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The Antimony Price Rise Crisis – a Lower Cost Pathway for Lead-Acid Batteries

Report contributors:

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- Energy Storage Publishing Ltd
- Ecotech Energy Solutions Ltd

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The personnel and participating companies

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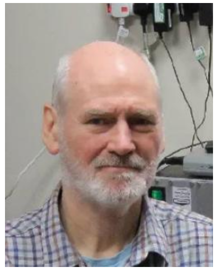

- Mike McDonagh – Ecotech Energy Solutions, Microtex Energy Ltd, Bestmag

- Madhusana Reddy – Microtex Energy Pvt. Ltd, Chief Engineer

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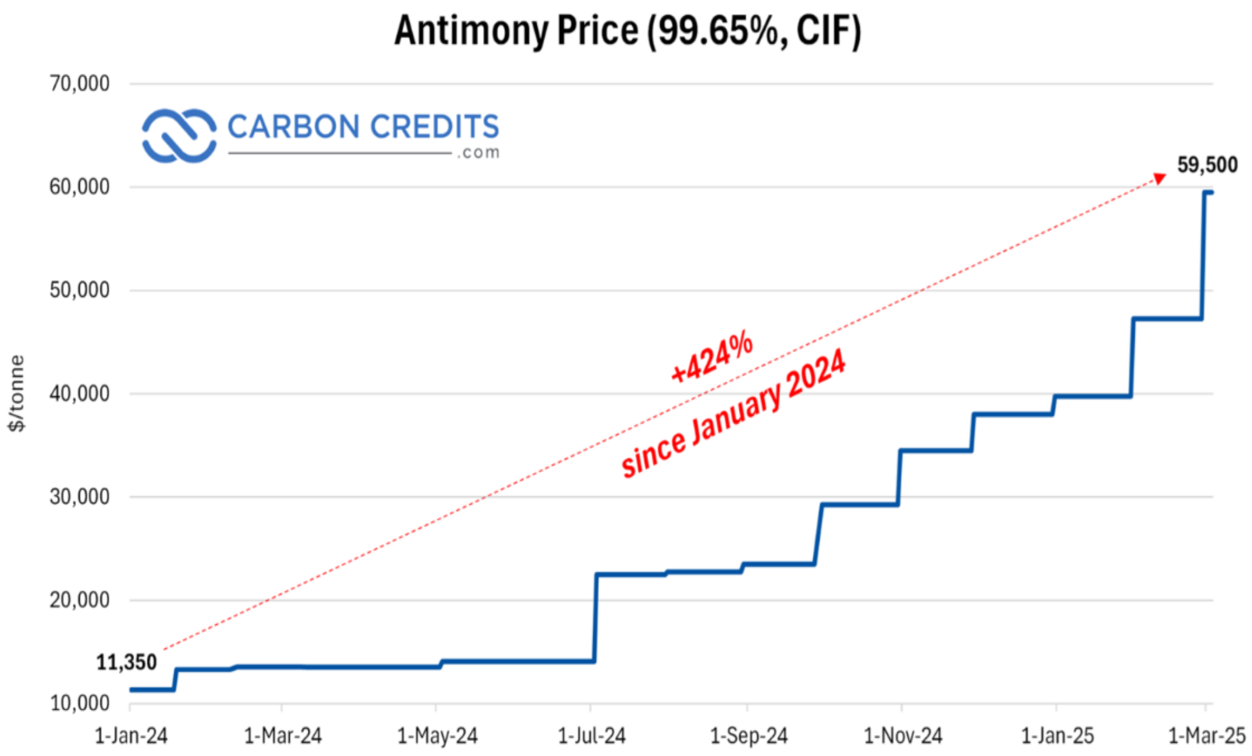
Economics of antimony price rise



Source: S&P Global

- The Future of Antimony: Rising Prices, Supply Chain Risks, and Demand Growth • Carbon Credits

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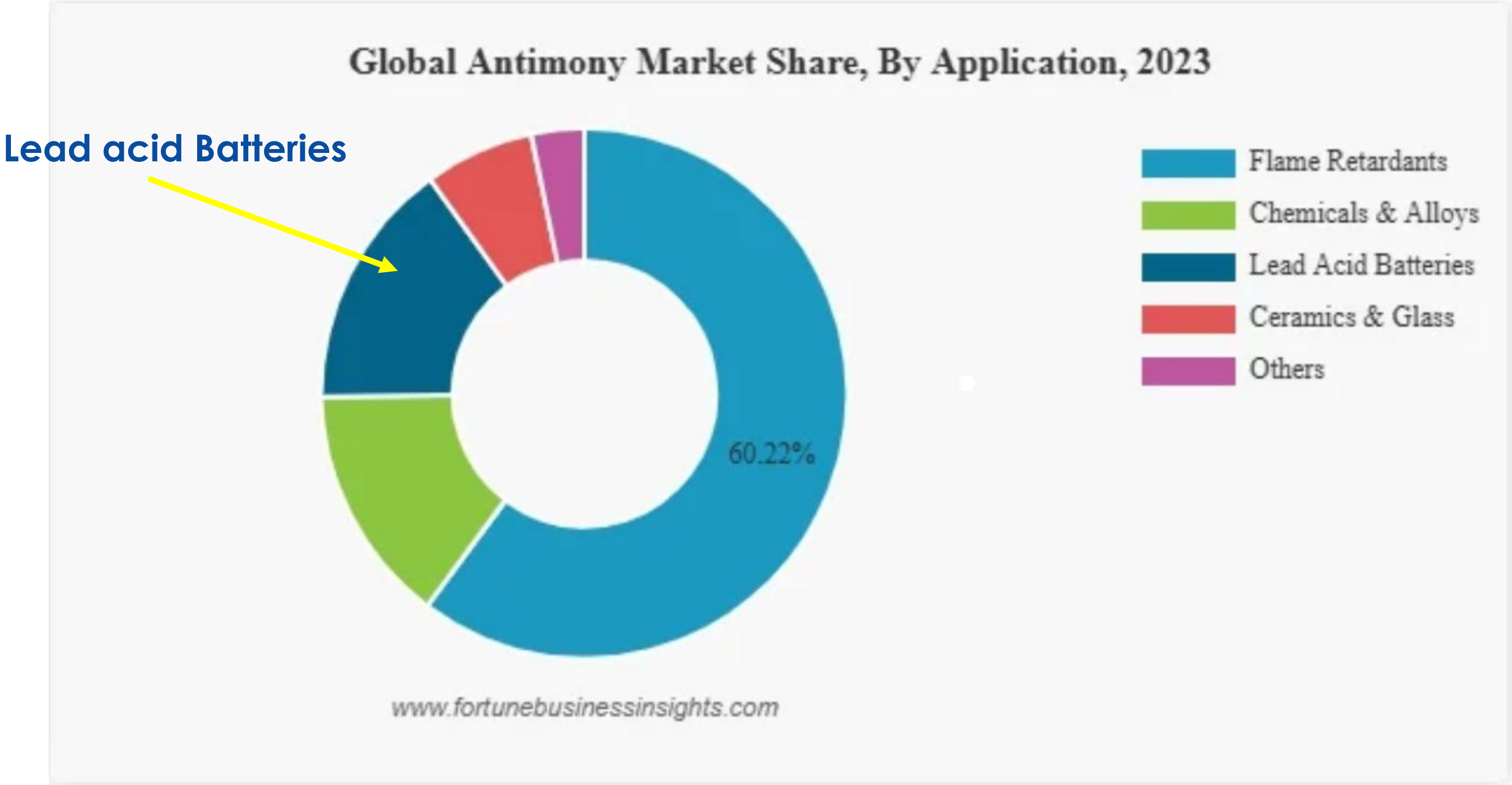
Uses of antimony

Lead acid batteries approximately 17% of global market

Antimony price is outside of the control of the lead acid battery industry



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Role of antimony in lead acid battery grids and components

Principle reasons for addition of antimony to lead

- Hardens lead and prevents component damage/ distortion
- Prevention of passivation in deep discharge of batteries
- Mechanical processing of battery grids and plates
- Prevention of grid growth for batteries in service
- Typical concentrations 1.5 to 9 wt% (components and grids)

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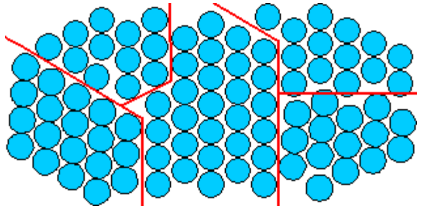
Hardness, mechanical properties and role of alloying elements in improving alloy strength

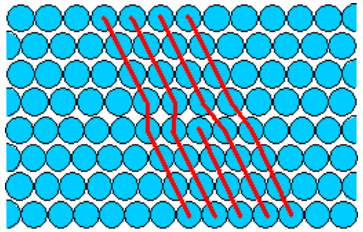
Metals deform by movement of dislocations (imperfections in the crystal lattice).

Alloying elements can pin dislocations into place to make movement more difficult

Deformation by dislocation movement.

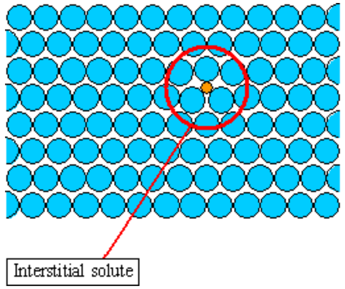


Grain boundary slip

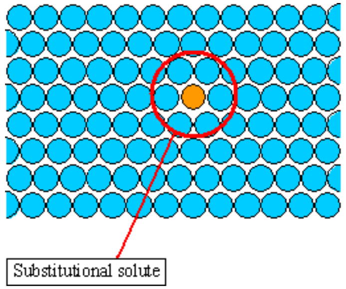


Matrix imperfection

Pinning of dislocations by solute atoms.



Dislocation pinned by interstitial atom



Dislocation pinned by substitutional atom

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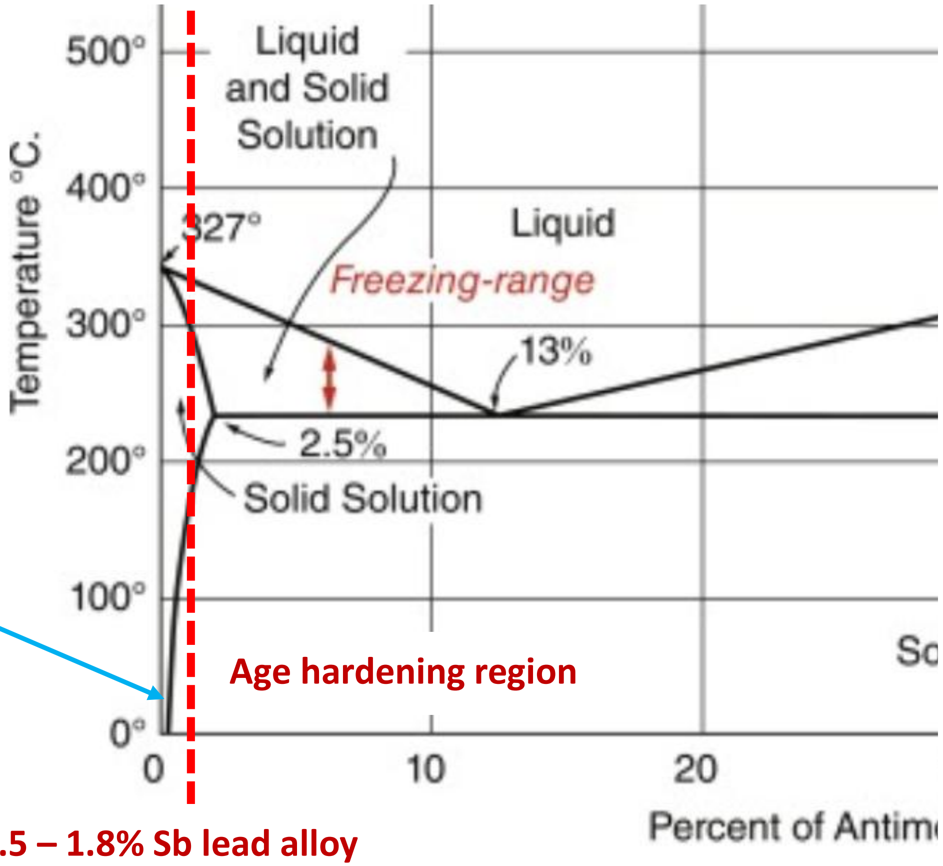
Age hardening - alloy choices to reduce antimony in lead acid battery grids and components

PbSb SS preciptn
=1.6 – 0.004
=1.596%

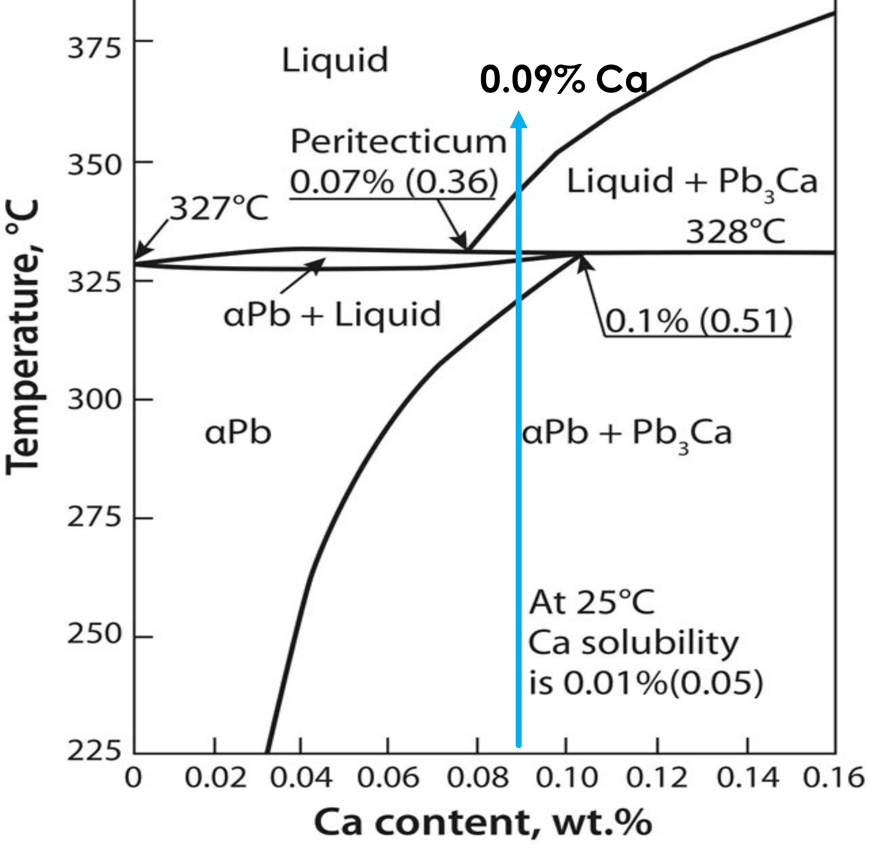
PbCa SS preciptn
= 0.1 – 0.03
= 0.07%

0.004% Sb

Pb-Sb Phase diagram



Pb-Ca Phase diagram



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Properties needed by new lead alloys

The connectors and grids require different mechanical and corrosion properties due to their very differing lifetime environments

Formation connector

- Processability
- Hardness and wear resistance
- Corrosion resistance

Battery grids:

- Processability
- Mechanical strength
- Creep strength
- Corrosion resistance

- **Alloys available:**
- 1. Low antimony lead alloy (Pb-Sb)
- 2. Lead calcium Pb-Sb-Sn)

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Case Study 1 – UK Powertech

Lead alloy battery component.

Formation connector

Principle requirements are:

Processability

damage resistance

corrosion resistance

Formation connector with Pb-8% Sb alloy push fit head

Test samples

Connector internal component from casting process.

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Critical properties for a formation connector

Corrosion resistance/low interface electrical resistance
- Antimony provides electron conduction when incorporated into the surface corrosion layer
- Tin acts in a similar way and can substitute for antimony

Processability
Casting – Gravity and injection moulding.
- Fluidity: Antimony reduces the MP and aids metal flow and filling.
- Tin is a suitable alternative to antimony

Hardness and wear resistance
Connectors have daily operational, removal and replacement on terminals
- Resistance to scratching and chipping
- Retention of shape – deformation resistance
- Age hardening by heat treatment for low Sb alloys is effective
- Arsenic is a powerful age hardening agent for low Sb alloys

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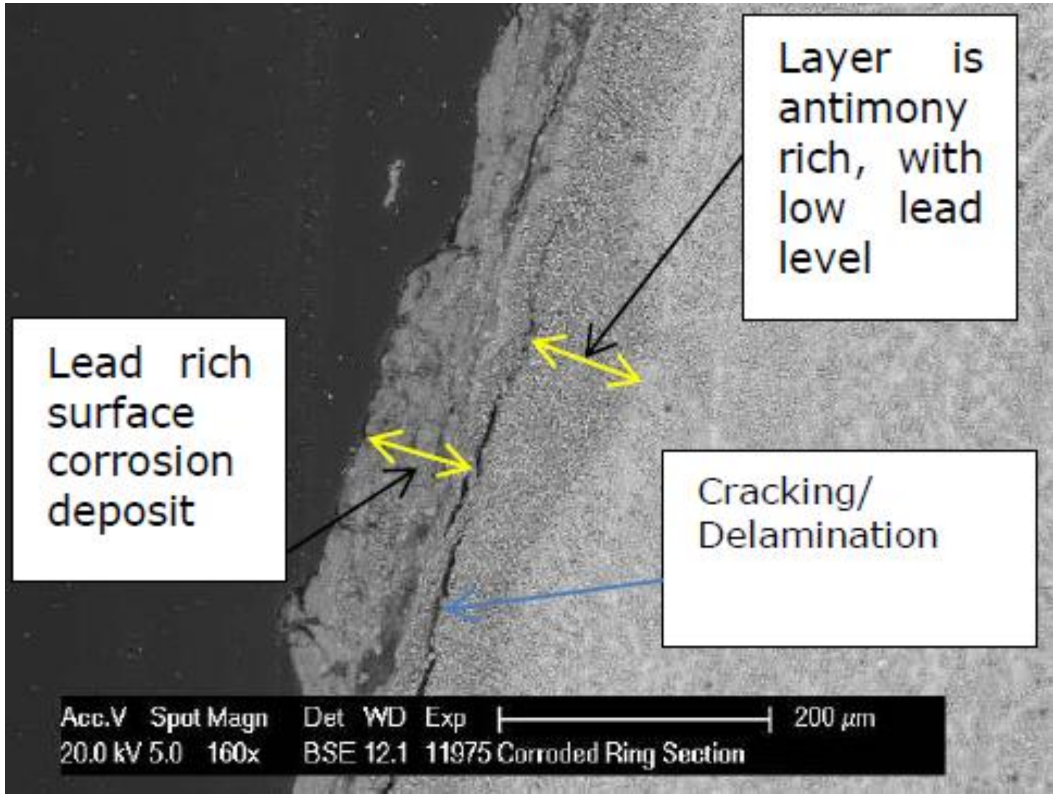
Corrosion resistance – Surface corrosion layer of used connector head

EDX Composition Data

	Cone				Ring
Element	Reference	Corroded Surface	Crumbly Surface	Nodular Background	Inside Average
Oxygen		63.1	60.9	57.6	58.4
Sodium			0.5		0.8
Arsenic			0.3		0.2
Sulphur		19.2	16.9	21.3	19.9
Lead	73.5	16.4	12.3	19.1	16.2
Antimony	26.6	1.4	8.8	2.0	3.0
Iron			0.3		0.9
Nickel					0.5



Corrosion deposits on inner curved surface – depth of 160µm.

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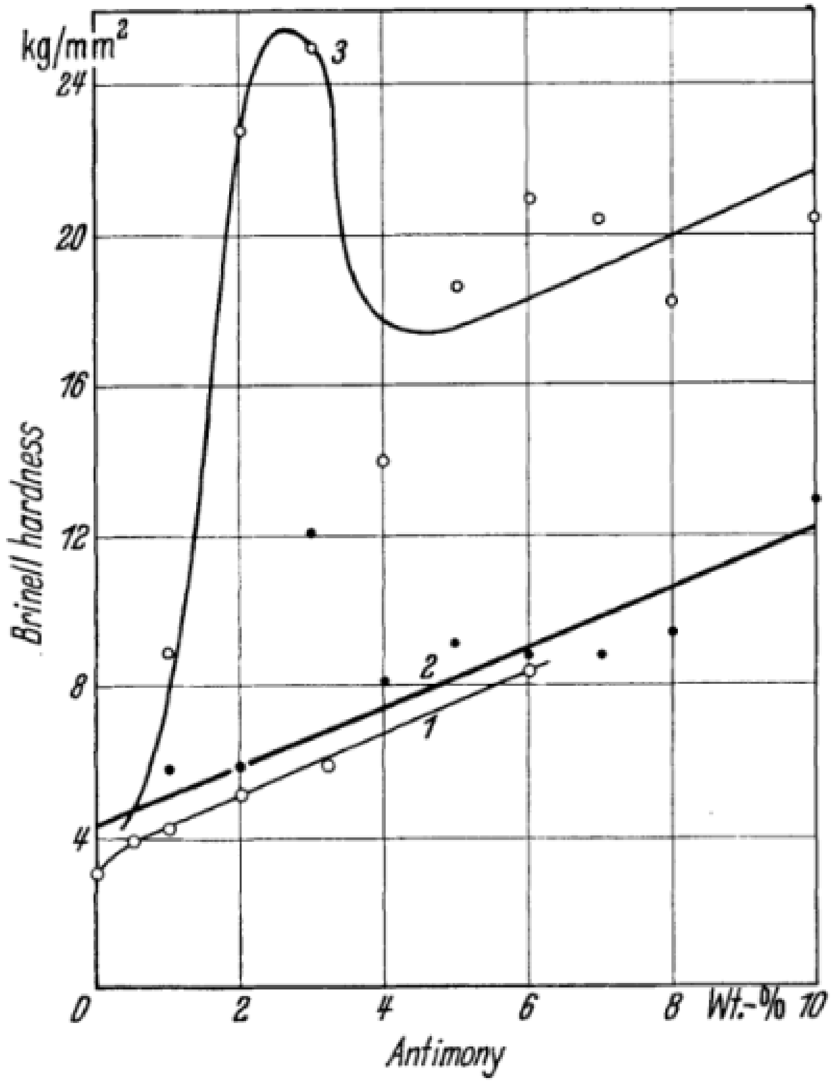
Reduction of antimony content

Hardness of Binary Lead Antimony Alloys – No Secondary Elements

Curve 1 Heat treated and quenched - no ageing
Curve 2 Quenched from 235 C- no ageing
Curve 3 Preceding samples age hardened



W Hoffman Lead and lead alloys properties and technology

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Sample preparation hand casting trials for connector components

Hand casting set-up

Pouring temperature: 340 C

Mould temperature: 130 C

Quenching water temperature: 30 C

Ambient temperature: 18 C

Test samples
Lead alloy: 1.7% Sb, 0.25% Sn, 0.027%As, 0.03% Se

Procedure:

1. Water quenching direct from the mould
2. Ambient air cooled direct from mould

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Summary of alloy choice and required characteristics

Alloy components and their function

Antimony : Hardness, fluidity for casting, conductivity in corrosion layer

Tin: Corrosion resistance and fluidity for casting

Arsenic: age hardening improvement

Selenium: Grain refinement, also aids hardness and improves corrosion resistance

New alloy specification for low antimony formation connector heads

AN	Element	Min	**Value**	Max
29	Cu	0,0000	**0,0043**	0,0500
33	As	0,1400	**0,1654**	0,1800
34	Se	0,0300	**0,0369**	0,0500
47	Ag	0,0000	**0,0033**	0,0400
50	Sn	0,2000	**0,2836**	0,3000
51	Sb	1,6000	**1,7058**	1,8000
80	Pb	residue	**residue**	residue
83	Bi	0,0000	**0,0410**	0,1000

Cost saving per connector: 0.57 USD

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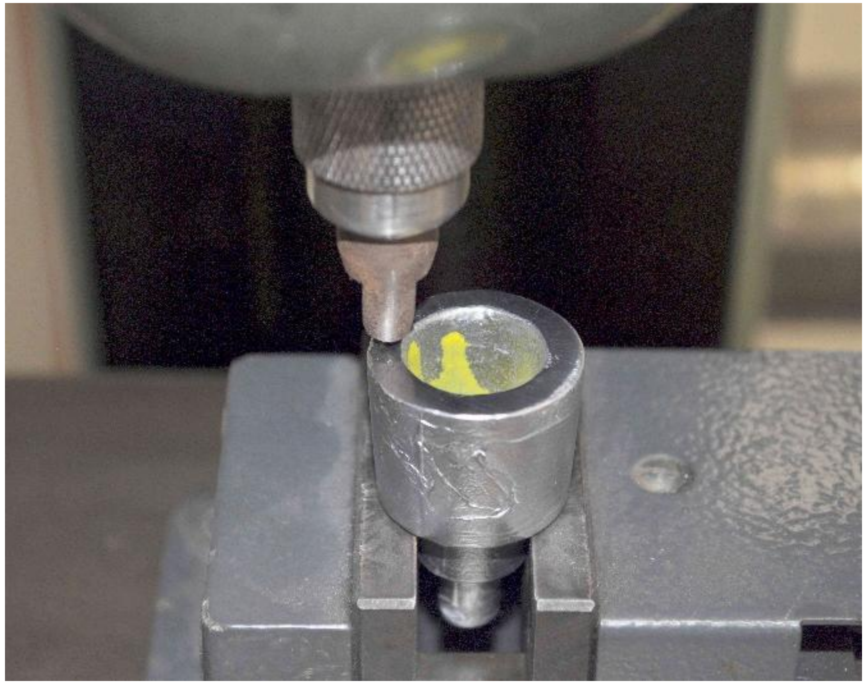
Hardness testing

Samples aged for 1 month

LPD ID	Client Batch Identification/Description	Average Hardness (HV1.0)
Z293-B	New Alloy Untreated age hardened	12.6
Z293-A	8% Sb Alloy Untreated age hardened	18.4
Z293-D	New Alloy Control Quenched 240°C	23.9
Z293-C	New Alloy Quenched from casting	21.8

LPD Lab Services Limited



Vickers hardness tool and connector sample

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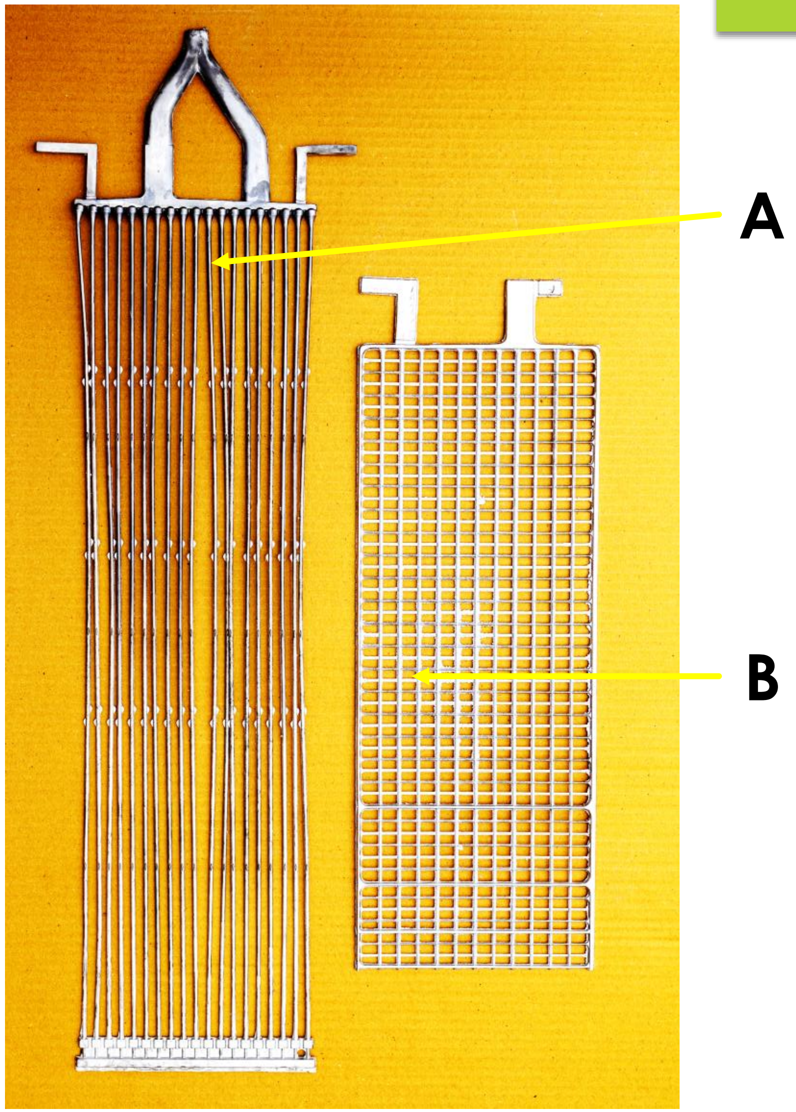
Case Study 2 – Microtex Pvte Ltd

Grid types used in A flat plate and B tubular positive plate Microtex lead acid batteries

Current lead alloys:
A: Lead – 5% antimony pressure diecast alloy
B: Low antimony (1.6% Sb-selenium alloys



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Relationship between hardness, Young's Modulus UTS, creep strength

The higher the UTS the lower the higher the creep resistance

$$\text{Young's Modulus} = E = \frac{stress}{strain} = \frac{\frac{Force}{Area}}{\frac{\Delta length}{original\ length}} = \frac{normal\ stress}{normal\ strain}$$

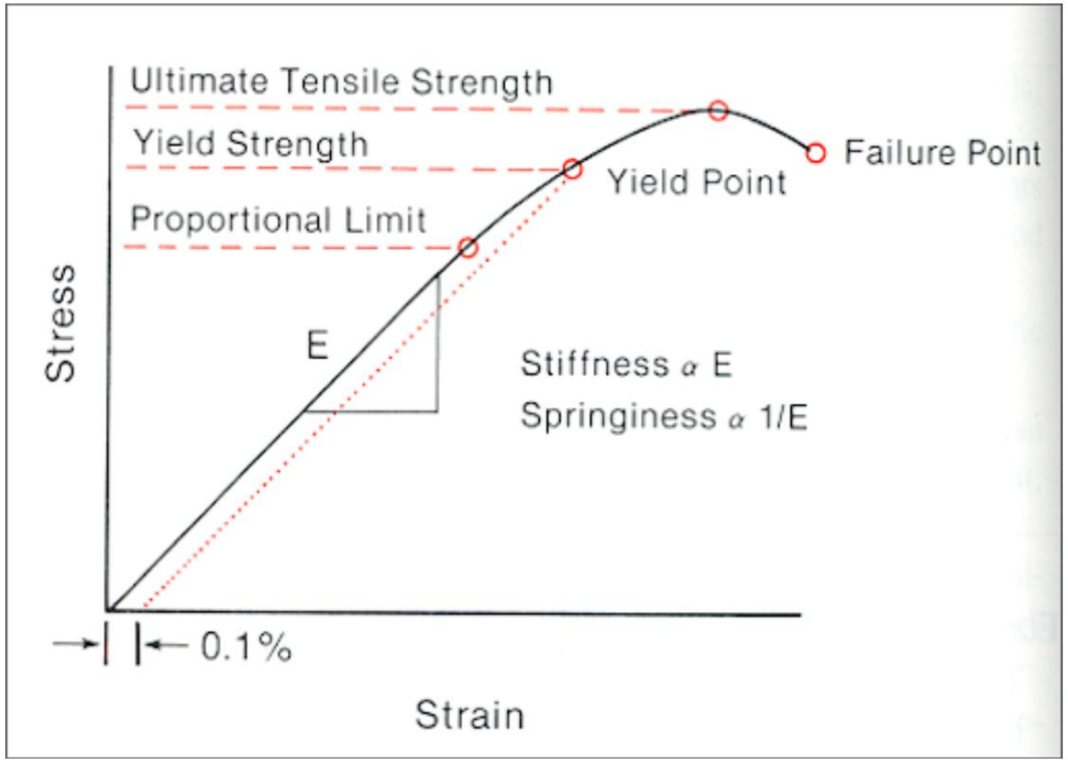
The higher the Young's modulus the greater the force needed to create strain (deformation)

Creep propagates by dislocation movement over long time periods.

Higher Young's modulus means less deformation and lower creep strain.

UTS is proportional to Yield Strength

Higher UTS = higher creep resistance.



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Corrosion resistance of various lead alloys.

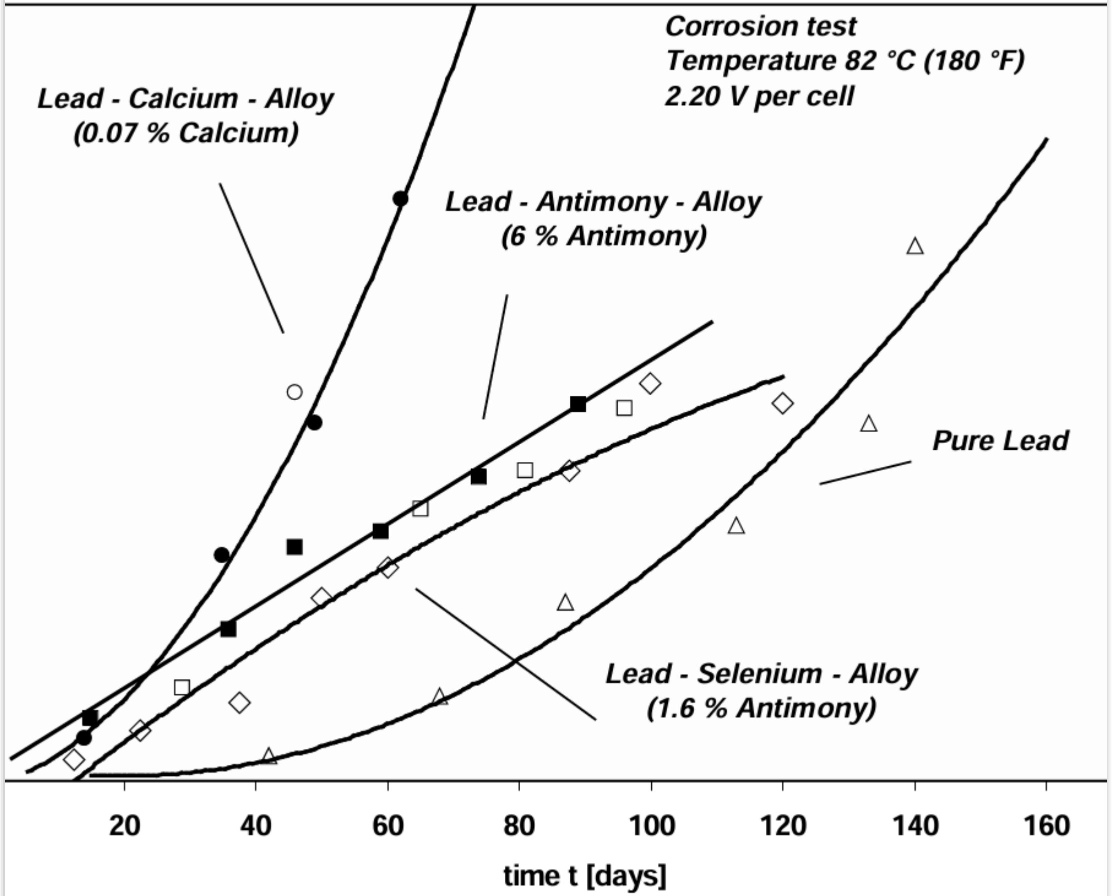
The amount of creep is related the amount of corrosion

Lead selenium (1.6%Sb) alloy has the lowest corrosion rate of all the alloys listed.

Lead calcium has the highest corrosion rate. It would be expected that grid growth would be higher due to creep with this alloy.

Improving the UTS of the alloy would reduce the creep strain and reduce the grid growth.

Corrosion of Lead Alloys



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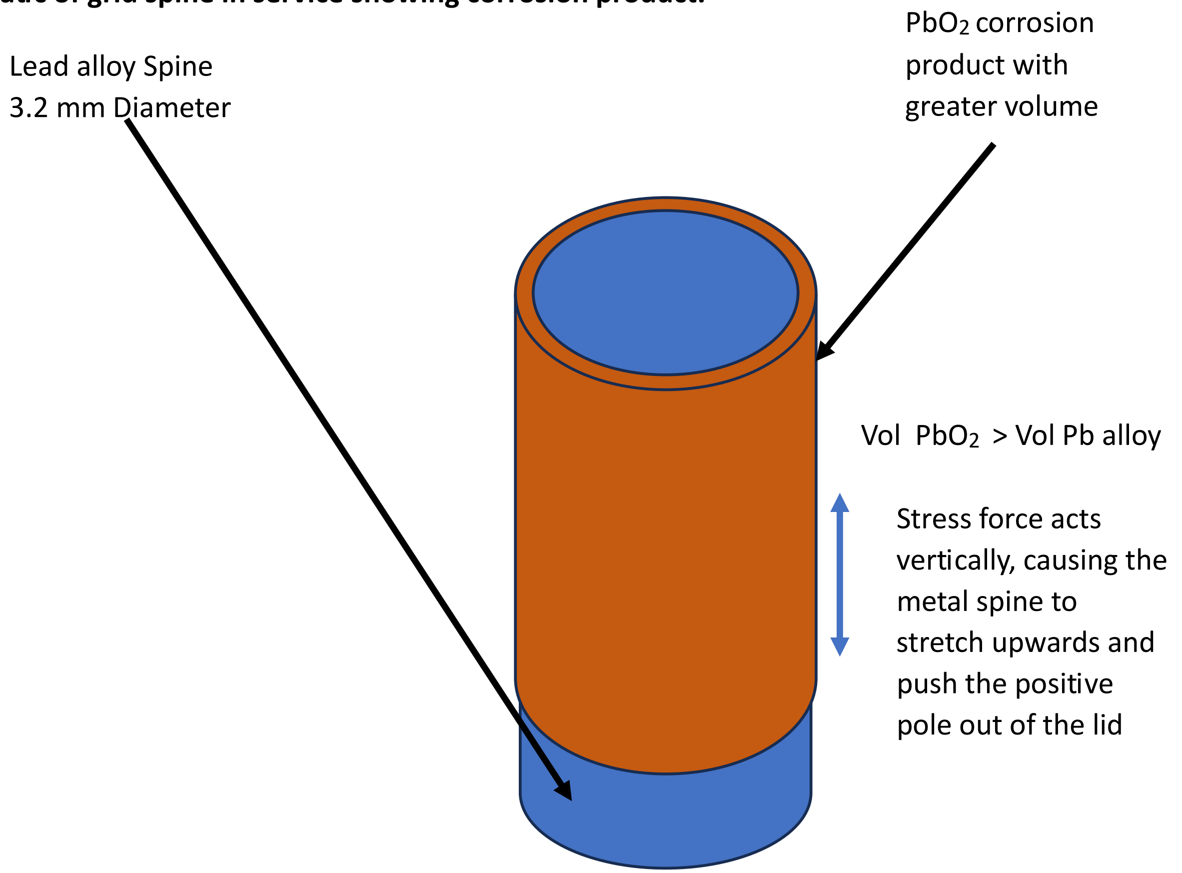
Schematic of a grid spine in service showing a positive corrosion layer

For deep cycle applications Pb/Sb alloys prevent formation of a passivation layer.

Pb/Ca alloys can suffer from premature capacity loss

Mechanical strength and creep resistance is higher with Pb/Sb alloys

a. **Schematic of grid spine in service showing corrosion product.**



The greater volume of PbO_2 creates a s volume stress that causes strain reaction below the yield stress. The subsequent spine growth is a cause of cell failure.

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Tensile tests for heat treated low antimony alloys

Spine samples of grids that had been cast then either air cooled or quenched were subjected to tensile testing.

The same spine castings were sampled after 1 week age hardening

The samples tested were all 1.6% Sb alloy

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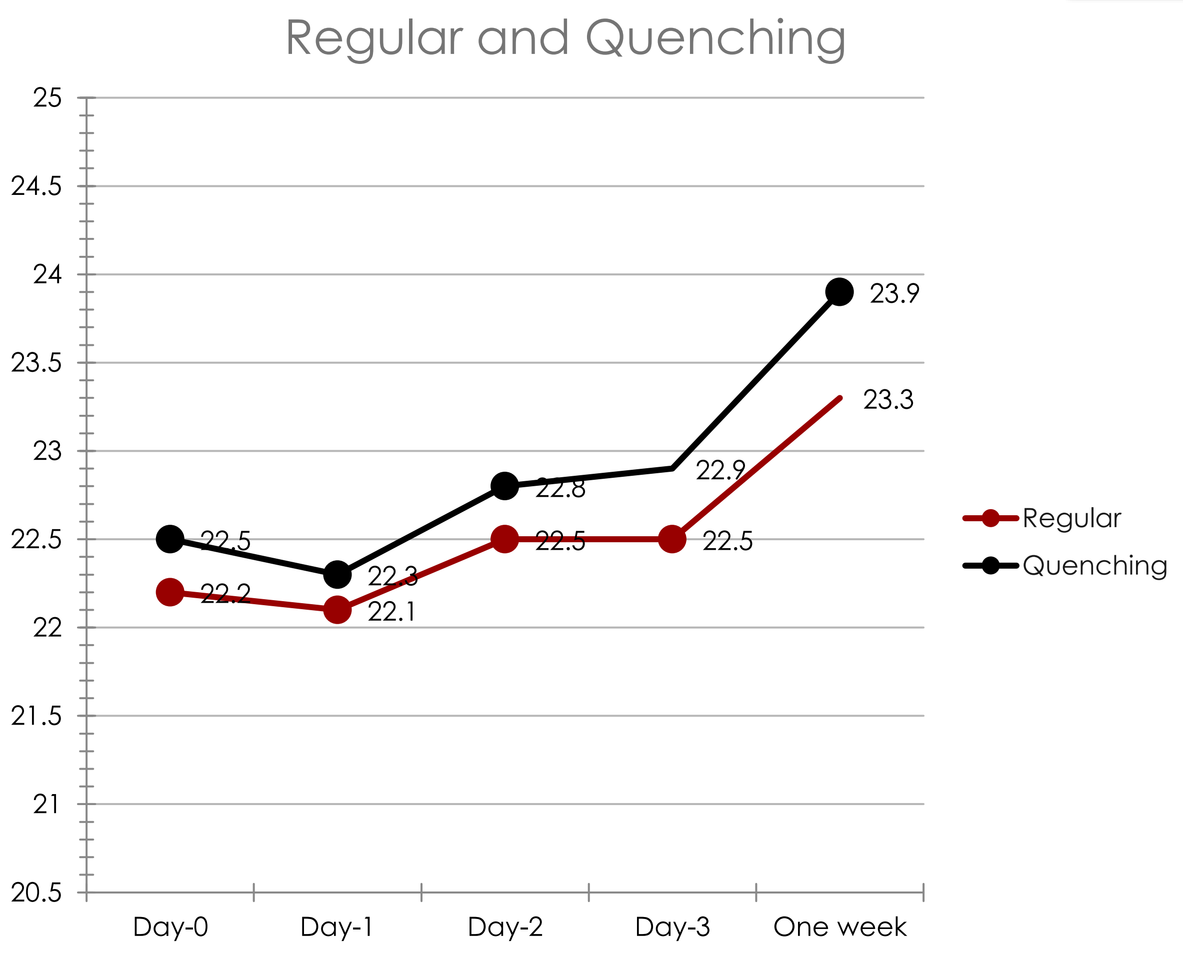
UTS testing results for spines

Two batches of samples were tested, quenched and age hardened and air cooled and age hardened

The results show a slight increase in UTS for spines water quenched immediately after casting

Quenching was achieved by placing the entire gid into a water container straight from the machine and before cropping.

Further tests are continuing with heat treatment and alternative alloy content.



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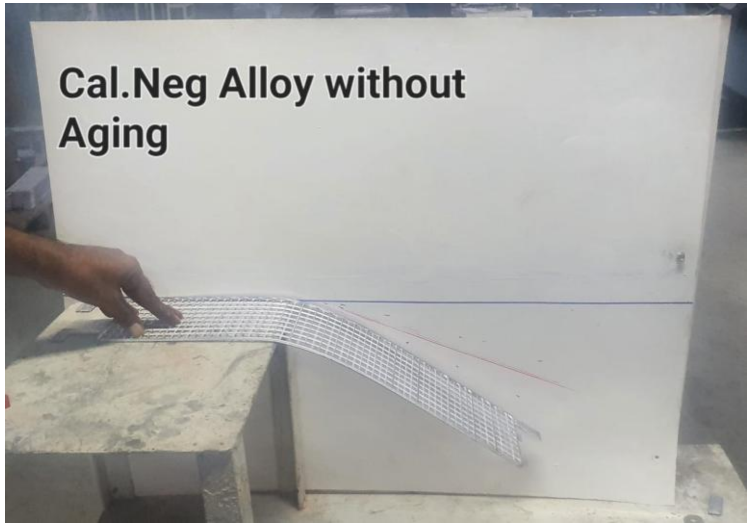
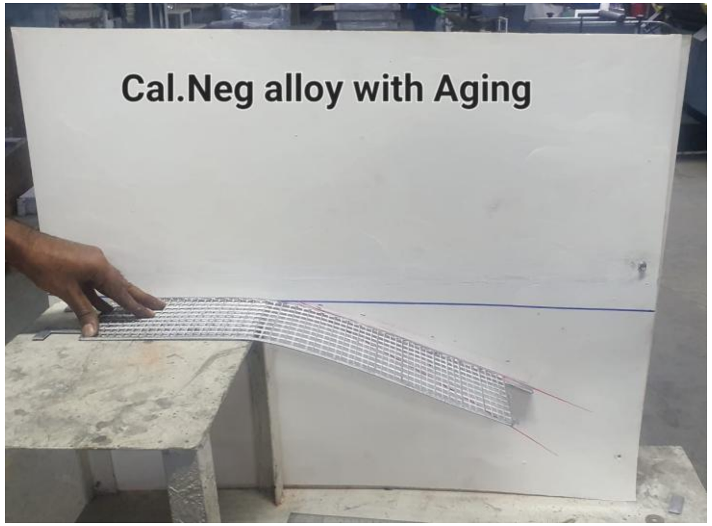
Processing guidelines low antimony and calcium lead alloys

* Flat plate grid hardening – lead calcium alloys

Shown here is a simple method to measure the grid strength for pasting

Lead calcium grids are inherently softer than lead antimony grids. They harden with ageing. It is necessary to check the strength of the grids before pasting to avoid scrap due to deformation of grids. By holding a fixed position of the grid on a flat surface then releasing the free edge, the angle of droop will indicate the stiffness of the grid. A position can be found which indicates the grids' suitability for the pasting process. In many cases the strength of PbCa grids can be improved by heat treatment before pasting.





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Surface dross lead calcium alloys – removal and minimisation of secondary element loss.

Secondary elements of tin, selenium and arsenic at the pot surface are oxidised. If they are removed by normal drossing methods the surface concentration becomes zero. This creates a concentration gradient causing further diffusion of the additive metals to the surface. If they are continually removed these additives will become depleted and ineffectual.

Surface dross contains secondary alloy elements. High tin levels cause a sticky, shiny pot dross.

Typical dross removal, takes out the secondary elements. This causes further depletion within the bulk molten metal.

Dross should be stirred into the pot before removal

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Processing guidelines low antimony and calcium lead alloys.

Current alloy specifications with casting conditions for flat plate grids

Lower Sb and Pb/Ca alloys require higher operating temperatures.

Alloy	%Ca	%Sb	%Sn	%As	%Se	%Al
Low Sb	-	1.6 – 1.8	0.2 – 0.4	0.12 – 0.18	0.02 – 0.04	-
Ca Pos	0.06 – 0.08	-	0.8 – 1.5		-	0.02 – 0.04
Ca Neg	0.08 – 0.12	-	0.3 – 0.6		-	0.02 – 0.04

Current lead alloy specifications

Machine settings and drossing method

Alloy	Pot Temp. ⁰C	Feed line Temp. ⁰C	Ladle Temp ⁰C	Drossing method
Low Sb	480 – 500	500 - 510	500 - 510	Stir and remove
Ca Pos	500 – 520	510 – 530	510 – 530	Stir and remove
Ca Neg	500 – 520	510 – 530	510 – 530	Stir and remove

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Lead alloy component costs
Case 1 Formation connector
Case 2 Battery spine grid

Alloy	component weight	2024 cost	2025 cost	component cost increase	Cost saving
	Kg	USD	USD	USD	USD
Pb - 8%Sb	0.24	0.81	1.65	0.84	
Pb - 1.7%Sb	0.24	0.68	0.86	0.18	0.79
Pb - 5%Sb	0.60	1.70	3.19	1.49	
Pb - 1.6%Sb	0.60	1.70	2.12	0.42	1.07

2025 Lead price (USD/Kg) = 2.7
2025 antimony price (USD/Kg) = 55.0

2024 lead price (USD/Kg) = 2.4
2024 antimony price (USD/Kg) = 11.0

Component price = weight (Kg) x SMPb x (100- sb%)/100 + weight (Kg) x SMSb x (sb%/100)

SMPb = Stock market price lead/Kg
SMSb = Stock market price antimony/Kg

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Properties needed from PbA grids for different market applications

The duty cycle of a lead acid battery varies greatly according to its application.

Stationary back-up and standby power require corrosion resistance and low gassing rates.

Traction and regular discharge duties such as solar, require recovery from deep discharges without paste shedding. Long cycle life increases the ROI.

CHARACTERISTIC	*LEAD SELENIUM*	*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)	Fair (3 Months)	Good (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	Fair (Typ. 1% per Day)	Good (Typ. 0.5% 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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Contact details

Follow BESTmag (esp) for full coverage of these and future testing results.

For more information on this presentation or lead acid battery alloys, or for any other questions on lead acid batteries, contact Mike McDonagh at

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