

## Advances in the refining and alloying of low-bismuth lead

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### Abstract

A programme has been initiated to improve the performance and eliminate the environmental concerns of the traditional Kroll–Betterton process for bismuth removal from lead. The work has resulted in the development of a new generation of debismuthizing reagents that are comprised of a magnesium–calcium alloy, specially designated as Mag-Cal<sup>TM</sup>. The most common Mag-Cal<sup>TM</sup> alloy contains 70 wt.% magnesium and 30 wt.% calcium. Extensive testing has revealed that addition of Mag-Cal<sup>TM</sup> to the vortex at approximately 480–500 °C, followed by mixing for 5–15 min, provides the best results. With Mag-Cal<sup>TM</sup>, bismuth levels of 0.005 wt.% Bi, or less, are readily achieved without the need for supplemental calcium and antimony additions. Calcium–aluminum master alloys (known as CAL-AL<sup>TM</sup>) have been developed which enable battery-grid manufacturers to achieve target calcium and aluminum specifications with consistently high and predictable recoveries. A new process has been developed for alloying calcium and aluminum into lead. The process has been proven in an extensive campaign of pilot-scale trials. The process uses pure calcium and aluminum in the form of granules of particulates and offers many advantages that will be of significant benefit to lead–calcium alloy producers.

*Keywords:* Refining; Alloys; Lead; Bismuth

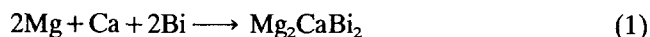
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### 1. Lead debismuthizing with Mag-Cal alloys

For most of this century, the established method for bismuth removal from lead has been the Kroll–Betterton (KB) process in which magnesium and calcium are added to the unrefined lead. Historically, this was done by adding pure magnesium ingots and calcium crown or turnings, either by plunging in a basket or stirring into a vortex. The preferred temperature for making the additions was in the range 380–450 °C. Below this temperature range, the reaction is sluggish, whereas at higher temperatures excessive oxidation of the calcium occurs. Oxidation gives rise to bright flaring, excessive fume generation, higher processing costs, and unpredictable final bismuth levels. Furthermore, the addition of calcium metal to a lead bath is often accompanied by an increase in the bulk temperature of the lead due either to an exothermic release of heat during the reaction and/or to heat generated by the oxidation of calcium metal. Another disadvantage of calcium metal is that it is highly reactive with atmospheric oxygen and humidity. Hence, calcium metal must be packaged, shipped and stored in such a way as to eliminate contact

with air and moisture. For these reasons, the authors' company developed a new generation of debismuthizing reagents comprised of a magnesium–calcium alloy, specially designated as Mag-Cal<sup>TM</sup>.

Davey [1] has summarized the thermodynamic relationships that govern the removal of bismuth from lead by the KB process. The removal of bismuth from lead is governed by the reaction:



Upon dissolution of magnesium and calcium in lead, cooling of the lead bath to near the liquidus (320 °C) will result in precipitation of bismuth according to the above stoichiometry and the following solubility relation:

$$\log([\text{Mg}]^2[\text{Ca}][\text{Bi}]^2) = -7.37 \quad (2)$$

At 320 °C, the dross containing Mg<sub>2</sub>CaBi<sub>2</sub> crystals is normally removed and can be processed further to recover bismuth. Optimization techniques have been employed by many companies to minimize the cost of the addition according to the price of the individual calcium and magnesium reagent metals.

Fig. 1 shows that the minimum alloy requirement usually results when the reagents include 35–40 wt.% Ca. When cost optimization is done, however, because of the higher price of calcium, the lowest cost reagent addition is in the range 30–35 wt.% Ca. Higher initial bismuth levels tend to favour a higher calcium percentage, and lower final bismuth levels tend to favour higher magnesium contents, but the deviation from 30 wt.% is not great.

Because the stoichiometry of the reaction sets a defined ratio of Mg:Ca in the crystals (i.e., 2 mol Mg per 1 mol Ca), the weight ratio of Mg:Ca in the crystals is always 48.6:40.1. Thus, in a 70/30 Mag-Cal reagent, the amount of calcium contained will always determine the amount of reagent required to combine with the bismuth as  $Mg_2CaBi_2$  crystals, i.e.,

Amount of alloy required to remove Bi  
(kg alloy/tonne Pb)

$$= \frac{40.1}{(2 \times 209) \times 0.3} \times (Bi_{\text{final}} - Bi_{\text{initial}}) \times 10 \quad (3a)$$

$$= 3.197 \times \Delta Bi \quad (3b)$$

where Bi is in wt.%.

The excess magnesium contributes to satisfying the solubility relation:

%Mg excess in lead

= amount added – amount consumed by Bi

$$= \left( \frac{3.197 \times 0.7}{10} - \frac{24.3}{209} \right) \times \Delta Bi \quad (4a)$$

$$= 0.1075 \times \Delta Bi \quad (4b)$$

To satisfy the solubility requirement, the amounts in solution are:

$$\%Mg_{\text{total}} = Mg_{\text{excess}} + Mg_{\text{added}}$$

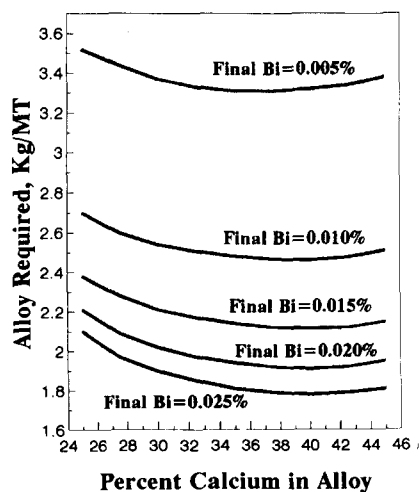


Fig. 1. Effect of calcium percentage on Mag-Cal alloy requirements for lead debismuthizing. Initial bismuth content = 0.50 wt.%.

$$= 0.1705 \Delta Bi + \frac{0.7}{10} \times A \quad (5)$$

where A is the amount of alloy added ( $kg\ t^{-1}$ ) to satisfy the solubility equation

$$\%Ca_{\text{total}} = \frac{0.3}{10} \times A \quad (6)$$

Expanding the logarithms of Eq. (2), and substituting for the dissolved magnesium and calcium yields:

$$\log Ca + 2 \log Mg + 2 \log Bi_{\text{final}} = -7.37 \quad (7a)$$

or

$$\log (0.03 A) + 2 \log (0.1075 \Delta Bi + 0.07 A) + 2 \log Bi_{\text{final}} + 7.37 = 0 \quad (7b)$$

Eq. (7b) can be solved to define the amount of alloy required to saturate the bullion at any initial and final bismuth level. The solutions can then be approximated by a linear equation. In conjunction with Eq. (3), the total alloy requirement (in  $kg\ t^{-1}$ ) can be determined, for example:

$$0.015\ \text{wt.\%}\ Bi_{\text{final}} \quad 1.030 - 0.740\ Bi_{\text{initial}} \text{ to saturate bullion} \quad (8)$$

$$-0.048 + 3.197\ Bi_{\text{initial}} \text{ to remove bi} \quad (9)$$

$$0.982 + 2.457\ Bi_{\text{initial}} \text{ total} \quad (10)$$

$$0.004\ \text{wt.\%}\ Bi_{\text{initial}} \quad 2.644 - 0.933\ Bi_{\text{initial}} \text{ to saturate bullion} \quad (11)$$

$$-0.013 + 3.197\ Bi_{\text{initial}} \text{ to remove Bi} \quad (12)$$

$$2.601 + 2.264\ Bi_{\text{initial}} \text{ total} \quad (13)$$

When analyzing these relationships, it becomes clear that in the case of primary producers, where initial bismuth levels are in the range 0.5–0.6 wt.% and if the final required bismuth is 0.02 wt.%, the majority of the alloy is required to remove the bismuth. To achieve low final bismuth levels, however, significantly more alloy is required to satisfy the solubility requirement, regardless of the initial bismuth level (see Fig. 2).

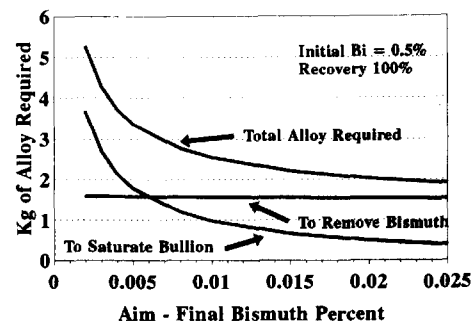


Fig. 2. Contribution of bismuth removal and bullion saturation to total 70/30 Mag-Cal alloy requirement.

1.1 Dissolution characteristics of Mag-Cal™ alloys

In the initial work on Mag-Cal™ development, it was shown that the average dissolving rate of magnesium metal increases linearly with increasing temperature. Magnesium metal does not exothermically release heat over the measured temperature range. Fig. 3 indicates that, compared with magnesium, the dissolution rate of calcium is extremely slow at normal debismuthizing temperatures. Nevertheless, the rate increases exponentially at temperatures in excess of 600 °C. The dissolution of calcium is characterized by the sudden release of heat due to the onset of a highly exothermic dissolution reaction.

Studies of the dissolution of magnesium/calcium alloys show that magnesium-rich alloys behave similarly to magnesium metal, namely, no exothermic heat release and an increased dissolving rate with increasing temperature. Magnesium-rich alloys have excellent shelf life and exhibit virtually 100% reagent recovery with virtually no flaring or fuming when added to liquid lead.

Fig. 4 summarizes the dissolving rate of magnesium and calcium metals and alloys at two temperatures, 425 and 500 °C. As shown, the dissolving rate of 70/30 alloy increases rapidly at higher temperatures and particularly with stirring. Industrial trials have

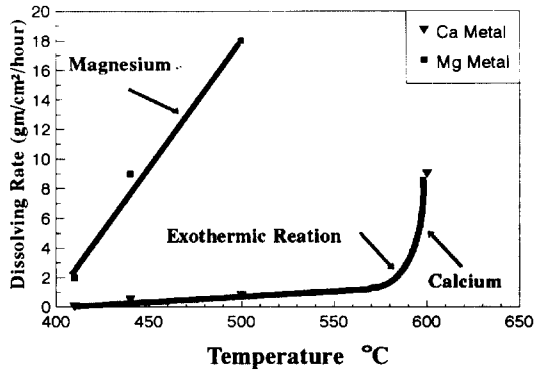


Fig. 3. Dissolution rate of pure magnesium and calcium metals in lead as a function of temperature (results of laboratory tests).

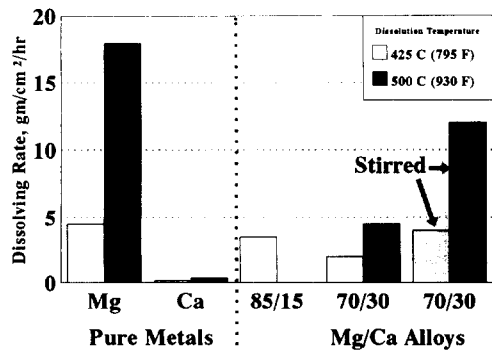


Fig. 4. Dissolution rates of pure magnesium and calcium metals and of Mag-Cal alloys in molten lead (results of laboratory tests).

confirmed that a typical charge of 20 kg Mag-Cal™ ingots to a large lead kettle at 500 °C will completely dissolve in 15–20 min when the ingots are added to a well-stirred vortex.

1.2. Obtaining low-bismuth lead with the KB process

The importance of using higher lead temperatures becomes apparent when the KB process is used to obtain low-bismuth lead (i.e., <0.005 wt.% Bi). Due to the higher amounts of magnesium and calcium required to achieve low final bismuth levels, the initial solubility product of  $[Mg]^2[Ca][Bi]^2$  can be exceeded when conventional (low) lead temperatures are used. Thus, unless the lead temperature is increased, dissolution of magnesium and calcium will become extremely difficult and slow because the intermetallic will start to precipitate (i.e., the lead is saturated) before the reagent addition has completely dissolved. Higher temperatures will require use of Mag-Cal™ due to the violent exothermic reaction when calcium metal is added to lead at higher temperatures.

Hancock and Harris [2] recently defined the solubility product of  $Mg_2CaBi_2$  in lead as a function of temperature:

$$\log([Mg]^2[Ca][Bi])^2 = 12.007 - 11\,437/T \tag{14}$$

where  $T$  is in K. To debismuthize from 0.5 to 0.004 wt.% Bi, according to Eq. (13), requires  $3.733\text{ kg t}^{-1}$  of 70/30 Mag-Cal™ which corresponds to 2.631 kg Mg/tonne + 1.120 kg Ca/tonne. Therefore, the amounts dissolved initially in the kettle are 0.263 wt.% Mg, 0.112 wt.% Ca and 0.5 wt.% Bi. Using Eq. (14), and calculating the solubility product based on these percentages, it can be shown that the minimum temperature required for complete dissolution is 500 °C. Fig. 5 shows the difference between the amount of magnesium and cal-

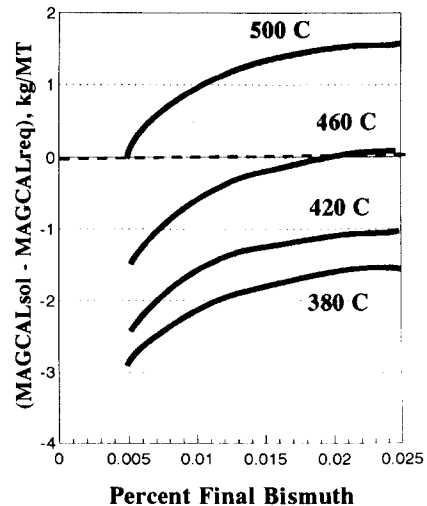


Fig. 5. Mag-Cal requirements vs. 70/30 Mag-Cal solubility as a function of temperature. Initial bismuth content=0.5 wt.%.

cium that can be dissolved and the amounts of magnesium and calcium required to achieve various final bismuth levels  $\Delta$  ( $\text{Mag-Cal}_{\text{sol}} - \text{Mag-Cal}_{\text{req}}$ ) as a function of temperature. A number greater than zero indicates that all the required reagent can be dissolved into the lead. This indicates the importance of using higher temperatures and Mag-Cal<sup>TM</sup> to achieve low-bismuth lead.

### 1.2.1. Example I: debismuthizing of primary lead

Since the introduction of Mag-Cal<sup>TM</sup>, debismuthizing trials have been conducting at many lead refineries throughout the world. Most of these refineries are now using Mag-Cal as their standard debismuthizing reagent.

Table 1 summarizes some of the initial trial results achieved when aiming for various final bismuth levels. It was quickly proven that the most efficient method is to add 10 or 20 kg Mag-Cal ingots to a well-stirred vortex. Using this method, dissolution is rapid and efficiency high, provided the correct melt temperature is used. Fig. 6 summarizes the effect of melt temperature on the dissolution time in 200-t lead kettles.

Actual debismuthizing efficiency achieved at a particular plant will be dependent on variables such as stirring effectiveness, and the efficiency of dross/crust removal and pumping, which affects whether residual debismuthizing dross is carried over to the next stage of the process. The lowest bismuth levels (i.e., 0.003 wt.% Bi) can be achieved if the newly formed dross is skimmed from the oxidation kettle after pumping.

The data of Table 1 show that it is very easy to achieve efficiencies of 100% when aiming for bismuth levels down to 0.010 wt.% Bi. When aiming for very low final bismuth (i.e., 0.005 wt.%), alloy recovery is very temperature sensitive, with the highest recoveries achieved only at addition temperatures approaching

500 °C. This is due to the solubility limit being reached as discussed previously. Fig. 6 shows the great importance of temperature on dissolution when aiming for low bismuth.

### 1.2.2. Example II: debismuthizing of secondary lead

Using a Mag-Cal 75/25 alloy, a test was conducted at a secondary lead smelter. A 60 MT kettle containing lead with 0.0092 wt.% bismuth was prepared. The metal kept at 480 °C was stirred to obtain a good vortex and 200 kg of Mag-Cal 75/25 were added. The addition was completed in 10–15 min. After addition, the lead bath was allowed to cool down. During the cooling cycle, several samples were taken for the spectrochemical analysis of bismuth. The bismuth level of the lead is a function of the bath temperature as shown in Table 2.

The debismuthization process occurs at a lead temperature below 340 °C. At a temperature in the 320–325 °C range, the solubility of calcium and magnesium in lead is low enough to obtain the formation of the ternary  $\text{CaMg}_2\text{Bi}_2$  compound. Finally, a bismuth level in the order of 0.005 wt.% is reached. To attain low bismuth levels (0.005 wt.%), it is necessary to lower the lead temperature close to the freezing point.

## 2. Alloying of lead with calcium and aluminum

### 2.1. Lead–calcium–aluminum alloys

A major step forward in lead/acid battery technology took place with the development of lead–calcium battery grids. These enabled the development of ‘maintenance-free’ batteries. To achieve better deep-discharge characteristics, ‘hybrid’ batteries have also been developed

Table 1  
Summary of average debismuthizing trial results at various primary lead refineries (total no. of tests > 50)

| Target final wt.% Bi | Company | Addition temperature (°C) | kg t <sup>-1</sup> added | Av. dissolution time (min) | Initial wt.% Bi | Final wt.% Bi | Alloy recovery (%) |     |
|----------------------|---------|---------------------------|--------------------------|----------------------------|-----------------|---------------|--------------------|-----|
| 0.020                | A       | 470 (basket)              | 1.80                     | 90                         | 0.37            | 0.021         | 92                 |     |
|                      |         | 505 (vortex)              | 2.40                     | 15                         | 0.60            | 0.011         | 100                |     |
|                      | B       | 400                       | 2.00                     | 57                         | 0.46            | 0.014         | 100                |     |
|                      |         | 460                       | 2.11                     | 28                         | 0.46            | 0.015         | 100                |     |
| 0.010                | C       | 465                       | 3.55                     | N/M                        | 0.83            | 0.013         | 90                 |     |
|                      |         | D                         | 445                      | 1.87                       | 80              | 0.076         | 0.0074             | 100 |
|                      |         |                           | 460                      | 1.73                       | 65              | 0.073         | 0.0072             | 100 |
|                      |         | 480                       | 1.60                     | 35                         | 0.078           | 0.0097        | 100                |     |
| 0.005/0.006          | B       | 420                       | 4.22                     | 56                         | 0.46            | 0.0057        | 73                 |     |
|                      |         | 450                       | 4.26                     | 53                         | 0.45            | 0.0050        | 76                 |     |
|                      |         | 450                       | 3.77                     | 54                         | 0.44            | 0.0050        | 88                 |     |
|                      | E       | 505                       | 2.80                     | 20                         | 0.46            | 0.006         | 100                |     |

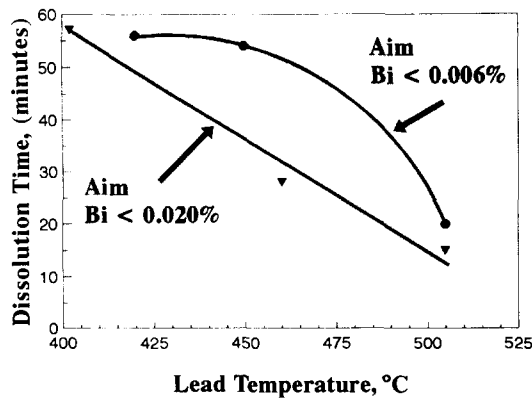


Fig. 6. Effect of melt temperature on Mag-Cal dissolution time in 200-t lead kettles.

Table 2  
Bismuth levels in secondary lead after treatment with Mag-Cal

| Temperature (°C) | Bismuth (wt.%) | Calcium (wt.%)       |
|------------------|----------------|----------------------|
| 480              | 0.0092         | 0 before addition    |
| 480              | 0.0092         | 0.068 after addition |
| 360              | 0.0095         |                      |
| 340              | 0.0095         |                      |
| 325              | 0.0063         |                      |
| 319              | 0.0055         |                      |
| 318              | 0.0049         |                      |

in which low antimony–lead is used for negative grids while calcium–lead is used for positive grids.

Manufacturing difficulties experienced during the initial development of lead–calcium alloys were attributed to variability in the calcium content of the metal. This problem was virtually eliminated by the addition of small amounts of aluminum (0.005–0.05 wt.%) to the molten lead alloy. Aluminum provides a thin surface oxide layer on the molten pool of lead and, thereby, prevents the calcium from oxidizing. At present, lead–calcium–aluminum alloys, with or without tin, are used widely as battery grid material.

## 2.2. Current alloying practices

Lead–calcium–aluminum alloys can be produced by adding calcium metal and aluminum metal, in the form of ingots, pieces or granules, to molten lead. Basket and vortex additions are the most common methods used to add calcium and aluminum. Several problems exist, however, when adding pure calcium and aluminum metals to molten lead. Calcium addition is accompanied by an increase in the temperature of the lead bath as well as significant burning, flaring and fuming. Hence, for safety and environmental reasons, pure calcium metal is usually added to molten lead at as low a temperature as possible and rarely exceeding 420 °C. On the other hand, the dissolution of aluminum in

molten lead is very difficult, due to the tenacious protective oxide layer on the surface of aluminum metal, and due to the extremely low solubility of aluminum in molten lead at normal processing temperatures (350–500 °C). The lead–aluminum phase diagram shows that aluminum and lead are virtually immiscible with the solubility of aluminum in molten lead being extremely low and strongly affected by the melt temperature. Fig. 7 shows this relationship between aluminum solubility and lead temperature. Aluminum dissolution is improved by increasing the molten lead temperature up to the melting point of aluminum (660 °C). Nevertheless, disadvantages of this practice include higher energy costs, long processing times, shorter kettle life, and excessive calcium fade.

## 2.3. Calcium–aluminum master alloys; CAL-AL™

Many of the afore-mentioned problems associated with the addition of pure calcium metal and aluminum metal are overcome with the use of calcium–aluminum master alloys. Standard alloys range in composition between 60 and 85 wt.% calcium (the balance is aluminum), and are known by the trade name CAL-AL™. As shown in Fig. 8, these alloy compositions are centred around the 540 °C low melting-point eutectic.

Use of CAL-AL™ offers several advantages over other alloying additions, as follows:

- Improved dissolution in molten lead: CAL-AL™ alloys begin melting at approximately 545 °C, which is substantially lower than the melting points of each of their pure metal components (i.e., 660 °C for aluminum and 840 °C for calcium). These lower melting points enable CAL-AL™ to dissolve readily into molten lead at melt temperatures ranging from 560 to 600 °C. At these processing temperatures, calcium and aluminum recoveries are consistently high, typically 90% for calcium and 80% for aluminum. Lower addition temperatures can result in sluggish dissolution rates and less than optimum recoveries.

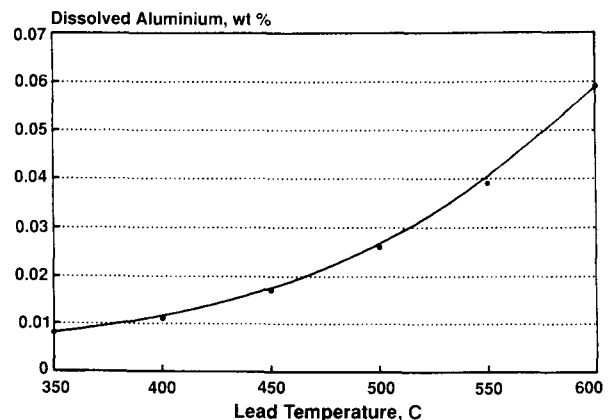


Fig. 7. Estimated aluminum solubility (wt.%) as a function of lead temperature.

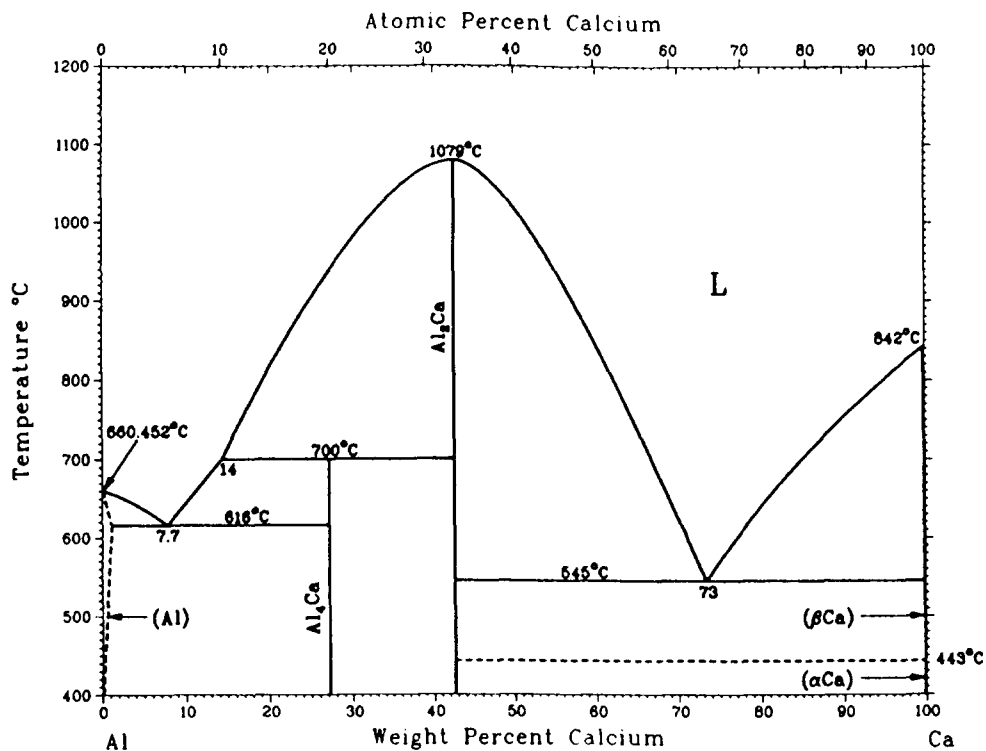


Fig. 8. Calcium–aluminum phase diagram.

- Little or no burning, flaring or fuming: addition of CAL-AL™ using the vortex method has proven to be the preferred technique. The stirring action also ensures rapid dissolution of CAL-AL™ and homogenization of the melt.
- Unlike pure calcium and aluminum metal that require two separate alloying steps, CAL-AL™ can be added in a single addition at one process temperature.
- Safety: since CAL-AL™ is an alloy of calcium and aluminum, it is much less reactive and safer to handle than pure calcium metal.

Fig. 9 is a plot of the expected percentage of calcium and aluminum recovered in the lead alloy for each of the three CAL-AL™ compositions (assuming recoveries

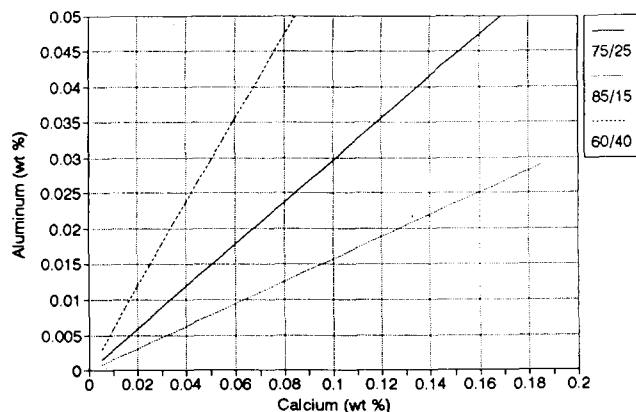


Fig. 9. Expected range of calcium and aluminum levels obtained with CAL-AL alloys (75/25, 85/15 and 60/40).

of 90% Ca and 80% Al). It is possible to control the dissolved Ca/Al ratio in the lead according to Fig. 9. An alternative method to achieve different Ca/Al ratios in lead is discussed in the last section of this paper.

#### 2.4. Improvements to the dissolution performance of calcium–aluminum alloys in lead

In response to increasing demands placed on lead alloy producers for tighter quality standards, the production technology for CAL-AL™ was recently re-examined. The overall objective was to improve the dissolution characteristics of CAL-AL™ and, thereby, ensure consistently high calcium and aluminum recoveries.

#### 2.5. Melt cleanliness

Due to the reactive nature of calcium and calcium–aluminum alloys in the molten state, there is significant potential for oxidation of the melt to occur if air comes in contact with the alloy during processing. Although CAL-AL™ alloys have traditionally been processed under inert-gas protection, an analytical investigation revealed that in some instances higher than desired levels of ‘insolubles’ (mainly oxides of aluminum) were present in the melt. In these cases, because some of the aluminum was contained as an oxide, the sum of the analyses of metallic Ca + Al in the alloy did not total 100%. This could result in the amount of aluminum

actually added being lower than desired. Furthermore, the insoluble oxide content of the alloy appeared to impede the dissolution performance of the alloy.

A new alloying and processing procedure was tested and was found to achieve consistently very low levels of insolubles in the CAL-Al™ alloy. A trial run of 31 casts was conducted, and Table 3 compares CAL-AL™ produced with the traditional method and the new, improved production practice. The results show that not only has the level of insolubles been substantially reduced, but the analysis of metallic calcium and aluminum in the alloy is higher and more consistent, due to the lower oxidation of the melt. Total metallic analysis (%Ca + %Al) is now greater than 99% for all casts whereas, by the traditional method, total metallic analysis was typically in the range 96–97%.

### 2.6. Dissolution performance and metallic recoveries

A significant number of dissolution tests has been conducted using both small (50 kg) and larger (1250 kg) experimental lead melts. Table 4 shows typical results of the experiments, where calcium and aluminum recoveries are compared between traditional CAL-Al™ processing methods, and the new improved processing method. The data show that the new processing method, which produces cleaner CAL-Al™ with increased metallic concentrations, results in an improvement in Al recovery by typically 11.5%, as compared with the traditional CAL-Al™ processing method. Calcium recovery from the new product remains very high and is typically virtually 100%. (Actual aluminum recoveries in practice may vary somewhat depending on the particular processing conditions employed.)

Table 3  
Comparison of CAL-AL™ by traditional and new processing methods (results of 31 casts)

| Component            | Traditional process | New process |
|----------------------|---------------------|-------------|
| Calcium (%)          | 72–74               | 75–77       |
| Aluminum (%)         | 20–24               | 23–24       |
| Total metallics (%)  | 96–97               | 99–100      |
| Insoluble oxides (%) | 1.0–4.0             | 0.1–0.7     |

Table 4  
Comparison of typical CAL-AL™ recovery by traditional and new processing methods (results of pilot-scale tests at 560 °C)

|                            | Recovery (%) |          |
|----------------------------|--------------|----------|
|                            | Calcium      | Aluminum |
| Traditional CAL-AL™ method | 98.5         | 70.0     |
| New CAL-AL™ method         | 100.00       | 81.5     |

### 2.7. New method for alloying calcium and aluminum into molten lead

The lead industry has shown an interest in improved, more flexible alloying methods. In particular, many lead alloyers are required to achieve a variety of different ratios of calcium to aluminum in the lead. Often, the aluminum specification is below what can be achieved by a simple addition of CAL-AL™, without exceeding the calcium specifications. In these cases, CAL-AL™ is often used solely to achieve the target aluminum level, and supplemental additions of pure calcium are made to achieve the desired calcium level. In addition, aluminum contained in the CAL-AL™ is an expensive form of aluminum (due to the specialized processing required to make the alloy). Thus, there is an interest in being able to alloy aluminum in its pure form, at normal processing temperatures (500–560 °C), and in being able to vary the ratio of calcium/aluminum added from one melt to another.

### 2.8. New process

A novel method for adding calcium and aluminum to lead has been designed and tested. The basic principle of the process is that a blend of calcium and aluminum pure-metal granules or particulates is fed into the vortex of a high speed mixer within an inert-gas purged, partially submerged, bell. The process takes advantage of the exothermic dissolution of calcium in lead to facilitate efficient aluminum dissolution.

Fig. 10 is a schematic diagram that shows the basic components of the equipment. The system includes a mixer located inside the bell and a screw feeder connected to a main container or hopper. These components are easily affixed to a steel 'bridge' beam, which is normally used in primary and secondary lead refineries to set mixers on the kettles.

While mixing, molten lead is caused to flow from the bell's interior to the exterior through the bottom open area of the bell. The lead is replenished from the outside through holes or slots located along the periphery of the bell near the melt surface. Thus, a circulating flow of metal through the bell is achieved where lead with the least amount of dissolved calcium and aluminum is brought into the reaction zone, while lead containing the highest concentrations of calcium and aluminum is brought out of the reaction zone and mixed into the bulk melt. The ability to use inert gas inside the bell is beneficial because oxidation and burning of the calcium is prevented and results in a consistently high recovery.

The high-speed mixing action inside the bell is important in order to overcome density differences between lead and the calcium/aluminum blend, and to achieve intimate contact for dissolution to occur. Because of

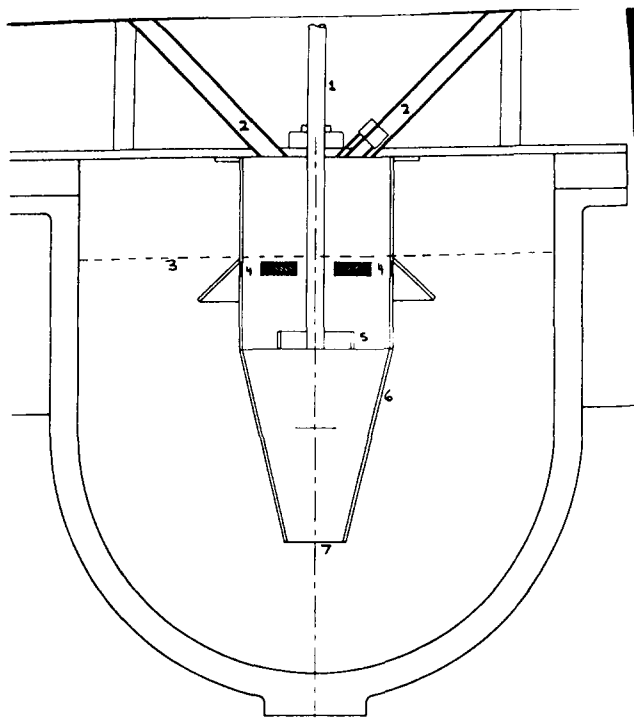


Fig. 10. Calcium and aluminum dissolution in lead by new submerged bell process: (1) driveshaft for mixer; (2) reagent (Ca and Al) feeder inlet ports; (3) liquid lead melt surface; (4) inlet slots for liquid lead from bulk melt; (5) rotary mechanical mixer; (6) conical bell; (7) outlet for alloy lead from bell.

the difficulty of dissolving pure aluminum in molten lead, it is important to have an intimate contact between the calcium and aluminum granules. The heat generated by calcium dissolution in close proximity to the aluminum granules greatly enhances the aluminum dissolution which, as mentioned previously, is strongly temperature-dependent.

The initial design of the bell employed a straight cylindrical shell, rather than using a conical bottom as illustrated in Fig. 10. The reagent feed system was altered to facilitate the addition of: (i) calcium and aluminum metal particles simultaneously; or (ii) only aluminum metal particles. Tests with this method at 560 °C showed that when aluminum metal was added separately, that is without calcium addition, the aluminum recovery was zero. Hence, this method is unsuitable for adding only pure solid aluminum to molten lead at processing temperatures customarily used for producing lead/acid battery alloys.

Tests were then conducted with the straight cylindrical bell by simultaneously adding calcium and aluminum particles to a 1250 kg lead bath. Table 5 presents the results which prove that when aluminum and calcium particles are held in close proximity to each other in a well-stirred reaction bell, the heat released by calcium dissolution facilitates aluminum dissolution by locally increasing the lead temperature in the vicinity of the aluminum particles. Table 5 indicates that the calcium

Table 5

Calcium and aluminum metal recoveries with simultaneous addition using a straight cylindrical bell

| Lead temperature (°C) | Number of tests | Recovery (%) |             |
|-----------------------|-----------------|--------------|-------------|
|                       |                 | Calcium      | Aluminum    |
| 500                   | 4               | 86.6 ± 17.4  | 39.0 ± 19.9 |
| 540                   | 3               | 90.6 ± 6.0   | 48.8 ± 7.2  |
| 560                   | 9               | 91.9 ± 6.8   | 60.0 ± 9.6  |

Table 6

Calcium and aluminum metal recoveries with simultaneous addition using a conical bell

| Test no. | Analysis (ppm) |     | Recovery (%) |      |
|----------|----------------|-----|--------------|------|
|          | Ca             | Al  | Ca           | Al   |
| 1        | 1140           | 140 | 96.1         | 83.2 |
| 2        | 1068           | 140 | 90.0         | 83.2 |

and aluminum recoveries both increase as the lead bath temperature increases from 500 to 560 °C. The results also show, however, that there is a high degree of variability in the test-to-test aluminum recovery; while the calcium recoveries are in the 90% range, aluminum recoveries are typically in the 60–70% range. The lower aluminum recovery is attributed to the loss of undissolved aluminum particles through the open bottom area of the bell due to inadequate retention time.

The conical-shaped reaction bell (Fig. 10) was evolved in order to promote tangential velocity and maximize the retention time of particles inside the bell. Table 6 summarizes the results obtained to date with the conical bell. The results confirm that the conical reaction bell significantly increases the recovery of aluminum and reduces the previous test-to-test unpredictability encountered with the cylindrical reaction bell. This is attributed to the tangential fluid flow inside the conical bell that ensures close proximity of aluminum and calcium particles, and effective use of the heat released during calcium dissolution to promote aluminum dissolution. Industrial trials using a larger conical reaction bell on a 15-t lead kettle are now being coordinated.

### 3. Conclusions

#### 3.1. Mag-Cal™

A programme has been initiated to improve the performance and eliminate the environmental concerns of the traditional KB process. The programme has given rise to the development of a new generation of debismuthizing reagents that are comprised of a magnesium–calcium alloy, specially designated as Mag-



Cal<sup>TM</sup>. The most common Mag-Cal<sup>TM</sup> alloy contains 70 wt.% magnesium and 30 wt.% calcium.

Extensive testing has revealed that addition of Mag-Cal to the vortex at approximately 480–500 °C, followed by mixing for 5–15 min, provides the best results.

With Mag-Cal, bismuth levels of 0.005 wt.% Bi or less are readily achieved without the need for supplemental calcium and antimony additions.

### 3.2. Cal-Al<sup>TM</sup>

Calcium–aluminum master alloys (known as CAL-AL<sup>TM</sup>) have been developed. These enable battery-grid manufacturers to achieve target calcium and aluminum specifications with consistently high and predictable recoveries.

Work has been conducted to improve the quality of CAL-AL<sup>TM</sup> and to improve its dissolution performance when added to molten lead. This has resulted in a cleaner product with fewer oxides and more consistent

calcium and aluminum analysis. Consequently, an increase in both calcium and aluminum recoveries has been achieved when CAL-AL<sup>TM</sup> alloys are dissolved in molten lead.

### 3.3. Ca–Al bell

A new process has been developed for alloying calcium and aluminum into lead. The process has been proven in an extensive campaign of pilot-scale trials. The process used pure calcium and aluminum in the form of granules or particulates, and offers many advantages that will be of significant benefit to lead–calcium alloy producers.

## References

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