



Short communication

# The refining of secondary lead for use in advanced lead-acid batteries

Timothy W. Ellis, Abbas H. Mirza\*

RSR Technologies, Dallas, TX 75247, USA

## ARTICLE INFO

## Article history:

Received 22 October 2009

Received in revised form 9 December 2009

Accepted 23 December 2009

Available online 13 January 2010

## Keywords:

Secondary

Lead

Refining

Advanced

Acid

Batteries

## ABSTRACT

Secondary lead, i.e. material produced by the recycling of lead-acid batteries has become the primary source of lead in much of the world. This has been important to the secondary lead industry as other uses have dwindled, e.g. lead based pigments, chemicals, fuel additives, solders and CRT glasses [1]. Presently, battery manufacturing accounts for greater than 80% of lead consumption while recycled lead accounts for approximately the same market share of lead supply. These two facts strongly demonstrate the battery manufacturing and recycled lead are intimately coupled in everyday life. In this paper we will explore how recycled lead has become the material of choice for battery construction through the development of a recovery and refining process that exceeds the industries requirements. Particular focus will be on addressing the results presented by Prengaman [2] on the effects of contaminant or tramp elements on gassing in lead-acid batteries.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Secondary lead produced by recycling process has come to dominate much of the world market for lead. This has happened under immense societal pressure to mitigate the environmental and health hazards of lead use and supply the material necessary to support economic growth in the industrial and emerging economies. It is truly an odd juxtaposition of events that the use of lead in batteries for electric vehicles, telecommunications, and renewable energy is an integral part of building a high growth, green world economy while at the same time being arguably the most regulated metal in common industrial usage.

The basic flow of lead-acid battery recycling has been stable for sometime [1]. Spent batteries are mined from the industrial economy through a reverse distribution channel covering all business sizes from the largest retailer to local garage being passed back to either battery distributors/manufactures or entering through the car dismantling/scrap metal network. The spent batteries find themselves at the recycling facility to undergo pyrometallurgical operations, most commonly, to produce refined metals. An ineliance of lead recycling is that much of the recycled lead is produced as soft lead, i.e. 99.95+ purity for the production of lead oxide for active material in the battery. Of course a great deal of the material coming back from spent lead batteries is lead oxides/sulfates. The energy and time used to convert oxide/sulfates into metal, which is subsequently reconverted to oxides, is a glaring area for improvement in present practice.

## 2. The process

Upon arrival at the recycling facility, the spent batteries are broken/crushed in hammer or toothed mills to begin the disaggregation of the components. After breaking, the material is passed to a sink/float operation. This hydrodynamic separation step uses Stoke's law to separate the lead from the separators and casing material into two different streams. The casing material is usually polypropylene (PP), although acrylonitrile butadiene styrene (ABS) is becoming more common for batteries requiring high case strength. Stoke's law states that separation can be accomplished by virtue of the density difference between materials using a fluid of intermediate density between the solid phases. Since the density of PP is less than that of water, while the density of lead metal/compound is much higher than that of water, sink/float operation is an effective methodology to achieve almost complete quantitative segregation. The polymers are subsequently cleaned and sent for recycling into new battery cases or for alternate uses. The lead metal and paste, a combination of the  $PbO_2$ ,  $PbO$ ,  $PbSO_4$  and lead metal from the active material, is removed from the bottom of the sink/float operation and sent to storage for water removal prior to smelting. A typical flowsheet for secondary lead recycling is shown in Fig. 1.

## 3. Sulfur removal

Sulfur management is the first-order of business in producing refined metal. Sulfur is removed from the spent material in one of two general ways: (i) by producing  $SO_2$  gas in the pyrometallurgical, carbothermic reduction of  $PbSO_4$ , or (ii) by the

\* Corresponding author. Tel.: +1 214 242 0357; fax: +1 214 631 6092.

E-mail address: [amirza@rsrtechnologies.com](mailto:amirza@rsrtechnologies.com) (A.H. Mirza).

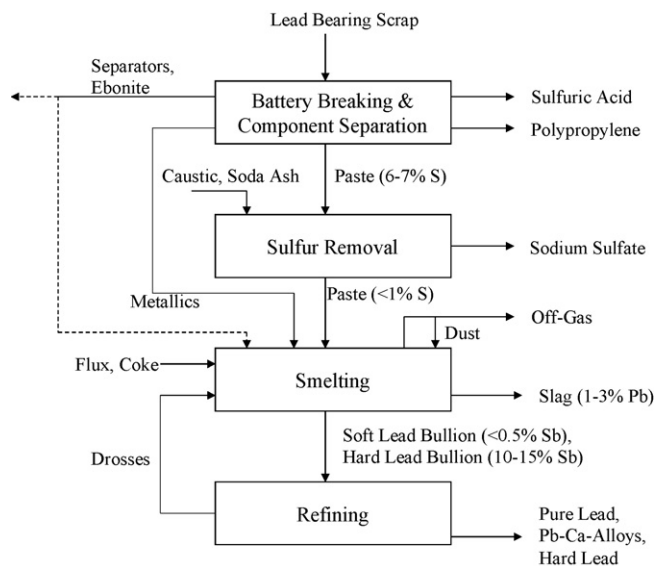


Fig. 1. Typical flow diagram of secondary lead recycling.

hydrometallurgical conversion of  $\text{PbSO}_4$  to  $\text{Pb(O, OH, CO}_3)$  by reaction with aqueous alkali carbonates ( $\text{CO}_3^{2-}$ ) or hydroxides ( $\text{OH}^-$ ).

### 3.1. Pyrometallurgical carbothermic reduction of $\text{PbO}_2/\text{PbSO}_4$

Pyrometallurgy is the predominant methodology for the recycling of spent lead-acid batteries. This is accomplished in a two-stage process, namely, producing  $\text{SO}_2$  from pyrometallurgical carbothermic process and sulfur capture by scrubbing  $\text{SO}_2$ .

#### 3.1.1. Producing $\text{SO}_2$ from pyrometallurgical carbothermic process

The battery paste consisting of a mixture of lead oxides and sulfates is carbothermally reduced, generally in accordance with the following reactions in either a single batch rotary furnace or a continuous smelting furnace of the reverberatory, blast or Isa-smelt/Aus-smelt type. The basics of this process can be followed by inspection of the following Ellingham diagram which outlines the thermodynamics of the process (Fig. 2).

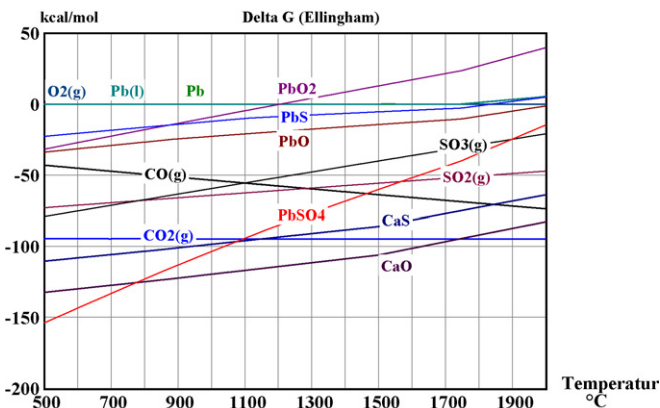
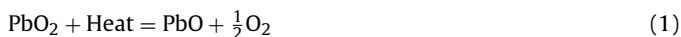


Fig. 2. Ellingham diagram of secondary lead smelting (HSC Chemistry 6.1) [15].

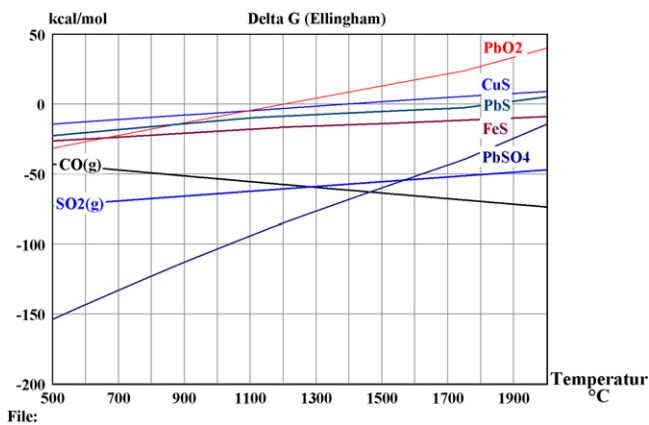
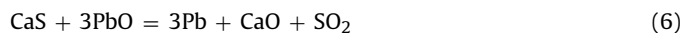


Fig. 3. Ellingham diagram showing the PbS–FeS matte (HSC Chemistry 6.1) [15].

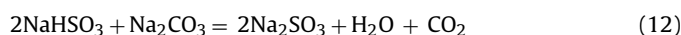
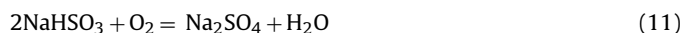


The Ellingham diagram indicates that a temperature of  $>1500^\circ\text{C}$  is necessary to reduce  $\text{PbSO}_4$  to form lead,  $\text{PbS}$  and  $\text{SO}_2$ , if not driven by Le Châtelier's principle. Lime ( $\text{CaO}$ ) is very important in eliminating the  $\text{SO}_2$  from the  $\text{PbSO}_4$  input to the furnace. A sufficient quantity of lime must be added to evolve sulfur as  $\text{SO}_2$ . Adding excess carbon does not help produce more lead from  $\text{PbSO}_4$  because carbon promotes the formation of  $\text{PbS}$  in accordance with reaction (8) below. It does not involve the formation of lead and does not eliminate the sulfur. On the other hand, it produces matte ( $\text{PbS}$ ) and a slag with high lead content. The Ellingham diagram below, Fig. 3, shows that  $\text{PbS}$  is stable over the entire temperature range from 500 to  $2000^\circ\text{C}$ .



#### 3.1.2. Sulfur capture by scrubbing $\text{SO}_2$

The  $\text{SO}_2$  from the pyrometallurgical operation is captured in off-gas scrubbing by reaction with carbonates or hydroxide in aqueous solution as outlined in the reactions (9)–(13) below. The normal cation for the carbonates and/or hydroxide is sodium or calcium to produce  $\text{Na}_2\text{SO}_4$  or  $\text{CaSO}_4$  as byproducts for sale or disposal. Sulfur dioxide in flue gases is dissolved in an aqueous, alkaline solution producing water with high concentrations of sodium sulfite.



Sulfite salts are oxygen scavengers which are stable in basic solutions; they are unstable in acid solutions decomposing to  $\text{SO}_2$ . At lower concentrations, sulfite is easily oxidized by oxygen to sulfate. The formation of sulfite is reversible with pH while the formation of sulfate reaction is not. Although the Eh–pH diagram for the S–Na– $\text{H}_2\text{O}$  system, Fig. 4, indicates  $\text{Na}_2\text{SO}_4$  as the predominant species over the pH range from pH 2 to 14, the sulfite oxidation reactions listed here apply to alkaline scrubbers only when the sulfite loading on the scrubber is less than the rate of sulfite oxidation.

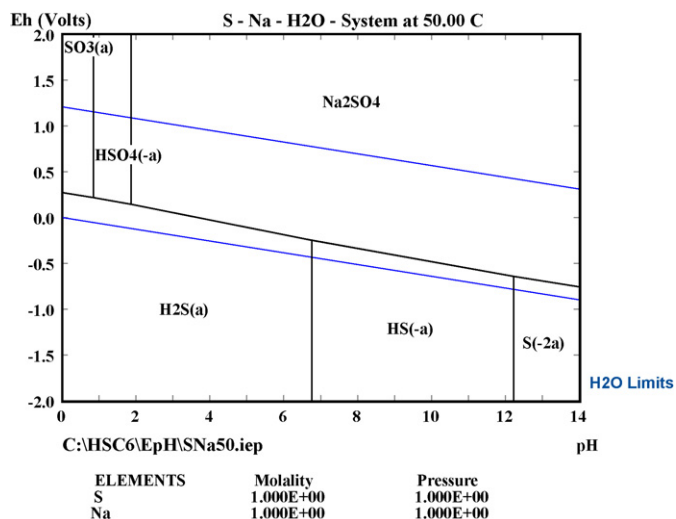


Fig. 4. Eh–pH diagram for SO<sub>2</sub> scrubbing system (HSC Chemistry 6.1) [15].

When the sulfur loading is greater than the rate of sulfite oxidation, the classic sulfite oxidation chemistry seldom applies. In this case, other difficult to oxidize metastable sulfur oxy-anions such as bisulfite, disulfite, trithionate, tetrathionate and dithionate will form, but are not represented in the equilibrium Eh–pH diagram for the S–Na–H<sub>2</sub>O system. The Eh–pH diagram was constructed for 50 °C because sulfite oxidation is exothermic and the temperature of the oxidation tanks is typically >50 °C.

### 3.2. Hydrometallurgical desulfurization of PbSO<sub>4</sub>

Hydrometallurgical removal of sulfur is an environmentally favorable option. It involves conversion of lead sulfate to carbonate, hydroxide or hydroxycarbonate [3], Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> without evolving SO<sub>2</sub> in accordance with reactions (14)–(17). The following reactions are based on the fact that Pb(OH)<sub>2</sub> or PbCO<sub>3</sub> have much lower solubility compared to PbSO<sub>4</sub>. As is clear from the Eh–pH diagram below, PbCO<sub>3</sub> is the predominant equilibrium species at pH > 5 and Pb(OH)<sub>2</sub> at pH > 13 (Figs. 5 and 6).

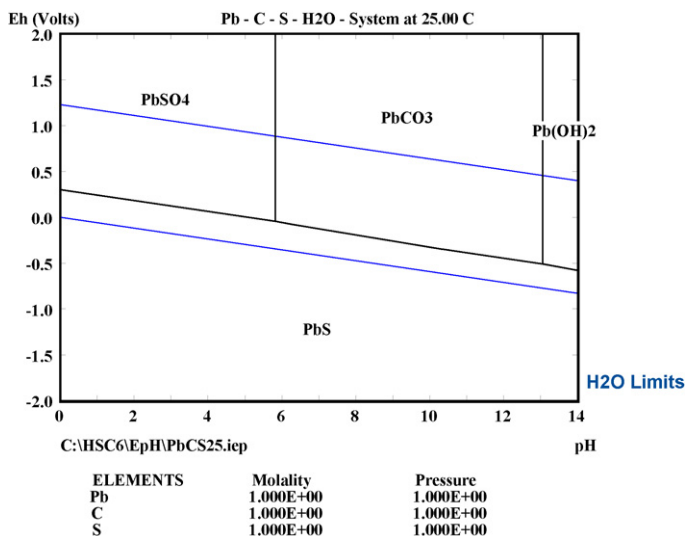
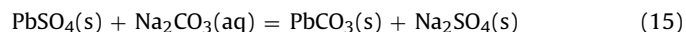
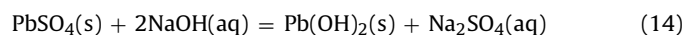


Fig. 5. Eh–pH diagram of PbSO<sub>4</sub> desulfurization w/Na<sub>2</sub>CO<sub>3</sub>/NaOH [15].

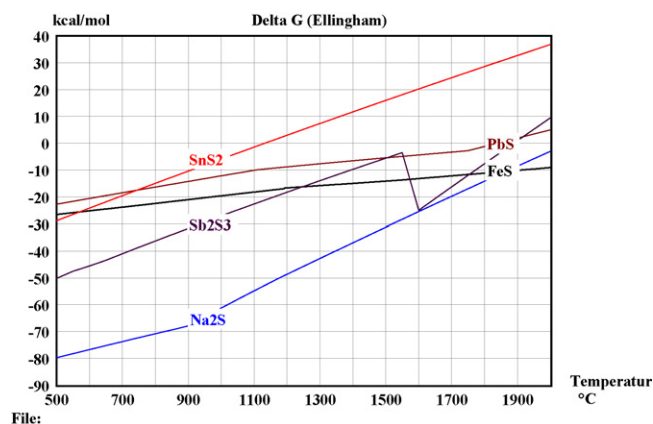
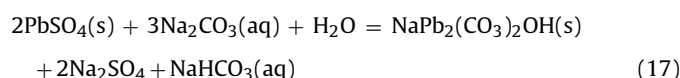
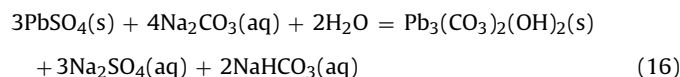


Fig. 6. Ellingham diagram showing the slag species [15].



## 4. Pyrometallurgical slags

Slag management is an extremely important issue because at temp > 1200 °C, slag is a universal solvent, and often serves as the sink for tramp contaminants. This prevents them from building up in the refinery due to the high number of internal recycling streams of drosses and production scrap. Slag also forms a layer on the top of the metal preventing further oxidation of the underlying metal. The thermodynamics of the secondary reduction step where lead is reclaimed from the matte by reduction with iron is represented below. The iron used in this step is often obtained from post consumer sources and can bring along significant quantities of metals common to ferrous metallurgy, e.g. nickel, chromium, copper, tin, zinc, which will need to be removed in subsequent lead refining steps. Antimony, aluminum, tin, and calcium report to the slag as oxides while iron and copper report to the slag as sulfides.

Two general types of slags are used in the pyrometallurgical processing of Pb, namely carbonate based (Na<sub>2</sub>CO<sub>3</sub>), also known as the soda slag and calcium iron silicate based. Silicate slags have become more prevalent in recent years to mitigate issues related to the leachability of residual elements within the slag.

## 5. Management of elements of electrochemical significance

The Advanced Lead Acid Battery Consortium (ALABC) has funded Dr. Lan Lam's group [4] at CSIRO in Australia to investigate the role of various common contaminants in lead on the gassing of lead-acid batteries. This is an important issue in lead-acid batteries as the production of gas, i.e. hydrogen and oxygen, within the battery leads to water loss and rapid failure. However, in the discussion below, we will present how the modern refinery manages these contaminants to produce material which is suitable for the production of conventional and advanced lead-acid batteries. Table 1 presents in a condensed form of the effect of 16 common contaminants in secondary lead [2]. It is important to note that many of these contaminants come from the alloys developed in support of modern lead-acid batteries, unlike primary lead where the impurity elements present are determined

**Table 1**  
The results of the hydrogen, oxygen, and float currents [2].

Elements	Upper level (ppm)	Rate of change (mA Ah <sup>-1</sup> per ppm)			Level		
		Float	Hydrogen	Oxygen	Float	Hydrogen	Oxygen
Ni	10	0.03772	0.00019	0.03772	4	16	4
Sb	10	0.0186	0.00059	0.01828	6	5	6
Co	10	0.04332	0.00109	0.04252	4	7	4
Cr	5	0.01782	0.00016	0.01774	7	16	7
Fe	10	0.01958	0.00014	0.01951	6	19	6
Mn	3	0.04643	0.0008	0.04543	5	5	5
Cu	10	0.00625	0.00038	0.00583	33	13	34
Ag	20	0.00097	0.00006	0.00103	76	165	66
Se	1	0.1041	0.005	0.0995	2	1	2
Te	0.3	0.10167	0.00933	0.11233	1.5	0.5	1.4
As	10	0.00887	0.0003	0.00881	15	15	14
Sn	10	0.00393	0.00002	0.00399	49	150	48
Bi	500	-0.00026	-0.00001	-0.00026	500 <sup>?</sup>	500 <sup>?</sup>	500 <sup>?</sup>
Ge	500	0.00041	0.00001	0.00042	673	250	658
Zn	500	-0.00003	-0.00002	-0.00001	500 <sup>?</sup>	500 <sup>?</sup>	500 <sup>?</sup>
Cd	500	0.00027	0.00001	0.00026	901	706	903

<sup>?</sup> indicates that currents could be higher than measured values.

by the geochemistry of the specific deposit from which metal is produced.

Table 1 presents summarizes the effect of 17 of the most important impurity elements in lead on the change in the production of oxygen at the positive plate and hydrogen at the negative plates in VRLA batteries on float charge [2]. The change in gassing current is given as mA Ah of battery capacity per ppm of the element.

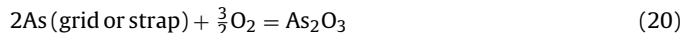
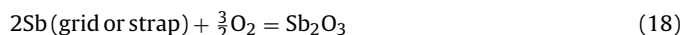
This first question to be asked is “are all contaminants harmful to a lead-acid battery by enhancing gassing?” Or, to turn the question around, “are some contaminants actually helpful, i.e. reduce gassing?” The presence of bismuth and zinc actually reduces gassing behavior which enhances the reliability and performance of a battery. Therefore, spending time and money to remove these elements from the recycled stream is counterproductive. Silver which is usually very low in lead from primary sources is present in recycled lead in the range of 50–70 ppm. Silver has been added purposefully to cast Pb–Ca–Sn grid alloys in the past to prevent penetrating corrosion through the thickness of the grid wires at higher temperatures. Even Pb–Sn alloys for stationary batteries now utilize silver to extend life at elevated temperatures. Although it would appear that silver is detrimental particularly for hydrogen generation, it has been shown that in use the silver migrates from the positive to negative plate, thereby, eliminating this concern [2].

### 5.1. Removal of copper, nickel, tellurium and selenium

Some processes in lead refining such as removing copper from lead by a drop in solubility with decreasing temperature and the oxidation of antimony, tin and arsenic to form oxide dross are carried out under equilibrium conditions. Other processes such as decopperization with pyrite/sulfur and caustic refining steps are governed by kinetics [5]. Investigation of Table 1 indicates that the most important trace elements in lead to manage/remove are nickel, tellurium and selenium. Nickel is removed along with copper in refining kettles by treatment with pyrite (FeS<sub>2</sub>) and sulfur. The refining action is due to the formation of (Cu, Ni)FeS<sub>x</sub> compounds, e.g. chalcopyrite (CuFeS<sub>2</sub>) and/or bornite (Cu<sub>5</sub>FeS<sub>4</sub>) and analogous ternary nickel sulfides, which remove both nickel and copper from the lead melt. This lowers the nickel and copper content to a range of <0.005%. A subsequent treatment with phosphorous or zinc–aluminum alloy removes nickel to trace levels as NiP or NiAl intermetallics which float off as dross. Tellurium and selenium removal to a range of <0.0001% is accomplished by the addition of sodium to form intermetallics that float to the surface as dross.

### 5.2. Removal of tin, antimony, arsenic, calcium, aluminum, iron, manganese, and chromium

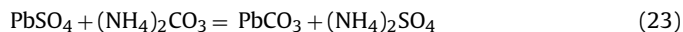
The metallic portion of the feed material contains various alloying elements such as antimony, tin, arsenic, calcium, aluminum, cadmium, copper, barium, etc. These are all oxidized in the reverberatory furnace. The SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, chlorine and bromine from the separators/plastics, CaO from the lime, CaSiO<sub>3</sub> from lime and silica, FeO from the waste water treatment sludge and MgO and Cr<sub>2</sub>O<sub>3</sub> from the furnace bricks are also removed in the slag.



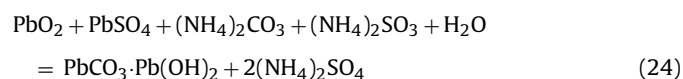
Since, tin and antimony oxides have high free energies of formation, oxygen sparging in refining kettles is used to remove tin and antimony down to a range of <0.0005%. The reduction of antimony by oxygen is commonly used to soften lead. However, lead is also oxidized in this process. Therefore, the minimum antimony content available is related to acceptable lead loss. High antimony alloys can also be produced by oxygen sparging which removes the lead from solution as an oxide. In this process the maximum antimony content obtainable is ~35 wt.%.

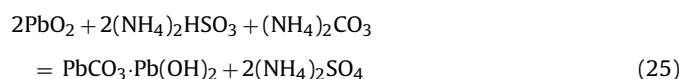
## 6. Electrochemical practice

Prengaman [6–10] investigated the RSR process of hydrometallurgical processing of lead-acid battery paste followed by electrowinning to recover lead. Lead sulfate was first desulfurized with ammonium carbonate (or other alkali carbonates) as follows.

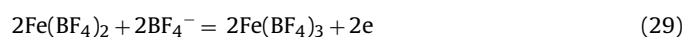
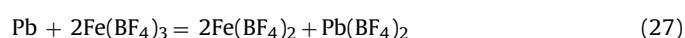
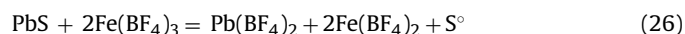


The PbO<sub>2</sub> in the lead-acid battery paste may be reduced by SO<sub>2</sub> added to the alkali carbonate. SO<sub>2</sub> dissolves in the alkali carbonate to form alkali sulfites or bisulfites which then react with PbO<sub>2</sub> and PbSO<sub>4</sub> or PbO<sub>2</sub> alone to produce lead hydroxocarbonate and ammonium sulfate.





The FLUBOR process, developed by Engitec Impianti (Milan, Italy), is an aqueous, electrochemical process to recover pure lead from the metallic grids in lead-acid battery scrap [11] and from lead concentrates (PbS) [12,13].



A pilot plant trial (45 kg day<sup>-1</sup>) performed at Asarco's East Helena Lead Smelter [14] using granulated lead bullion in the mid 1990s was successful in producing lead sheets of 99.9% purity. FLUBOR is essentially a simple process in which lead is dissolved as lead fluoborate by ferric oxidation. The electrolyte for lead electrowinning is a solution of lead fluoborate obtained above in ferric fluoborate–fluoboric acid. The solution flows to the cathode compartment where lead is electrodeposited. The anolyte with the ferric ion regenerated is then fed to the leaching reactor. As an intermediate purification step, the leach liquor is purified by cementation with lead granules to precipitate antimony, arsenic, bismuth, copper and silver. Since elements such as zinc and cadmium cannot be removed by cementation, they will accumulate in solution and may have to be removed by a bleedstream.

Several researchers [6–14] have investigated the hydro- and electro-metallurgical routes to produce lead from scrap lead-acid batteries over the last few decades. In spite of the fact that hydro-/electro-metallurgy is inherently attractive from an environmental point of view, it has not been used commercially because the pyrometallurgical process is economically favorable. Besides, there have been continuous developments in the pyrometallurgical processing of scrap batteries, viz. furnace and burner designs, feed drying, materials handling, ventilation, environmental technologies such as baghouses, scrubbers, wet electrostatic precipitators, etc.

## 7. Conclusion

The main difference between primary and secondary lead is the bismuth and silver content. Research at ALABC [4] has shown that the elements that cause the highest gassing are selenium, nickel, arsenic, tellurium, cobalt, copper, chromium and antimony

of which selenium, nickel, and tellurium are particularly bad. Other elements such as silver, bismuth, zinc, tin, and cadmium actually compensate for the effect of some of the elements that cause gassing. Silver, bismuth, and zinc are the most beneficial. Silver in the positive active material is transferred to the negative and has no effect on the gassing current of the positive and there was no increase in gassing at the negative active material up to a silver content of 100 ppm [2]. Further, it was found in the same study that silver improved the discharge capacity in the 50–100 ppm range in addition to enhancing the conductivity and rechargeability of the negative plate.

Going forward, secondary lead will become the major portion of worldwide lead supply as we recycle more batteries especially as it is refined to remove the impurities that cause gassing. Although, the secondary lead will contain significantly higher quantities of bismuth and silver, these two elements are not detrimental to battery performance. On the contrary, they are both beneficial. Secondary soft lead can also be alloyed with calcium and tin to get the same grid life as produced from primary lead containing low bismuth and silver.

## References

- [1] R.D. Prengaman, T.W. Ellis, 12th International Battery Material & Recycling Seminar, Fort Lauderdale, FL, 2008.
- [2] R.D. Prengaman, Improvements to active material for VRLA batteries, *J. Power Sources* 144 (2) (2005) 426–437.
- [3] A.G. Morachevskii, et al., Removal of sulfur from the active mass of lead battery scrap, *Russ. J. Appl. Chem.* 74 (7) (2001) 1103–1105.
- [4] L.T. Lam, H. Ceylan, N.P. Haigh, T. Lwin, C.G. Phyland, D.A.J. Rand, D.C. Vella, L.H. Vu, ALABC Project No. 3.1 Final Report, ILZRO, June, 2002.
- [5] T.R.A. Davey, in: John M. Cigan, Thomas S. Mackey, Thomas J. O'Keefe (Eds.), *Lead-Zinc-Tin'80*, Metall. Soc. AIME, Warrendale, PA, 1980, pp. 477–507.
- [6] R.D. Prengaman, Recovering lead from batteries, *J. Met.* (January) (1995) 31–33.
- [7] R.D. Prengaman, H.B. McDonald, Process for reducing lead peroxide formation during lead electrowinning, U.S. Patent 4,230,545 (October, 1980).
- [8] R.D. Prengaman, H. McDonald, in: T.S. Mackey, R.D. Prengaman (Eds.), *Lead-Zinc'90*, TMS, February 1990, pp. 1045–1056.
- [9] R.D. Prengaman, H. McDonald, Method of recovering lead values from battery sludge, U.S. Patent 4,229,271 (October, 1980).
- [10] R.D. Prengaman, H. McDonald, Stable lead dioxide anode and method for production, U.S. Patent 4,236,978 (December, 1980).
- [11] M. Olper, P.L. Fracchia, Hydrometallurgical process for an overall recovery of the components of exhausted lead-acid batteries, U.S. Patent 4,769,116 (6 September, 1988).
- [12] M. Olper, P.L. Fracchia, Process for producing electrolytic lead and elemental sulfur from Galena, U.S. Patent 5,039,337 (13 August, 1991).
- [13] M. Olper, M. Maccagni, in: J.B. Hiskey, G.W. Warren (Eds.), *Hydrometallurgy*, TMS, Warrendale, PA, 1993, pp. 1147–1167.
- [14] F. Ojebuoboh, S. Wang, M. Maccagni, *J. Met.* 55 (4) (2003) 19–23.
- [15] HSC Chemistry 6.1 Chemical Reaction and Equilibrium Software©Outokumpu Research.