Cu 2007 Short Course

Fundamentals and Practice of Copper Electrorefining and Electrowinning

Performance of Lead Anodes during Cu Electrowinning

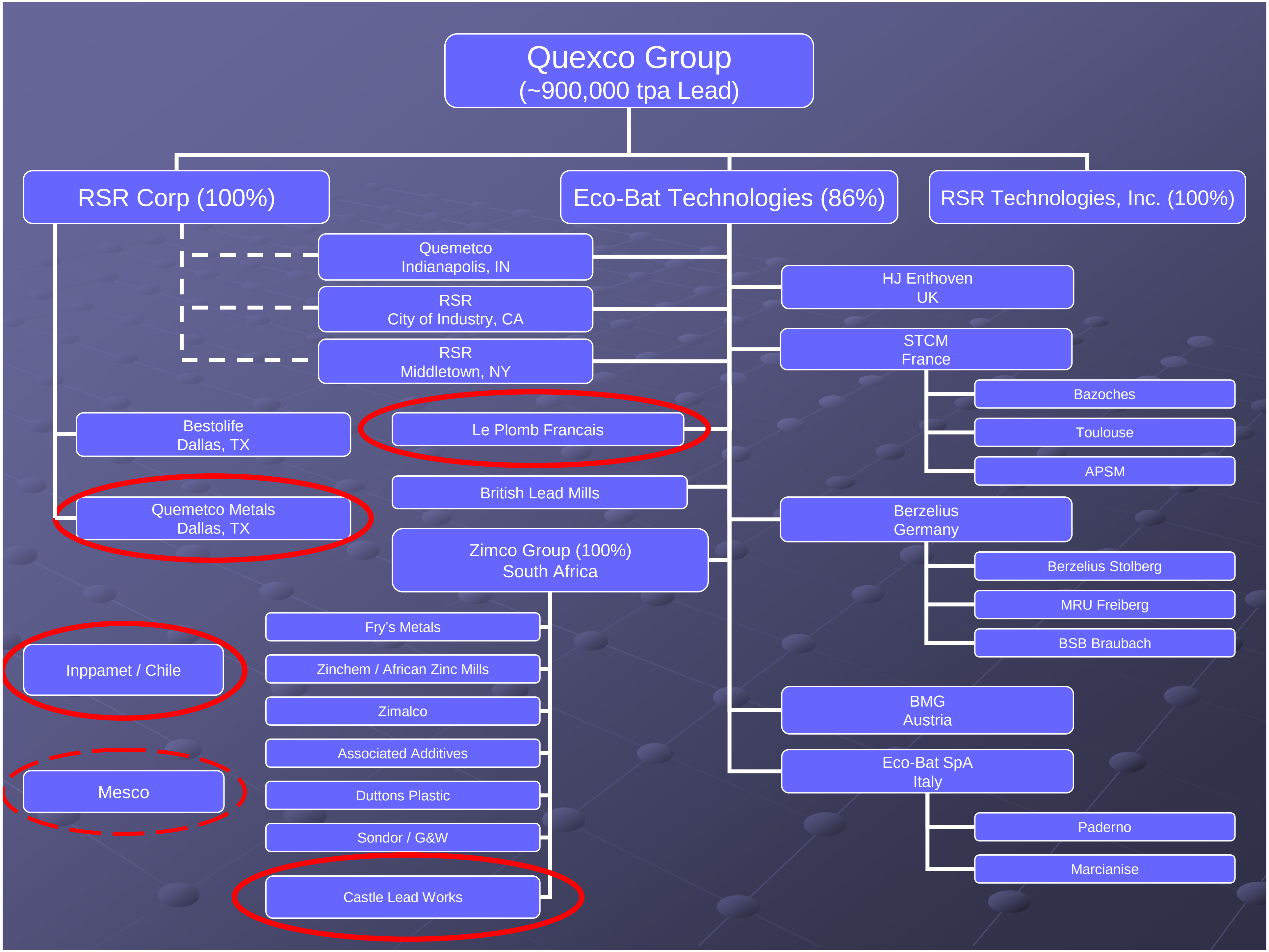
Dr. Andreas Siegmund
Quemetco Metals, Inc.
A subsidiary of RSR Corporation

Toronto, August 25, 2007

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%)
Eco-Bat Technologies (86%)
RSR Technologies, Inc. (100%)
Quemetco
Indianapolis, IN
RSR
City of Industry, CA
RSR
Middletown, NY
HJ Enthoven
UK
STCM
France
Bazoches
Toulouse
APSM
Bestolife
Dallas, TX
Le Plomb Francais
British Lead Mills
Quemetco Metals
Dallas, TX
Berzelius
Germany
Zimco Group (100%)
South Africa
Berzelius Stolberg
MRU Freiberg
BSB Braubach
Fry's Metals
Inppamet / Chile
Zinchem / African Zinc Mills
Zimalco
BMG
Austria
Associated Additives
Mesco
Duttons Plastic
Eco-Bat SpA
Italy
Sondor / G&W
Paderno
Marcianise
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

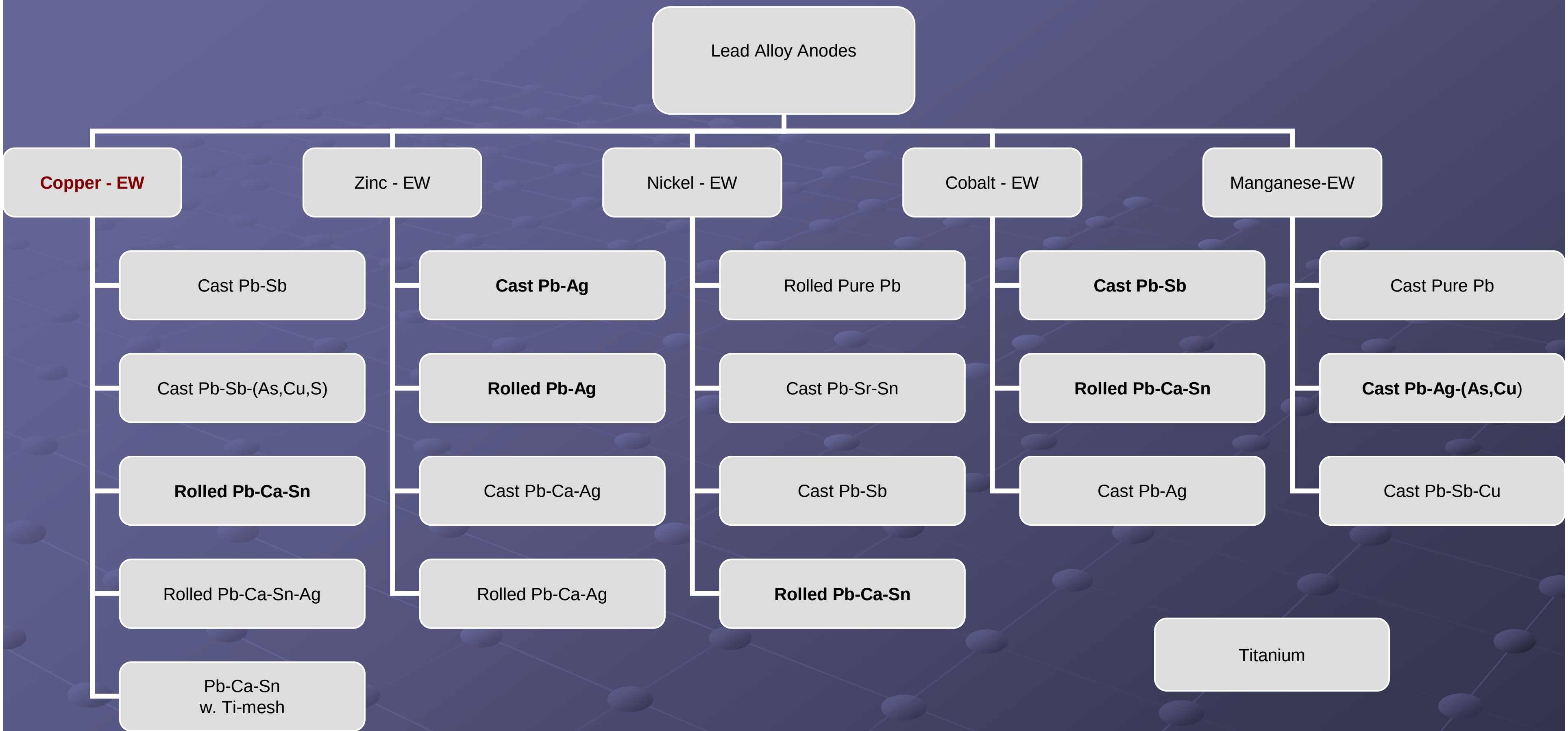
- Cast or rolled lead/silver (0.5-1.0%) anodes are used in zinc electrowinning
- RSR Corp./Quemetco Metals, Castle Lead & Le Plomb Francais supply cast and rolled lead/silver and rolled lead/silver/calcium anodes for zinc electrowinning
- RSR developed rolled lead/calcium (0.07) / silver (0.35%) anode 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

Industrial Anode Materials for Non-ferrous Metals EW



- 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

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

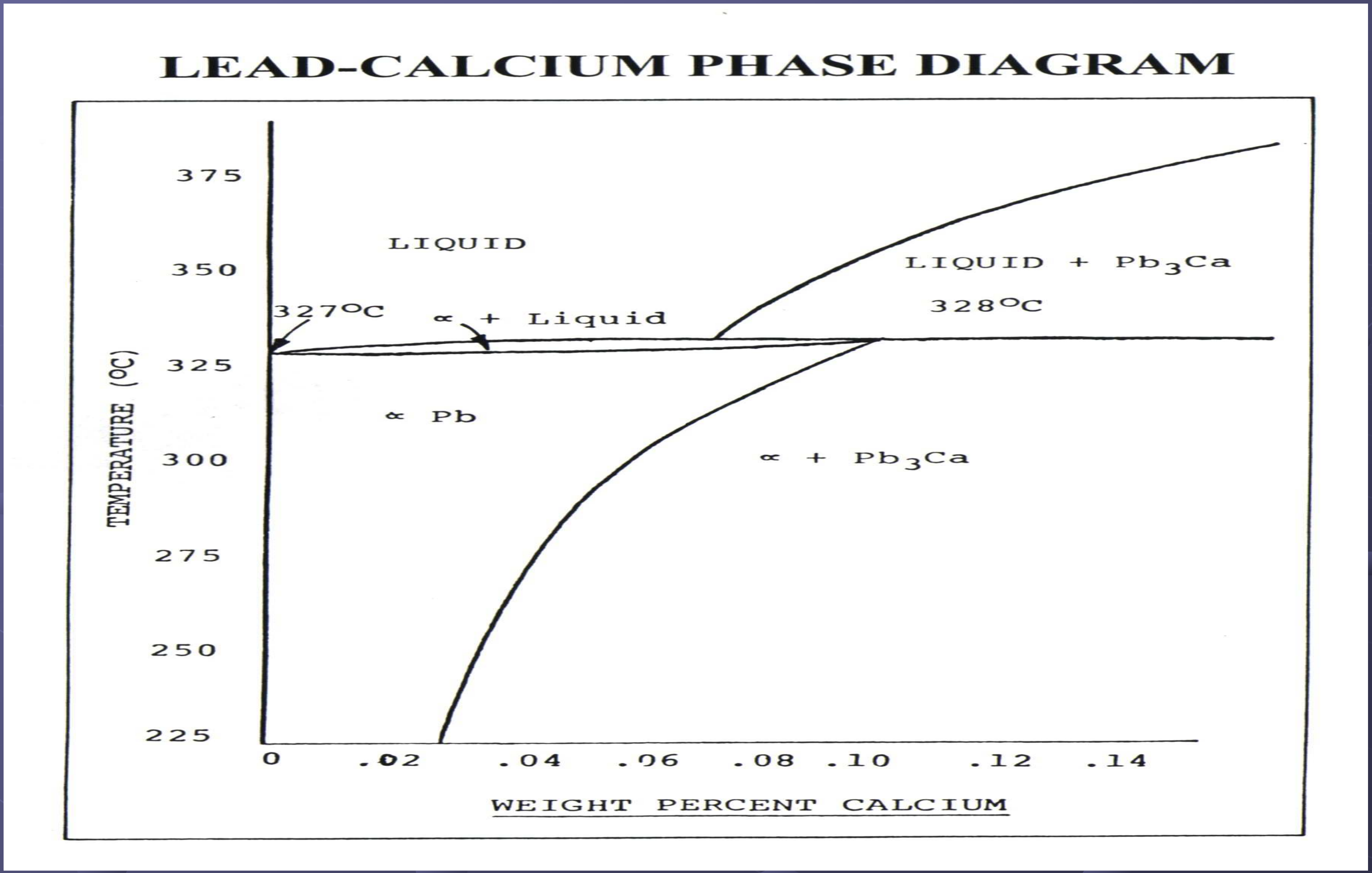
Effect of Silver in Anodes for Electrowinning

- 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

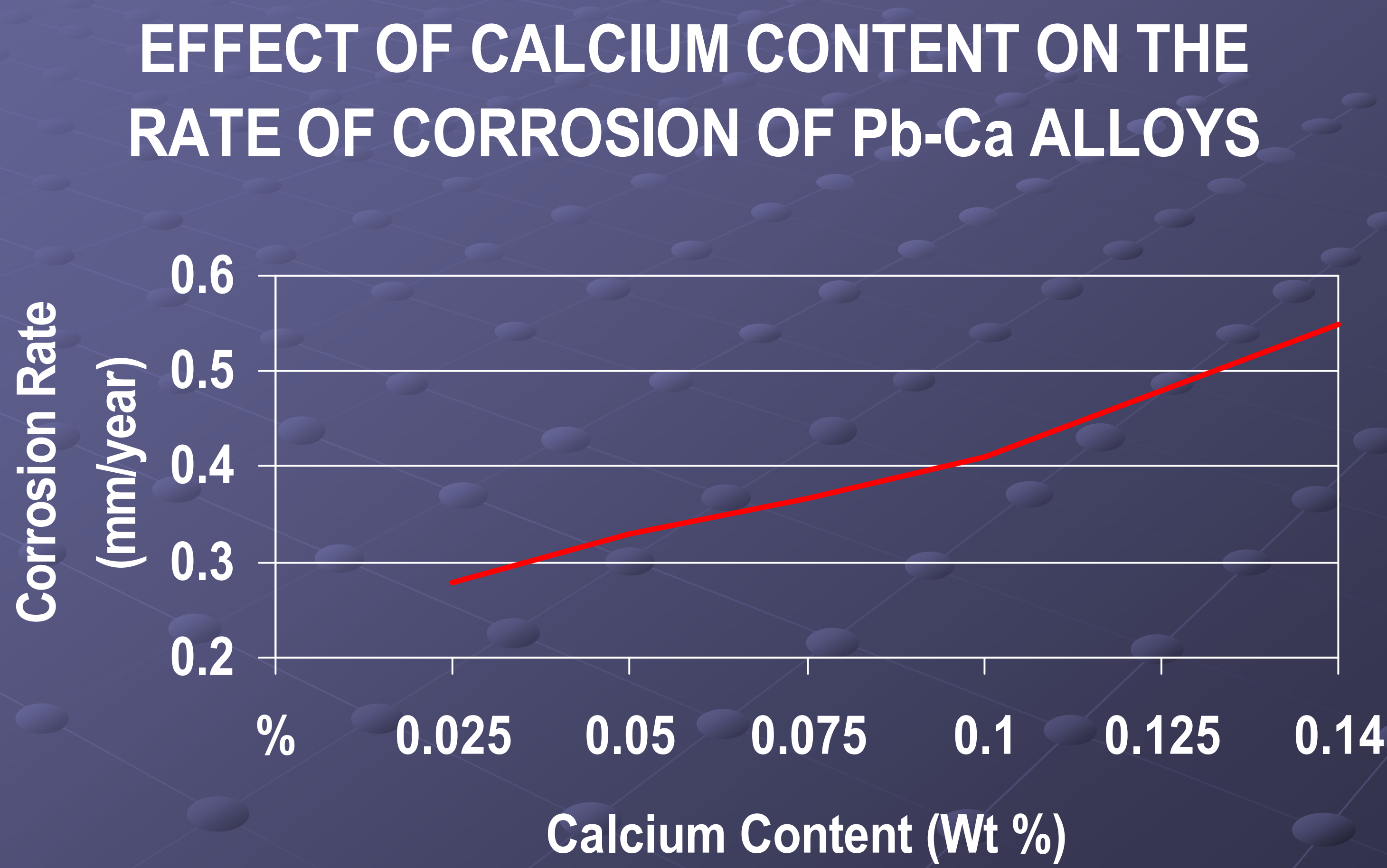
Effect of Calcium in Anodes for Electrowinning

- Increases Rate of Anode Corrosion
  - Particularly above 0.08% Ca because of Pb_3Ca formation
- Increases Mechanical Properties of Anode
- Decreases the Anode Potential

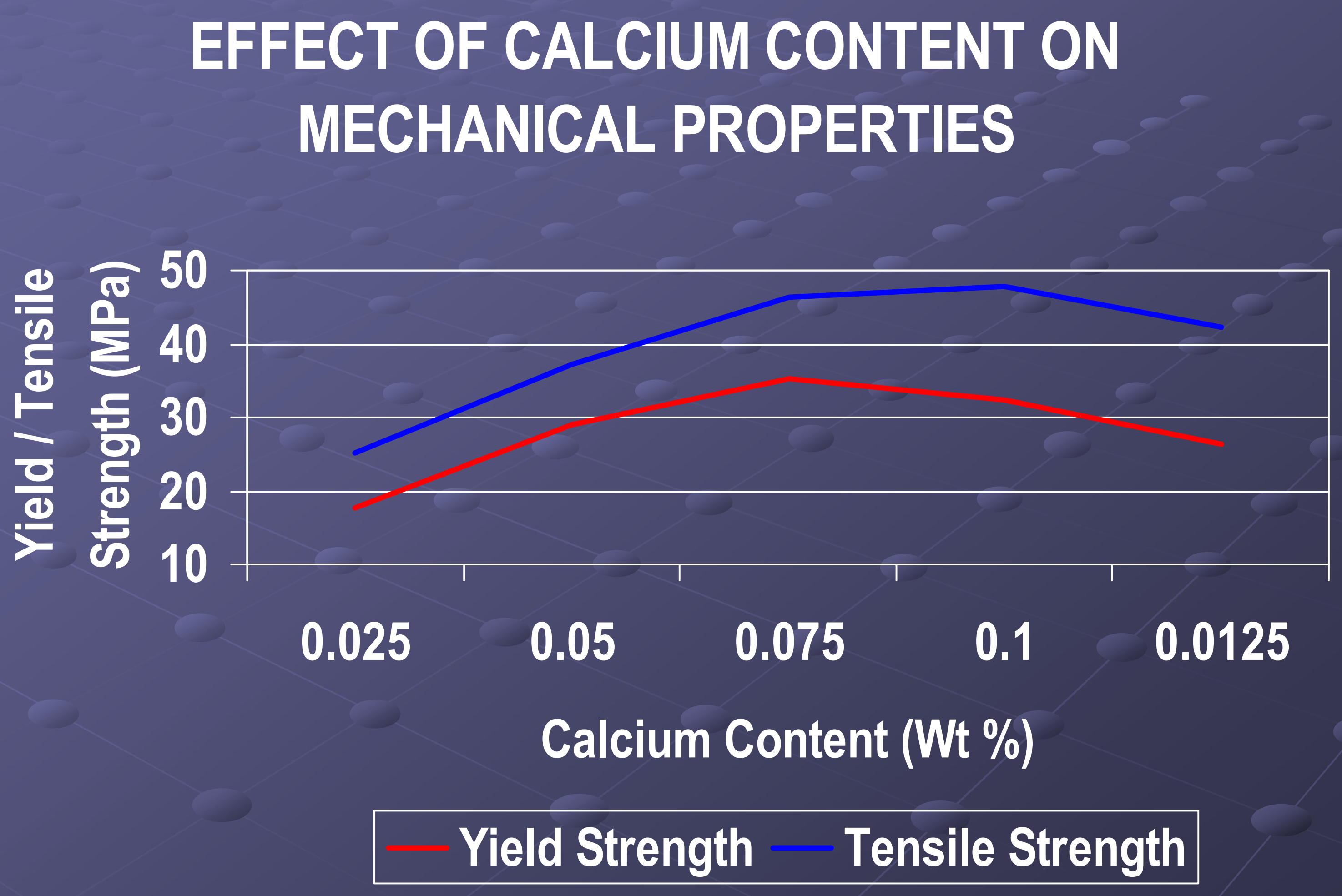
Properties of Pb-Ca-Sn Anodes



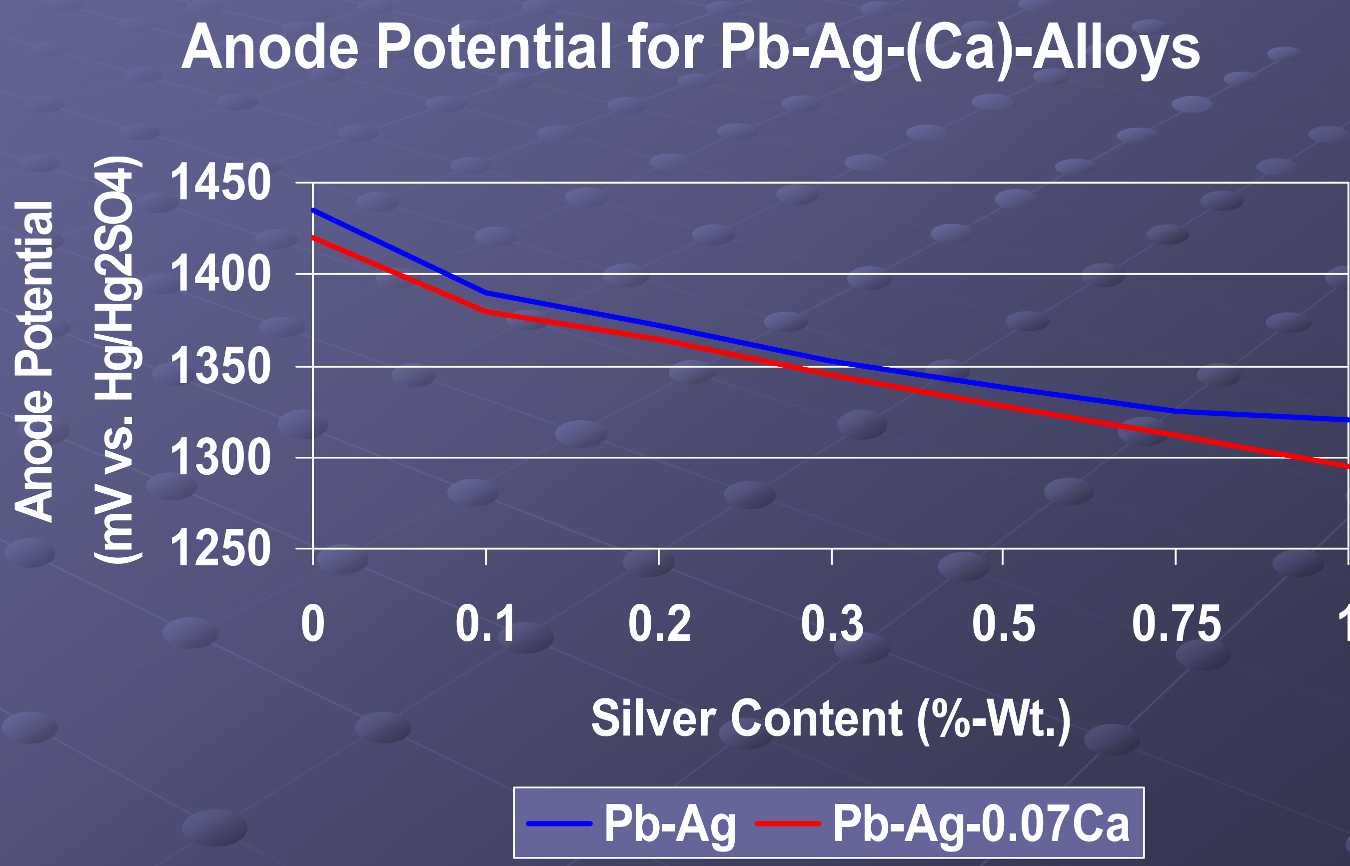
Mechanical Properties of Pb-Ca-Sn Anodes



Mechanical Properties of Pb-Ca-Sn Anodes



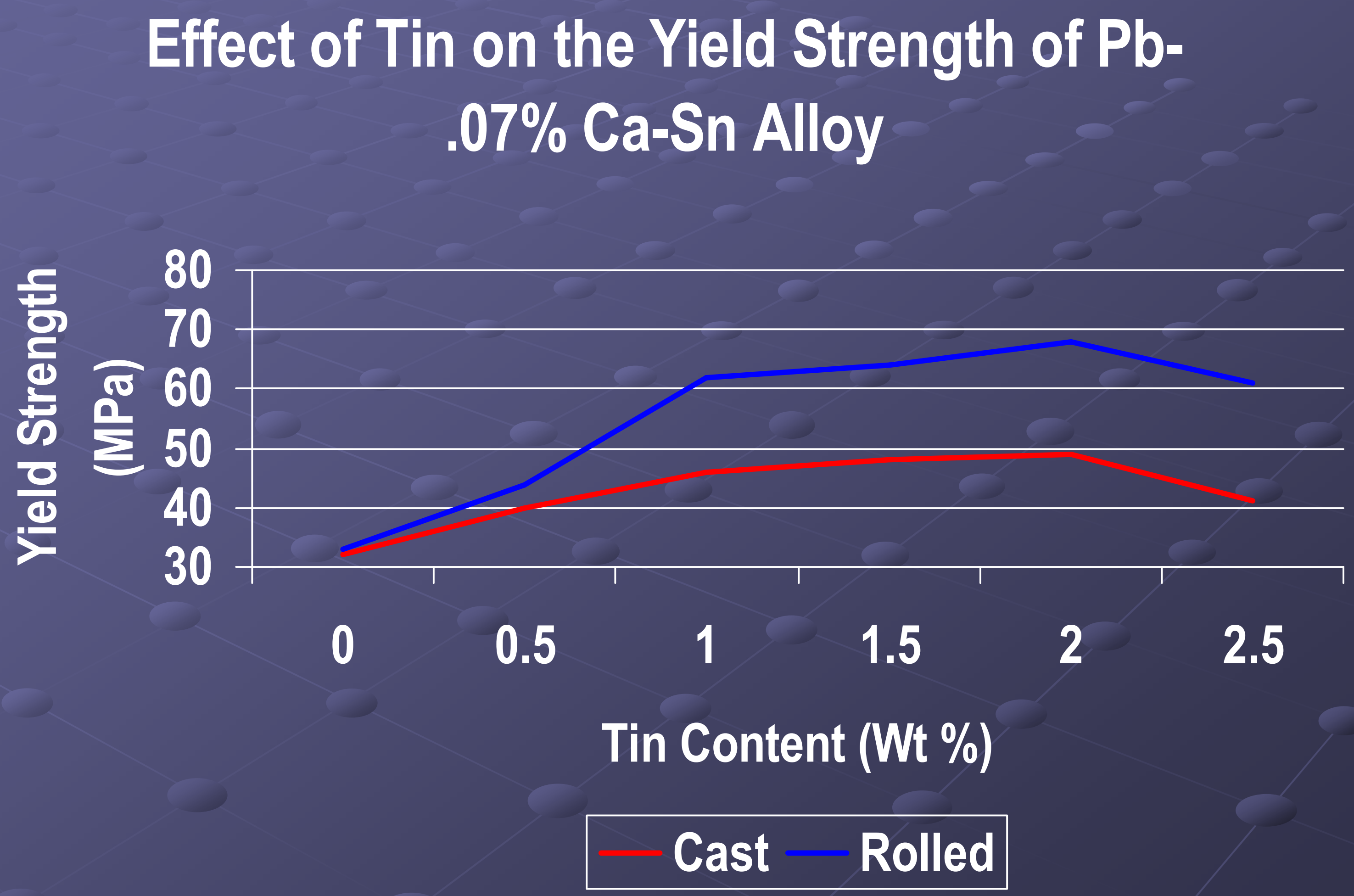
Mechanical Properties of Pb-Ca-Sn Anodes



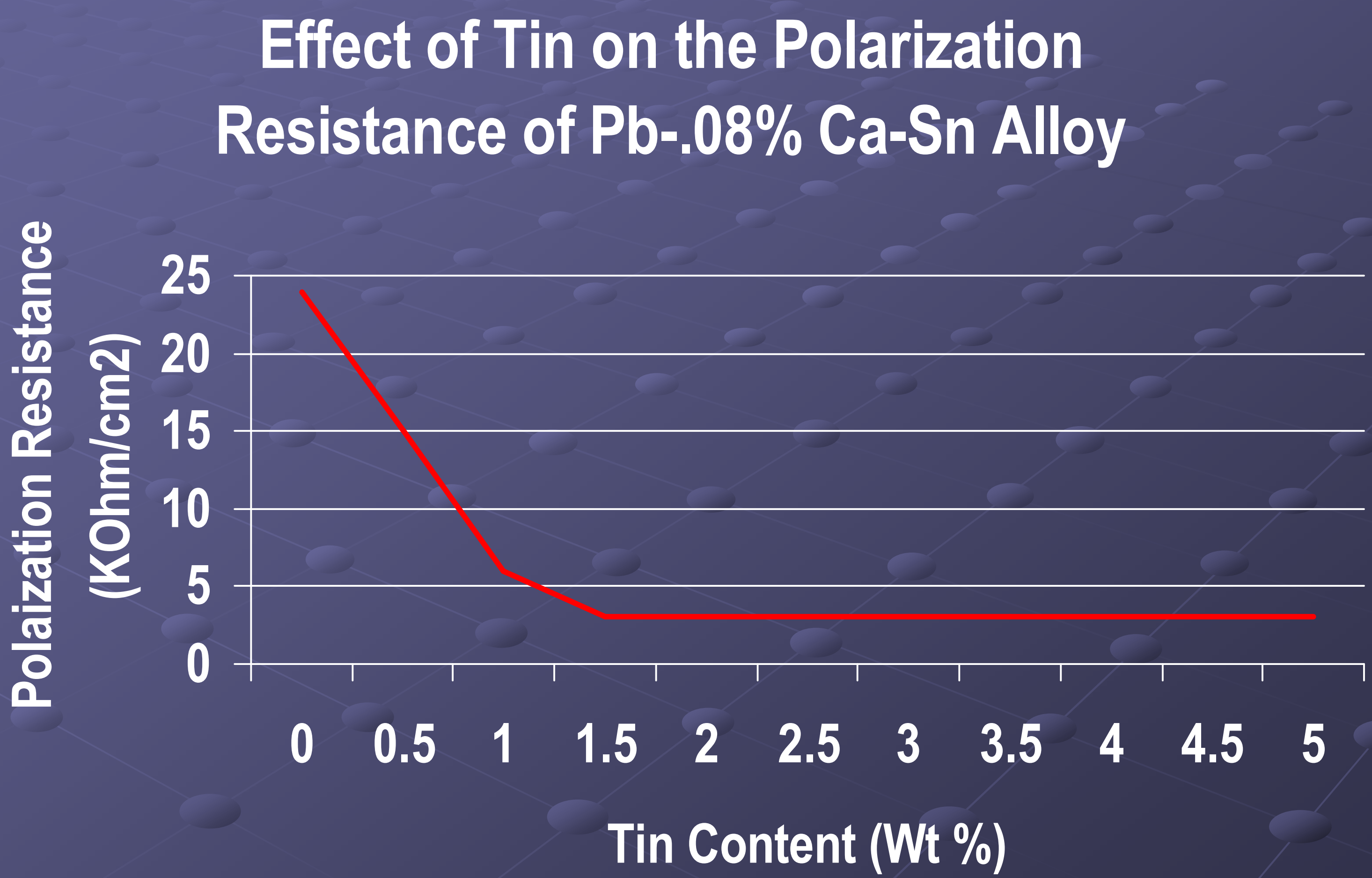
Effect of Tin in Anodes for Electrowinning

- Imparts Strength to the Lead Alloy and Reduces Creep
- Reduces Corrosion by Segregation into Interdentritic 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

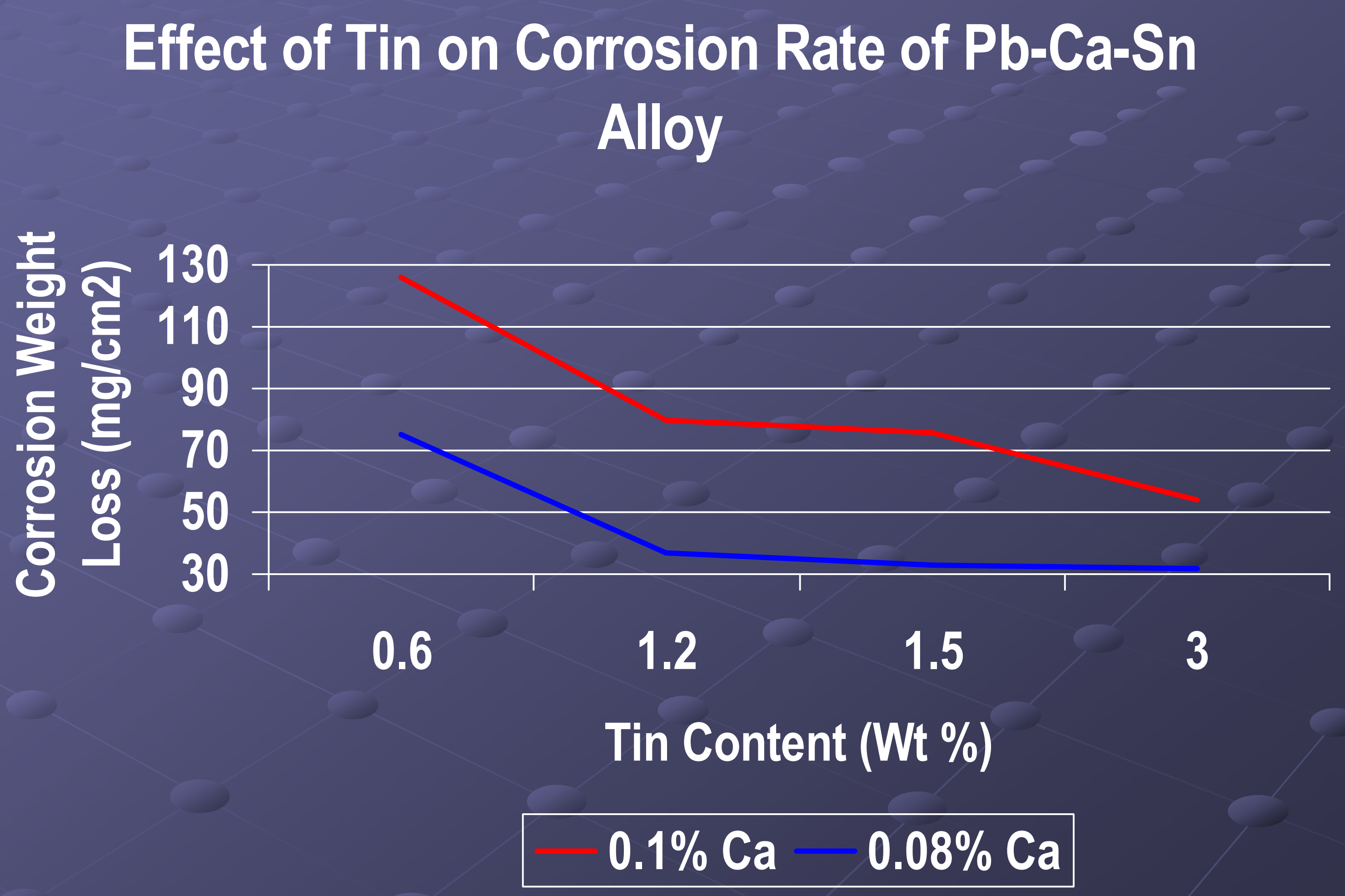
Mechanical Properties of Pb-Ca-Sn Anodes



Mechanical Properties of Pb-Ca-Sn Anodes



Mechanical Properties of Pb-Ca-Sn Anodes



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 Interdentritic and Grain Boundaries

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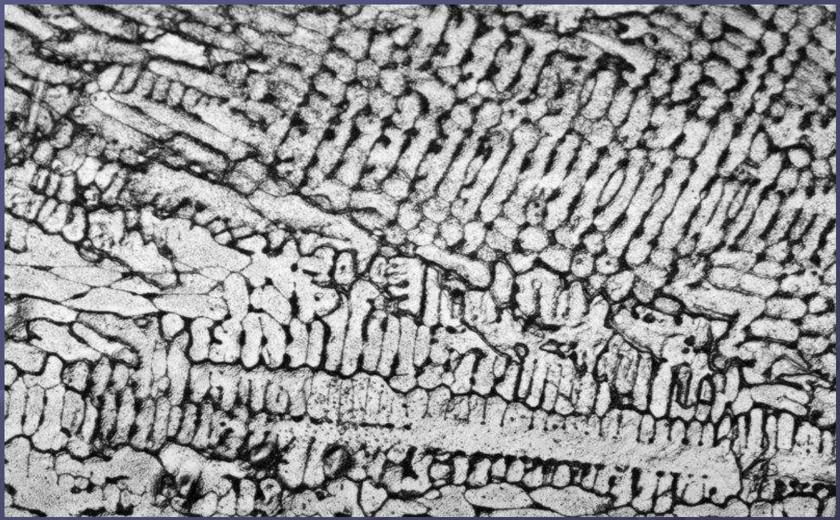
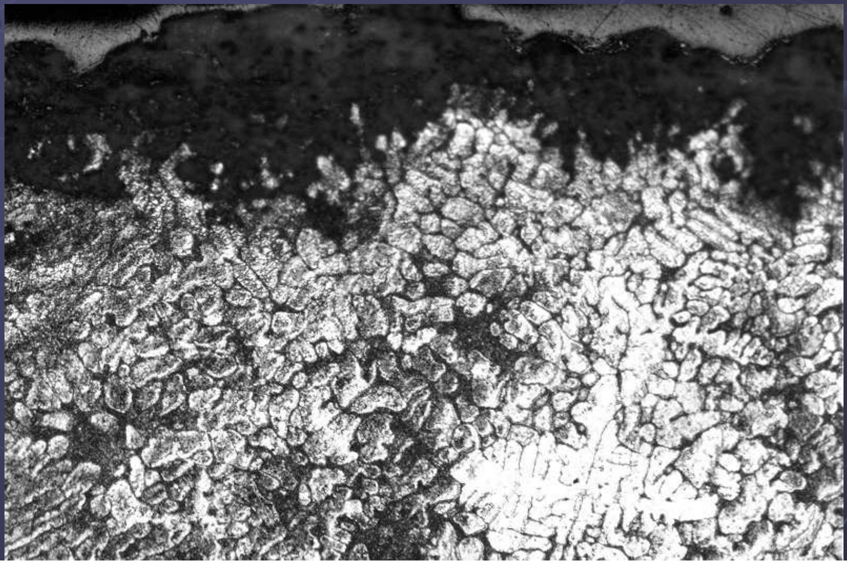
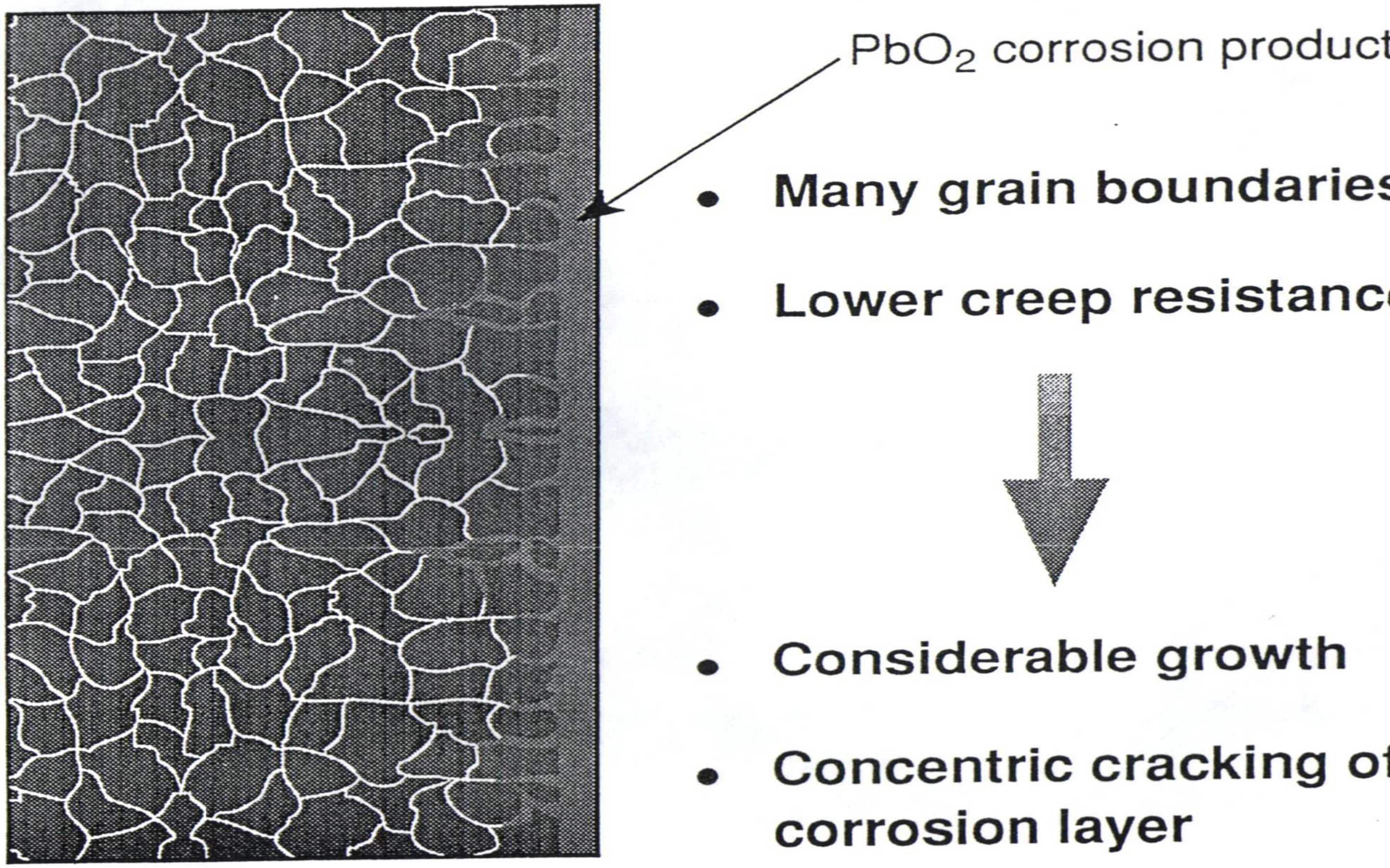
- Casting Defects
- Porosity
- Considerable creep
- Concentric cracking of corrosion layer





Cast Anodes

Fine-grained, cast Pb-Ca



- **Many grain boundaries**
- **Lower creep resistance**

↓

- **Considerable growth**
- **Concentric cracking of corrosion layer**

Anode Density and Porosity Top Cast

2.6	2.0
2.0	0.9
1.7	1.2
3.1	1.4
2.2	1.8
1.6	2.9

Cajamarquilla Anodes

Anode 1

0.5	0.5
1.1	0.8
1.1	1.1
1.5	1.3
1.9	1.5

Anode 2

0.7	0.8
0.9	0.8
1.2	1.3
1.4	1.9
1.8	1.7

Cominco Trail
ρ_{ave} = 11.11 g/cm^3
Ø 2.0 ± 0.7%

Cajamarquilla
ρ_{ave} = 11.19 g/cm^3
Ø 1.2 ± 0.4%

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

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

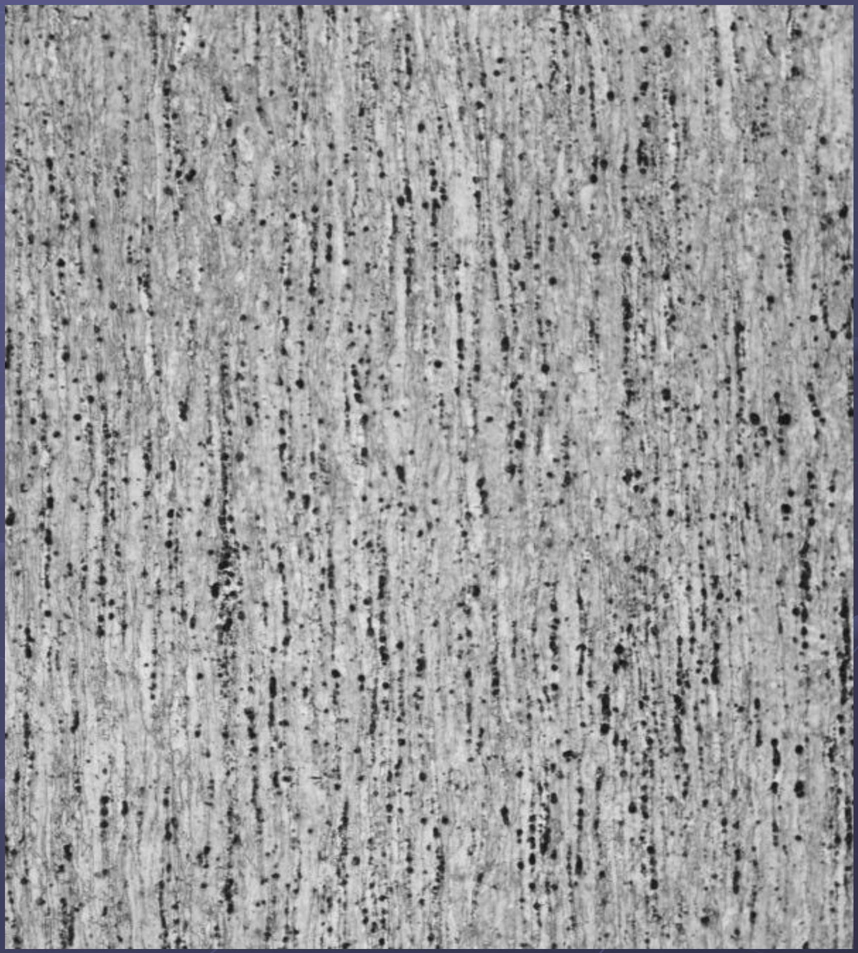
Castle Lead Works

ρ_{ave} = 11.30 g/cm^3
Ø 0.3 ± 0.2%

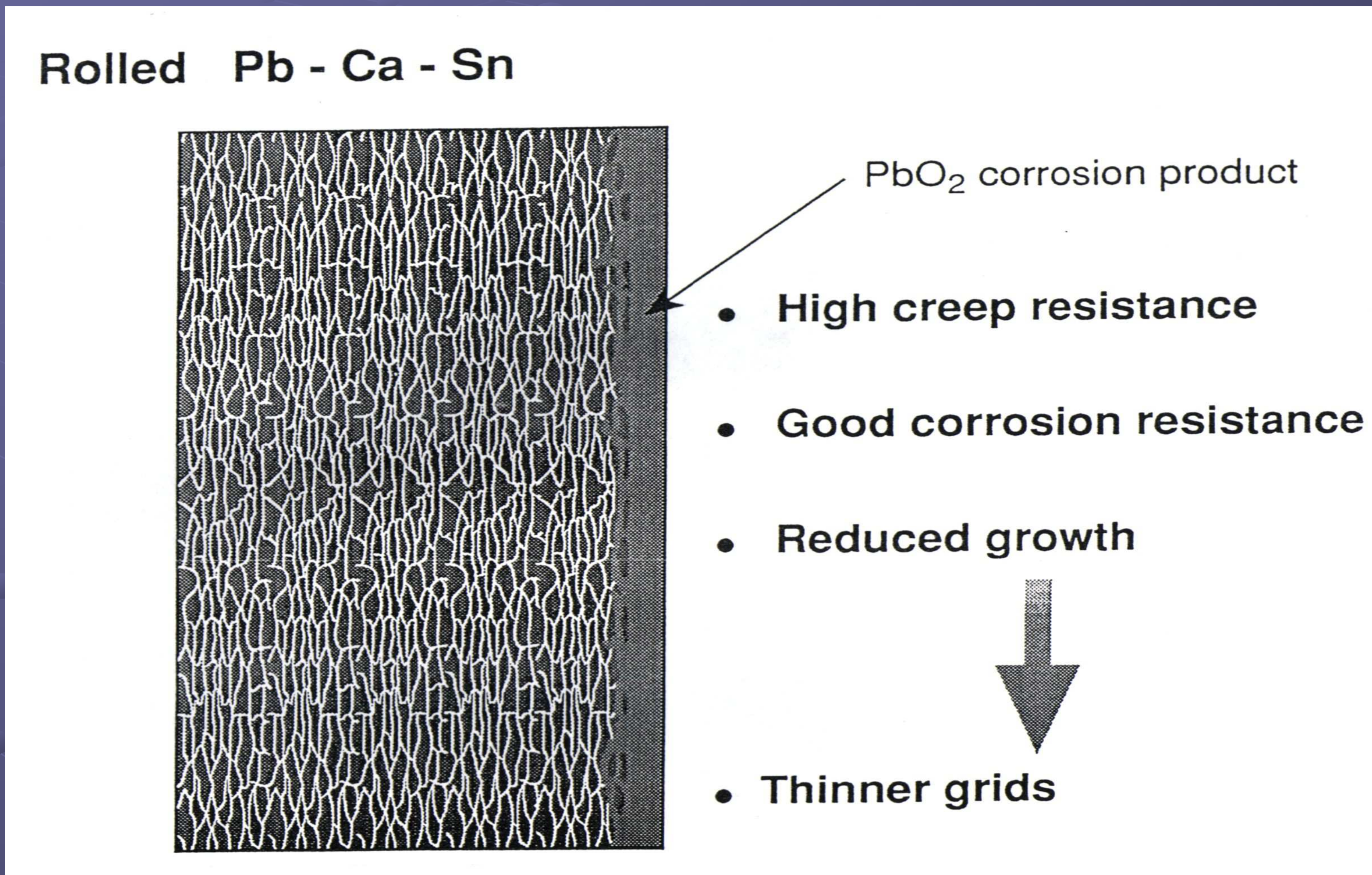
ρ_{ave} = 11.28 g/cm^3
Ø 0.4 ± 0.2%

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

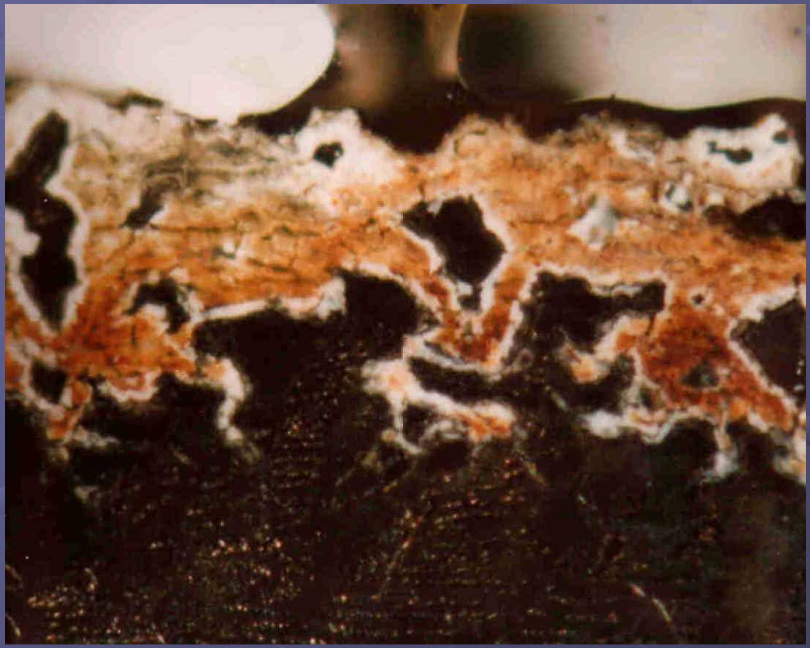


Rolled Pb-Ca-Sn Anodes

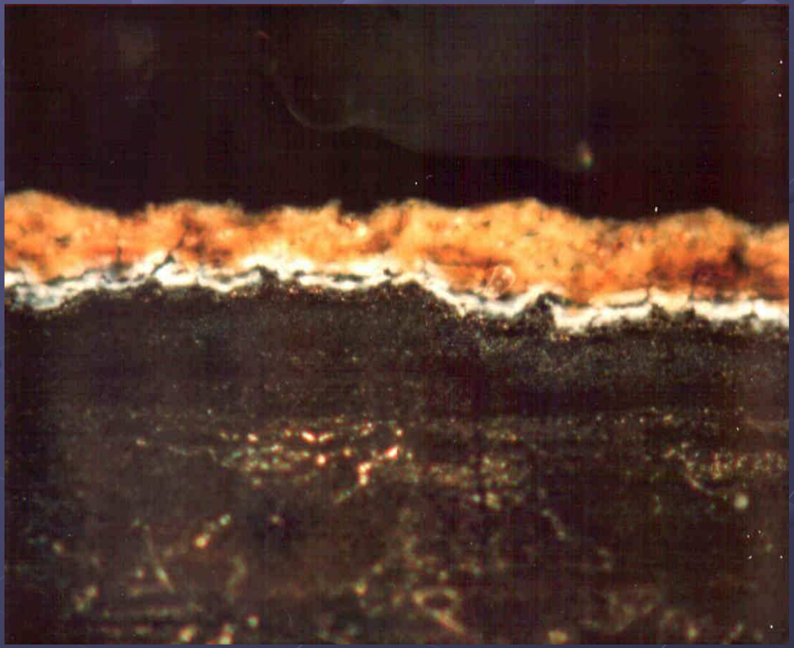


Anode Corrosion Products

Cast Anode



Rolled Anode

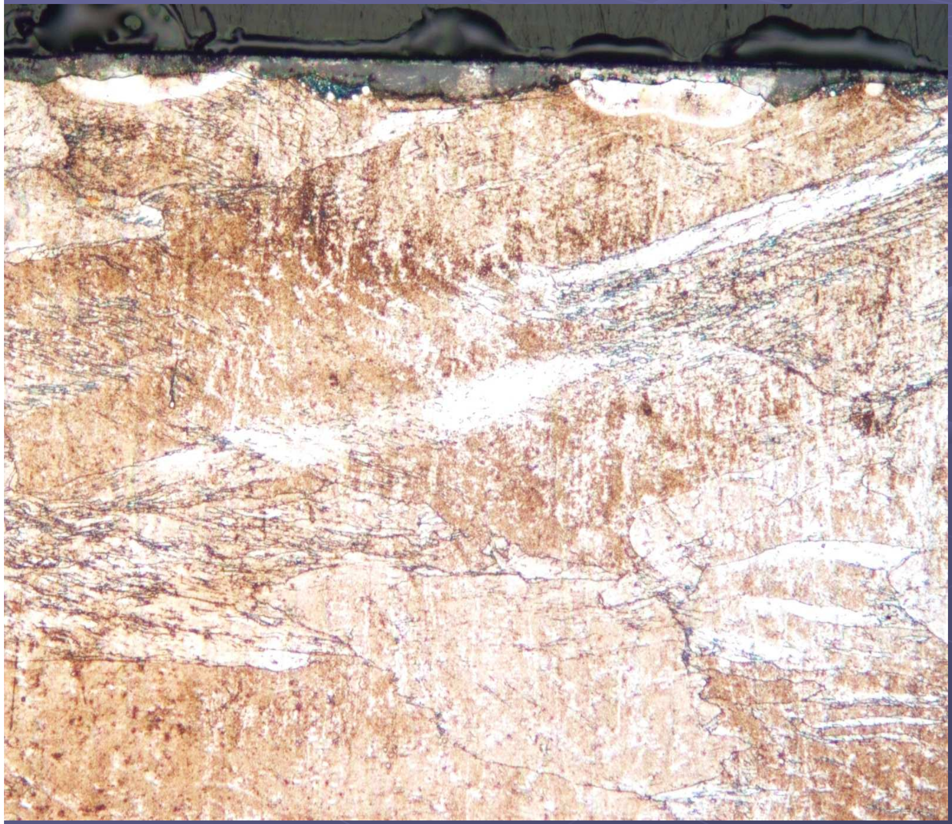


Differences in Anode Rolling

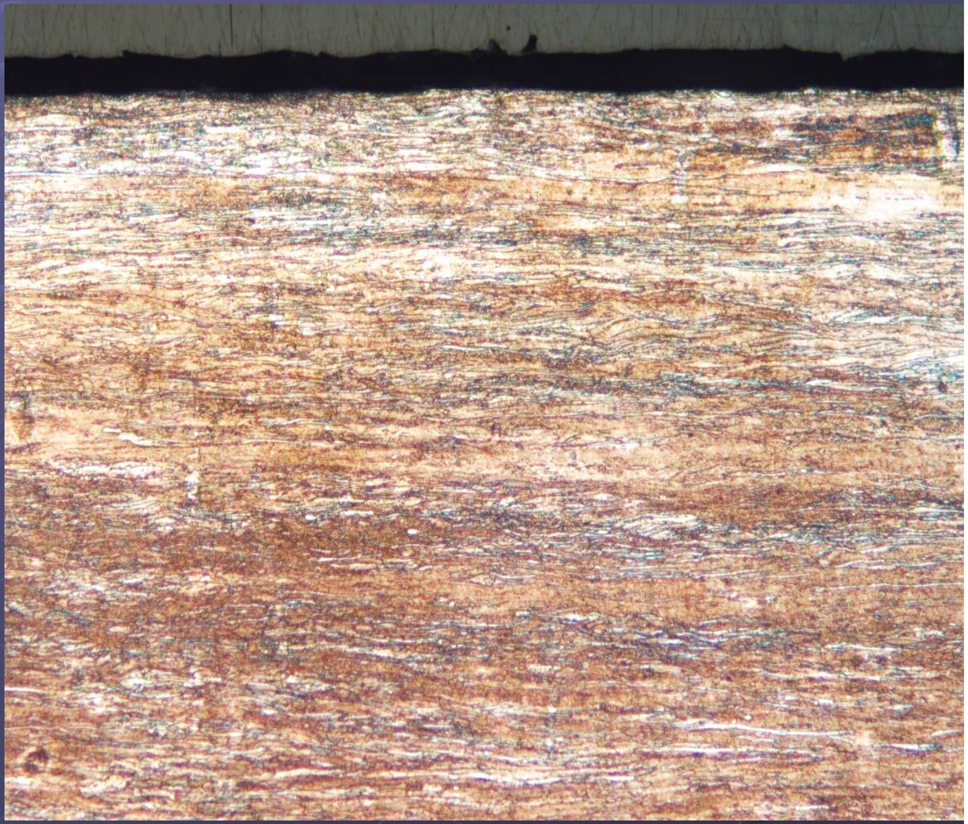
Anode Rolling

- At ratio 2:1 start to deform but still spherical grain structure
- At ratio 4:1 fully bent; Larger 4:1 stretched
- Optimum Mechnical Properites @ 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



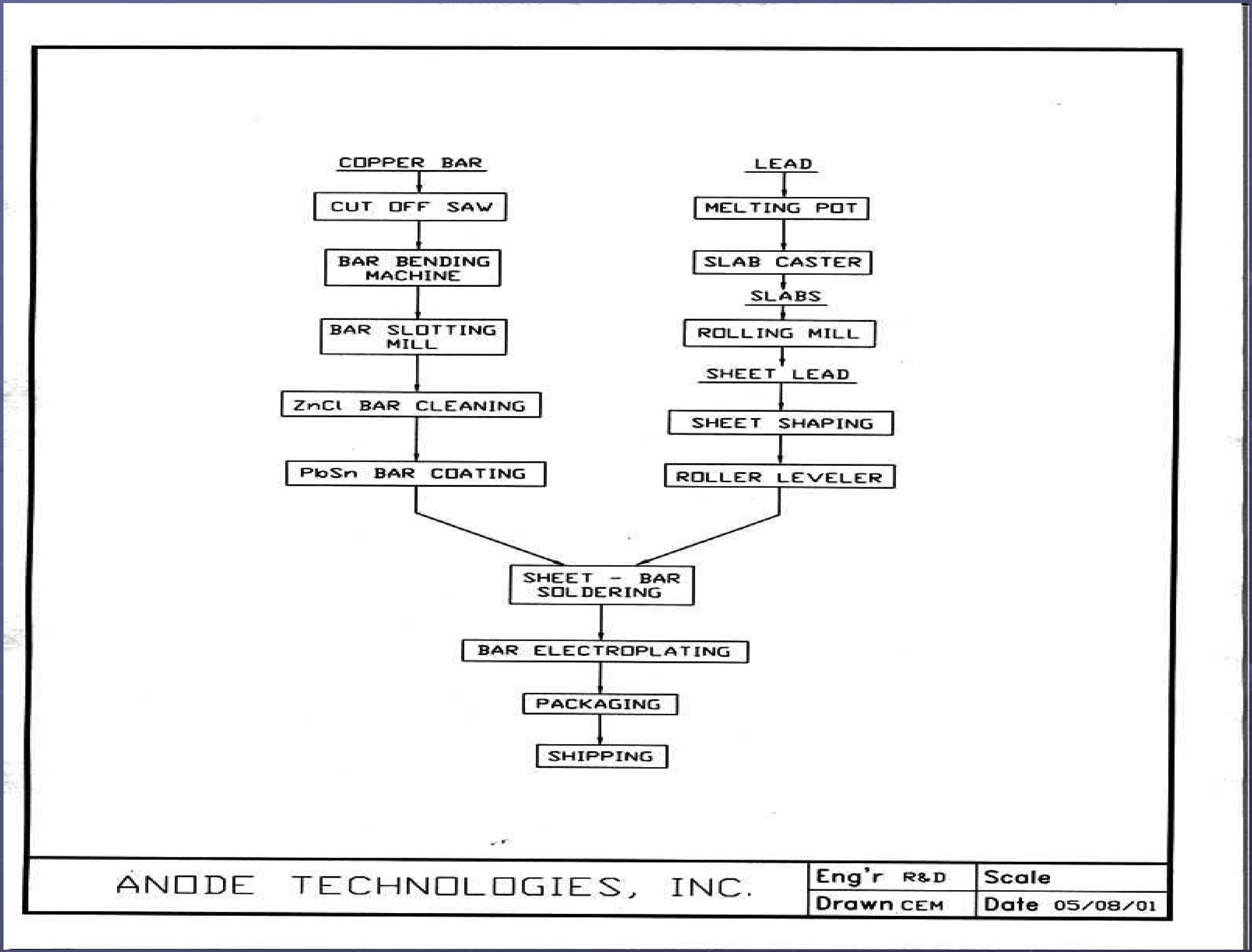
Deformation Ratio 15 : 1

Mechanical Properties of Typical Pb-alloys for Electrowinning

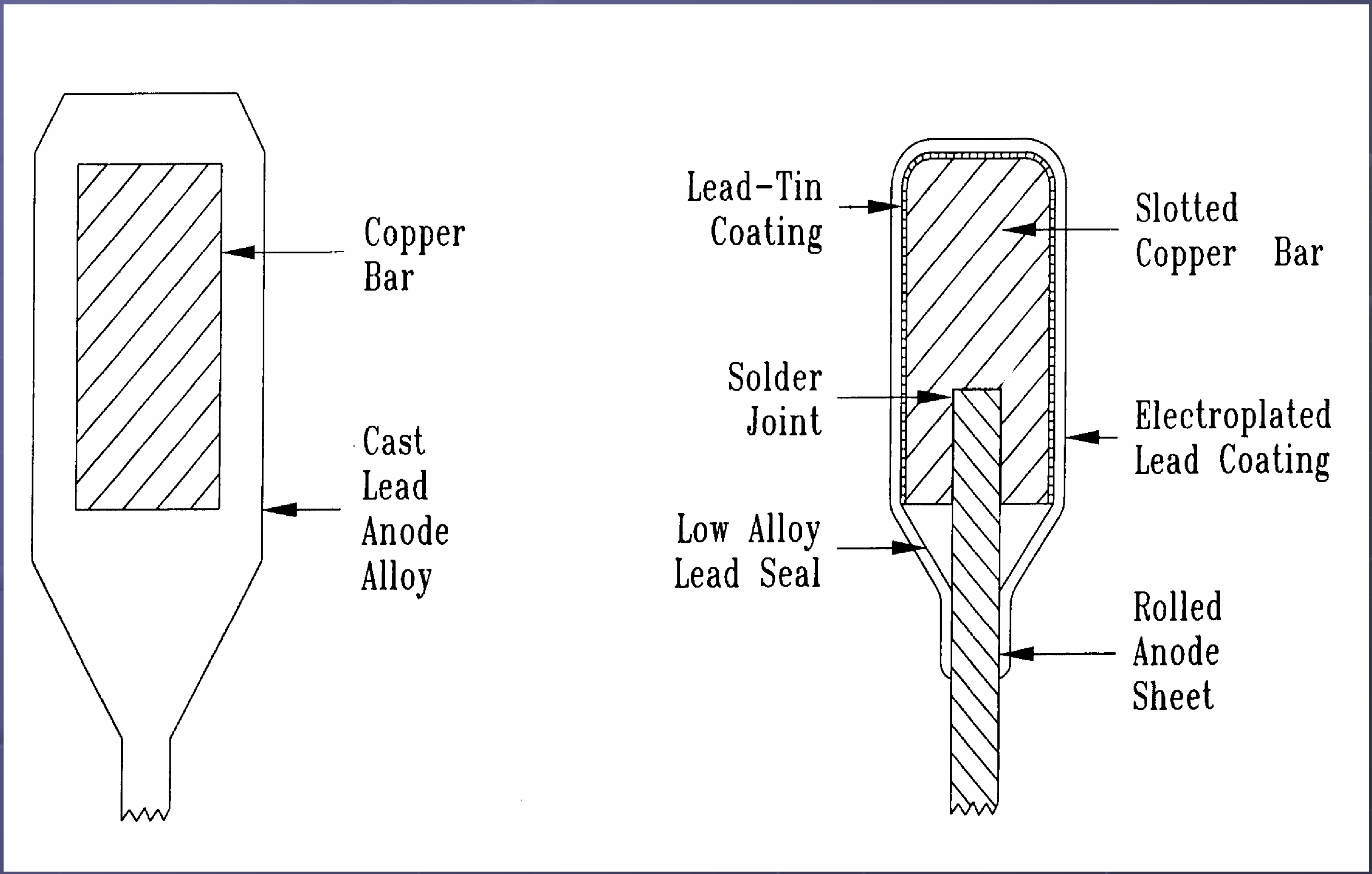
Alloy	UTS (MPa)	0.2% YS (MPa)	Elongation (%)	Hardness (RR30)
Pb-(3%)Sb Cast	65.5	55.2	10	85
Pb-(3%)Sb Rolled	24.6	16.3	40	64
Pb-(6%)Sb Cast	73.8	71.0	8	87
Pb-(6%)Sb Rolled	30.6	19.5	35	65
Pb-(0.07%)Ca-(1.35%) Sn Cast	46.4	35.3	29	71
Pb-(0.07%)Ca-(1.35%) Sn Rolled	**71.0**	**65.3**	**14**	**85**
Pb-(0.07%)Ca-(1.35%)Sn-(0.05%)Ag 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

Anode Assembling

Process Block Diagram Anode Manufacturing

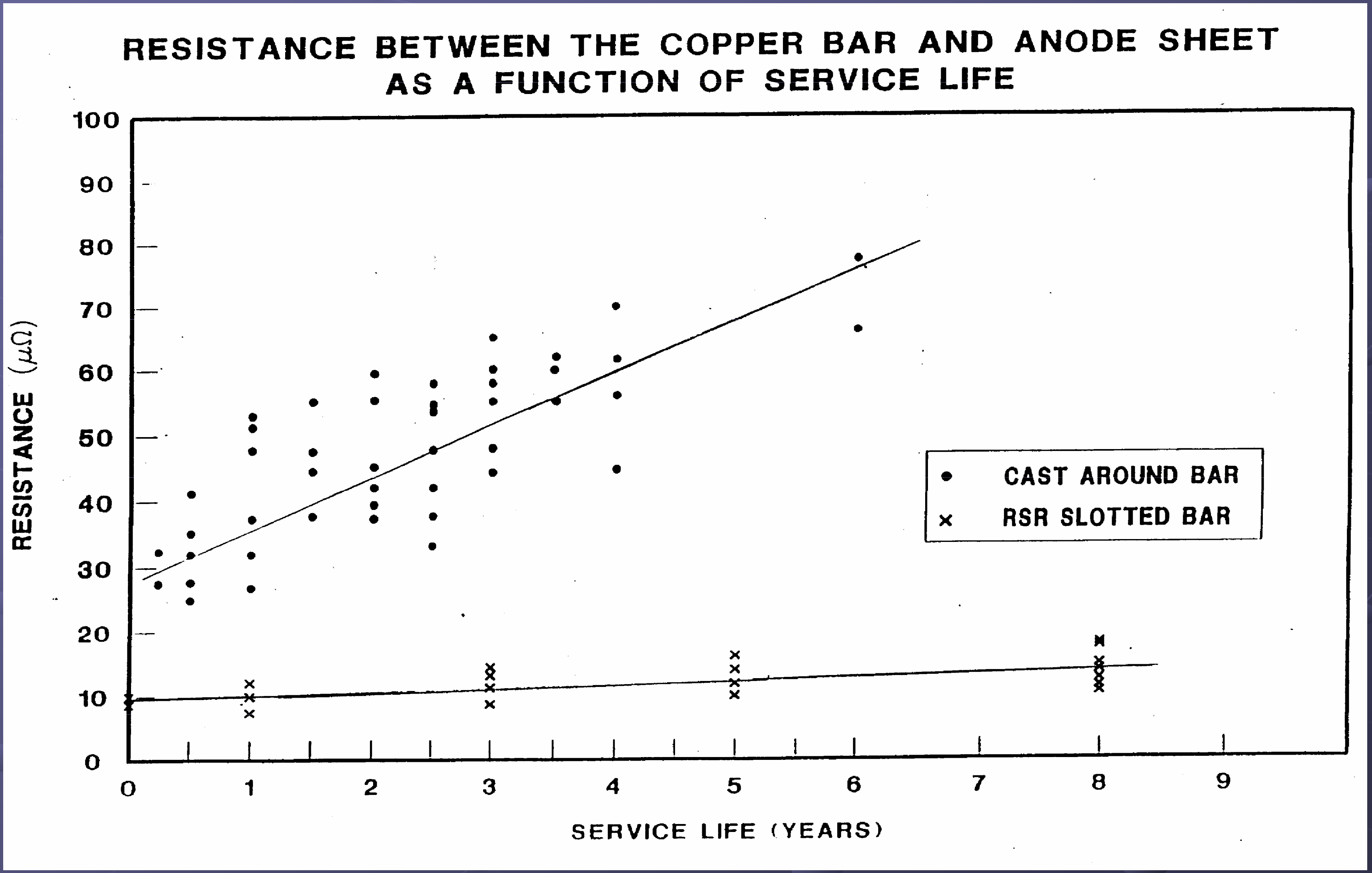


Advances in Anode Sheet Assembling



Assembling Sheet / Busbar

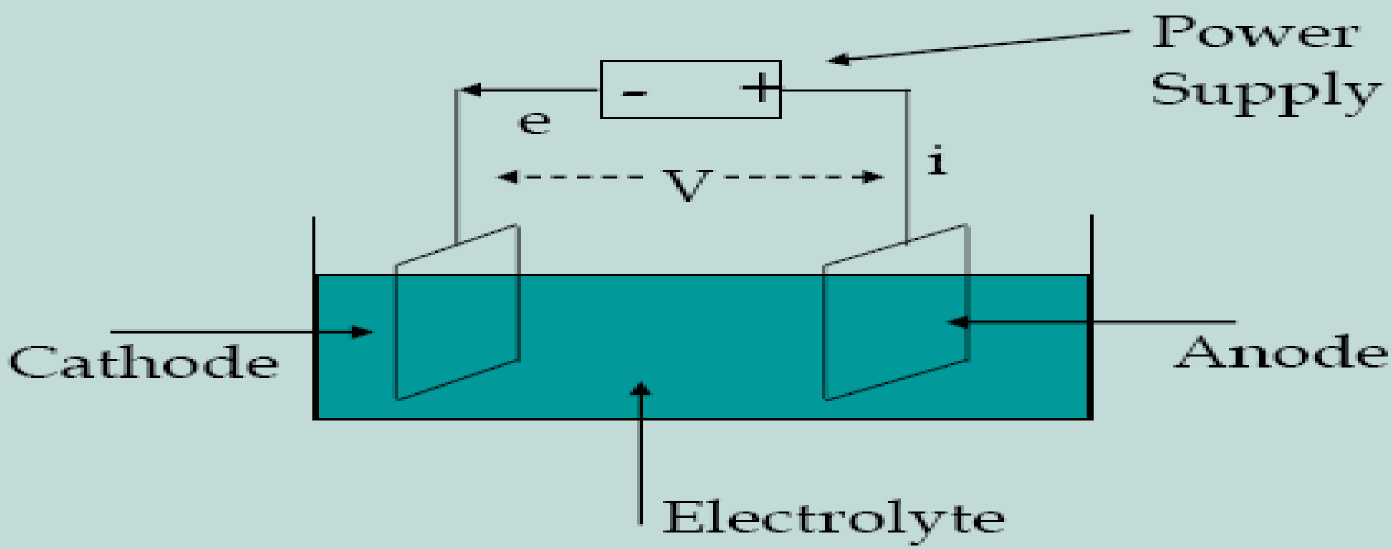
Advances in Anode Sheet Assembling



Advances in Anode Sheet Assembling

EFFECTS OF ANODIC OXYGEN EVOLUTION IN COPPER ELECTROWINNING

Electrolytic Cell



- Reduction occurs at the cathode

e.g. $Cu^{2+}(aq) + 2e = Cu(s)$

$H^{+}(aq) + e = 1/2H_2(g)$

- Oxidation occurs at the anode

e.g. $Cu(s) = Cu^{2+}(aq) + 2e$

$2H_2O = O_2(g) + 4H^{+} + 4e$

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

- **Oxidation of Manganese**
  - ☹ 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

$$O_2 + 2RH \rightarrow 2\,R^+ + H_2O$$

$$R^+ + PbO_2 \rightarrow PbO + R{=}O$$

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$$

  - ☹ 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

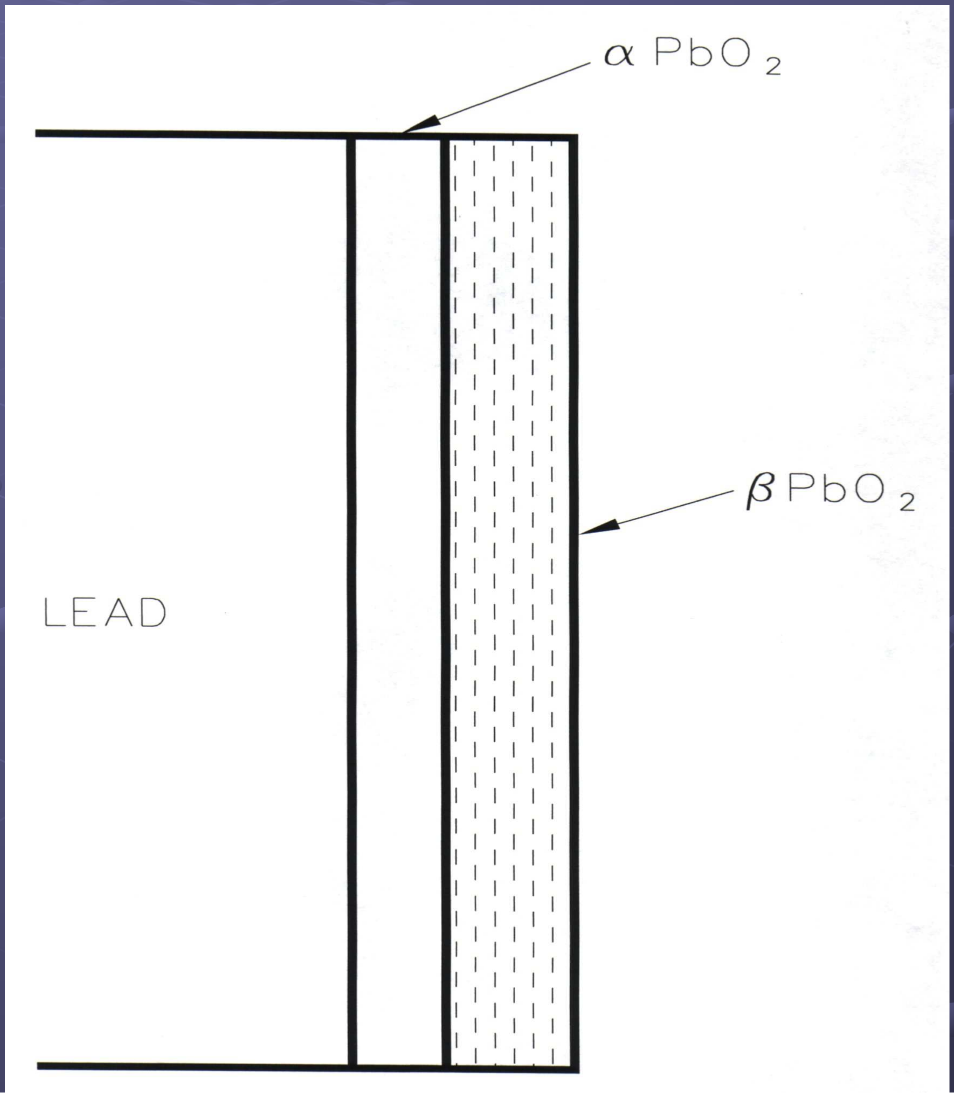
- **Major Consequence is Corrosion of Lead Anode on the Anode Surface**
  - ☺ **αPbO_2 (rhombic, large closely packed crystals, dense, hard, brownish color, formation at higher pH, temperature, pressure = metastable)**
  - 😐 **ßPbO$_2$ (tetragonal, fine needle-shaped crystals, black color, formation 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 ßPbO$_2$**
  - **Oxygen diffusion through ßPbO$_2$ and formation of αPbO_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

Anode Corrosion

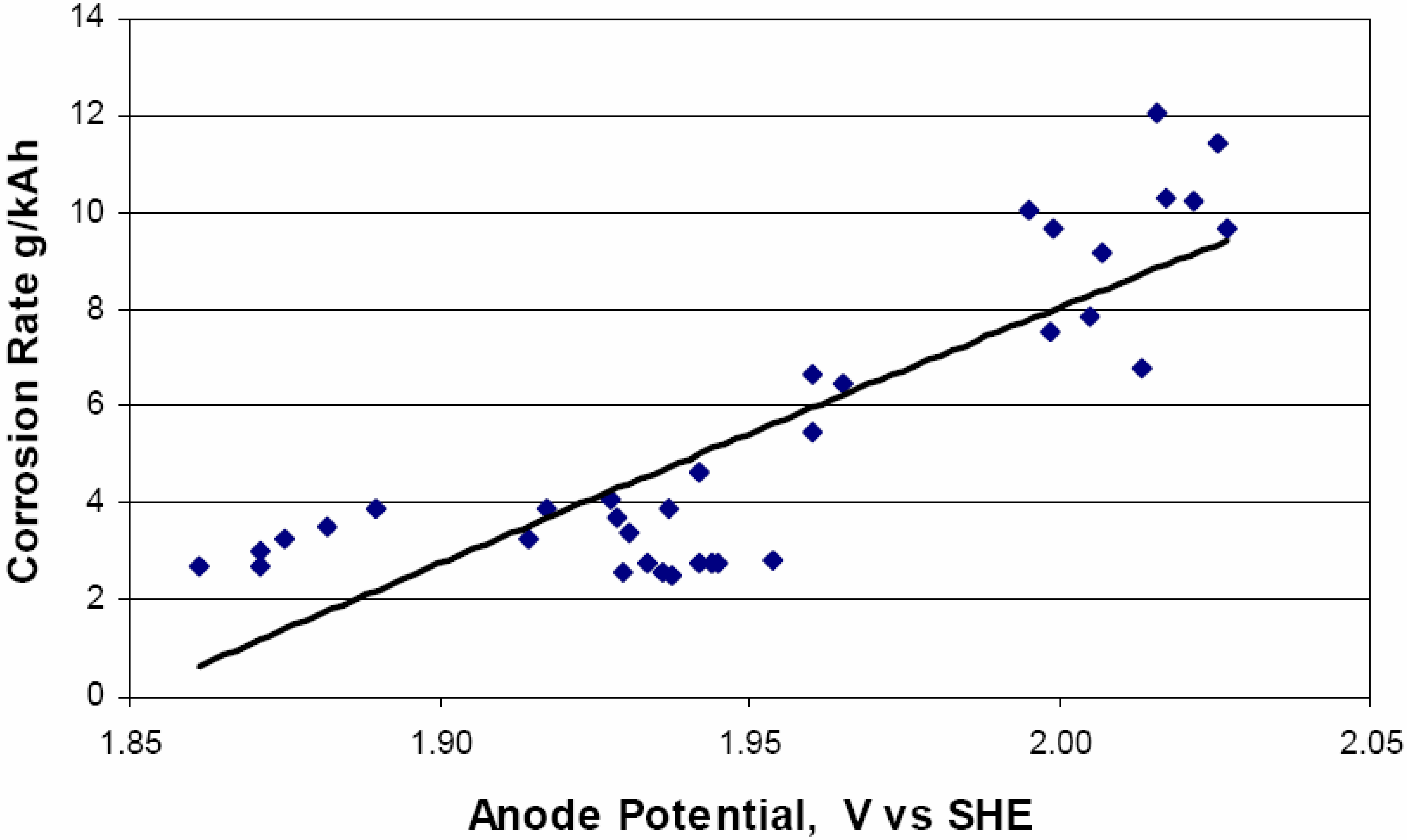


Figure 2: Effect of anode potential on corrosion rate

Anode Corrosion

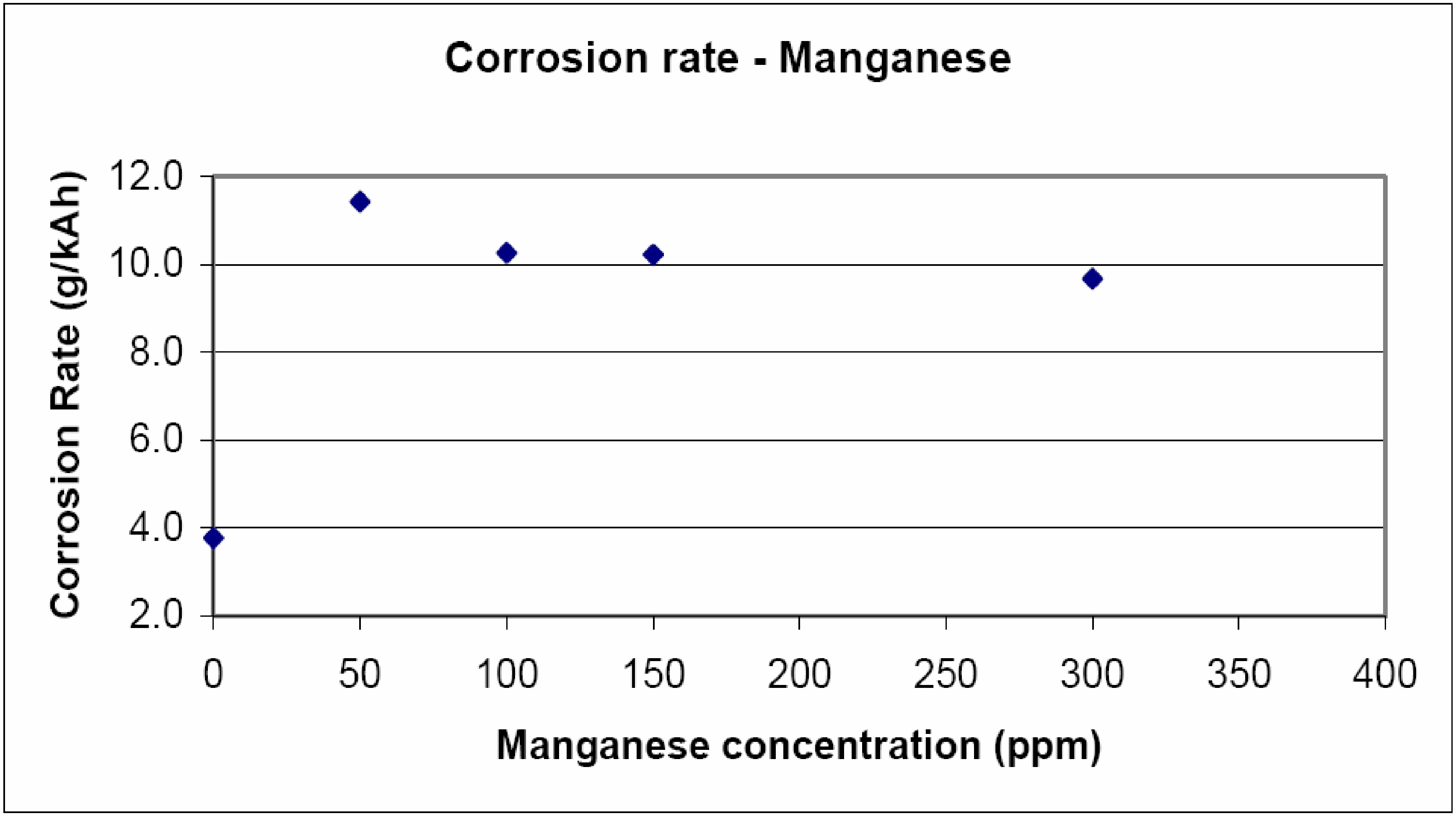


Figure 3: Effect of manganese on anode corrosion rate

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

$$Mn^{3+} + Fe^{2+} = Fe^{3+} + Mn^{2+}$$

$$MnO_2 + 2Fe^{2+} + 4H^+ = Mn^{2+} + 2Fe^{3+} + 2H_2O$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ = Mn^{2+} + 5Fe^{3+} + 4H_2O$$

- ☺ Mn:Fe ratio of 1:10 apparently required

Anode Corrosion

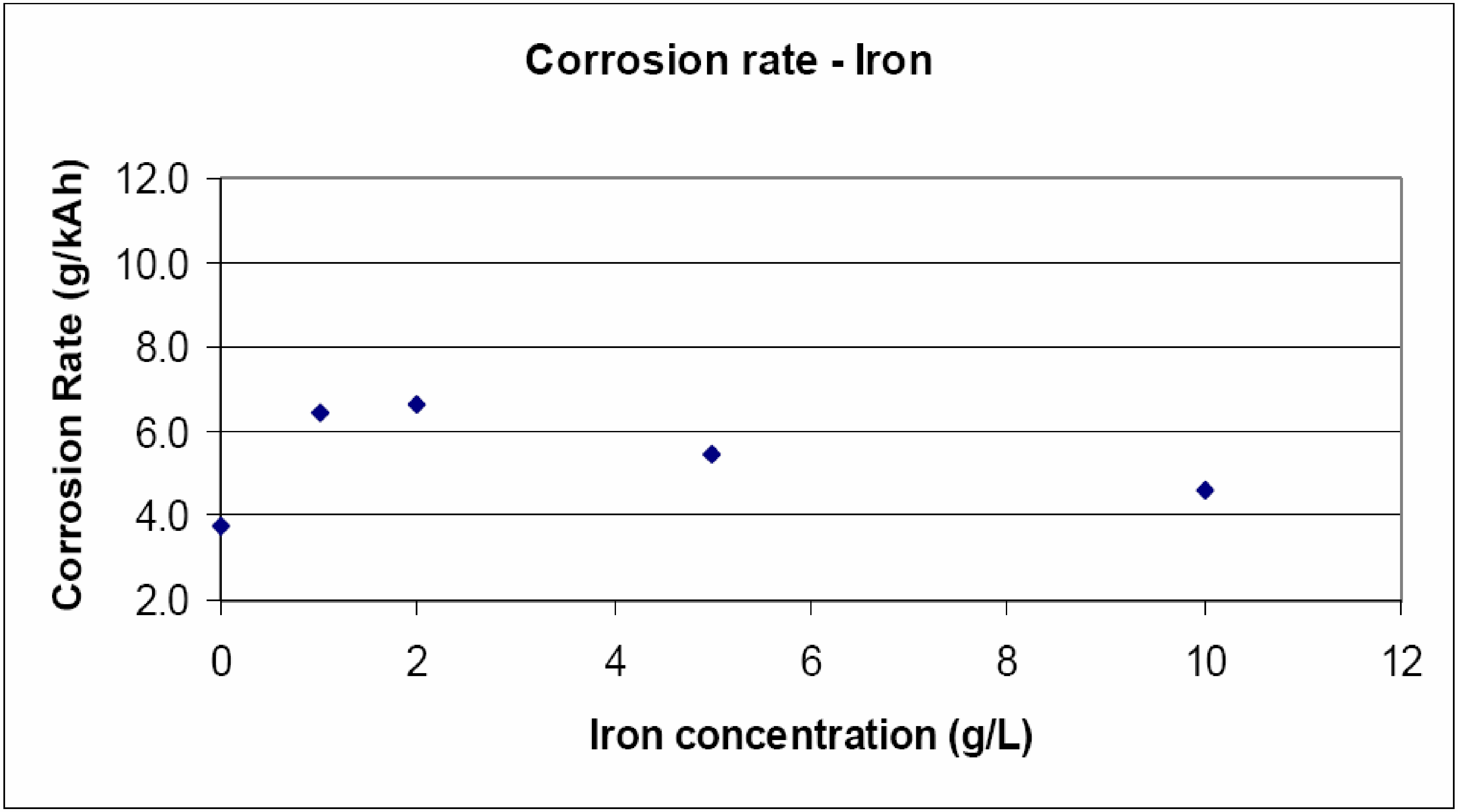


Figure 2: Effect of iron on anode corrosion rate

Anode Corrosion

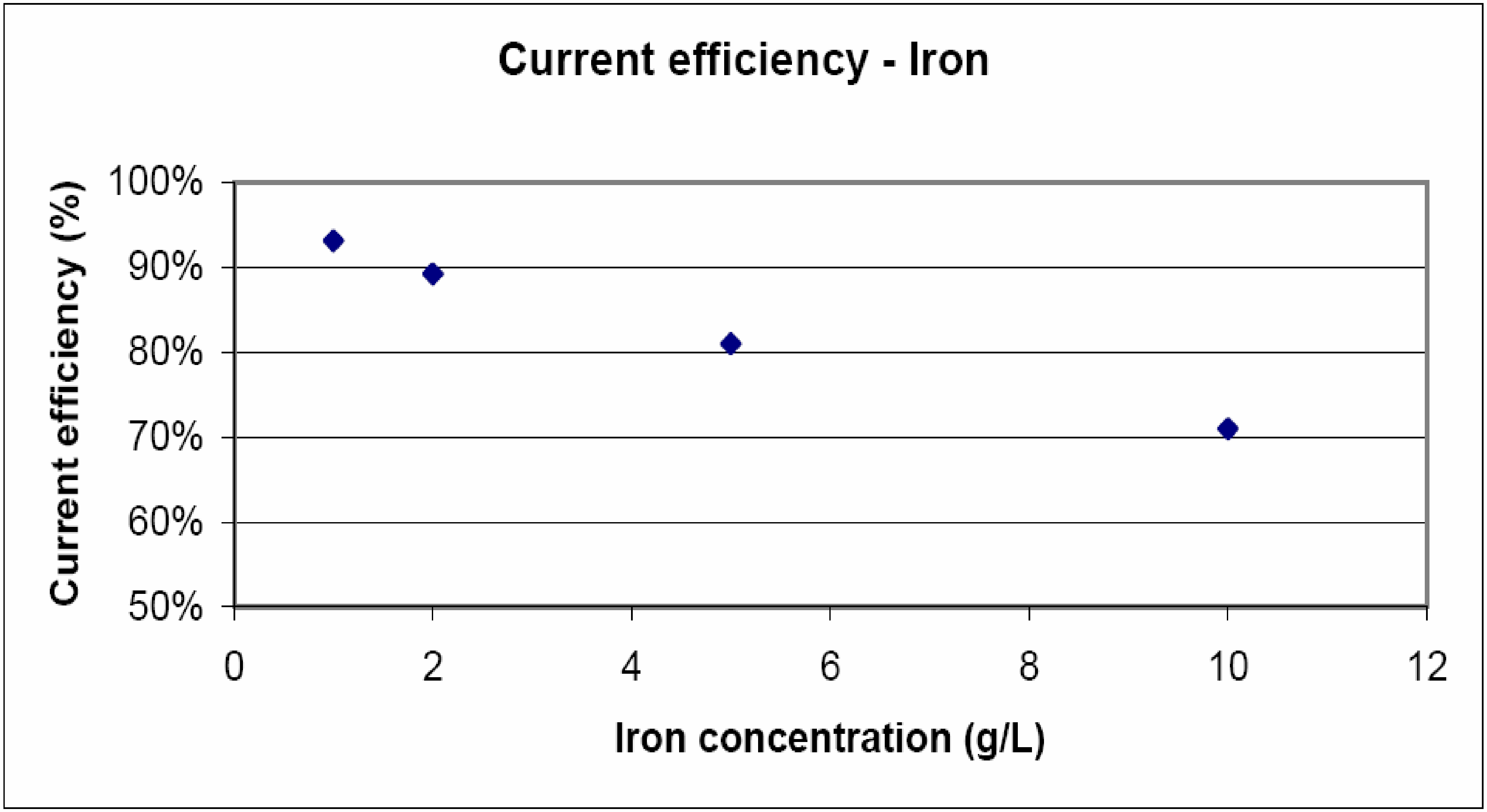


Figure 9: Effect of concentration of iron on cathode current efficiency

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 PbO_2 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

Industrial Methods for Surface Roughening

- Anode Surface pretreatment and applied method has effect on:
  - Required time initial anode conditioning
  - Anode behavior
  - Deposit morphology
  - Manganese sludge generation

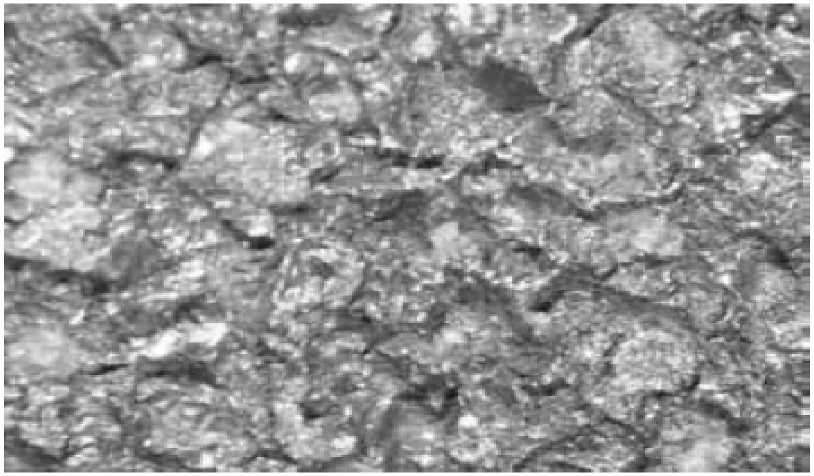
Industrial Methods for Surface Roughening

- KMnO4 Treatment
  - Chemical deposition of a flaky, initial MnO_2 corrosion layer; subsequent spalling of layer associated with break up of underlying $PbSO_4/PbO_2$ 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 MnO_2 layer with multiple PbO_2 sub-layers; labor, energy and cost intensive

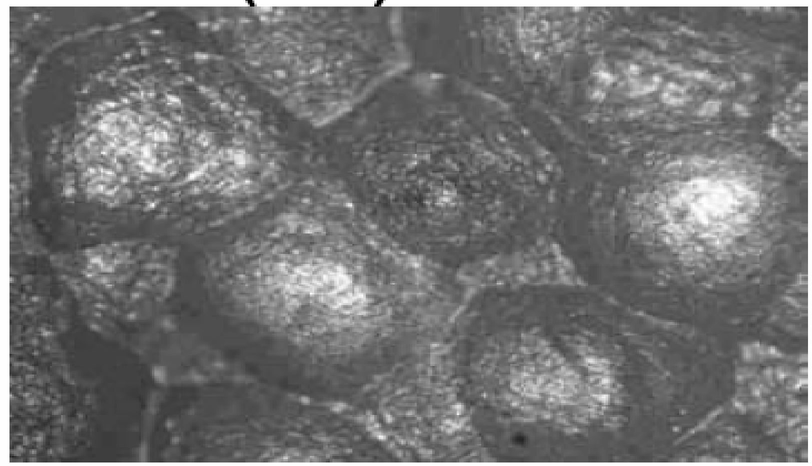
Industrial Methods for Surface Roughening

- 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

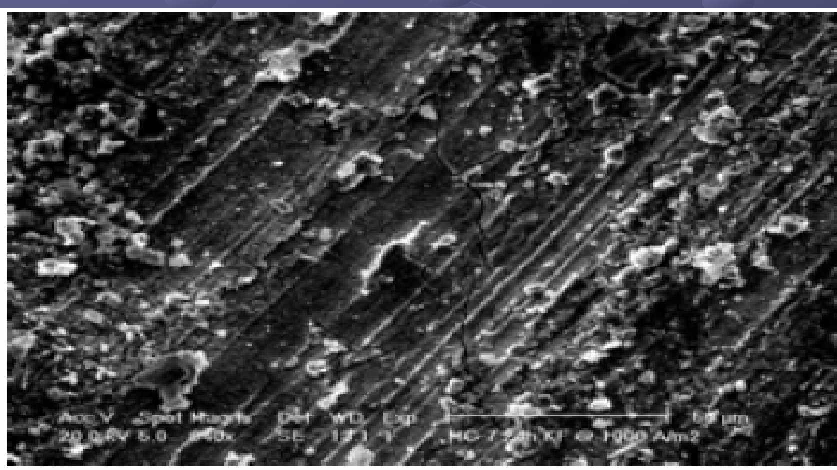
Surface Area after Treatment



b) 0.85-1.65mm Graded Gravel (x20)



e) 0.6-0.85 mm steel shot (x50)



a) KF pre-treatment (x640)

b) $KMnO_4$ 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**
  - **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**
  - **f (i, Mn-concentration)**
  - **No economical benefit above 200 mg/l**

Effect of Cobalt Addition

- In the presence of cobalt, the amount of PbO_2 formed on the anode surface is markedly decreased. Several interpretations for the reduction of PbO_2 formation in the presence of cobalt have been given in the literature:
  - Adsorption of Co^{3+} ions or CoO_2 on the lead anode probably forming a dense film and blocking the penetration of PbO_2 by O radicals.
  - Decrease of radicals due to recombination reaction of adsorbed Co^{3+} with water or hydroxide ion producing a complex, which inhibits formation of PbO_2
  - Co^{2+} increases the amount of labile oxygen containing species and decreases number of adsorbed OH^- radicals, which inhibits formation of PbO_2 film.
  - Co^{2+} inhibits formation of more soluble PbO underneath the $PbSO_4$ film

Effect of Cobalt Addition

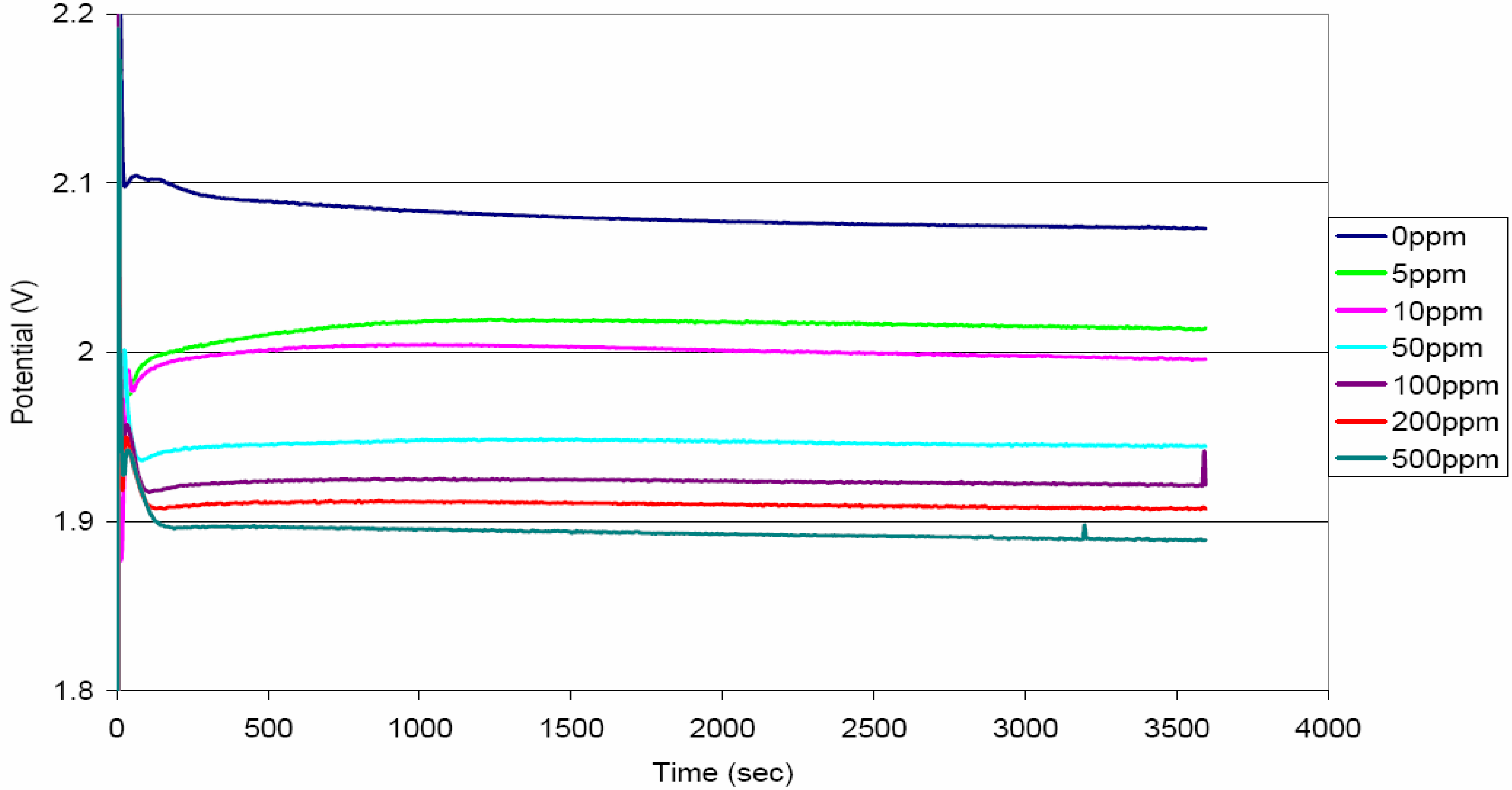


Figure 4.18. The effect of cobalt on the potential for oxygen evolution on a Pb-Ca-Sn anode

Effect of Cobalt Addition

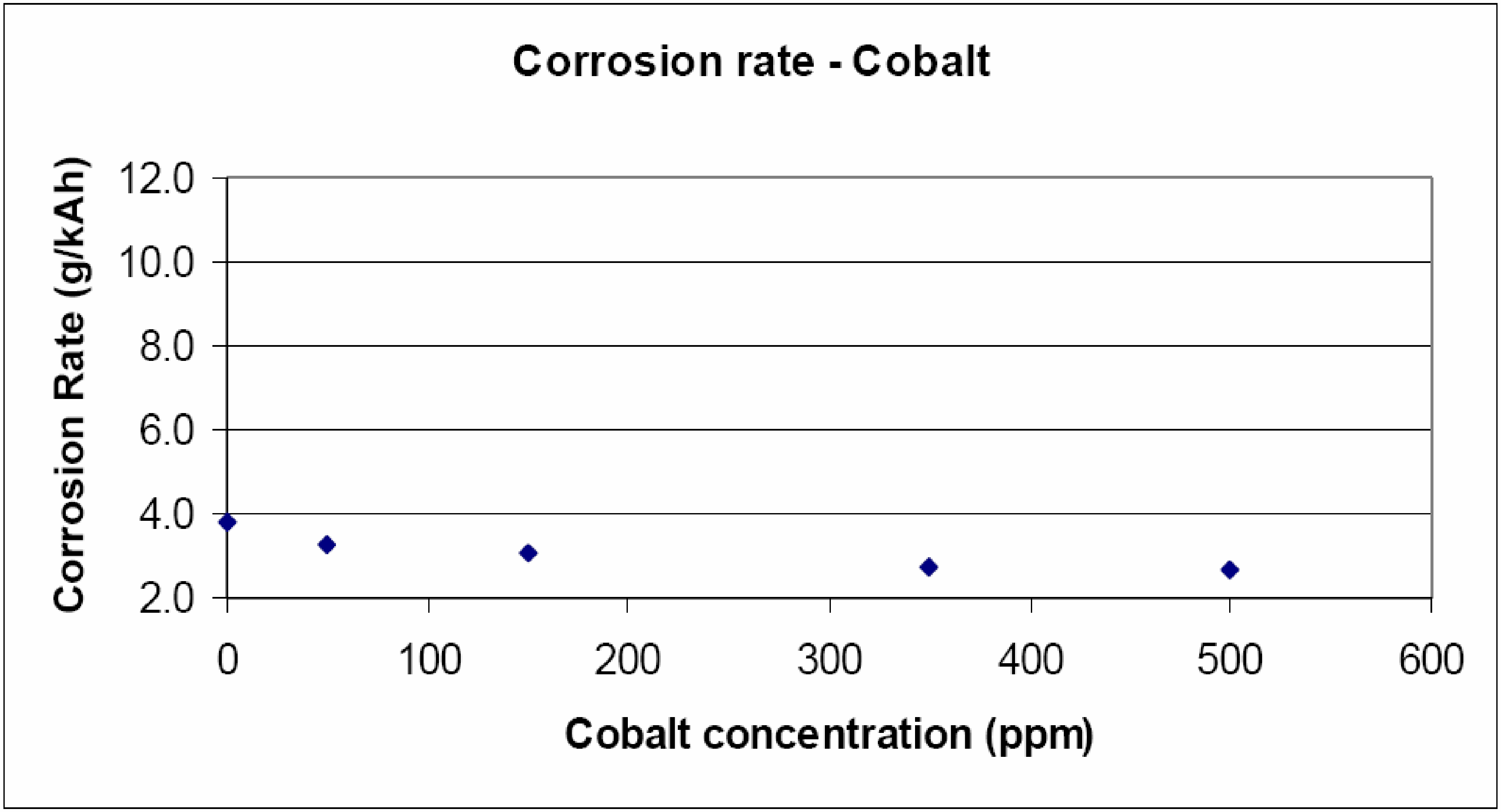


Figure 1: Effect of cobalt on anode corrosion rate

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 α-PbO_2
  - Porous material consists of ß-PbO_2
    - 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

  $Cu^{2+} + 2e^- \leftrightarrow Cu$ $E^0 = 0.34$ V

  $PbSO_4 + 2e^- \leftrightarrow Pb + SO_4^{2-}$ $E^0 = -0.36$ V

  $Pb^{2+} + 2e^- \leftrightarrow Pb$ $E^0 = -0.13$ V

- No co-reduction of Pb ions
- Only physical occlusion of particulate Pb species

- PbO_2 reduction to $PbSO_4$ or PbO possible

  $PbO_2 + SO_4^{2-} + 4H^+ 2e^- \leftrightarrow PbSO_4 + 2H_2O$ $E^0 = 1.69$ V

  $PbO_2 + H_2O + 2e^- \leftrightarrow PbO + 2OH^-$ $E^0 = 0.25$ V

- No further reduction of PbO

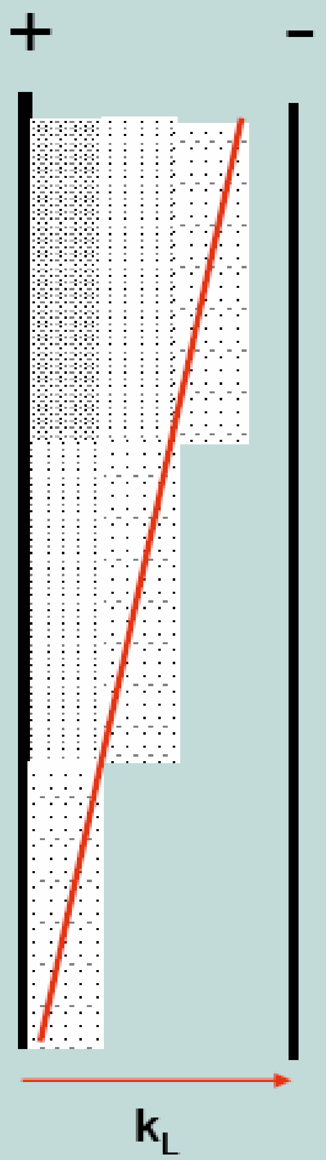
  $PbO + H_2O + 2e^- \leftrightarrow PbO + 2OH^-$ $E^0 = -0.58$ V

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



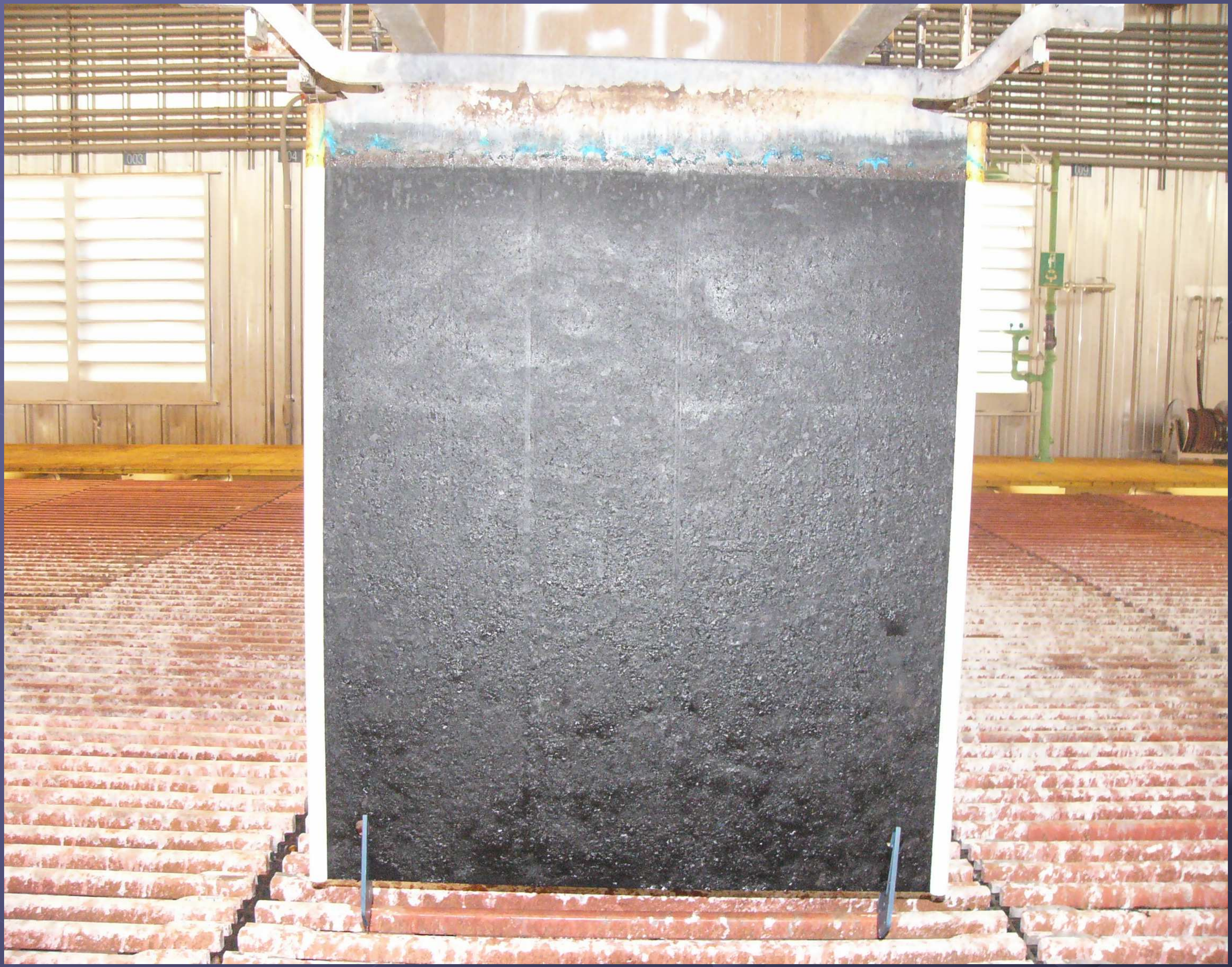
Enhanced Mass Transport Due to Oxygen Evolution At Anode

k_L (anode) >> k_L (cathode)

k_L (top) > k_L (bottom)

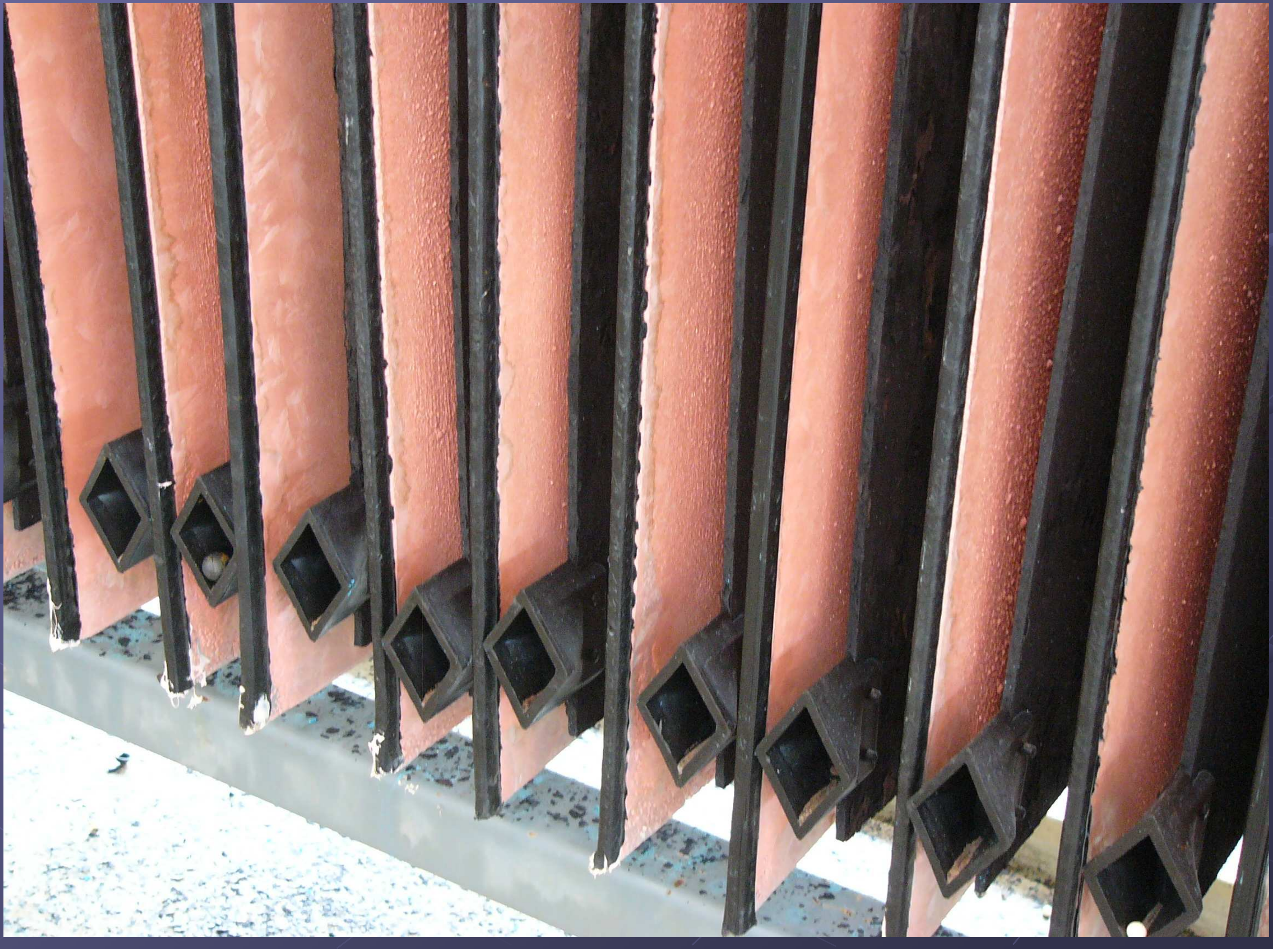
Manifold for Electrolyte Distribution

Anode Insulators

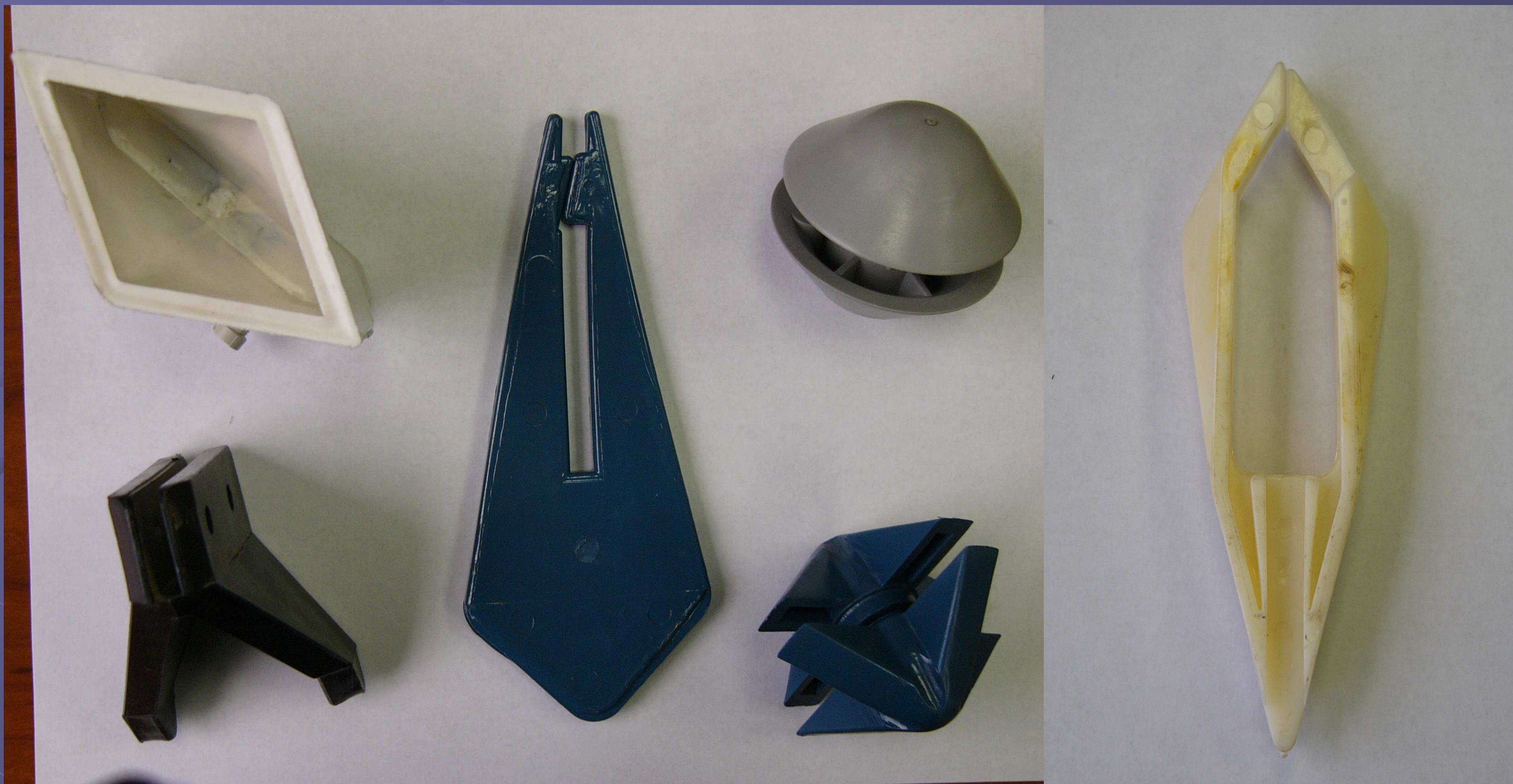


Anode Insulators

Anode Insulators



Anode Insulators



Lead Contamination in Copper Deposit

- PbO_2 more readily incorporated than $PbSO_4$
- Addition of Sr or Ba Carbonate
  - Formation of double salt (Pb, Sr or Ba) $(SO_4)_2$
  - Negative effect on Pb contamination
  - Increase in dendritic growth of Cu deposit
- Addition of Iron (2 g/l)
  - Possible Reduction of PbO_2 to $PbSO_4$ by Ferrous (Fe^{2+})
  - Significant reduction in current efficiency (8 – 10%)
- Filtration of Electrolyte
  - Reduction of Pb-levels with or w/o additives

Power Loss

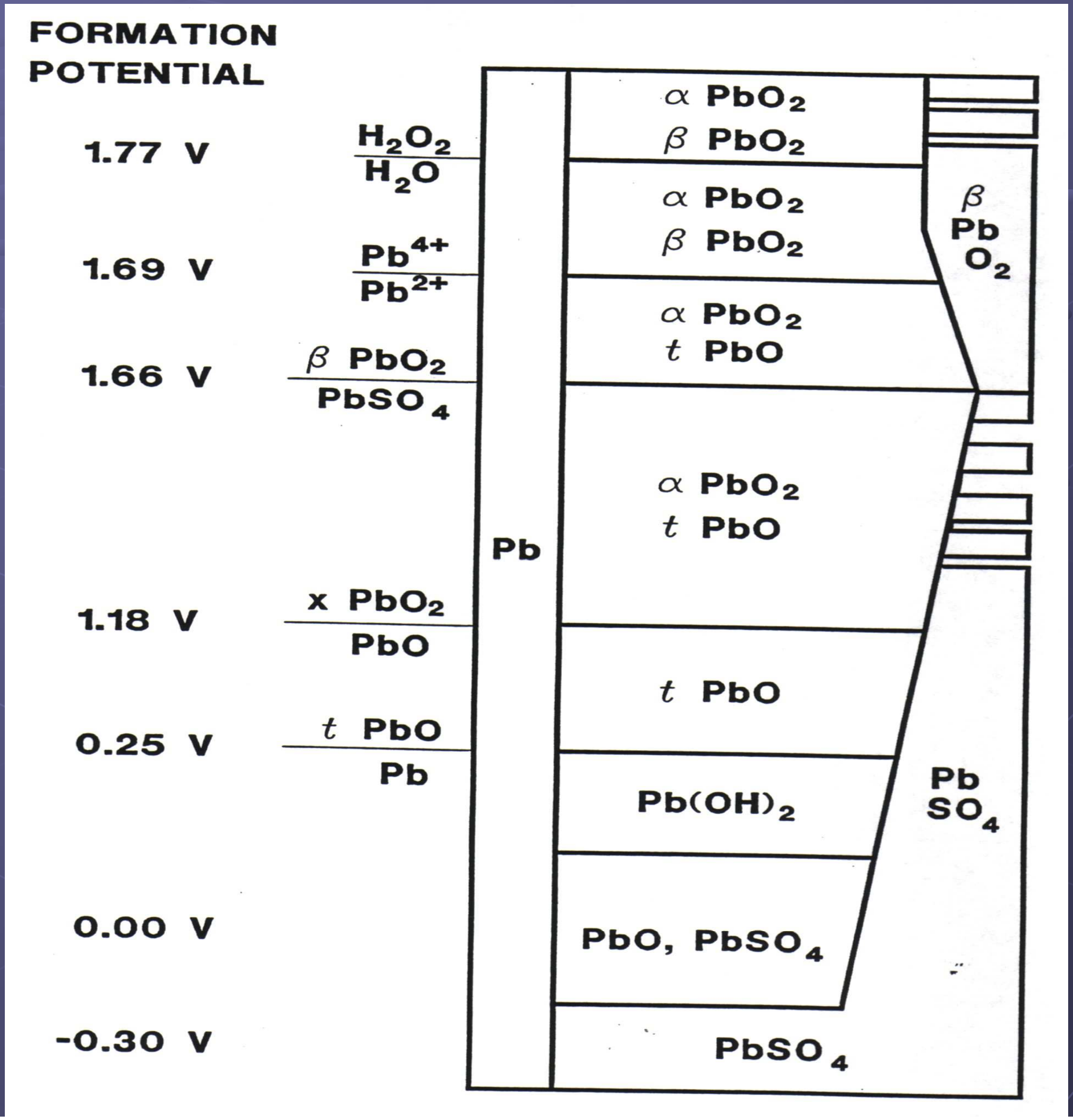
Power Loss

SULFATION REACTIONS OF ANODE WHEN POWER IS LOST:

$$Cu + PbO_2 + 2H_2SO_4 \rightarrow CuSO_4 + PbSO_4 + 2H_2O$$

$$Cu + MnO_2 + 2H_2SO_4 \rightarrow CuSO_4 + MnSO_4 + 2H_2O$$

Lead Corrosion Films



Power Loss

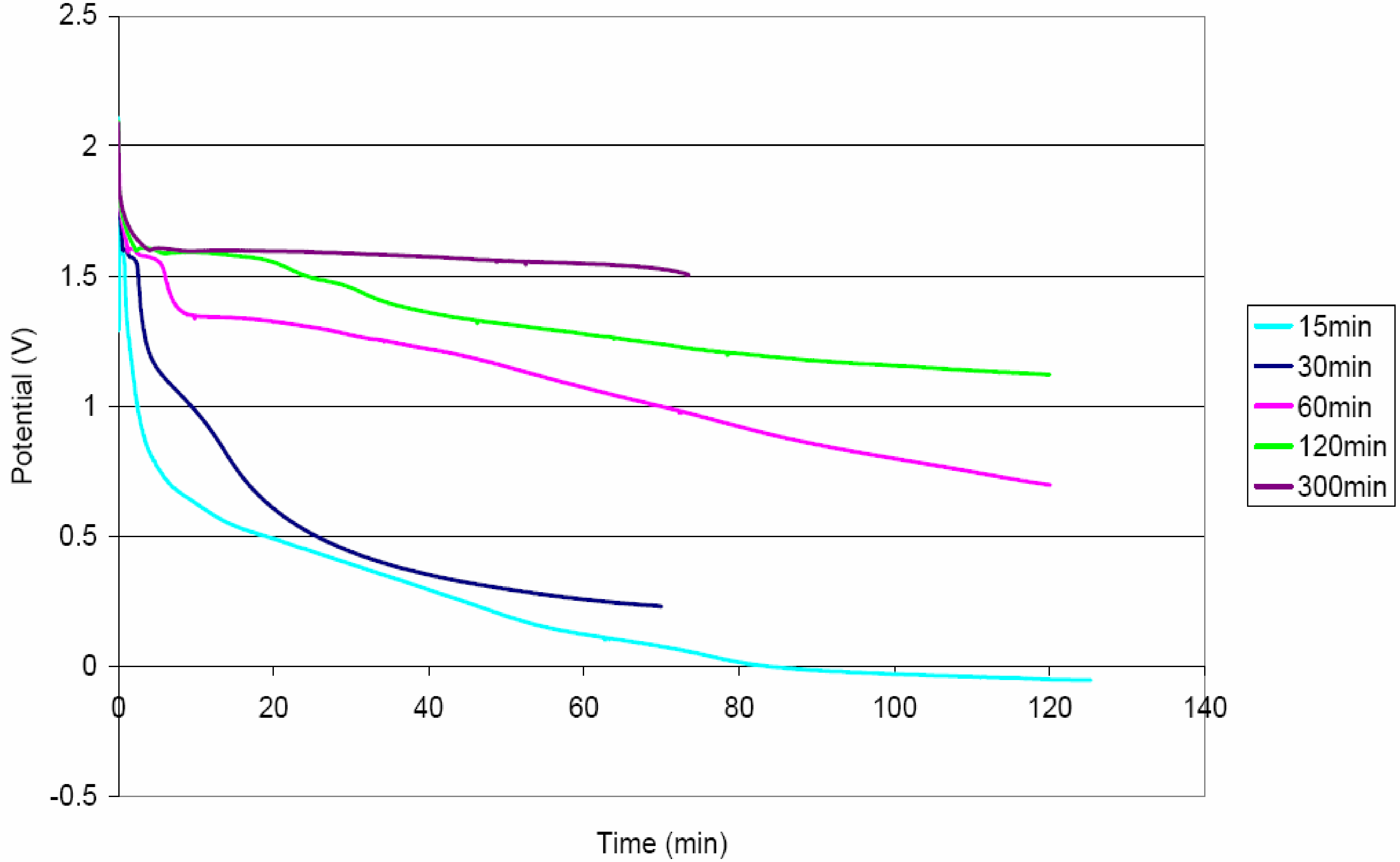


Figure 4.8 Open circuit potential transients after anodization for various times

Power Loss

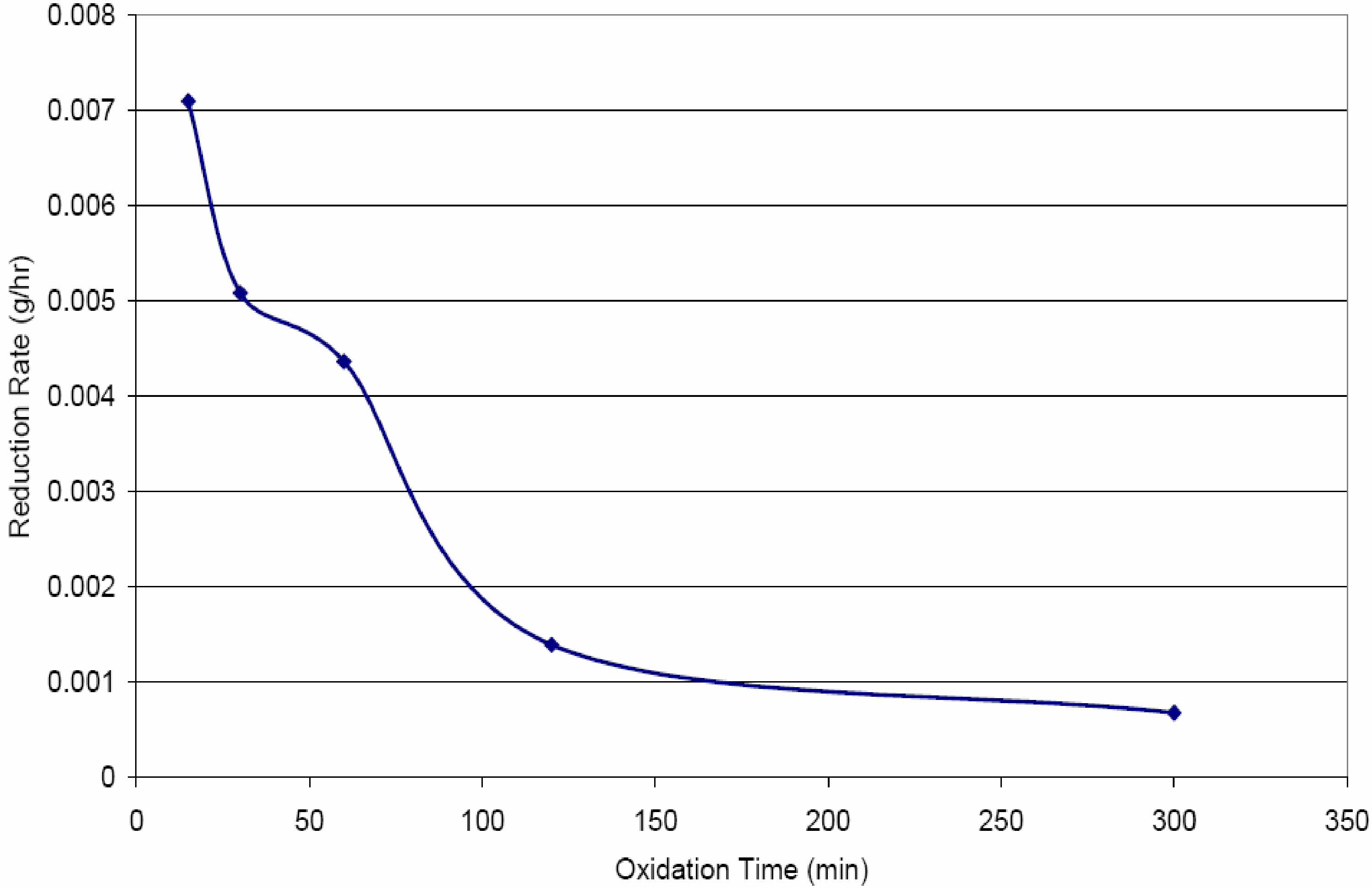
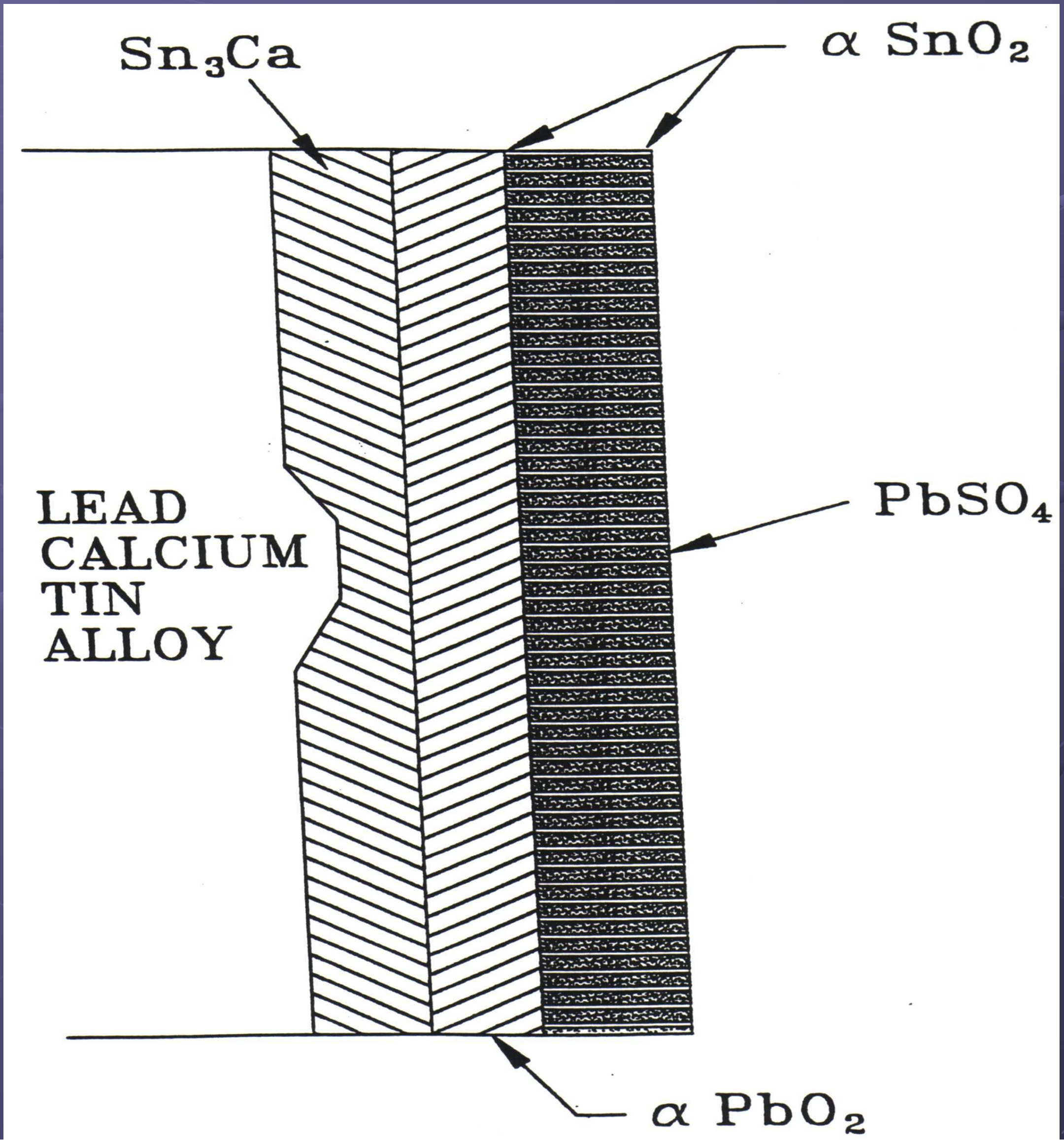


Figure 4.9 Rate of reduction of PbO_2 to $PbSO_4$ after various oxidation times.

Corrosion Product on Rolled Pb-Ca-Sn-Anode



Re-Start after Power Loss

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

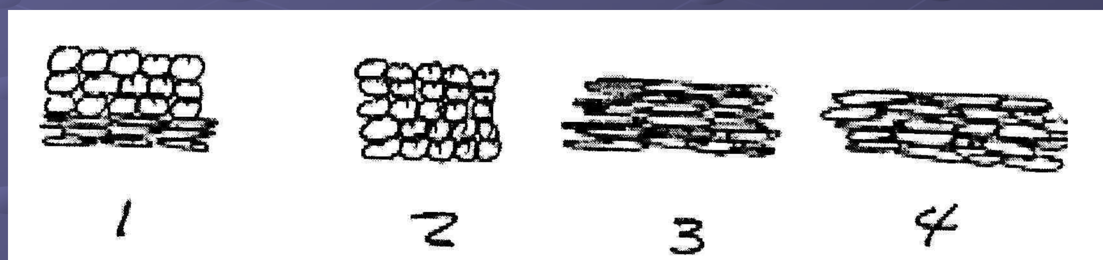
Anode Warping

Possible Reasons for Anode Warping

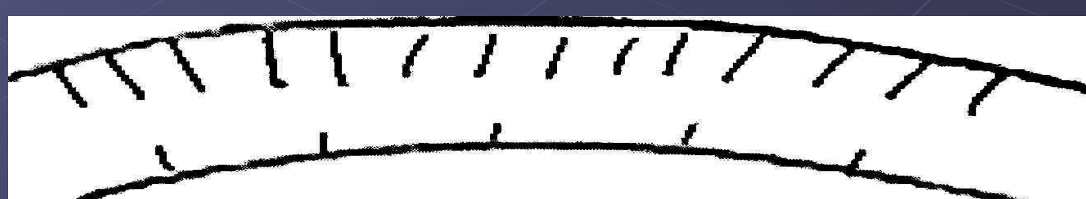
- Ca-content above 0.08%
- Rolling of Anode Sheet
- Assembling of Sheet to Hanger Bar
- Transportation
- Storage
- Tankhouse Operation
- Anode Cleaning
- Spacers

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-Mechnical Anode Treatment
- Polymer Coating
- Co_3O_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_2 or RuO_2 with Ta_2O_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_2 deposition) and Fluoride Ions Present
- Passivation of Ti-surface through TiO_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, MnO_2) 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/m^2)
- 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-Co_3O_4 Composite Coating

- Lead Alloy Anode with Pb-Co_3O_4 Composite Coating on Surface
  - Electroplating of Composite in $NH_2SO_3NH_4$- 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 – 45^0 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 ($\leq$ 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

D E T A I L S
Cast in blocks,stamp CSN and lot number.
Cast at 950-1000F.

C O L O R C O D E

E L E M E N T S

Sb < 0.0010	Sn 1.3000 - 1.5000
As < 0.0010	Cu < 0.0010
Ni < 0.0010	Te < 0.0010
S < 0.0005	Ca 0.0700 - 0.0800
Al 0.0150 - 0.0400	*Ag 0.0120 max
Cd 0.0010 max	Bi 0.0250 max
Fe 0.0010 max	Zn 0.0010 max

C O M M E N T S
On certificate of analysis list all elements indicated.