ADVANCES AND APPLICATION OF LEAD ALLOY ANODES FOR ZINC ELECTROWINNING

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ABSTRACT

Lead alloy anodes employed in Zn electrowinning (EW) typically contain between 0.25 to 1.0% wt Ag. These anodes are either cast or rolled and have a flat or corrugated shape. New lead alloy anodes require a relatively long time to form an adherent, protective PbO_2/MnO_2 layer that can evolve O_2 without excessive Pb contamination of the Zn cathode. To minimize cathode contamination, the anode surface is often mechanically, chemically or electrochemically pre-treated before anodes are placed in the EW process.

Anode quality and performance have a significant impact on the Zn EW process. Technological advances in anode performance in the last 2 decades have derived from optimization of the anode fabrication step, anode pre-treatment procedures and changes in the composition and microstructure of the alloy, design modifications like perforated anodes, improved anode cleaning, and increased attention to detection and correction of short circuits. Still, cast anodes have significant porosity that can lead to enhanced localized corrosion and formation of short circuits. Usage of improved casting techniques has helped to reduce anode porosity but the industrial trend is to migrate to rolled anodes which have no measurable porosity. The microstructure of cold-rolled anodes is elongated and highly oriented with homogenous grain size distribution throughout the anode sheet matrix. Several plants are now exclusively using rolled PbAg anodes.

In this paper recent developments in anode technology are described and an overview of anodes used in the Zn EW industry is presented. Physical and mechanical properties of these anode systems and associated pre-treatment methods are compared. Operational and economic issues associated with the use of different types of anodes are presented.

Keywords: Zinc, electrowinning, anodes, rolled, cast, density, porosity

INTRODUCTION

Despite the large number of publications [1-6] on the use of various anode compositions for Zn EW, most Zn EW plants still use binary PbAg alloys with [Ag] between 0.25% and 1% [1]. Worldwide, conventional Zn EW processes [1] are usually carried out in electrolytes saturated with gypsum ([Ca] ~ 0.6 g/L), with 0.6 to 15 g/L Mn, 1 to 20 g/L Mg, 5 to 200 mg/L F, and 50 to 200 mg/L Cl among other impurities. The only plant in the world currently using only cast PbAgCa anodes is the Kumba Resources Zincor plant in South Africa. Despite its good electrochemical behaviour [2, 8] the PbAgCa alloy is not widely used. New developments in the consistent fabrication of PbAgCa anodes [1, 9] may expand the use of this alloy in the future.

Prior to its use in the Zn EW process, anodes are pre-treated in either a H_2SO_4–KF electrolyte, or immersed in a H_2SO_4 – $KMnO_4$ bath to promote the formation of a stable PbO_2 layer [11]. Primarily, as a result of Mintek's work [12,13] sandblasting has been found to aid in the formation of good PbO_2 layers and many Zn EW plants are now routinely using sandblasting as a pre-treatment step.

Comprehensive literature reviews on anodes for EW have been published by Ivanov et al. [14, 15]. To simplify the experimental setup, researchers have chosen to work in pure H_2SO_4 solutions often in absence of Mn and halogens. From Ivanov's literature review, it is evident that:

1) The higher the [Ag] in binary PbAg alloys, the lower the corrosion rate. Increases in [Ag] above 1% provide little additional anodic protection.
2) The corrosion rate of PbAg anodes increases with current density (CD).
3) In absence of Mn^{+2} in the electrolyte, the corrosion rate increases as the acid and Zn^{+2} contents increase.
4) PbAgTl alloys have lower weight losses than binary PbAg alloys: In a Cl-free electrolyte, a Pb0.5Ag2Tl anode had a weight loss 18 times lower than a Pb0.5Ag alloy whereas in the presence of 500 mg/L Cl, a Pb0.5Ag0.2Tl had a weight loss 7 times lower than a Pb1Ag alloy.
5) A Pb0.5Ag2Bi anode had a similar weight loss as a Pb0.5Ag alloy.
6) In presence of 100 mg/L Cl, Pb1Ag1Ca anodes had weight losses 7 times lower than those seen in Pb1Ag anodes.
7) The lowest weight losses observed in long-term tests in the presence of 100 mg/L Cl were those obtained from quaternary Pb1Ag0.3 Sn0.02Co alloys.
8) In absence of Cl, the lowest Pb deportment (3 ppm) was obtained from quaternary Pb1Ag0.3Sn0.02Co alloys, whereas with Pb1Ag, 33 ppm Pb was found on Zn cathodes. Pb1Ag0.1As0.5Ba alloys also produce cathodes with low levels of Pb (11 ppm).
9) Pb0.97Ag0.13Mn and Pb0.97Ag0.83Sb1Mn can produce low lead in cathode (6 to 9 ppm). These alloys gain weight during EW because of the growth of MnO_2 on the anode.

10) High corrosion resistance was observed from Pb0.75Ag0.5Ti alloys
11) Additions of Co^{+2}, Ag^+, Fe^{+3}, or F^- ions to the electrolyte can decrease the corrosion rate of the anodes. However some of these ions are harmful to Zn EW and cannot be used to protect the anode.
12) Metal-Ceramic anodes have been tested under laboratory conditions with promising results. PbAg and PbCo are the most promising anodes tested so far.

In a recent paper O'Keefe et al. [5] showed that in H_2SO_4 the most stable alloys are PbAg and PbAgCa and that Co^{+2} was an effective anode depolarizing agent. Noble metal-coated electrodes have been tested for EW applications [4, 17] but their cost and limited service life have precluded their use in Cu and Zn EW. Recently, DeNora has been testing DSA anodes with some success. Similarly, Eltech Systems [18] has developed an anode that has a Pb-substrate over which a Ti-mesh, coated with a noble metal, is placed. These anodes have not been thoroughly tested for Zn EW and the limited service life of the coating and the detrimental effects of the corrosion products (which could affect the cathodic current efficiency) are a serious hindrance to their industrial use. Merrlin [19] has also been developing new composite anodes but these are still at the development stage and several years away from commercial use.

The mechanical and electrochemical properties of the anodes used in the Zn EW process depend to a large extent on the anode fabrication procedure which varies from plant to plant. Most plants in the world still use cast anodes and only a few use rolled anodes. At Teck Cominco's Trail Operations' plant, Pb0.75Ag (0.75% wt Ag) flat anodes are cast vertically using a book mould design. Molten metal is poured in from the top of the air-cooled mould and the header bar is attached to the anode in a separate step. At Votorantim's Cajamarquilla plant, anodes are corrugated and the header bar is cast in place. In vertical casting with pouring from the top, solidification and melting take place continuously, creating layers of metal with uneven properties. Furthermore, metal shrinkage is severe near the middle and top of the anodes, dramatically changing the anode's physical-chemical-mechanical properties in those areas.

Most Zn plants using PbAg cast anodes produced in a similar way to the ones in Trail or in Cajamarquilla report an average anode service life in the order of 2-4 years (a lower service life is reported for cellhouses operating at current densities greater than 600 A/m^2).

An alternative way of casting anodes is used by Castle Lead Works (like RSR Corporation, a subsidiary of the Quexco Group), which produces anodes using a water-cooled mould by injecting the molten metal from the bottom or from the side. Application of this casting system produces more homogeneous anodes with lower porosity and longer service life. Zincor in South Africa employs PbAgCa anodes produced this way and is achieving average anode service lives close to 5 years [12, 13]. Rolled PbAg anodes with reported service lives in excess of 5 years are being used in several plants (e.g., Asturiana, Hudson Bay, Norzink). Rolled PbAgCa anodes are now

being tested in several plants with the expectation that these anodes can have improved mechanical properties, uniform corrosion and a service life in excess of 6 years [1, 9, 20, 21].

In this paper, experimental results comparing the porosity and microstructure of PbAg and PbAgCa cast anodes are presented. The effect of alloying elements on the physical and mechanical properties of these anode systems and associated pre-treatment methods is reviewed. An update on industrial tests of rolled and cast PbAgCa anodes being carried out in different plants and an overview of operational and economic issues associated with the use of different types of anodes are described in this paper.

ANODE DENSITY AND MICROSTRUCTURE

Density measurements were made on several industrial "typical" cast anodes from Trail, Cajamarquilla and Castle Lead (RSR). The dimensions of the tested anode sheets are shown in Table I.

Table I - Description of Cast Anodes Tested		
Anode Composition (% wt)	Anode Source	Anode Plate Dimensions
Pb – 0.75 Ag	Trail Operations	157 cm length x 95 cm width
Pb – 0.75 Ag	Cajamarquilla	150 cm length x 85 cm width
Pb – 0.50 Ag	Castle Lead Works	100 cm length x 55 cm width
Pb – 0.50 Ag, 0.062 Ca, 0.015 Al	(South Africa)	100 cm length x 55 cm width

Each anode was cut into several pieces (to divide them in 10 to 21 individual pieces). Density was measured by the hydrostatic weighing method. The pieces were weighed in air and also in water. From the weight difference and the water density, the density of the anode section was determined. Select anode sections were X-rayed. Because of the thickness of the anodes and the relatively large number of areas that needed to be X-rayed, the gamma radiation source was used. Similar measurements were carried out using rolled PbAg and PbAgCa plates and no measurable porosity was observed in these plates. Select samples of the anodes were subject to optical microscopy and SEM analysis.

Results

Anodes from Trail

The vertically cast PbAg anode sheet fabricated in Trail Operations had an average density ρ_{ave}, of 11.11±0.08 g/cm^3, whereas a void-free plate has a theoretical density of 11.33 g/cm^3. Thus, the average porosity in this anode sheet was 2.0±0.7%. The average porosity of different sections of a typical anode produced in Trail is shown in Fig. 1. It can be seen that there are sections of the anode that have porosities as high as 3.1%. These large porosities are an indication of the presence of voids in the anode.

These voids are evident in the X-ray taken in one of the sections of the anode shown in Fig. 1b (the section with porosity of 1.2%).
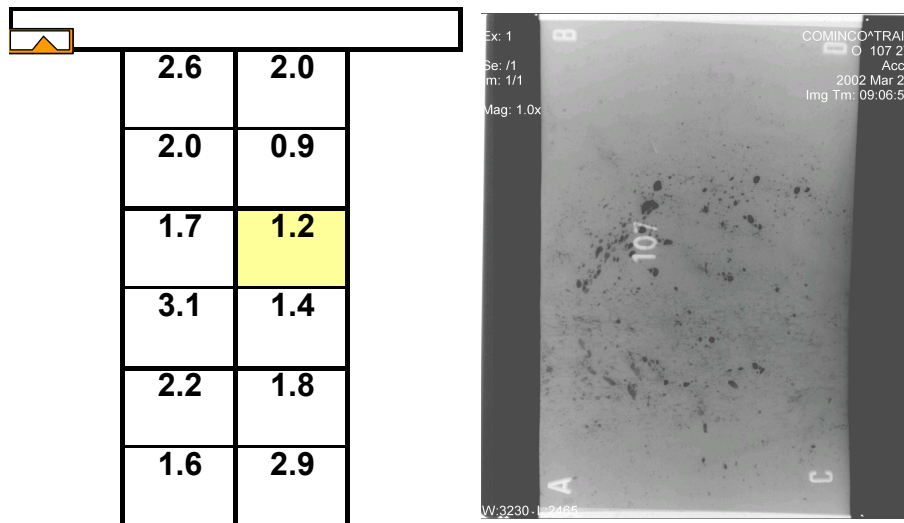

Figure 1 - Porosity of a typical anode used in Trail Operations (left) Volume % porosity in different anode sections (right) X-ray of the 1.2% porosity section

Not only was the anode porosity different in every section of the anode, but the thickness of the anode also changed from section to section by as much as 1 mm. The average thickness of the Trail anode was 12.14 mm with a variation from a minimum thickness of 11.80 mm to a maximum thickness of 12.80 mm.

To verify the results shown in Fig. 1, six additional anode plates were sectioned from different anodes. One anode from each of the anode casting moulds was selected. Pouring times were close to 10 s and the temperature of the molten alloy held in the pouring box holding the molten metal was 496 °C to 515 °C. As most of the anode failures tend to occur on the bottom of the anodes, the density of the bottom pieces (32 cm x 25 cm each) was measured, and some of these sections were studied metallographically. The average porosity for each of the sections at the bottom of six new anodes was very high: from 1.5% to 3.9%. This confirmed that anode plates consistently have higher porosity in this region, which is where a significant number of anode failures are found to occur in the Zn EW plant.

Fig. 2 shows a typical photomicrograph of one of the bottom anode sections. It can be seen that there is heterogeneity and voids in these anodes. The presence of voids was also confirmed from the X-ray images.
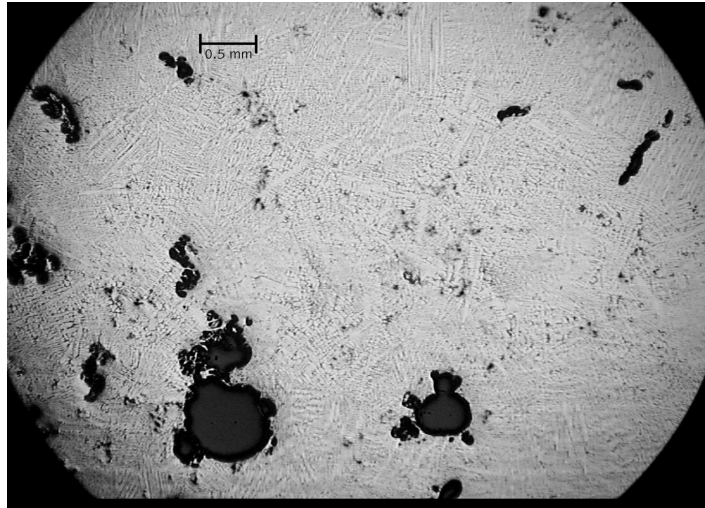
Figure 2 - Optical micrograph of a section of a cast PbAg anode as used in Trail
Operations

Anodes from Cajamarquilla

Two anodes from Cajamarquilla were sectioned. It was found that regular, vertically cast PbAg anode sheets fabricated in Cajamarquilla had a ρ_{ave} of 11.19±0.05 g/cm^3 which is equivalent to an average porosity of 1.2±0.4%. Porosity results for these two anodes are shown in Fig. 3. There are sections of these anodes with porosity as high as 1.9%. Thus, it appears that the anodes used in Cajamarquilla are more homogeneous and have less porosity than the anodes currently used in Trail Operations. However, Cajamarquilla anodes still have problems similar to those seen in Trail: the bottom sections have higher porosities than the top sections.

0.5	0.5
1.1	0.8
1.1	1.1
1.5	1.3
1.9	1.5

Anode 1

Cajamarquilla Anodes

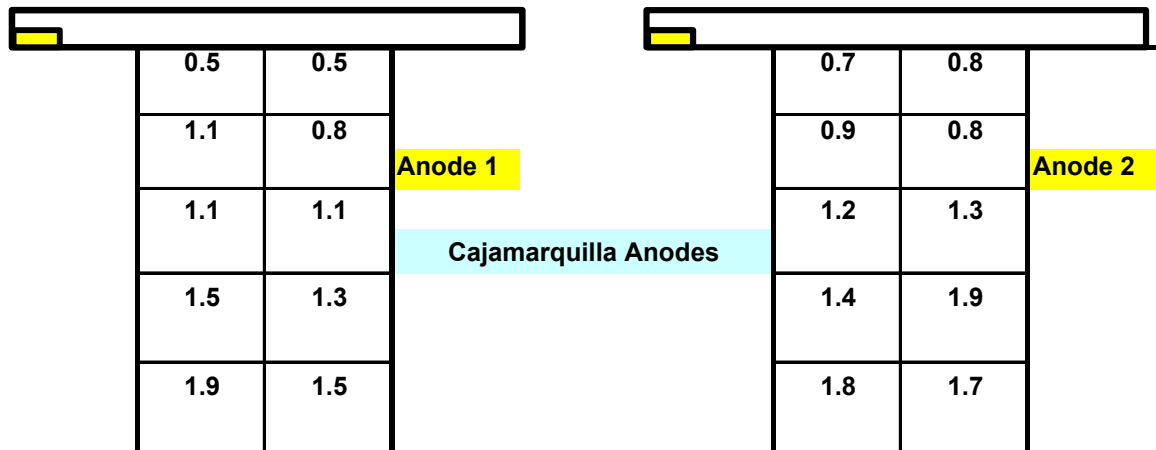| 0.7	0.8
0.9	0.8
1.2	1.3
1.4	1.9
1.8	1.7

Anode 2

Figure 3 - Volume porosity (in %) of two typical anodes used in Cajamarquilla

Fig. 4 shows a macroscopic cross sectional view of one of the pieces of anode No. 2 from Cajamarquilla. It can be seen that porosity seems to be localized in the centre. If this is generally true, it might explain why porosity-induced problems are not as severe in Cajamarquilla as in Trail.

By measuring the individual thickness of different anode sections, it was found that the bottom sections of the new Cajamarquilla anodes were significantly thinner than their top sections. The difference in thickness was between 0.5 and 1.0 mm. This small difference in thickness, and the larger porosity found in the bottom sections could lead to premature anode failure in Cajamarquilla. However, anode service life in Cajamarquilla is still tolerable at around 4 years.
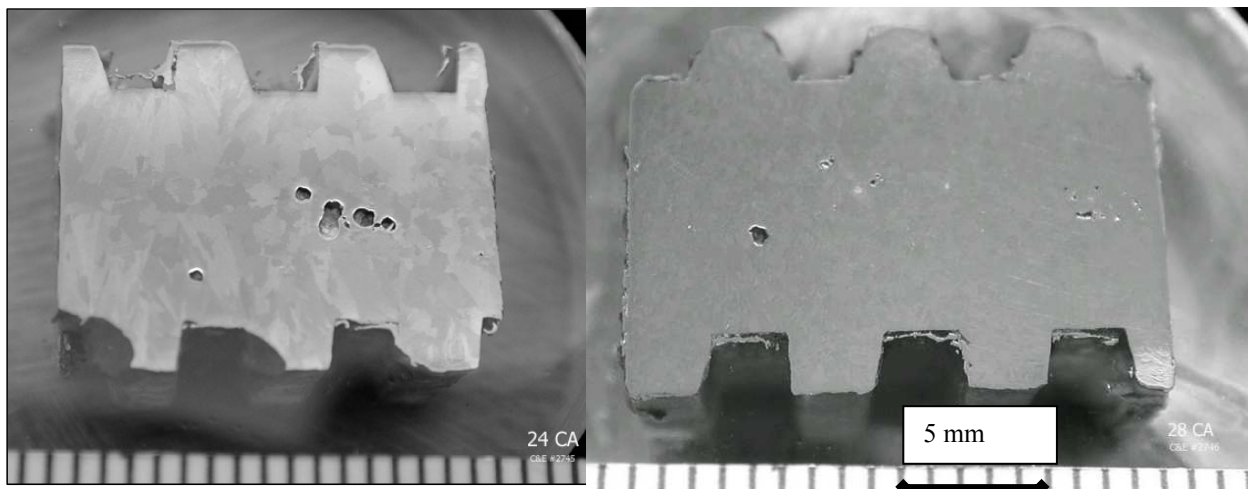

Figure 4 - Cross-Sectional macroscopic view of two anodes from Cajamarquilla

Anodes from Castle Lead Works

The anodes produced by Castle Lead Works in South Africa (in 2003) were found to have the lowest porosity of all the cast anodes tested. The Pb0.5Ag anode plate had a ρ_{ave} of 11.30±0.02 whereas the PbAgCaAl (0.5% Ag, 0.6%Ca, 0.025% Al) alloy had a ρ_{ave} of 11.28±0.02. These densities correspond to average porosities of 0.3±0.2% and 0.4±0.2% respectively.

The maximum porosity found in the Pb0.5Ag anodes was 0.5% whereas maximum porosity in the PbAgCaAl anode was 0.9%. Fig. 5 shows the average density obtained in different anode sections. The PbAgCaAl anodes had localised regions with higher porosity than the PbAg anodes. Although there was more segregation and heterogeneity in the PbAgCaAl anodes than in the PbAg anodes, these anodes were significantly more homogeneous than the anodes currently used in Trail and in Cajamarquilla. Optical microscopy/SEM and X-rays of selected samples confirmed these

findings. In addition, these anodes had very uniform thickness (10.00 mm±0.13 mm). The maximum difference in thickness between any two points was only 0.5 mm.

Anode 1 Pb-Ag

0.1	0.2
0.2	0.5
0.1	0.3
0.2	0.2
0.2	0.2
0.0	0.3

RSR Anodes

Anode 2 Pb-Ag-Ca-Al

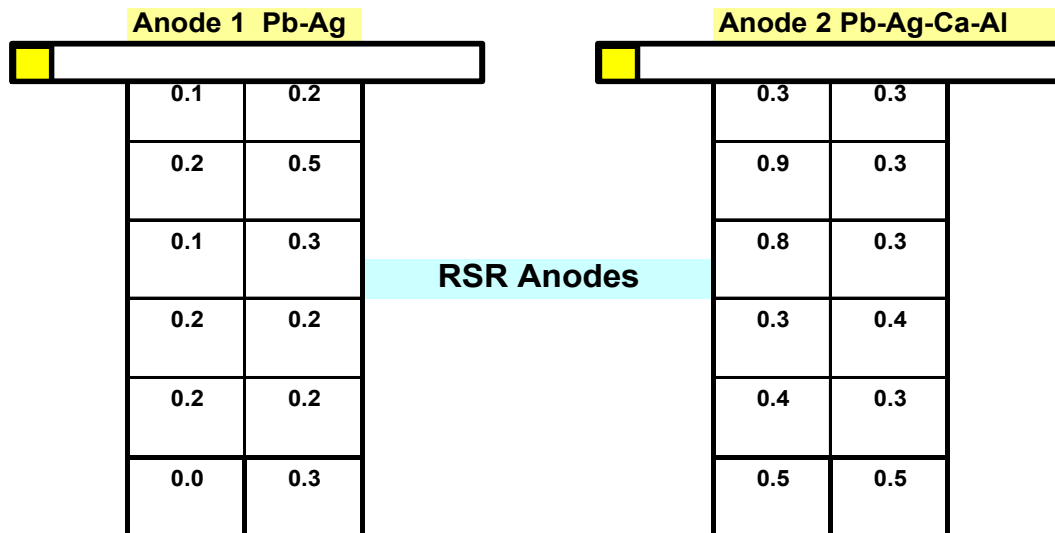|	
0.3	0.3
0.9	0.3
0.8	0.3
0.3	0.4
0.4	0.3
0.5	0.5

Figure 5 - Porosity of Castle Lead PbAg and PbAgCaAl anodes

From these results, it is clear that the casting system used by Castle Lead Works with controlled cooling of the mould can produce anodes with more homogeneous properties than the anodes cast in either Trail or in Cajamarquilla. While the Castle Lead anodes are not porosity-free, they have the lowest porosity of any cast anode that has been measured. Zincor uses anodes produced by Castle Lead Works and is currently achieving a service life close to 5.7 years (using the PbAgCa alloy). This service life is based on an average corrosion rate of 9.5 g/m^2/day, and an acceptable mass loss of 27% of the total anode mass (including header bar). The operating conditions were as follows: average anode current density of 558 A/m^2; 187 mg/L Cl$^-$; 38 – 43 ^{o}C; 165 g/L H_2SO_4; 10-17 g/L Mn; 8-15 g/L Mg; <2 mg/L F$^-$. The mass loss converts into an average decrease in the sheet thickness of approximately 3.3 mm (for a new anode thickness of 10 mm).

Whilst the lower porosity undoubtedly contributes to lower corrosion rates, the effect is enhanced by the beneficial effects of sandblasting. Sandblasting creates new grain boundaries by destroying larger grains due to the impact of the sandblasting medium but this only takes place in the outer surface layer of the anode. Overall, the beneficial effects of sandblasting include work hardening of the alloy, partial re-crystallization of the outer layer of the anode sheet, which combined with the roughened surface, promotes the formation of a very adherent and uniform corrosion layer and consequently a low and uniform corrosion rate.

ANODE COMPOSITION AND MECHANICAL PROPERTIES

Lead has been the preferred anode material for aqueous electrowinning applications over the last century. This is mainly attributed to the fact that lead oxidizes to its highest valence on the anode surface. The oxidized surface becomes coated with a smooth, adherent layer of PbO_2. The PbO_2 corrosion layer inhibits further oxidation to prevent excessive oxidation of the anode. In Zn EW this phenomenon is supported by the prevailing Mn-concentration in the electrolyte forming a protective PbO_2/MnO_2 layer. Additionally, the corrosion layer is conductive, allowing several electrochemical processes to take place. Pure Pb is a heavy metal but is mechanically very weak. It cannot support its own weight and will tend to creep when employed as an electrowinning anode. The resulting elongation of the material causes breaking off or cracking of the adherent, protective PbO_2 layer, which exposes new metallic Pb to oxidation and accelerated corrosion. It can also easily be damaged or deformed during the electrowinning process due to mechanical impact or corrosion-related tensions. This may lead to short circuits, low current efficiencies, high Pb contamination of the cathodic deposits and short anode service life. Therefore, Pb is normally alloyed to increase the mechanical properties during use while preventing cracking of the oxide layer due to creep and increasing its resistance against deformation.

The ideal anode alloy would be relatively strong with fine uniform grains and limited segregation of alloying elements to the grain boundaries. The alloy should be resistant to corrosion, be extremely conductive and oppose the formation of passivating films. Moreover, it should be ductile and not become embrittled in service. In anodes used in Zn EW, Ag is added to impart strength while reducing creep. Ag additions help to lower the corrosion rate, increase electrical conductivity and resist passivation effects. However, the overall mechanical properties of Pb-Ag alloy anodes such as yield strength, tensile strength, elongation and hardness are inferior relative to other Pb alloys used in non-ferrous metal electrowinning (as shown in Table II).

PbAg anodes become warped and bend quite easy, for example, when removed or returned to the electrolytic cell for cleaning purposes, when struck by cathode blanks during metal harvesting or as a result of variations in corrosion conditions. Alloying elements such as Ca and Sr have been added to the Pb-Ag alloy to further improve the mechanical properties of Pb anodes. Both Ca and Sr additions strengthen the Pb alloy through a cellular precipitation hardening process. The amount of these alloying elements has to be carefully controlled to produce a fine-grained structure with minimal alloy segregation. The fine precipitates not only strengthen the alloy due to their alignment (much like reinforcing rods in the metal matrix), but also because they form uniform corrosion sites preventing penetrating corrosion. The overall corrosion rate increases with Ca contents above 0.07%. Raising the Ca content to 0.08% or above increases the segregation to the grain centers to more than 0.10% Ca. These high calcium concentrations produce primary Pb_3Ca particles, which are associated with a significant increase in corrosion of the grains.

Production of cast PbAg or PbAgCa(Al) anode sheets often results in the formation of porosity in the anode as already described above. These holes or voids as shown in Figs. 2 and 4 can initiate internal corrosion in localized areas, which can weaken the anode and may cause localized cracking and enhanced anode warpage.

During the solidification of cast PbAg alloy anodes some Ag is displaced from the solidifying grain front to the remaining liquid. Ag is highly segregated at the interdentritic and grain boundaries. Because of this segregation, the alloy may exhibit different corrosion characteristics in different parts of the casting. Sheets cast from alloys containing higher [Ag] may form a low-melting-point final freezing liquid. The slower the rate of solidification of the alloy, the higher is the amount of segregation of silver to the interdentritic sub-boundaries and grain boundaries. The Ag in these areas is responsible for much of the corrosion resistance but also can cause external or internal cracking during casting promoting penetrating corrosion. In general, cast Pb-Ag alloys have a very good corrosion resistance but its mechanical weakness, structural defects and the resulting corrosion effects in cast anode sheets reduce the achievable service life.

Table II - Mechanical Properties of various lead alloy anode sheets

Alloy	UTS (MPa)	0.2%YS (MPa)	Elongation (%)	Hardness (RR30)
Pb-(3%)Sb Cast	65.5	55.2	10	85
Pb-(3%)Sb Rolled	24.6	16.3	40	64
Pb-(6%)Sb Cast	73.8	71.0	8	87
Pb-(6%)Sb Rolled	30.6	19.5	35	65
Pb-(0.07%)Ca-(1.35%) Sn Cast	46.4	35.3	29	71
Pb-(0.07%)Ca-(1.35%) Sn Rolled	71.0	65.3	14	85
Pb-(0.07%)Ca-(1.35%)Sn-(0.05%)Ag Rolled	80.0	76.8	10	88
Pb-(0.07%)Ca-(0.35%)Ag Rolled	37.8	35.5	42	68
Pb-(0.75%)Ag Alloy Rolled	18.8	9.0	54	-26*

*extrapolated value.

A method to significantly enhance the mechanical properties is to roll the PbAg anode alloy. Moreover, the elongation decreases markedly, the stress rupture resistance increases and a more uniform corrosion behavior than on cast anode alloys can be observed. Rolled sheets do not contain measurable porosity or inclusions because the cast billet for sheet rolling cools sufficiently slowly to allow all air and dross to rise to the top and be removed. Due to the acceptably large deformation ratio of the rolling process, the original as-cast grain structure is broken up during the rolling to generate a more uniform

but elongated grain structure which is highly orientated in the rolling direction. The anode structure still retains the Ag segregation but the Pb grains have been extended and elongated, as shown in Fig. 6. Less grain boundaries are exposed. Thus, only a minimal preferential or penetrating corrosion takes place at the grain boundaries and a uniform thinning of the anode sheet is achieved. Whilst this makes the alloy extremely corrosion resistant, it causes tremendous difficulties to condition the anode at the beginning of its service cycle. In order to expedite the formation of the desired adherent PbO_2 corrosion layer at the surface during the initial anode conditioning, pre-treatments of the anodes are carried out in many plants. These pre-treatment methods roughen or corrode the lead alloy structure by creating new grain boundaries for improved adhesion of the initial corrosion layer.
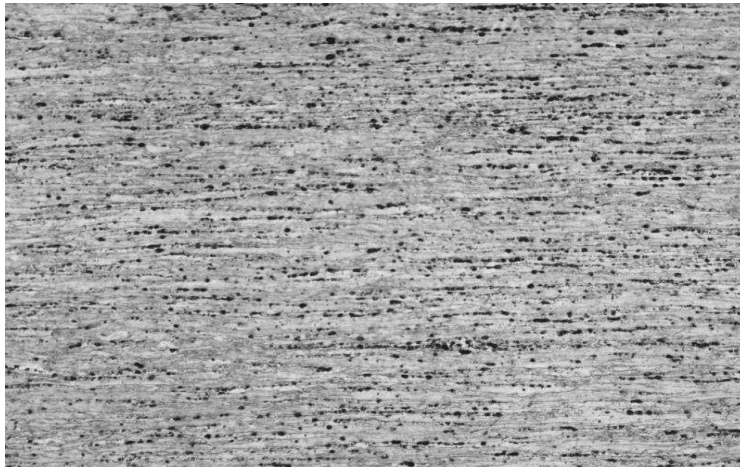

Figure 6 - Rolled Pb-(0.75%)Ag Anode sheet

When the rolling operation is performed at elevated temperatures above 100^0 C, much of the forced rolling orientation is removed due to re-crystallization effects and the grain structures as well as the mechanical properties are more uniform than in cold rolled material. At adequately sustained sheet temperatures during the rolling process a fine uniform grain structure both at the surface and throughout the sheet is obtained as depicted in Fig. 7. The fine grain structure has multiple boundaries exposed at the surface, which serve as areas of attachment for newly formed PbO_2. They are attacked by the evolved O_2 of the anodic electrochemical reaction and the multitude grain boundaries enable the rapid formation of an adherent corrosion layer during the initial conditioned process.

Figure 7 - Hot rolled Pb-(0.07%)Ca-(0.35%)Ag anode sheet

ANODE PRE-TREATMENTS

It is well known that new anodes that have not been subjected to a conditioning or pre-treatment process are more efficient at oxidizing Mn to MnO_2 than aged or mature anodes. The generation of MnO_2 mud can be up to ten times higher on such anodes compared to mature ones. Whilst the presence of MnO_2 on the anode surface is necessary to prevent excessive corrosion and subsequent contamination of the Zn deposit with Pb, excessive generation of MnO_2 mud can have a detrimental effect on electrowinning. New, untreated anodes generate very fine, non-adherent particulate MnO_2 solids, which tend to remain suspended in the electrolyte. The cell discharge containing high levels of suspended MnO_2 solids has a characteristic brownish color. Suspended solids are known to interfere with the deposition process, contributing to the formation of pin-holed deposition morphology and a decrease in current efficiency, which is directly related to a lowering in the H_2 overvoltage at the cathode surface. The pin-holed deposit morphology also contributes to increased dross generation during melting.

Higher levels of Pb contamination in the cathode Zn occur during the initial period, which is attributed to the absence of an adherent protective MnO_2 on the anode surface. This contributes to a higher corrosion rate and consequently a higher concentration of $Pb-PbSO_4$ species in the electrolyte, which are then electrochemically and physically incorporated into the deposit. An additional effect of increased levels of suspended solids, which has been observed at Zincor, is an increase in bubble or blister formation on the cathode deposit. The blister formation is the result of increased deposit stresses, which under extreme conditions can lead to detachment of the deposit from the cathode substrate. As the anode matures, the anode surface roughens due to chemical attack promoting the formation of a stable layer of PbO_2 and a thicker adherent surface layer of MnO_2. Eventually, the MnO_2 begins to slough off the surface as a flaky material. At this stage, the MnO_2 layer stabilizes with the rate of formation being equal to the rate at which the material sloughs off. The transition from particulate to more adherent MnO_2

can take up to two weeks, while the stabilization of the MnO_2 layer can take up to five months.

The pre-treatment of anodes ensures that new anodes operate like mature ones from installation and effectively eliminates all of the above-mentioned problems. Anode pre-treatment methods can be divided into three categories, namely, electrochemical, chemical and physical. The electrochemical treatment involves immersion of the anodes in a KF-H_2SO_4 electrolysis bath for a number of hours at elevated temperatures to produce a stable, adherent layer of PbO_2 onto which MnO_2 naturally adheres. Chemical treatment involves immersion of anodes in an H_2SO_4-$KMnO_4$ bath so that when the anodes are installed a slightly adherent MnO_2 layer develops without generation of particulates. Physical treatments include brushing, shot-peening and sandblasting, the latter being practiced at Zincor. With sandblasting, an adherent PbO_2 layer is rapidly generated, onto which a shiny, adherent MnO_2 layer forms initially. This layer thickens and eventually sloughs off after a few months. The advantage of sandblasting over other pre-treatments is that it also work-hardens the alloy, which enhances the mechanical properties of the anode and promotes the rapid formation of an adherent corrosion layer.

ANODE PERFORMANCE AND OPERATIONAL ISSUES

PbAgCaAl anode tests in Cajamarquilla

The Cajamarquilla Zn plant in Peru has unique capabilities to carry out industrial tests with new electrodes in its industrial-sized pilot cell [11]. Forty-nine (49) rolled anode PbAgCaAl (0.38% Ag, 0.07 Ca) plates of 1495 mm x 843 mm x 10 mm were fabricated in Chile by RSR and assembled in Peru. The plates were not pre-treated and the anodes were put into operation in April 2004. For comparison purposes, regular, corrugated, chemically conditioned (with $KMnO_4$-H_2SO_4) anodes were placed in a regular cell at the same time. The composition of the spent electrolyte in these tests ranged between the following values: 16 to 20 g/L Mn, 46 to 52 g/L Zn, 180 to 190 g/L H_2SO_4. The main impurities present in the feed electrolyte were: 0.25 mg/L Co, 0.01 mg/L As, 2 mg/L Fe, 0.14 mg/L Cu, 60 to 80 mg/L Cl, and less than 10 mg/L F. Spent electrolyte temperature was 38 to 41 ºC. Additives used included gelatine, licorice and strontium carbonate. Average current density in these tests was close to 490 A/m^2. Cathodes were harvested every 48 hours and anode plates were cleaned every 20 days. Cell mud was removed on-line as frequently as needed in the pilot cell and every 20 days in the regular cell. Results from these still ongoing tests indicate the following:

- The PbAgCaAl anodes generated very large quantities of cell mud during the first three months of operation (up to 10 times more than the amount of mud produced using regular anodes). Mud formation eventually decreased, and after 4 months the amount of cell mud generated in this test cell was similar to that generated in the regular cell.

- Anode mud buildup was very even on the rolled PbAgCaAl anodes and the mud was easy to remove during the anode cleaning step. There was about 30% less mud on these anodes than on regular anodes.
- Pb in Zn cathode values between 30 and 40 ppm were obtained during the first 4 months of operation of the PbAgCaAl anodes. After the fifth month of operation, Pb in Zn cathode values below 30 ppm were consistently obtained in the pilot cell. By comparison, regular, chemically conditioned anodes consistently produced Zn cathodes with less than 30 ppm Pb after the 2nd plating cycle.
- Current efficiency (90 to 93%) and cell voltage values (3.25 to 3.35 V) were similar in the regular and in the pilot cell.
- No warping was observed on the PbAgCa anodes and they did not need flattening.

Overall these anodes appear to be working well in Cajamarquilla with no anodes rejected after 1 year of operation. The main issue with the use of these anodes in Cajamarquilla was the large amount of cell mud that they initially generated. This was somewhat expected, given the fact that these anodes were not pre-conditioned.

PbAgCaAl anode tests at Big River Zinc

Big River Zinc in Sauget, USA installed 31 rolled Pb0.35Ag0.07Ca0.015Al anodes from RSR in one commercial electrolytic cell of their operation at the beginning of May 2001. These anodes were not pretreated. For comparison purposes, 31 new rolled and sandblasted PbAg anodes were placed in an adjacent cell at the same time. As at Cajamarquilla, the PbAgCaAl anodes produced a larger quantity of anode mud than the regular anodes during the first months of operation, which was somewhat expected due to not pre-treating these anodes. This conditioning phenomenon diminished after that period. Within 2 weeks of operating the PbAgCaAl anodes the zinc deposit at the cathodes was comparable to the standard zinc produced at Big River Zinc. Current efficiencies initially measured during the first months of operation were reported to be about 0.6% higher with the PbAgCaAl anodes. No warpage of the anodes was observed and no short circuits have been observed related to dimensional instabilities. The anodes formed a very uniform and adherent initial corrosion product on which an evenly distributed and adhesive MnO_2 layer formed. On the other hand, this protective MnO_2 layer was easily removed, thus simplifying anode cleaning and maintenance. An investigation of the anode microstructure after almost 2 years of operation showed virtually no penetrating corrosion. Unfortunately, the test was terminated after more than 3 years of continuous operation. The decision to stop the test with these anodes was attributed to a non-conformity of the copper hanger bars causing increased labor to remove them from the cell. The plant did not experience any other operational issues with the anodes. The anodes themselves were still in an excellent working condition and it was generally expected that they could have remained in service for several more years. Moreover, an extended test program with a total of 372 rolled PbAgCaAl anodes had been implemented at Big River Zinc since February 2004. These anodes had the

commonly used copper hanger bar type. The operation of these anodes confirmed the anode performances of the initial test cell. Based on the demonstrated results in the test cell as well as the expanded test, Big River Zinc is currently considering extending the use of PbAgCaAl anodes in their cellhouse.

PbAgCaAl anode tests in Trail

One hundred and two rolled PbAgCaAl (0.30-0.33%Ag and 0.06%Ca) anode sheets from RSR have been tested at Teck Cominco's Trail Operations' Zn EW plant since October 2004. Anode plates were pre-treated by sandblasting with coarse metallurgical slag. The performance of the rolled PbAgCaAl anodes was compared to that of the typical cast, flat, sandblasted (with olivine) PbAg (0.75% Ag) anodes produced in Trail Operations The results obtained so far with the rolled PbAgCa anodes being tested in Trail Operations indicate that:

-   The PbAgCaAl anodes are capable of producing reasonable quality Zn with low concentrations of Pb (< 20 ppm) at high current efficiency. No major process-related issues have been identified with these anodes.
-   No significant warpage has been observed on the rolled anodes. However, if the anodes are accidentally warped during their handling, the existing flattener cannot straighten these anodes as the PbAgCa alloy is harder than the PbAg alloy.
-   Anode mud adhered strongly and evenly on the rolled anodes whereas it was less evenly distributed on the cast anodes. Anode mud collected from the rolled anodes contained 37% Mn, 15% Pb, 0.14% Ag, 0.22% Ca, 6.6% SO_4 , and 1.1% Zn whereas anode mud collected from the cast anodes contained 24% Mn, 41% Pb, and 0.36% Ag, 0.17% Ca, 6.4% SO_4, and 0.9% Zn. Thus, the rolled anodes produced an anodic oxide layer with much less Pb and Ag and more Mn than that produced by the cast anodes. Remarkably, there was almost three times more Pb in the anode mud produced from the cast anodes than in the anode mud produced by the rolled anodes. This may suggest that rolled, sandblasted, PbAgCa anodes do not need to form as much PbO_2 as the cast anodes in order to produce a firmly adhered and protective anodic oxide layer.
-   Because of the rougher sandblasting procedure used on these anodes, less cell and anode mud is expected to be produced from the rolled anodes than from the cast anodes.

Unfortunately, some of the rolled PbAgCa anodes used in Trail Operations showed significant localized corrosion defects within 40 days of their use in the Zn EW plant. The low amount of Ag in some of these anodes (0.30% Ag), and the use of metallurgical slag (containing free Fe particles that became embedded in the anode sheet creating localized corrosion cells) for sandblasting may have significantly affected the behavior of these anodes.

Trail Operations intends to carry out a second industrial test of PbAgCa rolled anodes in 2005. These anodes will contain 0.35% Ag and will be sandblasted with silica sand using the procedure developed by Zincor [12].

PbAgCa anodes at Zincor

Silver content

Fig. 8 shows the average corrosion rate of various anodes currently under investigation in industrial cells at Zincor. The anode data in the Fig. refers to the period from the year 2000 to mid-2005. The anodes were subjected to the following conditions: an average anode current density of 558 A/m^2; 187mg/L Cl$^-$; 38 – 43 ^{o}C; 165 g/L acid; 10-17 g/L Mn; 8-15 g/L Mg; <2 mg/L F$^-$; 22-day cleaning cycle.

The [Ag] in the anodes, which has traditionally been 0.5%, makes up a significant fraction of the total anode cost. Until 2001, no tests had been done to determine the optimum level of Ag in PbAgCaAl anodes. In discussions with RSR, it was indicated that the [Ag] in the rolled PbAg anodes could be decreased to 0.35% without any detrimental effect on the corrosion rate and therefore subsequent levels of Pb contamination of the Zn cathode. Anodes with 0%, 0.25% and 0.35% Ag were installed in 2001 and compared with the standard alloy containing 0.5% Ag. All the anodes were sandblasted before installation. As expected, the corrosion on the anodes with no Ag was excessive at approximately 114 g/m^2/day (not shown in Fig. 8). These anodes were rejected after a service life of less than six months. The corrosion resistance of the anodes with 0.25% Ag improved significantly, however, their corrosion rate is still 34% higher than the anodes with 0.5% Ag (11.2 g/m^2/day vs. 8.35 g/m^2/day, after a service period of 59 months). The anodes with 0.35% Ag have a similar corrosion rate compared to those with 0.5% Ag (after a service period of 31 months). This appears to confirm the findings reported by RSR. The 0.35% Ag anodes need to be evaluated for at least another six months to determine whether the corrosion rate has stabilized, after which a decision will be taken to lower the silver content. However, any future reduction in [Ag] will be conducted in a phased manner with small step changes of 0.025% with at least a two-year interval between each change. Even with conclusive evidence that 0.35% Ag is acceptable, it is unlikely that the [Ag] will be lowered below 0.4%. This might be the practical limit to accommodate any variances caused by segregation of Ag in the alloy which is characteristic of cast anodes.

Addition of Aluminum

Ca is difficult to alloy with Pb due to its low solubility, high vapour pressure and relatively low density. The addition of about 100 - 200 ppm of Al to the PbAgCa alloy, in the form of a Ca-Al master alloy, results in improved control of Ca levels in the final alloy composition. The presence of Al is claimed to contribute to grain refinement, which implies enhanced corrosion resistance of the anode. A test batch of PbAgCaAl anodes was installed in the year 2000 for evaluation; all these anodes are still in service. The results in Fig. 8 show that the addition of Al within the specified range may produce an

anode with a higher corrosion resistance when compared with the standard PbAgCa anode. Based on the present corrosion data and an acceptable mass loss of 27% the service life of these anodes is expected to exceed six years. All anodes installed at Zincor since 2003 contain Al.
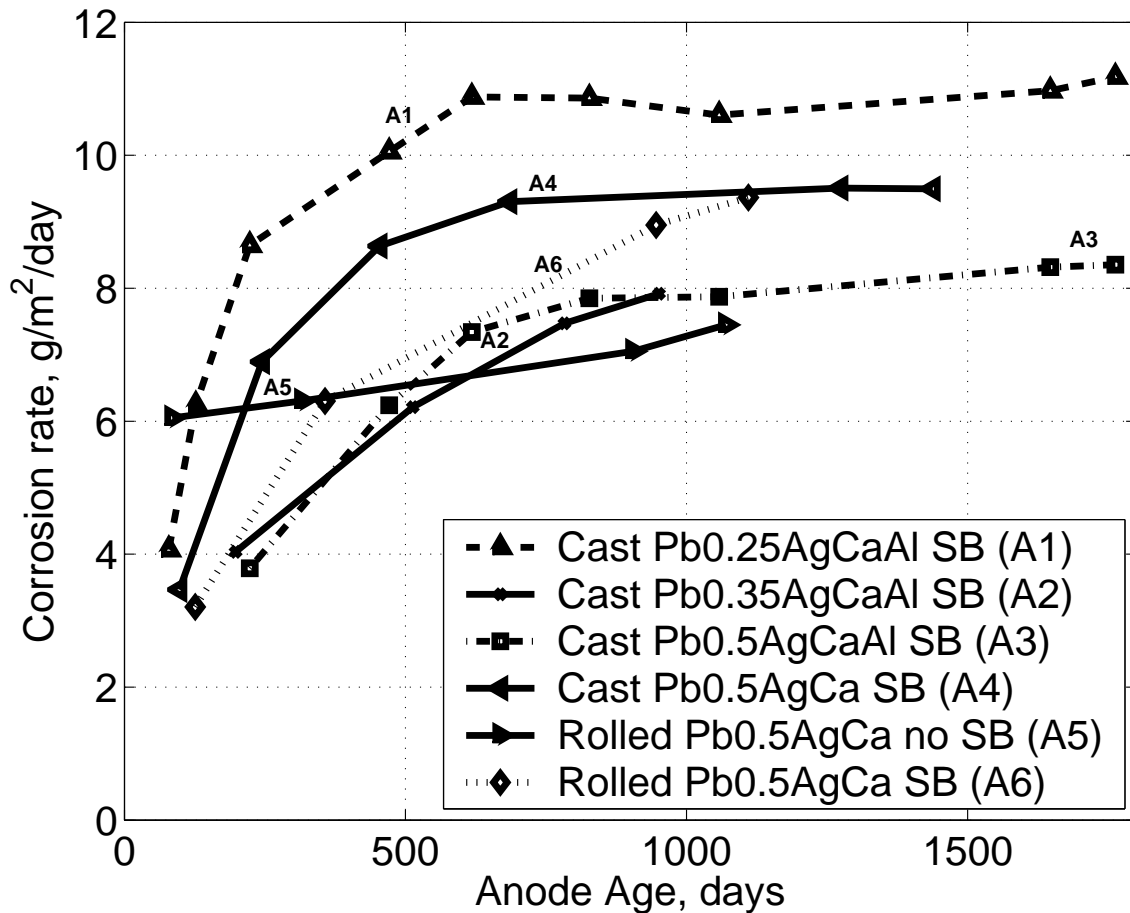

Figure 8 - Corrosion data for various cast and rolled anodes currently being tested at Zincor (SB = sandblasted anodes)

Rolled versus cast anodes

There is no doubt that rolled anodes can have superior properties than cast anodes. However, after accounting for several economic factors, rolled anodes can be more expensive to fabricate than cast anodes. In Zincor's case, the issue was whether rolled anodes are significantly better than the current technology of cast-sandblasted anodes to justify the additional cost. Rolled-untreated and rolled-sandblasted anodes were installed in 2002 for evaluation. These anodes did not contain any Al.

The data shown in Fig. 8 shows that rolled untreated anodes have a significant advantage over cast-sandblasted anodes with corrosion rates of 7.45 and 9.44 $g/m^2/day$ respectively, after a service period of 36 months (1095 days). However, the corrosion rate is only marginally better than that for cast-sandblasted Pb0.5AgCaAl alloy (7.45 versus 7.87 $g/m^2/day$). Sandblasting of rolled anodes seems to have a detrimental effect on the corrosion rate. This may be due to the grain refinement and destruction of the highly oriented and elongated grain structure on the rolled anode surface. It was observed that the MnO_2 layer on rolled anodes is generally thicker and sloughs off as large flakes. Given the higher production cost, the rolling process difficulties, and the small difference in corrosion rate between the cast and rolled PbAgCaAl alloys, at this time, there is no incentive at Zincor to convert to rolled anodes.

Perforated end-anodes

Whilst the enhanced mechanical strength of the PbAgCa alloy and the work hardening effect achieved by sandblasting combine to produce a very stiff anode sheet, these characteristics have little beneficial impact on the end-anodes. This is evidenced by the fact that the end-anodes are prone to severe warping, requiring regular flattening. Generally, new end-anodes start to warp within two months after installation, and flattening is necessary during each cell cleaning thereafter, which at Zincor is generally every 22 days. It has been found that regular flattening of anodes eventually decreases their stiffness, which in turn contributes to more pronounced warping. Apart from normal chemical attack, the corrosion on end-anodes is exacerbated by the formation of cracks in the sheet, created by the process of flattening and also by an increase in short circuits, which occur on the bottom edges due to pronounced warping.

One way to deal with the consequences of warping (i.e. short-circuiting), is to increase the spacing between the cathode and the end-anodes. This is practiced at Trail Operations and is easy to implement in cell houses with inter-cell busbars. Since the Zincor cell house does not have inter-cell busbars, increasing the spacing is not a practical option. Therefore, another method had to be found to eliminate or at least minimize the extent of the warping on the end-anodes. One practical option is to swap the end-anode on the feed side with the end anode on the discharge side of the cell; this practice was implemented in 2004. Since warping always occurs toward the cathode, swapping end-anodes ensures that warped sheets face outwards. At Zincor it usually takes two cleaning cycles for the anodes to warp inwards again toward the cathode. Whilst this method effectively eliminates the need for flattening, and is relatively effective in preventing short circuits, it does not address the root cause of the problem.

Warping is the result of imbalanced stresses in the anode sheet caused by differential corrosion rates on each side. Since the end-anodes only carry current on one side, referred to as the working surface, only this side is protected by the formation of a stable PbO_2 layer as well as the formation of an adherent MnO_2 coating. By contrast, the non-working surface has significantly less MnO_2 on it. The presence of MnO_2 on the

non-working surface is an indication that there is some current there, but not enough to form a substantial protective coating. Consequently, the effects of increased corrosion attack become visible on the non-working surface after only a few months. Any attempt to stop the corrosion on the non-working surface by, for example, applying a resin coating, has been found to exacerbate the warping problem. This is because the working surface is now the only side that is subjected to corrosion, and so once again, there is a relative difference in corrosion rates inducing mechanical stress in the sheet and eventually warping.

The solution to the warping problem lies in equalizing the corrosion rates on either side of the anode, which implies a near equal distribution of current. One way to achieve this is to perforate the anode by drilling holes, which effectively provides a path for the current to be driven by the electric field around to the back of the anode. Test trials at Zincor on the perforated end-anodes have thus far been very encouraging. Initially, the anodes were perforated with 25 mm holes at 75 mm centers. The latest test anodes have perforations of 32 mm at 75 mm centers. The perforations are machine-drilled, followed by the normal process of sandblasting before installation. The perforated sandblasting anodes behave similarly to the solid sheet anodes with an initial formation of a shiny, adherent MnO_2 on the working surface, which gradually blisters and begins to slough off normally after a few months. The MnO_2 on the non-working surface is similar to that on the working surface.

The 25 mm holes eventually closed up with the MnO_2 over a period of six months. The MnO_2 in the holes tends to be extremely hard compared with the relative soft material formed on the working surface. The anodes with the 32 mm holes have been in service for four months and whilst there is some buildup of MnO_2 in the holes, the anodes are expected to operate for approximately 10 months before the holes eventually close up completely. The build-up of MnO_2 in the holes need not pose a problem if the holes are cleaned regularly, which can be done by simply placing the anode on a steel plate with pins that line up with the holes on the anode sheet. The perforated anodes are definitely less prone to warping than solid anodes even with partially blocked holes. However, warping does increase when the holes are completely blocked.

The data shown in Table III shows that corrosion rate on the solid end-anodes, both rolled and cast-sandblasted, is significantly higher than on the perforated ones. In fact, the performance of the perforated anode is comparable to that of the solid inner anode over similar service periods. Since the solid end-anodes were straightened during each cell cleaning (every 22 days), the measured corrosion rate is attributable to chemical attack only and not short-circuit corrosion from warping. Thus, the higher corrosion rate on these anodes is due to the presence of high current densities, especially at the bottom of the anode, a consequence of warping, and increased corrosion in cracks that develop as a consequence of frequent flattening. By contrast, the perforated end-anode is not prone to warping and provided that the holes are kept open, corrodes rather normally.

The lower corrosion rate on the perforated anode results in not only improved anode service life but also in lower Pb levels in the cathode Zn, arising from either natural or short-circuit-induced corrosion. Additionally, the elimination of short circuits will also contribute to an improvement in current efficiency. Whilst these anodes are slightly more expensive, the cost is more than justified given the benefits. Based on the above results, Zincor has decided to replace all end-anodes with perforated anodes over the next three years.

Table III - End-anode corrosion rates			
	Corrosion rate, $g/m^2/day$	Service life, months	Comments
Solid end-anode – cast and sandblasted	19.54	33	Warping after 2 months; regular straightening thereafter
Solid end-anode – rolled	18.62	19	Warping after 5 months; regular straightening thereafter
Perforated end-anode – cast and sandblasted	6.32	22	No warping over first 6 months; slight warping as holes become blocked
Inner anode – cast and sandblasted	6.94 9.46	22 58	No warping during entire service life

ECONOMIC IMPLICATIONS OF USING ROLLED ANODES

In an economic model, low Ag (0.35%), rolled PbAgCa anodes could be considered to have a service life in excess of 6 years. However, so far, no plant in the world is exclusively operating with rolled PbAgCa anodes, and therefore it will be a few years more before reliable data on the expected service life of these anodes becomes available. On the other hand, rolled PbAg anodes can be considered to have a service life of at least 5 years as reported by their use in the Hudson Bay, Norzink, and Asturiana Zn EW plants. Plants that are contemplating to migrate to a new anode technology should carry out a comprehensive review of their existing and possible anode fabrication costs. The model should include the following:

- Existing anode and anode header bar fabrication costs and costs of maintaining/upgrading any existing anode fabrication/sandblasting facilities.
- Use of a model to simulate anode replacement rates during the conversion to the new technology.
- Inclusion of conversion costs/savings associated with migrating to a new anode technology.
- Estimates for inflation, cost of capital, and raw materials.

- Estimates on the fabrication, assembly, and salvage values of the anode header bars.
- Estimates of the recycling, transportation, re-melting, rolling, header bar, assembly and sandblasting costs associated with the fabrication of the rolled anodes.

CONCLUSIONS

The standard lead alloy currently applied in zinc electrowinning is a binary Pb-Ag alloy with silver concentration typically between 0.45 – 1.0%. Other alternative anode systems have been developed but their cost and limited service life has precluded their commercial application. Many plants are employing the PbAg alloy in an as-cast form manufactured on the plants premises. The service life of these anodes is typically limited mainly due to elevated porosity, insufficient control of obtaining a more corrosion resistant microstructure and mechanical weakness. A more sophisticated casting system implemented at Castle Lead Works results in lower porosity and semi-controlled microstructure, and thus, extended anode service life.

In recent years a trend has been observed towards the application of rolled anodes. In general, rolled anodes have improved mechanical properties, virtually no porosity, and a uniform and highly oriented microstructure making them more corrosion resistant.

Further enhancement in mechanical properties of anodes can be achieved by the addition of alloying elements such as calcium and aluminum. Cast and rolled PbAgCaAl anodes with low silver contents are commercially applied and tested in several Zn EW plants worldwide with encouraging results. With the exception of end-anodes, no warpage with the latter anode type has been observed during operation and no flattening of the anodes is required, which eliminates sheet elongation, cracks and reduces the potential of short circuits. Despite a lower silver content comparable corrosion rates have been obtained compared to different conventional anode types.

New cast and in particular new rolled anodes have detrimental effects on the electrowinning efficiency for an extended period of time until they are matured due to their high corrosion resistance. Chemical, electrochemical and mechanical pre-treatment methods have been developed to effectively minimize this phenomenon. End-anodes carry current only on one side. The resulting differential corrosion rates on each anode side may cause severe warping of these anodes. It has been demonstrated that perforating the end-anodes assists in equalizing the corrosion rates and makes them less prone to warping. Advances in understanding the impact of the anode performance on the electrochemical system promoted the introduction of these improvements and, in conjunction with preventive anode maintenance, anode service lives of 5 years or more can be realized. However, migrating to new anode technologies has to be carefully investigated and its economical feasibility carefully analyzed.

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