

The Electrorefining and Winning of Copper

Proceedings of the Symposium sponsored by the TMS
Copper, Nickel, Cobalt, Precious Metals and Electrolytic
Processes Committees, and held at the TMS 116th Annual
Meeting in Denver, Colorado, February 24-26, 1987.

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A Publication of



The Metallurgical Society, Inc.

NEW INSOLUBLE LEAD ANODES FOR COPPER ELECTROWINNING

R. David Prengaman

Vice President, Research & Development
RSR Corporation
1111 W. Mockingbird Lane; Dallas, TX 75247

Abstract

During the past several years a new insoluble lead anode has been developed for copper electrowinning. The new anode consists of a rolled lead-calcium-tin alloy sheet attached to a slotted copper bus bar by a soldering process which produces a complete metallurgical bond between bar and sheet.

The metallurgical bond greatly reduces the resistance between the bus bar and the lead sheet and the high conductivity does not deteriorate during the life of the anode. The rolled anode thins uniformly and does not suffer preferential grain boundary or internal corrosion commonly seen in cast anodes. The lead-calcium alloy containing a high tin content corrodes slowly because the rolling process produces a uniform, fine grained structure. The wrought product is very strong and ductile; and contains no internal defects, segregation, cracks, or pores which can reduce the life of the anode.

Because the anodes corrode uniformly, a high percentage of the anode thickness can be utilized thus extending the life of the wrought anodes. The anode alloy composition which is stable only in wrought form, produces exceptional resistance to passivation during current interruptions. First introduced into liberator cells, the new electrowinning anodes have been specified as the anodes of choice for every new SX-EW tankhouse constructed in the last two years. This paper describes the new anode, its method of construction, service history, and how it differs from present copper electrowinning anodes.

Background

In the early 1970's the solvent extraction - electrowin (SX-EW) process for producing copper was developed (1). High purity copper cathodes could be produced directly from leached ore. Prior to the SX-EW process, leach solutions were very impure and the cathodes needed further refining to produce salable product.

Initially, the anodes used for the SX-EW process were lead 6-10% antimony (2). The lead-antimony alloys used for insoluble anodes suffered severe intergranular corrosion of the antimony phase. This corrosion caused spalling of fine pieces of PbO_2 or $PbSO_4$ corrosion product and metallic lead from the anode surface. The intense agitation of the oxygen evolution caused some of the small particles to be transferred to the cathode where they were reduced to metallic lead producing significant lead contamination of the copper cathodes.

At about the same time as the introduction of the SX-EW process for copper, lead-calcium-(tin) alloys were developed for maintenance free lead acid batteries (3,4). Soon after lead-calcium insoluble anodes were introduced into copper electrowinning cells to reduce the lead contamination of the electrowon cathodes (5,6,7). Lead-calcium anodes along with cobalt additions to the electrolyte to aid in oxygen evolution greatly reduced the lead levels in the cathodes by forming a hard, dense PbO_2 layer which does not spall easily (8).

Maintenance free batteries used both cast and rolled lead-calcium alloys, but severe corrosion problems greatly restricted the use of cast alloys for the positive battery grids (9,10,11). Initially, all the lead-calcium anodes used for SX-EW plants were cast. These cast anodes, while providing low cathode lead levels, suffered the same severe corrosion problems seen in the anode grid of lead acid batteries. Newer cast anodes produced from lead-strontium-tin alloys suffered the same corrosion problems as the lead-calcium anodes (12).

In the late 1970's and early 1980's wrought lead-calcium-tin anodes were introduced for copper electrowinning (13). Like the rolled alloys for battery grids, the rolled anodes suffered none of the performance limitations seen in cast anodes, however attachment of the rolled lead sheet to the copper bus bar remained a problem. The attachment problem was overcome by the development of a process to permanently bond the rolled lead alloy sheet to the copper bus bar (14). The following sections of this paper describe the mechanical properties, corrosion behavior, manufacturing methods, and performance of the new insoluble rolled lead-calcium-tin anodes for copper electrowinning compared to the conventional cast alloy anodes.

Lead-Calcium-Tin Alloys

Lead-calcium-(tin) alloys are very reactive. The calcium in the alloy can react rapidly with oxygen in the air, water, or other oxides to produce calcium oxide when the alloy is in the molten state. Lead-strontium alloys have similar behavior. To produce rolled sheets, large slabs of lead-calcium-tin alloy are cast into open molds. Control of the calcium content is difficult even for large castings because of the reactivity of the calcium. When lead-calcium or lead-strontium alloys are cast into anodes in permanent molds, the oxides, dross, and air trapped in the molds can present problems (15).

Figure 1 shows air and dross trapped in a permanent mold cast anode. Each bubble of trapped air has a coating of calcium oxide around it due to the reaction between the calcium in the alloy and the oxygen in the air. The oxide skin on the outside of the air bubble exerts a drag on the upward movement of the air bubble and prevents it from escaping from the mold.

As the lead alloy streams flow into the mold during casting, the calcium from the molten alloy reacts with air to form an oxide skin on the surface of the stream. If the mold is not at the proper temperature, the metal may solidify before the oxide skins can float out of the molten metal. This can lead to laminations in the cast metal where the solidified alloy is surrounded by oxide skins. Figure 2 shows the oxide skins which formed laps at the grain boundaries in a cast Pb-Sr-Sn alloy anode after solidification. These can cause severe corrosion problems.



Figure 1 - Cast Pb-Ca-Sn alloy anode cross section. Note air bubbles and dross (oxides) trapped in the metal.

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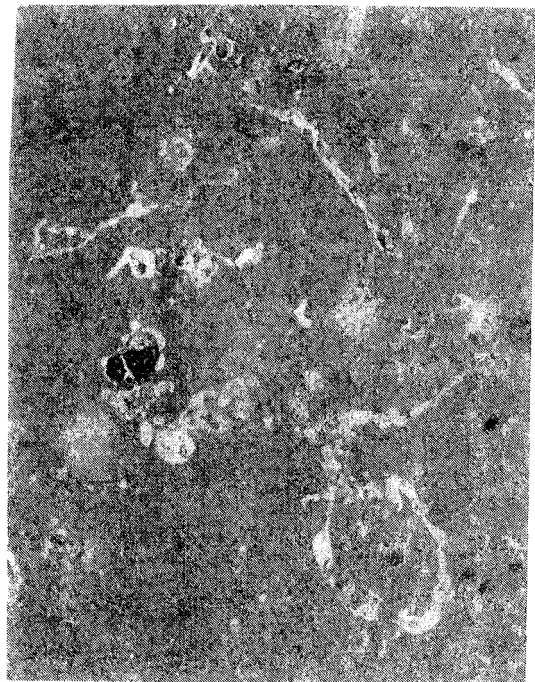


Figure 2 - Cast Pb-Sr-Sn alloy anode. Note oxide skins trapped between solidified metal streams.

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When the lead-calcium alloys are cast into large slabs for rolling there is sufficient time prior to solidification for the lead and calcium oxides and any included gases trapped during pouring to rise to the surface of the casting and be removed from the lead prior to solidification. By drossing the castings very well and allowing long solidification times, oxide dross and pore free slabs can be cast. Thus, slabs for rolling are virtually free of casting defects. There may, however, be significant segregation of calcium and tin in the casting.

Rolling

All as-cast lead-calcium-(tin) alloys initially contain very large dendritic grains. Figure 3 shows the typical as-cast structure of a lead-calcium-tin alloy whether cast in a permanent mold or in a slab for rolling. As soon as the slabs have completely solidified, they are rolled. The deformation introduced by the rolling mill in reducing the thickness of the slab at elevated temperatures results in breaking up of the large cast grains. In addition, the hot rolling results in recrystallization of the rolled sheet.

Lead-calcium alloys used for anodes generally contain tin as an additional alloying element. Tin significantly strengthens and increases the fluidity of the alloy (16). Tin additions also prevent lead-calcium anodes from becoming passivated during power interruptions or tankhouse downtime (17,18). Binary lead-calcium alloys are subject to passivation during power outages. While the tin is beneficial, it also segregates in the cast alloy. Tin segregation can be seen in figure 1 as the white lines between the dendrite arms. Tin also segregates to grain boundaries and sensitizes them to corrosion (10).

During recrystallization, the large deformed grains are reduced in size. The grain boundaries which move through the metal during deformation produce a uniform distribution of calcium and tin throughout the sheet. Tin greatly increases the mechanical properties of the rolled lead-calcium alloys and makes it resistant to structural changes when operated at elevated temperatures in the tankhouse. The hot deformation uniformly distributes the tin throughout the material allowing much higher levels to be used than in cast alloys without the formation of deleterious grain boundary precipitates (19).

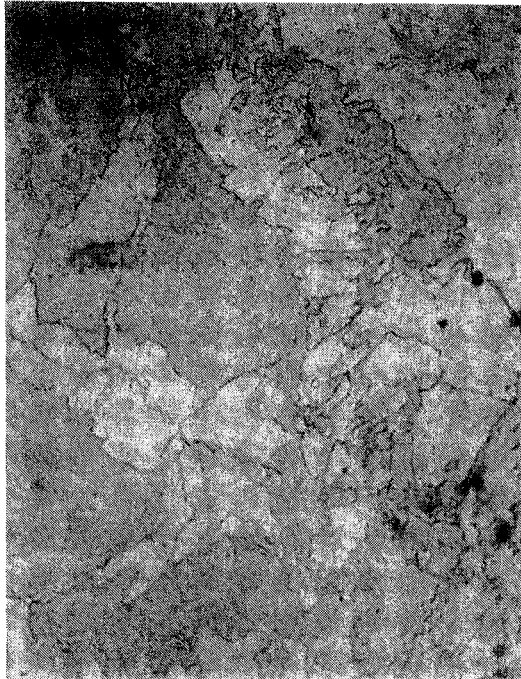


Figure 3 - Grain structure of typical cast Pb-Ca-Sn alloy anode.

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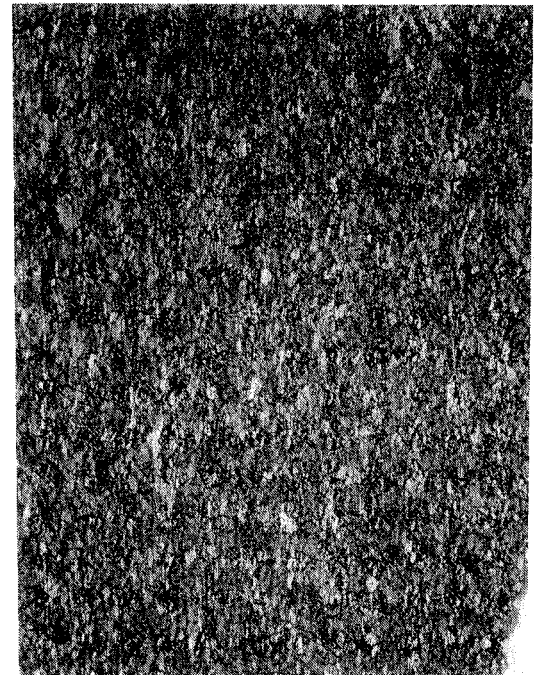


Figure 4 - Grain structure of rolled Pb-Ca-Sn alloy sheet used for anodes.

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During rolling the grain size of the sheet is gradually reduced and a fine grain structure oriented in the rolling direction is produced. Figure 4 shows the typical grain structure of the rolled lead-calcium-tin alloy sheet used for anodes. If desired, the hot rolled material may be further cold rolled to greatly increase the mechanical properties and further refine the grain structure. The energy imparted during deformation enhances the precipitation of extremely small, uniform Sn_3Ca intermetallic compound particles throughout the metal. The rolling force causes the Sn_3Ca particles to be precipitated in the form of small rods or needles in preferred orientations.

Cast Anode Production

Cast lead-calcium-(tin) or other alloy anodes are produced by pouring the molten alloy into a permanent mold in the shape of the anode. A copper bus bar is located in the lower portion of the mold. The molten lead alloy is poured into the mold, flows around the copper bar, and fills the mold to form the anode sheet or blade. The top portion of the mold serves as a hot top to feed the molten metal back down into the mold to prevent piping and collect oxides and gases trapped during pouring. The hot top (bottom of the anode) is cropped to produce the final length of the anode. The joint between copper bus bar and the cast lead alloy of typical cast anode is seen in figure 5. Production of cast anodes is relatively simple. However, producing castings without the trapped dross, air, or laps is virtually impossible.

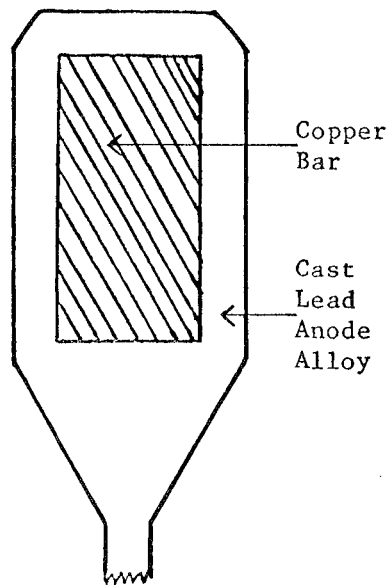


Figure 5 - Cross section of copper bar anode interface in cast anode.

Wrought Anode Production

Wrought anodes are generally produced from rolled lead-calcium-tin alloy sheet. Other alloys may also be rolled into sheet to produce anodes, however, these alloys tend to be more expensive than lead-calcium-tin alloys. To produce a complete anode, the rolled sheet must be joined to the copper bus bar. The rolled sheet can be produced in any size or thickness and windows or holes for insulators may be placed in any location without the expense of a permanent mold. While rolled sheet anodes have been used for several years, the method of attachment to the bar was a major problem. The problem was solved by a process to solder the sheet to a slotted copper bar. The cross section of this joint is seen in Figure 6.

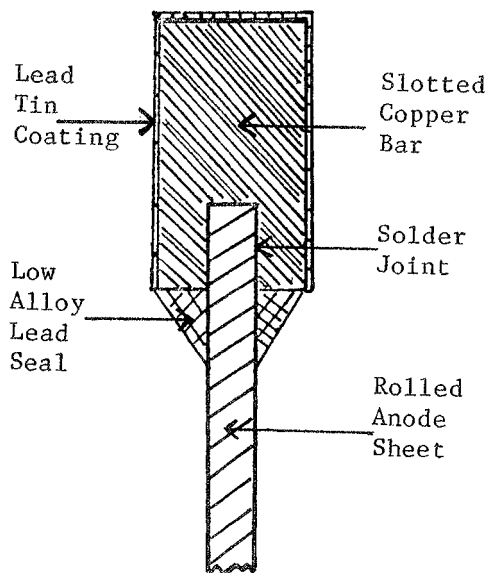


Figure 6 - Cross section of copper bar-sheet attachment for rolled sheet anode.

To produce a sound, stable anode, the rolled lead-calcium-tin or other alloy sheet must be permanently joined to the copper bus bar. The bottom surface of the copper bar is milled to produce a slot of proper dimensions to produce optimum clearance between sheet and bar for soldering. For thicker rolled sheets the milled slot is deeper.

The slotted bar is bent to the desired shape, and dipped into a flux bath to remove oxides, cutting oils, chips from the milling of the slot as well as to preheat the bar for subsequent operations. The cleaned copper bar is removed from the flux bath and dipped into a solder bath. In the solder bath the bar is heated to the proper temperature for joining to the lead alloy sheet, coated with a corrosion resistant lead-tin alloy layer, and the slot filled with enough solder to permit joining to the sheet. While heating in the solder bath, the slot in the copper bar widens slightly.

When the copper bar is removed from the solder bath, it is placed into a stand and the rolled sheet which has been cut to the proper dimensions is lowered into the slot filled with solder. The solder joins the lead alloy sheet to the copper bus bar by forming a Cu-Sn bond with the copper and a Pb-Sn bond with the rolled sheet. As the joint solidifies and cools the slot contracts slightly bonding the sheet even more firmly to the copper bar. The complete metallurgical bond between copper bar and the rolled lead-calcium-tin alloy sheet is seen in figure 7.

To prevent corrosion and possible deterioration of the solder joint, the bond area is sealed with a low alloy lead bead. The sheet in the completed anode is so firmly attached into the slotted copper bus bar that the resistance to pull out of the sheet is greater than the tensile strength of the rolled lead-calcium-tin alloy.

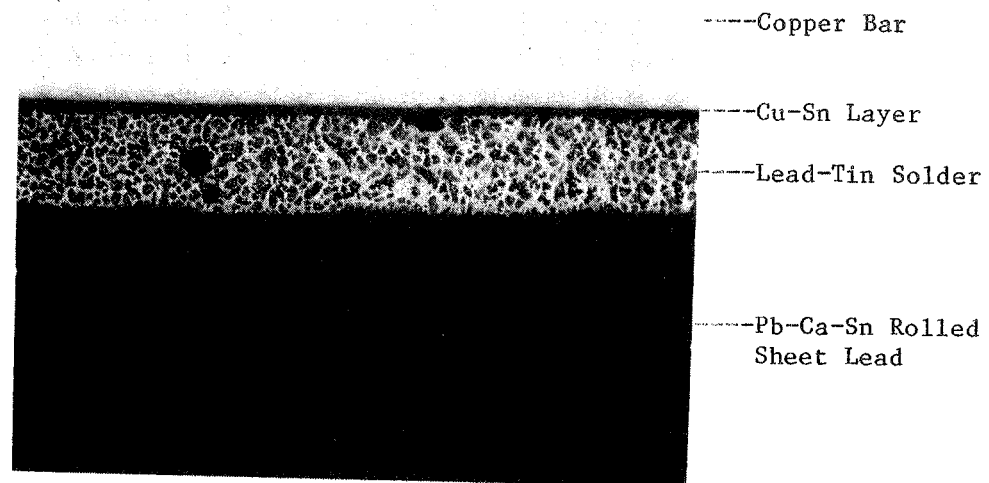


Figure 7

Solder bond between copper bar and rolled Pb-Ca-Sn anode sheet.

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Anode Performance

Mechanical Properties

The mechanical properties of the lead alloy used to produce the anode is important. The material must be strong and stable enough to resist the stresses of corrosion and elevated temperatures. Table I shows the mechanical properties of the materials normally used to produce anodes for copper electrowinning.

	Rolled	Cast	Cast	Cast
	Pb-Ca-Sn	Pb-Ca	Pb-Ca-Sn	Pb-Sr-Sn
Ultimate tensile strength (psi)	8,000	5,500	7,500	4,500
Yield strength 0.2% offset (psi)	6,500	3,500	5,500	3,200
Elongation (%)	15	30	30	40
Creep resistance Time to failure at 3,000 (psi)	1,000	10	100	5

The rolled lead-calcium-tin alloys are stronger and significantly more creep resistant than any other alloy used for copper electrowinning. Creep resistance is the most important property because high creep resistance allows less warping and more stable anode dimensions during service. The rolled lead-calcium-tin anode sheet is 10-200 times more creep resistant than anode alloys in the cast form.

Corrosion

Figure 8 shows the typical corrosion product on a rolled lead-calcium-tin alloy sheet anode from a SX-EW tankhouse. The corrosion product consists of a thin, uniform adherent layer. The orientation of the Sn₃Ca intermetallic particles and the fine oriented grain structure produce extremely uniform corrosion. Because the corrosion is so uniform, the rolled anode thins uniformly allowing complete use of the anode thickness before replacement is necessary.

Figure 9 shows the typical corrosion product on a cast anode. Note that the corrosion penetrates into the anode along the grain boundaries. In areas where the oxide produced during pouring is trapped, internal porosity is present, or grain boundary precipitates caused by tin segregation occur; the corrosion can penetrate deeply into the anode causing excessive shredding of the corrosion layer and early failure of the anode. Internal corrosion can be seen in figure 10. Because casting defects cannot be eliminated from cast anodes, the life is normally about 1/2 that of the rolled anodes.

Conductivity

Because the joint formed in soldering the rolled lead-calcium-tin alloy sheet to the copper bar is a complete metallurgical bond, there is very little resistance between the copper bar and the anode sheet. At normal electrowinning current densities of about 200 amps per square meter, there is a potential drop of less than 1 millivolt between copper bar and anode sheet. This low resistance continues for the life of the anode.

The conductivity of the soldered joint is significantly higher than that of the bond between copper bar and cast lead anode sheet where the lead is cast about the copper bar. In most cases there is no bond between the copper bar and lead cast around it shown in figure 5. The weight of the cast anode pulling on the copper bar produces the contact between bar and anode. The typical potential drop between copper bar and cast anode sheet is 2-10 millivolts for a new anode.

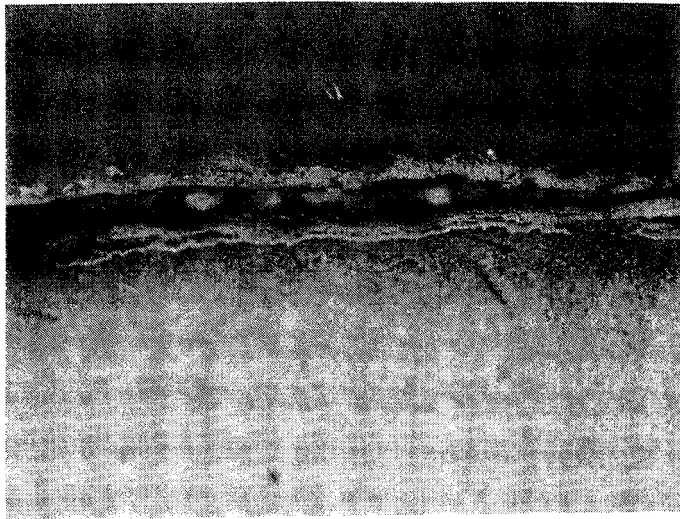


Figure 8 - Uniform corrosion layer on the surface of rolled Pb-Ca-Sn anode.

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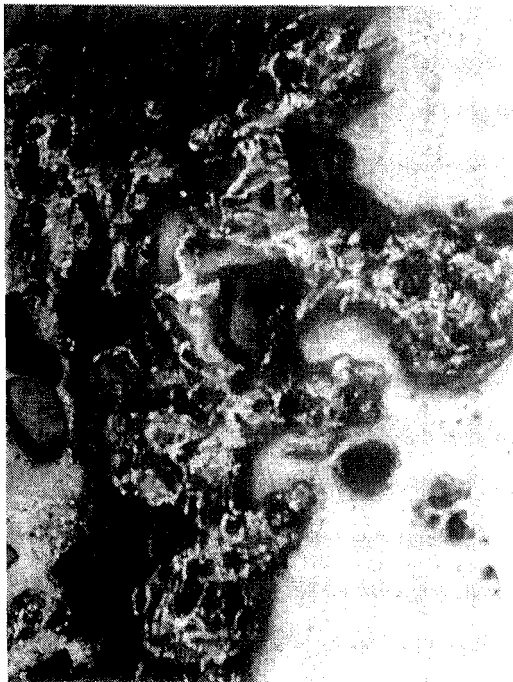


Figure 9 - Typical corrosion layer on the surface of a cast Pb-Sr-Sn anode.

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Figure 10 - Internal corrosion of casting defects in cast Pb-Ca-Sn anode.

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Because the attachment is not a complete metallurgical bond, acid mist or moisture can cause oxidation or sulfation of the lead adjacent to the copper bar causing an extremely high potential drop across the bond as the anode remains in service. Typical performance of cast and rolled (soldered) anodes during service life is seen in Table II.

Table II

Potential Drop Between Copper Bar and Anode Sheet (MV)

<u>Service Life</u>	<u>Cast Pb-Sr-Sn</u>	<u>Rolled (Soldered) Pb-Ca-Sn</u>
Initial	2-10	<1
6 months	5-50	<1
2 years	10-500	<1

As seen in Table II the cast anode can experience much higher potential drop as the anode ages. In some cases the resistance due to the buildup of an oxidation layer or dross trapped between bar and sheet during casting becomes so high that the lead cast around the copper bar melts. The high resistance between copper bar and cast anode can produce a cost penalty when using that anode compared to the rolled lead-calcium-tin sheet anode over the life of the anode. A 20 millivolt average potential drop between bar and sheet can result in an operating cost penalty of \$15.00 per anode over the life of the cast anode assuming a current density of 200A/m² and a power cost of \$.06/KWH.

Life

Rolled lead-calcium-tin alloy anodes of 6.4 mm (.250") thick have been in service in SX-EW tankhouses for over 5 years. This compares with an average life of under 3 years for 9mm (3/8") cast anodes. The rolled lead-calcium-tin anodes soldered to a slotted copper bus bar solves many of the problems of the cast anodes. The design flexibility, higher conductivity, higher mechanical properties, better corrosion resistance, and longer life makes the rolled lead-calcium-tin anode the anode of choice for modern SX-EW tankhouses.

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