A STUDY
OF THE PRODUCTION OF
SODIUM PERCHLORATE ELECTROLYTICALLY

Thesis
by
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A STUDY OF THE PRODUCTION OF SODIUM PERCHLORATE ELECTROLYTICALLY

The purpose of this work is to investigate the electrolytic production of perchlorate from chloride, and particularly to determine which anode materials serve best under the rigorous conditions imposed. In order that one may better understand what follows, it is necessary to briefly summarize the existing theory of the electrolytic formation of chlorate and perchlorate.

THEORY

When an electric current is passed into a neutral or alkaline solution of NaCl, the primary products formed are chlorine and sodium hydroxide, according to the equation

$$2 \text{Na}^+ + 2 \text{Cl}^- + 2\text{H}_2\text{O} + 2\text{e}^- = \text{Cl}_2 + 2\text{NaOH} + \text{H}_2 \quad (1)$$

If chlorine and sodium hydroxide are the products desired, they must be kept separate. If, however, the electrolyte is allowed to mix, a variety of products, dependent upon physical conditions, results from the interaction of the chlorine, sodium hydroxide, and water. The products that it is possible to obtain through interaction are chloride, hypochlorite, chlorate and perchlorate.

Just as soon as the liberated chlorine from the anode comes in contact with the cathodic sodium hydroxide, the following series of reactions takes place.
\[ \text{Cl}_2 + \text{OH}^- = \text{HOCl} + \text{Cl}^- \]  (2)

Hypochlorous acid reacts with unchanged sodium hydroxide to produce hypohlorite, according to the equation:

\[ \text{HOCl} + \text{OH}^- = \text{OCl}^- + \text{H}_2\text{O} \]  (3)

Only when there are at least two equivalents of hydroxide to every mol of chlorine does the following reaction, which is a summation of (1) and (2) hold. This is the usual equation written for the action which takes place.

\[ \text{Cl}_2 + 2 \text{NaOH} = \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O} \]  (4)

Starting from an initial zero concentration, the hypochlorite concentration will build up to, but not exceed a certain value which is dependent upon such factors as chloride concentration, temperature, current density, and the material of the anode. The reason for this is that almost from the start, the hypochlorite is itself decomposed, the rate of decomposition increasing as the hypochlorite concentration increases until finally the rates of production and decomposition of hypochlorite are equal.

There are three ways in which the hypochlorite ion in the cell is decomposed:

(1) Chemically,* by its action with free hypochlorite.

*Foerster and Jorre, 
J.F. prakt. Ch. 59, 53 (1899);

Foerster, ibid, 63, 141, (1901)
chlorous acid, whose formation has been described (Eq. 2). Chlorate ion is produced by this action.

\[ 2 \text{HOC}1 + \text{OC}1^- = \text{ClO}_3^- + 2 \text{Cl}^- + 2 \text{H}^+ \]  

(5)

The free hydrogen ion then combines to produce an equivalent amount of hypochlorous acid, which reacts with more hypochlorite ion, the process continuing, under suitable conditions until all the hypochlorite ion has been changed to chlorate ion and chloride ion.

\[ 2 \text{H}^+ + 2 \text{OC}1^- = 2 \text{HOC}1 \]  

(6)

(2) Cathodic reduction of hypochlorite ion by hydrogen.

\[ \text{OC}1^- + \text{H}_2 = \text{H}_2\text{O} + \text{Cl}^- \]  

(7)

(3) An electrochemical formation of ClO\textsubscript{3}\textsuperscript{-}

which takes place only on the cathode, and not throughout the solution. *

\[ 6 \text{ClO}^- + 3 \text{H}_2\text{O} + 6\text{e}^- = 2 \text{ClO}_3^- + 4\text{Cl}^- + 6\text{H}^+ + 1\text{O}_2 \]  

(8)

For the production of ClO\textsubscript{3}\textsuperscript{-} from NaCl, we must consider equations (5) and (6) and see what conditions are most favorable for each reaction.

Under the conditions we have been considering, i.e. a neutral or slightly alkaline solution the chemical formation of ClO\textsubscript{3}\textsuperscript{-} takes place but slightly. This is because the excess of hydroxyl ions prevents the formation of free hypochlorous acid. Hence at the equilibrium point; that is, when hypochlorite ion is... being

*Foerster and Muller, Z.f. Elektroch. 8, 567, (1902)
produced and decomposed at the same rate, in a neutral or alkaline solution the decomposition will be practically entirely electrochemical. By equations (1) and (4) it will be seen that two faradays are required to produce one mol of OCl\(^-\), or twelve faradays to produce six mols. Hence it requires twelve faradays to produce the OCl\(^-\) demanded by equation (8), while six faradays are required to decompose the hypochlorite thus produced, forming two mols of ClO\(_2\)^-. If the production of ClO\(_2\)^- is what is desired and, at the equilibrium point, as much OCl\(^-\) is to be produced as is decomposed, then it will require two thirds of the total current to produce OCl\(^-\) while one third is used to decompose OCl\(^-\), producing ClO\(_2\). Since, by the chemical formation of ClO\(_2\)\(^-\) (Eq. 5) no electrical energy is required for the decomposition of OCl\(^-\), all the current being employed in the production of OCl\(^-\), the electrochemical formation of ClO\(_2\)^- can, at its very best only attain a current efficiency of 66.7%.*

As has been said, in alkaline solution the chemical formation of ClO\(_2\)^- is very slow indeed, while after hypochlorite ion concentration has reached its limiting value, all the current is engaged in producing and decomposing OCl\(^-\). In acid solution however, the chemical formation of ClO\(_2\)^- is by far predominant. The excess of

H⁺ causes the formation of unionized HOCl (Eq. 6).

The HOCl thus formed reacts with OCl⁻ to form ClO₃⁻.

This action is enormously increased by an increase in temperature. If, before the OCl⁻ concentration in a neutral solution has come to its limiting value an amount of HCl equal to only a fraction of the hypochlorite present be added, the hypochlorite will be completely oxidized to chlorate. On further electrolyzing the solution, more hypochlorite will be produced, and the addition of more acid will cause its oxidation to chlorate.* It is necessary to keep adding small amounts of acid continuously because acid is decomposed by the current, forming chlorine and hydrogen. If the acid were not decomposed, a very small amount present at the start would serve to convert all the hypochlorite formed to chlorate.

Thus chlorate can be produced in acid sodium chloride solution with current efficiencies of over 90%. The best conditions are (1) high temperature, about 70 degrees C #, (2) suitable stirring of the electrolyte, (3) high anodic current density and (4) high initial sodium chloride concentration.

* Foerster and Muller, Z.f. Elektroch. 8, 13, (1902)

Perchlorate can be produced directly from sodium chloride in one operation, but it has not been found advisable to do so, because of the mixed chlorate and perchlorate thus obtained, and because the best conditions for producing chlorate are not those most suitable for the production of perchlorate. The best conditions for the production of perchlorate directly from sodium chloride are, (1) low temperature, (2) lower anodic current density than that employed for chlorate production and (3) low concentration of sodium chloride. A better way to produce perchlorate is in two steps, (1) the electrolysis of chloride to chlorate and (2) the separation of the chlorate from the mother liquor, redissolving it and electrolyzing to perchlorate.

The electrolytic production of perchlorate depends upon the discharge of chlorate ion and its subsequent reaction with water,*

\[ 2 \text{ClO}_3^- + \text{H}_2\text{O} + 2 \Theta = \text{HClO}_4 + \text{HClO}_2 + \frac{1}{2}\text{O}_2 \quad (9) \]

The oxygen produced immediately oxidizes the chlorous acid back to chloric acid

\[ \text{HClO}_2 + \frac{1}{2}\text{O}_2 = \text{HClO}_3 \quad (10) \]

In actual practice a slightly acid 60-70% solution of sodium chlorate is used for electrolyte. The temperature is kept below ten degrees by cooling coils.

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* Oeschli, Z.f. Elektroch. 9, 807, (1903)

# Allmand, "Applied Electrochemistry" p 402
and a good circulation is maintained. An anodic current density of about 8 amp./sq. decimeter, which is fairly high, is maintained. #

**EXPERIMENTAL WORK**

In view of existing theory on the formation of perchlorate electrolytically, the experimental work was planned to the end of producing perchlorate by the two stage process. It was planned to start with a concentrated solution of sodium chloride at a high temperature and using a high current density on suitable anodes, produce sodium chlorate. This sodium chlorate was then to be separated by decantation and crystallization and redissolved. A concentrated solution was to be electrolyzed at a low temperature and somewhat lower current density than that employed to produce sodium chlorate. The trend of experimentation was to be directed toward the channel of commercial production. Hence it would be necessary to seek some anode in place of platinum, which was considered too expensive for practical use. Some experiments were to be made on a small laboratory scale and if these experiments gave favorable results there were to be constructed cells that would produce chlorate and perchlorate on a semi-industrial scale.

The first problem to work out was to construct a laboratory cell for the production of sodium chlorate.

# Allmand, "Applied Electrochemistry" p 402
In view of the low current efficiency of the alkaline process, it was deemed highly advisable to work on the acid process. Allmand, in his "Principles of Applied Electrochemistry" lists as possible cathode materials for use in the acid process: Acheson graphite, nickel, copper and brass; and for anode materials: smooth platinum, platinum-irridium foil, hard artificial carbon, graphite, Fe₃O₄, and carborundum. Sheet copper was the material selected for cathode construction. Finding an anode material was not quite so simple, but some 3" graphite crucible covers were finally obtained and converted with but little trouble into suitable anodes. A motor generator set was the most available source of direct current. Since it would be difficult to obtain the high current required (about 20 amperes) at the low voltage of a single cell, it was found necessary to provide for four cells in series, which would make possible a practical voltage at the generator without having to use intermediate rheostats. It was not deemed necessary to preheat the electrolyte in each cell to 70 degrees, since the heavy current to be employed would soon bring the solution to a working temperature close to 70 degrees.

FIRST RUN ON NaCl

Each individual cell consisted of a one liter beaker suspended in which were two cathodes, at a distance apart of 3.1 cm. One anode was suspended midway
GENERAL ARRANGEMENT

FIRST TRIAL RUN ON NaCl

SECOND TRIAL RUN ON NaCl

CHANGED ANODE ARRANGEMENT

Khotinsky seal
Glass tube
between the two cathodes. The wiring was so arranged that each face of the anode was active—an arrangement which doubled the capacity of a single cell, or gave the effect of two cells in parallel. The anodes were originally graphite crucible covers 7.6 cm in diameter. These were reworked to flat disks. A small hole was drilled in near the outer edge, and the short leg of a copper wire with a 90 degree bend fitted in. This junction was then thoroughly coated over with cerasin wax, as was the copper wire for some distance away from the graphite, to prevent contact with the solution. The cathodes were cut in circular shape with a projecting lip to which was soldered a light copper lead wire.

In each beaker at the start was 900 cc of saturated brine solution, 2 cc dilute HCl and one gram of Na₂CrO₄. The purpose of the Na₂CrO₄ is to prevent the cathodic reduction of hypochlorite by hydrogen (Eq. 7). Its action, as first discovered by Imhoff and later more fully investigated by Muller * was ascribed to the reduction of CrO₄²⁻ to Cr³⁻ and the formation of a thin diaphragm of insoluble chromium chromate.

A diagram of the four cells in series, and some of the details will be found on the following page.

* Zeitsch., Elektrochem. 5, 469 (1899); 7, 398, (1901); 8, 909, (1902)
After the cells had all been set up as described and everything gotten in readiness, current was passed to determine how well the action would take place. The current used was 22 amperes, or, since the total anode surface was 2 x 45.5 or 91 sq. cm., a current density of 23.2 amp./sq. decimeter.

From the start of the passage of current, there was a vigorous evolution of gas, a very considerable amount of it being chlorine. There was a quite noticeable rise in temperature. Almost from the start, there was a very pronounced grayish green flocculent precipitate formed in each cell, but to a greater extent in cell 1, where the current first entered. This precipitate kept increasing rapidly, and a few drops of HCl added to each cell did not dispel it.

After current had passed for ten minutes, arcing across from anode to cathode occurred in cell 1, which necessitated stopping the run. Examination showed that, probably due to the heat generated, the cerasin coating had melted away, exposing the copper, which had completely disintegrated, allowing the anode to drop to the bottom. The precipitate before mentioned proved on examination to be copper hydroxide, indicating a very low remaining acid concentration.

In consequence of the unsuccessful outcome of this first run, it was decided to make another run, using the same apparatus and arrangement, but with the following
modifications:

(1) A glass tube was to be fitted over the copper anode lead and extend to the graphite. A seal between the end of the glass tube and the graphite was to be made with Khotinsky sealing compound.

(2) This junction was to be kept above the surface of the electrolyte.

(3) The electrolyte was to be made more strongly acid at the start, and the acid concentration maintained by frequent additions of more acid.

SECOND TRIAL RUN ON NaCl

A fresh brine solution was made up by dissolving 1225 gm recrystallized table salt in 3500 cc distilled water. The current used was only twelve amperes, or a current density of 16.2 amp./sq. decimeter for the 74 sq. cm of active anode surface. In each cell was 750 cc saturated brine solution, 5 cc dilute HCl and one gram Na₂CrO₄. The changes in apparatus mentioned above were made. A diagram of the changed anode arrangement may be found with the diagram for the first trial run.

During the passage of current, the electrolyte was kept as well stirred as possible by means of a stirring rod. Current was passed for forty-five minutes, during which time 15 cc of dilute HCl in 5 cc portions
was added to each cell. In spite of the frequent addition of HCl a flocculent, grayish green precipitate formed; the only effect of the HCl seemed to be to delay its formation. Due to the decomposition of HCl chlorine evolution was very bad; the stirring could not be made adequate to prevent its escape. The Khotinsky junction withstood the chlorine fairly well, although the heat generated caused it to take on a vitrified appearance.

As a result of these first two experiments with sodium chloride, the practical impossibility of obtaining satisfactory experimental results in the limited time on hand was seen, and it was decided to work on the second stage of the electrolytic process— the production of perchlorate from chlorate— since a somewhat lower current could be used, and there would be no chlorine evolution, making possible a somewhat wider selection of anode materials.

THE PRODUCTION OF PERCHLORATE FROM CHLORATE

FIRST TRIAL RUN

It was believed that the same arrangement of cells and electrodes could be used for perchlorate production as was used in the first two experiments on chlorate production. A concentrated solution of sodium chlorate was made up by dissolving 2000 gm. technical sodium chlorate in 2600 cc distilled water. This was analyzed for ClO$_3^-$ by the method shown in Appendix A(1) and found to
contain 0.578 gm NaClO$_3$ per cc.

In each cell was 625 cc chlorate solution and 5 cc 6 M HCl. Each cell was surrounded with an ice bath. The temperature at the start of the run was 6.5°C. The current used was 8 amperes, corresponding to a current density of 10.82 amp./sq. decimeter. This run lasted but a very few minutes. In cell 3, due to poor contact between graphite and copper lead wire, arcing of the current occurred. The graphite anodes gave evidence of very rapid deterioration. They became loose and crumbly, and a black scum of graphite floated on the surface of the electrolyte. Due to the increased porosity, electrolyte worked up through the graphite into the junction between graphite and copper, causing very poor contact and the arcing previously described.

SECOND TRIAL RUN ON NaClO$_3$

Due to the mechanical failure of the graphite anodes, and the difficulty of making good contact, anodes of ferro-silicon (Corrosiron) were substituted for graphite. These were small test disks 5 cm in diameter and 0.6 in thickness, with a hole 0.4 cm in diameter near the circumference. The copper lead wire was wrapped through the hole several times, then the wraps were soldered for rigidity and better contact. A glass tube was slipped over the wire and brought down as close as possible to the ferro-silicon disk. The balance of the insulation was
by means of Khotinsky and rosin melted together. The same cathodes and other arrangements as shown in the preceding diagram were used, except the cells were enclosed in an ice bath. The same electrolyte, filtered, was used in each cell, as in the first trial run. A current at the start of 2.9 amperes was employed which corresponded to a current density of approximately 11.1 amp./sq. decimeter for the 26 sq. cm of anode surface. Current was passed for forty minutes, at the end of which time, the anodes showing some signs of corrosion, the run was stopped temporarily. After a comparative test was made to determine how much iron had gone in solution,—there being no precipitate in the electrolyte,—current was again passed for one hour and thirty-eight minutes. At the end of this time, a slight reddish precipitate appearing in the electrolyte, the run was stopped. A summary follows:

<table>
<thead>
<tr>
<th>40 minute period</th>
<th>98 minute period</th>
<th>Av. for 138 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. I</td>
<td>3.09 Amp.</td>
<td>2.84</td>
</tr>
<tr>
<td>Av. E</td>
<td>5 Volts</td>
<td>4.7</td>
</tr>
<tr>
<td>Av. T</td>
<td>9 Degrees C</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Comparison tests made on the electrolyte at the end of the forty minute period and at the end of the run showed in each case about the same amount of iron—one milligram per cubic centimeter of electrolyte. At the end of the forty minute period, however, the iron was in solution and there was no precipitate, while at the end
of the run there was no iron in solution—it was all in the form of precipitate. Since there was no increase in iron concentration as the run went on, it seemed reasonable to suppose that the iron dissolved while the electrolyte was yet acid—then as the acid in the electrolyte disappeared, iron ceased to go into solution, and that already dissolved hydrolyzed. The electrolyte at the end of each period was also analyzed for ClO$_3^-$ (Appendix A,1), but the results were disappointing, as the analysis showed an increase in ClO$_3^-$ rather than a decrease. An attempt was made to locate faulty technique in the analysis, but the results were negative.

The ferro-silicon anodes it seemed, were on the whole worthy of another trial. They gave no trouble except for the slight amount of corrosion which took place. It seemed that in all previous experiments the electrolyte had not been made sufficiently acid at the start—hence it was determined to increase the acid concentration. The acid used was to be H$_2$SO$_4$, since there would then be no chlorine evolution, which had been noticeable in the first and second trial runs on sodium chlorate, with only 5 cc of 6 M HCl in the electrolyte. Although the failure of the first and second runs to give positive results was disturbing, it was believed that another run would throw some light on the cause.
THIRD TRIAL RUN ON NaClO₃

A solution of NaClO₃ and H₂SO₄ was made up in which the NaClO₃ concentration was 0.606 gm/cc and the acid strength approximately 0.18 N. The same arrangement of apparatus as for the previous run was used. Each cell contained, at the start, 650 cc. A current at the start of 2.8 amperes, or 10.8 amp./sq. decimeter, was passed for three hours. During the run, and especially toward the last, a reddish precipitate formed around the electrodes, but a little vigorous stirring with the glass rod which was employed to keep the electrolyte stirred soon dissipated it. The electrolyte was free of precipitate at the end of the run. A summary follows.

<table>
<thead>
<tr>
<th>Average temperature</th>
<th>13.2 degrees C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature at start</td>
<td>9</td>
</tr>
<tr>
<td>Average current</td>
<td>3.08 Amp.</td>
</tr>
<tr>
<td>Average voltage (single cell)</td>
<td>4.68 Volts</td>
</tr>
</tbody>
</table>

An analysis of the electrolyte was again disappointing because it did not indicate a decrease in chlorate ion but, rather, an increase. But the ferro-silicon anodes behaved on the whole satisfactorily, showing but small indications of corrosion, that it was thought advisable to construct a cell on a semi-industrial scale, which would necessitate sending to San Francisco for four Corrosiron castings 4"x 10"x ½". Meantime, until the
castings came, an investigation was to be made into the method of analysis employed, and the fault, if any existed, remedied or a new procedure adopted.

**INVESTIGATION OF ANALYSIS FOR CHLORATE ION**

The method of analysis followed was to analyze for \( \text{ClO}_3^- \) (Appendix A.1) at the start and at the end of the run. If \( \text{ClO}_3^- \) were oxidized to \( \text{ClO}_4^- \) there would be a diminution of \( \text{ClO}_3^- \), and in this way the amount of \( \text{ClO}_4^- \) formed could be determined. But, by the analysis, instead of a decrease in \( \text{ClO}_3^- \), there was an increase.

Either \( \text{ClO}_3^- \) was being produced from some material not thought to be present, or through faulty technique some \( \text{FeSO}_4 \) was being oxidized by the air, which would give high results. If \( \text{ClO}_3^- \) were being produced, it would be from \( \text{Cl}^- \) and since technical sodium chlorate was used in the cells, there would most probably be \( \text{Cl}^- \) present.

Several comparison tests however, showed that, per gram of sodium chlorate, there was only one milligram of \( \text{Cl}^- \). Even if this were changed to \( \text{ClO}_3^- \), with so much \( \text{ClO}_3^- \) already present, it would not account for the high results obtained. A close check on the technique of analysis did not show it to be at fault.

The reason the indirect analysis described above for \( \text{ClO}_3^- \) was adopted was because there was no simple analysis known for \( \text{ClO}_4^- \). The methods known were either cumbersome gravimetric procedures, or some such indirect
analysis as had been followed. With the uncertainty of this indirect method however, it became necessary to attempt a direct determination for ClO₄⁻. The procedure followed was modified from Treadwell-Hall's procedure for the determination of potassium. A description will be found in Appendix A (4). This attempt at direct determination of ClO₄⁻ was abandoned because:

(1) The excess FeSO₄ necessarily introduced to reduce ClO₃⁻ to Cl⁻ precipitated out as iron hydroxide in subsequent evaporations.

(2) The quite considerable amount of SO₄²⁻ present in the electrolyte necessitated a tremendous addition to BaCl₂.

Meantime word had come that it would not be possible to procure the Corrosiron castings, due to a disastrous foundry fire. There being a stock of sheet nickel on hand, it was decided to try out nickel anodes. Perhaps the analysis would show better results with nickel, indicating, if so, that some element of the ferro-silicon alloy anodes produced a disturbing effect on the analysis.

FOURTH TRIAL RUN ON NaClO₃

The same arrangement of apparatus was used as has been previously diagrammed, with the exception that for ferro-silicon anodes, rectangular sheet nickel anodes were substituted. These were 5.8 cm in width, 10.2 cm
in length and 3 mm in thickness. Two copper wires 1 mm in diameter and 35 cm long, one at each corner of an end were soldered to the anode for a means of suspension and for conducting in the current. A fresh sodium chlorate solution was made up which was approximately 0.6 N in H₂SO₄ and contained 0.573 gm NaClO₃/cc. In each cell was 500 cc of this electrolyte. The anodes were lowered into the solution until 5.2 cm of their length were immersed, which gave an active anode surface of 2 x 5.2 x 5.8 or 60.3 sq. cm. A current at the start of 3.65 amperes was used, corresponding to a current density of 6.35 amp./sq. decimeter.

After ninety-eight minutes the run was stopped, on account of cells 3 and 4 having ceased to evolve gas. On examination the anodes of these cells were found practically entirely disintegrated, while the electrolyte had the green color of a strong nickel solution. All anodes had been affected, though not to the same degree. An analysis of the electrolyte for NaClO₃ showed 0.562 gm NaClO₃/cc. Here at last the analysis showed a decrease in ClO₃⁻ rather than an increase. Had time permitted an interesting problem would have been to run down the trouble in analysis contingent upon the use of ferro-silicon anodes. A summary of results follows.


<table>
<thead>
<tr>
<th>Time in sec's</th>
<th>Av. I</th>
<th>Av. E</th>
<th>Coulombs</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>5880</td>
<td>3.76 Amp.</td>
<td>9.5 Volts</td>
<td>22,120</td>
<td>0.229</td>
</tr>
</tbody>
</table>

**TABLE B**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Beg.</td>
<td>End</td>
<td>Beg.</td>
<td>End</td>
<td>Decrease</td>
</tr>
<tr>
<td>500 cc</td>
<td>498</td>
<td>0.573</td>
<td>0.562</td>
<td>286.5</td>
</tr>
</tbody>
</table>

**TABLE C**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8.04 gm</td>
<td>2 x 8.04/122.5</td>
<td>0.1314</td>
<td>0.229</td>
<td>0.1314, 57.4%</td>
</tr>
</tbody>
</table>

It was quite evident that nickel was an entirely unsatisfactory material for anodes. Now, as time was getting short, in place of experimenting with other materials for anode construction it was thought advisable to try to obtain some quantitative results on perchlorate formation. For this purpose a piece of platinum was obtained and a last run on NaClO₃ made.

**FIFTH TRIAL RUN ON NaClO₃**

For this run only a single cell was used. The cathodes were two of the same copper cathodes as used in all previous runs. The anode was a strip of smooth platinum foil 5.07 cm wide and 12 cm long. A single 10 volt 80 ampere-hour Electra storage battery supplied the current. A solution of NaClO₃ was made up which was approximately 0.25 N in H₂SO₄ and contained 0.597
gm NaClO₂/cc. Of this solution 755 cc was placed in the cell and the electrodes lowered until 7.7 cm of the length of the anode was immersed, giving an active surface of 2 x 7.7 x 5.07 or 78.2 sq. cm. A current at the start of 3 amperes, corresponding to a current density of 3.84 amp./sq. decimeter was used. A diagram of the apparatus used will be found on the following page.

After current had passed for two hours and fifty-five minutes the run was stopped for an hour and a sample taken for analysis. Current was then passed for three hours more. A sample was taken for analysis. When a calculation was made to determine current efficiencies, on the basis of these analyses, over 100% current efficiency was obtained. A new analysis failed to give a different result. The only way in which such a result could be accounted for was that some ClO⁻₃⁻ was being reduced to Cl⁻ by the nascent hydrogen produced at the cathode. The removal of ClO⁻₃⁻ in this manner would give high results on the basis of the analysis used. An analysis for Cl⁻ (Appendix A,2) was made on samples of the original solution, on electrolyte after two hours and fifty-five minutes and on electrolyte after five hours and fifty-five minutes, and an increase in concentration of Cl⁻ was found. A correction was applied on the basis of these analyses to the calculations before
FIFTH TRIAL RUN ON \( \text{NaClO}_3 \)

GENERAL ARRANGEMENT

ANODE

CATHODES

Paper clip
fasteners

Liquid level

7.7 cm

5.07 cm

9.5 cm
mentioned. Furthermore, it was decided to pass more current into the same electrolyte, analyze, and calculate results to see what the trend would be. After four hours the run was stopped. There was a fine white precipitate, in the bottom of the cell of NaClO$_4$. The following tables give a summary of the whole experiment.

**CORRECTION FOR ClO$_3^-$ REduced TO Cl$^-$**

<table>
<thead>
<tr>
<th>Period</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Anal.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ass.*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgNO$_3$/ 2 cc elec.</td>
<td>1.90</td>
<td>1.060</td>
<td>1.230</td>
</tr>
<tr>
<td>AgNO$_3$/2 cc orig. solution</td>
<td>0.191</td>
<td>0.191</td>
<td>0.191</td>
</tr>
<tr>
<td>AgNO$_3$ to ppt. Cl$^-$ formed</td>
<td>1.709</td>
<td>0.869</td>
<td>1.039</td>
</tr>
<tr>
<td>AgNO$_3$ to ppt. Cl$^-$, per cc</td>
<td>0.855</td>
<td>0.435</td>
<td>0.520</td>
</tr>
<tr>
<td>Gm NaCl/cc elec.</td>
<td>0.00495</td>
<td>0.00252</td>
<td>0.00301</td>
</tr>
<tr>
<td>Corr.amt. NaClO$_3$ reduced/cc</td>
<td>0.00901</td>
<td>0.00458</td>
<td>0.00548</td>
</tr>
</tbody>
</table>

* Value calculated by assuming equal difference between 1 and 2, and 2 and 3. This value used in the following calculations.

In the above table, the high value obtained by analysis, for period 1, is to be accounted for by the fact that a high dilution of the original electrolyte was the only obtainable sample for analysis. (Appendix A, 3). The amount of AgNO$_3$ used in analysis had to be
multiplied five times to reduce to the same basis as analyses for the other two periods. Thus a small error in burette reading, or any AgNO₃ used to precipitate Cl⁻ already in the water, would be greatly increased.

**CALCULATION OF RESULTS**

<table>
<thead>
<tr>
<th>Time in Seconds</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average current</td>
<td>3.35</td>
<td>4.15</td>
<td>4.59</td>
</tr>
<tr>
<td>Average Voltage</td>
<td>3.73</td>
<td>4.26</td>
<td>4.55</td>
</tr>
<tr>
<td>Coulombs</td>
<td>35,180</td>
<td>44,800</td>
<td>66,200</td>
</tr>
<tr>
<td>Actual Faradays</td>
<td>0.3645</td>
<td>0.4650</td>
<td>0.6865</td>
</tr>
<tr>
<td>Volume in cell at Beginning</td>
<td>755</td>
<td>740</td>
<td>662</td>
</tr>
<tr>
<td>Volume in cell at End</td>
<td>750</td>
<td>735</td>
<td>656</td>
</tr>
<tr>
<td>NaClO₃ conc. at Beginning</td>
<td>0.597</td>
<td>0.573</td>
<td>0.543</td>
</tr>
<tr>
<td>NaClO₃ conc. at End</td>
<td>0.573</td>
<td>0.543</td>
<td>0.490</td>
</tr>
<tr>
<td>NaClO₃ red./cc at Beginning</td>
<td>------</td>
<td>0.00458</td>
<td>0.00548</td>
</tr>
<tr>
<td>NaClO₃ red./cc at End</td>
<td>0.00458</td>
<td>0.00548</td>
<td>0.00637</td>
</tr>
<tr>
<td>NaClO₃ conc. Total at Beginning</td>
<td>0.597</td>
<td>0.578</td>
<td>0.548</td>
</tr>
<tr>
<td>NaClO₃ conc. Total, at End</td>
<td>0.578</td>
<td>0.548</td>
<td>0.496</td>
</tr>
<tr>
<td>Total grams NaClO₃ at Beginning</td>
<td>451</td>
<td>427.5</td>
<td>363</td>
</tr>
<tr>
<td>Total grams NaClO₃ at End</td>
<td>433</td>
<td>403</td>
<td>325</td>
</tr>
<tr>
<td>Grams NaClO₃ Converted during Int.</td>
<td>18</td>
<td>24.5</td>
<td>38</td>
</tr>
<tr>
<td>Grams NaClO₄ Produced in Int.</td>
<td>20.7</td>
<td>28.2</td>
<td>43.7</td>
</tr>
<tr>
<td>Theoretical Faradays Required</td>
<td>0.338</td>
<td>0.459</td>
<td>0.713</td>
</tr>
<tr>
<td>Current Efficiency</td>
<td>92.8%</td>
<td>98.8%</td>
<td>103.8%</td>
</tr>
</tbody>
</table>
The 103.8% Efficiency obtained for the third period is, of course, not actual. The discrepancy is well within the range of experimental error. The calculation depends upon a small quantity—Gms NaClO₃ Converted during interval—which in turn depends upon the difference between two large quantities. A very small percentage error in calculation of the large quantities will cause a large percentage error in the small quantity.

This work was performed with the help and under the direction of Dr W. N. Lacey.

SUMMARY OF WORK DONE

1. A series of four cells, with graphite anodes and copper cathodes, was set up, and a concentrated brine solution electrolyzed, in an attempt to produce ClO₃⁻. Inadequate insulation of anode leads from the electrolyte was the cause of failure.

2. Using the same apparatus, with better insulation of the anodes and a more strongly acid solution, more success was attained. Chlorine evolution was however very bad, and the formation of a grayish green floculent precipitate of copper hydroxide interfered with the electrolysis.

3. The production of ClO₄⁻ was attempted, using graphite anodes, copper cathodes and a concentrated slightly acid solution of NaClO₃. Mechanical failure of the anodes occurred.
4. Two attempts were made, with ferro-silicon anodes and copper cathodes, to produce $\text{ClO}_4^-$. At first the acid concentration was not high enough to prevent the formation of iron hydroxide. In the second attempt, a more concentrated acid solution kept iron from the anodes in solution. Ferro-silicon withstood the electrolysis fairly well. The $\text{FeSO}_4$ method of analysis for $\text{ClO}_3^-$ did not give accurate results however. Some unknown disturbing element caused failure of the analyses.

5. Nickel anodes were used for $\text{ClO}_4^-$ production after it was found impossible to procure plates of ferro-silicon for building a cell on a semi-industrial scale. Nickel did not withstand the electrolysis at all, being very rapidly disintegrated.

6. Using a single cell, a platinum anode, copper cathodes and a concentrated fairly strongly acid solution of $\text{NaClO}_3$, an attempt was made to get some quantitative results. Cathodic reduction of $\text{ClO}_3^-$ to $\text{Cl}^-$ by nascent hydrogen was found to a small extent. The analytical methods were not sufficiently exact to give very reliable results, but high current efficiency was indicated.
CONCLUSIONS

There is a possibility of developing ferro-silicon into a suitable anode material for the conversion of ClO$_3^-$ to ClO$_4^-$. Some alteration in its composition may be found necessary. For any extensive work in this field, a really satisfactory method for the direct determination of ClO$_4^-$ will have to be developed. The ClO$_3^-$ to ClO$_4^-$ conversion is capable of giving very satisfactory yields.
1. **ANALYSIS FOR CHLORATE ION**  
*(After Treadwell-Hall, Analytical Chemistry, Volume II)*

By means of a pipette, a 10 cc sample is withdrawn from the electrolytic cell and drained into a one liter flask. Dilute up to the mark. Ten cc of this is withdrawn with a pipette, and drained into an Erlenmeyer flask fitted with a two hole stopper and an inlet tube. Carbon dioxide from a Kipp generator is passed in until all air is expelled, when 50 cc of freshly standardized ferrous sulphate is added. Boil gently for 10 minutes remove from the flame and pass in CO₂ immediately until cool. Add 10 cc MnSO₄ solution and 40 cc water. The excess FeSO₄ is then titrated with KMnO₄.

2. **ANALYSIS FOR CHLORIDE ION**  
*(After Treadwell-Hall, Volume II)*

Withdraw a 10 cc sample of the electrolyte, drain into a 250 cc flask, and add 25 cc AgNO₃ solution. Acidify with HNO₃, shake until coagulated, dilute to 250 cc and filter through a dry filter, rejecting the first 10 cc. Of the filtrate, take 50 cc for analysis, add 5 cc ferric alum indicator and 45 cc distilled water. Titrate with KCNS. The AgNO₃ used would be that required to precipitate the Cl⁻ in 2 cc of original electrolyte.
3. **ANALYSIS FOR CHLORIDE ION**
   *(After Treadwell-Hall, Volume II)*

   After the first period of the fifth trial run, all that was left to work on was the 1000 cc dilution from ClO₃⁻ analysis. One hundred cc of this was drained into a 250 cc flask, 25 cc AgNO₃ added, the solution acidified with HNO₃ and the flask well shaken and diluted up to the mark. This was filtered through a dry filter, the first 10 cc rejected, and 100 cc taken for analysis. The excess AgNO₃ was titrated against KCNS, using ferric alum indicator.

4. **ANALYSIS FOR PERCHLORATE ION**
   *(Modified Potassium determination, after Treadwell-Hall, Volume II)*

   Take a 10 cc sample of the electrolyte, drain into an Erlenmeyer flask, add 40 cc distilled water and 10 cc 12 N HCl; add sufficient solid FeSO₄ to reduce all chlorate present. Boil ten minutes and drain into a casserole. Heat to boiling, and treat, drop by drop, with boiling BaCl₂ solution (0.05 M) until no more BaSO₄ forms. Boil gently 15 minutes, and filter into an evaporating dish. Evaporate to dryness on a water bath. Agitate the residue with 50 cc of hot water, filter into an evaporating dish and wash thoroughly, and to filtrate add one gram c.p. KCl. Evaporate to dryness again. Wash the residue repeatedly with small amount of a 2% solution of HClO₄ in 97% alcohol, dry in an oven, and weigh. The residue is KClO₄.
REAGENTS AND STANDARD SOLUTIONS USED,
(After Treadwell-Hall)

1. KMnO\textsubscript{4} 0.1012 N. Approximately 6.4 grams KMnO\textsubscript{4}
were dissolved in two liters of distilled water. After
fourteen days the solution was filtered through an
asbestos filter and standardized against sodium oxalate.

2. AgNO\textsubscript{3} 0.0988 N. Approximately 17 grams c.p.
AgNO\textsubscript{3} were dissolved in one liter of distilled water.
After several days the solution was standardized against
c.p. NaCl using K\textsubscript{2}CrO\textsubscript{4} as indicator.

3. KCNS 1 cc KCNS equivalent to 1.031 cc AgNO\textsubscript{3}. Approximately 10 grams KCNS were dissolved in one liter
of distilled water.

4. FeSO\textsubscript{4}. Approximately 30 grams FeSO\textsubscript{4}.7H\textsubscript{2}O were dis-
solved in 900 cc distilled water. The volume was brought
to one liter by adding concentrated sulphuric acid. This
solution was freshly standardized against KMnO\textsubscript{4} each time
it was used.

5. (NH\textsubscript{4})\textsubscript{2}Fe(SO\textsubscript{4})\textsubscript{2}. Ferric alum indicator, for use
in the chloride determination. A saturated solution
of the salt was made up, and enough HNO\textsubscript{3} added to cause
the disappearance of the brown color.
6. MnSO$_4$ solution. For use as a catalyst in permanganate titrations. Sixty-seven grams of crystallized MnSO$_4$•4H$_2$O were dissolved in 500 cc distilled water, 138 cc phosphoric acid (sp. gr. 1.7) and 130 cc concentrated sulphuric acid (sp. gr. 1.82) added, and the mixture diluted to one liter.