

Lead Dioxide Anode in the Preparation of Perchlorates

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ABSTRACT

Lead dioxide deposited on graphite or carbon was used to make anodes suitable for the preparation of sodium perchlorate from sodium chlorate. This type of anode has been used successfully in the presence of certain addition agents as a replacement for platinum anode. The influence of anodic current density, temperature, pH, current concentration, and duration of electrolysis on the current efficiency of perchlorate formation was studied. Current efficiency was found to depend on anode surface transformation, which occurred with repeated use. Such changes could be observed visually and were confirmed by anode potential measurements. High current efficiency could be obtained even under slightly alkaline conditions of electrolysis, but addition of fluoride improved results. Addition of fluoride together with sulfate (as sulfuric acid) had the maximum effect on current efficiency under acidic conditions of pH.

This investigation is a result of preliminary studies carried out with the ultimate objective of setting up a pilot production unit to meet the requirements of perchlorates in India.

Use of platinum as anode material in the preparation of perchlorate from chlorate is well known. Many workers (1-6) have reported results obtained by using this anode in the preparation of perchlorates. The mechanism of anodic formation of per-

chlorates from chlorates, employing platinum anodes, has also been studied (7-10).

The high cost of platinum prompted several attempts to replace it by a cheaper material. In recent years, lead dioxide as the anode has been very much in evidence. This is seen in the considerable amount of work which has been carried out to obtain oxide deposits in a form suitable for use as anode in oxidation of chlorate to perchlorate.

Table I. Comparative statement of results obtained by different workers using lead dioxide anode

Conditions	Japanese workers (11-13)	Angel & Mellquist (17)	Grigger <i>et al.</i> (18)	Schumacher <i>et al.</i> (19)
Anode material	Lead dioxide coated over iron or nickel from lead nitrate bath	Lead dioxide coated on iron from tartrate bath	Lead dioxide on tantalum wire, rod or screen from lead nitrate bath	Lead dioxide deposited on platinum clad tantalum wires from lead nitrate bath
Electrolyte	Saturated solution of sodium chlorate at 20°C	Saturated solution of sodium chlorate	600 g/l of sodium chlorate	500 g/l of sodium chlorate
Addition agents	2 g/l NaF	2 g/l $K_2Cr_2O_7$	2.08 g/l $K_2S_2O_8$	0.5 g/l NaF
Cathode	Stainless steel	Mild steel	Stainless steel	Nickel or stainless steel
Bath voltage	4.5-5.0 v	4.9-6.2 v	5.0-6.5 v	4.75-5.1 v
Anode current density	20-31 amp/dm ²	20 amp/dm ²	30 amp/dm ²	15.5 amp/dm ²
Cathode current density	—	—	—	7.25 amp/dm ²
Temperature	29°-30°C	20°-25°C	25°-35°C	30°-45°C
pH	—	—	—	6.0-6.9 (controlled by 18% HCl)
Current concentration	80 amp/l	—	—	—
Current efficiency	70-71%	72-79%	61.2-75%	83.0-91.5%
Energy consumption (DC)	3.18-3.3 kwh/kg of NaClO ₄	—	—	1.04-1.23 kwh/lb of NaClO ₄

Preparation of lead dioxide electrodes in various sizes and shapes by deposition on nickel or iron base materials for the preparation of perchlorates was reported by Japanese workers (11-16). Angel and Mellquist (17) reported the use of lead dioxide anode prepared from a tartrate bath for the electrolytic preparation of perchlorates. Recently, Grigger *et al.* (18) reported on the use of lead dioxide deposited on tantalum, with the addition of 2.08 g/l of potassium persulfate to the electrolyte to increase current efficiency of perchlorate formation. Schumacher *et al.* (19) employed a lead dioxide anode coated over platinum clad tantalum.

Although the optimum conditions for electrolysis of chlorate to perchlorate using lead dioxide anodes have been described by earlier workers (Table I), there does not appear to be good agreement in current efficiency and in operating conditions of the cell. Earlier methods for obtaining suitable electrodes are not considered to be practical. For this reason, conditions for electrolytic production of perchlorate on a laboratory scale using a lead dioxide anode prepared by a procedure developed in this laboratory (20, 21) were investigated. The influence of addition agents and pH also was studied in an attempt to arrive at optimum conditions for the process.

Lead dioxide anodes.—The lead dioxide anode used by earlier workers was prepared by deposition of the same from a lead nitrate bath using tantalum or platinum clad tantalum as base material (18, 19). The use of iron and nickel as base materials for deposition of lead dioxide also has been mentioned in the literature (11, 12, 16).

The lead dioxide anode used in this investigation was prepared by depositing the oxide in a smooth and adherent form on graphite or carbon base material from a lead nitrate bath. Either a rotating technique for cylindrical rods, or a to-and-fro motion

technique for plate electrodes (20, 21), was used. A lead dioxide coating 0.5 to 1.0 mm thick proved to be just as effective as thick deposits, such as used by earlier workers (13, 18, 19). The graphite or carbon core acts as a support for deposited brittle lead dioxide and also serves as electrical contact for the same, thereby leading the current to the active anode. This type of anode allows preparation of light weight electrodes of desired dimensions to handle large currents on a commercial scale.

Experimental

Cell assembly.—The cell assembly consisted of a 250 ml tall-form beaker with a cell cover made of "perspex" with holes to introduce anode, cathode, and thermometer. The cell was placed in an outer vessel containing water and ice to control the temperature of the electrolyte in the cell. Two bent, perforated stainless steel plates (5.5 x 8.5 cm) acted as cathodes. Lead dioxide deposited on cylindrical graphite was used as anode (1.2 cm diameter x 8.0 cm long). Anode-cathode spacing was 1.5 cm.

Electrolyte.—The electrolyte was prepared by dissolving 600 g of sodium chlorate of A.R. quality in water to give 1000 ml of solution. The initial chlorate content of this solution was determined by the iodometric method (23).

Electrolysis.—In each electrolysis 200 ml of electrolyte was used. A selenium rectifier provided direct current. In each experiment the quantity of electricity theoretically required for complete conversion of chlorate to perchlorate (i.e., 2 Faradays) was passed unless otherwise stated.

Earlier it was established (6) that current efficiency calculated on the basis of perchlorate formed in an experiment by actual analysis with titanium trichloride (24) was within 1% of the value of current efficiency calculated by finding out the amount

Table II. Results of the preliminary investigation on perchlorate preparation

Anode, PbO₂; cathode, cobalt-tungsten alloy plated mild steel rods; volume of electrolyte, 850 ml; temperature, 35°-45°C; pH, 6.4-6.8 (maintained by the addition of hydrochloric acid)

Expt. No.	Motion of anode	Initial chlorate concentration, g/l	Final chlorate concentration after theoretical time, g/l	Addition agent	Current passed, amp	Anode current density, amp/dm ²	Bath voltage, v	Current efficiency, %	
								Half the theoretical time	Theoretical time
1.	Stationary	582.2	250.3	2 g/l NaF	18	14.9	4.4	61.1	57.6
2.	Stationary	582.2	133.2	2 g/l NaF	32	26.6	4.8-5.2	80.1	76.5
3.	Stationary	593.2	147.4	2 g/l NaF	31	26.4	4.7-5.2	90.4	74.9
4.	Stationary	572.3	142.4	2 g/l NaF	32	26.8	4.9-5.2	88.5	74.9
5.	Stationary	491.9	261.3	2 g/l NaF	39	35.1	5.8	46.7	46.9
6.	Stationary	616.9	317.5	Nil	31	26.4	5.0-5.4	51.7	46.9
7.	Rotation 1000-1250 rpm	580.2	374.5	Nil	32	26.8	5.1-5.2	41.1	34.4

of chlorate used up employing iodometry. The latter method therefore was adopted. A known amount of electrolyte (5 ml) was pipetted out for analysis, after electrolysis for half the theoretical time and also after full theoretical time. Results of experiments showing the effect of addition agent, anodic current density, pH, current concentration, temperature, and duration of electrolysis on current efficiency of perchlorate formation are given in the attached tables. Experiments were carried out in duplicate, and results were found to be reproducible within experimental error.

Discussion of results.—Table II gives the results of preliminary experiments using a 1 in. diameter cylindrical lead dioxide anode. Experiments 2 to 4 show that 75% current efficiency could be obtained using cobalt-tungsten alloy deposited cathodes at an anodic current density of 26.6 amp/dm² at a pH of 6.4-6.8. Both higher and lower current density decreased current efficiency as seen by experiments 5 and 1. Rotation of the anode lowered current efficiency as seen by experiments 6 and 7. It has been confirmed that sodium fluoride in the electrolyte leads to an increase of current efficiency of perchlorate formation. Schumacher (19), after exhaustive investigation, found that nickel or stainless steel were the best cathodes for perchlorate preparation, but in these experiments cobalt-tungsten alloy plated (22) mild steel rods have been employed

successfully. In subsequent experiments, however, stainless steel cathodes were employed.

Effect of addition agents.—Angel and Mellquist (17) reported that reasonable current efficiency (72-79%) for perchlorate formation could be obtained without any addition agent using lead dioxide anodes prepared by depositing from tartrate bath. Others (11-14) showed that practical efficiencies could be obtained only by adding 2 g/l sodium fluoride when lead dioxide anodes were prepared by depositing from a lead nitrate bath. Schumacher *et al.* (19) restudied that work and obtained best results with addition of only 0.5 g/l sodium fluoride to the electrolyte. The use of persulfate as addition agent instead of fluoride has been reported recently (18). Data in Table III indicate that without any addition agent current efficiency is very low. Normally electrolysis is carried out under acidic conditions (below pH 7) by the addition of either hydrochloric or perchloric acid (25). The addition of sulfuric instead of hydrochloric acid was tried and gave better results. This may be due to oxidation of SO₄²⁻ to S₂O₈²⁻ which in turn gives a better efficiency as found earlier by Bennett and Mack (8) and later by Grigger *et al.* (18) who employed persulfate as addition agent. The presence of both sodium fluoride and sulfuric acid gave still better results.

Under alkaline conditions current efficiency (Table III, experiment 5) was as good as that obtained

Table III. Effect of addition agents on current efficiency

Anode, PbO₂—stationary, previously used anodes; cathode, stainless steel; volume of electrolyte, 200 ml; anode current density, 23.2 amp/dm²; current concentration, 35.0 amp/l; temperature, 28°-30°C

Expt. No.	Initial chlorate concentration, g/l	Final chlorate concentration after theoretical time, g/l	Addition agents	pH	Bath voltage, v	Current efficiency, %	
						Half the theoretical time	Theoretical time
(a) Acidic condition							
1.*	609.0	324.9	9 ml of 3.11N HCl	6.6-6.8	4.5	53.0	42.2
2.	609.0	233.3	3.1 ml of 3.11N H ₂ SO ₄	6.6-6.8	4.4-4.5	70.1	57.6
3.	609.0	147.7	2 g/l NaF + 6.2 ml of 3.11N HCl	6.6-6.8	4.5	84.2	73.0
4. (a)	609.0	94.6	2 g/l NaF + 3.0 ml of 3.11N H ₂ SO ₄	6.6-6.8	4.5	93.6	82.3
(b)	613.0	89.1	2 g/l NaF + 2.3 ml of 3.11N H ₂ SO ₄	6.6-6.8	4.3	94.52	82.8
(b) Alkaline condition							
5.	607.0	156.9	No addition agent	8-10.9	4.5-4.7	80.6	71.2
6.	607.0	88.5	2 g/l NaF	8-10.8	4.3-4.4	93.0	83.1
7.	599.5	237.3	3.35 g/l of Na ₂ SO ₄	8.2-10.6	4.7-4.8	64.2	56.4
8.	599.5	124.8	3.35 g/l of Na ₂ SO ₄ + 2 g/l NaF	8.2-10.5	4.2-4.5	86.5	76.7

* Fresh anode.

Table IV. Effect of pH on current efficiency

Anode, PbO₂—stationary, previously used anodes; cathode, stainless steel; volume of electrolyte, 200 ml; current density, 23.2 amp/dm²; current concentration, 35.0 amp/l; temperature, 28°–30°C

Expt. No.	Initial chlorate concentration, g/l	Final chlorate concentration after theoretical time, g/l	Addition agents	pH	Bath voltage, v	Current efficiency, %		Remarks
						Half the theoretical time	Theoretical time	
1.	609.0	147.7	2 g/l NaF	6.6-6.8	4.5	84.2	73.0	pH maintained by addition of 6.2 ml of 3.11N HCl.
2.	609.0	94.56	2 g/l NaF	6.6-6.8	4.5	93.6	82.3	pH maintained by addition of 3 ml of 3.11N H ₂ SO ₄ .
3.	599.5	128.7	—	6.0-10.4	4.5-4.6	85.1	74.4	After initial pH adjustment, no acid was added during electrolysis.
4.	607.0	116.6	—	6.9-10.7	4.5-4.6	83.7	78.6	
5. (a)	609.0	124.7	—	8.0-11.0	4.5-4.6	91.2	77.8	
(b)	599.5	119.3	—	8.0-10.9	4.3-4.6	88.8	77.7	
6.	599.5	115.4	—	9.0-10.7	4.4-4.6	85.0	77.8	
7.	607.0	112.7	—	10.0-10.8	4.3-4.5	89.0	79.8	
8.	599.5	116.6	2 g/l NaF	6.6-10.8	4.2-4.6	91.4	77.5	
9. (a)	607.0	88.5	2 g/l NaF	8.0-10.8	4.3-4.4	93.0	83.1	
(b)	607.0	96.5	2 g/l NaF	8.0-10.9	4.6-4.7	89.0	81.2	
10.	609.0	77.3	2 g/l NaF	8.5-11.0	4.5-4.7	91.7	84.9	

under acidic conditions by addition of hydrochloric acid (Table III, experiment 3) and was further improved by the addition of fluoride (Table III, experiment 6). Addition of sodium sulfate, however, was found to lower current efficiency slightly under alkaline conditions of electrolysis (compare experiments 6 and 8 as well as 5 and 7, respectively, in Table III).

Effect of pH.—The effect of pH alone does not appear to have been studied systematically by previous workers. It is taken for granted that oxidation should be carried out under acidic conditions. Using platinum anodes, several workers (7-9) reported low efficiencies for alkaline conditions of electrolysis although high current efficiency was reported by Hampel and Leppla (5). The authors noted that the pH of the bath becomes alkaline during electrolysis and the efficiency remains fairly high when using lead dioxide anodes under these conditions. If the starting pH is on the alkaline side (approximately pH 8), cell

efficiency is improved and the presence of fluoride improves it even more.

When the starting pH was 8, it was observed that the pH of the electrolyte in the immediate vicinity of the anode was acidic (pH 2-3 as found by a few drops taken out with a glass rod and tested with pH indicator paper), but the final bath pH approached 11. Above this value of pH, disintegration as well as dissolution of the anode has been observed, leading sometimes to deposition of lead on the cathode.

Experiments in Table IV were all carried out with used lead dioxide anodes. Experiments 1 and 2 show the effect of maintaining pH during electrolysis by addition of hydrochloric acid or sulfuric acid with the addition of sodium fluoride also, a difference of nearly 9.3% in current efficiency being obtained. If the pH of the electrolyte is adjusted to 6.0 and then allowed to rise during electrolysis, as usually happens, the current efficiency was only 74.4%. Experiments 3 to 7 show the influence of starting pH on

Table V. Effect of current density and current concentration on current efficiency

Anode, PbO₂—stationary, previously used anodes; cathode, stainless steel; volume of electrolyte, 200 ml; addition agent, 2 g/l NaF; temperature, 30°C

Expt. No.	Initial chlorate concentration, g/l	Final chlorate concentration after theoretical time, g/l	Anode current density, amp/dm ²	Current concentration, amp/l	Bath voltage, v	Current efficiency, %		Remarks
						Half the theoretical time	Theoretical time	
1.	609.0	77.3	23.2	35.0	(a) pH: 8.0-11.5 4.5-4.7	91.7	84.9	
2.	611.5	85.1	30.0	45.0	4.5-4.7	95.6	84.1	
3.	603.5	63.1	40.0	45.0	4.8-5.3	94.6	88.1	
4.	603.5	70.5	40.0	60.0	5.1-5.3	95.2	86.6	
5.	603.5	63.1	50.0	45.0	5.2-5.6	96.4	88.1	
6.	603.5	74.2	50.0	75.0	5.8-6.1	94.0	85.9	
7.	613.0	89.5	15.3	23.0	(b) pH: 6.6-6.8 3.9	94.3	82.9	2.1 ml of 3.11N H ₂ SO ₄ added
8. (a)	597.5	66.8	23.2	35.0	4.3-4.6	93.4	86.8	2.7 ml of 3.11N H ₂ SO ₄ added
(b)	613.0	89.0	23.2	35.0	4.3	94.5	82.8	2.3 ml of 3.11N H ₂ SO ₄ added
9. (a)	597.5	155.7	30.0	45.0	4.5-4.9	77.2	71.3	3.0 ml of 3.11N H ₂ SO ₄ added
(b)	613.0	137.4	30.0	45.5	4.5-4.8	76.4	74.8	3.1 ml of 3.11N H ₂ SO ₄ added
10.	597.5	163.4	39.8	45.0	4.3-4.8	82.2	70.0	3.7 ml of 3.11N H ₂ SO ₄ added

the current efficiency obtained. A starting pH of 7 or higher gave almost identical current efficiency. Acidic starting conditions (pH 6) give low efficiencies. The influence of pH is perhaps not as much evident with a used anode as with a fresh anode. This is seen from experiments 1, 3, and 5 in Table VII where the starting pH of the electrolyte with fresh anodes is 6.1, 7.0, and 8.0, respectively. The current efficiency figures under these conditions were 52.6%, 61.0%, and 71.2%. It also was observed that the surface transformation of the anode referred to below is favored by high pH. This explains why the influence of pH becomes less marked in the case of anodes which have already been used, as in the experiments in Table IV. Experiments 8, 9, and 10 again show the influence of starting pH, 6.6, 8.0, and 8.9; the corresponding current efficiencies being 77.5, 82.2 (average of two experiments), and 84.9%. It can be argued that the influence of pH is not very significant and trends are due only to experimental errors. The definite increase in current efficiency observed in the 3 sets of experiments referred to above in passing from acidic to alkaline starting condition cannot be just due to error or to chance alone. It can, therefore, be stated that the perchlorate formation at lead dioxide anode is influenced by the pH of the electrolyte used.

Effect of current density and current concentration.—Experiments 1, 2, 3, and 5 in Table V show that current efficiency is almost independent of current density employed in the range 23.2–50 amp/dm² under alkaline pH condition of electrolysis. Current concentration normally is not expected to affect this reaction which takes place at electrode surface. However, it has been observed that the pH at the immediate vicinity of the anode is highly acidic and different from that of the bulk pH and therefore is very much affected by the current concentration and hence the geometry of the cell. The comparatively small influence of pH on the current efficiency observed also has shown itself in current concentration studies under alkaline conditions of electrolysis. At 40 amp/dm² increase of current concentration from 40 to 65 amp/l decreased current efficiency from 88.1

to 86.6%. Similarly, at 50 amp/dm², increase of current concentration from 45 to 75 amp/l decreased current efficiency from 88.1% to 85.9%. The effect, although small, is definitely observed. The simultaneous increase of cell-voltage is also to be noted especially from the point of view of cell design and conditions for commercial scale production. In experiments under acidic conditions, the study was carried out with simultaneous change of both current density and current concentration. One point is obvious from this. The corresponding increase of current concentration resulting from an increase of current density in a given cell greatly contributes to the pH of the anode diffusion layer and the low pH developed is obviously detrimental in maintaining current efficiency so that it drops from 84.8% [average of experiments 8(a) and (b), to 70%, experiment 10]. This explains the influence of high current density on the current efficiency of perchlorate formation under acidic conditions of electrolysis. At low current densities, the anode potential does not attain a value high enough for the perchlorate formation to occur at an appreciable rate so that the efficiency is low. An optimum current density for highest current efficiency has thus been found under acidic conditions of electrolysis.

Effect of temperature.—Table VI shows that current efficiency is affected differently depending on whether acidic or alkaline pH conditions are used to start with. Thus it could be seen from experiments 1 to 4 in Table VI that, when the starting pH of the electrolyte is 8, current efficiency dropped from 88.1 to 85.8%, on increasing the bath temperature from 30° to 60°C (2.3% decrease for 30° increase) which is not very significant. However, increase of temperature to 75°C not only decreased current efficiency but also disintegrated the anode. When the pH is maintained by addition of acid at 6.6 to 6.8 as is done usually, it is observed that a maximum current efficiency is obtained for an optimum temperature condition (30°C), thereby making it imperative to maintain the temperature at this desired level to obtain this efficiency. Experiments 8 to 11 show a

Table VI. Effect of temperature on current efficiency

Anode, PbO₂—stationary, previously used anodes; cathode, stainless steel; volume of electrolyte, 200 ml; addition agent, 2 g/l NaF

Expt. No.	Initial chlorate concentration, g/l	Final chlorate concentration after theoretical time, g/l	Temp, °C	Bath voltage, v	Current efficiency, %		Remarks
					Half the theoretical time	Theoretical time	
(a) Alkaline condition: (pH: 8 to 11.5); anode current density, 40 amp/dm ² ; current concentration, 45 amp/l							
1.	603.5	63.1	30	4.8-5.3	94.6	88.1	Electrode became intense brown in color and disintegrated
2.	603.5	59.4	40	4.7-5.1	91.5	88.6	
3.	603.5	74.3	50	4.6-4.9	91.5	85.6	
4.	597.5	78.0	60	4.3-4.8	90.9	85.8	
5.	597.5	178.2	74	4.5-4.7	49.8	66.2	
(b) Acidic condition: (pH: 6.6 to 6.8); anode current density, 23.2 amp/dm ² ; current concentration, 35 amp/l							
6.	583.0	185.6	20	4.5-4.9	86.0	64.3	7.7 ml of 3.11N H ₂ SO ₄ added
7.	614.5	147.7	25	4.2-4.4	94.7	74.2	2.5 ml of 3.11N H ₂ SO ₄ added
8.	613.0	89.1	30	4.3	94.5	82.8	2.3 ml of 3.11N H ₂ SO ₄ added
9.	583.0	106.5	35	4.0-4.2	81.0	79.3	2.9 ml of 3.11N H ₂ SO ₄ added
10.	583.0	118.8	40	4.0	83.5	77.6	2.8 ml of 3.11N H ₂ SO ₄ added
11.	604.5	154.5	60	3.9-4.1	88.6	71.5	3.2 ml of 3.11N H ₂ SO ₄ added

Table VII. Effect of fresh and used anode on current efficiency

Anode, PbO_2 —stationary; cathode, stainless steel; volume of electrolyte, 200 ml; anode current density, 23.2 amp/dm²; current concentration, 35 amp/l; temperature, 28°–30°C

Expt. No.	Nature of anode	Initial chlorate concentration, g/l	Final chlorate concentration, after theoretical time, g/l	Addition agents	pH	Bath voltage, v	Current efficiency, %	
							Half the theoretical time	Theoretical time
1.	Fresh	607	225.2	—	6.1–10.9	4.2–4.5	57.1	52.6
2.	Used	599.5	128.7	—	6.0–10.4	4.5–4.6	85.1	74.4
3.	Fresh	607	209.2	—	7.0–11.0	4.3–4.7	61.8	61.0
4.	Used	607	116.6	—	6.9–10.7	4.5–4.6	83.7	78.6
5.	Fresh	607	156.9	—	8.0–10.9	4.5–4.7	80.6	71.2
6.	Used	599.5	119.3	—	8.0–10.9	4.3–4.6	88.8	77.7
7.	Fresh	615.5	173.2	2 g/l NaF	8.0–10.9	4.5–4.75	77.7	70.6
8.	Used	607.0	88.5	2 g/l NaF	8.0–10.8	4.3–4.4	93.0	83.1
9.	Fresh	613.0	143.2	2 g/l NaF + 3.2 ml of 3.11N H_2SO_4	6.6	4.5–4.8	81.2	73.6
10.	Used	613.0	89.1	2 g/l NaF + 2.3 ml of 3.11N H_2SO_4	6.6	4.3	94.5	82.8

drop in current efficiency from 82.8 to 71.5% when the temperature was raised from the optimum level of 30°C to 60°C (11.3% drop for 30° increase).

The effect of temperature on perchlorate formation has been ascribed to various factors by early workers in this field. According to Oechsli (7), the decrease in perchlorate formation caused by the increase of temperature at a given current density may be due to the increase in hydroxyl ion concentration caused by the increased dissociation of water at higher temperatures. Bennett and Mack (8) state that an increase in electrolyte temperature tends to lower the active oxygen concentration and consequently gives a lower oxidizing power.

The effect of temperature on current efficiency can be explained perhaps on the basis of extent of decomposition of chloric acid at different temperatures. It is well known that all chemical reactions are accelerated by a rise in temperature due to activation energy effect. This is also true of the decomposition of chloric acid. Therefore, it is to be expected that a rise in temperature should bring about an increased rate of decomposition and lowering of current efficiency.

The rate of decomposition of chloric acid also depends on the anode layer pH. According to Oechsli (7), stability of chloric acid is favored greatly by diminished acidity. Therefore it is necessary to consider the effect of rise in temperature on anode layer pH. Due to electrode reaction, anode layer pH would be lower than bulk pH. The extent of lowering however would depend on diffusion which in turn is dependent on temperature. Higher temperatures would be expected to bring about a rise in anode pH due to increased rate of diffusion.

From the above discussion, it is clear that the rise in temperature has two opposite effects on current efficiency, *viz.*, (i) decrease in current efficiency due to higher rate of decomposition of chloric acid caused by activation energy effects and (ii) increase in current efficiency due to diminished instability of chloric acid caused by the rise in anode layer pH consequent on the increase of diffusion. The net effect would depend on which of the two would predominate. The rise of current efficiency with temperature up to the optimum is due presumably to the second factor predominating over the first, whereas above the op-

timum temperature the opposite trend is to be interpreted as due to the predominance of the first factor. The relatively low dependence of the current efficiency with temperature at a pH of 8.0 can be interpreted as due to an approximate compensation of the two opposing factors referred to above. In this connection, it is of interest to note that anode layer pH was found to be 1 to 2 when bath pH was 6.6 to 6.8, whereas it was 3 to 4 when bath pH was 8 at room temperature.

Effect of repeated use of anodes.—Results in Table VII show that current efficiency obtained with a fresh anode is lower than with an anode which has

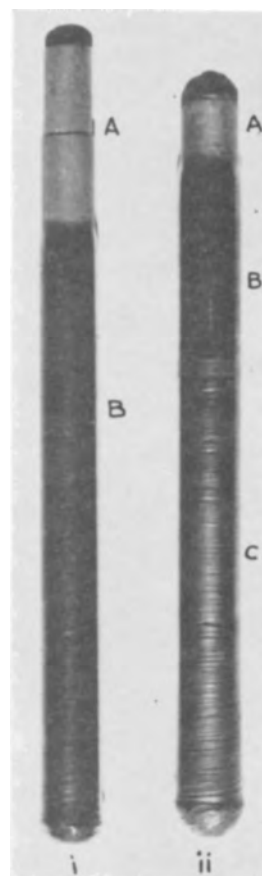


Fig. 1. Photograph showing fresh and used anodes (i) fresh anode, (ii) used anode. A, Graphite core; B, surface of deposited lead dioxide; C, surface of lead dioxide after use.

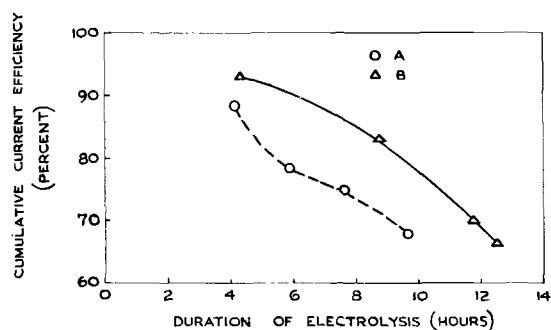


Fig. 2. Variation of current efficiency with duration of electrolysis. A, Acidic condition; B, alkaline condition.

been used before. A fresh lead dioxide anode has a smooth, black metallic sheen which soon changes to a brownish color on use. The addition of fluoride accelerates this change. Figure 1 is a photograph of the electrode showing the change that occurred during electrolysis. The development of the brown color always coincided with best anode performance. The cumulative current efficiency of perchlorate formation is shown in Fig. 2 and was found to decrease with duration of electrolysis to a greater extent under acidic than under alkaline conditions. This is more so with low chlorate concentrations.

Effect of chloride.—Table VIII shows the effect of the presence of chloride in the electrolyte. Concentrations of sodium chloride less than 8.1 g/l do not affect the final efficiency, whereas copious evolution of chlorine occurred when more chloride was present, leading to poor efficiency by oxygen evolution due to the highly alkaline conditions developed by electrolysis of sodium chloride and simultaneous formation of sodium hydroxide.

Anode potential measurements.—Attempts were made to measure the anode potential using a Heath-kit vacuum tube voltmeter. It was observed that

under any experimental conditions steady anode potential could not be obtained. Therefore it is possible to make only certain general observations. The anode potentials measured *vs.* SCE are expressed on the hydrogen scale by adding 0.2377 v (at 30°C). The potentials generally were higher under alkaline conditions (2.45–2.75 v) than under acidic conditions (2.1–2.3 v). The surface transformation occurring as a result of the use led to high fluctuations in anode potential. Addition of fluoride and sulfate under acidic conditions normally led to an increase in anode potential, especially with fresh anodes. The effect was erratic under alkaline conditions and was not great in extent.

The optimum conditions of electrolysis for perchlorate formation can be given as follows, although a fairly wide variation in conditions is possible when pH is alkaline.

	Alkaline condition	Acidic condition
pH	8 to start with	6.4–6.8
Anode current density	40 amp/dm ²	23.2 amp/dm ²
Current concentration	45 amp/l	35 amp/l
Addition agent	2 g/l NaF	2 g/l NaF + dil. H ₂ SO ₄ for pH maintenance
Temperature	40°C	30°C
Energy consumption per kg of NaClO ₄ (D.C.)	2.37 kwh	2.22 kwh

Conclusion

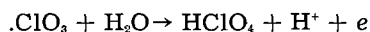
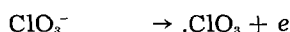
In any case, it is definitely to be considered that perchlorate formation is believed to occur at the anode surface as a result of adsorption of discharged

Table VIII. Effect of chloride addition on current efficiency

Anode, PbO₂—stationary; cathode, stainless steel; volume of electrolyte, 200 ml; addition agent, 2 g/l NaF; anode current density, 40 amp/dm²; current concentration, 45 amp/l; pH, 8.0 at the start and allowed to increase

Expt. No.	Initial chlorate concentration, g/l	Final chlorate concentration after theoretical time, g/l	Initial chloride concentration, g/l	Final chloride concentration, g/l	Duration, hr-min	Bath voltage, v	Current efficiency, %	Remarks
1.	614.5	—	50	39.20	1-20	4.1	—	Copious evolution of chlorine; pH turned alkaline rapidly, surface of lead dioxide changed; solution turned brown; Pb deposition on cathode—experiment stopped
2.	614.5	—	25	—	0-30	4.0	—	Copious evolution of chlorine; pH turned alkaline rapidly, surface of lead dioxide changed; solution turned brown; Pb deposition on cathode—experiment stopped
3.	614.5	199.3	12.3	4.06	6-50	4.1–4.2	65.2	Evolution of Cl ₂ in the beginning; pH change gradual
4.	614.5	106.5	8.13	1.35	6-50	4.2	81.06	Cl ₂ evolution only in the beginning; pH change gradual
5.	614.5	147.7	4.10	2.70	6-50	4.4–4.6	74.3	Cl ₂ evolution in the initial stages (fresh PbO ₂ anode was used); pH change gradual

chlorate radicals. This is assumed mainly because perchlorate formation takes place at a potential more positive than for oxygen evolution at a platinum anode (10). This is analogous to the Kolbe reaction which also occurs on platinum at a potential more positive than for oxygen evolution. We have also observed, by anode potential measurements on lead dioxide, that the reaction occurs at potentials more positive than the oxygen evolution potential on a lead dioxide anode. Further, anode potentials are more positive under alkaline conditions than under acidic condition during electrolysis. The formation of perchlorate probably occurs mainly as a result of the reaction of the discharged chlorate radical with water as indicated below.



This reaction shows that high acidity should develop at the anode interface, and actually during electrolysis it was observed that the pH at the interface was lower than the bulk pH. High acidity at the anode leads to decomposition of chloric acid and to lowering of current efficiency. Experiments carried out at different current concentrations under acidic and alkaline electrolyte conditions confirm this. Use of a rotating lead dioxide anode lowers current efficiency especially when bulk pH is alkaline but the lowering is not as much when bath pH is 6.6-6.8 (26).

Whether bath pH is maintained alkaline or acidic it has been observed that anode layer pH is acidic and perchlorate formation occurs under an acidic environment. The degree of acidity determines the experimental conditions to give maximum current efficiency for perchlorate formation. This explains the varying current efficiency values reported by different workers (see Table I). The current density suggested by different workers therefore depends on the different pH conditions they employed. One factor which has been overlooked by earlier workers is the transformation of the lead dioxide anode surface which definitely appears to influence perchlorate formation. The authors are at present investigating this aspect further and the results will be reported in a later communication.

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REFERENCES

1. F. Winteler, *Z. Elektrochem.*, **5**, 50 (1898); *ibid.*, **5**, 217 (1898); *ibid.*, **7**, 635 (1901).
2. J. G. Williams, *Trans. Faraday Soc.*, **15**, 134 (1919).
3. A. J. Allmand, "Applied Electrochemistry," p. 402, Edward Arnold, London (1912).
4. J. C. Schumacher, *Trans. Electrochem. Soc.*, **92**, 45 (1947); J. C. Schumacher, *Chem. Eng. Progr.*, **43**, 117 (1947); J. C. Schumacher, *Chem. & Met. Eng.*, **51**, No. 12, 108 (1944).
5. C. A. Hampel and P. W. Leppla, *Trans. Electrochem. Soc.*, **92**, 55 (1947).
6. K. C. Narasimham, A. Narayanaswami, and B. B. Dey, *J. Sci. Ind. Research (India)*, **16A**, 512 (1957).
7. W. Oechsli, *Z. Elektrochem.*, **9**, 807 (1903).
8. C. W. Bennett and E. L. Mack, *Trans. Am. Electrochem. Soc.*, **29**, 323 (1916).
9. N. V. S. Knibbs, *Trans. Faraday Soc.*, **16**, 424 (1920).
10. K. Sugino and S. Aoyagi, *This Journal*, **103**, 166 (1956); K. Sugino and S. Aoyagi, *Bull. Chem. Soc., Japan*, **26**, 185 (1953).
11. Y. Kato, K. Sugino, K. Koizumi, and S. Kitahara, *Electrotech. J. Japan*, **5**, 45 (1941).
12. S. Kitahara and T. Osuga, *J. Electrochem. Assoc., Japan*, **10**, 409 (1942).
13. K. Sugino, *Bull. Chem. Soc., Japan*, **23** (4), 115 (1950).
14. K. Sugino and Y. Shibasaki, *J. Electrochem. Soc., Japan*, **16**, 9 (1948).
15. Y. Kato and K. Koizumi, *ibid.*, **2**, 309 (1934).
16. T. Osuga and K. Sugino, *This Journal*, **104**, 448 (1957).
17. G. Angel and H. Mellquist, *Z. Elektrochem.*, **40**, 702 (1934).
18. J. C. Grigger, H. C. Miller, and F. D. Loomis, *This Journal*, **105**, 100 (1958).
19. J. C. Schumacher, D. R. Stern, and P. R. Graham, *ibid.*, **105**, 151 (1958).
20. K. C. Narasimham and H. V. K. Udupa, "Preparation of Lead Dioxide Electrodes—Part I." Presented at the symposium on "Electrolytic Cells" held at Karaikudi (India) in December 1958 (under publication).
21. H. V. K. Udupa and K. C. Narasimham, *Indian Pat.* No. 66,195, Dec. 22, 1958.
22. A. Brenner, P. Burkhead, and E. Seegmiller, *J. Research Natl. Bur. Standards*, **39**, 351 (1947).
23. Julius Grant, "Clowes and Coleman's Quantitative Analysis," p. 176, J. & A. Churchill Ltd., London (1947).
24. D. C. Eagles, *Chem. & Ind.*, 1002 (1954).
25. E. H. Karr, U.S. Pat. 2,772,229, Nov. 27, 1956.
26. K. C. Narasimham, S. Sundararajan, and H. V. K. Udupa, Unpublished work.