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A COMPARISON OF LEAD CALCIUM & LEAD SELENIUM ALLOYS

Separating Fact From Fiction

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Background

- Debate between lead antimony vs. lead calcium has been ongoing for almost 70 years
- Both are mature ‘technologies’, with major battery producers and users in both camps
- Batteries based on both alloy types have huge installed bases around the globe
- Time to take another look for US applications:
  - New market forces at work
  - Significant improvements in alloy compositions
  - Recognize that users are looking for viable options

Objectives

- Provide a brief history of the development and use of both lead selenium (antimony) and lead calcium; objectively compare and contrast the performance and characteristics of each type
- To attempt to draw conclusions about the performance, reliability, and life expectancy of each alloy type; suitability of each for use in the US

Then & Now:
Primary Challenges in Battery Manufacturing

- The improvement of lead alloy compositions for increased tensile strength, improved casting, & conductive performance
- Developing better compositions & processes for the application and retention of active material on the grids

Alloy Debate: Lead Calcium Vs. Lead Selenium

- Continues to dominate & define much of the technical and market debate in US
- Good reasons for this:
  - Impacts grid & product design, long-term product performance & reliability
  - Directly affects physical strength & hardness of grid; manufacturability
  - Influences grid corrosion & growth, retention of active material

History of Antimony

- First used in lead alloys back in 1881
- A boon to battery manufacturing, giving grids improved strength, handling, castability - yields
- Originally used in 8%-12% concentrations, gradually reduced to 5%-8%
- Led to rapid growth of lead-acid battery applications
- But along with the proliferation of lead antimony batteries came a growing awareness of certain problems associated with antimony:
  - Increased levels of outgassing, higher water consumption
  - Problems increased with age

Identifying The Problem

- Bell Labs in 1930 began research to better understand problems, experiment with new alloys
- Published findings in 1935, and found:
  - Confirmed phenomena of 'antimonial poisoning' (migration of freed antimony from positive to negative plates)
  - Antimony deposited on active material of negative plate led to increased local reactions (decreased potential of the negative) and reducing charging efficiency
  - Over time cell needs increasing levels of float charge, accelerating hydrogen evolution & watering requirements
  - Problems accelerated with age of battery

American Response: Lead Calcium Alloy

- Bell Labs team pioneered development of lead calcium alloys (original Ca concentrations at 0.065% to 0.090%, not to exceed 0.10%)
- Gave grids comparable grid density, tensile strength, and conductivity to antimony
- Good stability under float charge
- Significant reduction in outgassing & water consumption, at a rate that stayed constant w/ age
- Improved self-discharge characteristics
- First specified by Bell Labs in 1951; rapid adoption in the US subsequently for stationary battery applications

European Response: Lead Selenium Alloy

- Like US, driven to find solution to antimonial poisoning
- Different approach focused on lowering antimony concentrations to significantly reduce problems; eventually settled on antimony levels under 2% - made possible with new casting processes (e.g. pressure casting)
- **Key to this approach was the addition of selenium**
  - Stabilized antimony
  - Created a more hardened lead with finer, denser lead grain structure
  - Grain refinement created more corrosion resistant grid; less growth, inter-granular corrosion, creep resistance
  - Saw this as a solution that combined advantages of both lead antimony and lead calcium, & reduced disadvantages

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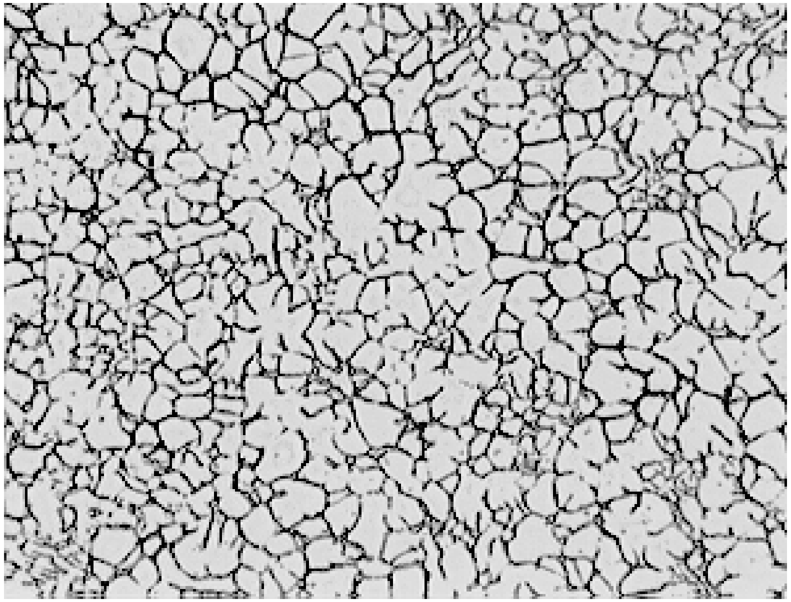
Lead Selenium Grain Refinement



Lead Selenium Alloy

Pressure Casting

- high cool down time leads to small grains
- globulitic structure
- low corrosion

Pros and Cons:

Comparing Strengths & Weaknesses of Lead Selenium vs. Lead Calcium

Lead Selenium: Pros

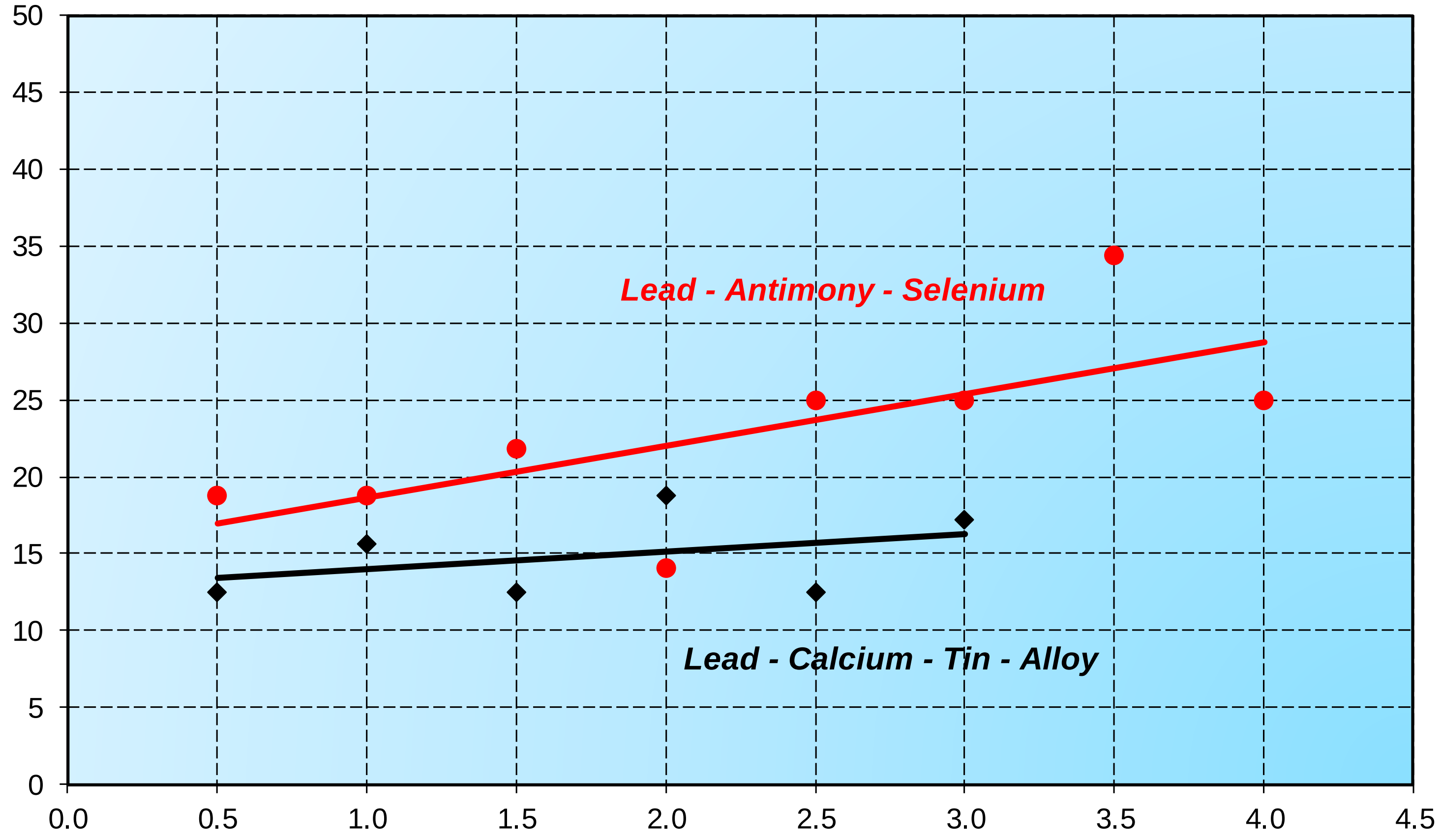
Benefit Summary

- Good grid density, conductivity, & tensile strength
- Reduced antimony migration and water requirements
- Stability under float charge; consistent cell voltages
- Little plate growth (max. 5-10mm over life)
- Increased corrosion resistance, little or no inter-granular corrosion
- Superior cycling & deep discharge performance

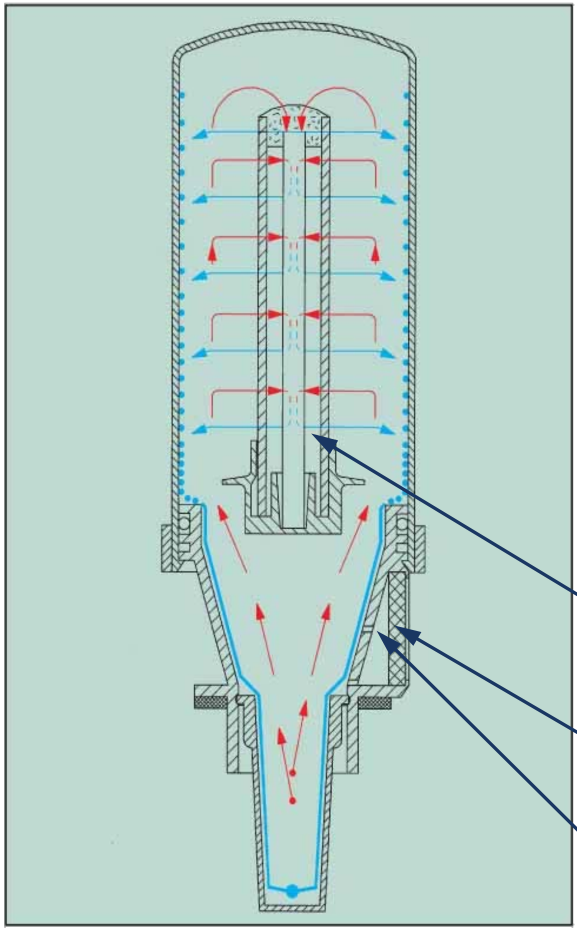
Lead Selenium: Cons

- Demonstrated water requirements, while greatly reduced (1.8% Se), still higher than calcium as battery ages
- Higher self discharge characteristics (typically 0.1% per day at 25°C)
- Shorter shelf-life (open circuit) 3 months vs. 6 months for lead calcium

Water Consumption: PbCa vs. PbSe



Recombination Catalyst



- Extends maintenance intervals up to the level of maintenance free (reducing maintenance costs)
- Reduces ventilation requirements
- Protects against flashback
- No significant escape of gas or of electrolyte fumes

Palladium catalyst

Ceramic protection

Allows the escape of gas during overcharge

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Lead Calcium: Pros

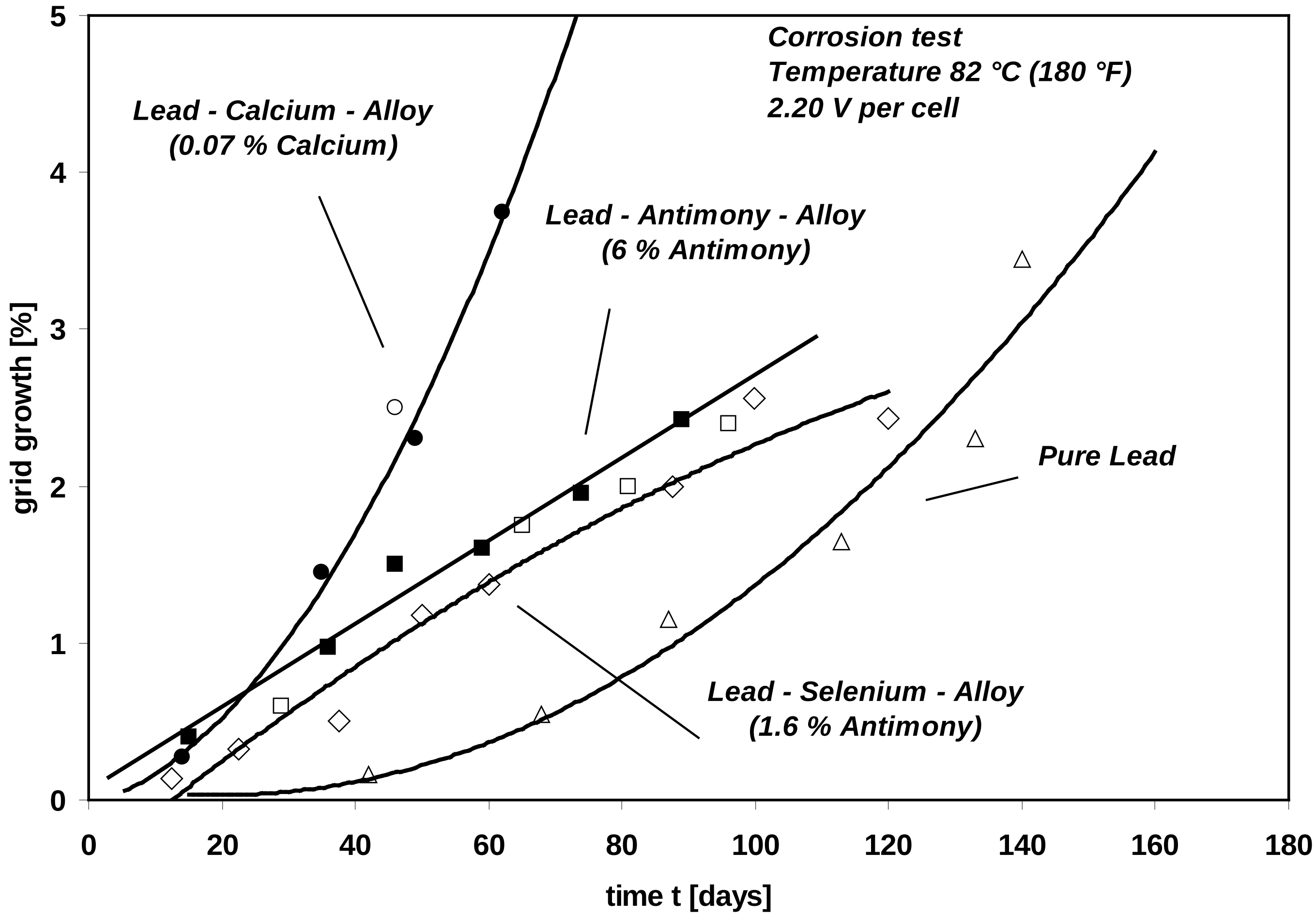
Benefit Summary

- Good grid density, conductivity, & tensile strength
- Reduced water consumption over life of battery
- Reduced electrolyte evolution & hydrogen gas
- Better self-discharge characteristics- (typically .05% per day at 25°C)
- Stable rate under float charge over the life of the battery; constant current draw

Lead Calcium: Cons

- Potential for creep resistance leading to positive plate growth when calcium levels exceed 0.09% (requires tight control in mixing & manufacturing processes)
  - Corrosive precipitation (Pb3Ca) penetrates lead grain boundaries & increases plate volume (positive plate growth)
  - Can create stress and failure of terminal post, jar cover seals
- Potential for passivation (premature capacity loss)
  - Caused by a passivating layer of lead sulfate between the grid and the active material
  - Over time this isolation of the active material from the grid reduces conductivity of active material & causes uneven current distribution throughout cell
  - Can in some cases cause unpredictable loss of performance & uncertainty

Corrosion of Lead Alloys



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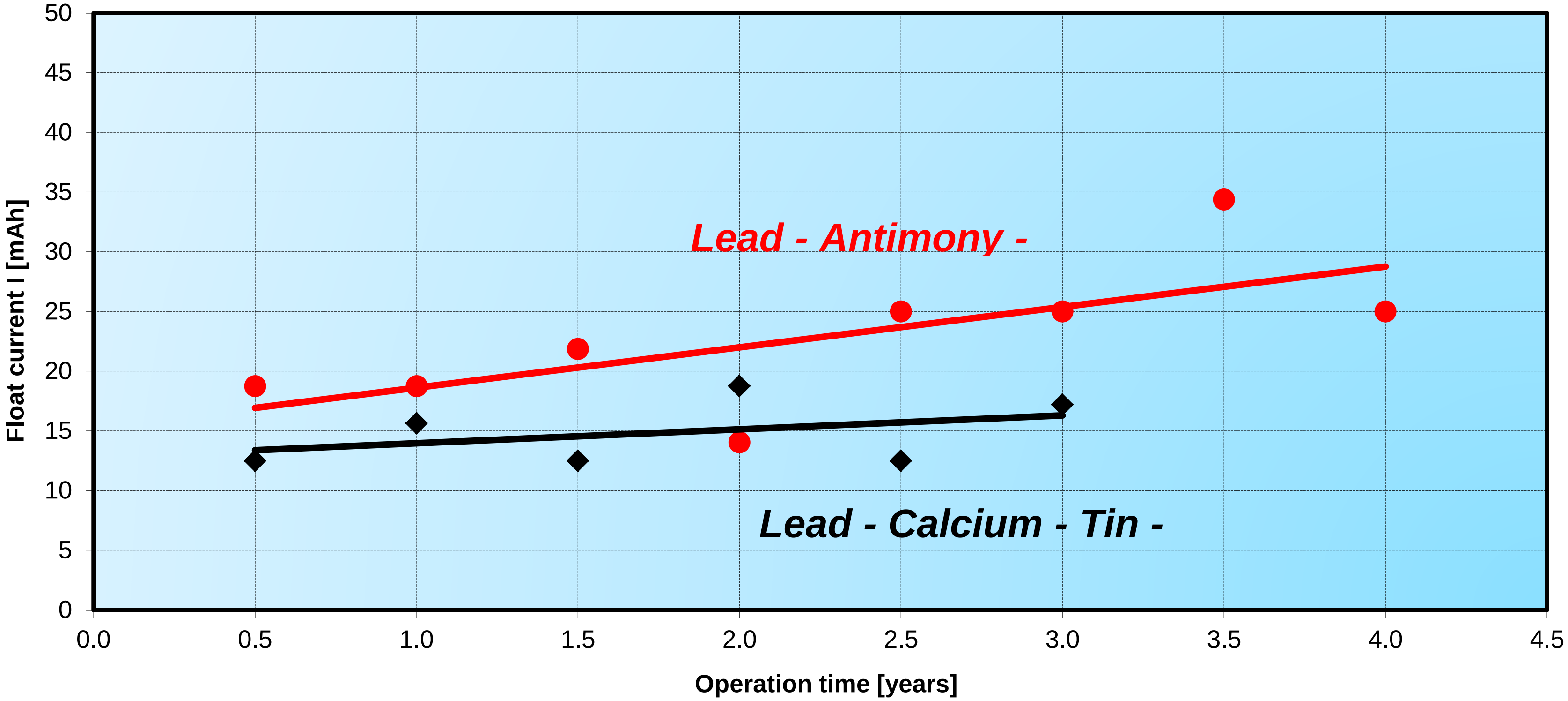
Float Voltages of Lead Alloys



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Lead Selenium (low antimony) vs. Lead Calcium

CHARACTERISTIC	*LEAD ANTIMONY*	*LEAD CALCIUM*
Voltage	**2 Volts**	**2 Volts**
Electrolyte Solution	**Dilute Sulfuric Acid**	**Dilute Sulfuric Acid**
Electrolyte Specific Gravity	**1.220 to 1.290**	**1.215 to 1.250**
Requires Specific Gravity Checks	**Yes**	**Yes**
Float Charge Voltage	**2.15 to 2.25 Volts**	**2.17 to 2.30 Volts**
Boost Charge Voltage	**2.30 to 2.40 Volts**	**2.35 Volts**
Use of Standard Battery Charger	**Yes**	**Yes**
Expected Service Life at 77° F (CV Float)	**20 Years**	**20 Years**
Cycle Life to 80% D.O.D. at 77° F	**800 to 1200**	**200 Maximum**
Water Intervals at 77° F	**Fair**	**Good**
Recommended Operating Temp Range	**50° to 90° F**	**50° to 90° F**
Storage Time at 77° F (Filled)	**3 Months**	**6 Months**
Storage Time Discharged	**Max. 24 Hours**	**Max. 24 Hours**
Vented Gas Composition	**Hydrogen, Oxygen, Acid Vapor**	**Hydrogen, Oxygen, Acid Vapor**
Self-Discharge at 77° F	**0.1% per Day**	**0.05% per Day**
Capacity at End of Life	**80%**	**80%**
Recharge time at float	**3 days**	**6-7 days**
Plate Growth Resistance	**Good**	**Fair**
Corrosion Resistance	**Good**	**Fair**
Predictability	**Good**	**Fair**

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Comparative Summary

- **Both Lead Calcium & Lead Selenium exhibit very comparable performance characteristics in primary battery operation**
  - Both alloy types have good stability under charge/discharge
- **Differences in secondary (negative) characteristics**
  - Lead calcium has lower water usage/gas evolution rates, and better self-discharge (higher shelf life); greater tendency for positive plate growth, potential for premature & sudden capacity loss (passivation)
  - Lead Selenium has better creep resistance (less positive plate growth), better inter-granular corrosion resistance, superior cycling/deep discharge performance, predictability; higher water usage (without catalyst), higher self discharge (lower shelf life)

Conclusions

General performance parity between alloys

- No real differences in primary battery performance metrics
- Both support 20 year battery life designs
- Both operate under typical float applications (telecommunications, utility/switchgear, data center)
- No discernible differences in recommended temperature operating ranges
- No significant differences in maintenance & testing requirements

Conclusions

- Both are mature technologies with years of design, production, and field data to support claims
- Both alloy types today have extensive, global installed bases with loyal customers
- Both alloy types are supported by large, experienced, and reputable manufacturers who are committed to constant refinement and improvement

Which of these alloy technologies is suited to meet the requirements for mission-critical applications in the US?

BOTH!

Win-Win

- The comparative data supports the idea of general performance parity between PbCa and PbSe
- Users win when the range of viable battery options is increased; global competition places severe pressure on organizations & supply chains
- **Users win when the final decision metrics become:**
  - Reputation & history of the manufacturer
  - Quality commitment and processes
  - Warranty policy and support
  - Commitment to customer service and support
  - Specified product performance levels
  - Price & Delivery