Presentation Overview

- Introduction
- Anode Systems and Requirements
- Effect of Alloying Elements (Calcium, Tin, etc.)
- Cast vs. Rolled Anodes
- Differences in Anode Rolling
- Anode Assembling
- Effect of Oxygen during Electrowinning
- Mechanism of Anode Corrosion
- Roughening of Anode Surface
- Depolarizers
- Pb-Contamination in Cu-Deposit
- Power Loss
- Anode Warping
- Maintenance
- Alternatives in Anode Technology
- Summary
Introduction
Quexco Group
(~900,000 tpa Lead)

RSR Corp (100%)

- Quemetco
  - Indianapolis, IN
- RSR
  - City of Industry, CA
- RSR
  - Middletown, NY

- Bestolife
  - Dallas, TX
- Quemetco Metals
  - Dallas, TX

- Inppamet / Chile
- Mesco

Eco-Bat Technologies (86%)

- Le Plomb Francais
- British Lead Mills
- Zimco Group (100%)
  - South Africa

- HJ Enthoven
  - UK
- STCM
  - France

- Bazoches
- Toulouse
- APSM
- Berzelius
  - Germany
  - Berzelius Stolberg
  - MRU Freiberg
  - BSB Braubach

- BMG
  - Austria
- Eco-Bat SpA
  - Italy
  - Paderno
  - Marcinise

- Fry's Metals
- Zinchem / African Zinc Mills
- Zimalco
- Associated Additives
- Duttons Plastic
- Sondor / G&W
- Castle Lead Works

RSR Technologies, Inc. (100%)

- Zimalco
- Associated Additives
- Duttons Plastic
- Sondor / G&W
- Castle Lead Works
**Anodes for Cu-EW Quexco Group & Inppamet**

- Cast or rolled lead/calcium/tin anodes are used in copper electrowinning.
- RSR developed rolled lead/calcium (0.07) / tin (1.35%) anode for copper electrowinning.
- RSR Corp/Quemetco Metals, Castle Lead, Inppamet & Le Plomb Francais supply rolled lead/calcium/tin anodes for copper, nickel, cobalt electrowinning.
- Castle Lead supplies cast lead/antimony anodes for copper, nickel and cobalt electrowinning.
- Recycling of anode scrap and anode sludge offered as part of service & environmental obligation.
Anodes for Zn-EW Quexco Group & Inppamet

- Cast or rolled lead/silver (0.5-1.0%) anodes are used in zinc electrowinning

- RSR Corp./Quemetco Metals, Castle Lead & Le Plomb Francais supply cast and rolled lead/silver and rolled lead/silver/calcium anodes for zinc electrowinning

- RSR developed rolled lead/calcium (0.07) / silver (0.35%) anode for zinc electrowinning; worldwide patented

- Recycling of anode scrap and anode sludge offered as part of service & environmental obligation
Anode Systems and Requirements
Standard Requirements

- High Mechanical Strength against Warpage and Creep (Form Stability)
- Low Oxygen Overpotential for Oxygen Evolution
- Quick and Stable Formation of Hard, Dense and Adherent Protective Corrosion Layer (Conditioning)
- High Corrosion Resistance
- Long Service Life
- Minimized Production Cost
- Design and Material Integral Part of Tankhouse Concept
Lead Alloys are Preferred Material for EW Anodes from Acidic Sulfate Solution

- Insoluble
- Ability to form protective PbO₂ layer
- Corrosion resistant
- Economical
- Acceptable Operating Voltage
Anode Development

Major advances in understanding the impact of anodes in electrochemical systems on
- Electrode Kinetics and Overpotentials
- Anode Corrosion Effects
- Mass Transport Processes (Convection, Diffusion, Migration)
- Cell Voltage
- Energy Consumption
- Current Distribution (Macroscopic & Microscopic areas on individual electrodes)
- Current Efficiency
- Cathodic Metal Deposit Morphology and Contamination

Efficiency of electrowinning step is strongly governed by anode performance

Main advances characterized by and resulted in:
- Substitution of Lead Alloys by Different Lead Alloys
- Structural Evolution of Anode Microstructure

Standard Cu-EW: Pb-(0.07-0.08%)Ca-(1.35%)Sn
Effect of Alloying Elements
Lead Alloying Elements

**Major**
- Antimony
- Silver
- Calcium
- Tin
- Aluminum

**Minor**
- Strontium
- Arsenic
- Selenium
Effect of Antimony in Anodes for Electrowinning

- Low Melting Point; Easy to Cast
- Enhances Mechanical Properties in As-Cast
- Intergranular Corrosion especially at Higher Sb-Levels
- Corrosion Resistant in Electrolytes with Low Acid Concentrations
- Corrosion Resistant at higher Electrolyte Temperatures Applications
Effect of Silver in Anodes for Electrowinning

- Increases Electrical Conductivity
- Lowers Oxygen Overpotential
- Resists against Anode Passivation
- Enhances Corrosion Resistance
- Increases Time for Initial Conditioning Process
- Virtually no Effect on Mechanical Properties
Effect of Calcium in Anodes for Electrowinning

- Increases Rate of Anode Corrosion
  - Particularly above 0.08% Ca because of Pb₃Ca formation

- Increases Mechanical Properties of Anode

- Decreases the Anode Potential
Properties of Pb-Ca-Sn Anodes
Mechanical Properties of Pb-Ca-Sn Anodes

EFFECT OF CALCIUM CONTENT ON THE RATE OF CORROSION OF Pb-Ca ALLOYS

Corrosion Rate (mm/year) vs. Calcium Content (Wt %)

- Corrosion Rate increases with increasing calcium content.
- The rate of corrosion is relatively low for calcium contents below 0.075%.
- There is a noticeable increase in corrosion rate as the calcium content exceeds 0.1%.
Mechanical Properties of Pb-Ca-Sn Anodes

EFFECT OF CALCIUM CONTENT ON MECHANICAL PROPERTIES

Yield / Tensile Strength (MPa) vs. Calcium Content (Wt %)

- Yield Strength
- Tensile Strength
Mechanical Properties of Pb-Ca-Sn Anodes

Anode Potential for Pb-Ag-(Ca)-Alloys

- Anode Potential (mV vs. Hg/Hg₂SO₄)
- Silver Content (%-Wt.)

Pb-Ag
Pb-Ag-0.07Ca
Effect of Tin in Anodes for Electrowinning

- Imparts Strength to the Lead Alloy and Reduces Creep
- Reduces Corrosion by Segregation into Interdendritic Eutectic Phase Forming Layers of Tin-Rich Material; Parallel to Surface for Rolled Anodes
- Improves Conductivity and Reduces Anode Polarization
- Prevents Formation of Tetragonal PbO
- Produces Conducting Paths through Corrosion Layer
Mechanical Properties of Pb-Ca-Sn Anodes

Effect of Tin on the Yield Strength of Pb-0.07% Ca-Sn Alloy

Yield Strength (MPa)

Tin Content (Wt %)

- Cast
- Rolled
Mechanical Properties of Pb-Ca-Sn Anodes

Effect of Tin on the Polarization Resistance of Pb-.08% Ca-Sn Alloy

- Polarization Resistance (KOhm/cm²)
- Tin Content (Wt %)

The graph shows a decrease in polarization resistance as the tin content increases from 0 to 5%. The resistance drops sharply with increasing tin content, indicating improved anode performance.
Mechanical Properties of Pb-Ca-Sn Anodes

Effect of Tin on Corrosion Rate of Pb-Ca-Sn Alloy

Corrosion Weight Loss (mg/cm²)

Tin Content (Wt %)

0.1% Ca  0.08% Ca
Effect of Aluminum in Anodes for Electrowinning

- Anti-Drossing Agent
- Grain refiner
Effect of Minor Elements in Anodes for Electrowinning

- **Strontium**
  - Imparts Strength via Precipitation Hardening
  - Uniform Corrosion Forming Larger Flakes
  - Prevents Penetrating Corrosion

- **Arsenic**
  - Grain Modifier to Less Needle Like
  - Reduces Corrosion Rate
  - Increases Ultimate Tensile Strength

- **Copper, Sulphur**
  - Refines Crystal Structure
  - Prevents Cracking

- **Selenium**
  - Refines Crystal Structure
  - Improves Castability of Pb-Sb Alloys
  - Reduces Corrosion Rate
Cast vs. Rolled Anode Sheets
Cast Anodes

- Randomly Oriented, Dendritic Grain Structure
- Many grain boundaries exposed
- Low creep resistance
- Tin / Silver Segregation to Interdendritic and Grain Boundaries

↓

- Casting Defects
- Porosity
- Considerable creep
- Concentric cracking of corrosion layer
Cast Anodes

Fine-grained, cast Pb-Ca

- Many grain boundaries
- Lower creep resistance
- Considerable growth
- Concentric cracking of corrosion layer

PbO₂ corrosion product
# Anode Density and Porosity Top Cast

<table>
<thead>
<tr>
<th></th>
<th>Anode 1</th>
<th>Anode 2</th>
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<tbody>
<tr>
<td>Cominco Trail</td>
<td>2.0</td>
<td>2.6</td>
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<td>0.9</td>
<td>2.0</td>
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<td></td>
<td>1.2</td>
<td>1.7</td>
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<td>1.4</td>
<td>3.1</td>
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<tr>
<td></td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>2.9</td>
<td>1.6</td>
</tr>
<tr>
<td>密度平均值 $\rho_{ave}$</td>
<td>11.11 g/cm³</td>
<td>11.19 g/cm³</td>
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<tr>
<td>直径 $\varphi$</td>
<td>2.0 ± 0.7%</td>
<td>1.2 ± 0.4%</td>
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Cajamarquilla Anodes

<table>
<thead>
<tr>
<th></th>
<th>Anode 1</th>
<th>Anode 2</th>
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<td>0.5</td>
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<td>1.1</td>
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<td>1.9</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Advances in Cast Anodes

- Controlling of Grain Structure
  - Controlled Heating and Cooling

- Reduction in Porosity and Dross Entrapment
  - Controlled Cooling
  - Vertical Cast
  - Low turbulent cast from bottom
Anode Density and Porosity Top Cast

<table>
<thead>
<tr>
<th></th>
<th>Anode 1 Pb-Ag</th>
<th></th>
<th>Anode 2 Pb-Ag-Ca-Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>0.2</td>
<td>0.5</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>0.1</td>
<td>0.3</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>0.0</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
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</tbody>
</table>

Castle Lead Works

ρ_{ave} = 11.30 g/cm³
Ø 0.3 ± 0.2%
ρ_{ave} = 11.28 g/cm³
Ø 0.4 ± 0.2%
Rolled (Cold) Anodes

- Breaks up Original Cast Grain Structure
- Elongated and Highly Oriented Grains
- Sn/Ag Segregation Remains
- Homogeneous Grain Size Distribution
- No Casting Defects and Porosity
- High Creep Resistance
- Good Corrosion Resistance
- Higher Resistance to Initial Conditioning
Rolled Pb-Ca-Sn Anodes

- High creep resistance
- Good corrosion resistance
- Reduced growth
- Thinner grids

PbO₂ corrosion product
Anode Corrosion Products

Cast Anode

Rolled Anode
Differences in Anode Rolling
Anode Rolling

- At ratio 2:1 start to deform but still spherical grain structure
- At ratio 4:1 fully bent; Larger 4:1 stretched
- Optimum Mechanical Properties @ deformation ratio of 4:1
- Elimination of porosity @ ratio 4:1
- Optimum corrosion resistance at ratio 4:1
- Recrystallization effects occurring during EW
- Results in reduced hardness and microstructure = reduced service life
- Microstructure elongated and stretched
Anode Rolling

Deformation Ratio 1.5 : 1

Deformation Ratio 15 : 1
## Mechanical Properties of Typical Pb-alloys for Electrowinning

<table>
<thead>
<tr>
<th>Alloy</th>
<th>UTS (MPa)</th>
<th>0.2% YS (MPa)</th>
<th>Elongation (%)</th>
<th>Hardness (RR30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-(3%)Sb Cast</td>
<td>65.5</td>
<td>55.2</td>
<td>10</td>
<td>85</td>
</tr>
<tr>
<td>Pb-(3%)Sb Rolled</td>
<td>24.6</td>
<td>16.3</td>
<td>40</td>
<td>64</td>
</tr>
<tr>
<td>Pb-(6%)Sb Cast</td>
<td>73.8</td>
<td>71.0</td>
<td>8</td>
<td>87</td>
</tr>
<tr>
<td>Pb-(6%)Sb Rolled</td>
<td>30.6</td>
<td>19.5</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>Pb-(0.07%)Ca-(1.35%) Sn Cast</td>
<td>46.4</td>
<td>35.3</td>
<td>29</td>
<td>71</td>
</tr>
<tr>
<td><strong>Pb-(0.07%)Ca-(1.35%) Sn Rolled</strong></td>
<td><strong>71.0</strong></td>
<td><strong>65.3</strong></td>
<td><strong>14</strong></td>
<td><strong>85</strong></td>
</tr>
<tr>
<td>Pb-(0.07%)Ca-(1.35%)Sn-(0.05%)Ag Rolled</td>
<td>80.0</td>
<td>76.8</td>
<td>10</td>
<td>88</td>
</tr>
<tr>
<td>Pb-(0.07%)Ca-(0.35%)Ag Rolled</td>
<td>37.8</td>
<td>35.5</td>
<td>42</td>
<td>68</td>
</tr>
<tr>
<td>Pb-(0.75%)Ag Alloy Rolled</td>
<td>18.8</td>
<td>9.0</td>
<td>54</td>
<td>-26</td>
</tr>
</tbody>
</table>
Anode Assembling
Process Block Diagram Anode Manufacturing
Assembling Sheet / Busbar
Advances in Anode Sheet Assembling

Graph showing resistance between the copper bar and anode sheet as a function of service life.
Advances in Anode Sheet Assembling
EFFECTS OF ANODIC OXYGEN EVOLUTION IN COPPER ELECTROWINNING
Electrolytic Cell

- Reduction occurs at the cathode
  - e.g. \( \text{Cu}^{2+} \text{(aq)} + 2e = \text{Cu(s)} \)
  - \( \text{H}^+ \text{(aq)} + e = 1/2\text{H}_2 \text{(g)} \)

- Oxidation occurs at the anode
  - e.g. \( \text{Cu(s)} = \text{Cu}^{2+} \text{(aq)} + 2e \)
  - \(2\text{H}_2\text{O} = \text{O}_2 \text{(g)} + 4\text{H}^+ + 4e\)
Effects of Oxygen Evolution in Electrowinning

- **Creation of Acid Mist**
  - 😊 Control methods = plastic ball or beads coverage, foam mist suppressants, mechanical shields, anode cap control systems, cell hoods & ventilation

- **Electrolyte Stirring**
  - 😞 May cause variations in the concentration layer at the surface of the cathode impacting quality of Cu-deposit
  - 😞 Stir up PbO$_2$ flakes from cell bottom; lead contamination

- **Transfer to Cathode and Oxidation of Cu-deposit**
  - 😞 Reduction in current efficiency
Plastic Ball Coverage in EW-Cell
Foam Surpressant in EW-Cell
Anode Cap Control System
Ventilation Hood Systems
MATERIAL OXIDATION IN SOLUTION

Oxidation of Iron

$password_flag

Oxidation of ferrous (Fe$^{2+}$) at anode and reduction of ferric (Fe$^{3+}$) at cathode reduces current efficiency.

Oxidation of Manganese

$password_flag

MnO$_2$ reacts with corrosion product PbO$_2$; Light PbO$_2$-MnO$_2$ layer may shed and can cause severe cathode contamination.

Addition of Fe and Co to reduce effects of manganese.
MATERIAL OXIDATION IN SOLUTION

- Degradation of Organic Additives Controlling Cu-deposit
- Oxidation of Organics from SX-Circuit / Additive
  - Formation of reactive radicals attacking the anode at electrolyte surface
    \[
    \begin{align*}
    O_2 + 2RH & \rightarrow 2R^+ + H_2O \\
    R^+ + PbO_2 & \rightarrow PbO + R=O \\
    PbO + H_2SO_4 & \rightarrow PbSO_4 + H_2O
    \end{align*}
    \]
  - Start of fires when sparks ignite flammable organic on surface
  - May soften flakes, which spall off easier
Organic Burn at Pb-Ca-Sn Anode
EFFECTS OF ANODE OXIDATION

Major Consequence is Corrosion of Lead Anode on the Anode Surface

- $\alpha\text{PbO}_2$ (rhombic, large closely packed crystals, dense, hard, brownish color, formation at higher pH, temperature, pressure = metastable)
- $\beta\text{PbO}_2$ (tetragonal, fine needle-shaped crystals, black color, formation at acidic condition, low temperature and pressure)
- Formation of PbO, Pb(OH)$_2$, PbSO$_4$, Complex Sulfates

Main Mechanism
- Formation of PbSO$_4$
- Oxidation to $\beta\text{PbO}_2$
- Oxygen diffusion through $\beta\text{PbO}_2$ and formation of $\alpha\text{PbO}_2$
Anode Corrosion
Anode Corrosion

**Primary Corrosion**
- Forms stable, adherent oxide layer on anode
- Formation ratio determined by chemical composition and macro-roughness of surface
- Surface pretreatment methods influence the anode corrosion behavior

**Secondary Corrosion**
- Occurs through periodic failure and re-growth of oxide layer
- Corrosion behavior of lead is dependant both on microstructure and chemical composition

Corrosion at and along the grain boundaries
Corrosion of Lead Anode
**Anode Corrosion**

FORMATION RATE AND STABILITY OF PbO$_2$ FILM 
MAINLY DEPENDS ON:

- **Current Density**
  - almost linear increase in corrosion rate with increasing current density

- **Electrolyte Temperature**
  - Temperature increase of 10$^0$ C doubles corrosion rate

- **Manganese Content**
  - Chemical attack of MnO$_4$–ions forming voluminous non-protective PbO & Pb(OH)$_2$
  - Forms MnO$_2$/PbO$_2$ flakes; larger, softer, lighter; tend to spall; <40 ppm desirable
Figure 2: Effect of anode potential on corrosion rate
Anode Corrosion

Figure 3: Effect of manganese on anode corrosion rate
Anode Corrosion

FORMATION RATE AND STABILITY OF PbO$_2$
FILM MAINLY DEPENDS ON:

- **Iron Concentration**
  - Increases anode corrosion
  - Reduces current efficiency
    - Fe$^{2+}$ - Fe$^{3+}$ reduction/oxidation at cathode and anode
  - Controls detrimental effect of manganese
    - 1g/l Fe reported to prevent high Eh levels in electrolyte preventing formation of stable permanganate

\[
\begin{align*}
\text{Mn}^{3+} + \text{Fe}^{2+} &= \text{Fe}^{3+} + \text{Mn}^{2+} \\
\text{MnO}_2 + 2\text{Fe}^{2+} + 4\text{H}^+ &= \text{Mn}^{2+} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \\
\text{MnO}_4^{-} + 5\text{Fe}^{2+} + 8\text{H}^+ &= \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}
\end{align*}
\]

- Mn:Fe ratio of 1:10 apparently required
Anode Corrosion

Figure 2: Effect of iron on anode corrosion rate
Anode Corrosion

Figure 9: Effect of concentration of iron on cathode current efficiency
Anode Corrosion

FORMATION RATE AND STABILITY OF PbO$_2$
FILM MAINLY DEPENDS ON:

- **Chloride Concentration**
  - Increases corrosion rate; MnCl$_2$, PbCl$_2$ formation;
  - 10 - 20 ppm desired to prevent dendrite formation at cathode; 100 ppm dangerous

- **Cobalt Concentration**
  - Reduces oxygen evolution potential; causes oxygen development instead of anode corrosion
  - Amount between 100 - 200 mg/l mainly depending on current density and manganese concentration
Anode Corrosion

FORMATION RATE AND STABILITY OF PbO₂ FILM MAINLY DEPENDS ON:

Grain Size

😊 small = too much corrosion; releases fast crystals; hard to form thick enough corrosion layer
😊 moderate = desired, if grains elongated in rolling direction; reduces creep resistance
😊 large = high corrosion; goes in and wedges it over; too less grain boundaries

Roughness of Anode Surface
Anode Pre-Conditioning
Anode Surface pretreatment and applied method has effect on:

- Required time initial anode conditioning
- Anode behavior
- Deposit morphology
- Manganese sludge generation
Industrial Methods for Surface Roughening

**KMnO₄ Treatment**
- Chemical deposition of a flaky, initial MnO₂ corrosion layer; subsequent spalling of layer associated with break up of underlying PbSO₄/PbO₂ scale

**Shot peening**
- Regular hemispherical indents up to 500 µm. Significant deformation and often warpage of lead sheet

**KF Electrochemical Pretreatment**
- KF electrochemical pretreatment forms thick, dense adherent MnO₂ layer with multiple PbO₂ sub-layers; labor, energy and cost intensive
Industrial Methods for Surface Roughening

Sandblasting

- Very rough irregular and enlarged surface area; indents up to 1 mm
- Creates new grain boundaries by destroying larger grains on outer surface layer (recrystallization) and high micro-roughness
- Produces rapidly thin adherent glass film of MnO$_2$ which forms adherent PbO$_2$
- Sand blasting appears to be the most suitable pretreatment generating the most adherent corrosion layer and to minimize initial anode mud formation
Surface Area after Treatment

b) 0.85-1.65mm Graded Gravel (x20)
e) 0.6-0.85 mm steel shot (x50)

a) KF pre-treatment (x640)
b) KMnO₄ pre-treatment (x100)
Lead Anode Depolarizers for Electrowinning

- Cobalt added as Cobalt Sulfate
- Sodium Sulfite
- Ammonium Sulfite
- Sparged Sulfur Dioxide
- Ethylene Glycol
- Ferrous/Ferric Oxidation
Effect of Cobalt Addition

- Reduces PbO$_2$ Formation and Anode Corrosion
- Reduces Oxygen Evolution Potential
  - $\downarrow$ 170 mV at 200 mg/l
- Oxidizes Preferentially Manganese
- Hardens Flakes; difficult to spall
- Reduces Pb Contamination at Cathode
  - Prevents deterioration of anode
  - No further improvements above 60 ppm Co
- Co-content between 100 - 200 mg/l
  - $\uparrow$ f (i, Mn-concentration)
  - $\downarrow$ No economical benefit above 200 mg/l
Effect of Cobalt Addition

In the presence of cobalt, the amount of PbO2 formed on the anode surface is markedly decreased. Several interpretations for the reduction of PbO2 formation in the presence of cobalt have been given in the literature:

- Adsorption of Co3+ ions or CoO2 on the lead anode probably forming a dense film and blocking the penetration of PbO2 by O radicals.
- Decrease of radicals due to recombination reaction of adsorbed Co3+ with water or hydroxide ion producing a complex, which inhibits formation of PbO2
- Co2+ increases the amount of labile oxygen containing species and decreases number of adsorbed OH- radicals, which inhibits formation of PbO2 film.
- Co2+ inhibits formation of more soluble PbO underneath the PbSO4 film.
Figure 4.18. The effect of cobalt on the potential for oxygen evolution on a Pb-Ca-Sn anode.
Effect of Cobalt Addition

Figure 1: Effect of cobalt on anode corrosion rate
Effect of Cobalt Addition

- Amount of PbO₂ decreases with increasing cobalt concentration

- Corrosion Layer in solutions without cobalt addition has a porous structure while the layer in solution with cobalt is more dense
  - Dense phase is composed of $\alpha$-PbO₂
  - Porous material consists of $\beta$-PbO₂
    - Higher the rate of oxidation.
    - Reflected by a darker, more black color of the corrosion layer.
Ferrous/Ferric Oxidation

- Substitute Anode Reaction with Ferrous/Ferric Couple
- Requires DSA or Activated Lead Anode
- Sparging with SO$_2$ for Ferric Reduction
- Stripping of Sulphuric Acid Required
- Electrolyte Distribution by Manifold
- Iron Concentration > 28 g/l (Fe$^{2+}$ > 26g/l, Fe$^{3+}$ <2 g/l)
- Significant Energy Savings
- No Acid Mist above Electrolyte but less than 1 ppm SO$_2$
- Ferric Reduction at Activated Carbon
- Fe-deposit in Copper Cathode
- No Commercial Operation; Pilot Plant Stage
Lead Contamination in Copper Deposits
Lead Contamination in Copper Deposit

- **Reduction Potential Electrodeposition**
  - $\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu} \quad E^0 = 0.34 \text{ V}$
  - $\text{PbSO}_4 + 2e^- \leftrightarrow \text{Pb} + \text{SO}_4^{2-} \quad E^0 = -0.36 \text{ V}$
  - $\text{Pb}^{2+} + 2e^- \leftrightarrow \text{Pb} \quad E^0 = -0.13 \text{ V}$

- **No co-reduction of Pb ions**

- **Only physical occlusion of particulate Pb species**

- **PbO$_2$ reduction to PbSO$_4$ or PbO possible**
  - $\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \leftrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \quad E^0 = 1.69 \text{ V}$
  - $\text{PbO}_2 + \text{H}_2\text{O} + 2e^- \leftrightarrow \text{PbO} + 2\text{OH}^- \quad E^0 = 0.25 \text{ V}$

- **No further reduction of PbO**
  - $\text{PbO} + \text{H}_2\text{O} + 2e^- \leftrightarrow \text{PbO} + 2\text{OH}^- \quad E^0 = -0.58 \text{ V}$
Lead Contamination in Copper Deposit

- High Electrolyte Temperature and Variations
- Elevated Manganese or Chloride Levels
- Increased Surface Roughness
- Increased Current Density
- Mass Transport though Oxygen Evolution
- Short Circuits

Electrolyte Distribution by Manifold
- Hole size and velocity of electrolyte injection = laminar flow
- Angle and angle direction
- Clearance between manifold - cell bottom & manifold - electrodes
Lead Contamination in Copper Deposit, cont.

- No frequent anode washing
- No sludge removal
- Short circuits
Enhanced Mass Transport Due to Oxygen Evolution At Anode

$k_L$ (anode) $>>$ $k_L$ (cathode)

$k_L$ (top) $>$ $k_L$ (bottom)
Manifold for Electrolyte Distribution
Anode Insulators
Anode Insulators
Anode Insulators
Anode Insulators
Lead Contamination in Copper Deposit

- **PbO₂** more readily incorporated than **PbSO₄**
- **Addition of Sr or Ba Carbonate**
  - Formation of double salt (Pb, Sr or Ba) (SO₄)₂
  - Negative effect on Pb contamination
  - Increase in dendritic growth of Cu deposit
- **Addition of Iron (2 g/l)**
  - Possible Reduction of PbO₂ to PbSO₄ by Ferrous (Fe²⁺)
  - Significant reduction in current efficiency (8 – 10%)
- **Filtration of Electrolyte**
  - Reduction of Pb-levels with or w/o additives
Power Loss
Power Loss

SULFATION REACTIONS OF ANODE WHEN POWER IS LOST:

\[
\text{Cu + PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{PbSO}_4 + 2\text{H}_2\text{O}
\]

\[
\text{Cu+ MnO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O}
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### Lead Corrosion Films

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Power Loss

Figure 4.8 Open circuit potential transients after anodization for various times
Figure 4.9  Rate of reduction of PbO₂ to PbSO₄ after various oxidation times.
Corrosion Product on Rolled Pb-Ca-Sn-Anode

Sn$_3$Ca

α SnO$_2$

LEAD CALCIUM TIN ALLOY

PbSO$_4$

α PbO$_2$
Proposed Ramping up of Power to avoid overheating of conductive SnO$_2$ tubes and subsequent spalling at interface metal corrosion product

- Initial Current: 50 A/m$^2$ or 5 (A/ft$^2$)
- After 5 Minutes: 100 A/m$^2$ or 10 (A/ft$^2$)
- After 15 Minutes: 150 A/m$^2$ or 15 (A/ft$^2$)
- After 25 Minutes: 200 A/m$^2$ or 20 (A/ft$^2$)
- Then raise 5 A / anode * minute
Anode Warping
Possible Reasons for Anode Warping

- Ca-content above 0.08%
- Rolling of Anode Sheet
- Assembling of Sheet to Hanger Bar
- Transportation
- Storage
- Tankhouse Operation
- Anode Cleaning
- Spacers
Possible Reasons for Anode Warping

- Non-uniform grain structure of sheet
  - large, equal-sized grains on one side
  - directionally oriented grains on other side

- Differential corrosion on each side of the sheet
Anode Maintenance
Maintenance of Pb-Ca-Sn Anodes

Built up of thick corrosion layers
- Anode cleaning with pressurized water to remove adherent flakes

Anodes have to be frequently checked for warpage and straightened, if necessary
- Before anode straightening remove corrosion product to bare metal
Alternative Developments in Anode Technology
Advances in Anode Technology

- Dimensional Stable Anode (DSA)
- Eltech Anodes
- Merrlin Anodes
- Gas Diffusion Anode
- Thermo-Mechanical Anode Treatment
- Polymer Coating
- Co$_3$O$_4$ Coating
- Graphite or Coke Particulate Anode
Dimensional Stable Anode

- Titanium Substrate Coated with Catalytic Layer
  - Platinum Group Metals (Pt, Pd, Rh, Ir, Ru)
  - Electrical Conductive Oxide (IrO\textsubscript{2} or RuO\textsubscript{2} with Ta\textsubscript{2}O\textsubscript{5} stabilizer)
  - Preparation by Painting or Cathodic Deposition

- Lower Anode Potential = Energy Savings
- No Anodic Gas Evolution
- No Cobalt Addition
- Very Expensive
- Coating Consumption/Peeling → Re-coating Required
- Prone to Passivation Effects particularly Limited Service Life when Manganese (= MnO\textsubscript{2} deposition) and Fluoride Ions Present
- Passivation of Ti-surface through TiO\textsubscript{2}-layer formation
- Less Robust than PbCaSn Anodes
- No Extended Commercial Operation / Data
Eltech Anode

- Lead Alloy Anode with Attached Titanium Mesh
  - Ti-mesh pre-coated with Electrocatalytic Layer (IrO$_2$ or RuO$_2$)
  - Mesh soldered to lead base

- Expensive
- Operates ca. 500 mV below Pb-anode → Commercial Operation = 13% Cost Savings plus 2 -4 % higher current efficiency after 13 months
- Achieved Service Life 16 months; Expected 4 yrs but not proven
- Coating Consumption → Re-coating required
- Limited Service Life when Manganese and Fluor ions present = Passivation Effects
- Recycling Issue
Merrlin Composite Anode

Lead Alloy Anode with Composite Coating
- Composite 90-95% Metal Compound (PbO, MnO₂) plus 5-10% Polymeric Binder (Polyethylene, Graphite, Carbon black or fiber)
- Composite Painted on Lead Base

Additional Production Costs vs. Conventional Anode
- Operates ca. 175 - 200 mV below Pb-anode
- Less Cobalt Required (30 – 50 ppm)
- Coating Consumption/Degradation through Graphite Oxidation → Frequent Re-coating required (0.5 – 1 year)
- Commercial tests abandoned; max. test 9 months
Hydrogen Gas Diffusion Anode

Hydrogen Oxidation to Hydrogen Ions
- Requires Gaseous Hydrogen; permeates through porous electrode structure, dissolves in electrolyte and diffuses to electrocatalyst, at which it oxidizes

Complex Anode Structure
- Gas Supplying Layer–Current Collector–Reaction Layer-Hydrophobic Layer

Lower Anode Potential = Energy Savings
High Currency Application (up to 5,000 A/m²)
No Anodic Gas Evolution
No Sludge Formation = No Cell Cleaning
High Capital Cost
Restricted Service Life of HGDA
No Commercial Operation in Primary Metal Electrowinning
Thermo-Mechanical Anode Treatment

- Lead Alloy Anode
  - Cold Rolling
  - Annealing at $T = 180^0 - 300^0$ C

- Homogenize of Grain Structure

- Re-crystallization of Microstructure = Avoid Segregation and Break up of Dendrites

- Additional Manufacturing Costs

- Minor benefits by Slightly Higher Resistance to Intergranular Corrosion
Conductive Polymer Coating

- Lead Alloy Anode with Conductive Polymer on Surface
  - Rely on Organic Structure to Carry Current
  - Coating through Electrochemical Deposition
  - Polymer = Poly-3,4,5-trifluorophenylthiophene (TFPT)

Additional Costs

- Only Lab Scale Test at Mild Operating Conditions
- Ability of Coating to Withstand Commercial Operating Condition over Extended Time Period ??
- Achievable Reduction in Corrosion Rate
Pb-Co₃O₄ Composite Coating

- Lead Alloy Anode with Pb-Co₃O₄ Composite Coating on Surface
  - Electroplating of Composite in NH₂SO₃NH₄- electrolyte
  - Layer Thickness approx. 90 µm

- Depolarization Effect vs. Pb-Sb Anodes Obtained
- Corrosion Rate 6.7x Lower
- Additional Costs
- No Commercial Tests, Only in Lab
- Re-Coating Required
Co-Treatment of Lead Alloy Anodes

- Lead Alloy Impregnation with Cobalt
  - Molten Cobalt Nitrate Bath Impregnation
  - Electrochemical Stabilization in Sulphuric Solution
  - Chemical Stabilization at Temperature 40 – 45°C below Pb Melting Point plus Controlled Stress Relieve Cooling

- Depolarization Effect Obtained = 100 – 200 mV
- Corrosion Rate Less than 1 mm/year
- Improved Copper Deposit Cathode
- Expensive Manufacturing Cost
- No Commercial Tests, Only in Lab
Summary
Anode Current Status

Lead Alloys are Preferred Material for EW Anodes from Acidic Sulfate Solution

- Insoluble
- Ability to form protective PbO$_2$ layer
- Corrosion resistant
- Economical
- Acceptable Operating Voltage

Alternative Technologies

- None can economically compete with Pb-alloy anodes
- Limited industrial test work carried out
- More developmental work required
Best Available Anode

- **Rolled Anode**
  - Microstructure has impact on anode corrosion rate

- **Chemical Composition for Cu-EW**
  - Lead alloy containing 0.07% Ca and 1.35% Sn
  - Impurity levels have impact on anode corrosion rate

- **Provides maximum mechanical properties and stability**

- **Resists Corrosion**

- **Resists Passivation**

- **Independent of Source for Raw Material**
  - Primary or Secondary Lead
  - Pyro-refined or Electrorefined

- **Conducting Current**
  - Low potential drop between sheet and hanger bar (≤ 1 mV) due to complete metallurgical bond at soldered joint
  - Low potential drop is maintained throughout anode life
Recommended Anode Alloy Specification

RSR CORPORATION PRODUCT SPECIFICATION

** REVISED **                  CSN                 ** REVISED **

Customer - QUEMETCO, LTD - FAB
Product No. 023001 CSN BLOCK LEAD    MSDS:088F
RSR Reference No. 04-2017M

Effective Date - May 10, 2004
Customer Revision Date - September 3, 2003

DETAILS
Cast in blocks, stamp CSN and lot number.
Cast at 950-1000F.

COLOR CODE

ELEMENTS
Sb < 0.0010
As < 0.0010
Ni < 0.0010
S < 0.0005
Al 0.0150 - 0.0400
Cd 0.0010 max
Fe 0.0010 max

Sn 1.3000 - 1.5000
Cu < 0.0010
Te < 0.0010
Ca 0.0700 - 0.0800
*Ag 0.0120 max
Bi 0.0250 max
Zn 0.0010 max

COMMENTS
On certificate of analysis list all elements indicated.