Lead-Zinc 2010
Edited by: A. Siegmund, L. Centomo, C. Geenen, N. Piret, G. Richards and R. Stephens
TMS (The Minerals, Metals & Materials Society), 2010

10 Years Experience with Rolled Lead-Calcium-Silver Anodes

**R. David Prengaman, Timothy Ellis,and Abbas Mirza*

RSR Technologies, Inc.
4828 Calvert St.
Dallas, TX 75247, USA
*(*Corresponding author: rdprengaman@rsrtechnologies.com)*

ABSTRACT

It has been 10 years since RSR Technologies introduced a new rolled anode for Zinc Electrowinning. The anode contains calcium and significantly less silver than the traditional cast or rolled lead silver anodes. The anodes are rolled to produce uniform dispersion of calcium and silver. These anodes have much higher mechanical properties than lead-silver which makes them more resistant to deformation. The calcium allows the anode to condition in several days.

The anodes have been extensively tested in Japan, North America, South America, Europe, and South Africa. Anodes have been service for up to 5 years without significant thinning or corrosion. The anodes remain straight and MnO_2 removal is easier than with cast or rolled lead silver anodes. The anodes yield a 1% improvement in current efficiency when compared to conventional anodes.

This paper describes the experiences with rolled lead-calcium-silver anodes, the resistance or inertia to their use, the manufacturing process, and improvements to surface treatment and handling which will enhance the use of the anodes in cellhouse operations. The paper also compares the significant economic benefits in utilizing RSR rolled lead-calcium-silver anodes in today's environment.

INTRODUCTION

It has been 10 years since the first introduction of rolled lead calcium silver anodes for zinc electrowinning. Despite extensive testing, these new anodes have not yet been placed in service in significant quantities or in an entire tankhouse. The anodes offer substantial savings in initial capital cost and perform as well as or better than comparable lead-silver anodes which cost more and represent an inferior product. Initial test results indicate higher zinc production, more rapid conditioning, longer life expectancy, and lower costs.

Why have these new anodes not been accepted throughout the industry? The anodes were introduced during a time of transition for zinc anodes and much economic stress in the zinc industry. Prior to year 2000 most zinc EW anodes were cast. (1) In fact most of the anodes in service today are cast in the same location as the tankhouse. The lead silver anodes are recycled in the cast shop at little additional cost as only a small amount of new metal is required. Cast anode quality is suspect due to porosity resulting in short anode life. Many attempts have been made to improve the porosity problem. (2, 3) Rolled anodes have solved many of the problems of cast anodes. To change from the cast anode to a rolled anode, however required an outside supplier for the rolled anodes and some additional costs.

ROLLED LEAD SILVER

The success of rolled lead-calcium-tin anodes for copper electrowinning produced by RSR with a life of 5 – 10 years has facilitated the change to rolled lead-silver anodes for zinc electrowinning. The excellent performance of rolled lead-silver anodes compared to cast lead-silver lead to the introduction of rolled lead-silver anodes for even jumbo and super jumbo applications. The silver content of the rolled lead silver anodes was also reduced from 0.7 – 1.0% silver in the cast anodes to 0.5 – 0.7% silver in the rolled anodes giving a reduction in the cost of the anodes (4).

CONDITIONING

Despite the benefits of the rolled anodes of uniform thickness and lack of internal porosity, the smooth surfaces of the rolled anodes required some treatment prior to introduction into the cells to permit development of a stable PbO_2 – MnO_2 corrosion layer (3,5,6,7,8). Sand blasting with silica sand was found to be very effective in roughening the surface of the anode so that the PbO_2 corrosion layer and MnO_2 layer could be developed in reasonable time of 2-3 weeks. The rolled lead-silver anodes were not much stronger than the cast anodes that they replaced and thus generally had the same initial thickness. The poor mechanical properties required a mechanism to flatten the anodes similar to that of cast anodes. (4)

For the past 10 years lead-calcium-silver anodes have been investigated by a number of individuals and organizations (8, 9, 10, 11). These investigations have led to better understanding of the formation of the initial corrosion layer of PbO_2 to which the productive MnO_2 layer is attached (12). In addition, research has determined that calcium addition to the lead silver anodes increases the oxygen evolution activity of the anode. This leads to more rapid formation of an adherent PbO_2 layer, but also delays the deposition of the MnO_2 on the anode surface giving significant sludge formation in the early life of the anode (13). Similar to the rolled lead-silver anodes, roughening of the surface of the lead-calcium-silver anodes is beneficial to reduce initial MnO_2 sludge formation, and permit the rapid development of the adherent MnO_2 layer.

ROLLED LEAD-CALCIUM-SILVER ANODE

The rolled lead-calcium-silver anodes from RSR have a much lower silver content (0.3 – 0.35%Ag) than the rolled lead silver anodes (0.5 – 0.7% Ag). Initially silver contents lower than 0.5% were not thought to be possible in zinc electrowinning. Now low silver rolled lead-calcium-silver anodes with a controlled grain structure and uniform dispersion of the silver throughout the structure permits better silver utilization (14). These grain structures were originally developed in lead-calcium-tin-silver alloys for battery grids (15). The calcium significantly increases the mechanical properties of the anode. In test service, if the lead-calcium-silver anodes are warped as an end anode or damaged in handling, the normal flattening process used for cast or rolled lead-silver alloys is ineffective in straightening these anodes. The rolled calcium silver anodes have four times higher yield strength of the cast or rolled lead silver alloy (3). The high mechanical strength and dimensional stability has been shown to be a major factor in the long life of rolled lead-calcium-tin alloys for copper electrowinning. These same advantages are seen with the rolled lead-calcium-silver anodes for zinc electrowinning and when treated properly should give exceptional life of well beyond 6 years.

The RSR rolled lead-calcium-silver alloys have a composition of 0.05 – 0.08% calcium and 0.3 – 0.35% silver. In most of the tests over the past 10 years the base lead has been well refined recycled lead form the RSR and Ecobat Group plants (16). The calcium content is designed to avoid the formation of Pb_3Ca particles which form in the melt when the calcium content exceeds 0.08% (17). In casting the billet for rolling, these Pb_3Ca particles can agglomerate on the top surface and give non-uniform corrosion between the sides of the anode leading to warping. By restricting the calcium content to this range the particles are prevented from forming and the anode has sufficient mechanical strength. To prevent the loss of calcium a small amount of aluminum is added to the alloy. This permits easy remelting of rolling scrap without loss of calcium. Alloys with calcium contents in this range also have the highest mechanical properties (18) of any lead-calcium-silver alloy.

The lead calcium silver alloy billet is hot rolled to control the precipitation of the calcium, produce a uniform grain structure, and maintain high mechanical properties. Calcium precipitates in lead-calcium alloys by the movements of grain boundaries leaving fine linear particles behind. These particles serve to strengthen the alloy. The silver in the alloy controls the grain diameter. When the material is hot rolled, the precipitation and boundary movement occurs during rolling. Any stresses of rolling or precipitation are relieved at these temperatures. Thus, when the rolled anodes are placed in service in the elevated temperature electrolyte, there is no recrystallization, warping, or loss of mechanical properties. Cold rolled lead-calcium-silver anode alloys induce stresses that are relieved in the cells and may cause warping.

Figure 1 shows the grain structure of the RSR rolled lead-calcium-silver anode blade. The silver is uniformly distributed. The calcium produces the unusual puzzle shaped grains.

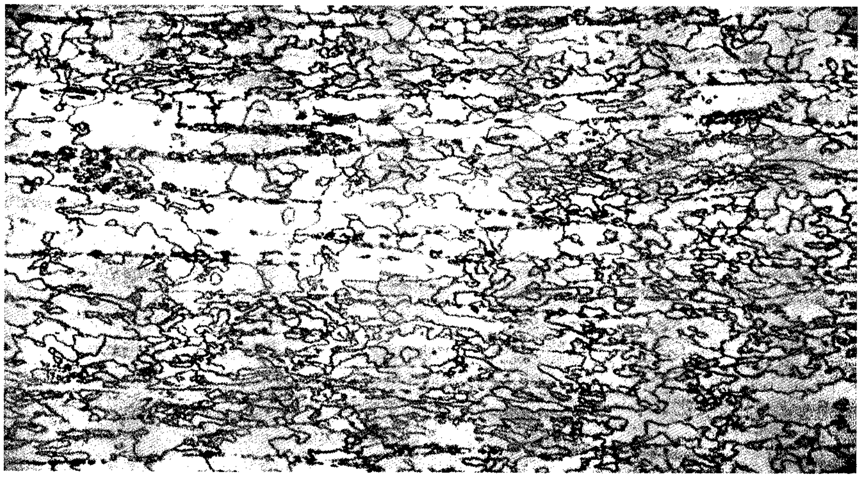


Figure 1- Grain Structure of Rolled Lead Calcium Silver Anode

TEST ANODES

Table 1 shows the program of rolled lead calcium silver test anodes conducted in various plants throughout the world. Extensive test data on the performance of the anodes compared to cast as well as rolled lead-silver anodes were obtained from anodes at Big River and Hikoshima.

Table 1 - Trials of Lead Calcium Silver Anodes

Zincor, South Africa	2000
Big River Zinc	2001, 2004
Nystar, Clarksville	2001
Cajamarquilla, Peru	2004
CEZ, Valleyfield	2004
Bouden, Kokkola	2004
Teck Metals, Trail	2004, 2005, 2010
Mitsui, Hikoshima	2005
Umicore, Auby	2005
Xstrata, Nordenham	2005
Ruhr Zink, Datteln	2006, 2008

Table 2 shows the comparison of 2 cells at Big River Zinc over a 2 year period. One cell had the RSR rolled lead 0.07% Ca – 0.35% silver anodes and the comparison cell had rolled lead – 0.55% silver anodes. During the first month there was a significantly more zinc deposited in the RSR lead-calcium-silver cell than the control cell. That advantage was maintained through the first 24 months of operation when detailed records were kept. For the first 24 months the lead-calcium-silver anodes produced 1% more zinc than the control cell. The anodes were very easy to clean as the MnO_2 removed easily. Unfortunately the testing was discontinued after 3 years. The anodes were in excellent condition with problems only with the end anodes warping due to the lack of a cathode on the opposite side. A perforated anode or wide spacing of the end anode can eliminate the warping. A whole section of rolled lead-calcium-silver anodes (3, 4) were installed in 2004, however, the plant closed shortly thereafter due to economic conditions.

Table 2 - Improved Zinc Production Rolled Pb-Ca-Ag vs. Rolled Pb 0.5% Ag

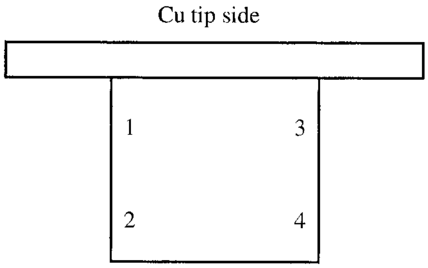
Time	Current Efficiency Rolled Pb-Ca-Ag %	Current Efficiency Rolled Pb0.5% Ag	
			% Difference
Month 1	90.46	86.59	3.8
Month 2	88.10	85.3	2.8
Month 9	90.6	88.9	1.7
Month 12	90.83	89.91	.93
Month 24	91.0	90.7	.20
		24 Month Cumulative	1.03

ANODE CORROSION

Table 3 shows the remaining thickness of 7 anodes which were installed at Teck Metals Trail Cellhouse in May 2005 with an initial thickness of 11mm. The plant had a 3 month plant shutdown and thus the anodes had been in service for over 4 ½ years when measured. The average remaining thickness of the 7 measured anodes is 9.2mm. The anodes have thus lost 1.8mm in thickness in 4 ½ years of operation or a wear rate o 0.4 mm per year. Because of the high strength and mechanical stability these anodes should be structurally stable even at a thickness of 5-6mm. If the anode are utilized to a thickness of 6mm and the rate of anode consumption is uniform in the future, these anodes may have a life of over 12 years.

Table 3

Anode	Thickness measurements (mm)			
	1	2	3	4
1	9.28	10.01	9.66	9.19
2	9.76	9.17	8.96	8.27
3	9.30	9.09	9.96	9.37
4	9.61	9.52	9.51	9.33
5	9.31	8.56	9.22	9.29
6	7.62	9.12	9.48	8.72
7	9.54	9.25	9.48	9.53
Avg.	9.20	9.25	9.47	9.10



SURFACE ROUGHENING

Despite the rapid formation of PbO_2 on the RSR rolled lead-calcium-silver anodes, plant tests have shown that a large amount of MnO_2 sludge is generated before an adherent layer is developed on the surface without surface treatment. Sandblasted anodes have been tested by Zincor and Teck Metals and have shown that roughening is adequate to produce the required adhesion. Sandblasting requires special ventilated rooms to protect workers from lead and silica exposure and produces significant amounts of lead contaminated silica sand which is a hazardous waste. RSR is currently testing several methods of surface roughening which may provide an adequate surface for the MnO2 and may eliminate the need for sandblasting. The sandblasted surface and one of the new surfaces produced by the time saver is seen in Figures 2 and 3. From surface analysis this should be superior to sand blasting. Various surface roughness samples are currently undergoing testing in a pilot cell and the initial results show virtually no difference between the two methods.

Figure 2 - Sandblasted Surface

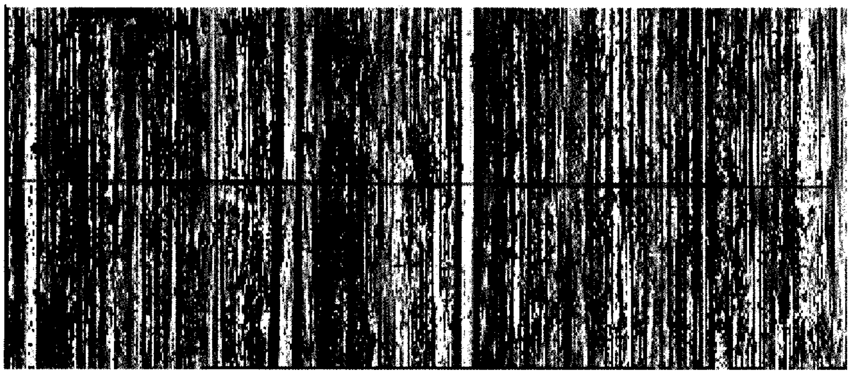


Figure 3- Timesaver Surface Roughening

ECONOMICS

With the test anodes performing well, the rolled lead-calcium-silver anodes are compared to conventional rolled lead-silver alloy anodes. The typical comparison is an anode of 1.6m x 1.0m x 11m thick. Table 4 compares the metal cost of the RSR rolled lead-calcium-sliver anode with the rolled lead-silver anodes of 0.5%, 0.55%, and 0.75% silver currently used in rolled lead silver anodes. The rolling, cutting, fabrication of the sheet, copper bus, surface treatment, and packaging are assumed to be constant. The only variable is the metal cost.

The analysis assumes a silver cost of $18.2 per troy ounce, a lead price of $1.02 per pound, and a calcium cost of $5.00 per pound. The RSR anode is assumed to have a calcium content of 0.07%, and a silver content of 0.33%.

As seen in Table 4, the rolled lead-calcium-silver has significantly lower metal costs than the comparable rolled lead-silver anodes used today. The cost is about $184 less than the lowest cost rolled lead-silver alloy (0.5% Ag) and up to $465 per anode less at the highest silver content. In addition, the increased zinc production during the first 1-2 years, and potentially longer anode life make the RSR lead-calcium-silver anode particularly attractive. A new straightening press developed by Brochot and the new surface treatment of the anode should solve the remaining problems with lead-calcium-silver anodes.

Table 4 - Comparison of Metal Costs of Rolled Anodes

Silver Cost $18.2 Per Troy ounce = $16.60 / oz
Lead Cost $1.02 per pound
Calcium Cost $30.00 per lead ton

Silver Content (%)	Anode Weight Pounds	Silver Cost $/Anode	Lead Cost $/Anode	Calcium Cost $/Anode	Total Cost $/Anode	Cost Difference $/Anode
0.75	424.43	845.50	429.70	--------	1275.20	465.10
0.55	424.43	620.00	430.50	--------	1050.50	240.40
0.50	424.43	563.65	430.70	--------	994.35	184.25
0.33	424.43	372.00	431.75	6.35	810.10	--------

The high silver cost in the last several years is expected to remain at the present levels or increase. The RSR rolled lead-calcium-silver anodes with lower silver content offer much lower costs than the conventional rolled lead-silver anodes.

CONCLUSION

After extensive testing, the RSR rolled lead-calcium-silver anodes may finally find applications. The lower cost, higher zinc production, rapid conditioning, high mechanical properties, along with the development of new conditioning and straightening equipment will overcome the inertia of the industry and permit full utilization of this improved anode.

There has been 10 years of development and testing of the rolled lead-calcium-silver anodes. The data from these tests indicates that these anodes perform very well and should replace the conventional rolled lead-silver anodes and the cast lead silver anodes.

REFERENCES

1. M. Sakata, T. Imai, A. Horriuchi, K. Morita, Y. Kondo, and M. Kusano, "Zinc Smelting Survey", T. Fujisawa Ed, Lead and Zinc '05, MMIJ, Kyoto, 2005, 139-202.

2. M. Sahoo, L. Centomo, G. Monfeitch, G. Cham Poux, G. Houlachi, S. Jim, and E. Ghali, "Effect of Casting Quality on the Electrochemical Properties of Pb-Ag Anodes for Application in the Zinc Electrowinning Process", and Lead and Zinc '05 Volume II, T. Fujisawa Ed., MMIJ, Kyoto, 2005, 1107-1121.

3. J.A. Gonzales, J. Rodrigues, and A. Siegmund, "Advances and Application of Lead Alloy Anodes for Zinc Electrowinning", Lead and Zinc '05 Volume II, T. Fujisawa Ed., MMIJ, 2005, 1037-1059.

4. Y. Lefevre and M.R. Pieterse, "The State of the Art and Constant Feasibility Upgrading of the Zinc Electrowinning Cellhouse of Austuriana De Zinc at San Juan De Nieva", Lead and Zinc Processing, J.E. Dutrizac, J.A. Gonzalez, G.L. Bolton, and P. Hancock, Eds., The Metallurgical Society of CIM, 1998, 367-377.

5. J.A. Gonzalez, "Zinc Electrowinning: Anode Conditioning and Current Distribution Studies", Electrometallurgy 2001, J.A. Gonzales, D.E. Dutrizac, and G.H. Kelsall, Eds., Met Soc, Canada, 2001, 147-162.

6. J. Rodrigues, and E. Meyer, "Improving the Performance of Anodes for Zinc Electrowinning", EPD Congress 1996, G.W. Warren, Ed., TMS, Warrendale, PA, 1995, 161-180.

7. D. Garbers, EHO Meyer, and J. Rodrigues, "Recent Development in the Zincor Cellhouse". Electrometallurgy 2001, J.A. Gonzalez, J.E. Dutrizac, G.H. Kelsall, Eds, MetSoc, Canada, 2001. pp. 163-178.

8. K. Koike, H. Watanabe and N. Masuko, "Energy Saving in Zinc Electrowinning with Modification of Lead Anode," Zinc & Lead '95, T. Azakami, N. Masuko, J.E. Dutrizac and E. Ozberk, Eds., MMIJ, Tokyo, Japan, 1995, 373-383.

9. Y. Takasaki, H. Watanabe, and K. Koike, "Anodic Behaviors of Pb-Ag-Ca Alloy Anodes for Industrial Zinc Electrowinning", Lead and Zinc '05 Volume II, T. Fujisawa Ed., MMIJ, Kyoto, Japan, 2005, 1025-1036.

10. R.D. Prengaman and A. Siegmund "New Wrought Pb-Ca-Sn Anodes for Zinc Electrowinning to Produce a Protective Oxide Coating Rapidly", Lead Zinc 2000, J.E. Dutrizac, J.A. Gonzales, S. Heuke. S. James, A. Siegmund, Ed., TMS, Pittsburgh, PA, 2000, 589-597.

11. M. Petrova, Z. Noncheva, T.S. Dobren, St. Rashkov, N. Kouchev, D. Petrov, St. Vlaev, V. Mihen, S. Zarev, L. Georgieva, and D. Buttinelli, "Investigation of the Processes of Obtaining Plastic Treatment and Anode Electrochemical Behavior of Lead Alloys in Their Capacity as Anodes During the Electroextaction of Zinc", 1. Behavior of Pb-Ag, Pb-Ca, and Pb-Ag-Ca Alloys, Hydrometallurgy, Volume 40, 1996, 293-318.

12. Y. Pu, and T.J. O'Keefe, "Evaluating of Lead Anode Reactions in Acid Sulfate Electrolytes II Manganese Reactions", Journal of the Electrochemical Society, Volume 149 No. 8, 2002, A558-A569.

13. A. Siegmund and R.D. Prengaman, Zinc Electrowinning Using Novel Rolled Pb-Ag-Ca Anodes, "Hydrometallurgy 2003, C.A. Young, A.M. Alfantazi, C.C. Anderson, D.B. Dreisinger, B. Harris, and S. James, Eds., TMS, 2003, 1279-1288.

14. R.D. Prengaman and C.E. Morgan, US Patent 6,224,723 B1, May 1, 2001.

15. R.D. Prengaman, "Challenges From Corrosion Resistant Grid Alloys in Lead Acid Battery Manufacturing", Journal of Power Sources, 95, 2001, 224-253

16. R.D. Prengaman and U. Buggelsheim, "Low Gassing Secondary Soft Lead: Effects of Bismuth, Silver, and other Impurities", Asian Battery Conference, Mancu, 2009 paper 1.5.

17. M. Hansen, Ed., Constitution of Binary Alloys, Second Edition, McGraw Hill Book Company, New York. USA 1958, 405-406.

18. Y. Kakasaki, K. Koike, and M. Masuko, "Mechanical Properties and Electrolyte Behavior of Pb-Ag-Ca Electrodes for Zinc Electrowinning", Lead-Zinc 2000, J.E. Dutrizac, J.A. Gonzales, S. Heuke. S. James, A. Siegmund, Ed., TMS, Pittsburgh, PA 2000, 599-614.