

Improved copper electrowinning operations using wrought Pb-Ca-Sn Anodes

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ABSTRACT

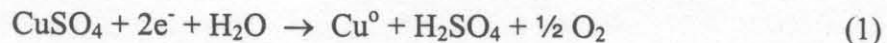
Wrought lead calcium anodes developed by RSR Corporation have improved performance compared to other lead alloy anodes. These anodes have been in continuous service in various locations around the world for as long as fourteen years. Calcium provides mechanical strength to the anode to prevent deformation while tin adds to the mechanical strength, reduces the rate of corrosion, prevents the formation of non-conducting layers on the anode surface, and dramatically improves the conductivity of the anode. Tin is also instrumental in developing the unique rolled structure of the anode which leads to reduced rates of corrosion, longer life, and improved oxygen evolution. Cobalt additions to the electrolyte further enhance oxygen evolution and improve anode life. Higher current densities and higher operating temperatures reduce life. The unique patented method of attaching the rolled anode sheet to the bus bar substantially reduces the resistance of this important joint and offers substantial savings in power over the life of the anode.

INTRODUCTION

In copper electrowinning oxygen is produced at the anode. Oxygen is either evolved as O₂ gas or corrodes the anode. The major goal of anode alloy development is to develop anode materials which resist anodic corrosion by oxygen. When oxygen corrodes the anode surface a new oxide layer builds up, spalls, and possibly contaminates the cathode. This paper describes the RSR rolled lead-calcium-tin anodes. These anodes resist oxidation and enhance oxygen evolution by the unique structure of the corrosion films. Cobalt additions to the electrolyte are particularly effective in enhancing oxygen evolution at the anode surface. Increased evolved oxygen results in greatly improved anode life. Tin additions to the anode produce conducting paths through the corrosion layer. Combined with low resistance at the sheet/bus bar interface, the anodes reduce resistive power losses.

CORROSION OF ANODES

The copper electrowinning reaction shown below:



generates oxygen at the anode while copper is deposited at the cathode. The oxygen, which is generated in the electrowinning reaction, has several possible consequences. Most of these are not beneficial. These are shown below in Table I.

Table I – Effects of Oxygen Generated in Copper Electrowinning

- | | |
|----|---|
| A. | Evolution of Oxygen at the anode surface as a gas |
| B. | Oxidation of materials in solution |
| C. | Formation of peroxides |
| D. | Corrosion of the lead anode |

Evolution of Oxygen as a Gas

The major effect of oxygen evolution is the creation of acid mist above the electrowinning cells. Various methods to control the acid mist have been developed including plastic balls or beads, foam mist suppressants, mechanical shields, and cell ventilation. Higher current density of the electrowinning process and greater efficiency of evolving oxygen as a gas has resulted in more severe acid mist which needs to be controlled.

The oxygen gas generated at the anode also tends to stir the electrolyte. The bubbles of oxygen are evolved at the anode surface and rise rapidly in the narrow region between the anode and cathode. As the rising oxygen bubbles are joined by oxygen gas generated higher on the anode, the stirring effect causes variation in the concentration diffusion layer at the surface of the cathode. This can have a effect of dramatically changing the quality of the copper deposit from top to bottom as well as increasing the number of short circuits in the bottom third of the cathode. In addition the oxygen generated by the intense current density at the bottom of the anode can stir up and suspend flakes of PbO_2 corrosion product from the bottom of the cell, leading to lead contamination of the bottom third of the cathode.

At high current densities and poor electrolyte circulation the oxygen evolved at the anode may be transferred to the cathode where it may oxidize the deposited copper reducing current efficiency. This may be particularly true at the edges of permanent cathodes protected by edge strips. The enhanced oxygen generated at the edges of the anode due to the higher current density in this area may reduce the thickness of the cathodic copper deposit.

Oxidation of Materials in Solution

The oxygen may oxidize materials in solution such as iron, silica, cobalt, and manganese to higher oxidation states as well as organics in solution or at the surface of the electrolyte.

Iron oxidized to ferric (+3) at the anode can be transported to the cathode by the intense oxygen stirring where it is reduced to the ferrous (+2) state causing reduced current efficiency.

The major problem with oxidation of materials in copper EW electrolyte solution is the oxidation of manganese to MnO_2 (1). The MnO_2 reacts with the corrosion product PbO_2 , deposits on the surface of the anode, and can cause severe cathode contamination when the mixed $PbO_2 - MnO_2$ layer is shed.

Iron and cobalt have been added to the electrolyte to reduce the effects of manganese. These elements are preferentially oxidized to manganese and in the case of cobalt reduce the oxygen evolution potential sufficiently to decrease MnO_2 deposition. Figure 1 shows how cobalt and iron prevent the formation of PbO_2 during electrowinning of lead from solution. (2) The same mechanism is believed to reduce oxidation of the lead anode surface to produce PbO_2 as well as to reduce the rate of oxidation of dissolved Mn ions to MnO_2 . The mechanism of O_2 evolution by cobalt has been explained by Hyvärinen. (3)

Oxygen in solution can also degrade organic additives to the electrolyte to control copper deposits at the cathode. In addition, organics carried over from the SX circuit can be partially oxidized creating reactive radicals which can attack the anode at the

electrolyte surface. High oxygen concentrations combined with reactive organics present on the surface of EW cells have resulted in fires when sparks ignite the flammable organic.

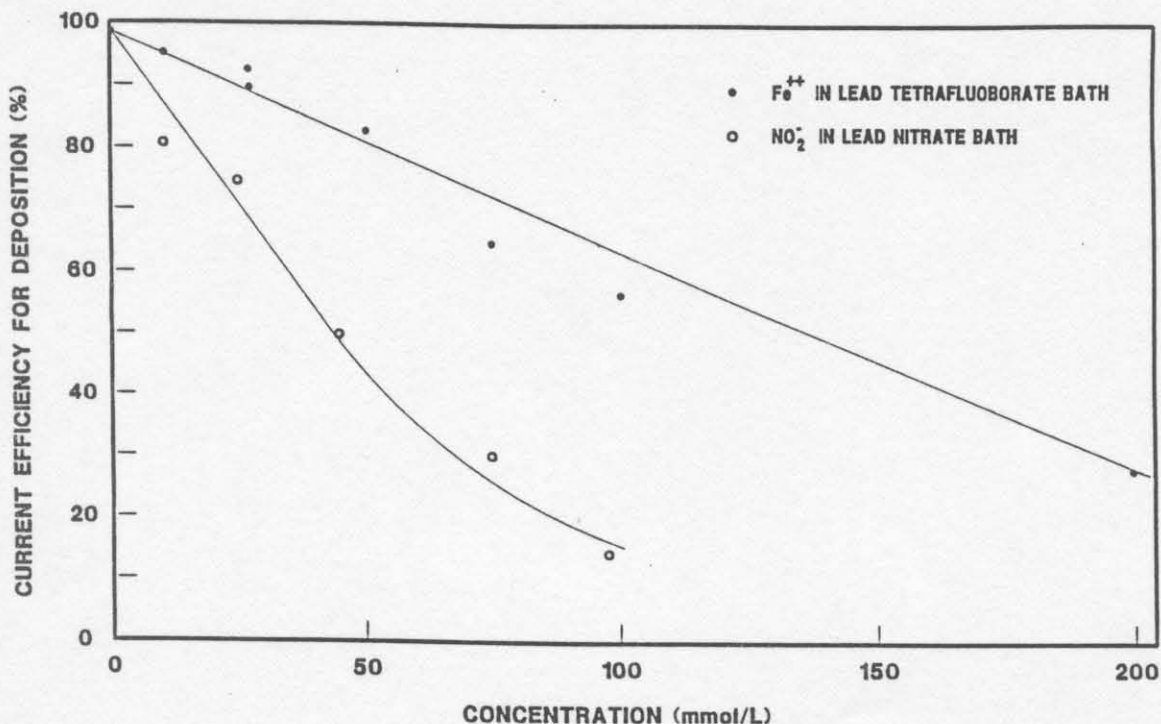


Figure 1 – Effect of Co and Fe on the Deposition of PbO₂ from Solutions

Formation of Peroxides

Peroxides can be formed during intense oxygen evolution at the surface of the anode. The most common peroxides are H₂O₂ and permanganate. These peroxides can damage pipes, tank liners, cathode edge strips, etc. due to their intense oxidizing power.

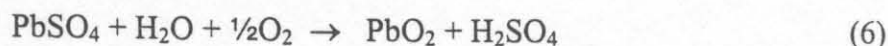
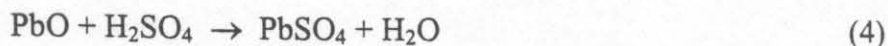
Oxidation of the Anode

The major consequence of the oxygen evolution is the corrosion of the lead anode. The oxygen corrodes the anode directly by the formation of PbO, PbSO₄, complex sulfates, βPbO₂, and αPbO₂ on the surface of the anode.

Figure 2 shows the corrosion of the surface of a lead anode. In the copper EW electrolyte, the high H₂SO₄ acid concentration always results in the formation of βPbO₂, at the external surface of the anode. The lead is corroded by the following reaction:

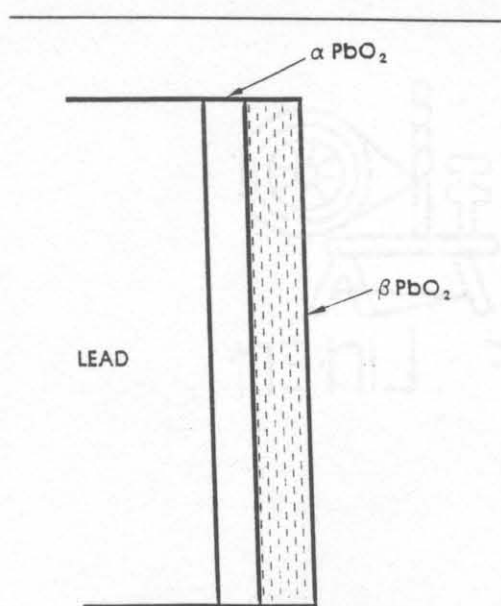


This reaction may actually have several steps. These are shown below:



The surface of a new anode inserted into the cell will form a layer of PbSO_4 on the surface of the anode sheet. As current is applied to the anode, the corrosion product can change from PbSO_4 to PbO to $\text{Pb}(\text{OH})_2$ and finally to PbO_2 as the potential is increased. When the potential is raised sufficiently high, oxygen will be generated at the surface of the anode.

Some oxygen generated at the surface of the anode diffuses back through the βPbO_2 surface corrosion film to further oxidize the lead at the anode/corrosion product interface. The first corrosion product is PbO . Some PbO reacts with H_2SO_4 to generate PbSO_4 and water. The other PbO beneath the PbSO_4 layer can react with water to form $\text{Pb}(\text{OH})_2$ which can raise the pH of the anode/corrosion product interface.



$\text{Pb}(\text{OH})_2$ is further oxidized to PbO_2 by oxygen diffusing through the corrosion layer, water is regenerated at the newly formed PbO_2 surface. The higher pH of the anode/corrosion product layer causes the formation of αPbO_2 at the surface of anode. The αPbO_2 is converted to βPbO_2 at the surface of the anode in contact with the high acid electrolyte.

As the corrosion product becomes thicker it begins to develop small micro cracks parallel to the surface of the anode. These micro cracks are eventually the source of larger cracks which cause flaking of the corrosion product from the anode as seen in Figure 2.

Figure 2 – Corrosion of Lead Anode

Pb-Ca-Sn Alloy Anodes

Anodes, however, are not produced from pure lead, but RSR anodes are produced by rolling cast Pb-Ca-Sn alloys to final gauge. These alloys introduce unique properties to the anodes. Figure 3 shows the effect of calcium content on the rate of corrosion of lead anodes (4). The higher the calcium content the higher is the rate of corrosion of the anode. When the calcium content is increased above 0.08% calcium, the rate of corrosion is increased. This is caused by the formation of Pb_3Ca particles in the melt which can segregate and cause severe non-uniform corrosion of anodes containing higher calcium contents.

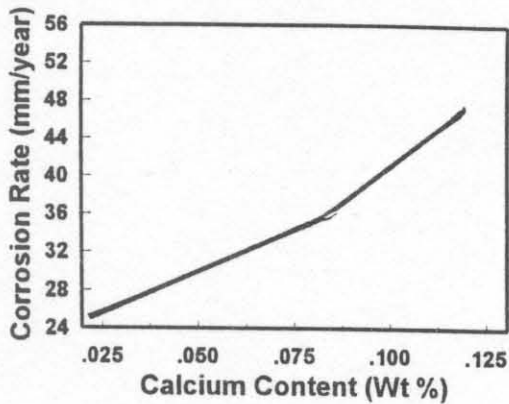


Figure 3 – Effect of Calcium Content on the Rate of Corrosion of Pb-Ca Alloy

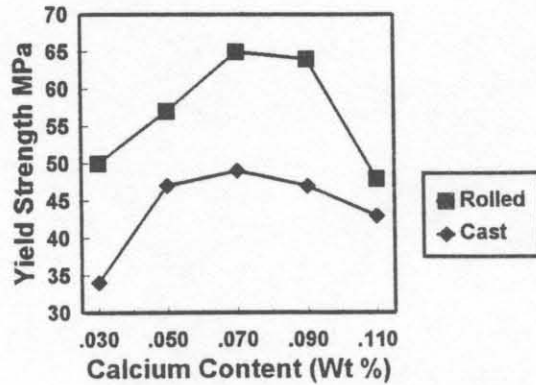


Figure 4 – Effect of Calcium Content on the Mechanical Properties (YS) of Pb-Ca-1.5% Sn Alloys

The calcium along with tin imparts strength to the anode. (5) Figure 4 shows the effect of calcium on the mechanical properties of Pb-Ca-Sn alloys. Note that the mechanical properties decrease at higher calcium contents. Figure 5 shows the effect of tin on the mechanical properties of Pb-Ca-Sn alloys. Rolling the Pb-Ca-Sn alloys further increases the mechanical properties.

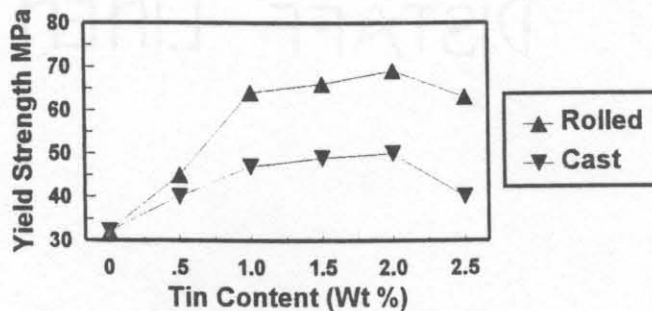


Figure 5 – Effect of Tin on the Yield Strength of Pb-.07% Ca-Sn Alloy

Effects of Tin and Rolling on the Corrosion of Pb-Ca-Sn Anodes

Tin additions to lead-calcium alloys dramatically reduce the rate of corrosion of these materials. As seen in Figure 6, as the tin content is increased, the corrosion rate of the anode decreases.

Tin Content (Wt. %)	Corrosion Wt. Loss (mg/cm ²)			
	0.6	1.2	1.5	3.0
0.1 Ca	126	80	76	54
0.08 Ca	75	37	33	32

Figure 6 - Effect of Tin on the Corrosion Rate of Lead-Calcium-Tin Alloys

In addition to reducing the rate of corrosion, tin has several other beneficial properties for rolled Pb-Ca-Sn anodes. During solidification of the billet prior to rolling into the anode sheet, the tin segregates within the material into subgrains. This segregation of tin is maintained during rolling, creating layers of tin-rich material parallel to the surface of the anode sheet. These tin-rich layers have substantial benefits. They maintain a fine grain structure parallel to the surface which prevents corrosion from penetrating into the anode.

Tin also reacts with the calcium to form fine uniform Sn₃Ca particles within the rolled grain structure. This dispersion of tin has significant benefits to the operation of the anode. Tin has been shown to improve the conductivity and reduce the polarization of anodes. (6, 7)

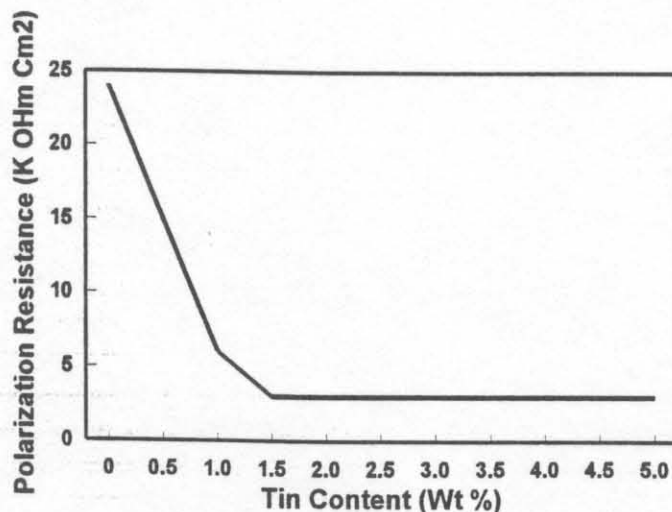


Figure 7 - Effect of Tin on the Polarization Resistance (RP) of Pb 0.08% Ca x Sn Alloys

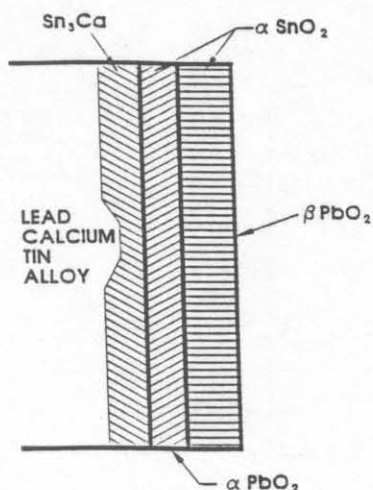
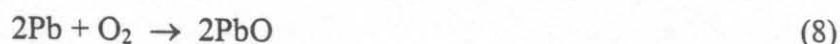


Figure 8 – Corrosion Product
on Rolled Lead Calcium
Tin Alloy Anode

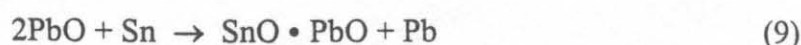
Figure 7 shows the conductivity of the anode as a function of tin content. As the tin content is increased approximately to 1.5%, the resistance of the corrosion product decreases significantly. (8) This decreased resistance or increased conductivity of the corrosion product is due to the formation of small conducting SnO_2 channels through the PbO_2 layers as shown in Figure 8.

These small conducting channels on the rolled anodes give the greatest resistance to long term passivation and improved oxygen evolution. The structure may further enhance oxygen evolution by Co additions to the electrolyte. (9)

In addition, tin prevents the formation of tetragonal PbO at the lead anode/ PbO_2 corrosion product interface by the formation of SnO_2 doped PbO_2 . The lead surface of the anode is corroded by the oxygen diffusing through the corrosion layer by the following reaction:



Tin in the area of the corroded lead, however, reduces the PbO to form PbO and SnO according to the following reaction:

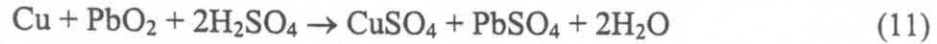


This SnO is soluble in the PbO and upon further oxidation forms SnO_2 doped PbO_2 . Once formed the doped PbO_2 is much more conductive and much less reactive than PbO_2 with lower tin contents. For EW anodes the higher tin content and the improved distribution of the tin in the rolled Pb-Ca-Sn anodes yields dramatically improved life. Because the lead/ PbO_2 corrosion product area is much more conductive, there is less resistive heating of this area by the EW current and, thus, rolled Pb-Ca-Sn anodes are much less prone to polarization and produce higher current efficiency.

Power Loss

When the power is lost in Cu EW circuits, the circuit can act like a battery and generate a back EMF. This is caused by a reverse of the electrowinning reaction, but

also a subsequent sulfation reaction of the PbO_2 surface of the anode. The reaction is shown below:



The $PbSO_4$ generated is an insulator and might make the anode become passivated when the power is reapplied. If the resistance is sufficiently high, the corrosion layers may be heated and spalled from the anode. With high resistance, the surface of the anode may not be fully polarized by the applied current. When potentials are applied to lead below the O_2 evolution voltage, rapid corrosion can occur, particularly in the presence of water generated by the anode corrosion reaction seen in Figure 9.

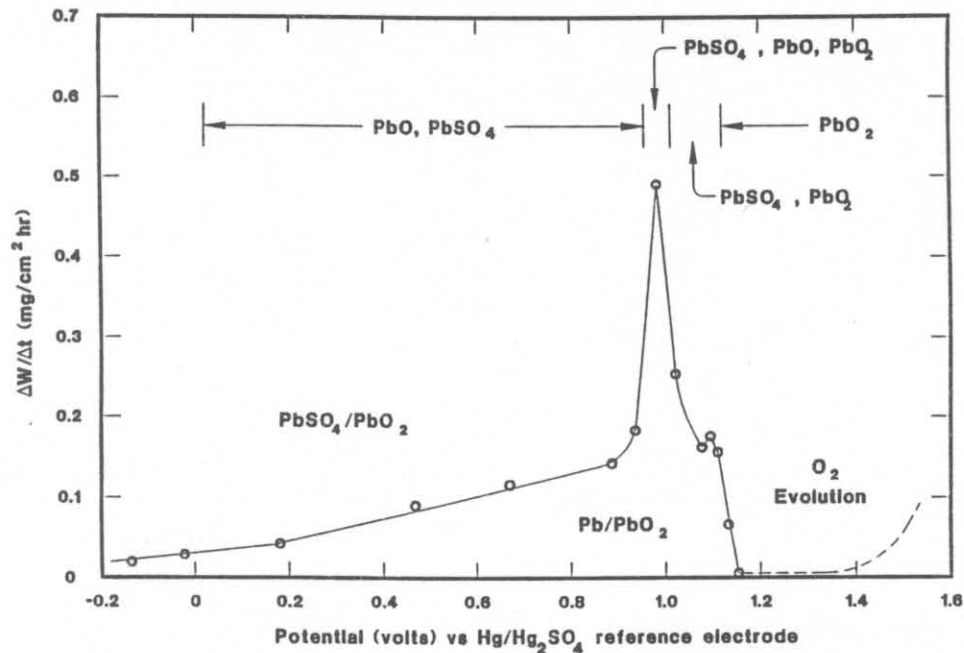
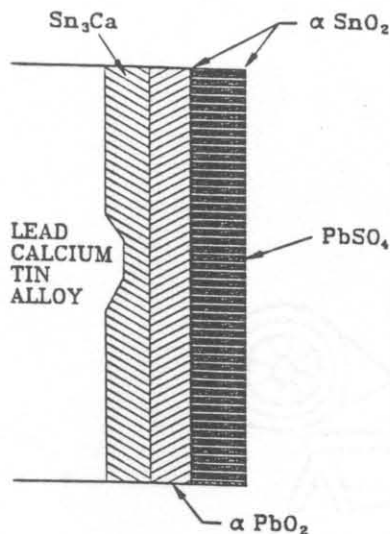


Figure 9 – Corrosion vs. Voltage



When the anode, however, has the rolled grain structure and sufficient tin content, the SnO_2 paths through the $PbSO_4$ will provide sufficient conductivity to prevent polarization of the anode as seen in Figure 10. The potential applied, however, must be sufficient to evolve oxygen or the anode can be corroded even with sufficient tin.

Figure 10 – Corrosion Product on Rolled Lead Calcium Tin Alloy Anode

Conductivity of the Sheet/Bus Bar Joint

The RSR rolled anode sheets are attached to the copper bus bar by a lead tin solder which gives a complete metallurgical bond between bar and sheet. (10) This bond is maintained for the life of the anode. The development of an electroplated layer of lead over the bus bar and joint serves to prevent deterioration of the joint in use. Competitive systems use lead cast around the bar and welding of the rolled sheet to the covered bar. These systems are shown in Figure 11.

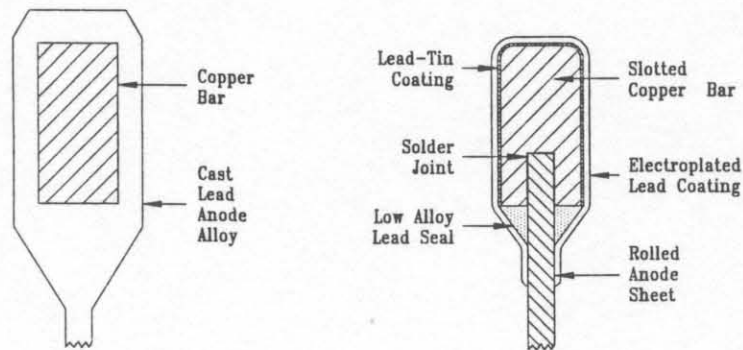


Figure 11 - Copper Bar

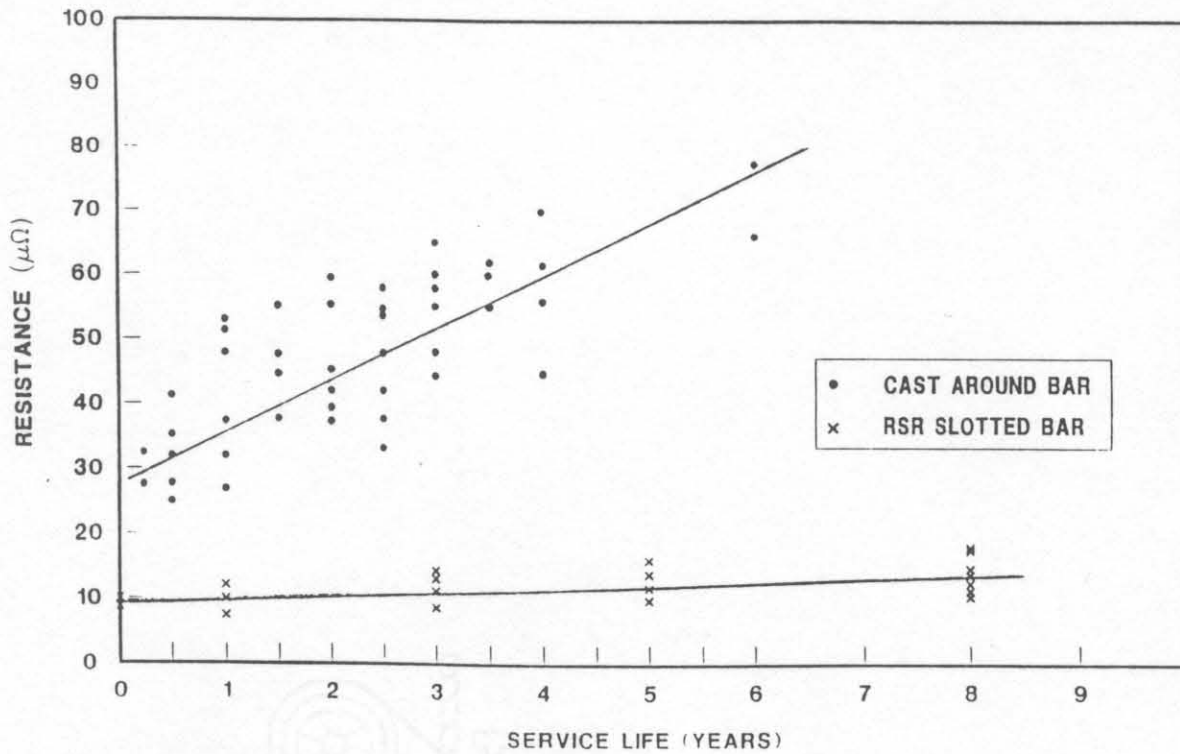


Figure 12 - Resistance between the Copper Bar and Anode Sheet As a Function of Service Life

The RSR system maintains the conductivity of the interface, while the cast around the bar system generally increases in resistance during the life of the anode. In some cases the resistance is so high that the lead covering is melted. Figure 12 shows the level resistance of the RSR anodes even after eight years of life while competitive anodes not using the slotted bar show significant increases in resistance. The cost of the increased resistance in additional power consumption from the competitive anodes can be as much as one half of the original cost of the anode.

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