15°C. (chromate-free solution). Under these conditions, no erosion or crack formation was observed. In the few cases in which anode failure occurred, the trouble was traced to foreign bodies on the base sheet on which the PbO_2 deposit had been formed. These investigators observed that immediately on closing the circuit, with new PbO_2 anodes, the resistance decreased by from 0.5 to 1.0 volts; thereafter the resistance began to increase slowly whether or not the electrodes were in use or standing idle.

In the oxidation of a 50% solution of sodium chlorate at 5°C., using a potential of 4.9 volts and a current density of 12 amps/dm.^{2}, Kato and Koizumi (67) found that the total current efficiency, from beginning to end, was 81% for platinum and 58% for a PbO_2 anode. It is observed (data not given) that while in reality a higher current density and consequently a higher voltage is required by a platinum anode, the watt consumption necessary for the preparation of the same amount of $NaClO_4$ is nearly equal for platinum and lead dioxide (1.00 to 1.02). Kitahara and Ohsuga (70) found that the current efficiency in the oxidation of chlorate with a PbO_2

anode could be increased from 41% to 70% by the addition of sodium fluoride to the electrolyte. Sugino and Yamashita (134) confirmed earlier results on the electrolytic conversion of chlorate to perchlorate with a PbO_2 anode, and also studied the preparation of $NaClO_4$ directly from NaCl in two steps by acifidying the solution first with HCl for $NaClO_3$ production and then adding sodium fluoride. The best yield was 99.9% with a current efficiency of 62-63%.

Lead dioxide anodes reported in the literature have been made in the following ways:

As anode for the electrodeposition of zinc (179), lead dioxide is packed into an earthenware sheath provided with holes to expose the dioxide to the solution. For the electrometallurgy of gold and silver, U.S. Patent 872,878 (175) employs a canvas sack sewed into a plurality of vertical compartments and packed with granular PbO_2, with a conducting wire passing through the compartments at the top.

U.S. Patent 1,043,937 (181) describes anodes prepared by mechanically compressing and heating a mixture of PbO_2 with manganese nitrate or manganese nitrate and manganese dioxide. These anodes were found suitable for electrodepositions from zinc sulfate and copper nitrate solutions.

According to U.S. Patent 598,193 (168), lead sheets that have been peroxidized in dilute sulfuric acid or in hot alkaline solution are suitable for use as anodes in the electrodeposition of gold or silver from cyanide solutions. Lead dioxide storage battery plates, which would appear to answer the requirements of the last-mentioned patent are made in several ways (136): (a) by electrolyzing sulfuric acid between lead electrodes; (b) by electrolyzing sulfuric acid solution containing a forming agent (a salt which has an anion that forms a soluble salt with lead, such as nitrates, chlorides, chlorates and perchlorates) between lead electrodes that have been mechanically etched; and (c) by electrolyzing sulfuric acid (sp.gr. 1.10-1.25) between lead-antimony grids that have been coated with a paste of litharge or red lead in sulfuric acid. Allmand (1) states that amalgamated lead surfaces show a higher O_2-overvoltage than pure lead and that, consequently, gas evolution is delayed with amalgamated lead and the useful production of PbO_2 continues for a longer time. U.S. Patent 935,250 (180) claims that storage battery plates are unsatisfactory as anodes for the electrodeposition of zinc because the underlying lead is attacked, with the result that lead deposits with the zinc on the cathode. The literature does not indicate whether or not PbO_2 anodes of the storage battery type would be suitable for chlorate oxidation.

Angel and Mellquist (4) produced PbO_2 anodes for their perchlorate production studies by electrolyzing an alkaline solution of lead tartrate. A typical solution is made by boiling 400-500 g. of finely ground litharge with 10 liters of a solution containing 50-100 g. of sodium hydroxide and

500 g. of Rochelle salt (192). From such a solution, $PbO_2 \cdot H_2O$ is said to plate out as a hard, dense, black, lustrous coating on iron, steel, or copper sheets that had previously been lightly electroplated with gold. The deposit was somewhat laminated at the edges, for which reason they were protected by a coating of Ebonit. Round electrodes, of course, obviated the need of such coatings. These investigators found no erosion or crack formation during chlorate oxidation at 20 amps/sq.dm., and no failures that could not be attributed to the presence of foreign particles on the base plate. Current densities above 20 amps/dm.^{2} damaged the electrodes.

In the electrodeposition of lead dioxide from nitrate solution, free nitric acid is formed and this is reduced to oxides of nitrogen by the lead depositing at the cathode. To avoid this and to replenish the lead content of the solution, German Patent 140,317 (153) suggests neutralizing the electrolyte repeatedly with lead oxide, hydroxide, carbonate or basic carbonate.

U.S. Patent 900,502 (177) (equivalent to German Patent 206,329) describes the electrodeposition of lead dioxide from a lead salt solution onto a rotating cylindrical body of electrically conducting material. After a layer of sufficient thickness has been deposited, the conducting body is removed (tightly stretched iron wire can be drawn out, carbon rods can be drilled out). German Patent 207,257 (154), to the same inventor, deposits lead dioxide electrolytically on a ceramic or other non-conducting base that has been given a primary coating of lead peroxide by chemical means.

According to U.S. Patent 1,740,291 (193), chemically resistant anodes for the electrolysis of halogen salts are made by electrodepositing PbO_2 from an acidic solution of lead nitrate onto a silver-lead alloy base. A suitable alloy contains 60% Ag and 40% lead and may contain up to 10% Mn or up to 20% Tl. The alloy surface is prepared for the PbO_2 coating by running it for a time in a halogen bath.

To prepare a suitable lead dioxide anode by the electrolysis of lead nitrate solution (30%), Kato and Koizumi (67) found that the presence of hydrophilic colloids (gelatin, dextrin, gum arabic, soluble starch, etc.) was helpful and that electrolysis at 80°C. with a current density of 100 amps/sq.dm. and a potential of 10 volts gave a compact deposit on graphite or nickel. The lead dioxide anodes so obtained showed an oxygen overvoltage of 0.5 volts in NaOH solution at 25°C. The electrical conductivity was about 1/10 that of mercury. These anodes were used successfully for the electrolytic production of sodium perchlorate.

Japanese Patent 175,166 (162) discloses that the presence of copper ions in the lead salt solution used to deposit PbO_2 prevents branch-like deposition of lead at the cathode. Sugino and Shibazaki (131) give the following conditions for producing good PbO_2 anodes by the electrolysis of lead nitrate solutions: (a) maintain the H^+ ion concentration below 0.25N, (b) maintain the current density within a narrow range corresponding to the bath temperature, and (c) add aluminum nitrate to the lead nitrate in a mol-ratio of 0.2 to 1 to prevent the dendritic growth of lead crystals at the cathode and to make the PbO_2 deposit uniform and compact. The addition of 3-10% sodium chlorate is said to produce the same effect. The dendritic growth of lead crystals may also be suppressed by the addition of 1-3% copper nitrate which also decreases lead nitrate consumption by half (131).

Kitahara and Ohsuga (70) prepared their electrodes by depositing PbO_2 on a section of nickel (or iron) pipe which was subsequently dissolved away. Kato, Sugino, Koizumi, and Kitahara (68) deposited PbO_2 on the inside of a nickel cylinder from a solution of lead nitrate containing gelatine. After the deposit had reached a thickness of 7 mm., the nickel was removed (to prevent its slow dissolving in the perchlorate bath in which the anode was to be used) by slitting the nickel cylinder and chilling. The PbO_2 form so produced served both as anode and as containing vessel. These investigators found that a small piece of platinum fastened to the PbO_2 anode raised the material efficiency to 99% at 50-60% current efficiency, apparently by dissolving and depositing on the iron cathode, thereby lowering the hydrogen overvoltage.

Manganese dioxide anodes have been investigated for several electrolytic reactions but not for perchlorate formation. For the electrolysis of zinc sulfate, copper sulfate, sodium chloride, etc. U.S. Patent 935,109 (179) proposes the use of a crystalline variety of MnO_2 produced by heating manganese nitrate at 150-200°C. The resulting coherent mass, which may be formed in molds of the desired dimensions, is said to possess sufficient strength to be used without supporting material. Alternatively, crystalline MnO_2 produced as described may be packed into molds with additional manganese nitrate and reheated at 150-200°C. to produce a coherent body. These anodes are said to be superior to natural manganese ore and to electrolytically deposited amorphous MnO_2. U.S. Patent 1,296,186 (187) improves on the preceding process by repeatedly impregnating the molded electrode with manganese nitrate and heating it, to fill the interstices with additional crystalline MnO_2 thereby increasing strength and conductivity. U.S. Patent 1,143,828 (182) describes anodes of natural MnO_2, chemical purified with H_2SO_4 and/or HNO_3. The purified ore is mixed with manganese nitrate and heated to decompose the nitrate.

The literature on lead dioxide anodes suggests interesting possibilities for this material and further work on their preparation and their performance in perchlorate production is indicated.

2. Thermal Decomposition of Chlorates

a. Historical Background

The thermal "self-oxidation" of potassium chlorate was first observed by Serullas in 1831, about 15 years after the discovery of the electrolytic oxidation method. By heating molten potassium chlorate until oxygen evolution ceased, during which operation the fluid became thick and pasty, Serullas obtained 44% potassium perchlorate. Liebig confirmed these results by heating potassium chlorate until one-half the available oxygen was evolved; under these conditions 45% potassium perchlorate was recovered. Millon, in 1843, recognized that yields of perchlorate are lowered by heating for too long a period of time or at too high a temperature. Millon claimed to have observed crystals of $KClO_3$ and KCl in heated $KClO_4$, which led him to the conclusion that the $KClO_4$ obtained by heating $KClO_3$ reverts to $KClO_3$ on long heating.

Graham proposed the following equation for the thermal decomposition of potassium chlorate, which involves the loss of 33% of the available oxygen:

$$2\,KClO_3 \longrightarrow KClO_4 + KCl + O_2$$

Millon, according to Blau and Weingand (14), believed potassium chlorate to be a complex of potassium perchlorate and potassium chlorite and proposed the following reactions, which, however, do not provide for the evolution of oxygen which is invariably observed.

$$2\,KClO_3 \longrightarrow KClO_4 + KClO_2$$

$$2\,KClO_2 \longrightarrow KClO_4 + KCl$$

These reactions, in summation, would represent the maximum realization of perchlorate from chlorate by thermal means alone:

$$4\,KClO_3 \longrightarrow 3\,KClO_4 + KCl$$

Marignac (14) proposed that the reaction takes place in three steps. In the first stage, during which 4.5% of the total oxygen is liberated, the amount of potassium perchlorate increases to 65% with 12-15% of the potassium chlorate still undecomposed. In the second step, in which up to 8.5% of the oxygen is evolved, practically all of the remaining chlorate is decomposed without, however, increasing the amount of perchlorate present. In the third step, the perchlorate formed decomposes into potassium chloride and oxygen. He concluded that several equations would have to be used to express the course of the decomposition and proposed the following for the beginning of the decomposition:

$$6\,KClO_3 \longrightarrow 4\,KClO_4 + 2\,KCl + O_2$$

This equation is probably intended to cover roughly the first two stages mentioned above, since it represents the loss of about 11% oxygen. However, this equation indicates a yield of 75 g. $KClO_4$ per 100 g. $KClO_3$, rather than the 65% reported.

Teed (135) reported that the reaction could be expressed by any of several equations between these limits:

$$10\,KClO_3 \longrightarrow 6\,KClO_4 + 4\,KCl + 3\,O_2$$

$$22\,KClO_3 \longrightarrow 14\,KClO_4 + 8\,KCl + 5\,O_2$$

The latter equation represents the results obtained by the most careful heating. Frankland and Dingwall (41) proposed the equation

$$8\,KClO_3 \longrightarrow 5\,KClO_4 + 3\,KCl + 2\,O_2$$

which Teed later pointed out is an approximate average of his limiting equations.

Sodeau (126) concluded that chlorate undergoes self-oxidation according to the equation:

$$4\,KClO_3 \longrightarrow 3\,KClO_4 + KCl$$

and that the decomposition reaction which occurs at the same temperature

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

has no essential connection with it. Scobai (119) reached substantially the same conclusions and also appears to have eliminated the decomposition of perchlorate

$$KClO_4 \longrightarrow KCl + 2\,O_2$$

as a source of oxygen loss by showing that pure $KClO_4$ is not noticeably decomposed at 411°C. whereas oxygen evolution from heated chlorate occurs at 395°C. Scobai was aware of catalytic effects with ordinary glass and Jena glass vessels, but apparently did not consider as a result of his work that the decomposition of $KClO_4$ could be accelerated by the components of the heated reaction mixture. Later Farmer and Firth (34) showed that KCl did not catalyze the decomposition of $KClO_4$ (see Table XIV, page 49).

The basic principles proposed by Sodeau and Scobai are still accepted as explaining the reactions which occur when potassium chlorate is heated. The thermal decomposition of perchlorate, however, as a contributing factor to the inefficiency of the reaction has not been disproved.

b. Factors Affecting the Decomposition

The major part of the work on the thermal decomposition of chlorates has been done with potassium chlorate. In the absence of similarly detailed study of sodium chlorate, the work on the potassium salt is reviewed because the two salts are generally alike in behavior.

Potassium chlorate melts, without decomposition, in the range 356-368°C. At a somewhat higher temperature, certainly below 400°, the chlorate begins to decompose. Perez (101a) gives 364°C. as the decomposition temperature, that is, 8° above the melting point he reports. It is generally agreed that two reactions occur simultaneously and independently at least above 395°C.

$$4\,KClO_3 \longrightarrow 3\,KClO_4 + KCl \qquad [1]$$

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2 \qquad [2]$$

There is no evidence in the literature to indicate that reaction [2] can be entirely suppressed by any choice of operating conditions, except possibly by using a very high pressure. Brown (17a) has shown that mixtures of $KClO_3$ and MnO_2, which decompose almost explosively at temperatures below 300°C., may be heated for several hours at 320°C. under a pressure of 300 atm. with less than 10% decomposition. This pressure is well below the equilibrium pressure and, therefore, cannot have reversed the $2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$ reaction, but apparently it has reduced its velocity.

Scobai (119) observed oxygen evolution even at 395°C. The reactions are probably very slow at this temperature and most of the later investigators have worked at higher temperatures, with correspondingly shorter periods of heating, in attempts to arrive empirically at a set of conditions that would give the best conversion of chlorate to perchlorate.

At the higher temperatures, the possibility of perchlorate decomposition, according to the following equation, complicates the picture

$$KClO_4 \longrightarrow KCl + 2\,O_2 \qquad [3]$$

As was pointed out earlier in this review, there is no satisfactory agreement on the decomposition temperature of this compound. Marvin and Woolaver (82) say that pure $KClO_4$ begins to decompose sharply at 510°C., but some decomposition at 444° (138) has been reported. Tian and Svilovich report (138) that this reaction is 24.9% complete in 65 minutes at 520°C. Ishikawa and Hagisawa (56,57) observed complete decomposition at 550-580°C. Reaction [3] is probably very slow below about 520°C. (97) but nevertheless is a possible cause of low yields, especially if catalyzed by other substances present.

Blau and Weingand (14) have reported a detailed study of time-temperature relations. In their work, 5 to 15 g. portions of $KClO_3$ were heated over a free flame or in a sulfur or potassium nitrate bath until "from about 1/3 to 1/4 of the theoretically possible oxygen was evolved." The oxygen was measured over water. The residue was cooled quickly, powdered, and analyzed for chloride and chlorate, perchlorate being obtained by difference. Some of their results are given in the following tabulation (p. 45) in which the last two columns have been calculated by the reviewer. There are some obvious discrepancies in these results (Table XI, p. 45) which argue against their acceptance as quantitative. Qualitatively it appears that:

(a) Temperatures of 500-510°C. are too high even for short heating periods.

(b) Temperatures of 465-485°C. are optimum provided an adequate heating period is employed. One hour at 485° is insufficient; 4 hours at 480° or 8 hours at 465° gave best results (in glass vessels).

(c) For best yields, $KClO_3$ is never completely decomposed. The authors state that the decomposition of $KClO_4$ has already begun when 3-4% $KClO_3$ remain in the reaction mixture.

(d) The amount of O_2 evolved is not necessarily a criterion of optimum reaction conditions.

Mathers and Aldred (83), using an accurately controlled electric resistance furnace heated 1 g. and 50 g. portions of potassium chlorate for 1 hr. and 30 min., respectively, and reported product analyses which are of significance principally for their showing that time-temperature relations are meaningful only for the amount of material used for the measurements (see Table XII, p. 46).

The yield of potassium perchlorate obtainable by heating potassium chlorate cannot exceed $3\,KClO_4/4\,KClO_3$, or about 85 g. per 100 g. $KClO_3$. Actual yields reported in the literature are summarized in Table XIII, on page 47.

The presence of various foreign substances has been shown to have a marked effect on the course of the reaction. Scobai (119) found that the decomposition of $KClO_3$ into KCl and O_2 is more rapid in ordinary glass vessels than in Jena glass and attributed the difference to the alkali in the glass. Frankland and Dingwall (41) also showed the deleterious effect of glass; by adding powdered glass to the melt, the yield of perchlorate under otherwise similar conditions was reduced from 71 gms. to 56.4 gms. per 100 gms. of chlorate. Blau and Weingand (14) observed better yields in quartz vessels than in Jena glass (see Table XIII, p. 47); it should be noted, however, that their experiments in quartz were

TABLE XI

THERMAL DECOMPOSITION OF $KClO_3$ IN GLASS
FROM DATA OF BLAU & WEINGAND (14)

Run No.	Principal Temp. °C.	Heating time hrs.	Oxygen evolved Normal conditions cc.	Oxygen evolved Normal conditions % of available	Product composition gms./100 gms. $KClO_3$ used $KClO_4$	Product composition gms./100 gms. $KClO_3$ used KCl	Product composition gms./100 gms. $KClO_3$ used $KClO_3$ undecomp.	Oxygen evolved gms./100 gms. $KClO_3$ used calculated from cc.*	Oxygen evolved gms./100 gms. $KClO_3$ used calculated by diff.**
34	450	25.75	-	-	60.9	18.9	14.8	-	5.4
32	465	8.25	628	20.8	63.5	23.6	3.7	8.1	9.2
29	480	4.50	315	23.0	63.0	26.0	3.0	8.9	8.0
19	485	1.00	135	9.8	30.8	15.5	36.1	3.8	17.6
25	500	2.00	475	34.7	30.4	14.6	5.0	13.6	50.0
3	510	0.5	130	9.5	54.6	26.4	9.4	3.7	9.6
2	510	1.0	325	23.7	56.0	25.0	10.2	9.3	8.8

* Calc.: (cc. O_2 evolved ÷ 22,400) x 32 x (100 ÷ sample weight).

** Calc.: 100 gms. $KClO_3$ used − (gms. $KClO_4$ + gms. KCl + gms. $KClO_3$ undecomposed).

TABLE XII

ANALYSES OF MIXTURES RESULTING FROM
THERMAL DECOMPOSITION OF $KClO_3$
FROM DATA OF MATHERS & ALDRED (83)

	Temp., °C.	% $KClO_4$	% KCl	% $KClO_3$
1 gram 1 hour	450	2.9	11.7	83.4
	480	28.3	33.4	37.3
	510	39.8	24.5	32.2
	540	30.9	53.2	14.0
	570	3.8	80.0	14.0
50 grams 30 mins.	510	18.4	9.2	-
	540	56.4	33.9	-
	575	32.7	57.0	-
	600	11.8	77.2	-

TABLE XIII

YIELD DATA ON THERMAL CONVERSION OF $KClO_3$ TO $KClO_4$

Observer	Experimental Conditions and/or Equation Assigned	$KClO_4$ Yield g./100 g. $KClO_3$	$KClO_4$ Yield % of theory
Serullas (14)	Heating until O_2 evol. ceases and mass becomes frosty	44	52
Liebig (14)	Heating until half the available O_2 is evolved	45	53
Graham (14)	$2\ KClO_3 = KClO_4 + KCl + O_2$	56	66
Teed (135)	Limiting equations: $10\ KClO_3 = 6\ KClO_4 + 4\ KCl + 3\ O_2$ (Conditions not given) $22\ KClO_3 = 14\ KClO_4 + 8\ KCl + 5\ O_2$	68 72	80 85
Frankland (41)	S vapor bath (444°C.) $8\ KClO_3 = 5\ KClO_4 + 3\ KCl + 2\ O_2$	71	83
Marignac (14)	Heating until $KClO_4$ reaches maximum (4.5% O_2 evolved)	65	76
Mathers (83)	Heating at 480° for 4 hrs.	55	65
Farmer (34)	Heating at 480-500°; dominant reaction is $2\ KClO_3 = KClO_4 + KCl + O_2$	56	66
Hofmann (52)	Heating at 490° for 5 hrs.	72	85
Blau (14)	Heating at 465° for 8 hrs. or 480° for 4.5 hrs., in glass Heating at 475° for 7.7 hrs., in quartz	63 69	74 81
Meyer (157)	Heating in range 470-520	75-78	88-92
Theoretical	$4\ KClO_3 = 3\ KClO_4 + KCl$	85	100

carried out in a molten sulfur or saltpeter bath whereas the runs in glass were carried out over an open flame where temperature control and uniformity is probably more difficult to achieve. Mathers and Aldred (83) demonstrated that glass reduced the yield of perchlorate by varying the amount of charge (which varied the contact area per gram of chlorate) and by adding glass slugs to the melt. Blau and Weingand showed that the addition of powdered quartz to a chlorate melt in glass improved the yield of perchlorate, and suggested that the quartz eliminated the alkali of the glass:

at 450° for 25.75 hrs. in glass the perchlorate yield was 60.9 g./100 g. $KClO_3$

at 450° for 36.00 hrs. in glass, with quartz addition, the yield was 64.2 g./100 g. $KClO_3$

Farmer and Firth (34) also claimed that the addition of up to 30% of powdered quartz to the reaction mixture in either glass or quartz vessels improved the yield. The data presented by these investigators also show that the presence of potassium chloride and potassium sulfate have little effect on the yield of perchlorate, but that certain oxidizing agents materially reduce the yield (see Table XIV, p. 49).

Blau and Weingand demonstrated that aluminum, iron (whether bright or surface-oxidized), nickel, and copper were entirely unsuitable for decomposition vessels because of the low yields of perchlorate obtained.

Fowler and Grant (40) reported that heating potassium chlorate for a considerable time with HgO, Ag_2O, PbO_2 and BaO_2 at about 500°C. evolved no more than a trace of oxygen and that potassium perchlorate was found in the residue in each case. Mathers and Aldred (83), working on the guess that Fowler and Grant's results might be due to a beneficial catalytic effect, for example, of metallic silver, found that Ag_2O and HgO actually decreased the yield of perchlorate and that Pb_3O_4 (which Fowler and Grant had reported in the $PbO_2 + KClO_3$ reaction mixture) prevented the formation of perchlorate entirely. Farmer and Firth (34) confirmed the conclusions of Mathers and Aldred with respect to Ag_2O (see Table XIV, p. 49).

Mathers and Aldred (83) and Bancroft and Magoffin (7) stated that there is no known catalytic agent for the reaction

$$4\,KClO_3 \longrightarrow 3\,KClO_4 + KCl$$

Hofmann (52), on the other hand, claimed that this reaction is accelerated by KCl, KI, and KIO_3.

Bancroft and Magoffin (7) also stated that there is nothing known to inhibit the non-productive reaction

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

TABLE XIV

EFFECT OF ADDITIVES ON YIELDS OF $KClO_4$ (34)

Catalyst	Glass Reaction Tube Temp. °C.	Time min.	Conversion* %	Quartz Reaction Tube Temp. °C.	Time min.	Conversion* %
None	540	45	41.1	480	60	49.8
Quartz	510	75	46.0	500	75	59.3
KCl	540	30	41.4	480	60	50.4
K_2SO_4	540	30	41.7	480	60	52.0
$K_2Cr_2O_7$	510	75	20.2	500	75	23.5
Ag_2O	280-380	120	0-1.2	280-380	120	0-2.0

* In this work, %-conversion is given on a molar basis, e.g. 50% conversion means $2\ KClO_3 \longrightarrow KClO_4 + KCl + O_2$

On the other hand, many substances such as MnO_2 and CuO are known to catalyze this reaction. Similarly, the decomposition of potassium perchlorate is subject to catalytic effect. Low yields of perchlorate in the presence of alkali, copper, nickel, iron oxide, and boron trioxide were attributed by Blau and Weingand to the catalyzed decomposition of potassium perchlorate. Farmer and Firth (34) showed that CeO_2, ThO_2, and ZrO_2 decrease the yields of perchlorate. Ishikawa and Hagisawa (56,57) reported that sodium and potassium carbonates lowered the decomposition temperature of the corresponding perchlorates. Hofmann (52) stated that the decomposition of $KClO_4$ was accelerated by salts of heavy metals, especially copper, and that the conversion of chlorate to perchlorate is retarded by molten KNO_3 which exerts a solvent action on $KClO_4$ and promotes decomposition according to the equation

$$2\,KClO_4 \longrightarrow 2\,KClO_3 + O_2$$

Other substances are said to interfere chemically. Thus, sodium nitrite (52,138) reduces $KClO_4$ successively to $KClO_3$ and KCl. Ammonium halides also reduce perchlorate (44); in this reaction, activity increases in the order $Cl^- < Br^- < I^-$. At 525°C., the rate of oxygen evolution from a mixture of $KClO_4$ and NH_4I is too fast to be measured; at 400°C., the mixture is converted quantitatively to iodate chlorate, and chloride, with no evolution of oxygen.

All of the literature points to the conclusion that the lowest temperature and lowest reaction time consistent with good conversion should be used. No one appears to have considered the possibility of a continuous or cyclic operation in which a moderate yield of perchlorate would be taken under conditions that would give a minimum loss of $KClO_3$ via KCl and O_2, and following which fractional crystallization of the mixed product would return undecomposed $KClO_3$ to the system. (Probably some such purification step would be needed in any case since thermally produced perchlorate invariably contains several percent. of chlorate.) Results also indicate that all foreign substances should be rigorously excluded since many adverse catalytic effects are possible. Silica, or at least an alkali-free ceramic material is indicated as the material of construction for the reactor unless the wall-reaction can be eliminated, for example, by "atomizing" molten chlorate into a hot zone, and allowing the product to condense on a cold surface. Investigation of the operation under pressure should prove interesting, if the hazards can be eliminated. In any process, consideration must be given to the possible explosiveness of the reaction.

c. Decomposition of Sodium Chlorate

Data on the decomposition of sodium chlorate are meager. It appears to melt without decomposition in the range 248-268°C. Decomposition of the chlorate begins around 350°C. (101a) or almost 100° above the melting point. The decomposition temperature of sodium perchlorate lies in the range 460-480°C.

According to Marvin and Woolaver (82) the decomposition temperature of sodium perchlorate is 30° lower than that of the potassium salt; Perez (101a) found it to be only 15° lower.

In view of these facts, it is to be expected that the optimum temperature range for the sodium chlorate - perchlorate conversion would lie below that of the potassium salt reaction. German Patent 300,713 (157) recommends a range 30° lower than that used for potassium chlorate; this would mean the use of temperatures between 440 and 490°C.

Mathers and Aldred's very brief investigation (83) of the effect of temperature on the course of the reaction gave the following results for a one-hour heating of one-gram samples:

Temperature °C.	Analysis of Residue, %		
	$NaClO_4$	$NaCl$	$NaClO_3$
450	3.3	10.0	89.3
480	5.6	12.0	79.4
510	31.4	52.5	13.4
540	0	97.2	0

These results clearly indicate that 540° is too high a temperature. The highest yield was obtained at 510°C.; but when it is considered that of the 52.5 parts of NaCl formed only about 5 parts accompanied the formation of $NaClO_4$ (31.4 x $NaCl/3\ NaClO_4$), it is obvious that a very appreciable decomposition of $NaClO_3$ and/or $NaClO_4$ into $NaCl + O_2$ has taken place. At 480° and 450°C., the proportion of NaCl deriving from perchlorate formation is still low in comparison with that accompanying oxygen formation. Apparently Mathers and Aldred have chosen a set of conditions which throw little light on the subject.

It is very possible that the best yields of sodium perchlorate will be lower than those of potassium perchlorate, but is obvious that a basic study of time-temperature effects has still to be made.

4. <u>Decomposition of Other Chlorates</u>

Lithium chlorate (103), anhydrous, melts at 129°C. and begins to decompose at 270°C. The decomposition temperature of lithium perchlorate is given as 380°C. by Potilitzin (103) and as 440°C. by Marvin and Woolaver (82). Potilitzin found that the initial and final stages of the thermal decomposition could be represented by the equations

$$\text{initial:}\quad 6\,LiClO_3 \longrightarrow 2\,LiClO_4 + 4\,LiCl + 5\,O_2$$

$$\text{final:}\quad 10\,LiClO_3 \longrightarrow 2\,LiClO_4 + 8\,LiCl + 11\,O_2$$

Since these equations represent a realization, respectively, of only 39 g. and 24 g. of $LiClO_4$ per 100 g. of $LiClO_3$, the use of the latter compound would appear to offer no advantage.

Calcium chlorate, anhydrous, begins to give off oxygen before it melts (105). It melts at 300-350° after having lost 3-5% of its oxygen content. The rate of decomposition increases, at 330°C., until about 60% of the total oxygen is evolved. The calcium perchlorate content of the residue reaches a maximum at this point: 2.34%. Marvin and Woolaver (82) state that $Ca(ClO_4)_2$ begins to decompose at 405°C. and forms, besides oxygen, calcium chloride and calcium oxide in the ratio of 20 to 1.

Barium chlorate was found (102) to decompose according to the following equations:

$$330\text{-}400°C. \quad 2\,Ba(ClO_3)_2 = BaCl_2 + Ba(ClO_4)_2 + 2\,O_2$$

$$400\text{-}470°C. \quad Ba(ClO_3)_2 = BaCl_2 + 3\,O_2$$

Sodeau (124) noted the formation of some chlorine on heating this compound and observed that the amount of chlorine formed in the thermal decomposition of metal chlorates increased with the weakness of the base.

Strontium chlorate begins to give off oxygen at 290°C., and melts after 10% of its oxygen has been evolved (104). The maximum amount of perchlorate is produced when 75% of the chlorate has been decomposed, and the proportions of products formed has been expressed as:

$$11\,Sr(ClO_3)_2 \longrightarrow 2\,Sr(ClO_4)_2 + 9\,SrCl_3 + 25\,O_2$$

Lead chlorate decomposes in the following manner (125):

$$Pb(ClO_3)_2 \longrightarrow PbCl_2 + 3\,O_2$$

$$\text{or} \quad \left\{ \begin{array}{l} Pb(ClO_3)_2 \longrightarrow PbO_2 + Cl_2 + 2\,O_2 \\ PbO_2 + Cl_2 \longrightarrow PbCl_2 + O_2 \end{array} \right.$$

No perchlorate was detected.

There is thus no evidence in the literature that the chlorates of the alkaline earths or heavy metals offer any promise as starting materials for the production of perchlorates by thermal means.

3. Direct Chemical Oxidation

The literature on the direct chemical oxidation of chlorates to perchlorates is fragmentary and, at times, contradictory.

Oxygen, according to Sodeau (126), will not oxidize chlorate to perchlorate. Bennett and Mack (9) supported the theory that "active oxygen" could effect this change (in this connection, see also discussion of metal oxides, below) and suggested that the thermal conversion of chlorate to perchlorate was due to the liberation of active oxygen:

$$KClO_3 \longrightarrow KCl + 3\,O^*$$

$$3\,KClO_3 + 3\,O^* \longrightarrow 3\,KClO_4$$

However, on bubbling oxygen through a solution of sodium chlorate in a quartz flask under ultraviolet irradiation for long periods of time, they observed only 1.1% conversion over the first 24 hours and no additional conversion thereafter.

Fairley, in 1874, reported that ozone will oxidize hypochlorous acid or hypochlorites to perchloric acid or perchlorates, respectively (47,87). On the other hand, Oechsli (96) found that 6 vol.-% ozone was incapable of oxidizing chlorates to perchlorates. Bennett and Mack (9) felt that Oechsli's work was not conclusive, and repeated the work with a Siemen ozonizer supplied by a 10,000 v. transformer, of 1 KVA capacity, which delivered about 7 vol.-% ozone. In 19 hours at 22°C. they obtained 0.78% conversion to perchlorate; and in 22 hours, using silver oxide as a catalyst, they observed 1.86% conversion. At higher O_3 concentrations (one spot analysis giving 21 vol.-%), without a catalyst, they again obtained conversions of less than 1%. Knibbs and Palfreeman (72), in turn, expressed the opinion that Bennett and Mack's work with ozone, activated oxygen, and hydrogen peroxide was inconclusive. It must be concluded, therefore, that even though the oxidation of chlorate by active oxygen or ozone may be possible, the process would be very inefficient.

Tanatar (134) was unable to detect any reaction between hydrogen peroxide and potassium chlorate either in the hot or in the cold. Bennett and Mack (9) similarly found no reaction in basic or neutral solution, but claimed that some oxidation of chlorate to perchlorate occurred in acid solution. In this reaction, however, the hydrochloric acid formed interferes.

Sodium persulfate was found by Bennett and Mack (9) to oxidize sodium chlorate in acid solution. Using an excess of persulfate with a 5% aqueous chlorate solution, 17-18.5% conversion to perchlorate was obtained after 30 minutes' boiling. Under the same conditions, but in the presence of Ag^+ or BaO, conversions of 23% and 34%, respectively, were observed. Lenher, Stone, and Skinner (78) reported that persulfuric acid does not decompose chlorate.

Chlorate was not oxidized by potassium permanganate in aqueous solution (9). Yields of perchlorate by the thermal decomposition of potassium chlorate were lowered considerably by the presence of potassium dichromate (83).

The beneficial effect of certain <u>metal oxides</u> (Ag_2O, HgO, PbO_2, BaO_2) on the thermal conversion of chlorate to perchlorate, first reported by Fowler and Grant (40), were accepted without checking by Bennett and Mack (9) as substantiation of his active oxygen theory. These findings, however, have been disproven by Mathers and Aldred (83) and Farmer and Firth (34). Yields of perchlorate are actually substantially lower when these oxides are present.

<u>Sodium peroxide</u> would not oxidize chlorate in aqueous solution (9). On the other hand, <u>lead dioxide</u> was found by Ott (113) and Ehrhardt (31) to be a very effective oxidizing agent for making perchlorates. Ehrhardt reported that

$$\left.\begin{array}{l} 1394\ \text{g. } KClO_3 \\ 3382\ \text{g. } H_2SO_4\ (92\%) \\ 7890\ \text{g. } PbO_2 \\ 486\ \text{g. } PbO \end{array}\right\}\ \text{gave } 2054\ \text{g. } KClO_4\ (91.6\%\ \text{yield}),$$

and calculated the following material balance (for 1 mole of $KClO_4$).

122.5 g. $KClO_3$
300 cc. H_2O
330 g. H_2SO_4

Regenerated peroxide:
390 g. PbO_2
24 g. PbO

Agitation, 4 hrs. at 84°C.,
Mixture filtered and residue washed

<u>Filtrate</u>, 315 cc.
179.7 g. H_2SO_4
5.6 g. $KClO_3$
2.8 g. $KClO_4$

<u>Washings</u>, 215 cc.
37.0 g. H_2SO_4
1.93 g. $KClO_3$
5.35 g. $KClO_4$

<u>Washed residue</u>
Boiled with water and filtered hot

(filtrate cooled)

<u>Deposit</u>, 67 g.
$KClO_4$ (almost pure)

<u>Mother liquor</u>, 2200 cc.
39.0 g. $KClO_4$
0.9 g. $KClO_3$
6.6 g. H_2SO_4

<u>Residue</u>, 497 g.
142 g. PbO_2
319 g. $PbSO_4$
24 g. PbO
10 g. $KClO_4$
0.4 g. $KClO_3$

Three methods of regenerating the spent residue were considered:

(1) Treatment with bleach

$$PbSO_4 + 2\,NaOH + NaOCl \longrightarrow PbO_2 + Na_2SO_4 + NaCl + H_2O$$

was rejected because the energy necessary for the regeneration is supplied in the form of an electrolytically manufactured product and hence the method would offer no savings in material or energy over direct electrolytic oxidation.

(2) Fusion with sodium nitrate

$$2\,PbSO_4 + 2\,NaOH + 2\,NaNO_3 \longrightarrow 2\,PbO_2 + 2\,Na_2SO_4 + NO + NO_2 + H_2O$$

was eliminated because saleable by-products were not produced and because apparatus and materials problems would not be easy to solve.

(3) Stepwise treatment, as follows:

$$PbSO_4 + 2\,NH_3 + CO_2 + H_2O \longrightarrow PbCO_3 + (NH_4)_2SO_4$$
$$PbCO_3 + 2\,Ca(OH)_2 \text{ at } 800°C. \longrightarrow Ca_2PbO_4 + H_2O + CO_2$$
$$Ca_2PbO_4 + 4\,HNO_3 \longrightarrow PbO_2 + 2\,Ca(NO_3)_2 + 2\,H_2O$$

was considered as the most suitable method, technically, because electrical energy is not required and because a ready and continuing market for the by-products should exist. For the entire process, the manufacture of 100 kg. of $KClO_4$ would require:

Oxidation	Regeneration of PbO_2	By-product credits
115 kg. $KClO_3$	421 kg. NH_4OH (sp.gr. 0.916)	132 kg. $(NH_4)_2SO_4$
368 kg. PbO_2	101 kg. CO_2	560 kg. $Ca(NO_3)_2$
311 kg. H_2SO_4 (92%)	190 kg. CaO	
	821 kg. HNO_3 (sp.gr. 1.36)	

Schlachter (113) predicted equipment difficulties for both the oxidation and regeneration operations.

__Chlorine__ will react with alkali carbonate (151a) or bicarbonate (196a) in warm aqueous solutions to produce alkali chlorates. Ishikawa, Muraoko, and Hagisawa (58) found, however, that when chlorine is reacted with dry sodium carbonate (prepared by heating $NaHCO_3$), the main reaction is

$$2\,Na_2CO_3 + 2\,Cl_2 \longrightarrow 4\,NaCl + 2\,CO_2 + O_2$$

but some sodium perchlorate is also formed at temperatures below 450°C. Chlorine is said not to oxidize chlorate (135a).

4. Reaction of Strong Acids with Chlorates

The decomposition of chlorates by strong acids has been known for many years, but very little study has been given to the reaction. Following the early observations of Stadion, Penny and Millon in the early 1800's, no work appears to have been done until 1922 when Lenher, Stone, and Skinner (78) studied the action of a number of acids. The reaction with sulfuric acid was reported to yield perchlorate and oxides of chlorine (principally the tetroxide). It was stated that this reaction could be carried out without danger by adding the sulfuric acid slowly and preventing the reaction mixture from becoming warm. Yields with various acids were given as follows:

H_2SO_4 conc., 50 cc./2-5 g. $KClO_3$, 5 hrs.	- 11%
HNO_3 conc., repeated evap. on steam bath	- 30%
H_3PO_4, 85%, boiled	- 15%
CrO_3 with enough water to effect solution	- 11%

Formic acid
Trichloroacetic acid
Hydrofluoric acid
Hydrochloric acid
} decomposed $KClO_3$ but yielded no perchlorate

Chloric acid
Persulfuric acid
Permanganic acid 20%
Arsenic acid, 50%
Acetic acid, glacial or dilute
Monochloroacetic acid
Oxalic acid, saturated
Tartaric acid, 25%
Lactic acid, 25%
} did not decompose $KClO_3$

Hampel, in U.S. Patent 2,489,571 (200), discloses a cyclic process for producing perchlorates and chlorites of different metals by the action of a mineral acid (H_2SO_4, HNO_3, H_3PO_4, $HClO_4$, H_2SiF_6 or HF) on a chlorate in a chloride-free medium. The basic reaction (M= metal, R= acid radical) is

$$2\,HR + 3\,MClO_3 \longrightarrow MClO_4 + 2\,ClO_2 + 2\,MR + H_2O$$

In this reaction the yield of perchlorate, in the case of the sodium salt, would be $NaClO_4/3\,NaClO_3$ = 38.3%. However, the chlorine dioxide can be absorbed in an alkaline solution

$$2\,ClO_2 + 2\,MOH \longrightarrow MClO_3 + MClO_2 + H_2O$$

Thus, one mole of chlorate is recovered and the overall yield of sodium perchlorate would be $NaClO_4/2\,NaClO_3$ = 57.4%. By a proper choice of acid and by using the chlorates of two metals in the proper proportions, the separation of the perchlorate from the other salt formed can be readily accomplished on the basis of difference in solubility.

$$2\,HR + MClO_3 + 2\,M'ClO_3 \longrightarrow MClO_4 + 2\,M'R + 2\,ClO_2 + H_2O$$

A similar expedient can be used in the chlorine dioxide absorption

$$2\,ClO_2 + MOH + M'OH \longrightarrow MClO_3 + M'ClO_2 + H_2O$$

In this process, the excess acid required for the chlorate decomposition would have to be recovered and reconcentrated; and, since 33% of the chlorate is not converted to perchlorate, a market or use for the chlorite would have to be developed.

5. Electrolytic Production of Perchloric Acid

Perchloric acid can be made by the electrolysis of dilute hydrochloric acid solutions. Haber and Grinberg (48a) found that it was produced in amounts which were 25% of the theoretical current yields. Oechsli (96) reported 98% yields of perchloric acid in the electrolysis of 2.4N hydrochloric acid at 8.3 amps/sq.dm. in a diaphragm cell. U.S. Patent 1,271,633 (185) discloses the electrolysis of 0.1 to 1.0N HCl at 50 amps/sq.dm., using temperatures up to 50°C. while the chloric acid concentration is building up, then lowering the temperature to favor oxidation to perchloric acid. Goodwin and Walker (46) found that with 0.1N hydrochloric acid, 50% of the HCl went to $HClO_4$ and 50% to Cl_2; and that with 1N hydrochloric acid, almost 100% of the HCl went to Cl_2. They report that increasing the current density and decreasing the temperature increases $HClO_4$ formation slightly. In an actual run producing 50 lbs. of 50% perchloric acid, they electrolyzed 0.5N hydrochloric acid in three stages at 18°C. with a current of 150 amps., a current density of 16 amps/sq.dm., and a potential of 8 volts, recirculating the electrolyte at the rate of 25-30 liters per hour. At the end of first and second stages, HCl was added to the electrolyte to restore its concentration to 0.5N.

	Composition of Electrolyte at End of		
	1st Stage	2nd Stage	3rd Stage
HCl	0.0179 N	0.0171 N	0.0112 N
$HClO_3$	0.0255	0.0089	0.0078
$HClO_4$	0.0738	0.2015	0.286

The product from the third stage was then concentrated in a cascade evaporator. The authors state that this process has been perfected and put in use by the Genesee Chemical Co.

In the work cited, platinum anodes were used. U.S. Patent 1,271,633 suggests, however, that magnetite anodes are also suitable. If perchloric acid can in reality be made economically with magnetite anodes, the acid so produced could be neutralized with soda ash to yield the desired sodium salt.

Newham and Mathers (93a) made crude aqueous perchloric acid at a concentration of 2N by electrolyzing between a Pt anode and Fe cathode a saturated solution of sodium chlorate in a 2-diaphragm, 3-compartment cell. The anode compartment was formed of porous porcelain cup, and the cathode compartment of an asbestos paper cup. At 3.5 amps/sq.dm. a 60% current efficiency and an 80% material efficiency were observed, with a power requirement of 3 KWH per lb. of 70% $HClO_4$ produced. It may be possible that magnetite or other platinum substitute could be used at this low current density.

6. Electrolysis of Chloride and Hypochlorite Solutions

Winteler (147) observed that in the electrolysis of alkali metal chlorides no primary formation of perchlorate occurs; it appears only when the chloride ion concentration falls to a minimum through oxidation to chlorate. Allmand (1) confirms this by stating that no perchlorate will form in the chlorate process if the NaCl concentration is kept up. Pamphilov and Fedorova (99,100) found that small quantities of $NaClO_4$ are formed in the electrolysis of $NaClO_3$ even in the presence of 18% NaCl, provided the current density is high (200 amps/sq.dm.). French Patent 704,325 (152) noted that magnetite anodes showed a greater tendency to produce perchlorate during chlorate manufacture than either platinum or graphite. Kato, Sugino, Koizumi and Kitahara (68) recognized the stepwise nature of the conversion of NaCl to $NaClO_4$, but carried out that operation in a single cell using a PbO_2 anode. Using saturated NaCl solution, a potential of 5 volts, a current density of 21 amps/sq.dm. and a temperature of 32°C., 98% conversion to perchlorate was obtained at a current efficiency of 49% and an expenditure of 17.9 KWH per kg. of perchlorate. They explained that if the first phase of the electrolysis had been carried out at a higher temperature, a higher current efficiency would have resulted.

The electrolytic oxidation of alkaline earth chlorides to perchlorates appears to occur more readily than with the alkali metal chlorides. Blau and Weingand (14) found that the electrolysis of $BaCl_2$ solutions between platinum anodes and nickel cathodes at 60°C. and with a current density of 15 amps/sq.dm., gave $Ba(ClO_4)_2$ in current yields of 50-60%. The addition of acetic acid, hydrochloric acid, calcium chloride or carbon dioxide was said to favor the reaction. Izgaryshev and Khachaturyan (59,60) studied the electrolysis of small volumes of alkali and alkaline earth chloride solutions between smooth platinum electrodes at a current density of 50 amps/sq.dm. Yields of perchlorate were low for NaCl and KCl, but high for LiCl.

Using 3.6N solutions, the following results were obtained:

	Gm. equivalents of perchlorate per amp. hour	Current Efficiency, %
LiCl	0.0041	94.4
NaCl	.00105	48.9
KCl	.0011	47.3
$MgCl_2$	.00195	36.8
$CaCl_2$	.0047	89.3
$BaCl_2$	.0022	54.7

With a graphite cathode, calcium chloride gave up to 99.84% perchlorate in 8 hours, at 25°C. In the electrolysis of NH_4Cl under the same conditions, explosive NCl_3 appeared during the early stages of the electrolysis; at the end of the electrolysis NH_4^+ had disappeared, the electrolyte had become strongly acid, and ClO_4^- was present.

Japanese Patent 129,657 (160), according to Chemical Abstracts, discloses the electrolytic oxidation of sodium hypochlorite to perchlorate at a PbO_2 anode.

The behavior of alkaline earth chlorides, on electrolysis, presents some interesting variations from that of sodium and potassium chloride, but it is not apparent from the literature how these differences might affect the choice of a substitute anode material.

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\- British Pat. 179, 636. (Febr. 7, 1921). See (190) U.S. Pat., 1,470,577.

\- British Pat. 198,246. (July 7, 1922). See (191) U.S. Pat. 1477,099.

\- British Pat. 220,944 (Aug. 18, 1924). See (192) U.S. Pat. 1,595,675.

(151) British Pat. 212,871. (Mar. 16, 1923). Chile Exploration Company.

\- British Pat. 486, 728. (June 9, 1938). See (196) U.S. Pat. 2,258,435

(151a) Canadian Patent 370,954 (Jan. 4, 1938). C. Carter to Canadian Industries, Ltd.

\- French Pat. 704,324. (May 18, 1931) See (194), U.S. Pat. 1,880,927.

(152) French Pat. 704,325. (May 18, 1931). I. G. Farbenindustrie, A.G.

\- German Pat. 92,612. (Aug. 7, 1895). See (165) U.S. Pat. 568,229.

\- German Pat. 136,678, (June 11, 1902). See (169) U.S. Pat. 693,035.

(153) Germ. Pat. 140,317. (March 18, 1903). P. Ferchland.

\- German Pat. 193,367. (Jan. 2, 1908). See (178) U.S. Pat. 931,513.

\- German Pat. 206, 329. (Febr. 4, 1909). See (177) U.S. Pat. 900,502.

(154) German Pat. 207, 257. (Aug. 25, 1906). P. Ferchland.

(155) German Pat. 298.991. (Dec. 5, 1919) Oberschlesische A.-G. fur Fabrikation von Lignose, Schiesswollfabrik fur Armee & Marine.

(156) German Patent 300,021. (Nov. 26, 1919) Oberschlesische Springstoff A.-G.

(157) German Pat. 300, 713. (Aug. 30, 1919) F. Meyer.

\- German Pat. 423,058 (1926). See (192) U.S. Pat. 1,595,675.

- German Pat. 514,340. (Dec. 11, 1930). See (194) U.S. Pat. 1,880,927.

(158) Japanese Patent 34,913. (Sept. 11, 1919). E. Sato & Kabafuto-Kwako Co.

(159) Japanese Pat. 38,818. (June 4, 1921). S. Tsukata, E. Sato, et al.

(160) Japanese Pat. 129,657. (Apr. 7, 1939). K. Sugino, K. Koizumi, & S. Kitahara.

(161) Japanese Pat. 174,440. (Jan. 23, 1947). R. Kikuchi & K. Yamagata.

(162) Japanese Pat. 175,166. (Oct. 23, 1947). Y. Shibasaki.

(163) Russian Pat. 69, 700. (Nov. 30, 1947). N.N. Tumanov

(164) U.S. Pat. 546,328. (Sept. 17, 1895). C. Hoeffner.

(165) U.S. Pat. 568,229. (Sept. 22, 1896). H. Blackman.

(166) U.S. Pat. 568,230. (Sept. 22, 1896). H. Blackman.

(167) U.S. Pat. 568,231. (Sept. 22, 1896). H. Blackman.

(168) U.S. Pat. 598,193. (Febr. 1, 1898). E. Andreoli

(169) U.S. Pat. 693,035. (Febr. 11, 1902). P. Lederlin.

(170) U.S. Pat. 727,813 (May 12, 1903). P. Lederlin.

(171) U.S. Pat. 732,753 (July 7, 1903). P. Lederlin.

(172) U.S. Pat. 788,631 (May 1905).

(173) U.S. Pat. 800,181. (Sept. 26, 1905) H. Specketer to Chemische Fabrik Griesheim A.M.

(174) U. . Pat. 860,657. (July 23, 1907). H. S. Hatfield.

(175) U.S. Pat. 872,878. (Dec. 3, 1907). R.J. Wisnom

(176) U.S. Pat. 882,169, (Mar. 17, 1908). M. Ruthenburg.

(177) U.S. Pat. 900,502. (Oct. 6, 1908). P. Ferchland & J. Nussbaum.

(178) U.S. Pat. 931,513. (Aug. 17, 1909). H. Specketer to Chemische Fabrik Griesheim Electron.

(179) U.S. Pat. 935,109. (Sept. 28, 1909). M. Huth to Siemans & Halske A.-G.

(180) U.S. Pat. 935,250 (Sept. 28, 1909). V. Englehardt & M. Huth to Siemans & Halske A.-G.

(181) U.S. Pat. 1,043,937 (Nov. 12, 1912). M. Huth to Siemans & Halske A.-G.

(182) U.S. Pat. 1,143,828. (June 22, 1915). P.C.C. Isherwood

(183) U.S. Pat. 1,173,346. (Feb. 29, 1916). A. E. Gibbs.

(184) U.S. Pats. 1,226,121-3. (May 15, 1917). A. P. Scott to Chile Exploration Co.

(185) U.S. Pat. 1,271,633. (July 9, 1918). E. C. Walker.

(186) U.S. Pat. 1,279,593. (Sept. 24, 1918). E.C. Schoch & R. H. Pritchett.

(187) U.S. Pat. 1,296,188. (Mar. 4, 1919). M. Huth to Siemans & Halske A. F.

(188) U.S. Pat. 1,302,959. (May 6, 1919). W.K. Page to Chile Exploration Co.

(189) U.S. Pat. 1,311,096. (July 22, 1919). E.A.C. Smith.

(190) U.S. Pat. 1,470,577. (Oct. 9, 1923). O. Liebknecht.

(191) U.S. Pat. 1,477,099 (Dec. 11, 1923) G. Baum to Chem. Fabr. Weissenstein.

(192) U.S. Pat. 1,595,675. (Aug. 10, 1926). J. H. Mellquist.

(193) U.S. Pat. 1,740,291. (Dec. 17, 1929). C.G. Fink to Baric Metal Corp.

(194) U.S. Pat., 1880,927. (Oct. 4, 1932). U. Ehrhardt to I.G. Farben,

(195) U.S. Pat., 1,965.457 (July 3, 1934). U. Ehrhardt to I.G. Farben.

(196) U.S. Pat. 2,258,435. (Oct. 7, 1941). G. Adolph & M.E. Bretschger to Buffalo E.-C. Co.

(196a) U.S. Pat. 2,287,061. (June 23, 1942). S.G. Osborne et al. to Hooker Electro-bhem. Co.

(197) U.S. Pat. 2,305,133. (Dec. 15, 1942). T.A. Campbell to Chile Exploration Co.

(198) U.S. Pat. 2 392,769. (Jan. 8, 1946). J.R. Ryan to Buffalo E.-C. Co.

(199) U.S. Pat. 2,475,157. (July 5, 1949). J.C. Schumacher to Western Electro-chemical Co.

(200) U.S. Pats. 2,489,571 to 2,489,575. (Nov. 29, 1949). C.A. Hampel to Cardox Corp.

(201) U.S. Pats. 2,496,288 to 2,496,290. (Feb. 7, 1950). C.A. Hampel to Cardox Corp.

(202) U.S. Pat. 2,511,686. (June 13, 1950). J. Andre to Cie. de Products Chimique et Electrometallurgique Alais, Forges & Camarque.

(203) U.S. Pat. 2,512,973. (June 27, 1950). J.C. Schumacher to Western Electro-chemical Co.

CONFIDENTIAL

INVESTIGATION OF METHODS TO PRODUCE SODIUM PERCHLORATE
WITHOUT THE USE OF PLATINUM

PART II - Laboratory Work

PROJECT NR 352-263/2-19-51

CONTRACT NUMBER - NONR 372(00)

OFFICE OF NAVAL RESEARCH

PENNSYLVANIA SALT MANUFACTURING COMPANY

RESEARCH AND DEVELOPMENT DIVISION

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August 31, 1951

Pennsalt File No. 4-00036-60
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SUBJECT

Sodium Perchlorate, Methods of Producing Without the Use of Platinum (Project Number NR 352-263; Contract Number NONR 732(00)).

OBJECT

An investigation in respect to the determination of a method for producing sodium perchlorate without the use of platinum, to include, but not necessarily to be limited to, the following:

(1) literature and patent review, both domestic and foreign, on possible substitutes for platinum as anode materials in the production of sodium perchlorate;

(2) preliminary laboratory experiments with the more promising anode materials;

(3) literature and patent review, both domestic and foreign, on the thermal decomposition of sodium chlorate for the production of sodium perchlorate; and

(4) preliminary laboratory experiments to indicate the feasibility of a thermal decomposition method.

SCOPE

The rapid expansion of the production of perchlorates during the last few years and the decreasing reserves of platinum, the metal now used in the production of sodium perchlorate (the starting material for potassium and ammonium perchlorate), make it desirable at this time to search for new methods to produce perchlorates that will be less wasteful of platinum. Part I of this report, bound separately, comprises a review of the technical literature, including patents, of all methods reported for the production of perchlorates, and of all apparatus and techniques that might be adapted to such production. Part II, bound in this cover, is a short but critical laboratory study of the methods described in the literature, and of other methods that were suggested during the course of the work.

SUMMARY OF LABORATORY WORK

1. Of 75 samples of various anode materials that were made in this laboratory or were secured from several outside sources, only magnetite, lead dioxide, silicon-silicon carbide mixture, ilmenite, platinum plated tantalum and certain metal carbides with platinum as a binder, looked sufficiently good in a screening test to warrant further testing as anode materials in a perchlorate cell.

2. A number of metals; several chemically resistant alloys; several varieties of graphite; a number of metal silicides, borides, carbides, and nitrides; and surface-oxidized or sulfided iron and nickel proved unsatisfactory.

3. Larger anodes of lead dioxide, silicon-silicon carbide, carbon, and magnetite were tested in a 5 to 10 ampere laboratory cell:

a. Magnetite anodes did not seriously erode but failed to make perchlorate under the conditions tested.

b. Electrolytic-plated lead dioxide anodes failed because of pinholes in the plated surface.

c. Silicon-silicon carbide produced perchlorate with little or no surface erosion; however, the anodes were seriously damaged by a cracking and shattering phenomenon that always accompanied the electrolysis.

d. Carbon anodes produced perchlorate but they were always seriously attacked. The attack was a function of pH, temperature, and current density.

4. Carbon anodes produced perchlorate when operated in a diaphragm-type cell as disclosed in a U. S. patent. The carbon was eroded but less severely than in a diaphragmless cell. Graphite failed completely in a diaphragm cell.

5. Laboratory study on the thermal conversion of both sodium and potassium chlorate ~~chlorate~~ confirmed the yields reported in the literature; also, the slowness of the conversion and the required temperature (ca. 470, 482°C.) were confirmed. Yields as high as 73.1% were observed in quartz, while Pyrex and Vycor apparatus gave very poor yields.

6. Ozone failed to oxidize either an alkaline or acid solution of sodium chlorate.

7. Sodium chlorate is slowly oxidized to perchlorate by lead dioxide in a strong sulfuric acid solution.

8. Sulfuric acid converted 45% of sodium chlorate to perchlorate. Chlorine dioxide and chlorine were formed also.

9. An analytical procedure was developed for the determination of perchlorate ion in the presence of chlorides and chlorates.

CONCLUSIONS

1. No anode material was found to produce perchlorate as well as platinum or platinum-coated tantalum.

2. Lead dioxide, silicon-silicon carbide mixtures, and carbon anodes require further development before they can be completely appraised as practical anode materials.

3. Magnetite anodes did not produce perchlorate under the conditions used.

4. Metal carbides with platinum as a binder, manganese dioxide, and ilmenite appear promising but were not tested in sufficient detail in this work to permit definite conclusions. Better specimens of some of these materials must be found before further work is undertaken.

5. The high temperature, the poor yields, and the sensitivity of the reaction to trace impurities makes the thermal method look unattractive.

6. The chemical oxidation of chlorate to perchlorate by lead dioxide in sulfuric acid solution is practical only if a good method is found to convert lead sulfate to lead dioxide.

7. The good yields and the ease with which by-products can be handled makes the conversion of chlorates to perchlorates by strong acids attractive when operated in conjunction with a chlorate plant.

8. The analytical procedure for perchlorate ion in the presence of chlorides and chlorates is rapid and accurate.

RECOMMENDATIONS

1. It is recommended that more work be done on the silicon-silicon carbide, carbon, and ilmenite materials. This work should be carried out in close cooperation with a laboratory equipped to formulate electrodes made from these high refractory materials.

2. Further work should be carried out to develop a lead dioxide anode that will not develop pinholes. This should include work on the electrolytic bath, preparation of the base metal, and a study of the best operating conditions for the perchlorate cell using a lead dioxide anode.

3. A laboratory study should be made on the decomposition of chlorate by sulfuric acid to determine conditions to produce the fewest problems of separation and purification, and the best utilization of by-products. This process should be considered in connection with a sodium chlorate plant for the best utilization of by-products.

4. If all other methods fail, the lead dioxide oxidation of chlorates should be studied with special emphasis on a study of the hazards of the process, and on methods of recycling the lead compounds.

5. Several classes of anode materials not fully studied here should be re-examined. The metal silicides and cerments would be included. The use of ozone as a possible oxidizing agent should be more fully evaluated.

6. For the present, no further work is recommended on the thermal decomposition method.

LABORATORY STUDY

A. Introduction

The various methods for the preparation of sodium perchlorate may be classified as follows:

(1) Electrolysis of an aqueous sodium chlorate solution, in which process the chlorate is oxidized anodically to perchlorate.

(2) Thermal decomposition of sodium chlorate, in which process the chlorate undergoes oxidation-reduction to perchlorate and chloride.

(3) Direct chemical oxidation of sodium chlorate to perchlorate by means of such oxidizing agents as persulfates, lead dioxide, ozone, etc.

(4) Reaction of a strong mineral acid on sodium chlorate to produce sodium perchlorate, chlorine dioxide, sodium chloride and chlorine.

(5) Electrolytic production of perchloric acid from hydrochloric acid, followed by neutralization of the acid with soda ash to yield sodium perchlorate.

(6) Electrolysis of sodium chloride and sodium hypochlorite solutions to produce sodium perchlorate.

In this preliminary work, the first four methods have been studied.

B. Electrochemical Oxidation of Sodium Chlorate

1. Introduction

Since, sodium perchlorate is apparently made industrially exclusively by the electrochemical method, it was considered desirable to spend the major effort in a preliminary study of the possibilities of finding a substitute for the platinum now used as anode material in commercial cells. The literature reports the testing of a relatively small number of substances as anodes in the perchlorate cell. Since there has apparently been no attempt in the past to examine a comprehensive list of possible anode materials, it was deemed advisable to test all likely materials that were readily available.

Many specimens for study were received as a result of a blanket request for metallic borides, carbides, nitrides, and silicides that was made to a selected list of government, industrial and research foundation laboratories. Further requests were made for anode materials that appeared promising on the basis of the Literature Study. (Table I) Other anode materials used in this study were either on hand from previous electrochemical investigations in this laboratory or were prepared during the course of this study. This section of the report covers this work in detail.

TABLE I

LIST OF GOVERNMENT, INDUSTRIAL AND RESEARCH FOUNDATION LABORATORIES

CONTACTED AS POSSIBLE SOURCES OF ANODE MATERIALS FOR PERCHLORATE CELLS

Acheson Graphite Corporation, Niagara Falls, New York

Adamas Carbide Corporation, 1000 South Fourth Street, Harrison, New Jersey

American Abrasive Company, 100 Union Street, Westfield, Mass.

The American Brass Company, Waterbury (20), Connecticut.

American Electro Metal Corporation, 320 Yonkers Avenue, Yonkers 2, N. Y.

Baker and Company, Inc., 113 Astor Street, Newark 5, N. J.

Battelle Memorial Institute, Columbus 1, Ohio

A. S. Behrman, Chemical Consultant, 9 South Clinton Street, Chicago 6, Ill.

Belmont Smelting and Refining Works, Inc., 320 Belmont Avenue, Brooklyn 7, N. Y.

Carboloy Department of General Electric Company, Detroit 32, Michigan

The Carborundum Company, Globar Division, Niagara Falls, New York

Ethicon Suture Laboratories, Division of Johnson and Johnson, New Brunswick, New Jersey

Fansteel Metallurgical Corporation, North Chicago, Illinois

Firth Sterling Steel and Carbide Corporation, McKeesport, Pa.

Fisher Scientific Company, 717 Forbes Street, Pittsburgh, Pa.

Foote Mineral Company, 18 W. Chelten Avenue, Philadelphia 44, Pa.

General Abrasive Company, Inc., 2107 College Avenue, Niagara Falls, N. Y.

General Tool and Die Works, East Orange, N. J.

Haynes Stellite Division, Union Carbide and Carbon Corporation, 30 East 42nd Street, New York 17, New York

International Graphite and Electrode Corporation, Saint Marys, Pa.

Kennametal, Inc., Latrobe, Pa.

Metals Disintegrating Company, Inc., Elizabeth (B), New Jersey

National Carbon Company, Inc., Unit of Union Carbide and Carbon Corporation. Carbon Products Division, P. O. Box 6087, Cleveland 1, Ohio

Norton Company, 50 N. Bond Street, Worcester, Mass.

Powell Duffryn Research Laboratories, Ltd., 140 Battersea Park Road, London, S. W. 11, England

Revere Copper and Brass Incorporated, Rome Division, P. O. Box 151, Rome, N. Y.

Stackpole Carbon Company, St. Marys, Pa.

Titanium Alloy Manufacturing Division, National Lead Company, Niagara Falls, New York

Tungsten Electric Corporation, Union City, New Jersey

U. S. Bureau of Mines, Washington, D. C.

Vascoloy-Ramet Corporation, 800 Market Street, Waukegan, Illinois

Ward's Natural Science Establishment, Inc., P. O. Box 24, Beechwood Station, Rochester (9), New York

2. Screening Tests

(a) General Description

This phase of the investigation involved the testing of many different kinds of materials that might be used as substitutes for platinum in the sodium perchlorate cell. For convenience in reporting, these materials are divided into the following classes:

(1) platinum group metals
(2) pure metals and metal alloys
(3) graphite and carbon
(4) globar rod material
(5) metal silicides
(6) metal oxides
(7) oxide and sulfide coatings
(8) metal borides
(9) metal carbides
(10) metal nitrides
(11) miscellaneous undesignated materials

The preliminary testing of these materials was designed to eliminate from further consideration those whose performance proved to be wholly unsatisfactory.

The electrolyte used in all tests contained 600 grams of $NaClO_3$ per liter. This solution was found to have a specific gravity of 1.594 at 28°C. The electrolyte also contained 4 grams per liter of sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$, except where its omission is so noted in the experimental data. The electrolyte, in beaker-type cells, was cooled either by an external ice bath or by an internal glass cooling coil with tap water flowing through the coil.

The cathodes, of low-carbon steel, were generally placed on opposite sides of the anode being tested.

The direct current source was an autotransformer-rectifier combination which was capable of delivering from 0 to 30 volts. The total cell current was varied, depending upon the size of the anode material available, to give the desired anode current density. The anode materials were tested at a current density of 200 to 300 ma./sq. cm.

For the most part, the substances tested eroded rapidly and their failure was observed by one or more of the following changes: (1) a decided color change in the electrolyte, (2) a precipitate or sediment in the electrolyte, and (3) an actual weight loss of the anode material tested. In some cases the anode material polarized and the cell failed to pass current at the applied voltage. The length of time for the tests varied depending upon the time necessary to make the above observations.

Anode materials that appeared promising as a result of these preliminary screening tests were studied more thoroughly in a large 10 ampere sodium perchlorate cell. This work is covered in Section B.3(b) "Extended Evaluation of Screened Materials", on page 42.

(b) Materials Tested, by Classes

(1) Platinum Group Metals

Background

The major industrial installations have accepted platinum as the only suitable anode material in spite of the high initial investment and subsequent erosion loss due to electrochemical attack and mechanical disintegration.

Platinum alloys with cheaper noble metals may be a solution to this problem and indeed it has been found by Yamaga and coworkers (149) that platinum alloys containing a small quantity of gold, iridium and rhodium showed almost the same oxygen over-voltage as pure platinum in the electrochemical oxidation of ammonium sulfate to persulfate.

A platinum plated tantalum base has been proposed by Baum (191) as an anode for making persulfates.

Experimental Observations

In the preliminary screening tests, platinum was tested briefly as an anode in the sodium perchlorate cell merely to observe how a satisfactory anode material behaved. No platinum alloys were procured and tested since it was the purpose of this study to avoid the use of expensive platinum.

However, since platinum plated tantalum sheet (0.005 g. Pt per sq. cm.) from the J. Bishop & Co. Platinum Works, Malvern, Pa. was on hand, it was tested in the perchlorate cell. It was found that platinum plated tantalum sheet performed entirely satisfactorily as an anode material. This anode was studied in greater detail in the 10 ampere cell (see section B.3(a) page 35).

Rhodium plated tantalum sheet (0.0041 g. Rh per sq. cm.), also from the J. Bishop & Co. Platinum Works, proved unsatisfactory because the rhodium eroded from the tantalum, turning the electrolyte black.

(2) Pure Metals and Metal Alloys

Background

Howard (57) reported that all the common metals and some of the rarer metals corroded very rapidly when used

TABLE II

PLATINUM GROUP METALS SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Platinum	3	400	6.3-7	45-50	No noticeable erosion	
Rhodium plated tantalum sheet	4		8.6	20-40	Erodes appreciably	Black color appearing in electrolyte
Platinum plated tantalum sheet	4		7.5	20-45	No noticeable erosion	

as anodes in the perchlorate cell. Angel (3) found that tungsten and molybdenum were strongly attacked. Certain lead alloys have been mentioned as "insoluble" anodes in other electrochemical processes (37, 38, 197).

Experimental Observations

It was found that aluminum and magnesium eroded rapidly in the perchlorate cell.

Molybdenum metal, obtained from the Fansteel Products Company, completely eroded away in the electrolyte after current had passed for 30 minutes.

Pure tantalum metal, obtained from the Ethicon Suture Laboratories, polarized immediately, and the cell failed to pass any current.

Pure titanium metal in the form of an arc melted sheet was obtained from the Foote Mineral Company. This anode material when tested in a simple sodium perchlorate cell completely disintegrated after 40 minutes of electrolysis (4 amperes at start falling off to 0 amperes at end of electrolysis period).

Pure zirconium metal in the form of an arc melted sheet was also obtained from the Foote Mineral Company and tested in a similar manner. Zirconium eroded very rapidly and after current had passed for 30 minutes (4 amperes at start falling off to 0 amperes at end of electrolysis period), all the zirconium beneath the surface of the electrolyte had completely eroded away.

All of the stainless steels tested were rapidly attacked as shown by the appearance of a reddish-brown precipitate in the electrolyte.

A sample of cast cobalt-chromium-tungsten alloy (Tantung G, No. 166 alloy) from the Vascoloy-Ramet Corporation tested in a beaker cell showed considerable erosion after 30 minutes as evidenced by anode weight loss and a very large amount of green precipitate in the electrolyte.

With a lead alloy consisting of 40% lead, 59% silver and 1% indium, a copious amount of yellow precipitate appeared in the electrolyte after 5-10 minutes electrolysis.

Since all of the above materials either polarized, eroded rapidly or disintegrated entirely in the sodium perchlorate cell, none was considered sufficiently promising to warrant further testing as anode materials.

TABLE III

PURE METALS AND METAL ALLOYS SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Aluminum (Aluminum Company of America)	3.8	200	5.5	20	Erodes appreciably	
Magnesium (Dow Chemical Company)	3	200	2.3	20	Erodes appreciably	
Molybdenum (Fansteel Metallurgical Corp.)	1			30	Disintegrates	
Lead-silver-indium alloy	4		8-9	25-35	Erodes appreciably	
Tantalum (Ethicon Suture Laboratories)					Polarizes immediately	
Titanium (Foote Mineral Company)	4		10-22	30-45	Disintegrates	Disintegration complete after 40 minutes
Zirconium (Foote Mineral Company)	4		9-18	40-80	Disintegrates	Disintegration complete after 30 minutes
Stainless Steel Type 302	4	540	6.5-7.3	30-45	Erodes appreciably	
Stainless Steel Type 304	4	540	7.0-9.0	30-45	Erodes appreciably	
Stainless Steel Type 309	4	540	6.0	30-60	Erodes appreciably	
Cast Cobalt-chromium-tungsten alloy (Tantung G No. 166 - Vascoloy-Ramet Corporation	2.4	200	3.6	20	Erodes appreciably	

(3) <u>Graphite and Carbon</u>

<u>Background</u>

Ullmann (140) reports that graphite is too strongly attacked to be serviceable in perchlorate production. Sihvonen (123) says that no perchlorate is formed at a graphite electrode.

On the other hand, U. S. Patent 1,279,593 (186) claims that impregnated retort carbon may be used in a diaphragm cell, with an anode loss of 9% by weight of the perchlorate produced, at a current efficiency of 50% or greater.

<u>Experimental Observations</u>

Of the nine different samples of graphite tested, all eroded too rapidly to be considered useful, thus confirming the literature report. The two carbon materials gave the same result. Both the graphite and carbon anodes were softened by use and the accompanying erosion colored the electrolyte black.

Diaphragm cell experiments showed conclusively that perchlorate can be produced at a high density carbon anode, such as Powell-Duffryn PS-1910, with a current efficiency of 5%. The anode, however, is considerably softened and swollen, and the electrolyte is blackened by finely dispersed carbon particles resulting from attack on the anode. Perchlorate could not be produced at a graphite anode in the diaphragm cell, and in addition the graphite completely disintegrated within 2 to 3 hours.

Powell-Duffryn dense carbon when operated as anode in a diaphragmless cell under conditions similar to those used with the diaphragm cell were eroded at a much faster rate. Perchlorate was formed in this cell, although probably at a lower current efficiency than in the diaphragm cell. It was also noted that perchlorate formation was much more efficient in a mildly alkaline bath than in a bath in which the pH was maintained between 4 and 6 by the addition of hydrochloric acid during the electrolysis.

(4) <u>Glober Rod Material</u>

<u>Background</u>

Russian Patent 49,700 (163) claims the use of silicon carbide or "silicided graphite" electrodes in place of platinum for the electrolytic production of perchlorates and persulfates. However, Howard (53) states that carborundum is "valueless" as an anode material in perchlorate formation.

TABLE IV

GRAPHITE AND CARBON SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
International Graphite H	4	300		40-50	Erodes appreciably	oil treated
International Graphite 850T (oil treated)	4	300		40-50	Erodes appreciably	erodes slowly at first; then as rapidly as untreated
International Graphite #90	4	300		40-50	Erodes appreciably	
International Graphite 185 NOT	4	-		15-30	Erodes appreciably	
International Graphite 185 CT (oil treated)	4	-		25-40	Erodes appreciably	Oil treated erodes the least
Stackpole Carbon #C1HP	4	-		40-50	Erodes appreciably	
Acheson Graphite	4	-		30-45	Erodes appreciably	Acheson Graphite best
Grade 10 Graphite	4	-		30-50	Erodes appreciably	When compared with the two samples of Grade 10 Graphite
Grade 10 Graphite soaked 1.5 hrs. in molten CH-73 at 110°-120°C.	4	-		30-60	Erodes appreciably	CH-73 is a chlorinated hydrocarbon, 73% chlorine
High Density Carbon (Powell-Duffryn, Ltd.)	4	300	7.4-7.5	45-50	Erodes appreciably	Softens

TABLE V

A. **TESTING OF GRAPHITE AND CARBON AS ANODE IN DIAPHRAGM-TYPE PERCHLORATE CELL**

Run No.	Electrode Material	Catholyte Composition	Voltage	Current Amps.	Bath Temp. °C.	Electrolysis Period Hours	Condition of Electrodes After Electrolysis	Analysis of Anolyte after Electrolysis	
1	High density carbon Powell-Duffryn, Ltd.	1:1 (v/v) H_2SO_4 with H_2O	Rises from 7.9 to 13.5	6.3	25	2.3	Anode - softened Cathode - unchanged		
2	"	1:2 (v/v) H_2SO_4 with H_2O	Rises from 8.1 to 8.9 in 1st hour, then drops to 7.4	6.3	25	5.2	Anode - considerably softened and noticeably swollen Cathode - unchanged	NaCl 0 g./l. $NaClO_3$ 548 g./l. $NaClO_4$ 96 g./l.	Not neutralized pH = <2
3	"	10% H_2SO_4	Rises from 9.3 to 14.9	6.3	21	12.0	Anode swollen and split Cathode - unchanged	NaCl 0 g./l. $NaClO_3$ 332 g./l. $NaClO_4$ 103 g./l.	*Neutralized with Na_2CO_3 when removed from cell
4	Dense Graphite	10% H_2SO_4	Rises from 9 to 11	6.4	26	7.5	First anode completely eroded in 5 hours. Second anode eroded to one-half thickness. (Initial anode cross-section: 1" x 1/2")	NaCl 0 g./l. $NaClO_3$ 606 g./l. $NaClO_4$ 0 g./l.	Neutralized with Na_2CO_3 when removed from cell

Cell Body - Glass, museum-type jar; 1/8" thick porous ceramic plate, used to divide cell into two compartments, was set in with a wax.

Anolyte - Sodium Chlorate, 600 g./l.
Current Density - 200 ma./cm.^{2}

*Note: The original concentrations of chlorate and perchlorate changed because of the loss of H_2O from the cell and also because of the subsequent addition of Na_2CO_3.

B. **TESTING OF HIGH DENSITY CARBON AS ANODE IN DIAPHRAGMLESS PERCHLORATE CELL**

Run No.	Electrode Material	Voltage	Current Amps.	Bath Temp. °C.	Electrolysis Period Hours	Condition of Electrodes After Electrolysis	Analysis of Electrolyte After Electrolysis	
5	Powell-Duffryn High Density Carbon PS 1910	Rises from 9 to 10	5.0	19 to 28	26	Anode swollen and surface layer split off. Cathode - unchanged	NaCl 2 g./l. $NaClO_3$ 545 g./l. $NaClO_4$ 93 g./l.	pH = 10
6	"	9	8.7	26 to 35	11	Anode - one half of thickness eroded Cathode - unchanged	NaCl 9 g./l. $NaClO_3$ 621 g./l. $NaClO_4$ <10 g./l. (HCl was added during electrolysis of Run #6 only)	pH = 4

Experimental Observations

In the experimental work covered here, Globar rod materials obtained from the Carborundum Company were tested. The first work was done with sections of a regular Globar rod element cut with a diamond saw.

The end sections of the regular Globar rod element are silicon-silicon carbide mixtures. Such an end section, tested as an anode, showed surface disintegration, apparently caused by mild explosions occurring beneath the porous surface of the Globar end section. The particles which had flaked off the surface of the anode sample dropped to the bottom of the cell; there was no change in the color of the electrolyte.

A further test was run with a center section of a Globar rod, which is chiefly silicon carbide. This material polarized after about 30 minutes of electrolysis.

Following this initial work, larger specimens of more definite description were secured from the Carborundum Company. With both a Globar element section (SiC) and a Durhy rod #1 section, polarization occurred after 2 to 3 minutes.

With a Durhy rod #2 section (Si-SiC mixture), analysis of the electrolyte definitely showed the formation of sodium perchlorate, and a very approximate calculation indicated a current efficiency of between 50 and 60%. Since the Durhy rod #2 section showed only slight surface disintegration, it may be considered one of the most promising of the materials of this class. The behavior of this material was studied further in [illegible] cell [illegible] (b), par. 42)

(5) Metal Silicides

Background

The literature (164, 176, 189) indicates the use of high-silicon alloys and metal silicides as corrosion-resistant electrodes in a variety of electrochemical processes. However, Howard (53) states that high silicon alloys are "valueless" as anode materials in perchlorate formation.

Experimental Observations

Of the samples tested, Duriron, and siliconized steel from the Battelle Memorial Institute were strongly attacked with visible erosion evident on the anode sample and considerable reddish-brown precipitate in the electrolyte.

Since only a small number of possible materials of this class has been investigated, further tests should be made on metal silicides because of their generally outstanding inertness.

TABLE VI

GLOBAR ROD MATERIAL* SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq. cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
End section of Globar Rod	1-4		16-23	25-50	Slight surface disintegration, Polarizes	
End section of Globar Rod	1		6-15	25-50	Slight surface disintegration	No dichromate used
Center section of Globar Rod	-	-	-	-	Polarized	
Globar Element Section (SiC)	0-0.4		15 to greater than 30	16-20	Polarized	
Durhy Rod #1 section	0.1		40	9	Polarized	Data after current had passed for 2 minutes
Durhy Rod #2 Section (Si-SiC mixture)	2-3	100	5-9	16-20	Slight surface disintegration	

*All samples obtained from the Carborundum Company.

TABLE VII

METAL SILICIDES SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq. cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Duriron	4	-----	9-10	20-40	Erodes appreciably	Reddish-brown precipitate in electrolyte
Siliconized Steel (Battelle Memorial Institute)	1		5.3	20-30	Erodes appreciably	Reddish-brown precipitate in electrolyte
Molybdenum Silicide (Battelle Memorial Institute)	--	-----	---	5	Polarizes	No dichromate in electrolyte
Silicided Molybdenum (Fansteel Metallurgical Corporation)	4	200	5-10	20	Erodes appreciably	

(6) Metal Oxides

The materials investigated under this classification include magnetite (pages 18, 19), lead dioxide (pages 18, 20-27), manganese dioxide (pages 25, 28, 29) and ilmenite (page 28).

Magnetite

Background

Fabricated magnetite electrodes have been used in a number of electrolytic operations: (a) electrolysis of acidic copper sulfate solutions (26, 173), (b) manufacture of chlorine and chlorinated lime (13) and (c) in I. G. Farben's electrolytic sodium chlorate plant at Bitterfeld (80). No reference was found to indicate the successful use of magnetite as anodes in the sodium perchlorate cell.

Experimental Observations

A specimen of natural magnetite obtained from Ward's Natural Science Establishment indicated some promise when tested. However, a fabricated magnetite electrode, made by compressing magnetite powder mixed with Carbowax #1500 as a binder in a mold to 16000 psig in a Carver press and then carefully firing the sample to a maximum temperature of 1300°C., proved to be a poor conductor. Thus, a cell using this magnetite as anode passed only low current.

After a considerable search for a source of fabricated magnetite anodes, they were finally obtained from the Carborundum Company. These fused magnetite anodes showed good conductivity and when used in the perchlorate cell showed only slight erosion after 22 hours. However, only a very small [illegible] a current efficiency of only 5%.

Thus, it appears that fabricated magnetite anodes are very inefficient in the production of sodium perchlorate. The reason for this is not clear. Perhaps iron dissolved from the anode has an adverse catalytic effect upon the electrode reactions. Time did not permit elucidation of this observation.

Lead Dioxide

Background

In 1923, Howard (53) stated that lead dioxide anodes are decomposed very quickly under the conditions prevailing in the chlorate-perchlorate cell. However, Angel and Mellquist (4),

TABLE VIII

MAGNETITE SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq. cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Natural Magnetite	4		13-15	40-50	Erodes slightly	Some reddish-brown precipitate in electrolyte
Sintered magnetite (formed in Carver Press and fired at a maximum temperature of 1300°C.					Only low current through cell	
Fabricated magnetite (Carborundum Company)	3.1	200	5.8-6.7	18	Erodes slightly	Some reddish-brown ppt. in electrolyte after 22 hours. Very small amount of perchlorate formed.

Kato and Koizumi (67), Kitahara and Ohauga, (70) and Sugino and Yamashita (134) have reported the use of lead dioxide anodes in a laboratory sodium perchlorate cell. Lead dioxide anodes described in the literature have been made by: packing lead dioxide into an earthenware sheath provided with holes (179), packing lead dioxide in a canvas sack (175), compressing and heating a mixture of lead dioxide with manganese nitrate or manganese nitrate and manganese dioxide (181), by electrolyzing sulfuric acid between lead electrodes (136), and by the electrodeposition of lead dioxide from lead salt solutions (4), (192), (153), (177), (154), (193), (67), (162), (131), (70), (68).

Experimental Observations

For this work the electrodeposition method of preparing lead dioxide anodes was chosen as offering the best opportunities for success. The following paragraphs describe the work involved in testing and developing a suitable lead salt bath that would give lead dioxide plate of desirable characteristics for an anode in the sodium perchlorate cell.

The equipment used for the anodic electroplating of lead dioxide consisted of a cell and a low voltage direct current power source. Beakers were used as cell bodies to hold the electrolyte, and were heated, when necessary, on an electric hot plate. For electroplates #1 to #20, (see Table X, page 22) the cell consisted of a 600 ml. beaker with double cathodes of platinum plated tantalum placed opposite each other at the wall of the beaker. The anode, usually a 1 1/2" x 4" sheet of metal was suspended centrally in the beaker between the two cathodes. When metal rods, 1/2" in diameter and 9" long, were to be plated, as in electroplates #21 to #26, the cell body was a three liter beaker and the cathode a sheet of thin flexible steel coiled to cover the entire inside circumference of the beaker. A circular piece of the same metal with suitable current leads was used as a botton plate inside the beaker. A plexiglass lid served as support for the centrally suspended anode rod and thermometer, and to decrease solution evaporation when operating above room temperature for long periods. The power source was an autotransformer-rectifier combination.

A number of lead salt baths were tried to determine the best composition to give a good lead dioxide plate. These bath compositions are summarized in Table IX, page 21, and the conditions under which the lead dioxide electroplates were made are outlined in Table X, page 22.

It was found in some experiments of a preliminary nature that a satisfactory lead dioxide plate could not be secured from an acid lead plating bath based on lead nitrate

TABLE IX

COMPOSITION OF BATHS USED IN ANODIC ELECTROPLATING OF LEAD DIOXIDE

Bath #1 - 200 grams lead nitrate, $Pb(NO_3)_2$.
45 grams aluminum nitrate, $Al(NO_3)_3 \cdot 9\ H_2O$.
Water to make 1 liter of solution.
2-3 ml. nitric acid to lower pH to 3.

Bath #2 - 200 grams lead nitrate, $Pb(NO_3)_2$.
Water to make 1 liter of solution.

Bath #3 - 300 grams lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$
95 grams sodium hydroxide, NaOH
Water to make 1 liter of solution.

Note: Dissolve the chemicals individually in water and mix. Various precipitates are formed during mixing. Final mix contains one-third solids. Filter for use.

Bath #4 - Add 5 grams of gelatine powder to 1 liter of Bath #3 composition and filter.

Bath #5 - 300 grams lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$
Water to make 1 liter of solution.
5 grams gelatine. Filter solution.

Bath #6 - 250 grams lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$
200 grams sodium acetate, $NaC_2H_3O_2$.
Water to make 1 liter of solution.
2.9 grams gelatine powder. Filter solution.

Bath #7 - Composition of example #2 in U. S. patent 1,595,675 (Aug. 10, 1926)

In 1 liter of water, dissolve:

50 grams sodium potassium tartrate, $NaKC_4H_4O_6 \cdot 4\ H_2O$
10 grams sodium hydroxide, NaOH
50 grams lead oxide, PbO

Note: Solution takes place best at about 60°C., but even then only 46 grams of the PbO dissolves. Filter solution when cooled below 40°C. On standing at room temperature several hours, the solution contains a heavy white flocculent precipitate of a lead salt. This precipitate dissolves on reheating the solution above 45°C.

Bath #7M - In 1 liter of water, dissolve:

50 grams of sodium potassium tartrate, $NaKC_4H_4O_6 \cdot 4\ H_2O$
25 grams sodium hydroxide, NaOH
48 grams lead oxide, PbO

Note: Dissolve at 40°-60°C; filter after cooling to below 40°C. Solution remains clear and no precipitate forms on standing at room temperature.

TABLE X

ANODIC ELECTROPLATING OF LEAD DIOXIDE

Electro-plate No.	Bath* No.	Anode Base Metal	Current Density $Amps/Ft^2$	Bath Temp. °C.	Plating Period Hours	Description of Electroplated Lead Dioxide Surface
1	1	steel, sheet	20	26	1	Brittle, poor adherence to steel, and poor coverage on edges.
2	1	steel, sheet	20	85	0.5	No lead dioxide on anode; pH of bath dropped to below 2; bath is opaque and a reddish brown color.
3	2	steel, sheet	20	26	0.7	Brittle, poor adherence; bath pH is below 2, initial pH = 4.
4	2	steel, sheet	20	85	0.6	No lead dioxide on anode; bath pH is below 2.
5	3	steel, sheet	20	67	0.4	Black, smudgy, poor adherence.
6	3	lead, sheet	35	67	0.4	Black, smudgy, poor adherence.
7	4	lead, sheet	35	67	0.5	As for #6, except somewhat finer grained.
8	4	lead, sheet	7	67	0.8	No lead dioxide on anode, except along edges.
9	4	steel, sheet	12	28	0.7	Blisters and crumbles on drying.
10	4	steel, sheet	12	50	0.6	As for #9; pH of bath drops from 6 to 4.
11	5	steel, sheet	15	28	0.7	Blistered into small fragments, poor adherence to steel.

TABLE X (CONT'D)

ANODIC ELECTROPLATING OF LEAD DIOXIDE

Electro-plate No.	Bath* No.	Anode Base Metal	Current Density Amps/Ft^2	Bath Temp. °C.	Plating Period Hours	Description of Electroplated Lead Dioxide Surface
12	6	nickel, sheet	15	28	0.6	Fairly adherent, but dull and rough; some dendrites on edges.
13	6	nickel, sheet	7.5	28	1	Semi-lustrous, fairly smooth, fair to good adherence; several nickel spots exposed by breaking off of dendrites on one edge
14	6	nickel, sheet	0.8	28	5	Bright, adherent, but brittle; 8 to 10 spots of pin-head size not covered.
15	6	tantalum, sheet	0.9	28	5	Lustrous deposit scattered over 40% of surface on one side and 20% on the other side.
16	6	platinum plated over tantalum	0.9	28	1.4	Lustrous, continuous deposit.
17	7	nickel, sheet	0.54	30	1.7	Smooth, adherent deposit; a heavy white floc formed in bath.
18	7	nickel, sheet	0.6	50	0.3	Somewhat dull, but adherent deposit.
19-1	7M	platinum plated over tantalum	0.69	28	5	Discontinuity over 5% of surface; remainder smooth and adherent.
19-2	7M	steel, sheet	0.69	28	5	Smooth, dull, and adherent.
19-3	7M	nickel, sheet	0.69	28	5	Smooth, dull, adherent.
20-1	7M	platinum plated over tantalum	0.69	54	5	Smooth, semi-lustrous, adherent.

TABLE X (CONT'D)

ANODIC ELECTROPLATING OF LEAD DIOXIDE

Electro-plate No.	Bath* No.	Anode Base Metal	Current Density Amps/Ft^2	Bath Temp. °C.	Plating Period Hours	Description of Electroplated Lead Dioxide Surface
20-2	7M	Steel, sheet	0.69	54	5	Smooth, bright, and lustrous, adherent
20-3	7M	nickel, sheet	0.69	54	5	Smooth, semi-lustrous, adherent
21	7M	steel, rod	0.67	51	41.5	Smooth, lustrous, adherent
22	7M	steel, rod	0.73	51	75	Smooth, lustrous, adherent
23	7M	Monel, rod	0.57	56	96	Smooth, lustrous, adherent; smaller grain size than when on steel.
24	7M	nickel, tube (Crimped at lower end)	0.58	60	96	Smooth, lustrous, adherent
25	7	Monel, rod	0.57	53	66	Rough, dull, but adherent
26	7M	gold plated over Monel rod	0.50	54	94	Developed very unevenly in multiple layers due to a yellow smut formation of surface during electroplating. Smut probably caused by acetone adsorbed into gold surface in precleaning treatment.

*See Table IX for composition of electroplating baths.

nor from an alkaline bath based on lead acetate. Such a strikingly superior lead dioxide plate was easily produced in a bath containing lead tartrate that further development work on the nitrate and acetate baths was dropped. The composition of the first lead tartrate plating bath (#7), as taken from the patent literature, was improved (bath #7M) to provide stability at room temperature and a more lustrous deposit on plated objects.

Lead dioxide platings on monel and nickel were found to be of somewhat smaller grain size and superior in luster to those on steel. One anode was prepared by flash plating a monel rod with copper, then with gold to a thickness of 0.001 inch and finally with lead dioxide using bath composition #7M. Due to faulty precleaning of the gold surface, the lead dioxide coating failed prematurely. It is felt that the use of relatively inert platings such as copper, silver or gold over Monel or nickel before the lead dioxide plating was not sufficiently evaluated in this work to permit any definite conclusions as to their value.

After the lead dioxide anode samples had been prepared by electrodeposition as described in the preceeding paragraphs, they were tested in the small sodium perchlorate cell. These trials are summarized in Table XI, page 26.

It was found that a lead salt bath solution of formula #7 and 7M (Table IX, page 21) gave the best erosion-resistant lead dioxide plate when Monel or nickel rod was used as the base material. Steel did not appear to be a satisfactory base material. As a result of these preliminary tests, larger lead dioxide electrodes were prepared for testing in the 10 ampere cell.

Manganese Dioxide

Background

The preparation of manganese dioxide anodes has been described in the literature (179, 182, 187) but there is no indication that they have been successfully used for perchlorate formation. In fact, Howard (53) states that manganese dioxide is decomposed very quickly under the conditions prevailing in the perchlorate cell.

Experimental Observations

Managanese dioxide anodes were prepared in the following manner. Nine (9) parts by weight of manganese nitrate solution (approximately 80%) was mixed with 70 parts by weight of manganese dioxide to make a slightly damp mixture. This

TABLE XI

LEAD DIOXIDE SCREENING TESTS

Description of Anode Material	Electro-plate No. from Table X	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Lead dioxide plated on lead	6	4		7-9	30-40	Disintegrates (after 17 minutes)	
Lead dioxide plated on nickel	12	4		9-10	30-40	Disintegrates (PbO_2)	Pinholes in plate after 10 minutes
Lead dioxide plated on nickel	14	1		5	28	Erodes appreciably (PbO_2)	Pinholes in plate after 30 minutes
Lead dioxide plated on tantalum	15					Polarizes as PbO_2 plate dropped off	Polarization occurred over a period of 5 minutes
Lead dioxide plated on platinum on tantalum	16	1		5.3	24-27	Erodes appreciably (PbO_2)	PbO_2 rapidly dropping off after 7 minutes
Lead dioxide plated on nickel	17	2	200	6.6-7.2	16-20	Erodes appreciably	Pinholes in plate after 40 minutes
Lead dioxide plated on nickel	18	2	200	6.4-8.2	14-21	Erodes slightly. No pinholes after 3 hours	No dichromate used.
Lead dioxide plated on platinum on tantalum	20-1	3	200	5.7	16-25	Erodes slightly	No pinholes after 2 hours

TABLE XI (CONT'D)

LEAD DIOXIDE SCREENING TESTS

Description of Anode Material	Electro-plate No. from Table X	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Lead dioxide plated on steel	20-2	3	200	5.9-6.4	18-24	Erodes appreciably.	Pinholes after 2 hours.
Lead dioxide plated on nickel	20-3	3	200	5	16-17	Erodes slightly.	No pinholes after 1 1/4 hours.
Lead dioxide on monel rod	25	0.4-0.9	30	greater than 30 V	16-20	Erodes appreciably. Pinholes after 7 hours.	No dichromate used.
Lead dioxide on cold on copper on monel rod	26	5	175	4.5-6.2	16-26	Erodes appreciably. Pinholes after 30 minutes.	No dichromate used.

mixture was then pressed in a mold to 16000 psig using the Carver press. The pressed cake was then carefully heated to a maximum temperature of about 300°C., thus converting manganese nitrate into manganese dioxide. With the first sample, good electrical contact was not obtained with the cylindrical manganese dioxide anode. With the second sample, a strip of tantalum was imbedded in the manganese dioxide anode as a current lead. This anode slowly polarized, with some erosion and finally fracture of the anode sample.

A sample of pyrolusite, MnO_2 + 2% H_2O, obtained from Ward's Natural Science Establishment, was tried as anode in the sodium perchlorate cell. In this trial good electrical contact with the mineral pyrolusite was not obtained, but in intermittent operation the change in color of the electrolyte indicated erosion of the sample.

Manganese dioxide anodes, therefore, do not look sufficiently promising to warrant further study as anodes in the sodium perchlorate cell.

Ilmenite

A U. S. Patent (166) proposes using ilmenite ($FeO \cdot TiO_2$) as a substitute for platinum or graphite. Another U. S. Patent (167) claims electrodes made of a magnetite-ilmenite mixture.

A preliminary trial was run using ilmenite mineral obtained from Ward's Natural Science Estaglishment. Current was passed through the cell for three hours at 1-2 amperes at 13-16 volts. There seemed to be no serious erosion of the ilmenite anode sample and only a slight amount of reddish-brown precipitate was formed in the electrolyte.

Further study should be made to ascertain whether perchlorate is formed when ilmenite is used as the anode material.

(7) Oxide and Sulfide Coatings on Various Base Substances

Background

Fedotiev (35) reported the production of insoluble iron oxide electrodes by partially oxidizing 1 cm. diameter rods of commercial (not electrolytic) iron. Best results were obtained with air and steam at 1000-1100°C., under which conditions a smooth continuous surface was obtained. However, Kameyama and Naka found that they could not produce firmly adhering Fe_2O_3 coatings on iron rods in an atmosphere of oxygen (66) or by heating iron plates in contact with MnO_2 or MnO_2-SiO_2 mixtures (65).

TABLE XII

MANGANESE DIOXIDE SCREENING TESTS

Description of Anode Material	Average Dc Current (amperes)	Anode Current Density (approx.) ma./sq. cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Manganese Dioxide (pressed and heated to 300°C.)	Unble to obtain good electrical contact with sample.					
Manganese Dioxide (pressed and heated to 300°C. with strip of tantalum imbedded in one end as a current lead)	10	80	29.5	18-20	Erodes appreciably and polarizes	
Pyrolusite (Ward's Natural Science Establishment)	[illegible]		13	17	Unable to obtain good electrical contact with sample. Intermittent operation with electrolyte turning green.	

Experimental Observations

Along similar lines, iron oxide coatings on steel were formed (a) by heating a steel rod in an air-steam mixture at 900°C., (b) by heating in a gas-oxygen flame, (c) by allowing stainless steel plate to stand in 30% hydrogen peroxide at 38°C. for three months, (d) by heating steel for three hours in an electric furnace at dull red heat and (e) by dipping a steel rod in molten sodium hydroxide.* All these iron oxide coatings failed in the sodium perchlorate cell.

Oxide coatings on nickel and on Duriron, formed by heating for four hours at dull red heat in an electric furnace, eroded appreciably when used as anodes in the sodium perchlorate cell.

Sulfide coatings on copper, steel and Duriron, formed by immersing these materials in molten sulfur, also eroded appreciably.

This, it appears that the specific oxide or sulfide coatings studied are valueless in the chlorate-perchlorate cell.

(8) Metal Borides

Background

No literature reference was found to suggest the use of a metal boride as an insoluble anode. However, these materials have been readily available only within the past few years.

Experimental Observations

Two metal borides, chromium boride and titanium boride were obtained from the Battelle Memorial Institute. When these materials were tested in a sodium perchlorate cell they showed an excessive weight loss, visual evidence of anode erosion and a change in color of the sodium chlorate electrolyte.

Thus, chromium boride and titanium boride were unsatisfactory anode materials in the sodium perchlorate cell.

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*The 1/2" steel rod was soaked in an aqueous alkaline solution to remove grease, pickled in 10% sulfuric acid at 80°C. for 3 to 4 minutes, and finally dried. The clean steel rod was then dipped into molten caustic at 400°-500°C. for 1/2 hour. On removal from the caustic, and after rinsing and drying, the treated steel was coated with a smooth brown deposit.

Possible future work would be to treat the steel with molten caustic at higher temperatures, for instance 800°-1000°C., and for longer periods, since this was the best of the oxide coatings tested. There might also be considered the addition of various oxidizing agents to the caustic to enhance the formation of a denser and heavior oxide coatings on the steel.

TABLE XLII

OXIDE AND SULFIDE COATINGS SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.)	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
Iron Oxide coating on steel formed by air and steam at 900°C.	4	–	–	30-40	Erodes appreciably
Iron oxide coating on steel formed by heating in gas-oxygen flame	4	–	–	30-40	Erodes appreciably
Oxide coating on #304 stainless steel formed by 30% hydrogen peroxide at 38°C. for about 3 months	1	–	–	20-30	Erodes appreciably
Oxide coating on steel formed by gas-oxygen torch	4		8.5	30-40	Erodes appreciably
Oxide coating on steel formed by molten NaOH	4		8.0	30-40	Of oxide coatings tested, formed least amount of reddish-brown ppt. in electrolyte.
Oxide coating on steel formed by heating 3 hours - dull red heat in electric furnace.	4	–	9.2	30-45	Erodes appreciably
Original oxide coating on steel rod	[illegible]		[illegible]-5.0	25-35	Erodes appreciably
Oxide coating on nickel formed by heating 4 hours at dull red heat in electric furnace	4		9.5-10	30-40	Erodes appreciably

TABLE XIII (CONT'D)

OXIDE AND SULFIDE COATINGS SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.)	Average Cell Voltage	Cell Temp. °C.	Result (Anode)
Oxide coating on Duriron formed by heating 4 hours at bright red heat in electric furnace	2	-	5.6-6.2	30-45	Erodes appreciably
Sulfide coating on copper rod formed by immersing in molten sulfur for 30 minutes	4	-	10	30	Disintegrates
Sulfide coating on steel rod formed by immersing in molten sulfur for 30 minutes	4		7.6	30-45	Erodes appreciably
Sulfide coating on Duriron formed by immersing in molten sulfur for 15 minutes.	4	-	-	30-40	Erodes appreciably

TABLE XIV

METAL BORIDES SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq. cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Chromium boride (Battelle Memorial Institute)	3	200	6.7-7.0	3-7	Erodes appreciably	No dichromate used
Titanium Boride (Battelle Memorial Institute)	3	200	10-11.5	0-15	Erodes appreciably	No dichromate used

(9) Metal Carbides

Background

In the class of metal carbides, only silicon carbide has been mentioned as an "insoluble" anode. Russian Patent 69,700 (163) claims the use of silicon carbide or "silicided graphite" electrodes in place of platinum for the electrolytic production of perchlorates and persulfates. However, many metal carbides are now available, and an experimental study was made of those which could be readily obtained.

Experimental Observations

Three different samples of boron carbide were tested as anode materials; one from Battelle Memorial Institute, one from the Norton Company and one whose source was unknown. All samples showed excessive weight losses, with erosion that turned the electrolyte black.

Twelve different samples of metal carbide compositions were secured from the Carboloy Department of the General Electric Company. Samples #1 to #5 were standard, readily available production items. The remaining samples were of an experimental nature. Upon testing these materials, only samples #11 and #12 showed sufficiently small erosion losses to warrant further study. Sample #11 was disclosed by the Carboloy people to be chromium carbide with 12% platinum by volume as a binder. Sample #12 was tantalum carbide also with 12% platinum by volume as a binder. Larger samples of these two materials were obtained and tested. The chromium carbide eroded at a rate of 0.3 grams per ampere-hour, which is too high, while the tantalum carbide showed an anode erosion rate of 0.008 grams per ampere-hour.

Pure silicon carbide samples (Fisher Scientific Company and General Abrasive Company, Inc.) polarized as was the case with Globar heating element sections (SiC) (see Globar Rod Material, Section B. 2. (b) (4), page 12).

Similarly, the pure tantalum carbide samples (Battelle Memorial Institute and U. S. Bureau of Mines) polarized.

All the various titanium carbide compositions were attacked too rapidly to be of use.

A sample of tungsten-titanium carbide (85% WC, 15% TiC) from the U. S. Bureau of Mines eroded too rapidly, while samples of tungsten carbide with various percentages of cobalt added as a binder (Adamas Carbide Corporation) polarized after 6-12 minutes of electrolysis.

Zirconium carbide secured from the U. S. Bureau of Mines showed a high anode erosion loss.

Of all the different metallic carbides tested, only chromium carbide and tantalum carbide, both with 12% platinum by volume added as a binder (Samples #11 and #12, respectively, Carboloy Dept.), showed sufficiently small erosion losses to warrant further study in the 10 ampere cell.

(10) Metal Nitrides

Background

The use of metal nitrides as insoluble anodes was not suggested by the literature. However, it was throught advisable to test those which became available in the requisitioning of anode materials.

Experimental Observations

The two anode materials tested in this class, titanium nitride and zirconium nitride, both obtained from the Battelle Memorial Institute, did not indicate that metal nitrides would be promising as anode materials in the sodium perchlorate cell. Both titanium nitride and zirconium nitride showed an excessive weight loss with the formation of a precipitate in the sodium chlorate electrolyte.

(11) Miscellaneous Undesignated Materials

These samples are grouped here since their chemical composition was not definitely disclosed by the manufacturer. However, they are chiefly metallic carbides with various percentages of cobalt added as a binder.

All the undesignated samples supplied by the Haynes Stellite Division of Union Carbide and Carbon Corporation and by the Vascoloy-Ramet Corporation proved to be unsatisfactory as anodes in the subject process.

3. Extended Evaluation of Screened Materials

(a) Description of 10 Ampere Cell and Its Operation with Platinum Anode

In order to become more familiar with the operation of the perchlorate cell and to provide a basis of comparison for the other anode materials tested, two 10-ampere cells of simple design (Figure 1) were made and equipped with platinum-plated tantalum anodes. The effective area of the anodes was varied to give a current density of 100 ma./sq. cm. in one cell and 300 ma./sq. cm. in the other cell. Using an electrolyte composition of 600 g./l. $NaClO_3$ and 4 g./l. $Na_2Cr_2O_7 \cdot 2H_2O$, these

TABLE XV

METAL CARBIDES SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Boron Carbide (unknown source)	4		6-11	25-55	Erodes appreciably	Electrolyte turns black
Boron Carbide (Battelle)	3	200	10-12.5	5-20	Erodes appreciably	No dichromate used
Boron Carbide (Norton Co)	1	200	10-12	18	Erodes appreciably	
Metal Carbide Compositions (Carboloy Department of the General Electric Company)						
Sample #1	0.4	200	3-28	15-20	Erodes appreciably and polarizes	
Sample #2	0.4	200	3-26	16-18	Erodes appreciably and polarizes	
Sample #3	0.4	200	3.5	15-18	Erodes appreciably	
Sample #4	0.4	200	4-5	16-18	Erodes appreciably	
Sample #5	0.4	200	3.3	15-17	Erodes appreciably	
Sample #6	0.4	200	5-12	15-20	Erodes appreciably	
Sample #7	0.4	200	4.0-4.7	16-17	Erodes appreciably	
Sample #8	0.4	200	3.5	16-17	Erodes appreciably	
Sample #9	0.4	200	3.3	17-18	Erodes appreciably	
Sample #10	0.4	200	3.3	15-16	Erodes appreciably	

TABLE XV (CONT'D)

METAL CARBIDES SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Sample #11 - Chromium Carbide with 12% by volume Platinum as a binder	4.0	200	4.7	19	Erodes slightly	
Sample #12 - Tantalum Carbide with 12% by volume Platinum as a Binder	0.2	200	4.3	16-18	Erodes slightly	
Silicon carbide crystal (Fisher Scientific Co.)	No current would pass through cell				Polarizes	
Silicon carbide (General Abrasive Company, Inc.)	0.1-0.2	Not convenient to measure area	22 to greater than 30	15-18	Polarizes	
Tantalum Carbide (Battelle Memorial Institute)	0.2-3	200 at start	9-21	10-30	Polarizes	No dichromate used
Tantalum Carbide (U.S. Bureau of Mines)	1.8	200	6.4-13.0	20	Slowly polarizing	
Titanium Carbide (Battelle Memorial Institute)	2	200	6.6-7	18-29	Erodes appreciably	No dichromate used

TABLE XV (CONT'D)

METAL CARBIDES SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Titanium Carbide (U.S. Bureau of Mines)	1.2	200	4.9-5.2	18-22	Erodes appreciably	
Titanium carbide plus 20% nickel (Kennametal, Inc.)	2	200	4.2-4.7	19-22	Erodes appreciably	
Titanium carbide plus 30% Nickel (Kennametal, Inc.)	2	200	4.1-4.4	19-22	Erodes appreciably	
Sintered titanium carbide (Titanium Alloy Mfg. Div., National Lead Co.)	4	200	5.4-5.8	18-20	Erodes appreciably	
Tungsten-Titanium Carbide (85% WC, 15% TiC) (U.S. Bureau of Mines)	1.55	200	4.5	16-18	Erodes appreciably	
Tungsten carbide with various percentages of cobalt added as a binder (3 samples obtained from Adamas Carbide Corp.)	0.1-2	200 at start	4-30	16-19	All samples polarized	
Zirconium Carbide (U.S. Bureau of Mines)	1.2	200	4.2	17-19	Erodes appreciably	

TABLE XVI

METAL NITRIDES SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq. cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Titanium nitride (Battelle Memorial Institute)	2	200	8-12	12-22	Erodes appreciably	No dichromate used
Zirconium nitride (Battelle Memorial Institute)	3	200	6.3-6.6	13-27	Erodes appreciably	No dichromate used

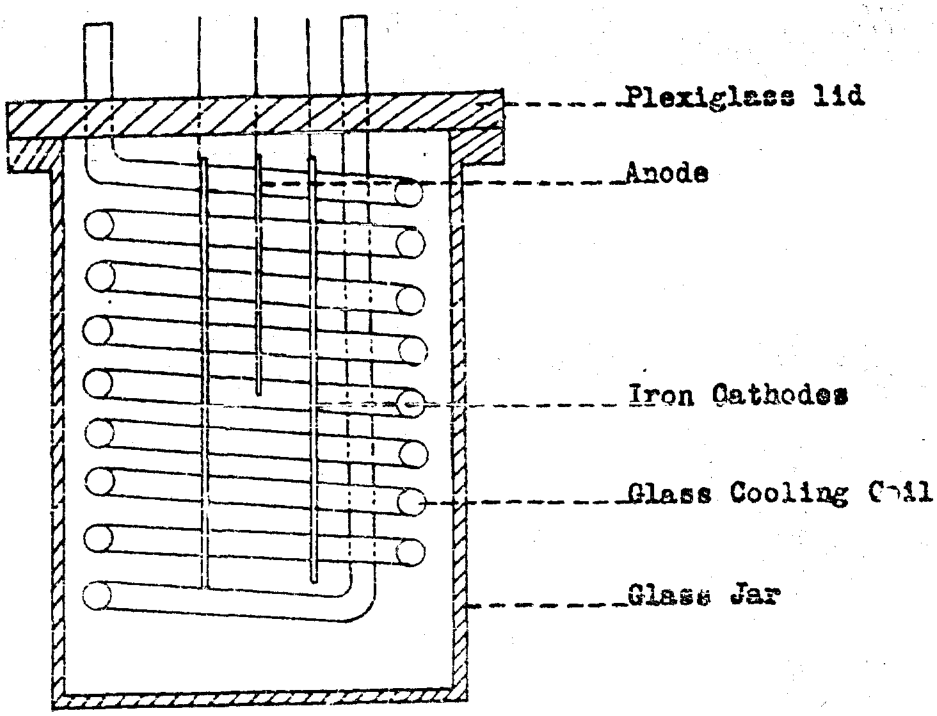
TABLE XVII

MISCELLANEOUS UNDESIGNATED MATERIALS SCREENING TESTS

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Result (Anode)	Remarks
Metanic LT-1 (Haynes Stellite Division, Union Carbide & Carbon Corp.)	2	200	3.8	17	Erodes appreciably	
Sample A.W. (Vascoloy-Ramet Corporation)	0.5	200	3.3-26	17	Erodes appreciably and polarizes	
Sample ZA 68 (Vascoloy-Ramet Corporation)	1	200	4.7-30	16	Polarizes	
Samples from Haynes Stellite Division						
Sample 4145-531-3T	2	200	10	17	Erodes appreciably	
Sample 4145-531-12T	2	200	4	17	Erodes appreciably	
Sample 4145-531-20T	2	200	4-6	19	Erodes appreciably	
Sample 4145-531-32	2	200	4.1	16	Erodes appreciably	

FIGURE 1

TEN AMPERE PERCHLORATE CELL



cells were operated for a period of about 43 hours, at a temperature of 10°-15°C., to give a final electrolyte composition in the low anode current density cell of 293 g./l. $NaClO_3$ and 380 g./l. $NaClO_4$, and in the high anode current density cell of 215 g./l. $NaClO_3$ and 466 g./l. $NaClO_4$. The current efficiency in the low anode current density cell was about 67%; in the high current density cell, about 80%. This confirms the reported observation that high anode current density is necessary for the efficient production of perchlorates.

This experiment also indicated that platinum-plated tantalum anodes could be used in place of pure platinum anodes in the perchlorate cell.

(b) Use of 10 Ampere Cell in Evaluation of Screened Anode Materials

Anode materials which appeared promising in the screening tests were re-examined in the larger 10 ampere cell for longer periods of time than were used in the screening tests.

Lead dioxide plate on mild steel rod, Monel rod and nickel tubing all failed after a relatively short period of operation apparently because of the presence of minute discontinuities or pinholes in the lead dioxide plate. Where such pinholes appeared, the base material (steel, monel or nickel) would be rapidly attacked. Figure 2 shows the result of such attack on lead dioxide plated on monel rod; the third anode has not been used.

Globar Durhy #1 sections from the Carborundum Company polarized whereas Globar Durhy #2 (SiC-Si mixture) operated with the production of perchlorates. There was surface disintegration of the Globar Durhy #2 especially at the top level of the electrolyte. Figure 3 shows Globar Durhy #2 sections before and after use in the sodium perchlorate cell.

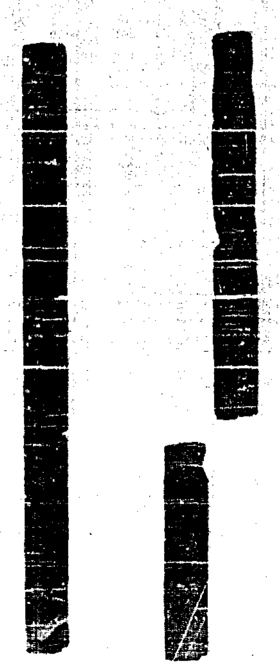
In the case of the lead dioxide anodes, the type of failure described above is not uncommon for electrolytically plated electrodes, and no doubt improvement could be worked out by a more detailed study. Improvements might be achieved by preparation of the base metal, by changes in the method of deposition of the plate, or some treatment of the anode after plating such as buffing. Future work should also establish the best condition of carrying out the electrolysis of sodium chlorate using lead dioxide anodes.

Further work with the Durhy #2 material would involve trials with a more dense type of silicon-silicon carbide, one impregnated with magnetite, or one plated with lead dioxide. Combinations of silicon carbide and carbon as suggested in the Russian Patent (163) should also be considered.

FIGURE 2

Anodic Attack on Lead Dioxide Plated on
Monel Rod

FIGURE 3



Globar Durhy #2 Section Before and After
Use as Anode in the Sodium Perchlorate Cell

Further tests in the 10 ampere cell should include ilmenite ($FeO \cdot TiO_2$), Carboloy Sample #11 (chromium carbide + 12% Pt) and Carboloy sample #12 (tantalum carbide + 12% Pt). These materials appeared promising in the screening tests, but samples of the size necessary for use in the 10 ampere cell could not be obtained in the period allotted for the experimental study.

C. Thermal Decomposition of Chlorates to Perchlorates

Date on the optimum temperature for the thermal conversion of sodium chlorate to perchlorate are meager, with German Patent 300,713 (157) recommending 440° to 490°. The larger body of information on potassium chlorate contains numerous conflicting statements on the optimum conversion temperature and on the effect of additives. It would appear, however, that the maximum yield of potassium perchlorate is obtained at a somewhat higher temperature than is necessary for the sodium salt. It was therefore considered desirable to determine experimentally, to within about 10 degrees, the minimum temperatures at which satisfactory yields of sodium and potassium perchlorates could be obtained by the heating of the corresponding chlorates, and to study the effect of reactor composition on the course of the reaction using Pyrex, Vycor, and Quartz flasks. It was not considered within the scope of these preliminary experiments to determine the catalytic effect of various addition agents suggested in the literature.

In carrying out the experiments, the chlorate salt was placed in a 500 ml. round-bottomed flask having a long neck. A glass tube, sealed at the lower end and extending down the neck of the flask to about 1 1/2 inches above the surface of the chlorate salt, served as a thermocouple jacket. The bulb of the flask was placed in a pot furnace with an insulating cover set around the neck of the flask. The gases given off during the reaction were led by Tygon tubing into the top of a 3 liter bottle filled with water. The water displaced from the bottle was forced out a bottom opening into a 1 liter burette connected to the bottle by tubing. The collected gases were maintained at atmospheric pressure by equalizing the liquid level in the burette with that in the bottle. Temperatures were measured by an iron-constantan thermocouple.

The normal procedure, in a typical run, was to place a chlorate sample in the flask which was then set into the cold furnace. The temperature of the pot furnace was rapidly raised to the desired level, control being maintained through an autotransformer. At the end of the heating period, the flask was removed from the furnace and allowed to cool to room temperature. The volume of oxygen evolved was then measured before the flask was opened and the solidified product removed for analysis. A summary of the results of these experiments is given in Table XIX, page 47..

Heating potassium chlorate in a quartz flask at 482°C. for three hours gave a product which analyzed 73.1% $KClO_4$. A higher temperature resulted in decreasing the perchlorate and increasing the chloride yield. Sodium chlorate under the same conditions gave a lower perchlorate and higher chloride yield indicating that the temperature may have been a little too high. However, heating at 456° for 20 minutes resulted in

TABLE XVIII

EVALUATION OF SCREENED MATERIALS USING 10 AMPERE CELL

Description of Anode Material	Average Cell Current (amperes)	Anode Current Density (approx.) ma./sq.cm.	Average Cell Voltage	Cell Temp. °C.	Results
PbO_2 plate on mild steel rod (75 hrs. plating time; Electroplate #22)	9.6-10	200	10-15	15-25	(No dichromate used) Cell ran 2 1/2 hrs. - Large number of pits in steel base rod, PbO_2 plate partially eroded away, large amount of reddish brown ppt. in electrolyte
Globar Durhy #2 Section (Si-SiC mixture) from the Carborundum Co.	5-10	200	7-30	12-25	Cell ran 8 hrs. Severe surface disintegration at top level of electrolyte. No change in color of electrolyte
PbO_2 plate on monel rod (Electroplate #23)	8-10	200	9.5-26	15-25	(No dichromate used) Cell ran 5 1/2 hrs. Anode severely pitted at top surface of electrolyte. Large amount of brownish-black precipitate in electrolyte.
Globar Durhy #1 Section from the Carborundum Company (4 samples)					All samples polarized after 2 minutes of operation.
PbO_2 plate on nickel tube (Electroplate #24)	5	100	14-21	8-11	Cell ran 2 hrs. Leak in tubular anode where tube was crimped together at top. Electrolyte leaking from cell through inside of tube to bottom of anode. Also electrolyte turned black.

TABLE XIX

THERMAL DECOMPOSITION OF CHLORATES TO PERCHLORATES

Batch No.	Compound Heated	Wt. of Compound Heated gms.	Reaction Flask	Ave. Max. Temp. °C.	Period at Ave. Max. Temp. Hours	Volume of Oxygen Evolved at 28°C.; ml.	Analysis of Furnace Product: XRD	Analysis of Furnace Product: Chemical
1	$NaClO_3$	5.0	Pyrex	482	3	1100	$NaCl$ $NaClO_3$ $NaClO_4 \cdot H_2O$	52.4% $NaCl$ 4.4% $NaClO_3$ 6.5% $NaClO_4$
2	$NaClO_3$	5.0	Quartz	480	2.7	820	$NaCl$ $NaClO_3$ (faint) $NaClO_4 \cdot H_2O$	40.0% $NaCl$ 5.3% $NaClO_3$ 51.1% $NaClO_4$
3	$NaClO_3$	5.0	Quartz	456	0.3 (furnace preheated)	70	$NaCl$ $NaClO_3$	
4	$NaClO_3$	5.0	Quarts	456	0.3	34	$NaCl$ $NaClO_3$	
5	$NaClO_3$	5.0	Quartz	480	0.3	165	$NaCl$ $NaClO_3$ $NaClO_4$	12.2% $NaCl$ 50.3% $NaClO_3$ 34.9% $NaClO_4$
6	$NaClO_4 \cdot H_2O$	6.6	Quartz	492	1.5	540		10.0% $NaCl$ 6.4% $NaClO_3$ 75.8% $NaClO_4$
7	$KClO_3$	5.0	Quartz	482	3	196	KCl $KClO_4$	19.5% KCl 6.6% $KClO_3$ 73.1% $KClO_4$
8	$KClO_3$	5.0	Quartz	512	3	710	KCl $KClO_4$	42.5% KCl 3.0% $KClO_3$ 52.7% $KClO_4$
9	$NaClO_3$	5.0	Vycor	481	2.3	1520	$NaCl$	86.5% $NaCl$ 2.4% $NaClO_3$ 6.8% $NaClO_4$

zero conversion to perchlorate. Therefore, it appears necessary to heat sodium perchlorate in the temperature range 460°-480°C. for one to three hours to obtain satisfactory yields of perchlorate together with minimum decomposition to chloride. The analyses for the sodium salts given in Table XIX give less than 100 percent analyzed ingredients due to the presence of water adsorbed by the very hygroscopic sodium chlorate and perchlorate.

It should be noted that the temperatures and heating periods given above may need adjustment according to the size of the chlorate charge.

Sodium chlorate heated in Pyrex and Vycor flasks gave poor yields of perchlorate compared to that obtained when it was heated in a quartz flask under approximately the same conditions.

Recent cost calculations showed a total manufacturing cost per pound of potassium perchlorate by the thermal decomposition method to be 17.1 cents per pound as compared to 13.8 cents per pound by the electrolytic method. Details of the cost estimates on the electrolytic and thermal method are given in Appendixes A and B, respectively, of this report on pages 68 and 72. Considering the high initial platinum investment and the operating loss of platinum in the electrolytic process, it becomes apparent that the thermal process is somewhat inefficient.

D. Chemical Oxidation of Chlorates

Background

Oxidizing agents that will convert chlorates to perchlorates are not well established in the literature. Lead dioxide has been reported to be a very effective oxidizing agent for making perchlorates (31, 113). Sodium persulfate was found by Bennett and Mack (9) to oxidize sodium chlorate in acid solution. Very small yields of perchlorate have been reported using ozone (9). Also, some oxidation of chlorate to perchlorate in acid solution was claimed using hydrogen peroxide (9). According to the literature reports, oxygen, potassium permanganate, sodium peroxide and chlorine will not oxidize chlorate in aqueous solution (126, 9, 135a).

Experimental Observations

A series of experiments was run to determine the time necessary to oxidize sodium chlorate to sodium perchlorate using lead dioxide and 50 weight-% sulfuric acid according to the following equation:

$$NaClO_3 + PbO_2 + H_2SO_4 \longrightarrow NaClO_4 + PbSO_4 + H_2O$$

In these experiments a 50% excess of lead dioxide (packaged product used) was mixed with sodium chlorate in an Erlenmeyer flask. A slight excess of 50 weight-% sulfuric acid was added to the dry mixture. The flasks were then heated on a steam bath (85°-95°C.) for varying periods of time. After heating, the slurries were filtered, washing the residue well with distilled water, and the combined filtrate and washings were analyzed for sodium chlorate content. The conversion to sodium perchlorate was then calculated, as exploratory experiments had shown that only sodium chlorate and sodium perchlorate were present in the filtrate.

The results are plotted in Figure 4 and it may be seen that about a 70% yield of sodium perchlorate may be obtained after 4-5 hours heating on the steam bath. Provision to insure more thorough mixing of the ingredients would probably improve the yield.

On the laboratory scale used in these tests, the reaction proceeded smoothly at 100°C. when 50 weight-% acid was used but became explosive when 65% sulfuric acid was used.

Based on this process for the production of potassium perchlorate, a preliminary cost estimate gives a manufacturing cost of 16.4 cents per pound. This figure does not include the cost of recovery of lead dioxide which may be a difficult process and which will increase the product cost several cents a pound. This total cost of 20 cents per pound or over is appreciably higher than the 13.8 cents per pound by the electrolytic method (see Appendix A, pages 68-71). Details of the cost estimate on the lead dioxide method are given in Appendix C, pages 75-78.

Preliminary tests were run to evaluate the oxidizing power of ozone on sodium chlorate. In the first experiment, a solution of 600 g./l. of sodium chlorate was mixed with an equal volume of 50 weight-% sulfuric acid. While still warm (30°C.), 250 ml. of this solution was placed in a gas washing bottle and ozone (O_3) from a Welsbach ozone generator was passed through the acidic sodium chlorate solution. All the gass passing through the acid chlorate solution was then passed through a 2% KI solution, which quantitatively absorbed all unreacted ozone. Tests on the KI solution indicated that all but about 10% of the ozone passed through the chlorate solution unchanged. Since the 10% ozone loss represents normal decomposition, it may be concluded that, in this experiment, ozone was a very inefficient oxidizing agent in changing chlorate to perchlorate. Chemical analysis of the chlorate solution also failed to show any perchlorate that would not have been formed by the strong acid.

In the second experiment, a similar test was made using a 600 g./l. sodium chlorate solution adjusted to a pH of 11 with sodium hydroxide. All but about 10% of the ozone passed through the chlorate solution unchanged, representing normal decomposition of the ozone. Here also, it appeared that ozone is a very inefficient agent in making perchlorate.

Since this work is preliminary, further work should be done to substantiate these results, and to try other methods of using ozone.

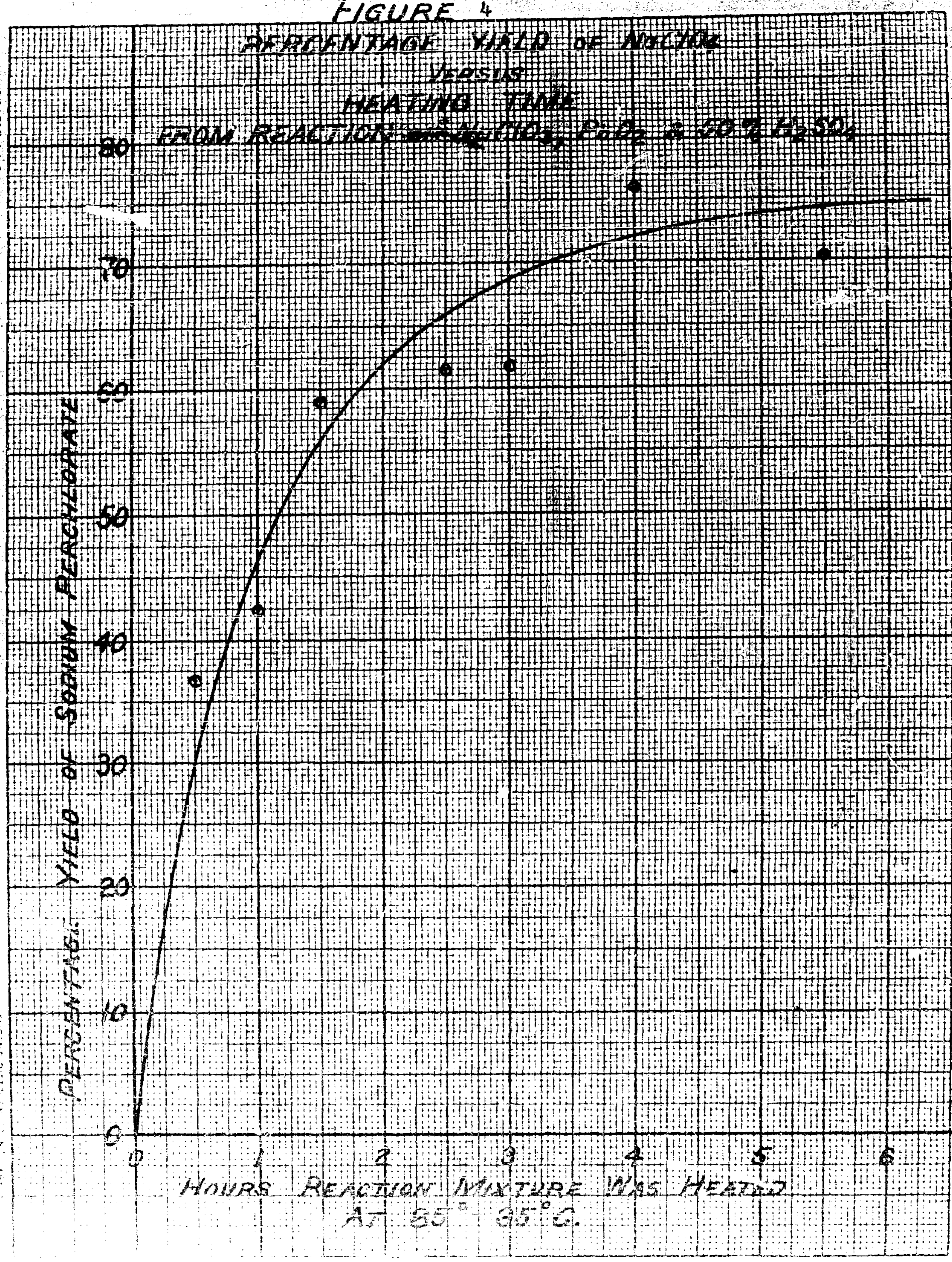


FIGURE 4
PERCENTAGE YIELD OF NaClO4
VERSUS
HEATING TIME
FROM REACTION NaClO3, PbO2 & 50 % H2SO4
PERCENTAGE YIELD OF SODIUM PERCHLORATE
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
HOURS REACTION MIXTURE WAS HEATED
AT 85° - 95° C.

E. Decomposition of Chlorates by Strong Acids

The decomposition of chlorates by strong acids has been known for many years. The reaction (M = metal, R = acid radical)

$$2\ HR + 3\ MClO_3 \longrightarrow MClO_4 + 2\ ClO_2 + 2MR + H_2O$$

is the basis for a patented process (200) for making perchlorates and chlorites of different metals. This process is of doubtful value because of the complex mixtures that must be separated, because of side reactions in which chlorine and chlorides are formed, and because of the large yield of chlorite necessarily associated with the production of perchlorate.

An adaptation of this process, which does not recover chlorite but returns all of the reduced chlorate to the chlorate cell to be reconverted may be practical.

The chlorine and chlorine dioxide can be separated from the reaction mixture safely and efficiently by blowing air through the mixture while the reaction is taking place. This dilute gas mixture, when absorbed in a caustic solution to form a solution of NaCl, NaClO, $NaClO_2$ and $NaClO_3$, can be added to a solution of sodium chloride to be used as the electrolyte of a chlorate cell. Such a cell would require less power to produce chlorate than one using sodium chloride only as the electrolyte (see Figure 5).

In a laboratory test, 15 gms. of sodium chlorate was mixed with excess sulfuric acid (50% by weight) and heated on a steam bath. After several hours the solution became colorless and was found to contain 7.8 gms. of sodium perchlorate with no chloride or chlorate. This was equivalent to 45% conversion of sodium chlorate to sodium perchlorate. Other laboratory tests showed that the chlorine and chlorine dioxide could be blown out of the solution by a vigorous stream of nitrogen.

F. Analytical Procedure for Perchlorate, Chlorate, and Chloride Mixtures

The lack of a proven method for the accurate determination of perchlorate ion, particularly in the presence of chlorides and chlorates, made the evaluation of the processes studied in this project difficult. A procedure for this determination was adapted from various literature sources and was proven to be rapid and accurate method in determining perchlorates, chlorates, and chlorides in the presence of each other.

The following table shows the accuracy of this procedure in determining these ions in known samples. (Table XX, page 53)

1. Procedure

a. Reagents

Standard silver nitrate solution 0.1 N
Standard potassium thiocyanate solution 0.1 N
Nitric acid, c.p., 6 N.
Nitrobenzene (purified)

FIGURE 5

VISUALIZED COMMERCIAL METHOD FOR THE PRODUCTION OF SODIUM PERCHLORATE BY ACID DECOMPOSITION OF SODIUM CHLORATE

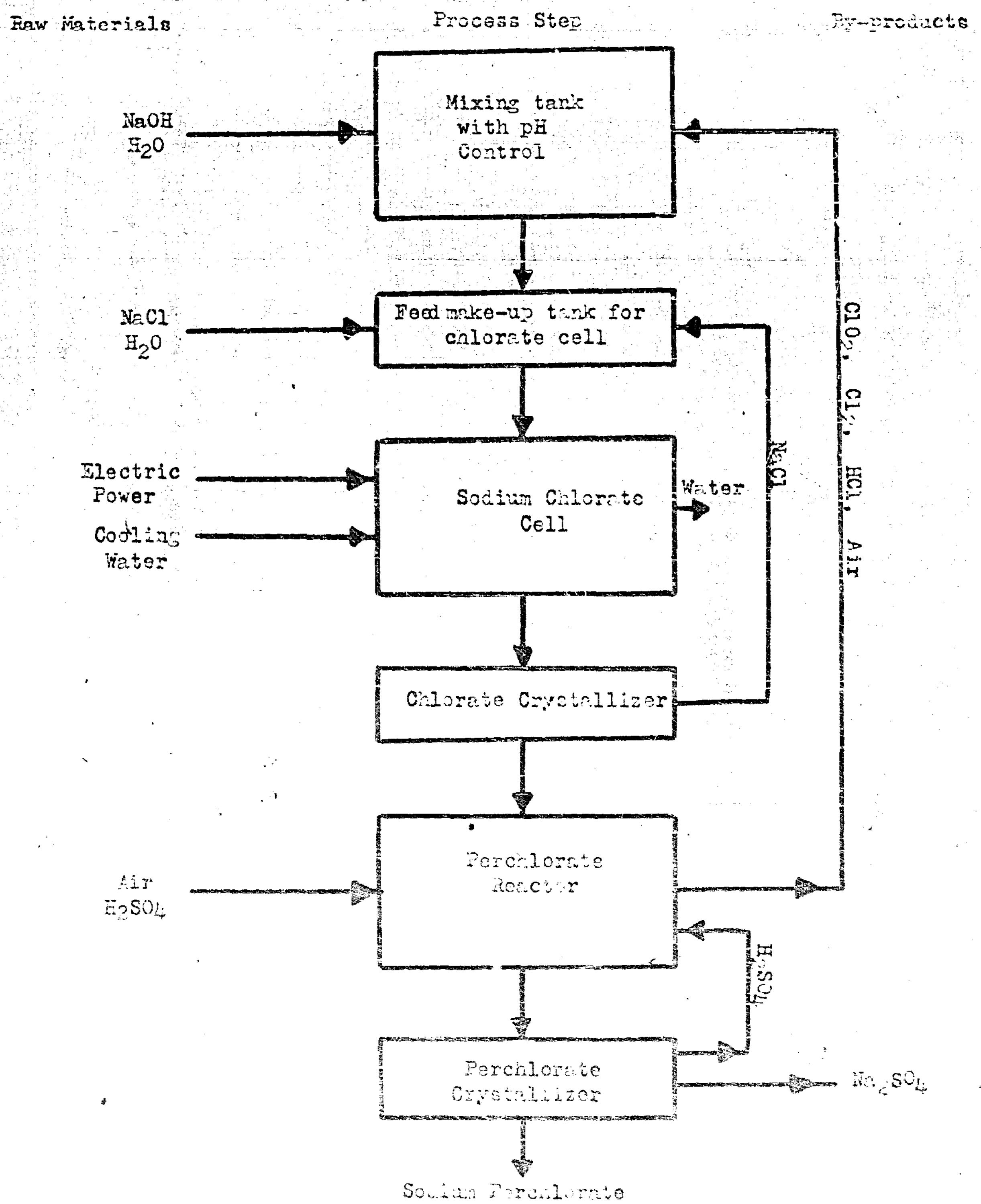


TABLE XX

PROOF OF THE ANALYTICAL PROCEDURE FOR THE DETERMINATION

OF PERCHLORATES, CHLORATES, AND CHLORIDES

Sample No.	Concentration of $NaClO_3$ made up gravimetrically grams per liter	Concentration of $NaClO_3$ found by Volumetric Analysis grams per liter	Concentration of $NaClO_4 \cdot H_2O$ made up gravimetrically grams per liter	Concentration of $NaClO_4 \cdot H_2O$ found by Volumetric Analysis grams per liter
I	600.0	602.8	0	-8
II	400.0	402.4	229.2	222.0
III	200.0	203.6	458.8	449.6
IV	100.0	105.6	573.2	588.4

Ferric alum indicator solution (saturated solution)
Crystalline ferrous sulfate, c.p.
Titanous sulfate solution, 20%
Sulfuric acid, dilute (1:1)

b. Preparation of the Sample

The samples are submitted as solutions produced by the electrolytic or the chemical process. As such, a reliable estimate of the chlorate and/or perchlorate content is possible for preparing the sample solution.

Measure out accurately a convenient volume of the sample containing not more than 5 grams of sodium chlorate and/or sodium perchlorate. Record the exact volume of sample taken ≡ S.

Transfer the sample quantitatively to a 500 ml. volumetric flask, dilute to the mark with water and mix thoroughly.

c. Determination of Chloride Content

Pipette 25 ml. of the filuted sample solution into a 500 ml. iodine flask. Add 150 ml. of water and 5 ml. of 6 N HNO_3.

Precipitate the chloride present by the slow addition of 0.1 N silver nitrate solution until a slight excess of the reagent is obtained. Record volume of $AgNO_3$ solution added ≡ A.

Add 2 ml. of ferric alum indicator and 2 ml. of nitrobenzene. Stopper flask and shake thoroughly for 1/2 minute.

Titrate excess $AgNO_3$ with the 0.1 N KCNS to a reddish-brown endpoint. Record volume of KCNS used ≡ B.

Calculation of chloride content. Neither the chlorate nor the perchlorate interfer with the direct determination of chloride by the Volhard procedure, the calculations are direct, thus

C = milliequivalents of chloride per 25 ml. of diluted sample =

$$(A \cdot N_{AgNO_3} - B \times N_{KCNS})$$

Expressed in terms of sodium chloride in the original sample,

$$\frac{C}{S} \times 1169 = \text{grams NaCl per liter}$$

d. Determination of the Chlorate Content

Measure approximately 150 ml. of water, 5 ml. of dilute H_2SO_4 (1:1) and 10 grams of ferrous sulfate (c.p.) into a 500 ml. iodine flask.

Pipette 25 ml. of the diluted sample solution into the iodine flask. Place on steam bath and heat for 1 hour.

Cool flask contents and precipitate the chloride by slow addition of 0.1 N silver nitrate until a slight excess is obtained. Record volume of $AgNO_3$ solution added ≡ D. Add 2 ml. of nitrobenzene and shake thoroughly for 1/2 minute.

Titrate the excess silver nitrate with 0.1 N KCNS to reddish brown endpoint. Record volume of KCNS used ≡ E.

Run blank determination on reagents simultaneously. Record volumes of $AgNO_3$ (≡ F) and KCNS (≡ G) used.

Calculations

The above procedure measures the chloride ion produced by the reduction of the chlorate as well as the chloride originally present. Hence, in calculating the equivalent of chloride due to chlorate a correction for the amount present originally as chloride (A) is made. In addition, a blank determination (for the chloride content of the reagents) is recommended. Hence for the 25 ml. of diluted sample taken; there results:

Milliequivalent of total chloride found = $(D \times N_{AgNO_3}) - (E \times N_{KCNS}) = H$

Milliequivalents of chloride in reagents = $(F \times N_{AgNO_3}) - (G \times N_{KCNS}) = J$

Milliequivalents of chloride originally present = A

Milliequivalents of chlorate found = $(H - (J + A.)) = K$

Expressed in terms of sodium chlorate in the original sample,

$$\frac{K}{S} \times 2129 = \text{grams } NaClO_3 \text{ per liter}$$

e. Determination of perchlorate content

Measure 25 ml. of water, 2 ml. of dilute H_2SO_4 (1:1), and 2 grams of ferrous sulfate (c.p.) into a 500 ml. iodine flask.

Pipette 25 ml. of the diluted sample solution into the iodine flask. Insert into opening of flask a short stem funnel to reduce vapor loss and place on steam bath for 1 hour.

Remove from bath and add immediately 20 ml. of the 20% titanous sulfate solution and 25 ml. of dilute sulfuric acid (1:1). Leave digest on hot plate without boiling for 1 1/2 hours.

Cool and add an excess of ferric alum solution to oxidize excess titanous sulfate. Precipitate the chlorides by slow addition of 0.1 N silver nitrate until a slight excess is obtained. Record volume of AgNO added ≡ M. Add 2 ml. of nitrobenzene and shake thoroughly for 1/2 minute.

Titrate the excess $AgNO_3$ with 0.1 N KCNS to a reddish-brown endpoint. Record volume of KCNS used ≡ N.

Run a blank determination on reagents used and record volumes of $AgNO_3$ (≡ P) and KCNS (≡ R) used.

Calculations

The titanous sulfate method measures the total amount of chloride ion present, i.e. that originally present, that produced by reduction of the chlorate, and that produced by reduction of the perchlorate.

Hence in calculation of the perchlorate content, the titers due to chloride and chlorate must be subtracted. In addition a blank determination is recommended to correct for chloride content of the reagents.

Hence, for the 25 ml. aliquot of the diluted sample,

Milliequivalents of total chloride found = $T = (M \times N_{AgNO_3}) - (N \times N_{KCNS})$

Milliequivalents of chloride in reagent = $U = (P \times N_{AgNO_3}) - (R \times N_{KCNS})$

Milliequivalent of chloride due to chlorate = K.

Milliequivalent of chloride due to original chloride = A.

Milliequivalent of perchlorate found = $(T - (U + K + A)) = W$

Expressed in terms of sodium perchlorate in the original sample solution,

$$\frac{W}{S} \times 2449 = \text{grams of } NaClO_4 \text{ per liter}$$

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APPENDIX

APPENDIX A

COST ESTIMATE ON POTASSIUM PERCHLORATE BY THE ELECTROLYTIC METHOD

SUMMARY SHEET

PRODUCT COST

A. ESTIMATED MANUFACTURING COST OF SODIUM PERCHLORATE VIA ELECTROLYSIS

Direct Cost

Including raw materials, labor, maintenance, utilities, etc. 11.2¢/lb.

Indirect Cost

Including plant overhead (superintendant, shift supervisors, chemists, office workers, plant guards, etc.) and administrative expense. 1.4¢/lb.

Total Cost

Not including depreciation, taxes, and insurance on Pennsalt operating fee. 12.6¢/lb.

B. ESTIMATED MANUFACTURING COST OF POTASSIUM PERCHLORATE VIA SODIUM PERCHLORATE

Direct Cost

Including raw materials, labor, maintenance, utilities, etc. 13.8¢/lb.

Indirect Cost

The plant overhead applied to the sodium perchlorate plant also covers this plant. 00.0¢/lb.

Total Cost

Not including administrative overhead and fee of the operator or depreciation, taxes and insurance. 13.8¢/lb.

Process

Sodium chlorate liquor is fed batchwise to electrolytic cells employing copper anodes plated with platinum. The product of electrolysis, sodium perchlorate, is converted to the potassium salt by the addition of a hot, concentrated solution of potassium chloride. The product is then cooled, crystallized, filtered and dried.

Investment Cost

On the same basis as stated in Appendix B, the investment is estimated to be \$2,270,000 for the sodium perchlorate plant, and \$1,865,000 for the potassium perchlorate plant.

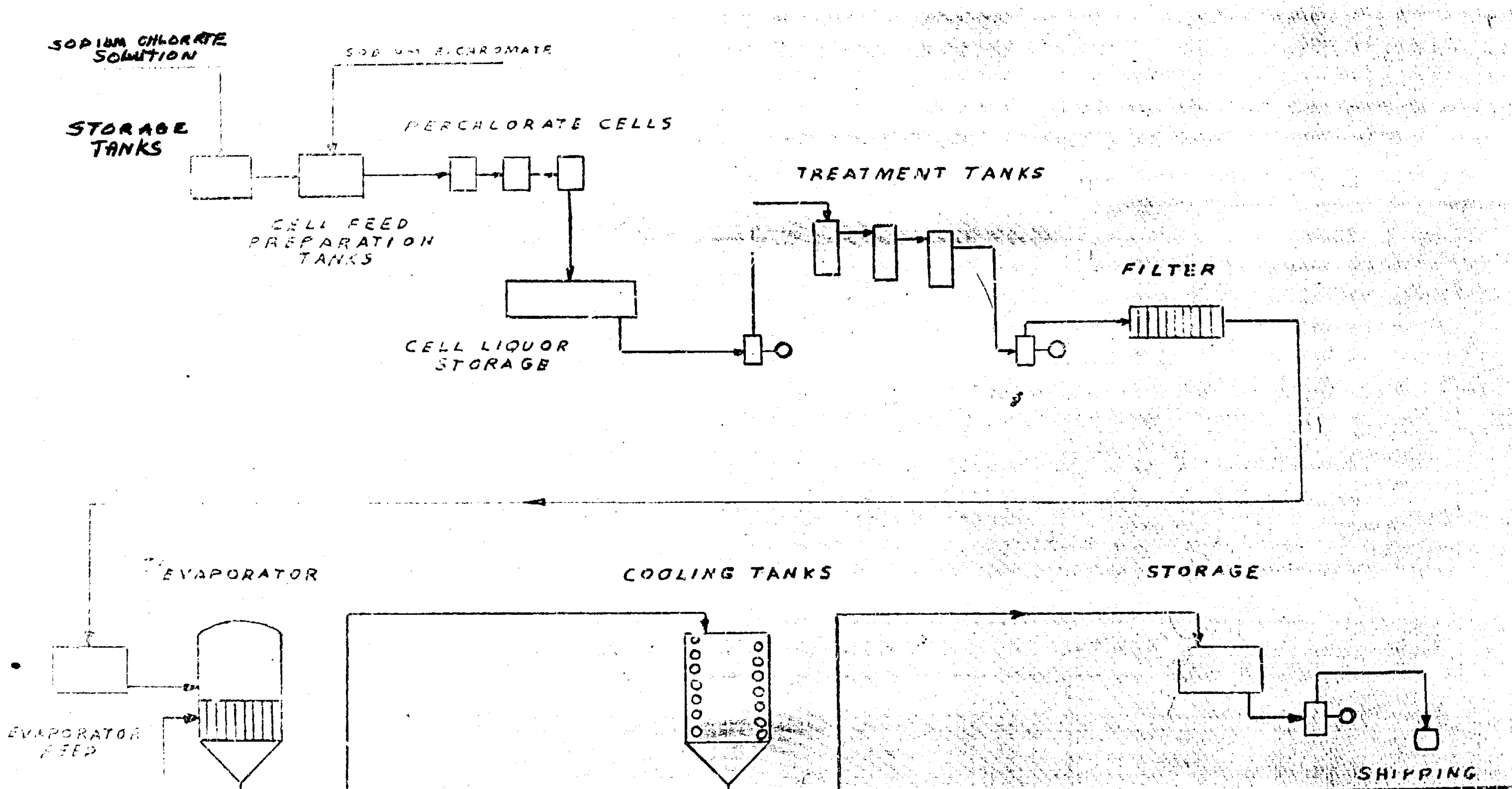
Productive Capacity

The potassium perchlorate plant is based on a production of 10,000 TPY.

The sodium perchlorate production is 9360 TPY. This production is equal to the raw material requirements of the potassium perchlorate plant.

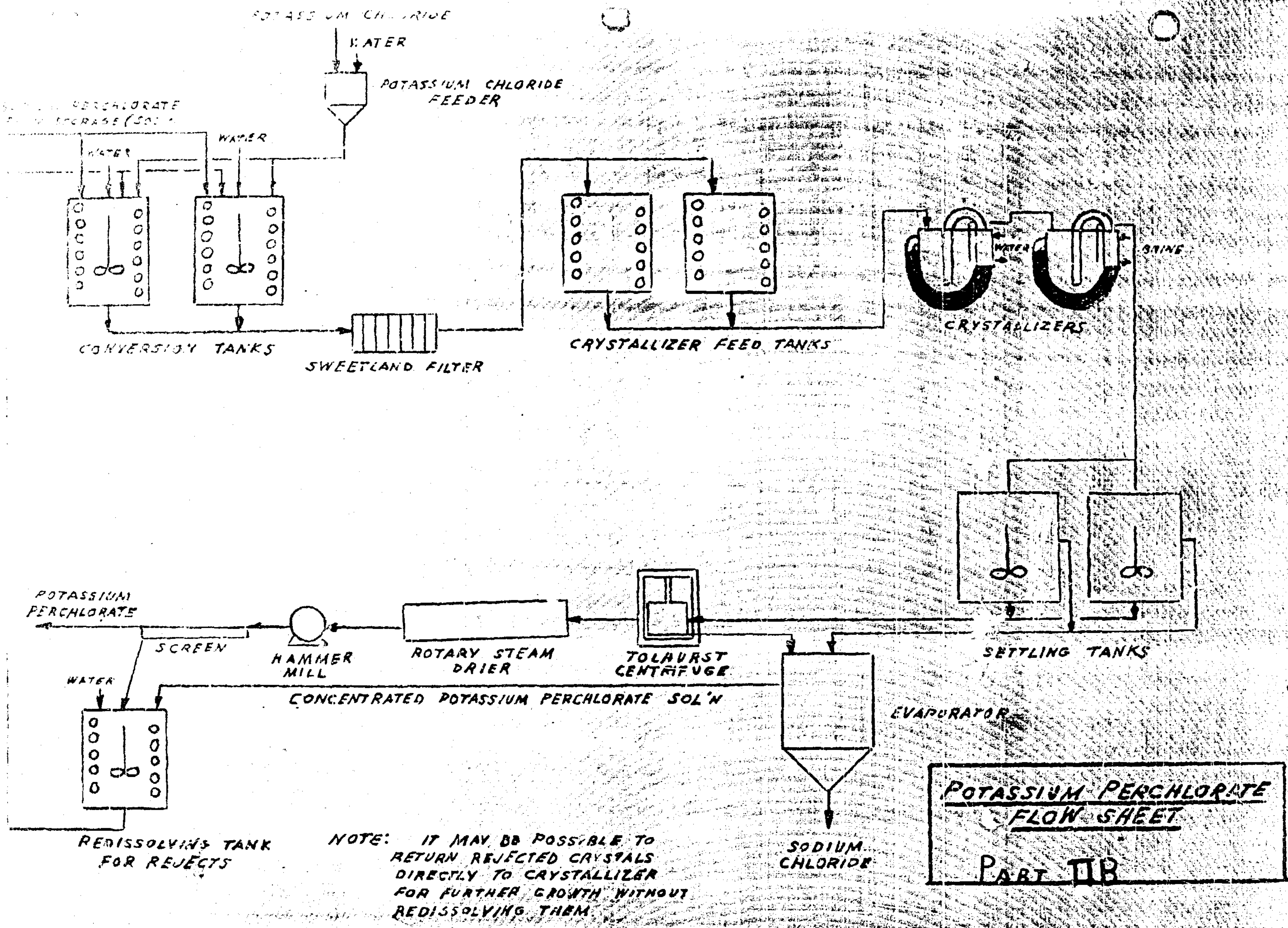
Probable Accuracy of Estimate

This estimate is believed to be accurate within ± 20%.



FLOW SHEET
SODIUM PERCHLORATE
PART II-A 8/17/51

ELECTROLYTIC METHOD



ELECTROLYTIC METHOD

APPENDIX B

COST ESTIMATE ON POTASSIUM PERCHLORATE BY THE THERMAL METHOD

SUMMARY SHEET

PRODUCT COST

ESTIMATED MANUFACTURING COST OF POTASSIUM PERCHLORATE VIA THE THERMAL METHOD

Direct Cost

Including raw material, labor, maintenance, utilities, etc. — 16.7¢/lb.

Indirect Cost

Including plant superintendant, shift supervisors, chemists, office workers, plant guards, etc. — 0.4¢/lb.

Total Cost

Not including administrative overhead and fee of the operator or depreciation, taxes and insurance. — 17.1¢/lb.

PROCESS

Potassium chlorate is heated to 900°F. for one hour in a silica brick lined rotary kiln. The molten kiln product is quenched and dissolved in water. The product is then crystallized, filtered and dried.

INVESTMENT COST

It is estimated that a plant to produce 10,000 TPY of potassium perchlorate at Calvert City, Ky., will cost $755,500. Included in the cost is $40,000 for a building. No warehousing or expansion space has been provided for in the estimate.

PRODUCTIVE CAPACITY

The potassium perchlorate plant is based on a production of 10,000 TPY.

PROBABLE ACCURACY OF ESTIMATE

This estimate is believed to be accurate within ± 20%.

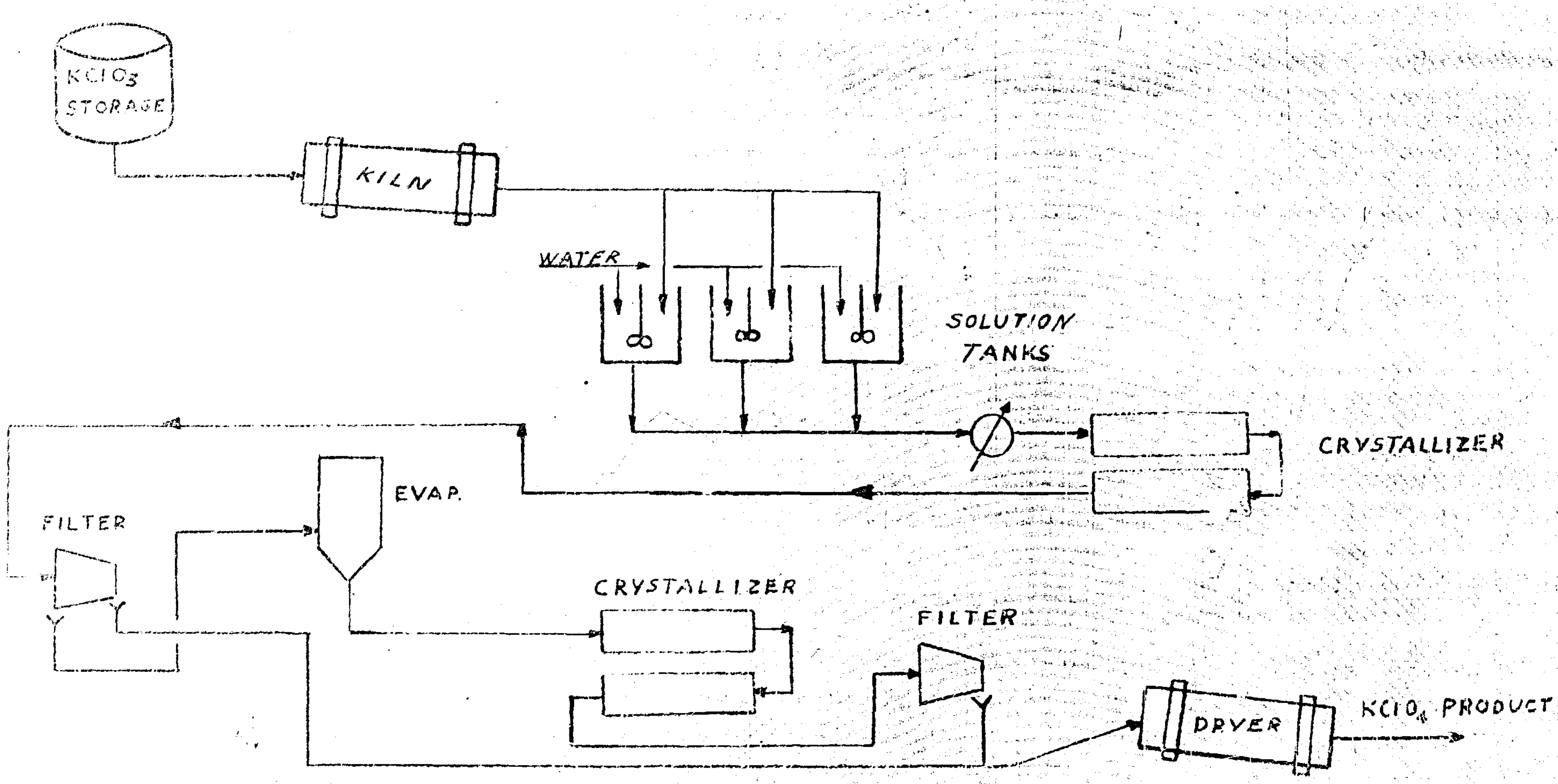
EQUIPMENT LIST

Item	Size	Visualized Materials of Construction
Storage Tank	10,000 gal.	Steel
Conveyors	one steel	three - SS304
Kiln	4'D x 14'	Steel lined with silica brick
Pumps	Four	SS304
Cooling Tanks with Agitators (three)	2500 gal.	SS304 Clad
Evaporator	1870 sq. ft.	SS304 Clad
Heat Exchangers	145 sq. ft.	SS304
	30 sq. ft.	SS304
Packaged Units		
Swenson Walker Crystallizers	9 - 40' L's	SS304 Clad
	1 - 40' L	SS304
	1 - 30' L	Clad
Bird Continuous Filters	2000 gal./hr.	SS304
	500 gal/hr.	SS304
Roto Louvre Dryer	3'10" D x 16' L.	SS304

POTASSIUM PERCHLORATE

FLOW SHEET

THERMAL METHOD



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APPENDIX C

COST ESTIMATE ON POTASSIUM PERCHLORATE BY THE LEAD DIOXIDE METHOD

INTRODUCTION

This estimate has been prepared for the purpose of obtaining a comparison between this process and the thermal or electrolytic process for manufacture of potassium perchlorate.

SUMMARY SHEET

PRODUCT COST

Estimated Manufacturing Cost of Potassium Perchlorate via the Lead Dioxide Method

Direct Cost

Including raw materials, labor, maintenance, utilities, etc. — 16.0¢/lb.

Indirect Cost

Including plant superintendant, shift supervisors, chemists, office workers, plant guards, etc. — 0.4¢/lb.

The recovery of lead dioxide will increase the product cost several cents a pound.

Total Cost

Not including administrative overhead and fee of the operator or depreciation, taxes and insurance — 16.4¢/lb.*

PROCESS

Powdered lead dioxide is added to a water solution of potassium chlorate and sulfuric acid. These ingredients are reacted for four hours at 100°C. to produce potassium perchlorate and lead dioxide. The products of this reaction are filtered. The filtrate is recycled and the cake digested in water for one hour at 100°C. The lead sulfate is removed by filtration, converted to lead dioxide by electrolysis and reused**. The potassium perchlorate is crystallized and dried.

INVESTMENT COST

The investment cost less purchase cost and recovery equipment for lead dioxide is $1,274,500 for a plant to produce 10,000 TPY of potassium perchlorate at Calvert City, Ky.

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*The recovery of lead dioxide will increase the product cost several cents a pound.

**The process for electrolysis of lead sulfate requires development.

PRODUCT COST

It is estimated that the bulk manufacturing cost of potassium perchlorate less depreciation, taxes, insurance, administrative charges and Pennsalt operating fee would be 16.4¢/lb.* at Calvert City, Ky., at a production rate of 10,000 TPY.

PRODUCTIVE CAPACITY

This plant is rated at a production of 10,000 TPY operating at a 90.5% plant efficiency.

PROBABLE ACCURACY OF ESTIMATE

This estimate is believed accurate within ±20%.

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*The recovery of lead dioxide will increase the cost several cents a pound.

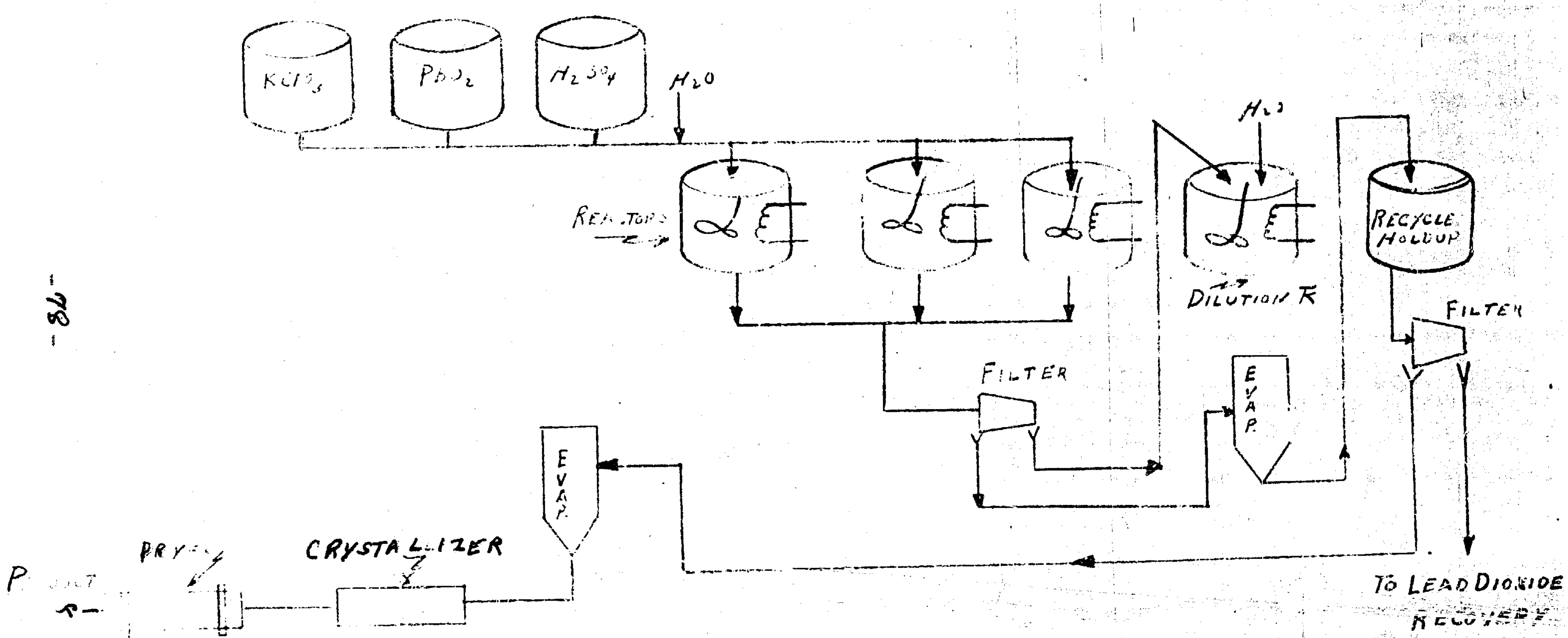
EQUIPMENT LIST

A. Delivered Equipment

Item	Size	Visualized Materials of Construction
Storage Tanks:		
Potassium Chlorate	10,000 gal.	Steel
Sulfuric Acid	10,000 gal.	Steel
Lead Dioxide	10,000 gal.	Steel
Recycle	5,000 gal.	Acid brick lining
Water Holdup	10,000 gal.	Steel
Holdup tank	5,000 gal.	Acid brick lining
Evaporators	4,650 sq. ft.	Duriron
	225 sq. ft.	Duriron
Reaction Vessels: (Coils and Agitated)		
Potassium Perchlorate (3)	2,500 gal.	Acid Resistant
Dilution Tanks (2)	7,000 gal.	brick lining
Pumps:		
Ten		Duriron
One		Steel
Conveyors:		
Four		Steel
Two		S.S. 316

B. Packaged Units

Item	Size	Visualized Materials of Construction
Bird Continuous Filters	1500 GPH	Duriron
	6000 GPH	Duriron
	300 GPH	Duriron
Swenson-Walker Crystallizers		
Three	40' long	Duriron
Refrigeration	14 Tons 50°F.	
Roto Louvre Dryer:		
One	3'10"D x 16'L	Duriron



POTASSIUM PERCHLORATE
VIA LEAD DIOXIDE
FLOW SHEET

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PENNSYLVANIA SALT MANUFACTURING CO., RESEARCH AND DEVELOPMENT DIV., WYNDMOOR, PA.

INVESTIGATION OF METHODS TO PRODUCE SODIUM PERCHLORATE WITHOUT THE USE OF PLATINUM - AND APPENDIXES A THRU C - PARTS 1 AND 2

P7/2

GALL, J.F.; MILLER, H.C.; GRIGGER, J.C.
31 AUG'51 155 PP PHOTOS, TABLES, DIAGRS, GRAPHS, DRWGS

USN CONTR. NO. NONR 372(00) * [illegible]

CHEMICALS - PRODUCTION
SODIUM PERCHLORATE

CHEMISTRY (52)
INORGANIC CHEMISTRY (1)

[redacted]

AD-A800 216

NTIS, auth: ONR, DN ltr, 21 Jan 77

Classification Changed To UNCLASSIFIED
* By Auth Director of CADO (re/ltr from Office of Naval Research dtd 1 Feb 52)
By John E. Moore, USO
Date 6 Feb 52

* classification rather than reclassification