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BY

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THE ELECTROLYTIC REDUCTION OF SODIUM
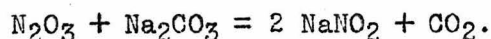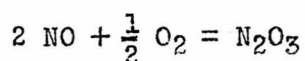
NITRATE TO SODIUM NITRITE

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THE ELECTROLYTIC REDUCTION OF SODIUM NITRATE

TO SODIUM NITRITE

In the commercial absorption by a sodium carbonate solution of the nitric oxide formed by the electric arc passing through air, approximately 95 per cent of the gas is converted into sodium nitrite according to the equations,

$$2\ NO + \tfrac{1}{2}\ O_2 = N_2O_3$$

$$N_2O_3 + Na_2CO_3 = 2\ NaNO_2 + CO_2.$$

The remaining 5 per cent of the gas is further oxidized forming nitrogen tetroxide, which by absorption forms sodium nitrate, as;

$$4\ NO + 3\ O_2 + 2\ Na_2CO_3 = 4\ NaNO_3 + 2\ CO_2.$$
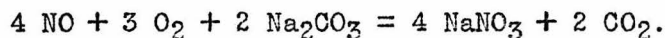
The solution coming from the absorption chambers therefore contains approximately 95 parts of sodium nitrite to 5 of sodium nitrate. Pure sodium nitrite is obtained from this liquor by evaporation and crystallization, the final solution containing about equal amounts of nitrite and nitrate. It has not yet proved profitable to separate more nitrite from this liquor, consequently it is evaporated to dryness and the residue placed in storage. At present there is no demand for this nitrite-nitrate mixture. Since sodium nitrite is more valuable than the nitrate, this investigation was undertaken with the object of discovering a commercial electrolytic method for reducing the nitrate in this mixture to nitrite.

Very little literature pertaining to this subject is available. Muller and Spitzer (Ber. **38**, 1190; 1905) give a short account of their work on the reduction of nitrate to nitrite. These investigators obtained a maximum current efficiency of 80 per cent when electrolyzing a solution containing 24 grams of sodium nitrate and 30 grams of sodium nitrite per 100 cc. of solution. The percentage of nitrate converted into nitrite was 5.6 per cent. Sponge copper was used as a cathode, sheet copper as the anode, and a small quantity of copper in solution as a depolarizing agent. They concluded that the production of pure nitrite in this manner was impossible.

It was decided in the present investigation first to study the conditions required for reducing a solution of pure sodium nitrate to sodium nitrite, and perhaps later to use a solution containing equal quantities of nitrite and nitrate.

Preliminary experiments indicated that nitrite was formed at the cathode and nitric acid at the anode. The cathode reaction may be represented by the equation

$$NO_3^- + H_2O + 2\ \Theta = NO_2^- + 2\ OH^-,$$
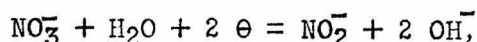
and the anode reaction by

$$H_2O + 2\ \oplus = 2\ H^+ + \frac{1}{2}\ O_2.$$
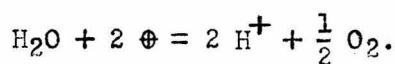
The nitric acid thus formed at the anode reacted with the electrode, causing trouble. This introduced another problem, namely that of finding a material, sufficiently inexpensive for commercial work, which is not attacked by nitric acid. Malleable and cast iron, steel, aluminum, copper, nichrome, carbon arc-light rods, carborundum, and silicon were used with but little success. This problem was temporarily eliminated by using a platinum anode and not attacked later.

According to Muller and Spitzer, sponge copper is the best cathode material. Experiments confirmed their statement and indicated that the reduction did not depend on the form of copper but upon the area of the electrode surface. A small current density favored nitrite formation while a large current density caused the reduction to proceed to ammonia. Thru out these experiments the cathode consisted of number 40 copper gauze. Current densities are therefore given in amperes per square centimeter of gauze.

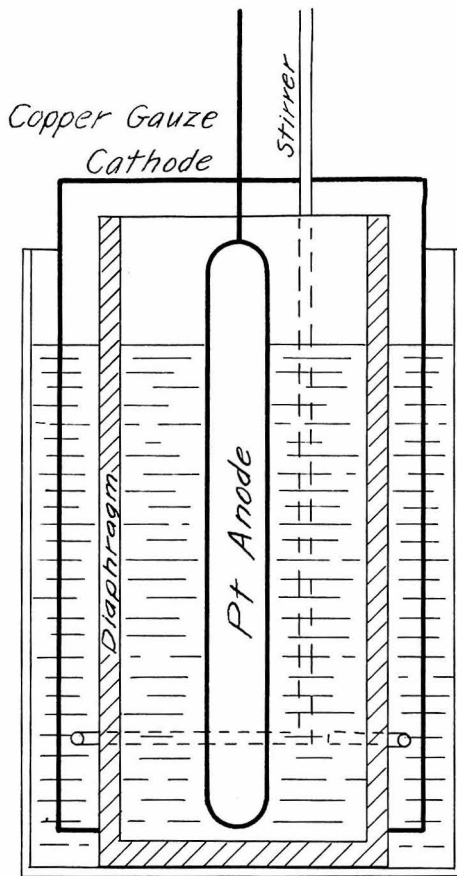Following are diagrams of the cells:

Copper Gauze Cathode

Stirrer

Diaphragm

Pt Anode

Fig. 1.

Solution Intake

Pt Anode
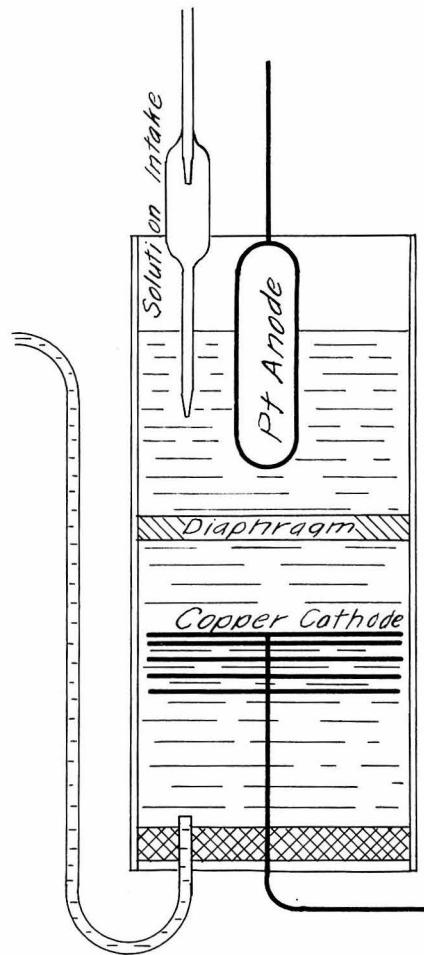
Diaphragm

Copper Cathode

Fig. 2.

It is evident that the cathode solution containing the nitrite should not be mixed with the anode solution since the anode reaction is an oxidizing one and would oxidize the nitrite to nitrate. Fig. 1 is a cell using a diaphragm and Fig. 2 one in which the solution is caused to flow from the anode to the cathode. Stirring was accomplished by means of a ring paddle moving between the diaphragm and the cathode in the first cell while the flowing of the solution regulated the contact with the electrodes in the second type. The paddle arrangement has disadvantages in that the amount of stirring was unknown and hard to duplicate.

In using the cell as shown in Fig. 1, 100 cc. of a 5 molal sodium nitrate solution were put in contact with the cathode and anode. The stirrer and then the electolysis was started. By knowing the amount of sodium nitrate in the cell and the current, the duration of each run was calculated. At the end of each run, a 10 cc. sample of the cathode solution was analyzed for nitrite. The 10 cc. sample was diluted to 500 cc. and added from a burette to 25 cc. of acidulated N 10 potassium permanganate which had been previously warmed to about 50 deg. C. The potassium permanganate was used as the indicator. As the formation of sodium nitrite was the object of the experiment, the nitrite determination was the only one made.

The following data were obtained:

Exp. No.	Amp.	Current density Amp sq.cm.	Faradays Used	Equiv. $NaNO_2$ Formed	Current Eff.	Volts
1.	8.0	0.026	0.273	0.074	0.27	24-12
2.	3.0	0.008	0.077	0.039	0.50	10
3.	1.0	0.003	0.261	0.257	0.98	10-5
4.	0.8	0.002	0.260	0.235	0.90	16-10
5.	0.7	0.002	0.457	0.385	0.84	17-11

When using the cell in Fig. 2, the flow of the solution was always greater than the migration of the nitrate radical. The intention was to free the cathode of nitrite ions as fast as they were formed and to allow as little polarization at the anode as possible. The solution was passed from the anode thru the cathode at a given rate. The duration of each experiment was such that the cell delivered a constant concentration of sodium nitrite. The nitrite was determined in a manner similar to that formed in the cell in Fig. 1.

Following are the data obtained:

Exp. No.	Amp.	Rate of Flow Cc. min.	Faradays Used	Equiv. $NaNO_2$ Formed	Current Eff.	Conversion	Volts
6.	4.0	4.9	0.051	0.011	0.224	0.011	6.7
7.	4.0	4.5	0.056	0.015	0.268	0.015	6.6

Exp. No.	Amp.	Rate of Flow Cc. min.	Faradays Used	Equiv. $NaNO_2$ Formed	Current Eff.	Conversion	Volts
8.	4.0	2.1	0.120	0.021	0.176	0.021	8.0
9.	2.7	4.8	0.027	0.018	0.665	0.018	8.0
10.	2.0	3.1	0.040	0.023	0.565	0.023	8.0
11.	2.0	0.9	0.100	0.028	0.282	0.028	6.0
12.	0.5	1.5	0.022	0.013	0.590	0.013	5.0
13.	0.5	1.3	0.024	0.017	0.710	0.017	5.0

The current efficiencies of the first cell were very satis-
factory when small current densities were used. The conversion of
nitrate to nitrite was not determined definitely but was estimated to
be less than 5 per cent. The conversion in the second type of cell
also was very low. An increase in the current density caused a
decrease in the current efficiency and for any current density, a
decrease in the rate of flow had the same effect. The most disappointing
result is not so much the low current efficiency found but is this low
efficiency with the small percentage of nitrate converted into nitrite.

These experiments do not indicate a satisfactory commercial
solution of the problem, but nevertheless some general conclusions may
be drawn. Sodium nitrate in solution may be at least partially reduced
electrolytically to either sodium nitrite or ammonia. The formation of
nitrite takes place when a small current density is employed, while the
formation of ammonia results from the use of a larger current density.