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Reduction in Chlorate Content in De-Nora Type Electrolytic Diaphragm Cells used for the Manufacture of Caustic Soda in Sri Lanka

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Abstract The sodium hydroxide produced in the De-Nora diaphragm cells at the Paranthan Chemicals Corporation, Sri Lanka, has 1.30 to 1.50 g sodium chlorate per 100 g of sodium hydroxide. Pilot cells were constructed in the laboratory with a single carbon anode and a double steel cathode, in order to investigate the optimum conditions under which the electrolysis of brine would lead to the maximum production of sodium hydroxide with a minimum proportion of chlorate. Reduction of chlorate contaminant was achieved by using a lowered catholyte level and a consequential increased flow rate. This led to a decrease in the back diffusion of hydroxide ions and a consequent decrease of chlorate formation in the anolyte. This however, also led to a decrease in the hydroxide concentration. Experiments done with simultaneous replenishment of anolyte liquor and pre-heating of feed brine have shown a reduction in anolyte chlorate and consequent reduction in catholyte chlorate. Repetition of these experiments at Paranthan Chemicals Corporation, *in situ*, at current loads of 3000 A, showed an even more significant chlorate reduction when simultaneous replenishment of anolyte liquor and pre-heating of feed brine was carried out. Experiments were also carried out with increasing replenishing rates at a constant feed brine temperature of 55°C. Anolyte chlorate concentration was thereby reduced to 0.1 to 0.08 g per 100 g sodium hydroxide. It is shown that spent anolyte liquor could be re-circulated to the cells *via* the saturators, thus eliminating the wastage of brine.

1. Introduction

Caustic soda is produced in the De-Nora type diaphragm cells at the Paranthan Chemicals Corporation, Sri Lanka. The cells are narrow and high consisting of a single anode comprising of twenty-six bars, made out of graphite material and a perforated double steel cathode on either side of the anode. On the anode side of the cathode, the diaphragm is pasted (on the periphery) and stitched at intervals. The diaphragm material consists of asbestos paper and cloth. The cathode is submerged. The design includes an arrangement by which the height, and therefore the hydraulic pressure of the liquid in the anode and cathode compartments of the cell may be varied according to the permeability of the diaphragm, as it changes with age. The hydrostatic pressure in the anode and cathode chambers may differ by as much as twenty-five inches.

The effluent of the cell contains 1.30 g to 1.50 g of sodium chlorate per 100 g of sodium hydroxide and all the cells suffer from this defect. In the manufacture of soap (85% of Sri Lanka's caustic soda being used for this purpose), caustic soda is treated with coconut oil, the resultant by-product being glycerine. Glycerine is one of Sri Lanka's non-traditional export products. The chlorate that is present in the caustic soda contaminates the glycerine thereby reducing the export value of glycerine.

The primary reactions that take place in the chlora-alkali cell are :

at the cathode : $2H_2O + 2e \longrightarrow H_2 + 2OH^-$ ———— (1)

at the anode : $2Cl^- \longrightarrow Cl_2 + 2e$ ———— (2)

Due to the following secondary reaction,

$Cl_2 + H_2O \longrightarrow HOCl + Cl^- + H^+$ ———— (3)

$HOCl \rightleftharpoons OCl^- + H^+$ ———— (4)

$2\ HOCl + OCl^- \longrightarrow ClO_3^- + 2Cl^- + 2Cl^- + 2H^+$ ———— (5)

$6\ OCl^- + 3H_2O \longrightarrow 2Cl_3^- + 4Cl^- + 6H^+ + 3/2\ O_2 + 6e$ ———— (6)

There exists a chloride, chlorine, hypochlorite and chlorate system.

Most of the chlorine, bubbles out of the solution as chlorine gas but a certain amount dissolves in the anolyte liquor, this amount depending on the chloride ion concentration (Figure 1)[9] and temperature. Foerster and Mueller[2,3] formulated the path taken by the dissolved chlorine ultimately leading to the formation of chlorate. The dissolved chlorine undergoes hydrolysis according to Equation 3. Ibl[5] has shown that the above reaction is fast and takes place in the bulk solution as well as in the diffusion layer, close to the anode where chlorine is generated. Hypochlorous acid produced dissociates according to :

$$HOCl \longrightarrow ClO^- + H^+$$

The dissociation constant for this dissociation is :

$$4 \times 10^{-8}\ \text{mol.}\ l^{-1}\ \text{at}\ 25°C.$$

Chlorate may be formed in either of two ways :

1. Chemical formation as represented by the Equations 3, 4 and 5.
2. Electrochemical formation at the anode as represented by Equation 6, with simultaneous oxygen evolution.

In strongly alkaline media[6] the electrochemical oxidation can be represented as follows :

$5ClO^- + 8H_2O \longrightarrow 3ClO_3^- + Cl^- + 6H^+ + 2O_2 + 16e$ ———— (7)

According to Ibl and Landolt[6] in alkali cells electrochemical chlorate is predominant.

The work reported here was directed towards finding optimum conditions under which the electrolysis of brine would lead to the production of sodium hydroxide with a minimum proportion of chlorate.

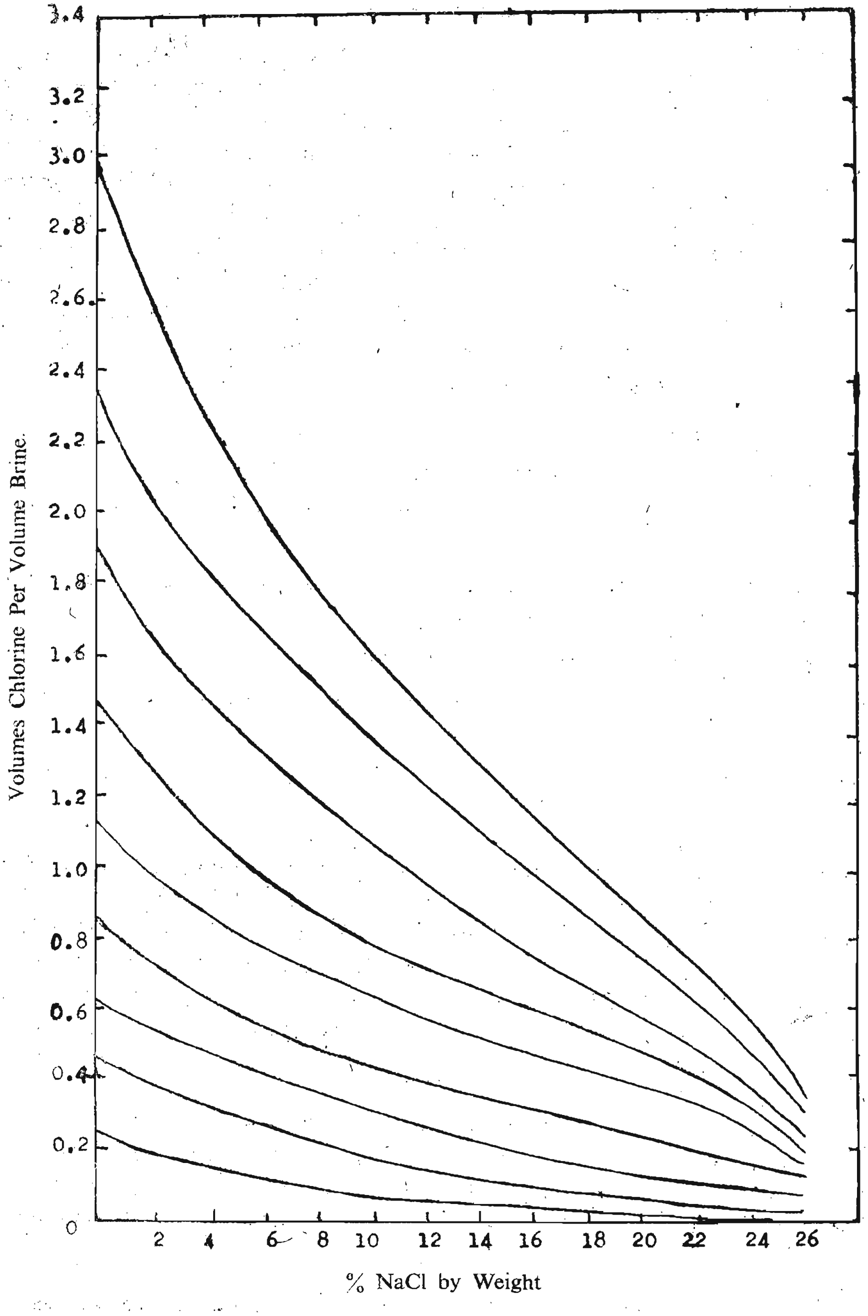

Figure 1. Solubility of Chlorine in Brine

2. Experimental

2.1. Preliminary Experiments

For our preliminary investigations, experimental cells were constructed in the laboratories of the Department of Chemistry on a design similar to those at Paranthan Chemicals Corporation, Sri Lanka. The current densities used were 0.06 and 0.07 A cm^{-2} at the cathode and anode respectively, similar to that used at Paranthan. The anode consisted of three bars of graphite. Cathodes were placed on either side of the anode and were made out of perforated steel plates to which was tightened the diaphragm made out of asbestos paper and cloth of the type KP 407. All materials were supplied by the Paranthan Chemicals Corporation. The power supply came from the mains via a variac shown in the circuit diagram (Figure 2). The cells (Figure 3) operated at a load of 40 A.

2.2. Pattern of Experiments.

Four categories of experiments were performed :

(A) under normal electrolysis* conditions i.e. in the manner carried out at Paranthan;

(B) electrolysis with replenishing of anolyte liquor (taking out of anolyte and introduction of fresh brine);

(C) electrolysis with pre-heated brine ; and

(D) electrolysis with simultaneous pre-heating of brine and replenishing of anolyte liquor.

At each catholyte level, the four categories of experiments were performed.

2.3. Procedure

Three catholyte levels were pre-selected corresponding to 15 cm, 12 cm and 8 cm. Feed-brine was maintained at concentrations between 304 to 312 gl^{-1} of sodium chloride. In replenishing experiments (categories B and D) the replenishing rate was maintained at one-third the cell feed rate (cell feed rate varied between 4.7 to 12.5 $cm^3 min^{-1}$). In pre-heating experiments (category C), the temperature of brine was maintained at 70°C. Duration of each experiment varied from 5 to 6 h.

2.4. Experiments conducted *in situ* at Paranthan

The above experiments were repeated at a load of 3000 A on one of the cells in the cell plant at Paranthan Chemicals Corporation. The concentration of sodium hydroxide in the effluent liquor was maintained between 100 to 120 gl^{-1}, and experiments were conducted for durations of 10 h. Sampling was carried out as before at the end of each hour.

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*Normal electrolysis—electrolysis carried out without any modification such as mentioned under category B, C and D.

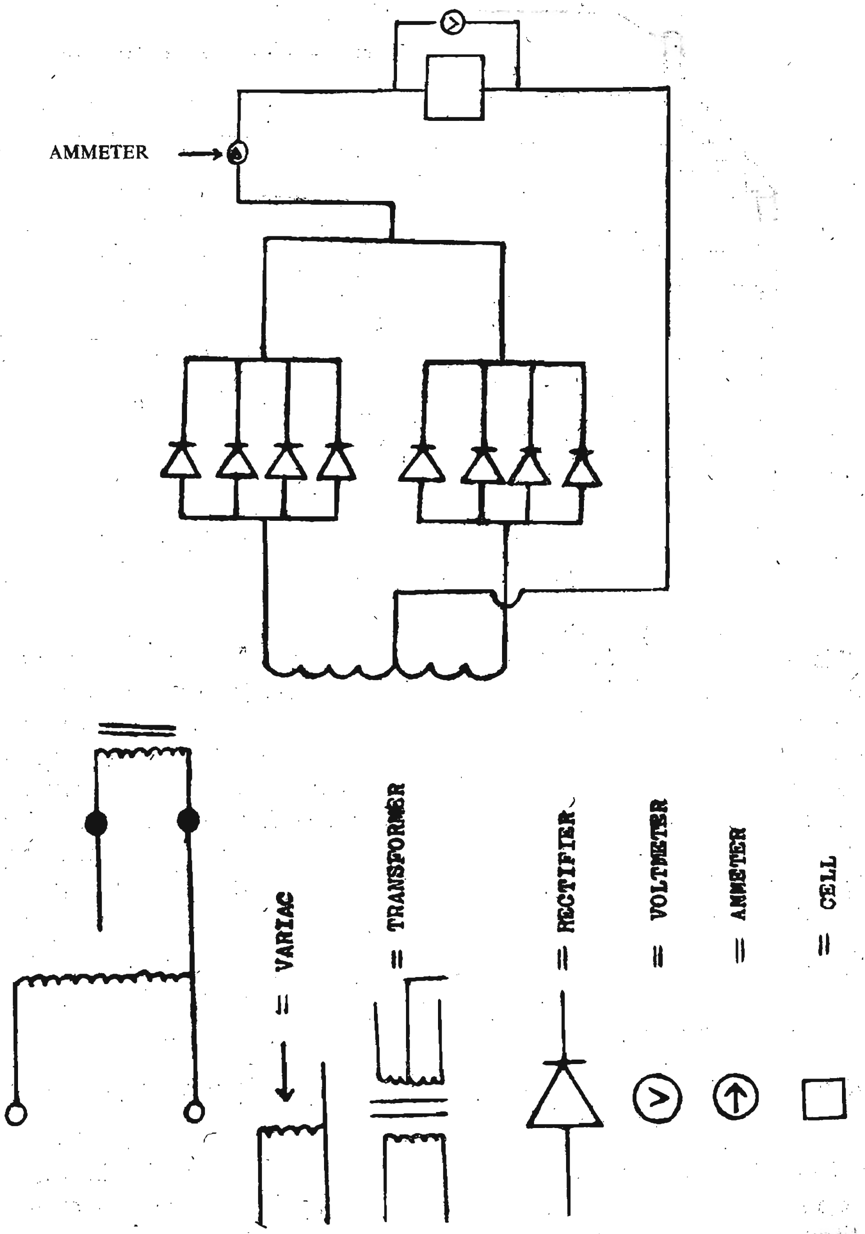


Figure 2. Circuit Diagram

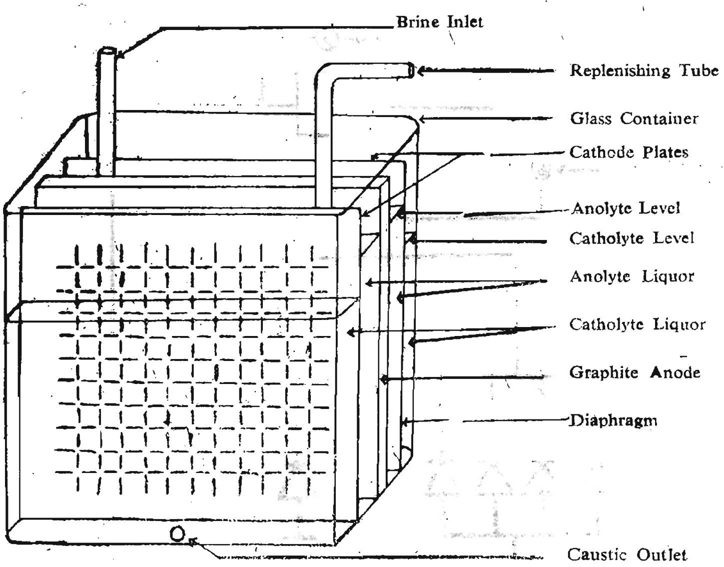


Figure 3. Diagramatic Section of the Cell

In this series of experiments we tried to derive the maximum replenishing rates that could be adopted by the cells in question to reduce the chlorate to the lowest possible value without reducing the efficiency of the cells. Increasing of temperature of feed-brine was limited to 55°C since P.V.C. pipes carrying brine cannot withstand a higher temperature. Normal electrolysis was carried out for 10 h maintaining the feed rate $40 \pm 2\ \mathrm{lh^{-1}}$. Cell was thereafter subjected to a replenishing rates of anolyte liquor $18 \pm 2\ \mathrm{lh^{-1}}$, $60 \pm 1\ \mathrm{lh^{-1}}$ and $66 \pm \mathrm{lh^{-1}}$, at the latter replenishing rate a drop in the anolyte temperature being recorded. As a result we were not able to increase the replenishing any further.

3. Analytical

For all quantitative analysis the following procedure was adopted :

NaOH–10.00cm^3 of a sample diluted with an equal volume of water was titrated against 0.1000N hydrochloric acid.

$NaClO_3$—10.00cm^3 of a sample was warmed with ferrous ammonium sulphate in the presence of 5N sulphuric acid. The remaining ferrous ammonium sulphate was titrated against standard 0.1000N potassium dichromate.

NaCl—5.00cm^3 of a sample was diluted upto 250cm^3 of water and 10.00cm^3 of the latter solution titrated against 0.100N silver nitrate.

4. Discussion

4.1. Relationship of Anolyte and Catholyte Chlorate

In experiments of category A as the catholyte level was lowered and hence flow rate increased, there was observed a decrease in anolyte chlorate (Figure 4). This could be attributed to a decrease in the back diffusing hydroxyl ions[4] caused by the low sodium hydroxide concentration in the effluent. Back diffused hydroxyl ions contribute to the chemical formation of chlorate in the anolyte liquor. Reference to Figure 5 shows that the anolyte chlorate is higher than the catholyte chlorate and the magnitude of the catholyte chlorate is determined by the anolyte chlorate. Figure 5 also indicates a possible cathodic reduction of chlorate during the passage of the anolyte liquor through the cathode plates.

$$ClO_3^- + 3H_2O + 6e \longrightarrow Cl^- + 6OH^-$$

$$ClO_3^- + 6H^+ + 6e \longrightarrow Cl^- + 3H_2O$$

In experiments done under category D at 15 cm and 12 cm catholyte levels it was observed that with an increased anolyte sodium chloride concentration there was a decrease in the anolyte chlorate ; however, a reduction in the catholyte chlorate was not observed as expected. The anolyte chlorate concentration fell below the catholyte chlorate concentration and the difference in concentration increased with increasing flow rate ; therefore, the presence of catholyte chlorate cannot be attributed solely to chlorate formation in the anolyte. It is partly due to a process of chlorate formation in the catholyte. Dissolved chlorine in the anolyte liquor which passes through the diaphragm undergoes reaction with hydroxyl ions in the catholyte to give rise to additional chlorate in the catholyte. The series of reactions leading to catholyte chlorate formation is thought to be as follows :—

$$Cl_{2(aq)} + OH^- \longrightarrow Cl^- + HClO$$

$$HClO + OH^- \longrightarrow ClO^- + H_2O$$

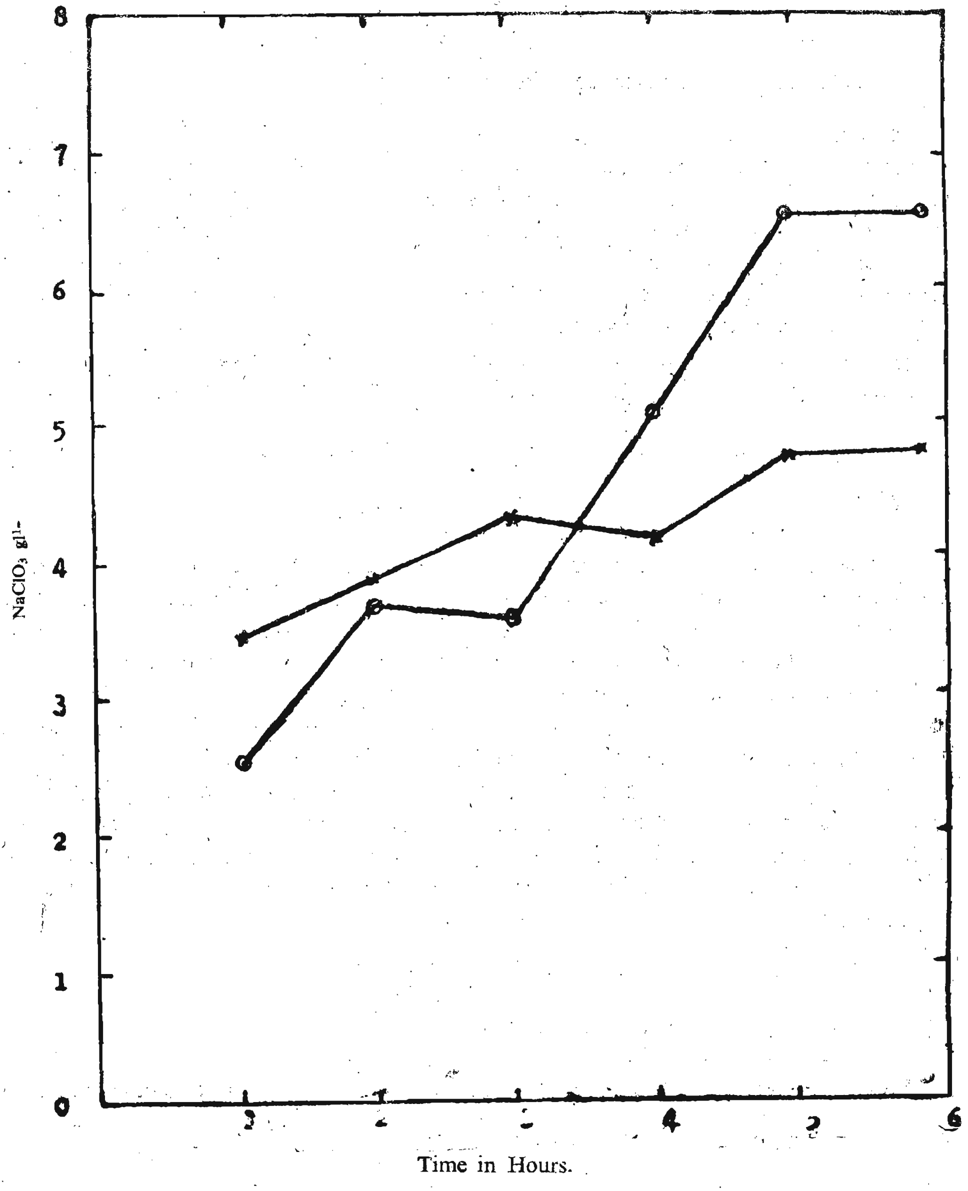
The process hereafter proceeds in two stages : the very slow bimolecular reaction

$$2ClO^- \longrightarrow ClO_2^- + Cl^-$$

being followed by the fast reaction

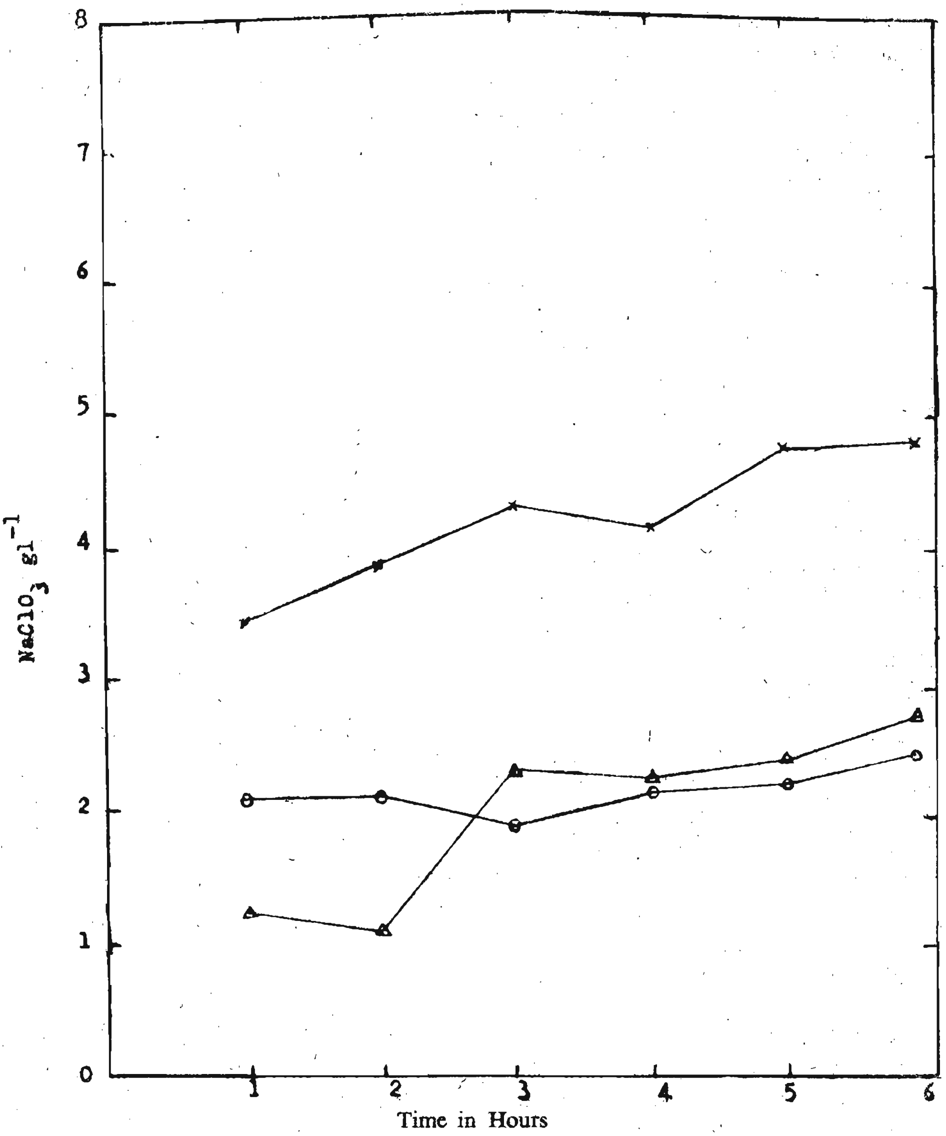
$$ClO_2^- + ClO^- \longrightarrow ClO_3 + Cl^-$$

In those experiments (category D) where replenishing of anolyte liquor and pre-heating of cell feed-brine was carried out reduction in anolyte chlorate, took place



o Anolyte Chlorate (catholyte level 15cm)
× Anolyte Chlorate (catholyte level 12cm)

Figure 4. — Variation of anolyte chlorate during normal electrolysis



× Anolyte $NaClO_3$
o Right Cell Effluent $NaClO_3$
Δ Left Cell Effluent $NaClO_3$

Figure 5. Variation of anolyte and catholyte chlorate during normal electrolysis at catholyte level of 12cm.

However equilibrium conditions were not well defined with respect of sodium hydroxide concentration and catholyte chlorate, i.e. there were large fluctuations in sodium hydroxide and catholyte chlorate concentrations when tested hourly. It was therefore thought that if the above experiments are repeated under control conditions* still further chlorate reduction could be expected.

When experiments were done at current loads of 3000 A under category A (normal electrolysis), the significant feature was a higher anolyte chlorate concentration as compared to the catholyte chlorate concentration, resulting in cathodic reduction of chlorate. In experiments under category B (replenishing of anolyte liquor) there was no significant reduction in chlorate observed either in the anolyte or catholyte. This is possibly due to low temperature of the anolyte which did not exceed 65°C. since replenishing rates were maintained at approximately 1/3 the cell feed rate (normal cell feed rate 40 $1h^{-1}$). The next series of experiments were conducted with simultaneous replenishing of anolyte liquor and pre-heating of feed-brine at 55°C There was a marked drop in both anolyte and catholyte chlorate. Thereafter the same cell was subject to a series of experiments introducing only pre-heated brine ; there was observed a marked increase in chlorate. To be sure that these changes were not experimental artifacts but due to pre-heating of feed-brine and replenishing of anolyte liquor, the same cell was subjected to normal electrolytic conditions and results were compared with the initial experiments of this nature done on the same cell ; similar results were observed.

Comparison of results of experiments conducted at catholyte levels 14.50 cm and 12.00 cm show that with increase in flow rate there was a 53% reduction in the concentration of sodium chlorate. Experiments done at catholyte level 8.00 cm shows that with further increase in flow rate, there was a 68% reduction in the concentration of sodium chlorate. Corresponding to each catholyte level, the lowest value for sodium chlorate was recorded in those experiments where replenishing of anolyte liquor with pre-heating of feed-brine was carried simultaneously.

Repetition of experiments in the industrial cells at Paranthan under control conditions, indicated that the lowest values of sodium chlorate concentrations were once again those corresponding to experiments with simultaneous pre-heating of feed-brine and replenishing of anolyte liquor.

Results[8] indicate that at high replenishing rates (approximately 66 $1h^{-1}$) chlorate has reduced to values of 0.08 g of sodium chlorate per 100 g of sodium hydroxide.

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*Equilibrium conditions—an instance where variable parameters such as temperature, sodium hydroxide and sodium chlorate concentrations remain almost constant., i.e. cells to be run for a longer period from the commencement of the experiment.

5. Conclusion

During normal electrolysis, only limited control can be maintained over the operating conditions of the cell. These include decomposition voltage, brine concentration and feed rates, the last of which depending largely on the porosity and flow rate through the diaphragm. On the other hand, in cells with replenishing of anolyte liquor, equilibrium conditions of the cell could be so adjusted for it to operate under desired conditions of anolyte Cl^-, temperature and cell liquor concentrations. Replenishing of anolyte liquor further maintains an uniform distribution of Cl^-, temperature and cell liquor concentrations. Replenishing of anolyte liquor further maintains a distribution of Cl^- within in the anolyte and inhibits the deplection of Cl^- within the pores of the graphite anodes. This reduces the discharge of OH^- which should give rise to active O_2 attack on carbon, leading to shortening of anode life and contamination of Cl_2 gas with CO_2. The present method of anolyte replenishment substantially reduced the need for individual cell attention due to changes in diaphragm porosity and hydroxide back diffusion. The cell could be worked under a desired pH range, if necessary, thereby attaining high catholyte NaOH concentration and hence reduce the cost of evaporation.

Since replenishment would lead to undue wastage of brine and hence uneconomical from an industrial point of view, the possibility of re-circulation of anolyte liquor via the saturators instead of replenishing it was considered. When the plant is at full working capacity, approximately 55 cells are in circuit and when each cell is replenished at the rate of 60 lh^{-1} ($1\frac{1}{2}$ the normal feed rate) a volume corresponding to approximately 3300 lh^{-1} of anolyte liquor has to be delivered to the saturators through a pumping device. The possibility of recontamination of ClO_2^- concentration at the present rate of replenishing is shown to be in the region of about 0.08 g of NaOH.

The anolyte pH was in the range of 4.8 to 6.7 and it was not possible to draw a relationship of pH with either anolyte or catholyte concentrations. When current densities were increased, the potential rose to such heights that the process was not economical; when decreased the cell efficiency was found to be low.

6. Economy of the Process

Expenditure involved in implementing the process industrially, would comprise the capital cost of the construction of the P.V.C. pipe line (150m long with a diameter of 10 cm) from the cell plant via a storage tank of capacity of 150 cm^3 to the saturators. Motors would be needed to pump anolyte from the storage tank to the saturators at an approximate velocity of 80m min^{-1}, to a height of 15 m.

A dechlorination plant before the introduction of anolyte liquor to the saturators was not considered to be necessary, since dissolved Cl_2 in the anolyte liquor would tend to decrease with re-saturation. The industrial implementation of the above technique (pre-heated cell feed brine and re-circulation of anolyte liquor) is found to be satisfactory and has been recommended. The proposed method, in addition to the reduction of ClO_3^- in NaOH, is also expected to improve the working conditions of the cells and give better quality NaOH and purer Cl_2 gas.

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