

## Lead Dioxide Anodes in the Large Scale Production of Potassium Chlorate from Potassium Chloride<sup>a</sup>

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Potassium chlorate, which is used mainly in the manufacture of matches, was prepared by the electrolytic oxidation of potassium chloride in an 800 A cell using graphite substrate lead dioxide anode and stainless steel cathode. The cell was operated at an anode current density of 5 A/dm<sup>2</sup>, a temperature of 55 to 60 °C and a pH of 6.0 to 7.0. A current efficiency of 82 to 85 % was obtained and an assay yield of 77 % was realised for the recrystallised product. The cell voltage was 3.2 to 3.3 V with an energy consumption of 6.3 to 6.5 kWh (d.c.)/kg of potassium chlorate produced.

The cell effluent, being clear and free from suspended impurities, could be processed further without filtration and pure potassium chlorate (>99%) was obtained by recrystallisation.

### 1. Introduction

Potassium chlorate is used mainly in the manufacture of matches. It may be mixed with certain organic compounds such as lactose to give a relatively cool flame, so that certain dyes may be incorporated in the mixture to give coloured flares. To a limited extent, potassium chlorate finds application in pharmaceutical preparations and for heating pads. The hygroscopic property of sodium chlorate renders it unserviceable in most of these instances and hence potassium chlorate is the natural choice.

The successful substitution of graphite for platinum as anode material and the discovery of the effect of chromate addition to the electrolyte to prevent cathodic reduction, with the proper maintenance of pH by the addition of acid, made the chlorate production purely an electrolytic method.<sup>1</sup> The use of graphite substrate lead dioxide anodes in the production of sodium chlorate has been engaging the attention of this Institute and it has been proved that lead dioxide deposited over graphite increases the life of the graphite anode at least by three to four times.<sup>2-5</sup>

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On the basis of the results obtained on a laboratory scale,<sup>6</sup> one 800 A cell was run for the production of potassium chlorate starting from potassium chloride and using graphite substrate lead dioxide anode<sup>7</sup> and the results of the same are presented in this paper.

## 2. Experimental

### 2.1. Cell assembly

The 800 A cell having 16 numbers of graphite substrate lead dioxide anodes and stainless steel cathode (Cell C1), which was used for the production of sodium chlorate<sup>5</sup> was used for the direct oxidation of potassium chloride to potassium chlorate. The cell was a rectangular tank (i.d. 80 cm long  $\times$  70 cm wide  $\times$  60 cm high with a wall thickness of 5 cm) of 250 l capacity made of reinforced (cement) concrete. Sixteen graphite substrate lead dioxide rods<sup>8</sup> (7.9 cm diam.  $\times$  60 cm long having a deposit of 2 to 2.5 mm thick up to 52 cm height) were used as anode and the contact to the anode was given through a copper rod (1.6 cm diam.) screwed to the top portion of the graphite rod. Stainless steel cooling coils (1.6 cm i.d. and 1.9 cm o.d. 1208 cm long) and perforated stainless steel sheets made up the cathode assembly and two such assemblies were used. Each row of anodes consisting of four rods of graphite substrate lead dioxide was suspended by means of iron flats. The four rows of anodes were placed in such a way that each anode was surrounded by the perforated cylindrical stainless steel cathode. The inter-electrode distance was 1.25 cm. PVC (polyvinyl chloride) (sheet) covers and putty were used for sealing the cells and to make the cover gas tight.

### 2.2. Electrolysis

Initially the cell was charged with 250 l of electrolyte containing 280 g/l potassium chloride. To avoid cathodic reduction of hypochlorite, sodium dichromate was added to the cell feed to the extent of 2 g/l. The pH of the cell was maintained between 6.4 and 7.0 by the addition of 2 N-hydrochloric acid. The cell gases were removed by means of exhaust arrangement. Direct current for the electrolysis was provided by a silicon rectifier (0 to 32 V and 1000 A). The temperature of the cell was maintained at 55 to 60 °C. When the potassium chlorate concentration came to about 110 g/l, circulation of potassium chloride solution (290 g/l) was commenced. The cell effluent contained 225 g/l potassium chloride and 106 g/l potassium chlorate. The hot liquor was cooled to room temperature in order to crystallise out the potassium chlorate. The liquor after cooling contained 218 g/l potassium chloride and 36 g/l potassium chlorate. This solution was resaturated with fresh solid potassium chloride when the concentration of the liquor became 286 g/l potassium chloride and 33 g/l potassium chlorate. This solution was fed to the cell at the rate of 20 l/h and this fast rate of circulation was maintained to prevent the crystallisation of any solid potassium chlorate. The concentration of cell liquor and effluent were maintained at 245 to 260 g/l potassium chloride and 80 to 106 g/l potassium chlorate. The salt in the crystalliser was centrifuged and recrystallised. The purity of once recrystallised potassium chlorate was > 99%. The conditions of electrolysis are given in Table 1.

TABLE 1. Operating conditions of the cell

Current passed (A)	:	800
Quantity of electricity passed (kA h)	:	172.8
Anode current density (A/dm <sup>2</sup> )	:	4.9
Current concentration (A/l)	:	3.2
Bath voltage (V)	:	3.2–3.3
Temperature (°C)	:	55–60
pH	:	6.0–7.0
Current efficiency (%)	:	82–85
Assay yield for the recrystallised potassium chlorate (%)	:	77
Energy consumption (d.c.) (kWh/kg of KClO <sub>3</sub> )	:	6.3 to 6.5

### 2.3. Analysis

The chloride and chlorate were estimated by Mohr's method<sup>9</sup> and iodometric method,<sup>10</sup> respectively.

The material balance study carried out during the oxidation of potassium chloride to potassium chlorate for 9 days is presented in Table 2.

The flow diagram of the process is shown in Figure 1.

TABLE 2. Material balance study in the production of potassium chlorate from potassium chloride

Sl. No.	Conc. of feed liquor			Concentration of liquor			KClO <sub>3</sub> present finally in solution after isolation of product	KClO <sub>3</sub> to be obtained as per current efficiency	KClO <sub>3</sub> isolated as solid	Percentage loss of KClO <sub>3</sub> during processing
	Volume	Conc. of KCl	Conc. of KClO <sub>3</sub>	Volume	Conc. of KCl	Conc. of KClO <sub>3</sub>				
	(l)	(g/l)	(g/l)	(l)	(g/l)	(g/l)	(kg)	(kg)	(kg)	
1	250	280.5 286*	— 33*	250	260.3	72.6	18.7	99	77.0	3.4

\* Concentration of cell feed during circulation.

### 3. Results and Discussion

It has already been proved that the graphite substrate lead dioxide anodes have the advantage of possessing a longer life than the conventional graphite anodes in the electrolysis for chlorate production.<sup>2–5</sup> Due to the low solubility of potassium chlorate a larger volume of liquor has to be kept in circulation for production. The cell voltage was practically constant throughout the period of electrolysis owing to the conversion of a small percentage of chloride. Since the chlorine overvoltage on lead dioxide anode is higher than on graphite, the cell voltage at the beginning was higher than the starting voltage using graphite anode. However, continuous disintegration of graphite anode increases the inter-electrode distance and the cell voltage increases with time in a cell using graphite anode. The average voltage of the cell using graphite anode is likely to be equal to that of a cell employing lead dioxide anodes. The advantage gained by the use of lead dioxide anode is due to the fact that the cell effluent, being clear and free from suspended impurities, could be further processed without filtration. Even if there are any particles in suspension, they readily settle because the lead

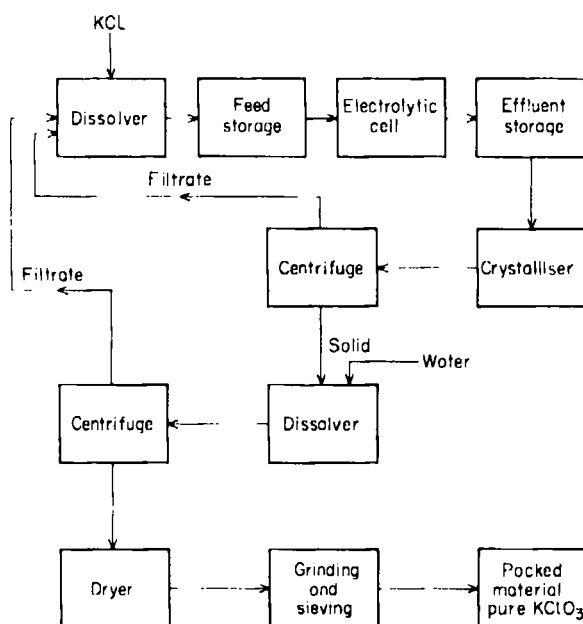


Figure 1. Flow diagram of the process for the production of potassium chlorate from potassium chloride.

dioxide particles are very dense. On the other hand, the processing of the solution free from colloidal graphite particles always involves one or more operational steps, when graphite is used as anode for chlorate production. Similarly, use of magnetite anodes present considerable difficulty in the removal of colloidal ferric iron from the product. The cell can be operated at a higher temperature using graphite substrate lead dioxide anode which is not possible using graphite anode, although this is possible with magnetite anodes.

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