

*Large-scale preparation of perchlorates directly from sodium chloride**

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Based on the optimum conditions arrived at in the laboratory experiments, large-scale trials have been carried out for the preparation of sodium perchlorate by the direct oxidation of sodium chloride in a single step using a graphite substrate lead dioxide anode.

Two cells of 75 A capacity and one 400 A cell were run continuously at an anode current density of 20 A/dm² and a temperature of 45°–50°C. The cell performance with these anodes is given.

Potassium and ammonium perchlorates formed by double decomposing the sodium perchlorate obtained by this method with the respective chlorides are pure and conform to the stringent specifications.

Introduction

With the increasing research activities in rocketry in India, a large demand for ammonium perchlorate is envisaged in the near future. Sodium perchlorate, which is the starting material for both potassium and ammonium perchlorates, has so far been prepared in two stages, the first stage being the oxidation of chloride to chlorate using graphite [1] or magnetite [2] or lead dioxide [3–5] anodes and the second stage being the oxidation of chlorate to perchlorate using platinum [6–9] or lead dioxide anodes [3, 10–14]. In between these two stages, the electrolyte obtained in the first stage has to be processed to isolate the sodium chlorate and recover the unconverted sodium chloride. Sugino [3] reported the direct oxidation of chloride to perchlorate using a lead dioxide anode, avoiding the intermediate processing of liquors, but there were two discrete electrochemical stages wherein the temperatures of electrolysis were different while other operating conditions remained the same. Oxidation of

chloride to chlorate was carried out at 60°–65°C and when chlorate formation was almost complete the temperature was lowered to 30°–35°C and a small amount of sodium fluoride (2 g/l) was added.

Bravo *et al.* [15] prepared lithium perchlorate from either lithium chloride or lithium hypochlorite using a platinum anode.

The present process consists of the preparation of sodium perchlorate by electrolysis of sodium chloride solution at high current density without addition of chromate but with initial addition of fluoride.

On the basis of the results obtained on the laboratory scale [16, 17], higher amperage cells have been set up to evaluate the life of the lead dioxide anodes during the direct oxidation of sodium chloride to sodium perchlorate in a single step electrolysis without recourse to intermediate processing to remove chromate or isolate solid chlorate. The results of this study are described in the present paper.

Experimental

Two cells, of 75 A and 400 A capacities, were run continuously for over 18 months.

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Cell assembly

(a) *75 A cell.* The cell consisted of an oval-shaped porcelain tank of 15 l capacity. The cell cover was a p.v.c. (polyvinyl chloride) sheet with suitable slots for the introduction of the electrodes. The anode was 30 cm long \times 7.5 cm diameter graphite rod having a deposit of lead dioxide 5 mm thick up to a height of 25 cm. The cathode was a stainless steel cooling coil (1.9 cm O.D. and 1.5 cm I.D.) to which a perforated cylindrical stainless steel cathode (10.5 cm diameter) was welded. The inter-electrode distance was 1.5 cm. The electrical connection to the anode was conveniently provided to the graphite through a threaded copper rod, screwed on to the top portion of graphite by means of flexible wires. The portion of the anode above the level of the electrolyte was painted with chlorinated rubber paint to avoid corrosion at the electrolyte-air-interface. A stainless steel bar, 6 mm thick, acted as current conductor to the cathode. The electrical connections to the cell were 2.5 cm \times 0.3 cm copper busbars. The porcelain tank rested on a mild steel stand, which supported wooden frames for holding the anode and cathode in position.

(b) *400 A cell.* The cell container was made of reinforced concrete (outer dimensions 81 cm long \times 72 cm wide \times 37 cm height with a wall thickness of 5 cm). A concrete slab, 2 cm thick, was placed on top of the container, with suitable holes for the introduction of anodes, cooling coils, thermometer, gas vent-pipe and solution feed inlet tube. The outlet was provided on one side of the cell, 10 cm from the top of the cell.

Six graphite rods (30 cm long \times 7.5 cm diameter) having a deposit of lead dioxide 5 mm thick up to a height of 25 cm were used as anodes. The contact to the anode was made through a copper rod (1.6 cm diameter) screwed on to the top portion of the graphite rod. A flexible wire was connected from each of the anodes to the common anode busbar.

Perforated stainless steel plates of cylindrical shape (11.0 cm diameter) welded on to stainless steel cooling coils (1.6 cm I.D. and 1.9 cm O.D., 580 cm long) acted as cathodes. Electrical connection was made by clamping the cooling

coils to busbars, which were connected to the rectifier.

Two rows of anodes, each row containing three graphite substrate lead dioxide rods, were placed in such a way that each anode was surrounded by a perforated cylindrical stainless steel cathode. The holes in the cell cover were closed with p.v.c. covers and putty. Two gas vents were provided and the gases were removed by an exhaust arrangement.

Electrolysis

A saturated solution of sodium chloride (about 300 g/l) was used as the cell feed. 2 g/l sodium fluoride was added to the cell feed at the beginning of the electrolysis. The pH of the electrolyte was maintained between 6.2 and 6.8 by adding the calculated quantity of hydrochloric acid. The loss due to evaporation was made up with such further quantities of sodium chloride solution that the cell liquor at the end of the electrolysis contained 650–700 g/l sodium perchlorate. A silicon rectifier (0–32 V and 1000 A) was the source of direct current. The temperature of the cell was maintained between 45° and 50°C by passing cold water through the cooling coils. The temperature of the outlet water was lowered by 5° to 6°C in a forced draft cooling tower prior to recirculation. Analyses were carried out for chloride, chlorate and perchlorate at intervals so as to follow the course of the reaction.

Fig. 1 represents the variation in concentration of chloride, chlorate and perchlorate with duration of the electrolysis under optimum conditions. Results are given in Tables 1 to 4.

Analyses

Chloride was estimated by Mohr's method [18] and the chlorate was estimated by iodometric method [19]. The total concentration of electrolytes in the solution was determined by passing the solution through a cation exchange (Amberlite IR-120) column; the perchlorate concentration was calculated by subtracting the combined concentrations of the chloride and chlorate from the total concentration. Later the current efficiency was calculated from the quantity of

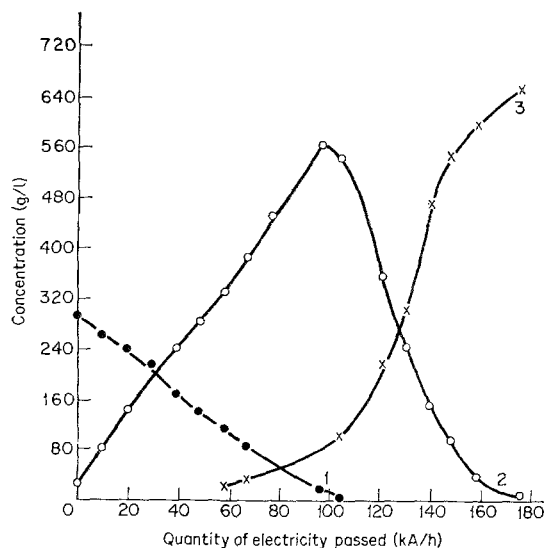


Fig. 1. Variation of the concentration of chloride, chlorate and perchlorate of sodium with quantity of electricity passed. 1 sodium chloride; 2 sodium chlorate; 3 sodium perchlorate.

electricity passed and the theoretical quantity of electricity required for the formation of chlorate and perchlorate.

Results and discussion

Tables 1 and 3 show typical results of the performance of 75 and 400 A cells respectively, under the optimum conditions of electrolysis. The results confirm the data obtained in laboratory scale experiments. Tables 2 and 4 give information about the life of each anode in the

preparation of sodium perchlorate from sodium chloride.

It is seen from Table 4 that most of the anodes have lasted for more than 450 days of continuous electrolysis. This confirms the earlier observation that lead dioxide deposits of 5 mm thickness on graphite can be used successfully for the production of perchlorates.

In the present process the constituent steps, the oxidation of chloride to chlorate, and the oxidation of chlorate in the presence of sodium fluoride to perchlorate, have been reported in published literature and are well known. The combination of these steps in a single process constitutes the novelty of this procedure. However, in the direct oxidation of chloride to perchlorate in a single stage, none of the commonly used electrodes, viz., graphite, magnetite or platinum can be employed as anode material. Lead dioxide is the natural choice at present. The use of lead dioxide anodes necessitates the addition of sodium fluoride to the bath and this addition, made at the beginning of electrolysis increases the current efficiency of the process [17] for perchlorate formation.

In the conventional two-stage process, the dichromate which is added in the first stage converting chloride to chlorate, must be completely removed before the electrolyte can be used in the second stage converting chlorate to perchlorate with a lead dioxide anode. No dichromate is required in the one-step process. Additional difficulties associated with the removal

Table 1. Operating Characteristics of 75 A cells.

Volume of electrolyte, 15 l; anode current density, 20 A/dm²; temperature, 47 ± 3°C; pH, 6.5 to 6.8; NaF, 2 g/l.

S. No.	NaCl at the beginning of electrolysis (g/l)	Quantity of electricity passed kA/h	Voltage (V)	Final concentration NaClO ₃ (g/l) NaClO ₄ (g/l)		Current efficiency with reference to NaClO ₄ produced (%)	Energy consumption (Kwh/kg of NaClO ₄ produced)	Remarks
1	302	30.8	3.5-4.0	4.7	610	53.0	12.8	
2	295	29.5	3.5-4.0	2.0	600	54.0	12.8	
3	302	28.2	3.5-4.0	5.7	615	58.0	12.1	
4	310	42.2	3.5-4.0	3.5	760	52.4	12.9	20 l of NaCl solution used
5	315	41.5	3.5-4.0	3.0	760	53.0	12.9	20 l of NaCl solution used

Table 2. Life of the anodes used in the 75 A cells for the production of perchlorate from chloride. Conditions of electrolysis same as in Table 1.

S. No.	Rod No.	Date on which put into the cell	Date on which removed from the cell	Quantity of electricity passed (kA/h)	Quantity of sodium perchlorate produced (kg)	Remarks
1	VIII	4.12.68	14.8.69	385	105	The deposit came out as a hood
2	D	22.1.68	19.5.69	768.2	320	The deposit came out as a hood

Table 3. Operating characteristics of 400 A cell.

Volume of electrolyte, 100 l; Anode current density, 20 A/dm²; Temperature, 47 ± 3°C; pH, 6.5–6.8; NaF, 2 g/l.

S. No.	Sodium chloride in the beginning (g/l)	Quantity of electricity passed (kA/h)	Voltage (V)	Final concentration NaClO ₃ (g/l)	NaClO ₄ (g/l)	Current efficiency with reference to NaClO ₄ (%)	Energy consumption (Kwh/kg of NaClO ₄ produced)
1	310	220	3.6–4.0	3.0	615	52	12.9
2	310	205	3.6–4.0	2.5	620	54	12.7
3	310	207.5	3.6–4.0	3.5	620	53	12.8
4	302	210.1	3.6–4.0	3.2	610	52.6	13.0
5	300	163.2	3.6–4.0	3.0	610	57	12.3
6	300	172.8	3.6–4.0	3.0	610	55	12.4

Table 4. Life of the individual anodes used in the 400 A cell for the production of perchlorate from chloride. Conditions of electrolysis same as in Table 3.

S. No.	Rod. No.	Date on which put into the cell	Date on which removed from the cell	Quantity of electricity passed through each anode (kA/h)	Quantity of perchlorate produced from each anode (kg)	Remarks
1	XI	6.12.68	16.6.70	637.4	256.6	The anode is still in good condition
2	XIV	6.12.68	16.6.70	637.4	256.6	The anode is still in good condition
3	E	6.12.68	12.1.70	424.0	175.0	The deposit came out as a hood
4	XIII	6.12.68	16.6.70	637.4	256.6	The anode is still in good condition
5	X	6.12.68	16.6.70	637.4	256.6	The anode is still in good condition
6	VI	6.12.68	16.6.70	637.4	256.6	The anode is still in good condition
7	X (Replacement for E)	12.1.70	7.2.70	29.3	11.6	The deposit peeled off
8	M (Replacement for X)	14.2.70	16.6.70	183.7	70.0	The anode is still in good condition

of graphite sludge and ferric hydroxide and isolating the sodium chlorate have all been obviated in this process. Even if a lead dioxide anode is employed in the chlorate process, the isolation of chlorate and the removal of dichromate cannot be avoided because dichromate is added not only to prevent cathodic reduction of hypochlorite but also to prevent the formation of perchlorate, especially at high concentrations of chlorate.

From Fig. 1 it is seen that the chloride is first converted to chlorate and to perchlorate only to a small extent. After all the chloride has been converted to chlorate, the conversion of chlorate to perchlorate proceeds. The sodium perchlorate liquor thus obtained contains less than 10 g/l sodium chlorate and is used for double decomposition with either potassium chloride or ammonium chloride to give potassium perchlorate or ammonium perchlorate. Potassium perchlorate and ammonium perchlorate which were prepared from this sodium perchlorate solution conformed to the stringent specifications. Nearly 1200 kg of sodium perchlorate was prepared and converted to potassium and ammonium perchlorates.

The advantages of this process are as follows.

- (a) Sodium perchlorate is prepared directly from the cheap raw material sodium chloride without intermediate processing or the isolation of solid sodium chlorate.
- (b) The use of lead dioxide anodes eliminates the consumption of either graphite, magnetite or platinum during the two stage production of sodium perchlorate.
- (c) The addition of a small quantity of sodium fluoride at the beginning of the electrolysis increases the current efficiency of the process.

Conclusion

The following are the main features of the process.

- (i) Direct oxidation of sodium chloride to sodium perchlorate in a single step in the same cell.
- (ii) The use of lead dioxide anodes, the only suitable anodes at present available.
- (iii) The addition of sodium fluoride made at the beginning of the electrolysis to give a high efficiency.

(iv) The avoidance of intermediate processing of the liquor to isolate sodium chlorate.

(v) A high concentration of sodium perchlorate is built up by adding sodium chloride solution to make up evaporative losses in the cell.

(vi) The preparation of potassium and ammonium perchlorates by double decomposition of the sodium perchlorate solution with potassium chloride and ammonium chloride respectively.

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