

EXPERIMENTS ON THE MANUFACTURE OF CHLORATES AND HYPOCHLORITES WITH A VIEW TO HIGH CURRENT EFFICIENCY.

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The following experiments were undertaken with the object of finding methods by which to increase the current efficiency in the manufacture of chlorate and hypochlorite electrolytically. The addition of alkali chromate has been found to increase the efficiency considerably and this method has been patented. It is used effectively in the manufacture of chlorate, but it is stated to be of no service in the manufacture of hypochlorite for bleaching purposes, owing to its strong color.

In these experiments cathodes and anodes of various kinds were used and various substances which would cause a deposit to be formed on the cathode were added as well.

The first experiment was an attempt to use deposited lead peroxide as anode, with the idea of finding, if possible, a permanent cheap anode. The peroxide was deposited on a carbon rod in the following manner. The rod was dipped into a 50 percent. caustic potash solution saturated with litharge, and made the anode, while a piece of sheet lead bent around it served as cathode. The current was passed for eight hours with a current density of 6 amperes per square foot. The rod was then taken out and washed and found to be covered with a fine hard coating of lead peroxide. The temperature of the caustic potash solution during the deposition was kept at 26°.

The rod was then used as anode in a 20 percent. potassium chloride solution, containing 2 percent. caustic potash. The cathode consisted of six small copper wires hung down into the solution from the sides of the beaker. The current was started with an anode current density of 24 amperes per square foot, and at once the peroxide began to fall off, as a fine brown powder. Temperature 26°. The solution was then heated to 60° and the current passed as before. At the end of three hours no signs of wear could be seen, but after running all night the surface was pitted and broken, though very little peroxide fell off. The temperature fell to 45° during the night.

The peroxide was deposited for other experiments at various temperatures and current densities and used as anode in the potassium chloride solution at different temperatures and current densities, but in every case the deposit peeled off in from five to ten hours. Of great importance is the proportion of caustic potash in the solution. It was found that with 1 percent. caustic potash the deposit came off rapidly, less rapidly with 2 percent. and hardly at all with 3 percent. It seems probable that with a temperature of 60° and a little higher percentage of caustic potash the lead

peroxide coating would remain firm and insure a permanent anode. The efficiency of chlorate and hypochlorite formation with this anode is practically zero, which seems remarkable.

Several determinations were made with platinum plates for electrodes, with the addition of various substances. We thought it probable that there were other materials than chromates which would prevent reduction at the cathode, especially compounds of those metals which might be partly reduced at the cathode to lower oxides or hydroxides, but not to metal. The deposition of spongy metal on the cathode would be worse than useless.

In these determinations a 25 percent. solution of potassium chloride was used, containing 1.5 percent. caustic potash and 3 percent. potassium chlorate, 75 cc. being used for each experiment. The current was measured in ampere hours by taking the reading of the ammeter each minute. The amount of chlorate produced was determined by taking a sample of the solution after electrolysis and boiling with a standard solution of ferrous sulphate and sulphuric acid and titrating with permanganate. The chlorate and hypochlorite were calculated from the amount of ferrous iron oxidized.

The figures for the efficiency found are as follows: In this first set the current was passed for from 35 to 45 minutes, the ampere hours averaging about three. Current density 0.25 to 0.4 amps. per sq. cm.

Addition	Temperature	Efficiency Per Cent
None	50—62°	43.2
Trace Sodium Tungstate	50—66°	55.1
“ Molybdic Acid	52—65°	55.2
Sodium Chromate (small amt)	55—60°	69.3
0.6% Molybdic Acid	62—67°	51.2
0.15% Thorium Nitrate	28—61°	59.2
0.15% Cerium Chloride	28—61°	48.0
0.15% Uranium Acetate	32—61°	58.5
Trace Vanadium	28—61°	47.4
0.15% Zirconium Chloride	43—63°	49.0

It can be seen from the above figures that addition of the salts of some of these metals increases the efficiency to a considerable extent, though none works as well as sodium chromate.

We had an idea that the harder the cathode used, the less might be the cathodic reduction. Molybdenum and tungsten under some conditions yield very hard suboxides, called bronzes, and it was thought films of these substances might form on the cathode. On account of the large proportion of caustic potash present the maximum yield would probably not be over that given by the solution to which chromate had been added. These experiments are rather qualitative than quantitative in scope.

Other cathodes were tried, our idea being to try all the harder cathodes available. It has been suggested that hardness and softness of cathodes is an important matter¹ and we pursued that idea to some extent in this work. For comparison the efficiency with a platinum wire was about 43 percent., and with platinum wire and chromate added to the solution, about 69 percent., which is about the maximum possible with the amount of caustic potash used. A hard steel razor used as cathode gave a good result, but is of doubtful practical value owing to the difficulty of keeping the surface bright and clean.

Cathodes of magnesium and aluminum were tried. The idea of using magnesium was that it would be always covered with a film of oxide or hydroxide, which would act as a diaphragm and prevent reduction. The idea is shown to be sound and we did further work with the magnesium cathode in making chlorate and hypochlorite.

Aluminum, which, it was thought, would also give an oxide coating was tried, but did not give a good result owing to its rapid solution in the alkali liberated at the cathode.

In these experiments, the anode was platinum wire. From three to four ampere hours were passed in each experiment, using 75 cc. of a 25 percent. solution of potassium chloride containing 1.5 percent. caustic potash and 2.0 percent. potassium chlorate.

Cathode	Temperature	Efficiency Per Cent	Notes
Iron Wire.....	60	57.0	High current density
Iron wire previously somewhat corroded..	59—60	15.4	
Magnesium and platinum wires fastened together }	34—60	57.0	
Magnesium Wire.....	34—60	65.0	
Steel Razor (polished).....	36—60	62.3	
“ “ with addition of little calcium chloride to the solution }	52—60	55.4	
Nickel Plate.....	60	59.0	

The nickel plate worked fairly well, but was blackened in the solution in a short time.

As magnesium wire gave an efficiency nearly equal to that produced by the addition of alkali chromate to the solution, further experiments were carried on with it on a larger scale.

300 cc. of a 25 percent. solution of potassium chloride in a 400 cc. beaker were used in these experiments. The ampere hours passed were measured with a lead voltameter. The anode was graphite. The E. M. F. 5 volts. Current density at cathode 0.17 amps. per sq. cm.

¹ Betts, Trans. Am. Electrochem. Soc. 7, 79 (1905).

Time	Temp.	Ampere hrs.	Theor. KClO ₃ grams	KClO ₃ made grams	Efficiency Per Cent
Start	42°	0	0	0	0
1 hr.	52°	1.6	1.2	1.08	90
2 hrs.	65°	3.32	2.5	1.83	73
4 hrs.	60°	6.5	5.0	2.95	60
6 hrs.	56°	9.2	6.9	4.2	61
8 hrs.	58°	11.3	8.5	4.9	58

A moderate current was allowed to pass for 18 hours and at the end of that time the wire was found to have lost 50 percent. of the magnesium, or about 0.096 grams, equal to 1 part magnesium lost per 50 parts chlorate made.

If magnesium was not too expensive, this method would probably be economical in the manufacture of chlorate, provided a little hydrochloric acid was added from time to time to keep the efficiency up.

The magnesium cathode was also tried in making hypochlorite where it also gave a high efficiency and was less attacked. 200 cc. of a 25 percent. sodium chloride solution was used in a 400 cc. beaker, with a graphite anode. The temperature was kept between 15 and 20°. The ampere hours passed were measured with a lead voltameter. Current density at the cathode 0.11 amps. per sq. cm.

Time	Amp.	Volts	Amp. hrs.	Theoretical Chlorine Grams	Chlorine made grams	Efficiency Per Cent
Start	1.3	4.7	0	0	0	0
1 hr.	1.32	1.56	1.6	100
2 hrs.	2.72	3.5	3.16	90
4 hrs.	5.6	7.0	5.73	82
6 hrs.	8.0	9.3	7.5	81
8 hrs.	9.2	11.5	8.48	74

After this run the magnesium wire lost 2½ percent. or 0.005 grs. of the metal.

Another run was made with 300 cc. of a 5 percent. salt solution. The temperature was kept below 20°. The surface of the wire was 20 sq. cm. The current density at the cathode 0.04 amp. per sq. cm.

Time	Amp.	Volts	Amp. hrs.	Theoretical Chlorine Grams	Chlorine made grams	Efficiency Per Cent
Start	.8	5.4	0	0	0	0
1 hr.	0.6	0.79	0.76	96
2 hrs.	1.42	1.87	1.66	89
4 hrs.	2.15	2.84	2.55	89
5 hrs.	3.15	4.16	3.43	82
6.5 hrs.	3.81	5.03	4.26	84
9 hrs.	4.45	5.87	4.4	75

At the end of nine hours the magnesium had lost 10 percent., or 0.02 grams.

An experiment was tried using both electrodes of carbon with a 12½ percent. salt solution. The efficiency dropped off very rapidly. Electrodes each 1.5 cm. in diameter and 19 cm. deep in solution. Current density .03 amp. per sq. cm.

Time	Amp.	Volts	Amp. hrs.	Theoretical Chlorine Grams	Chlorine made grams	Efficiency Per Cent	Temp.
Start	2.5	5.1	0	0	0	0	14
14 min.	2.5	5.1	0.54	0.71	0.666	94	14
30 min.	2.6	4.2	1.42	1.97	1.425	75	14

A run was made for six hours using three beakers each containing 300 cc. The current strength was 2.0 amperes. E. M. F. 5.4 volts. Temperature 15°. A 12½ percent. salt solution was used. Current density in first cell at the anodes was 0.04 amp. per sq. cm. and 0.02 amp. per sq. cm. at the cathode. In cells 2 and 3 the current density at the anodes was 0.04 amp. per sq. cm. and at the cathode 0.12 amp. per sq. cm.

Every 20 minutes 50 cc. were taken from the last beaker and put into a receptacle, 50 cc. from the second transferred to the third, 50 cc. from the first to the second, and 50 cc. of fresh solution put into the first. At the end of six hours the concentration in the receptacle was about 20 grs. active chlorine per liter.

The wire in the first cell was all broken into small pieces. The wire in the second cell had lost 13 percent. or 0.084 grams. The wire in the third cell had lost 7 percent. or 0.045 grams. In order to avoid the high loss of magnesium in the first cell in which the percent. of caustic soda is very low, the carbon cathode could be used, as it gives a high efficiency in the small concentration of active chlorine, and would not be badly attacked.

It was found to be easy to decompose one-third of the salt in 12½ to 25 percent. brines and still get a respectable current yield of from 60 to 70 percent. The loss of magnesium for 100 pounds of active chlorine varied from 0.06 to 0.5 pounds which would make a cost of from \$0.018 to \$0.15 for magnesium figuring the cost at \$0.30 per pound.

This result appears to be much better than present results with carbon cathodes.

Two further experiments were made using graphite electrodes in the first cell and graphite anodes and magnesium cathodes in the second and third cells. A 12½ percent. salt solution was used and allowed to run through the cells at a rate of 200 to 250 cc. per hour. The cells were wooden and were each 4.7" long, 1.4" wide and 3.8" deep. The temperature in these experiments was kept below 25°.

EXPERIMENT 1.

Cell	Amp.	Volts	C. D. Anode amps. per sq. cm.	C. D. Cathode amps. per sq. cm.	Cathode
1	3.6	4.5	0.06	0.03	Graphite
2	3.6	6.0	0.06	0.17	Magnesium
3	3.6	6.0	0.06	0.17	"
Amp. Hrs.	Theoretical Cl. Chlorine grams	Chlorine made grams	Chlorine per liter	Efficiency	
60	79	50.7	26.6	64%	
Loss of Magnesium					
Weight before	grams		Cell w 2	Cell 3	
" after	"		0.7	0.7	
" after	"		0.62	0.675	
Loss			0.08	11.5%	0.025 3.6%

EXPERIMENT 2.

Cell	Amp.	Volts	C. D. Anode amps. per sq. cm.	C. D. Cathode amps. per sq. cm.	Cathode
1	4.5	5.5	0.12	0.24	Graphite
2	4.0	6.0	0.064	0.19	Magnesium
3	4.5	6.5	0.074	0.21	"
Amp. Hrs.	Theoretical Chlorine grams	Chlorine made grams	Chlorine per liter	Efficiency	
62	82.4	48.2	25.4	58.5%	
Loss of Magnesium					
Weight of wire before			Cell 2	Cell 3	
" " " after			0.75	0.75	
" " " after			0.675	0.724	
Loss and per cent.			0.075	10%	0.026 3%

Power required for 100 lbs. chlorine is 450 H. P. hours.

Loss of magnesium for 100 lbs. chlorine is 1/5 lb. or less.

We also tried the addition of traces of caustic soda to the salt solutions, before electrolysis, and found this had a beneficial action in reducing the loss of magnesium from the cathode.

The great advantage in the use of the magnesium cathode would seem to be not only the lower power cost, but that a large quantity of the salt can be converted, it being possible to convert from 35 to 50 percent. of the salt with an efficiency of 60 percent. If more cells were used with magnesium cathodes, the efficiency would be increased owing to the decrease in the proportion of graphite used as cathode.

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THE DETERMINATION OF MELTING POINTS AT LOW TEMPERATURES. II.

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Further melting point determinations have been made by means of the method previously described¹. The ice point was taken, and could al-

¹ J. Chem. Soc. 87, 1037-42 (1905).