

A COMPARISON OF LEAD CALCIUM & LEAD SELENIUM ALLOYS: Separating Fact From Fiction

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Introduction

A significant chapter in the history of the lead-acid battery, and its development and use in the United States, has centered on the differences in technology between the antimony based lead alloys and those utilizing lead calcium. For many years, the most common battery chemistries used in the U.S. for lead-acid batteries were the high-antimony lead alloy compositions. Antimony was first identified and used as an alloy to lead grids as far back as 1881, because of the good properties it gave to the alloy in terms of strength, handling, and improved production casting.¹ Antimony is an alloy added to lead primarily to maintain the rigidity and structural integrity of the casted lead grids, thus improving the quality and yields during the battery manufacturing process. The concentrations of antimony to lead were initially in the 8% - 12% range for most flooded batteries built up to about 1955, with concentrations gradually being reduced to the 4% - 6% range.²

But along with the proliferation of applications requiring DC battery back-up, came a growing awareness of certain limitations and problems associated with high-antimony lead-acid battery design. These problems centered on the tendency of high-antimony lead alloy towards higher hydrogen evolution under both float and recharge conditions, leading to increased levels of out-gassing. This led to more frequent watering and maintenance of the antimony batteries as they aged. This issue motivated the US battery industry to find alternative alloys.

Five years of research at the Bell Labs led to the introduction of lead calcium alloy compositions in 1935, as a response to the problems with high antimony alloys. The lead calcium alloy offered the primary advantages of low water consumption and stable float charge characteristics over the life of the battery, and was intended to enhance flooded battery performance, reliability, and expected life.³ Once introduced, the adoption of the lead calcium battery design in the US was very rapid, and within a relatively short period of time high antimony battery designs had been eliminated by most users for use in stationary applications. It should be noted that though high-antimony battery designs were eliminated for typical float applications, they continue to be widely used here in the US throughout the 'calcium years' for a wide range of high-cycling motive applications.

What is far less known in the United States is how the European battery manufacturers responded to this issue, especially given that they faced the same field problems and issues with high antimony designs that US users experienced. Like their US counterparts, the European manufacturers experimented with a variety of different alloys and approaches, but in the end decided on a very different approach to the problem. The result was a lead acid battery utilizing lead alloys with far lower levels of antimony (< 2%) along with addition of selenium for stabilization and the refinement of the lead grains. This alloy is referred to as lead selenium.

The position of the lead selenium battery manufacturers is that modern lead selenium based batteries have dramatically improved performance with regard to watering cycles and maintenance over the older high antimony designs, and in fact, argue that in some key areas they can demonstrate performance advantages over modern lead calcium based products. They point today to decades of proven performance and reliability of the low-antimony designs throughout Europe, Asia, and even in the US for the same kinds of demanding, mission critical applications found throughout the US telecom, utility, data center, and industrial sectors. ⁴

Nevertheless for decades the Europeans have faced stiff resistance from US customers, resellers, and integrators, who have been reluctant to even re-examine the issue of lead calcium vs. lead selenium alloys. Much of the institutional resistance in the US to lead selenium batteries can be attributed to a long history of good performance by lead calcium battery products, good sales and marketing by US battery manufacturers, and long standing product specifications that are slow to change. There is also a distant industry memory of the old problems associated with high antimony batteries that still exists, making organizations reluctant to consider other potential options for lead acid batteries.

We recognize that many of these issues have been around for decades, and that a lot of thoughtful technical discussions have preceded this paper. Some might question why this issue should be resurfaced, given the decades of history and discussion that have already taken place. But while these issues are not new, we believe there are some driving forces in the

marketplace that warrant a re-examination of how these lead alloy compositions compare with each other. The accelerating drive towards the globalization of commerce, combined with the increasing need for a more efficient supply chain management process, is placing increasingly severe pressure on sourcing and materials management groups to broaden the potential base of viable product sources. Their primary interest is in identifying all possible vendors and products that will meet their requirements and give them more competitive options for sourcing. The 54-week lead times of a few years ago for flooded lead-acid batteries are still a painful memory for many, and the steady improvement of economic conditions combined with limited battery manufacturing capacity in the US brings the potential for a return to some of these critical sourcing issues.

There are two primary objectives of this paper:

1. To provide a brief history of the development and use of both lead selenium and lead calcium alloy compositions, and to objectively compare and contrast the design & performance specifications and capabilities of each type.
2. To draw conclusions about the performance, reliability, and life expectancy of each lead alloy composition, as a way to determine the overall suitability of each alloy type for both current and emerging mission critical applications in the US, particularly for the telecommunications, electric utility, and industrial sectors.

This exercise may be timely, given the external pressures that are now impacting organizations in their drive to improve the performance and reliability of their mission-critical systems, combined with severe pressure to reduce costs and increase supply-chain efficiency. Understanding all of our sourcing options for lead acid batteries, based on valid and current assumptions, could be a critical part of improving the management of this process.

Brief History of Lead Alloy Development

With regard to the subject of lead alloys and their differences, we should first recognize that the basic and positive reactions which occur in any lead acid battery are essentially the same, regardless of whether it is a lead antimony or lead calcium based grid. These are the normal, reversible actions and processes that deliver current during battery discharge, and the storage of energy during charge. The fundamental reactions involving the conversion of the sponge lead of the negative plate, the lead dioxide active material in the positive plates, and the electrolyte over to lead sulphate (and back) are essentially the same regardless of lead alloy composition.⁵ Interestingly, it is the second class of reactions occurring in the lead acid battery during cell operation, that are primarily negative or parasitic, which in some regards helps us identify and define the differences between these two lead alloys.

The lead acid battery goes back to Raymond Gaston Plante, who in 1860 performed the original research and development of batteries using lead material and sulfuric acid. Breakthrough development was also done by Faure, who first conceived and developed the process for pasting lead oxide active material on lead grids, which significantly reduced the costs and time involved in battery manufacturing. Even early on with the original lead battery designs, there were two primary challenges: 1.) the improvement of lead alloy compositions for better strength, improved casting, and conductive performance, and 2.) developing better compositions and processes for the application and retention of active material on the grids.⁶ These challenges are still with us today.

In one respect, lead-acid battery fundamentals today are very much the same as the turn of the century. Of course, the growth of the lead acid battery industry in the US has been rapid, with continuous refinement and improvement in the design, development of manufacturing equipment and processes, recovery methods, active material utilization and production, components, and battery packaging. But the debate between lead alloy compositions continues to dominate and define much of the technical and market debate within the US battery industry.

There are good reasons for this. The choice of grid alloy compositions used in a battery directly impacts the grid and product design, the plate manufacturing and assembly process, as well as long term product performance and reliability of the product. Manufacturability is a major issue, as the chosen alloy directly impacts the physical strength and hardness of the grid for the ability to handle without distortion and breakage. Grid alloy selection also influences grid corrosion and grid growth, which impacts battery performance and life via mechanical strength, conductivity, and the degree of positive active material adhesion to the plate grid.⁷

Lead, as a malleable metal, is generally too soft to be used as a production grid material, except for a few battery types that utilize pure lead for high performance and life (e.g. Plante thick plate designs, telecom Round Cell, DIN GroE designs).

Antimony was first identified and used as a lead alloy as far back as 1881, and it was immediately recognized that lead antimony alloys brought significant benefits to the performance and strength of lead plates used in battery production. Antimony is used to strengthen and harden the lead grids for improved handling and casting, as well as having good conductive properties. At one time almost all lead acid batteries were made with lead antimony grids, and the original antimony alloy concentrations were in the 8-12% range. (Today the more common concentration levels we see in batteries using lead antimony alloys are in the 4-6% range.)⁸

Identifying the Problem:

The use of lead antimony alloys spurred the growth of the battery industry and contributed to the improvements in manufacturing and the reduction of costs. But even with these benefits, there was a growing awareness by 1930 of some issues involving lead antimony alloys. As the use of lead-acid batteries grew rapidly, particularly in the telecommunications and utility/switchgear sectors, users began to experience increases in the watering requirements and increased float voltages as the batteries aged.

Beginning in 1930, researchers at Bell Labs began to work on developing a better understanding of the inner workings of the antimonial lead acid battery, and experimenting with different types of lead alloy compositions. Led by W.E.Haring, the team published its findings in 1935, where they confirmed a phenomena termed 'antimonial poisoning'. This described the freeing of antimony from the positive plate as a result of normal charge current corrosion and the charge/discharge operation of the battery. The freed antimony then dissolves and migrates to the negative electrode and is deposited on the active material of the negative plate. This migration of antimony over time leads to an increase in the local action between the antimony and the sponge lead of the negative plate, reducing charging efficiency.⁹

The long-term impact to the cell is an increase in the self-discharge rate of the battery, as well as lowering the gas potential of the cell, causing increased hydrogen evolution. Over time, the cell requires increasingly higher levels of float current in order to compensate for the local actions and losses, so the rate of gas evolution and water loss accelerates as the battery ages.¹⁰ The main impact to the user was seen as the loss of water due to increased hydrogen evolution, requiring more frequent watering and maintenance intervals. Once this phenomenon was identified and understood, the US telecom sector in particular pressed for a solution to this problem.

American Response: Lead Calcium Alloy

The solution found by Haring & Thomas at Bell Labs was the development of a lead calcium alloy composition, which addressed the maintenance issues while giving the lead grids good density, conductivity, and tensile strength (comparable to the lead antimony alloys). It was found that by adding calcium to the lead, with the best results in concentrations of 0.065% - 0.09% (not to exceed 0.10%), created a battery grid with some improved characteristics over the high antimony alloys.¹¹ Further research found that adding tin to the lead calcium alloy increased the grid hardness and strength, while imparting good melting, casting, and wetting properties. (Recently aluminum has been added to the lead calcium and lead-tin-calcium alloys, as a way to stabilize the calcium.)¹²

The net result was a battery that used less water, at a rate that stayed constant even as the battery aged. Additionally, the lead calcium batteries were stable under float current, with a broad float voltage range. Another advantage of lead calcium over the high antimony lead alloys was the reduced self-discharge characteristics, typically at 0.5%/day at 25°C.¹³ This reduction in maintenance and watering requirements, along with the good stability under float charge, led to the rapid adoption of lead calcium batteries by most users in the US. Bell Labs first specified the lead calcium alloy battery for stationary applications in 1951, and by the 1960's most stationary batteries used in the US were based on lead calcium alloy compositions.

Benefit Summary of Lead-Calcium Alloys:

- Good grid density, conductivity, and tensile strength
- Reduced water consumption over the life of the battery
- Reduced electrolyte evolution and generation of hydrogen gas
- Better self-discharge characteristics (typically 0.5%/day at 25C)
- Stable rate of under float charge over the life of the battery; consistent current draw

European Response: Lead Selenium Alloy

What is not as well known in the US is the European response to the problems that they were also experiencing with batteries manufactured with high antimony lead alloys. Like Bell Labs, the Europeans experimented with lead calcium alloys, but after identifying potential issues, they refocused their efforts on low antimony lead compositions that would significantly reduce and potentially eliminate the problems of antimonial migration. Over time antimony concentrations under 2% became the standard for stationary lead acid batteries in Europe. Key to this approach was the use of selenium in the alloy compositions, which acted as a stabilizer for the antimony, and led to a more hardened lead with a finer, denser grain structure. This grain refinement characteristic brought by the addition of selenium created a lead alloy that was more corrosion resistant and virtually eliminated inter-granular corrosion, a common cause of battery failure. The Europeans viewed the lead selenium alloy as a solution that combined the advantages of both the lead calcium and lead antimony alloys, while reducing the disadvantages. This position is recognized by David Linden, who noted "...because of the beneficial effects of antimony, its complete elimination may not be desirable, and low antimony-lead alloys are a useful compromise."

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Benefit Summary of Lead Selenium Alloys:

- Good grid density, conductivity, and tensile strength
- Reduced water consumption and little antimony migration
- Stability under float charge, consistent cell voltages
- No positive plate growth.
- Corrosion resistant and virtually eliminates inter-granular corrosion
- Superior cycling and deep discharge performance

Lead Calcium and Lead Selenium Disadvantages

As with any solution, there are compromises involved in the selection of either lead alloy composition. While the development of lead selenium alloys led to significant reductions in watering cycles, the demonstrated water requirements for lead selenium are still typically higher than lead calcium, particularly as the battery ages. Also, the self-discharge characteristics of lead selenium are higher than lead calcium, with a typical discharge rate of 1.0%/day (25°C) versus the 0.5% rate/day (25°C) for lead calcium. This translates to a typical shelf life of 3 months for a filled lead selenium battery versus 6 months for a filled lead calcium battery.¹⁵

A solution that was developed by certain lead selenium battery manufacturers to address the watering issue has been the development and implementation of recombination catalysts installed over the battery vents. These devices use a ceramic encapsulated palladium catalyst to recombine hydrogen generated under charge/overcharge conditions with oxygen, creating water which is returned to the cell. One manufacturer's device claims 98% efficiency in the recombination of outgassed hydrogen, with dramatic reductions in watering maintenance cycles that match and even exceed lead calcium. This technology has been used globally for over two decades, and the manufacturer points to empiric field data that supports the performance and results claimed.

Lead calcium alloys have their issues as well. One problem with lead calcium compositions is the gradual onset of creep resistance that leads to positive plate growth. This can occur in alloy compositions where the calcium levels exceed 0.09% in the lead alloy mix. What occurs is the precipitation of the corrosive compound Pb_3Ca at the lead grain boundaries, which over time penetrates the grains and leads to an increase in the plate volume. The net result of this positive plate growth can be the stressing and failure of the jar cover and terminal post seals.¹⁶

Another issue with lead calcium batteries that has been observed is the occasional premature loss of battery capacity. This is a phenomenon whose causes are not yet fully understood today. Tests on lead calcium batteries in the field have observed the presence of a passivating layer of lead sulfate between the grid and the active material. The primary effect is reduced conductivity of the active material and uneven current distribution throughout the cell. Over time we see the double sulphation reactions limited increasingly to the vicinity of the grid, while the active material remains isolated and undercharged. This passivation, or separation of the active material from the grid, leads to the loss of performance and unequal cell voltages, requiring more frequent equalization charges and introducing an element of uncertainty into the battery life and performance levels. This phenomenon was a driving force in the IEEE 450 recommendation to conduct capacity testing on lead calcium batteries on a regular basis.¹⁷

Batteries utilizing both lead calcium and lead selenium alloys exhibit outgassing during normal charge/discharge conditions, primarily in the form of hydrogen and oxygen. Under certain overvoltage conditions or excessive charge, acid vapor can be generated by any flooded lead acid battery. Early studies on antimony alloys by Haring reference the potential for the generation of trace amounts of the toxic gas stibine under overcharge conditions. Both Linden and Bode make no reference to stibine gas in their works, and studies by Sand, Grant, and Lloyd determined that stibine gas does not form very readily, and then is detected in trace amounts only under extreme charge densities and high acid concentrations. With both battery types, the primary concern is the potential build-up of explosive hydrogen gas levels; adequate ventilation precautions typically address this potential issue.

Comparative Matrix: Lead Calcium vs. Lead Selenium Alloys

The following matrix provides a good comparative summary of the primary characteristics of each lead alloy composition:

Behavior Characteristics of the Primary Lead Alloys

Antimony < 2%, Calcium < 1%

<i>CHARACTERISTIC</i>	<i>LEAD ANTIMONY</i>	<i>LEAD CALCIUM</i>
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	1% per Day	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

Both lead calcium and lead selenium alloys exhibit very comparable performance in terms of the primary, positive performance characteristics of normal battery operation. The matrix reveals that there are some differences in the lead alloy compositions, primarily in the secondary performance characteristics. Lead calcium performs better with regard to self-discharge rates, and (in the absence of a recombination catalyst for lead selenium batteries) typically will have some advantages in watering cycle intervals. Lead calcium alloys have good stability under charge/discharge conditions. The lead selenium has superior cycling characteristics, good stability under charge/discharge conditions, and has better corrosion resistance and resistance to positive plate growth. Lead selenium also has very predictable performance response and behavior.

But with regard to the primary electrochemical characteristics, it can be argued that there is general parity between the lead calcium and lead selenium performance levels. Batteries built with both alloy compositions are designed and manufactured for 20 year life, and will operate under all typical float applications. There are no discernible differences in the temperature ranges recommended for nominal operation and life. The comparative data indicates that there are no conclusive primary performance differences between lead selenium and lead calcium alloys that would discourage either from being considered for a typical mission critical application in the US.

Conclusion

Using the data and information above, we are led to ask the following questions as an aid to drawing conclusions about the suitability of each of these technologies for typical US telecom, utility, and industrial back-up applications:

1.) ***Which of these battery technologies is MOST suited for mission critical applications in the US?*** Based on the evaluation metrics above, it is not immediately clear what the answer is to this question. Battery manufacturers on each side of this issue can make good arguments in favor of their technology, highlighting the design and product advantages that they bring. At the same time, customers have positions on this issue, based primarily on their experience and product history. For example, the large RBOC and ILEC telecom customers in the US might see this issue one way, while on the other side of the Atlantic large telecom companies like Deutsch Telecom and British Telecom would see it another. Yet despite these differing product views, we should recognize what all of these end-users have in common: they are all demanding customers, with exacting battery product specifications, and high expectations for product quality, performance, and life expectancy. Current battery preferences aside, they share many common interests.

Attempting any qualitative final judgments about the suitability of each of these technologies for US applications runs the risk of continuing the endless partisan debate among the manufacturers, while missing the opportunity for a common sense resolution of this issue. Perhaps then it makes sense to slightly modify the primary question we need to be asking ourselves.

2.) ***Which of these technologies IS suited to meet the requirements for mission-critical applications in the US?*** We believe that the answer to that, backed by a review of common product specifications, test data, and decades of empiric field data, is both. We think all of the available data indicates that both the lead calcium and lead selenium battery technologies, properly designed and manufactured, meet the long-term requirements for today's mission critical applications in the US.

In some regards, the ongoing marketing battles and technical 'specmanship' between these two technology camps, even 45 plus years later, are at odds with the new forces and market drivers that are increasingly impacting the telecommunications, utility, and industrial sectors. Globalization, along with the accelerating drive to optimize efficiencies in our complex supply chains, is placing severe pressure on the operations, sourcing, and project management arms of the organization to seek and improve the availability of competitive solutions to their needs. This comprehensive retooling of our business processes requires that we constantly reevaluate our current sources of supply, to ensure that we are doing everything possible to make our customers more competitive and efficient. Expanding the availability of quality, reliable battery products, that offer our customers a wider range of viable solutions, is consistent with these market realities. It is the cornerstone of the principles of continuous improvement and value engineering, for our own organizations and those of our customers.

In our industry we are fortunate to have reputable, quality manufacturers on both sides of this issue, which are deeply committed to their chosen battery technology and its ongoing improvement. Lead calcium and lead selenium battery products are both mature technologies, utilized by companies with many years of business history, huge installed bases world wide, and extensive battery manufacturing and design experience. All of them have experienced the highs and lows of the battery industry, and are well traveled along the learning curve of success and failure with battery design, manufacture, and field performance.

By opening up the pool of qualified companies and products to our customers, and increasing their options to find competitive solutions, we will help alleviate the market-derived stresses on those groups within the organization that are tasked with the job of cutting costs, increasing efficiency, and improving project management. Modern organizations will benefit when the issues change from increasingly irrelevant arguments on the merits of battery products based on lead calcium vs. lead selenium, and turn instead to considerations such as: the reputation and history of the manufacturer, product manufacturing quality, specified product performance levels, commitment to warranty support, customer service, lead times, and of course, price and delivery. And ultimately, when we help these parts of the organization to better perform their jobs, it is also the best indication that we in this industry are doing ours.

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