

Electrolytic Production of Bromates

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ABSTRACT

An electrolytic process for the production of potassium or sodium bromate using a pure lead peroxide anode has been operated successfully. A concentrated bromate solution was electrolyzed continuously at a cathode of stainless steel with an anodic current density of 20 amp/dm² at 70°C; current efficiency, about 90%; anode consumption about 50-60 mg/K amp-hr. Pure crystalline bromate could be obtained by cooling the cell effluent at room temperature.

Among alkali metal halogenates, only chlorates have been produced commercially in Japan by the electrolytic process. New uses for bromate brought about its electrolytic production, although in much smaller amounts than chlorate. A new electrolytic process using a lead peroxide anode is described here.

Anode for Electrolytic Production of Bromate

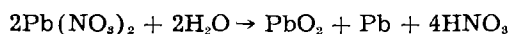
Electrolytic production of bromate is usually carried out at a graphite anode. However, the use of graphite has unfavorable effects. It spalls during electrolysis, forming a mud which makes continuous operation difficult. Also, the final product becomes slightly yellow¹ and can be decolorized only with difficulty. These two facts are the main reasons for the search for a better material.

A brief investigation showed that the lead peroxide electrode manufactured by a process reported earlier (2) was the most practical choice for an anode material.

A compact lead peroxide layer is deposited electrolytically from neutral lead nitrate solution upon the inner surface of an iron cylinder which acts as an anode. An example of the operating conditions is shown in Table I. Apparatus used is shown in Fig. 1.

During electrolysis, the acidity of the electrolyte

gradually increased and the concentration of Pb⁺⁺ decreased according to the following reaction.



The change of these two was found to give a brittle deposit of lead peroxide which could not be cut for finishing or not used for an anode of the electrolysis. Moreover, sudden change of pH due to direct neutralization of acid in the electrolytic bath gave a deposit consisting of heterogeneous layers which was also brittle. Therefore, the pH and the concentration of Pb⁺⁺ should be maintained as constant as possible during electrolysis. This was accomplished by flowing the electrolyte at constant rate and neutralizing the increasing acidity with Pb(OH)₂ by using the apparatus shown in Fig. 1.

The electrolysis was conducted until the thickness of the deposit reached about 8 mm. Each end of the mother cylinder 75 mm in length was cut off; then by cutting the iron part of the cylinder lengthwise, a lead peroxide cylinder of suitable strength and compactness as well as of a smooth outer surface was

Table I. Operating conditions

Electrolyte:	21-22% lead nitrate solution.
Anode:	iron cylinder with surface polished inside; length 500 mm, ID 204 mm, thickness 8 mm, weight 20.6 kg, available surface area 32 dm ² .
Cathode:	copper rod (diameter 25 mm)
Current:	172 amp
Current density, anodic:	5.4 amp/dm ²
Voltage:	7.4 v
Temp:	50°C
Flow rate of electrolyte:	4 to 5 l/min
Time:	66 hr

¹This coloration has been considered hitherto to be due to the presence of chromate added to the cell (1). By the use of a lead peroxide anode instead of graphite, colorless crystals were obtained as shown here.

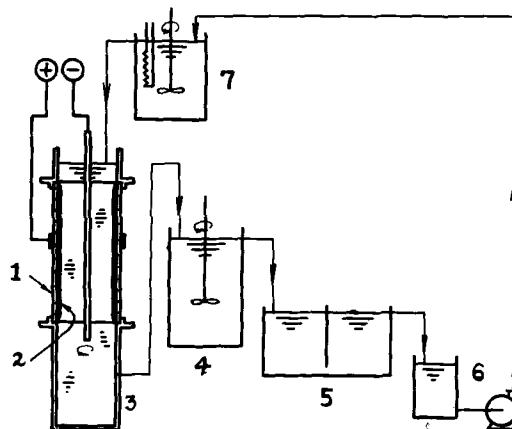
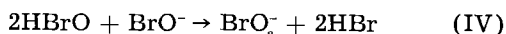
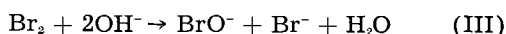
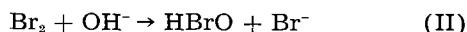


Fig. 1. Apparatus for electrodepositing lead peroxide layer. 1, Iron cylinder; 2, lead peroxide layer deposited; 3, electrolytic bath; 4, neutralization tank; 5, settling tank; 6, pump for recycling electrolyte; 7, preheating tank.

obtained (diameter, 200 mm; length, 350 mm). The lead peroxide cylinder was separated into twelve parts by cutting it again lengthwise. Each part of the lead peroxide thus obtained has the shape of a rectangular piece shown in Fig. 2. Its dimensions are as follows: length, 350 mm; width, 50 mm; thickness, 7-9 mm.

Important Factors in Electrochemical Formation of Bromate

Anodic reactions in bromate formation may be represented as follows.



These reactions are similar to those in chlorate formation, but some differences are seen between the two cases. Reaction (IV) is about 100 times faster than that in chlorate formation according to Kretzschmar (3). On the other hand, reactions (II) and (III) seems to occur imperfectly as compared with those in chlorate formation by comparing the hydrolysis constant of Br with that of Cl_2 (4).² Therefore, in the case of bromate, it may be preferable to maintain the pH of the electrolyte slightly alkaline in order to favor these reactions and thus obtain high current efficiency. This condition can be attained easily by using a neutral or slightly alkaline solution of bromide at the start of the electrolysis. Efforts to keep the pH in the desirable range is not necessary except to avoid discharge of hydroxyl ion.

Reactions (II) and (III) may also be accelerated by high temperature, which has a favorable effect on current efficiency. When reactions (II) and (III) are still slow and imperfect as compared with reaction (I), the current concentration and current density may have a marked influence on the current efficiency. Preliminary experiments showed that high current concentration and also high current density [for example, 50 amp/l to 100 amp/l (13-28 amp/dm²)] had no unfavorable effect on the current efficiency. This facilitates design of the cell and also the determination of the operating conditions.

² This was confirmed by the fact that bromine separated at the bottom of the cell when the initial pH of the electrolyte was less than 8 and the circulation of the electrolyte was inefficient.

Fig. 2. Lead peroxide anode

Cell Design

The cell design depends on the use of vertical lead peroxide anodes of rectangular shape and stainless steel cathodes. A diagram of the bromate cell construction is shown in Fig. 3.

The cell body is constructed of a sheet iron rectangular tank 900 mm long x 500 mm wide x 400 mm high. All inside surfaces of the body are lined with concrete. Cell volume was determined so as to keep the cell temperature as constant as possible by balancing the internal heating with natural cooling. Three sheets of hard vinyl chloride polymer rested side by side on top of the cell and covered it entirely. The central cover supported 10 anodes and 20 cathodes. These were arranged in 6 rows running the length of the cover. Down the middle were two rows of 5 anodes, and on either side was a row of 5 cathodes. In each cell all anodes and all cathodes were in parallel.

The lead peroxide anodes were 50 mm wide, 7-8 mm thick, and 350 mm long, and extend about 55 mm above the cover. The stainless steel cathodes (Avesta 832-SV) were 35 mm wide, 2.5 mm thick, and 400 mm long. The distance from an anode to the nearest cathode was about 13 mm.

Hydrogen discharged at the cathodes caused sufficient circulation of the cell liquor. It was vented through the roof from each cell.

Batch Experiments

The cell was operated batchwise with 90-95 l of potassium bromide solution. To decrease anode loss, the temperature was kept as constant as possible. The pH was not controlled and reached a maximum of about 10 when a slightly alkaline solution (less than pH 9) of bromide was used at the start of the

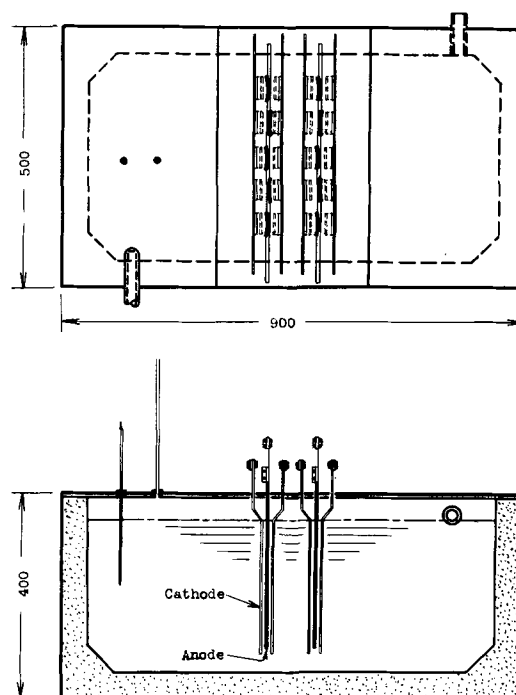


Fig. 3. Sanwa bromate cell. Dimension: length, 900 mm; width, 500 mm; height, 400 mm. Anode: lead peroxide bar; length, 350 mm; width, 50 mm; thickness, 7-9 mm. Cathode: stainless steel bar; length, 400 mm; width, 35 mm; thickness, 2.5 mm. Capacity: 95 l.

Table II. Operating conditions

Run No.	Starting electrolyte			Initial pH	Current, amp	Cell voltage, v	Temp, °C	Time, hr min		Amount of current, 1000 amp-hr
	KBr g/l	KBrO ₃ g/l	Vol, l							
1	186	4	95	8.3	494	4.0	69	47	10	23.2 ₈
2	173	6	90	8.9	506	3.9*	66	44	00	22.2 ₇
3	229	9	95	6.9	500	3.8	67	56	40	28.3 ₂
4	232	9	95	8.9	500	3.7	66	56	40	28.3 ₂
5	233	9	95	9.2	500	4.0	70	56	40	28.3 ₂

* Voltage reached about 4.6 v at the end of the electrolysis.

Results

Run No.	KBrO ₃ produced		Total kg	KBr unconverted, kg	Conversion of bromide to bromate, %	Current efficiency, %
	Crystal obtained, kg	In solution, kg				
1	17.3	5.6	22.9	1.0	94.2	94.6
2	15.7	5.4	21.1	0.4	97.4	91.3
3	22.7	3.9	26.6	2.7	87.4	90.5
4	22.7	4.4	27.1	2.4	88.9	92.2
5	24.0	3.1	27.1	3.0	86.7	92.2

electrolysis. All electrolyses were conducted at an anodic current density of 20 amp/dm². Operating conditions and results are given in Table II.

Two runs were made to determine what losses the anode might sustain (Table III).

Lead peroxide losses averaged 53-56 mg/1000 amp-hr and also 57-60 g/ton of product. It indicated that the loss amounted to about 2.2-2.6% of the original weight after the anode has been used for one year. Lead could not be detected in the product, the electrolyte, or in a black deposit which developed on the cathode. Lead was found in the slight amount of mud on the bottom of the cell.

An Example of Commercial Production

On a commercial scale, 24 cells were connected in series to make a circuit of 90 v and 500 amp. The cell system was divided into two solution series of 12 cells each. Electrolyte was introduced into the

cell by means of a glass tube through the cover at one end and was discharged by the same means through the cover at the opposite end. The flow maintained good circulation.

A potassium bromide solution (pH 8-9), containing approximately 210-220 g/l KBr, 19-24 g/l KBrO₃, and 2 g/l K₂Cr₂O₇, was fed from a constant head tank into the cells. The concentration of bromide was adjusted so as to prevent crystallization of bromate during electrolysis. In a single pass through the cell, about 140 g/l of bromide was converted to bromate. The composition of cell effluent was approximately 270 g/l KBrO₃ and 90 g/l KBr. Results obtained are summarized in Table IV.

Cell effluent was a very clear solution due to the insolubility of the anode, and filtration was not necessary. After electrolysis, the electrolyte was cooled to 20°-25°C with circulating water. About 87% potassium bromate crystallized out. Almost all of the remaining potassium bromate in the mother liquor can be crystallized by adding a suitable amount of potassium bromide to return the electrolyte to the original concentration for a new cycle in the bromate cells. By this method, 97% of the bromate produced can be crystallized out without evaporation.

Potassium bromate crystal thus produced has excellent purity without recrystallization. Following

Table III. Operating conditions

Electrolyte: 180-220 g/l KBr, 15-25 g/l KBrO₃,
2 g/l K₂Cr₂O₇,
pH 9-10 (during electrolysis)
Temp, 70°-85°C

Run No.	Current, amp	Amperage per one anode	Anodic current density, amp/dm ²	Time, hr	Amount of current per one anode, 1000 amp-hr
Cell 1 (10 anodes)	600	60	30	2970	178
Cell 2 (15 anodes)	750	50	20	6170	308

Results

Run No.	Weight of anode* before and after electrolysis, g		Loss, g	Loss per 1000 amp-hr, mg	Loss per ton KBrO ₃ , g
	before electrolysis, g	after electrolysis, g			
Cell 1	1146.5	1136.5	10.0	56.2	60
Cell 2	1043.6	1027.2	16.4	53.3	57

* Cell 1, mean value of 4 anodes; cell 2, mean value of 10 anodes.

Table IV. Characteristics of bromate production

Current: 510-550 amp
Voltage: 1st cell 3.8 v, 2nd cell 3.7 v,
other cells 3.5 v in 12 cells
Current density, anodic: 20-22 amp/dm²
Temperature: 65°-72°C (1st to 4th cells, less than 60°C)
pH: alkaline, less than about 10
Rate of flow: 32 l/hr
Current efficiency: 90-92%
Energy consumption: 3.84 kw/hr (d.c.)/kg KBrO₃
Cell feed: 210-220 g/l KBr, 19-24 g/l KBrO₃
Cell effluent: 260-280 g/l KBrO₃, 80-100 g/l KBr

are the chemical specifications of the final product currently being produced: colorless crystal, KBrO_3 assay, 99.2-99.5%; bromide as KBr , 0.05-0.1%; free acid, 0.35 cc 1/50N NaOH /5 g KBrO_3 , max; total nitrogen, 0.002% max; sulfate, 0.005% max; heavy metals, 0.0005% max; iron, 0.0025% max.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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High Temperature Oxidation of High Purity Nickel between 750° and 1050°C

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ABSTRACT

Kinetic studies on the oxidation of nickel using the vacuum microbalance method have been extended to 1050°C in order to determine the conditions and mechanisms of breakdown of the metal in oxidation. Below 900°C Ni oxidizes in the normal manner and the rate data fit in well with experimental rate relationship already established. At 900°C and higher, parabolic rate law plots of the data show increasing values of the constant with time. At 1000°C and higher, the oxide cracks away from the metal. It is suggested that Ni fails in protective oxidation due to a loss of adhesion at the oxide metal interface.

A number of studies have been reported on the oxidation of pure Ni. These studies were reviewed in an earlier paper (1). In recent years precise data have been obtained on the kinetics of the oxidation of pure Ni at temperatures up to 900°C. Moore (2), using a volumetric method, studied the reaction over the temperature range 400°-900°C while Gulbransen and Andrew (1), using a sensitive weight gain method, studied the reaction over the temperature range 400°-750°C. Considering the differences in method and metal, good agreement was found. In both studies the parabolic rate law was used to correlate the experimental data. Using the classical rate theory of oxidation, Gulbransen and Andrew (1) proposed a mechanism of reaction based on the diffusion of Ni ions through cation vacancies.

This paper extends the earlier work to 1050°C. Two objectives were of particular interest. First, to compare oxidation rate data with tracer studies (3) on the diffusion of Ni ions through nickel oxide and, second, to determine the conditions for transition in the mechanism of oxidation. Studies on several other metals (4) have shown that at some oxide thickness transition occurs from a slow protective oxide formation to a more rapid nonprotective type of oxide formation. If this transition phenomena is found to occur for all metals and alloys, we are dealing with a question of great technical importance.

Failure of metals in protective oxidation.—The use of metals and alloys at high temperature in many applications depends on the fact that the oxide film limits to a certain extent the rate of oxidation. In the protective range of reaction the rate of oxida-

tion decreases as the oxide film thickens. However, at some temperature, time, and oxygen pressure, or film thickness, the rate of oxidation undergoes a transition to a more rapid reaction in which the rate of reaction does not depend on the oxide thickness. This phenomena has been termed "catastrophic reaction," "breakaway corrosion," "transition reaction," etc., depending on the degree of change in the reaction kinetics. The change in kinetics is referred to here as "failure in protective oxidation"; the film or scale is no longer rate controlling. The following physical and chemical factors have been related to the onset of transition in the kinetics of the reaction: (a) volatilization of the oxide; (b) volatilization of the metal; (c) phase transformations in the oxide; (d) phase transformations in the metal; (e) melting of the oxide; (f) loss of adhesion of the oxide to the metal; (g) combustion.

Apparatus and Method

Kinetic measurements were made using a vacuum microbalance method which has been described (5). However, to extend the range of the method, a low sensitivity balance was used as well as specimens of smaller area. In this way film thicknesses of 2000 $\mu\text{g}/\text{cm}^2$ weight gain could be measured. In terms of film thickness for NiO , this weight gain is of the order of 126,000Å. The microbalance had a sensitivity of 4.75/division of 0.001 cm.

Samples were prepared from high purity nickel strip purchased from Johnson, Mathey and Company, London, and had no metallic impurities in excess of 0.0005%. Specimens were abraded through