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**Lead Dioxide-Plated Titanium Anode
for Electrowinning Metals
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UNITED STATES DEPARTMENT OF THE INTERIOR

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Lead Dioxide-Plated Titanium Anode for Electrowinning Metals From Acid Solutions

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LEAD DIOXIDE-PLATED TITANIUM ANODE FOR ELECTROWINNING METALS FROM ACID SOLUTIONS

by

L. W. Higley, Jr.,¹ W. M. Dressel,² and E. R. Cole, Jr.¹

ABSTRACT

Electrowinning metals from solutions leached from low-grade ores is becoming an increasingly important extraction method as the metal industry turns to pollution-free recovery processes. Lead-alloy anodes are used industrially in the electrolytic recovery of zinc and copper. However, associated with the use of these anodes are the inherent problems of stability and lead contamination of the cathode. In an effort to eliminate these problems, the Bureau of Mines has developed a relatively inexpensive lead dioxide anode for electrowinning metals from strong acid solutions.

The anode was prepared by depositing PbO_2 directly on a titanium blank in a strong HNO_3 - $Pb(NO_3)_2$ solution at 2.15 to 6.45 A/dm² and 60° C. This anode was tested in zinc and copper electrowinning cells containing 200 gpl H_2SO_4 and 35 to 100 gpl metal ions at the current density of 3.23 to 6.45 A/dm². Contamination of the cathode by lead was ≤ 0.005 pct. A 30-day test at 6.45 to 12.90 A/dm² in an electrolyte containing 200 gpl H_2SO_4 and no metal ions resulted in a slight change in surface morphology of the PbO_2 anode but no measurable change in anode weight or dimensions.

INTRODUCTION

Electrowinning metals such as copper and zinc is rapidly replacing pyrometallurgical methods (11).³ Electrowinning metal from acid solutions requires that stable, inert, and relatively inexpensive anodes should be used. Platinum-group metals meet the first two requirements but are extremely expensive. Other metals and alloys are relatively inexpensive but corrode readily in acid solutions under anodic current and therefore cannot be used unless precoated with a protective conducting coating.

In Europe, particularly in the U.S.S.R., Hungary, Germany, France, and England, metal substrates have been coated with PbO_2 and used as anodes in the

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³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

electrooxidation of alkali-chloride solutions (1-2, 5-7, 10, 12). The metal substrate on these anodes is usually titanium or tantalum on which a flash-coated surface of copper and/or nickel is applied prior to PbO_2 plating (1-2, 7-8). Good electrical conductivity and stability in acid solutions makes titanium and tantalum excellent choices for use as a substrate for coated anodes. Although these anodes are suitable for use in electrooxidation of the alkali-chloride solutions, they are not suitable for application in the electrowinning of metal from strong acid solution. They tend to fail after short service owing to the dissolution of the flash coating, when cracks and fissures develop in the PbO_2 layer. The dissolved copper or nickel coating interferes with zinc electrolysis (8-9). Furthermore, the PbO_2 layer loses its adherence to the metal substrate and creates additional problems.

In some of the processes for deposition of PbO_2 , F^- ions are present. If these ions are absorbed into the PbO_2 , they subsequently may be released into zinc electrowinning solutions and etch the aluminum cathodes upon which the zinc is deposited. The deposited zinc then can adhere so strongly to the aluminum cathode that stripping of the metal from the cathode becomes virtually impossible.

An extensive program of converting chlor-alkali cellrooms from graphite anodes to coated titanium anodes has resulted in more than 40 cellrooms being converted. As a result, about one-third of the total North American market is producing chlorine from titanium-based anodes. These anodes have resulted in expansion of plant capacity, either by permitting higher current density or by the addition of more cells on the same electrical circuit. Some converted cells now have completed 6 years of operation using the so-called "dimensionally stable anodes" (platinum-coated titanium). During 1972, 1 billion kwhr of electrical energy was saved using these anodes rather than graphite (4).

Stringent limitations on sulfur dioxide emissions are placing the copper industry in a particularly difficult position. Even though the industry is trying to achieve these limits by scrubbing techniques and hydrometallurgical processes, it is certain that to meet the standards in the time frame imposed will require considerable amounts of money, which will influence greatly the copper market in years to come (3). Thus, the development of stable metal anodes in conventional electrowinning facilities will permit electrowon-quality copper to be produced with a low lead content and could in itself prove to be a significant factor in helping determine an acceptable solution to the problem of pollution control.

Protective coatings of PbO_2 have been applied to lead-silver and lead-antimony alloys that are used for copper and zinc electrowinning. However, these anodes require long break-in or preconditioning times and are relatively unstable. Lead-silver anodes are expensive because the silver content may be as much as 1 pct (8).

At the beginning of electrolysis with a lead or lead alloy anode in a sulfate electrolyte, Pb^{++} ions from the dissolution of the anode react with $\text{SO}_4^{=}$ ions and PbSO_4 precipitates on the surface of the anode. Since PbSO_4 is a dielectric, the voltage rises and in the range of 900 to 1,200 mv (potential versus the $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode--0.667 v), a stable conductive film of

PbO_2 is deposited. Conditioning times of from a few hours up to several days are necessary before a stable PbO_2 coating is formed. Cathode deposits produced during the conditioning period are scrapped or their value is discounted owing to contamination by lead in the form of PbSO_4 that migrates from the anode. It is apparent that lead contamination can be an elusive and a costly problem in both zinc and copper electrowinning (9-10).

From the foregoing, one can readily see the importance and desirability of the development of a stable, inert, PbO_2 anode suitable for use in copper and zinc electrowinning. Consequently, because the electrowinning process is such an important part of the metals industry and is essentially nonpolluting, there is keen interest in any technical advancement that can be made in this area. The elimination of tankhouse problems, such as lead contamination, will not only improve recovery efficiency, but will reduce the energy requirements in electrowinning. The Bureau of Mines therefore undertook this effort to produce PbO_2 -coated titanium anodes for electrowinning metals in strong acid solutions.

EXPERIMENTAL PROCEDURE AND RESULTS

Preparation of the Plating Bath

The electrolyte for plating PbO_2 was prepared by dissolving 200 grams of corroding-grade lead and 0.1 gram of copper in a nitric acid solution made by diluting 225 ml of concentrated acid (69 pct to 71 pct HNO_3) to 1 liter. The lead was added slowly to keep the solution temperature below 80° C. After the addition of a small amount of HNO_3 to compensate for vaporized or decomposed HNO_3 during the dissolution, the composition of the electrolyte was 200 gpl Pb, 0.1 gpl Cu, and 100 gpl HNO_3 . Finally, 1 to 10 gpl glass beads (minus 325-mesh) were added to the electrolyte to avoid pitting of the PbO_2 deposit. Alternately, lead oxide powder was dissolved in concentrated nitric acid. The use of powdered lead oxide was more convenient and much faster than dissolving corroding-grade lead, and comparable deposits of PbO_2 were obtained. The acid concentration of the electrolyte was kept high enough so that the titanium blank did not passivate, and the lead concentration was kept near the maximum solubility to reduce concentration polarization at the anode at the initial stage of plating. The high acid concentration also prevented deposition of lead on the cathode. The hydrogen overpotential on the titanium cathode during the plating of PbO_2 was lowered by the deposition of the small amount of copper present in the electrolyte.

Preparation of the Titanium Blank

Anode blanks with various designs and sizes were prepared from titanium sheets 7.62 cm wide and 0.32 cm thick. The blanks were bored, slotted, or spiked, and the edges were rounded or serrated in several experimental designs. The blanks were sandblasted within 24 hours before the plating and were kept in a desiccator.

Surface preparation of the titanium blank to obtain good PbO_2 adherence was given careful attention. Etching with varying concentrations of HF or

HF + HCl solution was tried, but none of the treatments produced an acceptable surface. Sandblasting appeared to be best. Flash coating of the blank with various metals, except those in the platinum group, was not attempted because they would have dissolved in the plating bath when anodic potential was applied. A flash coating with 0.11 g/m^2 platinum produced a good adhesion of PbO_2 and the least electrical interface resistance, but this practice was abandoned for economic reasons.

The edges of the blank were spiked or serrated to increase the surface area and also to achieve a better mechanical bonding of the plated PbO_2 . Figure 1 shows an example of the titanium blank.

Lead Dioxide Plating

The plating of PbO_2 was carried out in a 3,850-ml glass cell, about 15 by 13 by 28 cm deep. The anode blank was placed between two titanium cathodes approximately the same size as the anode. The electrode spacing between the blank and the cathodes was 4 cm. The plating conditions were 2.15 to 6.45 A/dm^2 , 60° to 70° C , with continuous stirring to circulate the electrolyte and to suspend the glass beads. The glass beads were added to prevent oxygen bubbles from adhering to the titanium substrate during electrolysis and consequently to eliminate the formation of holes in the PbO_2 deposit.

Plating conditions of 2.15 to 6.45 A/dm^2 , 60° to 70° C , were established as the optimum conditions for obtaining good PbO_2 deposition on the anode with a minimum deposition of lead on the cathode. Deposition of lead on the cathode will deplete the lead ions in solution and will affect the deposition of PbO_2 since a high solution concentration of about 200 gpl of lead is required. Lead deposition at 2.15 A/dm^2 tended to be greater with cell temperatures maintained below 60° than with cell temperatures above 60° C . On the other hand, the plated deposits of PbO_2 tended to crack along the edges if the cell temperature was above 70° C or if the current densities exceeded 6.45 A/dm^2 . The anode current efficiency, which was above 95 pct when the lead content was above 175 gpl and the acid concentration was 100 to 120 gpl at 1.61 to 4.30 A/dm^2 , was drastically reduced by increasing the current density above 6.45 A/dm^2 . A problem was encountered with mixed PbO - PbO_2 oxide deposition, resulting in anode current efficiencies considerably greater than 100 pct and some as great as 160 pct. The precise reason for the mixed oxide deposition has not been ascertained, but it appears that time of deposition is an important factor. Short-time (2 hours or less) deposits result in mixed oxide deposition and current efficiencies greater than 100 pct, while longer time deposits in the same solution result in normal current efficiencies less than 100 pct. Figures 3 and 4 show the surface structure and cross section of the PbO_2 anode, which is shown in figure 2.

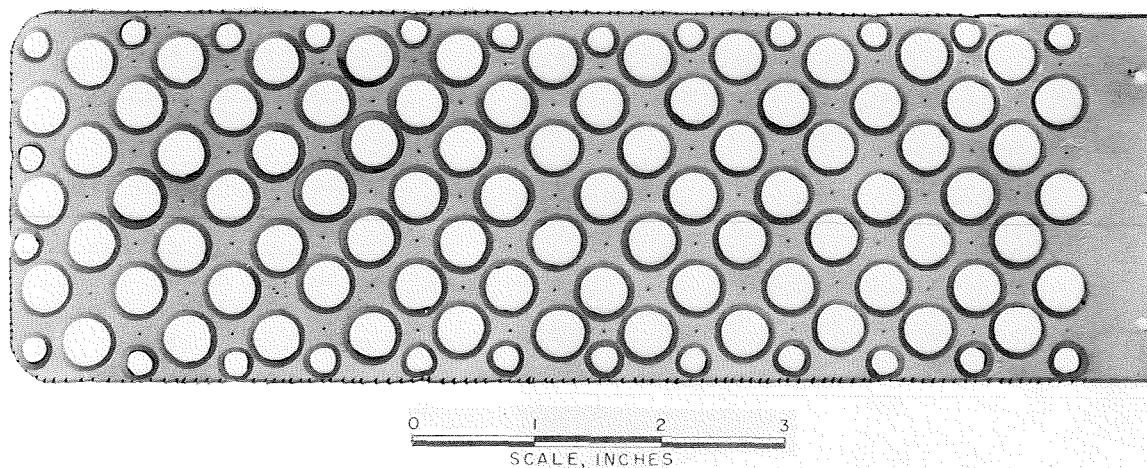


FIGURE 1. - Titanium blank.

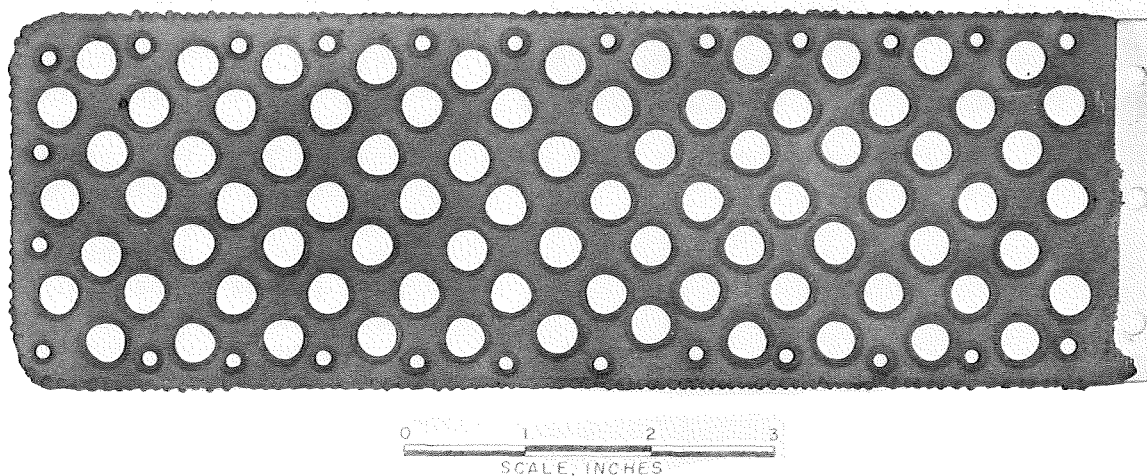


FIGURE 2. - PbO_2 anode plated on a titanium blank.

There was an electrical resistance between the titanium blank and PbO_2 surface, which varied with the conditions of the blank surface and the electroplating. Higher current densities increased the interface resistance; however, it was very difficult to quantify this phenomenon.

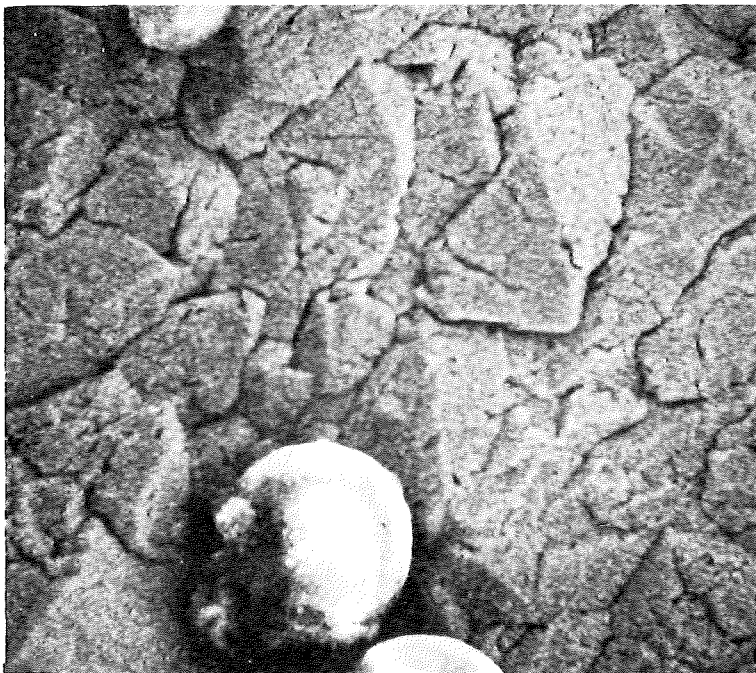


FIGURE 3. - Surface structure of the anode shown in figure 2 (X 1,000).

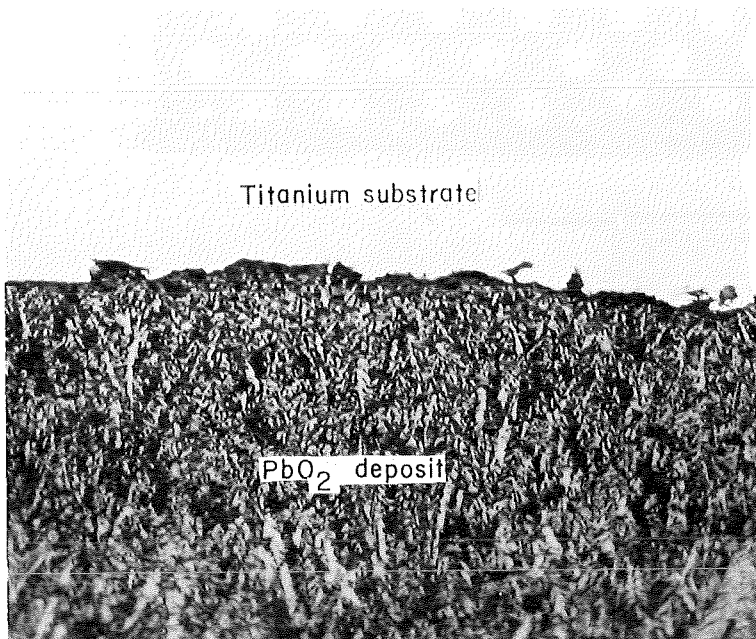


FIGURE 4. - Cross section of the anode shown in figure 2 (X 250).

Lead Dioxide Anode in Electrowinning Solutions

Some of the prepared anodes were used in electrowinning zinc and copper to determine the anode stability under simulated operating conditions. The electrowinning solutions contained 100 to 200 gpl H_2SO_4 , and 35 to 100 gpl metal ions. Small amounts of other agents were added in some instances. The addition of glue was necessary to make the zinc deposit smooth for long-time deposition. Mn^{+2} was added to determine whether or not MnO_2 adhered to the anode surface. (Mn^{+2} is present in industrial practice and MnO_2 adherence occurs on Pb-Ag anodes.) Depletion of Mn^{+2} proved to be rapid, however, and virtually no MnO_2 adhered to the PbO_2 in a 21-hour test. The surface morphology of the anode was examined by a scanning electron microscope (SEM) before and after use in the electrowinning process.

Zinc and copper electrolysis tests were run using "as produced" and "preelectrolyzed" PbO_2 anodes. It was observed that lead contamination of the zinc cathode deposit usually occurred within a few hours after the start of the electrolysis when "as produced" PbO_2 electrodes were used. It was reasoned, therefore, that a preelectrolysis treatment of the PbO_2 anode would remove any lead which might

tend to migrate to the cathode. This was demonstrated by tests in which the "as produced" PbO_2 anodes were preelectrolyzed for a period of only 2 hours at 3.23 A/dm^2 in a solution containing 200 gpl H_2SO_4 at 40°C to remove lead contamination. Zinc deposited from zinc electrolyte and copper deposited from copper electrolyte using preelectrolyzed anodes showed 0.001 pct or less lead contamination in the cathode deposits. The tests are summarized in tables 1 and 2.

TABLE 1. - Contamination of electrowon zinc¹ by lead

Electrolyte		Anode pretreatment	Deposition time, hr	Cathode current efficiency, pct	Pb in cathode, pct
Additives	Current density, amp/dm^2				
None.....	6.45	None, as deposited.	4	95.0	0.005
Do.....	6.45	Preelectrolyzed for 2 hr at 3.23 amp/dm^2 .	4	95.2	.001
2 gpl Mn and 10 mg/1 glue.	6.45	Preelectrolyzed for 2 hr at 6.45 amp/dm^2 .	21	94.6	<.001

¹Electrolyte contained 200 gpl H_2SO_4 and 65 gpl Zn. Temperature was 40°C .

TABLE 2. - Contamination of electrowon copper¹ by lead

Electrolyte		Anode pretreatment	Deposition time, hr	Cathode current efficiency, pct	Pb in cathode, pct
Additives	Current density, amp/dm^2				
454 g/metric ton glue, 45.4 g/metric ton thiourea.	3.23	Preelectrolyzed for 2 hr at 3.23 amp/dm^2 .	45	94.3	0.001
Do.....	6.45	From preceding test, 3.23 amp/dm^2 , 45 hr	11	98.2	<.001
454 g/metric ton glue, 45.4 g/metric ton thiourea, ceramic beads.	12.90	From preceding test, 6.45 amp/dm^2 , 11 hr	10	96.3	<.001

¹Electrolyte contained 100 to 200 gpl H_2SO_4 and 35 to 100 gpl Cu. Temperature was 40°C .

Anodes were tested also for a prolonged period in a solution containing 200 gpl H_2SO_4 and no metal ion using a current density of 6.45 A/dm^2 and an electrolyte temperature of 40°C . The PbO_2 anode was placed between two lead cathodes with a spacing of approximately 4 cm between the blank and each cathode. No visible deterioration or breakdown of the PbO_2 anodes was noticed after 2 hours of preelectrolyzing, nor was any apparent after 30 days of continuous testing. A slight change in surface morphology was noted as shown by a comparison of the scanning electron micrographs made before and after

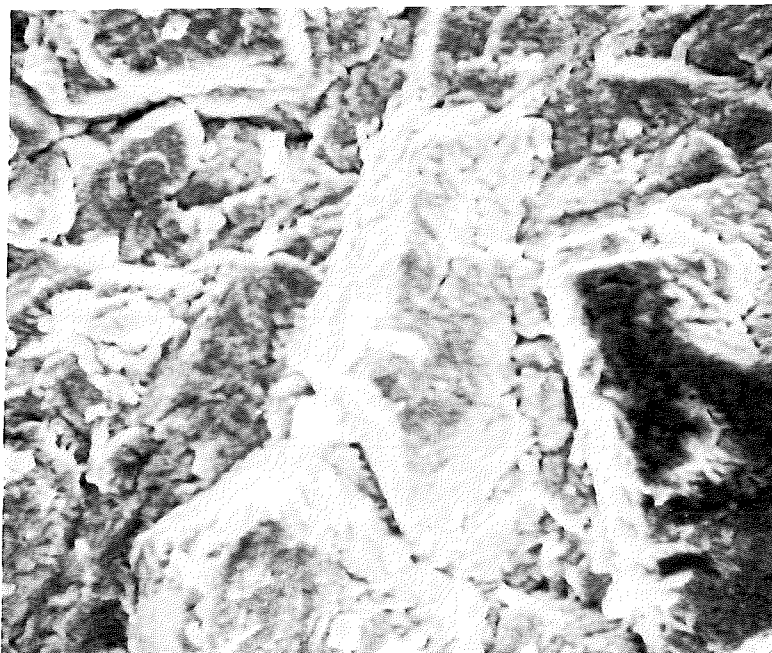


FIGURE 5. - Surface structure of the anode after pre-electrolysis (X 1,000).

treatment and displayed in figures 3 and 5. The same type of structure change is apparent in PbO_2 anodes after use in either copper or zinc electrowinning solutions.

Although surface morphology was slightly altered by preelectrolysis, no significant changes in crystal orientation of the anode were observed. Table 3 compares the crystal orientation pattern of standard plattnerite ($\beta\text{-PbO}_2$), as plated PbO_2 electrodes and/or PbO_2 electrodes after preelectrolysis. It was evident that the deposited PbO_2 on the titanium blank was $\beta\text{-PbO}_2$ but had strong (110), (211), and (220) preferred orientation; all other orientations were weak.

TABLE 3. - Crystal orientation of the PbO_2 electrode¹

Orientation	Intensity ² (1/1 strongest)			Orientation	Intensity ² (1/1 strongest)		
	JCPDS ³ standard	As plated PbO_2 electrode	After preelectrolysis		JCPDS ³ standard	As plated PbO_2 electrode	After preelectrolysis
(110)	1.0	1.0	1.0	(202)	0.5	-	-
(101)	1.0	.3	.4	(321)	.7	0.3	0.3
(200)	.7	-	.2	(400)	.2	-	-
(210)	.1	-	-	(222)	.5	-	-
(211)	1.0	.8	.7	(330)	.2	.1	.1
(220)	.6	.4	.4	(312)	.7	.1	.1
(002)	.4	-	-	(411)	.7	.1	.1
(310)	.6	.2	.1	(420)	.4	-	-
(112)	.7	-	-	(331)	.4	-	-
(301)	.7	.3	.3	(421)	.6	-	-

¹Plattnerite, or $\beta\text{-PbO}_2$.

²No intensity is given for those lines that are less than 10 pct of the strongest line.

³Joint Committee of Powder Diffraction Standards.

DISCUSSION AND CONCLUSIONS

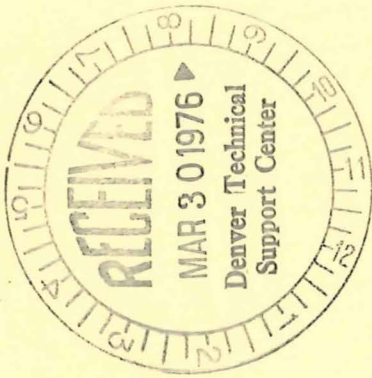
A method was developed for preparing stable, inert, and relatively inexpensive anodes for use in strong acid electrolytes. These anodes were tested in laboratory-prepared zinc and copper electrolytes to show that lead contamination of the cathode deposits was insignificant. The stability of the PbO_2 anode was demonstrated by testing in a strong acid electrolyte for 30 days.

The anode blanks used for depositing the PbO_2 were only 7.6 cm wide and approximately 23 cm long; hence, scaleup from laboratory to commercial size and testing in industrial plants is essential. Further efforts should be directed, in particular, to improving the physical characteristics of the PbO_2 deposit. Lead dioxide is brittle by nature, but it could be produced as a spongy deposit, reducing the possibility of cracking during handling. In addition, a spongy deposit also would permit higher current densities in electrowinning. It is not in the manufacture of industrial-size PbO_2 anodes that problems could arise, but in the handling.

Long-term electrowinning studies using the prepared anodes to recover zinc or copper from samples of the respective industrial electrolytes are needed to determine whether the lead contamination problems normally associated with the use of lead-silver or lead-antimony anodes can be eliminated or minimized by using the Bureau's PbO_2 -coated titanium anodes.

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