

## **NEW WROUGHT Pb-Ag-Ca ANODES FOR ZINC ELECTROWINNING TO PRODUCE A PROTECTIVE OXIDE COATING RAPIDLY**

R. D. Prengaman and A. Siegmund  
*RSR Technologies, Inc.*  
2777 Stemmons Freeway, Suite 1800  
Dallas, Texas, U.S.A. 75207

### **ABSTRACT**

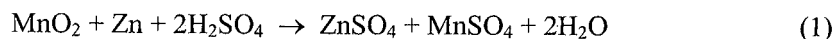
Lead anodes used in zinc electrowinning generally contain 0.5 – 1.0 % silver to reduce the rate of corrosion over the service life. For good quality zinc, the cathodes must contain less than 10 ppm lead. In order to reduce the lead contamination of the cathode, the lead anode must become coated with a protective layer of  $PbO_2/MnO_2$ . The formation of this layer may take as long as 30 – 60 days, during which time zinc production is substantially reduced and the cathodes are contaminated with lead. To improve the mechanical properties of Pb-Ag-anodes alloying elements such as calcium, strontium, barium and others are added. The production of cast lead-silver or lead-silver-calcium anodes often results in the formation of numerous holes, voids or laps in the anode surface that can initiate localized internal corrosion. Based on the experience as the major supplier of rolled anodes for copper electrowinning, RSR Technologies has developed an improved anode for zinc electrowinning. The anode consists of a rolled Pb-Ag-Ca-alloy with a controlled surface grain structure. It forms an adherent protective oxide coating within 2 – 3 days when placed in an electrowinning cell. The preferred calcium and silver contents of the alloy are 0.03 – 0.08 % and 0.3 – 0.4%, respectively. Rolling sheets significantly reduces the presence of internal porosity or laps. The lack of defects results in long anode life. The rolling also produces a uniform grain structure to which the corrosion product readily adheres, thus significantly reducing the conditioning period.

## INTRODUCTION

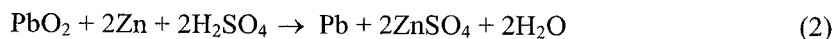
Lead contamination of the cathodes in zinc electrowinning is minimized by the formation of a stable protective coating of  $\text{PbO}_2$  on the surface of the anode. The formation of the stable  $\text{PbO}_2$  layer is a slow process on the normally utilized lead-silver anodes. Lead-calcium-silver alloys, investigated and applied in the past, also showed a very slow rate of formation of the protective  $\text{PbO}_2$  layer.

In the conditioning of the anodes to form a  $\text{PbO}_2$  layer, oxygen evolution on the anode surface causes small fine particles of  $\text{PbO}_2$ , which are not adherent, to be detached from the surface of the anode and become suspended in the electrolyte from where they contaminate the cathode with lead. The  $\text{PbO}_2$  particles are reduced to metallic lead at the cathode leading not only to lead contamination, but also to a detrimental morphology of the zinc deposits which can lead to dendrite formation and short circuits. The lead contamination, poor morphology, and poor current efficiency are common in cells containing new anodes.

In addition to oxidation of the lead surface to  $\text{PbO}_2$ , a competitive oxidation process also takes place at the anode. New anodes rapidly oxidize  $\text{MnO}_2$  from the manganese-containing electrolyte. The  $\text{MnO}_2$  not only builds up rapidly on the anode surface but the manganese in solution can also react with the newly formed  $\text{PbO}_2$  particles to produce even higher amounts of  $\text{MnO}_2$ , further reducing the rate of formation of an adherent  $\text{PbO}_2$  film. The result of the  $\text{MnO}_2$  deposition is the formation of large, soft,  $\text{MnO}_2$ - $\text{PbO}_2$  layers which are not well attached to the anode. Oxygen evolution at the anode surface dislodges these layers into a fine suspension of  $\text{PbO}_2$ / $\text{MnO}_2$  particles. These particles can be conveyed in the electrolyte to the cathode where they are reduced to manganese ions whereupon they reform manganese sulfate. The reduction of large amounts of finely divided  $\text{MnO}_2$  at the cathode dramatically reduces the zinc current efficiency via Equation 1.



Because the  $\text{MnO}_2$  sludge also carries  $\text{PbO}_2$  particles, contamination of the cathode with lead results from the spalling of the  $\text{MnO}_2$  layer (Equation 2). Only some of the  $\text{MnO}_2$ / $\text{PbO}_2$  layer contaminates the cathode. A large amount of sludge builds up in the cells and requires frequent cleaning.



Eventually, as the anodic process continues, a hard, dense, protective layer of  $\text{PbO}_2$  is formed on the anode surface. Once this protective film has been formed, cathode contamination decreases and the amount of sludge generated by the anode decreases as well. This process (called conditioning) may take 30-60 days or more depending on the anode composition and current density (1). Because of the difficulty in conditioning anodes, operators of zinc cellhouses are very reluctant to replace an entire cell of used, conditioned anodes with new, unconditioned anodes. Operators will normally replace only one or two anodes per cell or try to condition the anodes prior to use in the cells.

Cominco in the late 1960's developed a method to precondition the anodes in separate cells outside the circuit (2). The process involves the creation of a hard dense  $\text{PbO}_2$  layer on the surface of the anode by oxidation of the anode at high current density in an acidic fluoride-containing electrolyte. This preconditioning process takes 8-12 hours. In this process the

PbO<sub>2</sub> layer is created without the interference of the rapidly forming MnO<sub>2</sub> layer. The anode corrodes to form a very hard resistant surface.

In the early 1990's, an alternative process to anode preconditioning was developed by Mintek (3). This process involves sandblasting the surface of the cast anode with a relatively coarse silica sand at high pressures above 500 kPa. This process roughens the surface of the anode to enhance the formation of a hard adherent PbO<sub>2</sub> layer. Sandblasting has been shown to reduce the time to form an initial corrosion layer on the lead anode surface. It also increases the adherence of the newly formed PbO<sub>2</sub>/MnO<sub>2</sub> layers giving a conditioned anode within several weeks instead of several months, but raises environmental concerns for the manufacturer of the anodes.

As anodes have become larger, it has become much more difficult to cast the anodes to the preferred shape. Rolled lead-silver or rolled lead-calcium-silver sheets have been utilized alternatively in some tankhouses to form these jumbo anodes. The surfaces of the rolled anodes are much smoother than those of the cast anodes generating fewer places for the oxides to adhere. In addition, the texture is oriented in the rolling direction, producing a grain structure even more difficult to corrode and to form an adherent layer of PbO<sub>2</sub>.

RSR Technologies has developed a method to produce a surface on the anode, through controlled rolling and alloying, to which a hard, dense layer of PbO<sub>2</sub> adheres very quickly. In the rolling process a very fine, uniform non-elongated grain structure is developed which presents many fine grain boundaries. These grain boundaries are corroded by the anodic current causing PbO<sub>2</sub> to be produced at many uniformly dispersed sites. The large number of anodic sites cause the PbO<sub>2</sub> to adhere to the anode surface at multiple locations, and permit the anode to be conditioned in the cell within several days, without the need for preconditioning or sandblasting.

## CURRENT STATUS AND DEVELOPMENTS

### Pb-Ag Anodes

Lead-silver anodes have been used for many years for zinc electrowinning. The anodes are produced by casting a lead - 0.5-1.0% silver alloy into a mold containing a copper bus bar and having the anode shape. The anodes have been produced in flat, ribbed, or perforated designs for the body of the anode.

In general the cast anodes have an oriented, dendritic grain structure. Such a structure is shown in Figure 1. The silver in the alloy is segregated as a silver rich phase at the interdendritic boundaries as well as at the grain boundaries. During the initial conditioning or corrosion of the cast lead-silver anodes, these areas where attachment of the PbO<sub>2</sub> corrosion product would normally occur most rapidly (the grain and interdendritic boundaries) are rendered most corrosion-resistant by the concentration of silver. Only the small, lead-rich region between the interdendritic boundaries can be corroded. There are, however, no boundaries for the PbO<sub>2</sub> corrosion product to attach itself to the anode surface. It is only when the surface becomes significantly roughened because of the spalling of the non-attached PbO<sub>2</sub> particles and newly formed MnO<sub>2</sub> particles that the PbO<sub>2</sub> and MnO<sub>2</sub> particles finally form an adherent layer. The higher the silver content of the anode, the longer the process takes to fully form an adherent layer. The conditioning generally takes 30-90 days.



Figure 1 - Structure of a Cast Lead - 0.75% Ag Anode (magnification 160x)

Cast lead-silver alloys are extremely corrosion-resistant, but in general have a life of only 2-4 years. The short life is in general related to the presence of casting defects within the body of the anode. The internal corrosion of these defects, as seen in Figure 2, can lead to the production of holes and uneven corrosion conditions in certain areas of the anode leading to bending, warping and short circuits.



Figure 2 - Defects in a Cast Pb - 0.75% Ag Anode (magnification 320x)

Rolled lead-silver alloys have been used to overcome the problems caused by porosity and casting defects. In this process a billet of lead-silver alloy is cast, rolled to the desired thickness, cut to shape, and joined to the copper bus bar.

Rolling the alloy also breaks up the original cast grain structure, produces a smooth surface with less corrosion, and facilitates the removal of the  $MnO_2$  scale (4). One would think that rolling would produce a grain structure more compatible with rapid conditioning of the anode. The grain structure of a typical rolled lead-silver alloy is seen in Figure 3.

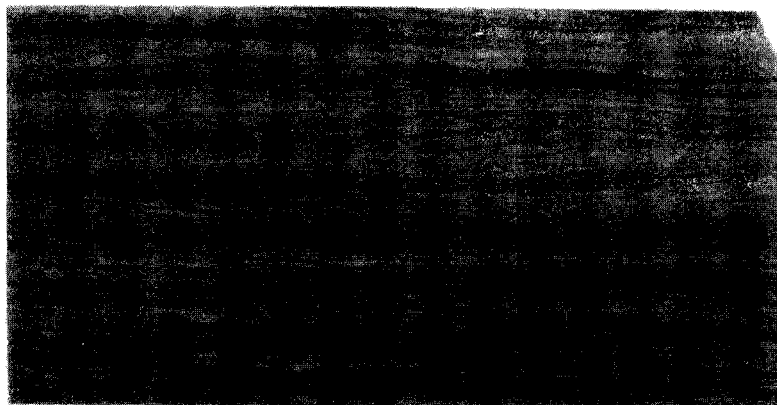


Figure 3 – A Rolled Pb-Ag Anode (magnification 160x)

The structure consists of grains which are oriented in the rolling direction. The extension of the grains during rolling, however, merely bends the grains to the rolling direction and extends them while retaining the original cast-in segregation. The anode structure at the surface still has silver segregation at the grain and sub-boundaries, but the lead areas have been extended and elongated. Very few new grain boundaries have been created and the rate of attachment of the newly formed  $PbO_2$  may not be significantly faster than in cast lead-silver alloys.

#### **Lead-Calcium-Silver Anodes**

Lead-silver alloys are extremely weak and bend easily in response to being struck by cathode blanks as they are removed or returned to the cells, during  $MnO_2$  removal, or in response to variations in corrosion conditions caused by cast-in defects. Calcium has been added to lead-silver alloys to increase the mechanical properties. The calcium content added is normally 0.05-0.07% calcium; however, some researchers report the addition of significantly higher amounts of calcium (5,6,7). Increasing the calcium content to about 0.10% Ca results in higher mechanical properties such as tensile and yield strength and hardness. However, as the calcium content is increased above 0.10% Ca, the mechanical properties decrease because of the segregation of calcium within the anode as primary  $Pb_3Ca$ .

Unfortunately, cast lead-calcium-silver alloys have the same problems of conditioning as lead-silver alloys. The calcium is primarily segregated upon casting to the lead-rich dendrites, while the silver is segregated primarily to the interdendritic region, as seen in Figure 4. Although the calcium slightly increases the rate of corrosion and the formation of  $PbO_2$  in these anodes, the lack of attachment areas makes conditioning as difficult as for lead-silver anodes.



Figure 4 - Grain Structure of a Cast Pb-Ca-Ag Anode

#### Sandblasted Lead Anodes

In an attempt to make lead-calcium-silver anodes more receptive to the formation of an adherent  $\text{PbO}_2/\text{MnO}_2$  layer, lead-silver and lead-calcium-silver anodes have been sandblasted. This technique was developed by Mintek and is employed by Castle Lead (3) and some other manufacturers. The sandblasting disrupts the cast Pb-Ag or Pb-Ca-Ag structure and creates some new grain boundary surfaces, but roughens the structure for better adhesion of the  $\text{PbO}_2/\text{MnO}_2$  film, as seen in Figure 5. Conditioning times have been reported to be significantly reduced using this technique.



Figure 5 - Surface Grain Structure of a Cast Pb-Ca-Ag Sandblasted Anode (magnification 160x)

### Rolled Pb-Ca-Ag Anodes

RSR Technologies has developed a special rolling technique to produce a unique grain structure in wrought lead-calcium-silver alloys. The process produces a fine uniform grain structure both at the surface and throughout the rolled sheet. The fine grain structure has many new grain boundaries which serve as areas of attachment for the newly formed  $\text{PbO}_2$ . The structure is seen in Figure 6. The new grain boundaries are free of silver particles and can be attacked by the oxygen generated in the electrowinning process to rapidly produce an adherent  $\text{PbO}_2$  layer. In tests, the anodes have produced an adherent layer of  $\text{PbO}_2/\text{MnO}_2$  in as little as two days. The lead level of the zinc cathodes was low and a high current efficiency was obtained basically from the first day of operation.



Figure 6 - Grain Structure of a Rolled Pb-Ca-Ag Anode (magnification 160x)

In tests of up to one year duration, the corrosion rate of the anode was very low because of the improved grain structure, showed reduced cell voltage, and maintained its rigidity and high mechanical properties. Although the average life of these anodes for zinc electrowinning is yet unknown, rolled lead-calcium-tin anodes for copper electrowinning have given up to ten years service in certain tankhouses (8).

In addition, assembling the RSR rolled anode sheets to the copper hanger bar is carried out by soldering the sheet to the slotted bar. This forms an intermetallic compound resulting in a complete metallurgical bond between the sheet and the bar (8). Subsequently either casting or electroplating a layer of lead around the bar protects the bond as well as the bar. The bond is maintained for the life of the anode and always provides a high conductivity at the interface. In contrast, conventionally cast around systems generally increases in resistance during the anode life. Figure 7 shows the level resistance of RSR anodes after eight years of operation in copper electrowinning that results in significant power cost savings compared to competitive anodes showing an evident increase in resistance.

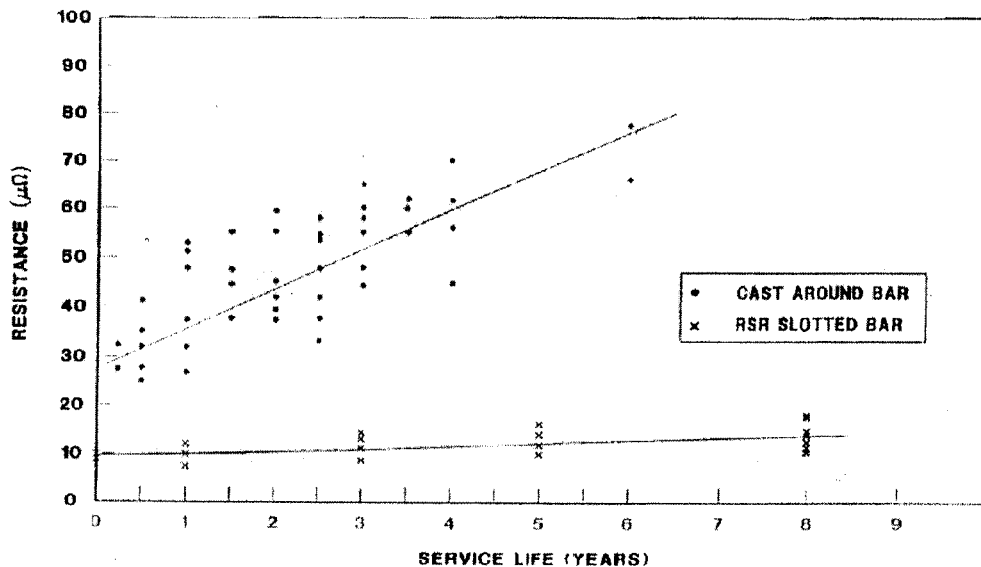


Figure 7 - Resistance Between the Copper Bar and Anode Sheet as a Function of Service Life

### CONCLUSIONS

Conditioning of lead anodes for zinc electrowinning has been a major problem. Rolled lead-calcium-silver alloys with controlled grain structure have been developed by RSR Technologies to enable the anodes to produce an adherent  $PbO_2/MnO_2$  deposit after a few days of operation. The reduced conditioning time produces less lead contamination of the zinc cathode and higher current efficiencies compared to conventional lead-silver or lead-calcium-silver anodes.

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