A STUDY

OF THE PRODUCTION OF

SODIUM PERCHLORATE ELECTROLYTICALLY

Thesis

by

Frederic A. Maurer

In partial fulfillment of the requirements

for the degree of Bachelor of Science

in Chemical Engineering.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

1923

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 form-
ed are chlorine and sodium hydroxide, according to the
equation

$$2\ Na^{\bullet} + 2\ Cl^{-} + 2H_2O + 2\underline{F} = Cl_2 + 2\ NaOH + H_2 \quad (1)$$
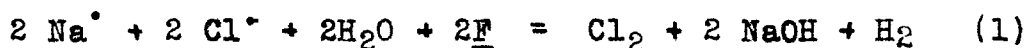
If chlorine and sodium hydroxide are the products desir-
ed, they must be kept separate. If, however, the elec-
trolyte is allowed to mix, a variety of products, depend-
ent upon physical conditions, results from the interac-
tion of the chlorine, sodium hydroxide, and water. The
products that it is 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 hydrox-
ide, the following series of reactions takes place.

$$Cl_2 + OH^- = HOCl + Cl^- \qquad (2)$$

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

$$HOCl + OH^- = OCl^- + H_2O \qquad (3)$$
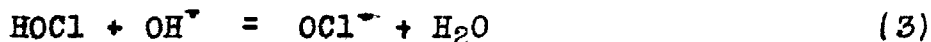
Only when there are at least two equivalents of hydroxide to every mol of chlorine does the following reaction, which is a summation of (1) and (2) hold. This is the usual equation written for the action which takes place.

$$Cl_2 + 2\ NaOH = Na\ Cl + NaOCl + H_2O \qquad (4)$$

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 hypo-

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* 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.

$$2\ HOCl + OCl^- = ClO_3^- + 2\ Cl^- + 2\ H^+ \qquad (5)$$

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.

$$2\ H^+ + 2\ OCl^- = 2\ HOCl \qquad (6)$$

(2) Cathodic reduction of hypochlorite ion
by hydrogen.

$$OCl^- + H_2 = H_2O + Cl^- \qquad (7)$$
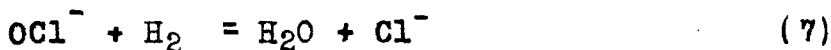
(3) An electrochemical formation of ClO_3^-
which takes place only on the cathode, and not
throughout the solution. *

$$6\ ClO^- + 3\ H_2O + 6\oplus = 2\ ClO_3^- + 4Cl^- + 6H^+ + 1\tfrac{1}{2}O_2 \quad (8)$$
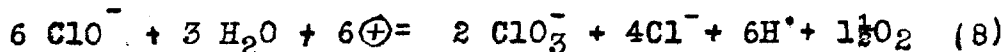
For the production of ClO_3^- from NaCl, we must
consider equations (5) and (8) and see what conditions
are most favorable for each reaction.

Under the conditions we have been considering, i.e.
a neutral or slightly alkaline solution the chemical
formation of ClO_3^- takes place but slightly.   This is
because the excess of hydroxyl ions prevents the form-
ation of free hypochlorous acid.   Hence at the equilib-
rium point;   that is, when hypochlorite ion is being

* Foerster and Muller, Z.f. Elektroch. 8, 667, (1902)

produced and decomposed at the same rate, in a neutral
or alkaline solution the decomposition will be practi-
cally entirely electrochemical.   By equations (1) and
(4) it will be seen that two faradays are required to pro-
duce 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 re-
quired to decompose the hypochlorite thus produced, forming
two mols of ClO_3^-.   If the production of ClO_3^- 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_3^-.   Since,
by the chemical formation of ClO_3^- (Eq. 5) no electrical
energy is required for the decomposition of OCl^-, all the
current being employed in the production of OCl^-, the elec-
trochemical formation of ClO_3^- can, at its very best only
attain a current efficiency of 66.7%.[*]

As has been said, in alkaline solution the chem-
ical formation of ClO_3^- is very slow indeed, while after
hypochlorite ion concentration has reached its limiting
value, all the current is engaged in producing and de-
composing OCl^-.   In acid solution however, the chemical
formation of ClO_3^- is by far predominant.   The excess of

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[*] Thompson, "Applied Electrochemistry" p 90. Macmillan 1914.

$H^\bullet$ causes the formation of unionized HOCl (Eq. 6).
The HOCl thus formed reacts with OCl^- to form ClO_3^-.
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 hypochlor-
ite present be added, the hypochlorite will be complete-
ly oxidized to chlorate.   On further electrolyzing the
solution, more hypochlorite will be produced, and the
addition of more acid will cause its oxidation to chlor-
ate. *   It is necessary to keep adding small amounts of
acid continuously because acid is decomposed by the cur-
rent, 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 chlor-
ide solution with current efficiencies of over 90%.   The
best conditions are (1) high temperature, about 70 de-
grees C #, (2) suitable stirring of the electrolyte, (3)
high anodic current density and (4) high initial sodium
chloride concentration.

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* Foerster and Muller, Z.f. Elektroch. <u>8</u>, 13, (1902)

Allmand, "Applied Electrochemistry", p 338,
        Longmans, Green and Co. (1912)

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 ôf 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,[*]

$$2\ ClO_3^- + H_2O + 2\ \oplus\ =\ HClO_4 + HClO_2 + \tfrac{1}{2}O_2 \qquad (9)$$
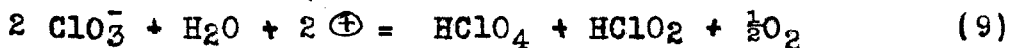
The oxygen produced immediately oxidizes the chlorous acid back to chloric acid

$$HClO_2 + \tfrac{1}{2}O_2\ \bullet\ HClO_3 \qquad (10)$$

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,

[*] Oechsli, Z.f. Elektroch 9, 807, (1903)

[#] Allmand, "Applied Electrochemistry" p 402

and a good circulation is maintained.   An anodic cur-

rent density of about 8 amp./sq. decimeter, which is

fairly high, is maintained. #

EXPERIMENTAL WORK

In view of existing theory on the formation of per-

chlorate electrolytically, the experimental work was

planned to the end of producing perchlorate by the two

stage process.   It was planned to start with a concentra-

ted 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 redis-

solved.   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 chlor-

ate 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 plat-
inum, platinum-irridium foil, hard artificial carbon,
graphite, Fe_3O_4, and carborundum. Sheet copper was the
material selected for cathode construction. Finding an
anode material was not quite so simple, but some 3" graph-
ite 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 intermed-
iate 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 solu-
tion 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 dis-
tance apart of 3.1 cm. One anode was suspended midway

GENERAL ARRANGEMENT

FIRST TRIAL RUN ON NaCl

I II III IV

G   A

ANODES   CATHODES

8mm   1.6 mm

76cm   9.5cm

2.8 mm D
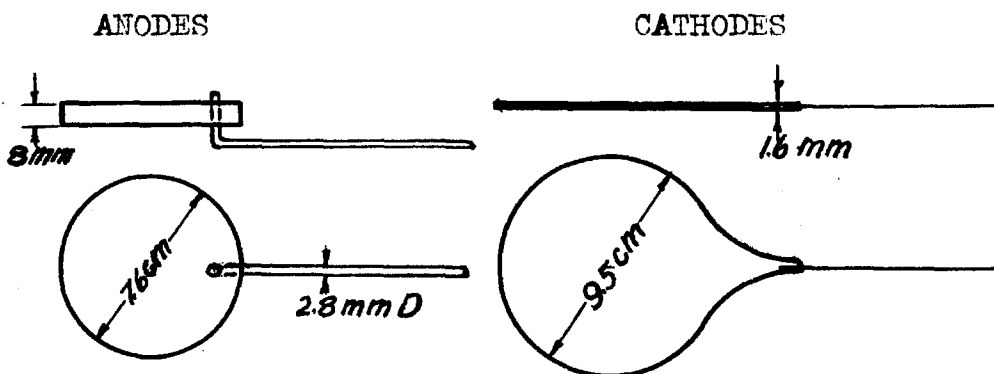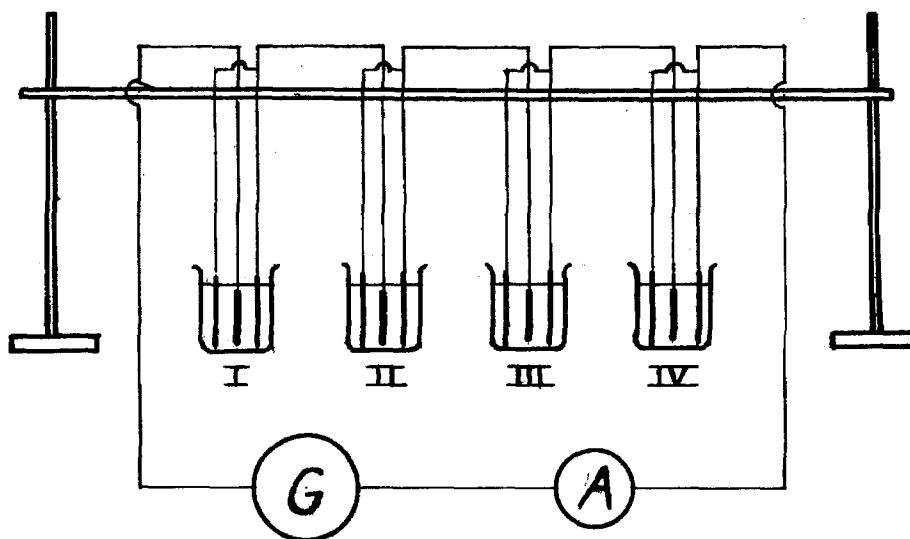
SECOND TRIAL RUN ON NaCl

CHANGED ANODE ARRANGEMENT

Khotinsky
seal   Glass tube
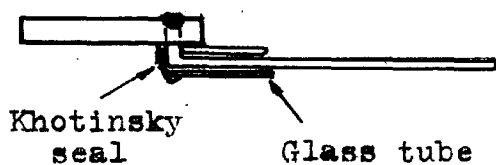
between the two cathodes. The wiring was so arranged
that each face of the anode was active--an arrangement
which doubled the capacity of a single cell, or gave the
effect of two cells in parallel. The anodes were orig-
inally graphite crucible covers 7.6 cm in diameter.
These were reworked to flat disks. 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 junc-
tion was then thoroughly coated over with ceresin 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 satur-
ated brine solution, 2 cc dilute HCl and one gram of
Na_2CrO_4. The purpose of the Na_2CrO_4 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 $CrO_4^=$ to $Cr^{···}$ 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.

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* Zeitsch, Elektrochem, $\underline{5}$, 469 (1899); $\underline{7}$, 398,(1901);
$\underline{8}$, 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 noticable 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 nec-
essitated stopping the run.   Examination showed that, prob-
ably due to the heat generated, the ceresin 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 Na_2CrO_4. 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 N 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 cur-
rent 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 circum-
ference.   The copper lead wire was wrapped through the
hole several times, then the wraps were soldered for rig-
idity 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 en-
closed 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 ap-
pearing in the electrolyte, the run was stopped. A sum-
mary follows:

	40 minute period		98 minute period	Av. for 138 minutes
Av. I	3.09	Amp.	2.84	2.91
Av. E	5	Volts	4.7	4.8
Av. T	9	Degrees C	9.7	9.5

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_2SO_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 N 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 NaClO$_3$

A solution of NaClO$_3$ and H$_2$SO$_4$ was made up in which the NaClO$_3$ 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.

Average temperature	13.2 degrees C
Temperature at start	9
Average current	3.08 Amp.
Average voltage (single cell)	4.68 Volts

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 so 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 $\frac{1}{4}$". 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 ClO_3^- (Appendix A,1) at the start and at the end of the run. If ClO_3^- were oxidized to ClO_4^- there would be a diminution of ClO_3^-, and in this way the amount of ClO_4^- formed could be determined. But, by the analysis, instead of a decrease in ClO_3^-, there was an increase. Either ClO_3^- was being produced from some material not thought to be present, or through faulty technique some $FeSO_4$ was being oxidized by the air, which would give high results. If ClO_3^- were being produced, it would be from Cl^- and since technical sodium chlorate was used in the cells, there would most probably be Cl^- present. Several comparison tests however, showed that, per gram of sodium chlorate, there was only one milligram of Cl^-. Even if this were changed to ClO_3^-, with so much 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 ClO_3^- was adopted was because there was no simple analysis known for 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 at least attempt a direct determination for ClO_4^-.   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 ClO_4^- was abandoned because:

(1)   The excess $FeSO_4$ necessarily introduced to reduce ClO_3^- to Cl^- precipitated out as iron hydroxide in subsequent evaporations.

(2)   The quite considerable amount of $SO_4^=$ present in the electrolyte necessitated a tremendous addition to $BaCl_2$.

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 $NaClO_3$

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 $\frac{3}{4}$ 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 $\underline{N}$ in

H_2SO_4 and contained 0.573 gm $NaClO_3$/cc.   In each cell

was 500 cc of this electrolyte.   The anodes were lower-

ed 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 prac-

tically 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 anal-

ysis of the electrolyte for $NaClO_3$ showed 0.562 gm $NaClO_3$/

cc.   Here at last the analysis showed a decrease in ClO_3^-

rather than an increase.   Had time permitted an inter-

esting 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 A

Time in sec's	Av. I	Av. E	Coulombs	F
5880	3.76 Amp.	9.5 Volts	22,120	0.229

TABLE B

Vol. of Elec.		$NaClO_3$ Conc.		Total $NaClO_3$		$NaClO_3$	$NaClO_4$
Beg.	End	Beg.	End	Beg.	End	Decrease	Prod.
500 cc	498	0.573 gm/cc	0.562	286.5	279.5	7 gm	8.04 gm

TABLE C

$NaClO_4$ Prod.	Theoretical F		F	Current Eff.	
8.04 gm	$\frac{2 \times 8.04}{122.5}$,	0.1314	0.229	$\frac{0.1314}{0.229}$,	57.4%

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 $NaClO_3$ made.

FIFTH TRIAL RUN ON $NaClO_3$

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 $NaClO_3$ was made up which was approximately 0.25 N in H_2SO_4 and contained 0.597

gm $NaClO_3$/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 appara-
tus 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 sam-
ple 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 effic-
iencies, on the basis of these analyses, over 100% cur-
rent 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 be-
ing 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 concen-
tration of Cl^- was found. A correction was applied on
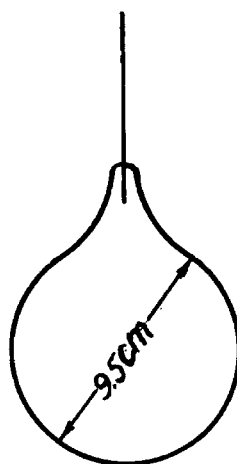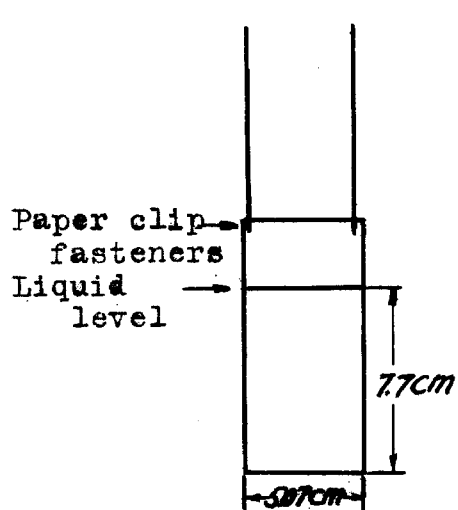the basis of these analyses to the calculations before

FIFTH TRIAL RUN ON NaClO₃

GENERAL ARRANGEMENT

ANODE   CATHODES

Paper clip
  fasteners
Liquid
  level

7.7cm

5.07cm

9.5cm
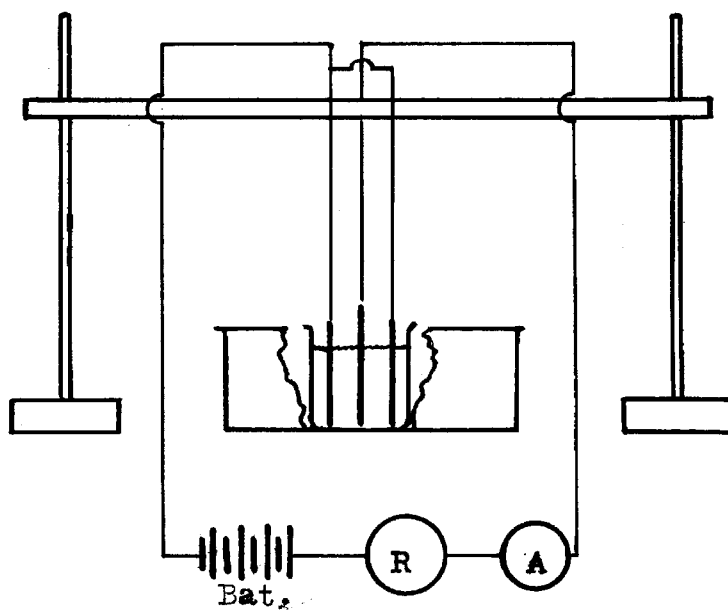
mentioned.   Furthermore, it was decided to pass more current into the same electrolyte, analyze, and calculate results to see what the trend would be.   After four hours the run was stopped.   There was a fine white precipitate, in the bottom of the cell of $NaClO_4$.   The following tables give a summary of the whole experiment.

CORRECTION FOR ClO_3^- REDUCED TO Cl^-

	Period			
	1		2	3
	Anal.	Ass.*		
$AgNO_3$/ 2 cc elec.	1.90	1.060	1.230	1,400
$AgNO_3$/2 cc orig. solution	0.191	0.191	0.191	0.191
$AgNO_3$ to ppt. Cl^- formed	1.709	0.869	1.039	1.209
$AgNO_3$ to ppt. Cl^-, per cc	0.855	0.435	0.520	0.605
Gm NaCl/cc elec.	0.00495	0.00252	0.00301	0.00351
Corr.amt. $NaClO_3$ reduced/cc	0.00901	0.00458	0.00548	0.00637

   * Value calculated by assuming equal difference be-
      tween 1 and 2, and 2 and 3.   This value used in
      the following caluclations.

   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 $AgNO_3$ used to precipitate Cl^- already in the water, would be greatly increased.

CALCULATION OF RESULTS

	Period		
	1	2	3
Time in Seconds	10,500	10,800	14,400
Average current	3.35	4.15	4.59
Average Voltage	3.73	4.26	4.55
Coulombs	35,180	44,800	66,200
Actual Farradays	0.3645	0.4650	0.6865
Volume in cell at Beginning	755	740	662
Volume in cell at End	750	735	656
$NaClO_3$ conc. at Beginning	0.597	0.573	0.543
$NaClO_3$ conc. at End	0.573	0.543	0.490
$NaClO_3$ red./cc at Beginning	------	0.00458	0.00548
$NaClO_3$ red./cc at End	0.00458	0.00548	0.00637
$NaClO_3$ conc. Total at Beginning	0.597	0.578	0.548
$NaClO_3$ conc. Total, at End	0.578	0.548	0.496
Total grams $NaClO_3$ at Beginning	451	427.5	363
Total grams $NaClO_3$ at End	433	403	325
Grams $NaClO_3$ Converted during Int.	18	24.5	38
Grams $NaClO_4$ Produced in Int.	20.7	28.2	43.7
Theoretical Farradays Required	0.338	0.459	0.713
Current Efficiency	92.8%	98.8%	103.8%

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 $NaClO_3$ 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 ClO_3^-. 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 flocculent precipitate of copper hydroxide interfered with the electrolysis.

3. The production of ClO_4^- was attempted, using graphite anodes, copper cathodes and a concentrated slightly acid solution of $NaClO_3$. Mechanical failure of the anodes occurred.

4. Two attempts were made, with ferro-silicon anodes and copper cathodes, to produce 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 $FeSO_4$ method of analysis for ClO_3^- did not give accurate results however. Some unknown disturbing element caused failure of the analyses.

5. Nickel anodes were used for 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 $NaClO_3$, an attempt was made to get some quantitative results. Cathodic reduction of ClO_3 to 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..

APPENDIX A

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 dioxid 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 CO_2 immediately until
cool.   Add 10 cc $MnSO_4$ solution and 40 cc water.   The
excess $FeSO_4$ is then titrated with $KMnO_4$.

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 $AgNO_3$ solution.   Acid-
ify with HNO_3, 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 $AgNO_3$ used would be that re-
quired to precipitate the Cl^- in 2 cc of original elec-
trolyte.

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 ClO_3^- analysis. One hundred cc of this was drained into a 250 cc flask, 25 cc $AgNO_3$ added, the solution acidified with HNO_3 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 $AgNO_3$ 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 $\underline{N}$ HCl; add sufficient solid $FeSO_4$ to reduce all chlorate present. Boil ten minutes and drain into a casserole. Heat to boiling, and treat, drop by drop, with boiling $BaCl_2$ solution (0.05 $\underline{N}$) until no more $BaSO_4$ 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 $HClO_4$ in 97% alcohol, dry in an oven, and weigh. The residue is $KClO_4$.

APPENDIX B

REAGENTS AND STANDARD SOLUTIONS USED,
(After Treadwell-Hall)

1. $KMnO_4$ 0.1012 <u>N</u>.   Approximately 6.4 grams $KMnO_4$ 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. $AgNO_3$ 0.0988 <u>N</u>.   Approximately 17 grams c.p. $AgNO_3$ were dissolved in one liter of distilled water. After several days the solution was standardized against c.p. NaCl using K_2CrO_4 as indicator.

3.   KCNS 1 cc KCNS equivalent to 1.031 cc $AgNO_3$.   Approximately 10 grams KCNS were dissolved in one liter of distilled water.

4. $FeSO_4$.   Approximately 30 grams $FeSO_4 \cdot 7H_2O$ were dissolved in 900 cc distilled water.   The volume was brought to one liter by adding concentrated sulphuric acid.   This solution was freshly standardized against $KMnO_4$ each time it was used.

5. $(NH_4)_2Fe(SO_4)_2$.   Ferric alum indicator, for use in the chloride determination.   A saturated solution of the salt was made up, and enough HNO_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 $MnSO_4 \cdot 4H_2O$ 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.