# Developments in lead–acid batteries: a lead producer's perspective

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## Abstract

Rapid progress is being made in many aspects of materials, design and construction for lead–acid batteries. Much of this work has taken place under the auspices of the Advanced Lead–Acid Battery Consortium (ALABC). From the general tone of the literature, it seems likely that several of these developments will be adopted in commercial products, and that there will be cross-fertilization between the emerging electric vehicle (EV) battery technology and the starting, lighting and ignition (SLI) battery. Given the impetus for improvement from several different factors, the development process appears to be accelerating. To those not intimately involved in the battery design and specification process, it is not clear which of the possible developments will make it from the laboratory to general commercial adoption. Some of the possible changes in materials, design and construction could have an impact on the recovery, recycling, smelting and refining of lead–acid batteries. Some of the possible developments are outlined and their possible impact is discussed. It is likely that negative effects may be minimized if battery developments are considered from other perspectives, largely based on the overall life-cycle, as early in the design phase of new products as possible. Three strategies for minimizing undesirable effects are advocated: first, improved communication between car manufacturers, battery manufacturers and lead producers second, use of life-cycle analysis (LCA) to identify and optimize all attributes of the product throughout its life-cycle third, concerted and coordinated action to deal with issues important to the industry once trends are identified. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

It is not intended that this paper should present new insights in the area discussed. Many people involved in the field have covered the same ground before, often very well, and many more will do so again. The message is so important to the future of the industry, however, that it bears regular repetition.

The lead–acid battery has been dominant in automotive applications almost since the birth of the motor car. The underlying principles of operation have remained unchanged, but there has been a steady trickle of technical improvements in starting, lighting and ignition (SLI) automotive batteries throughout this time.

Early pre-First World War commercial lead–acid batteries, in general, were contained in glass or earthenware jars, or hard rubber, celluloid, or lined wooden cases. They had separators of hard rubber, celluloid, wood, or glass and thick, hand-cast grids made of antimonial lead. They had from 2 to 12 wt.% antimony, quoted as typically 4 wt.% by a contemporary source [1], but as typically the eutectic composition of 11 wt.% in a more modern reference [2]. Automotive use for lighting was not uncommon in Denmark and the USA, but the electric self-starter was not invented until 1912 [3]. Very early on, electric vehicles (EVs) had proponents [4].

By the mid 1950s, use of lead–calcium alloys (in telephone batteries) was increasing. New separators had been developed, but wood was still most popular. Expanders had been improved, and vulcanised rubber was commonly used for cases [5]. Batteries still had relatively thick, cast grids made from alloys of typically 5 wt.% antimony according to one source [5], or 6–9 wt.% antimony according to another [2]. Alloys containing arsenic, tellurium and cadmium had been considered [5]. Punched grids were dabbled in and the normal voltage for an automotive battery increased from 6 to 12 V.

The rate of progress increased over the next 40 years. Today's typical automotive battery has a polypropylene (PP) case, high-performance separators, and thin grids. The grids can be wrought or cast and made often by modern high-tech machinery from optimized very low antimonial or lead–calcium–(tin)–(aluminium) alloys. A better understanding of battery additives has also been gained in recent

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years. During this process, the automotive battery has progressed to a low-maintenance, or maintenance-free battery design.

The pace of present research is accelerating rapidly. This is largely driven by the quest for a high-performance lead–acid EV battery, exemplified by the sterling work carried out under the auspices of the Advanced Lead–Acid Battery Consortium (ALABC). There are also strong driving forces to improve automotive batteries. These include greatly increasing electrical loads in vehicles due to the burgeoning crop of electronic and computerized devices fitted to cars [6–8], increasing under-bonnet temperatures, a requirement for better maintenance-free characteristics, the desire for lower weight, and possibly the use of much higher voltage batteries in cars than the current 12 V standard, possibly as high as 48 V [9]. This will require the adoption of some of the improvements in construction, materials and design that are being made in EV batteries, such as the use of valve-regulated lead–acid (VRLA) designs [10,11], and possibly in further refinements specifically tailored towards automotive batteries. It has been suggested that cars may be fitted with two batteries in the future [12], which may even be of completely different designs [9]. From the perspective of the lead producer, the course of these developments is by no means clear, as some of the issues and proposals will be confidential between battery manufacturers and their customers.

Batteries are the major use for lead today, with automotive batteries accounting for the major portion of this. The market is set to grow substantially into the next century if predicted EV use is included with the expanding automotive battery market [13]. Batteries are a non-dispersive application and, thus, environmentally friendly—provided that the recycling chain from lead producer, to battery manufacturer, to car, back to lead producer is closed. Lead is a particularly cheap and low-margin commodity, a factor which has helped to create the hugely successful battery market which exists today.

Users, car manufacturers and battery manufacturers are all used to cheap lead–acid batteries. It is important, therefore, not only that the recycling loop is closed, but that each step in the chain is performed as efficiently as possible. Battery materials, design and construction have the potential to influence significantly the economics which drive the loop. Unnecessarily complicated or expensive recycling processes can increase costs for everyone in the loop, and may also impact on the degree of recycling carried out. The latter would damage the environmentally sound position on which the industry now relies for its future.

Some factors which affect the recycling process, such as legislation, are outside the direct control of lead producers and recyclers, and their customers. Other factors which influence the economics and viability of recycling are more amenable to control. Part of the effort over the last few years by those involved in the ALABC has been aimed at these very questions. There has also been an appreciation in this work of the importance of considering implications for recycling as part of the development process. This culminated in publication last year of an excellent paper covering much of what is presented here [14]. It is not clear, however, that the message has been taken on board by the broader industry, as it seems to have been in the EV forum.

In this paper, present and proposed changes in materials and construction for lead–acid batteries are reviewed and implications for recycling are discussed. Suggestions are made as to possible 'problem' areas, and recommendations are made on the necessity for open dialogue between all parties in the manufacturing cycle, on the need to consider the battery from the perspective of the full life-cycle, not just as a 'factory gate' product, and on the need to address areas which are clearly of importance with cross-company cooperation at as early a stage as possible.

## 2. Alloys

In order to provide alloys of an acceptable quality, it is first necessary to remove the impurities to the level required. With primary lead, these vary according to the ore body from which the lead was mined. With secondary lead, the impurities depend upon the composition of the scrap that is to be treated. Some elements, such as antimony, copper, zinc and several others, are easily removed to fairly low levels, whilst others, such as bismuth and silver, can be extremely difficult and/or expensive to remove.

Britannia is particularly fortunate with primary lead, in that it comes from very high quality ore bodies in and around Mount Isa in Australia. The material is smelted and de-coppered in Australia, then sent to Northfleet, UK, where about 0.25 wt.% silver and 0.1 wt.% antimony are removed. There is sufficient silver recovered to pay for the quite expensive de-silvering process. The final silver content is typically 0.0005 wt.%. Bismuth is present at very low levels. The company is also a recycler of lead. Batteries are bought in and broken, separated and de-sulfurized in a CX plant, after which the recovered lead values are smelted and refined and the PP from the cases is reprocessed.

It is not possible, either environmentally or politically, to discard life-expired lead products and to replace them with articles made exclusively from high-quality primary lead. Secondary lead must be refined to standards which are acceptable to a sufficient number of lead users so that all the lead produced from secondary sources is absorbed by new products.

Previous changes in battery alloys have been gradual, the main change being a steady drop in the amount of antimony present in batteries. The antimony content of lead for recycling has reduced in line with this, but with a

time lag of several years due to the effect of product life. It has been relatively easy for recyclers to remove this antimony; the only problem is in inventory, as the lower demand for antimony in alloys has occasionally produced a stock pile. By contrast, future alloys may have an undesirable impact on recycling.

Many current and proposed alloying elements for use in battery alloys pose no real technical or safety problems in alloying, handling, or subsequent removal. Others however, may not be so straightforward. Many alloy systems have been considered. From 1960 to 1993, these included pure lead, lead–antimony, lead–calcium, lead–barium, lead–strontium, lead–lithium, and dilute arsenic–tellurium–silver–(tin). In the lead–antimony system, additions of arsenic, tin, silver, selenium, copper, sulphur and cadmium were considered, whilst in the lead–calcium system, additional elements investigated included tin, aluminium, and silver [2].

Lead alloys are used in a battery for grids and for top metal. The following discussion focuses on alloys for the former, as the demands made of a grid are far more complex and arduous and this area is where most development will take place. There is a problem, however, if inappropriate combinations of alloys are used. The use of an antimonial top metal with a new-generation grid alloy, or the use of certain combinations of alloy in hybrid battery designs, may increase refining costs.

## 2.1. Silver

Several sources [15–17] have suggested that silver be added to lead–calcium–tin alloys. Concentrations discussed are in the range 0.01–0.25 wt.% [2], with 0.1 wt.% being specifically mentioned in one source [17], and 0.05 wt.% in another [18]. A range of 0.015 to 0.045 wt.% silver has been patented [19]. Benefits which have been quoted are an improvement in mechanical properties [18], particularly at elevated temperatures, with a significant reduction in the rate of corrosion [15]. Silver has also been advocated for use in lead–antimony alloys, in which it is reported to have a marked effect on the durability of batteries where corrosion and grid disintegration are the normal modes of failure [2].

With a time delay of 6 years or so, any added silver would report to secondary smelting and refining circuits. Unlike Britannia, who remove silver from primary lead, no purely secondary refiner has the expensive equipment necessary to remove and refine silver. Unfortunately, even for those companies who have the plant, it costs as much to remove traces of silver as it does to remove large quantities. Without recovery of a substantial quantity of silver to pay for the exercise, the economics are quite poor. In practice, if present below an economic threshold, most of the silver would remain in the refined lead. This process would grow worse over several years, with the result that fewer and fewer lead users would be able to use secondary lead.

The adoption of silver is, however, not a certainty. Research carried out recently as part of the ALABC programme evaluated high-tin Pb–Ca–Sn–Al and Pb–Ca–Sn–Ag–Al alloys and concluded that because of the cost, gassing at end of charge, enhanced self-discharge and recycling difficulties, a high-tin, silver-free alloy is to be preferred [20,21]. Nevertheless, at a forum where the preference for tin over silver was presented, an opinion was expressed by another researcher that Pb–Ca–Sn–Ag alloys are preferred for advanced batteries [22].

## 2.2. Bismuth

There has been more disagreement over the effect of bismuth in batteries than for any other element. The quality of the data from some of the early work on the effect of bismuth in batteries, much of which showed a deleterious effect, seems not to be particularly high. The levels studied were sometimes extremely high in battery terms, and often not on real alloys under realistic conditions. More recent work aimed more carefully at battery service and conducted with more rigour seems to indicate that more realistic levels seem to be benign, or even beneficial. In particular, bismuth between 0.006 and 0.86 wt.% in a lead −1.5 wt.% antimony alloy was found not to influence cycle performance, self-discharge [23], age hardening behaviour, general microstructure or grain size. Moreover, the rate of corrosion decreases with increasing bismuth content [24]. Addition of bismuth to batteries is favoured in some quarters [9,25]. A fairly recent paper [26] cites previous work on the effect of bismuth in lead, reports on the effect on microstructure and concludes that bismuth may be beneficial under deep-discharge conditions in Pb–Ca–Sn alloys with high Sn: Ca ratios. An even more recent paper [27] concludes that addition of bismuth to Pb–Ca–Sn–Al alloys increases the passivating current density and improves the conductivity of the oxide passive film, and another [28] that bismuth in the same system reduces the rate of evolution of both hydrogen and oxygen.

Bismuth already makes up the majority of the difference in purity between 99.99 wt.% (primary lead) and 99.97 wt.% (secondary lead). An increase in bismuth levels in secondary lead would not be welcomed by most users if current customer specifications are used as a guide. Bismuth is another element that is only economic to remove from lead which bears high concentrations. There could be substantial cost and recycling implications if bismuth levels in returned material rose significantly.

## 2.3. Cadmium

Another element which has been advocated for use in lead–acid batteries is cadmium. Cadmium in low-antimony alloys is reported to form an intermetallic phase which renders the antimony much less likely to poison the cell [17]. Alloys containing 1.5 to 2.5 wt.% antimony and 1.5

to 2.5 wt.% cadmium have actually been used in commercial batteries in the USA [2].

Cadmium is currently a problem in recycling, due to stray nickel–cadmium batteries in returned materials. It is present in small amounts and concentrates in bag-house fume, which periodically must be treated to remove cadmium from the circuit. It is also difficult to control levels in water discharged from the site if more than a trace of cadmium enters the recycling process. Most lead recyclers will not have the plant required to treat the material in which the cadmium becomes concentrated, so cadmium-bearing materials will be sent to one of those metals refiners with such a capability.

Given the toxicity, combined with the fugitive nature of cadmium in smelting and refining, a greatly increased recycling burden would make it much more difficult, or impossible, to meet emission requirements for recycling processes and would, at best, impose additional recycling costs or, at worst, render plants inoperable. Deliberate addition of cadmium to alloys is to be strongly discouraged.

### 2.4. Arsenic

It has been well known for decades that small amounts of arsenic are beneficial, or even essential, to precipitation hardening in lead–antimony alloys; arsenic greatly accelerates the rate of hardening. In larger amounts, arsenic confers greater creep resistance. Despite considerable research effort [2] and widespread adoption of low levels in antimonial grids, alloys containing very large quantities of arsenic do not seem to have gained widespread popularity, although an alloy containing 0.5 wt.% arsenic has had commercial success.

The need to remove large quantities of arsenic from the circuit in a safe form would not endear such alloys to the recycler. It is not particularly difficult to remove, but outlets to anyone interested in recovering it in a useful form are strictly limited and in many plants it would tend to gravitate towards materials for disposal, where there are environmental overtones.

### 2.5. Selenium

A further safety matter concerns selenium. This is added to low-antimony alloys in small quantities as a grain refining agent. Selenium is toxic. Lead producers have equipment and procedures to allow safe handling, and it is quite safe when incorporated in a battery alloy. In use, it can be lost to the dross on excessive cooling or on freezing and remelting. Occasionally, requests have been received for selenium master alloys, or for advice on adding selenium to a melt which has become deficient. It is recom-

mended that anyone without the required equipment or expertise should not add selenium.

### 2.6. Tin

Tin, in both lead–calcium and lead–antimony alloys, has been the subject of considerable research. In comparatively large quantities in lead–calcium–tin alloys, it confers structural stability, corrosion resistance, and overcomes the 'antimony-free' problem with passivation on deep discharge if used in the positive grid [29]. In low–antimony alloys, in small amounts (0.02 wt.%), it greatly increases fluidity, and in large amounts (2.5 wt.%), it improves cycle-life [2]. Pure-lead–tin has also been developed for EV use [30].

High-tin is to be greatly preferred to silver-bearing alloys for recycling. Tin is easily removed from lead during recycling and its presence in any concentration poses no problems. Only a proportion is recovered in a useable form, however. Further, any contamination of the recovered tin with antimony will render it unsuitable for further use in batteries. Such contamination is hard to avoid unless batteries of different types are segregated, and impossible if they are not. The result of the foregoing is that there may be an appreciable life-cycle cost penalty associated with the use of high tin contents in battery alloys.

### 2.7. Nickel

Nickel is not added to battery alloys—even minute amounts are regarded as unacceptable. It is useful to mention here, however, that the return of nickel–cadmium batteries to the lead producer in lead recycling streams is a source of trace contamination [23]. Due to the physical nature of some consignments for recycling and the sheer quantity, hand-sorting to remove them is not a viable option. It is difficult to remove nickel from secondary lead to less than 5 ppm. This could give a real problem for supply of secondary lead and alloys for use in VRLA batteries, where the limits are more stringent. Improved control of all steps in the recycling chain would minimize the source of contamination and reduce the trace levels of nickel reporting to secondary lead.

### 2.8. Miscellaneous

Other actual or proposed additions of elements such as strontium, barium, aluminium, lithium, rare earths, do not pose any problems in removal.

Composite materials for grids have been both used and proposed [31,32]. Some, such as lead on aluminium, may pose some problems in economically recovering the metal values of both as metals using existing plant. Others, such as lead on copper, would be treatable in some types of

plant, but widespread adoption might require some adaptation and expansion of plant to cope. Grids of, or 'armouring' with, plastics might have implications for successful treatment with current battery-breaking plants.

### 2.9. Safe handling of drosses

A very important safety issue that is often overlooked with modern battery alloys is correct handling and segregation of drosses. When drosses containing calcium are exposed to moisture, either from direct contact with water, or with damp air, a reaction can take place that liberates nascent hydrogen. If this happens in a poorly ventilated area, the hydrogen concentration may build up. If the concentration exceeds 4 wt.%, there is a risk of an explosion. Further, if drosses from lead–calcium alloys are mixed with or stored with other materials which contain antimony or arsenic, or if the melt from which the dross is removed is contaminated with antimony or arsenic, any nascent hydrogen which is formed can react with them to produce the very poisonous, inflammable gases of stibine (hydrogen antimonide) and arsine (hydrogen arsenide). It is therefore essential not to mix drosses. It is also obviously important to ensure that any third party handling or receiving such drosses is competent to do so, and to inform them as to the general composition and associated hazards of these drosses, with firm instructions on passing the information on with the material when it changes hands again.

## 3. Oxide

A recent review of soft-lead specifications for use in VRLA batteries [9] proposes that elements which are harmful in VRLA batteries should be comprehensively specified. The proposed maxima for those elements (in ppm), are shown in Table 1, row 1. An earlier paper [26] suggested the specification, given in Table 1, row 2, for use in VRLA batteries. An earlier paper [31] still suggested that Bi, Ag, Sn and Cu limits did not need to be reduced for hermetically sealed batteries, but that the limits in Table 1, row 3 should apply.

Limits for many of the elements listed are considerably more stringent than has been the case historically, with explicit specifications for some elements not previously specified. Indeed, in some respects, the requirements are tighter than might have been inferred from comparatively recent work [23]. If there is widespread adoption of VRLA batteries for automotive applications, supply to the first specification in Table 1 would effectively limit supply of soft lead to the top-flight primary lead producers. Recycling would therefore be irrelevant to the supply of oxide. The second and third specifications might possibly allow use of high-quality recycled lead for oxide manufacture, bringing into play all the recycling issues discussed. Even

if a secondary circuit were able to achieve the stringent requirements laid down, the variable nature of feed-stock in recycling would not give confidence in the analysis from batch to batch.

A further problem exists with setting ultra-low limits for impurities: how does the producer, or the customer, decide whether the specification has been met? The analytical techniques commonly used are OES, AAS, and ICP. The detection limits by direct techniques are now in the same range as the specified maxima for As, Co, Mo and Sb, whilst for Se and especially Te, the maxima fall well below the detection limits. For the first group of elements, there can be little confidence in actual concentrations at these levels, and for Se and especially Te, none of the three direct techniques are adequate. To achieve any degree of accuracy close to the limits of detection requires great care and skill on the part of the analyst. Separation and pre-concentration can increase sensitivity, but the level of proficiency and diligence required of the analyst is then still greater. Certainly for tellurium, alternative routine analytical methods are required if each batch of lead is to be analyzed.

To underline the implications of the above situation, Table 1, row 4 shows the typical analysis of Britannia Refined Metals MIM primary lead, obtained by routine analytical techniques, quoted to a resolution at which an acceptable limit of confidence may be maintained [33]. Table 1, row 5 shows a one-off reference analysis conducted on a typical sample of MIM primary lead using GDMS. This is an expensive, time-consuming and exotic analytical technique which is totally unsuitable for routine analysis, but which can determine accurately, very low levels of impurities.

The material subjected to routine analysis might meet the most stringent of the above requirements, perhaps easily, but given the sub-1 ppm requirement for Te, Se and to a lesser extent, As and Sb, it is not possible to tell. The exotic, expensive, non-routine analysis shows that the material analysed meets easily all of the requirements for purity of the most stringent standard. While this situation exists, the only viable solution for a battery manufacturer who requires such a pure product is to form a good long-term relationship with a major lead supplier who they can trust, and who produces top-quality lead without significant variation from batch to batch, or preferably from year to year.

Is such stringent control of impurities essential with all elements, or is it a counsel of perfection? Recommendations have been made that the maximum silver content in soft lead for VRLA battery oxide should be 10 ppm [9]. In one study [23] where silver was added to the electrolyte, cyclic voltammetry suggests that silver is disastrous for gassing performance at both electrodes, whereas for battery oxide in a real battery, 40 vs. 5 ppm of silver showed a difference of 3% in the reduction of the capacity after storage for 8 weeks. Silver and zinc dopants have been

Table 1
Maximum impurity limits for lead for battery oxide in ppm, compared with detection limits and analyses

| Row | Ag | As[b] | Ba | Co[b] | Cr | Cu | Fe | Mn | Mo[b] | Ni | S | Sb[b] | Se[c] | Te[c] | V | Bi | Cd | Sn | Zn | Co+Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 1 | 10 | 1 | 5 | 10 | 5 | 3 | 3 | 2 | 10 | 1 | 1 | 0.3 | 4 | – | – | – | – | 10 |
| 2 | 35 | 0.5 | – | 1 | 5 | 10 | 5 | 0.5 | 1 | 1 | 5 | 0.8 | 0.5 | 0.2 | 1 | 250 | 5 | 10 | 5 | – |
| 3 | – | 1 | – | 1 | – | – | – | 0.5 | – | – | – | 1 | 0.5 | 0.3 | – | – | – | – | – | – |
| 4 | 5 | <1 | – | <1 | – | <1 | <1 | <1 | – | <1 | <1 | <1 | <1 | <1 | – | 15 | <1 | <1 | <1 | – |
| 5 | 4.6[a] | <0.005 | 0.02 | <0.005 | 0.87 | 1.3 | 0.02 | <0.001 | <0.005 | 0.03 | 0.02 | 0.01 | <0.01 | <0.005 | <0.001 | 21.6[a] | 0.51 | <0.01 | <0.01 | – |
| 6a | 2 | 2 | – | – | – | 0.5 | 2 | – | – | 2 | 2 | 5 | 5 | 5 | – | 10 | 2 | 5 | 2 | – |
| 6b | 2 | 5 | 100 | 2 | 5 | 2 | 5 | 2 | – | 2 | – | 20 | 10 | 20 | – | 20 | 2 | 20 | 1 | – |
| 6c | 0.06 | 5 | 3 | 1 | 0.2 | 0.1 | 0.3 | 0.1 | 2 | 0.3 | – | 10 | 4 | 2 | 0.2 | 1 | 0.3 | 5 | 0.3 | – |
| 7a | 0.5 | 1 | – | – | – | 0.5 | – | – | – | 0.5 | 2 | 1 | 5 | 5 | – | 1 | 0.5 | 1 | 0.5 | – |
| 7b | 1 | – | – | – | – | 1 | – | – | – | – | – | – | – | – | – | – | 0.1 | – | 0.5 | – |
| 8c | 0.5 | 5 | 0.5 | 1 | 0.2 | 0.1 | 1 | 0.05 | 2 | 1 | 2 | 2 | 5 | 2 | – | 1 | 0.1 | 10 | 0.2 | – |

[a] Ag and Bi figures in row 5 determined by inductively coupled plasma (ICP), as too much is present for accurate analysis by glow-discharge mass spectrometry (GDMS).

[b] Elements where proposed maxima are similar to detection limits for direct analysis by optical emission spectrometry (OES), atomic absorption spectroscopy (AAS) and ICP.

[c] Elements where proposed maxima are substantially less than detection limits for direct analysis by OES, AAS and ICP.

Row 1. Specification proposed by D.M. Rice and J.E. Manders of Pasminco [9].

Row 2. Specification proposed by R. David Prengaman of RSR [26].

Row 3. Specification proposed by A.I. Rusin of the Chemical Power Sources Institute, Belgrade [32].

Row 4. Typical impurity levels of Britannia Refined Metals primary lead refined from MIM bullion [33].

Row 5. Analysis of Britannia Refined Metals MIM primary lead, by GDMS.

Rows 6a,b,c. Detection limits by (a) OES, (b) AAS and (c) ICP using direct techniques, from R. Höhn and A. Ueberschaer [34].

Rows 7a,b,8c. Detection limits by (a) OES, (b) AAS and (c) ICP using direct techniques, current situation at Britannia Refined Metals.

found to suppress the evolution of hydrogen on negative electrodes [35,36].

Also, a comment has been made that bismuth is currently specified at levels too low to be beneficial [23]. Research has shown that bismuth in the positive active mass can be beneficial [37], and other work drew the conclusion that a minimum bismuth content for both positive and negative oxide should be specified [36]. This has culminated recently in the introduction by a major primary lead supplier of a bismuth-bearing primary lead, low in other elements, for battery manufacture [25].

## 4. Additives

Battery additives have been in use in one form or another almost since the beginning of the industry. Those currently in use have a negligible effect on recycling. Today, however, there are some additives under consideration which may be particularly pernicious.

### 4.1. Paste additives

Traditionally, barium sulfate, lignosulfonates and related compounds and finely divided carbon have been added to the negative paste as an 'expander'. Humic acid salts, tanning agents and other organics are also used. Sometimes, fine polymeric fibres are also added, as are stearic acid and carboxymethyl cellulose. None of these materials present any problem in recycling. Synthetic formaldehyde expanders have been developed [22]. It is not clear how these would behave in recycling.

One proposal for future additives is to add a conductive polymer powder to the active mass of the battery [38]. These polymers include polyaniline, polypyrrol, etc. Some of these polymers, and/or their decomposition products, may be potent carcinogens. These products may include dioxins. Careful consideration will be needed as to the implications for manufacturing of the battery, and especially for recycling.

Another additive which has been tested in the positive active-mass is carbon fibre. This seems unlikely to be adopted, but would pose no problems. Research under the ALABC programme has investigated the use of additives or layers of materials which create an osmotic driving force through the active mass [39]. Most of these are based on fluorinated polymers, such as polyvinylidiene di-fluoride (PVDF). Fluorinated compounds should be approached with extreme caution from the recycling perspective, as it is not clear whether fluorine compounds will report to the slag, or whether hydrogen fluoride will be produced [14]. If the former, leachable species might be present, giving potential groundwater pollution and, if the latter, there would be serious safety, gaseous emission and plant corrosion implications.

### 4.2. Acid additives

Phosphoric acid has been added to the electrolyte of lead–acid batteries since the 1920s. Recent work [40] suggests that there is some benefit in adding it to lead–acid EV batteries. Silica is used to gel electrolyte in VRLA batteries. Polyacrylamide-emulsion polymer has been advocated for gelled electrolytes [41].

Phosphoric acid should not cause any problems, provided that the quantity is small [14], except where a recycler intends to recover a high-grade acid, sulfate, or other product for sale, where there is a possibility that the contamination might be difficult or expensive to remove.

Gel batteries may be difficult to separate into their components and the water requirement in washing may be greater [14]. More potent gelling agents and stiffer gels would exacerbate this behaviour. A further problem is that electrolyte will be retained in a gelled battery, rather than being drained at the start of processing [14]. This also may complicate acid recovery where a saleable product is to be recovered, due to dilution effects and greater volumes to be treated. Fluctuating levels of silica gel entering the process could also affect process stability and performance.

## 5. Separators

Recyclers already cope with rubber, cellulosic, polyvinyl chloride (PVC), and polyethylene separators. These can contain fillers such as silica, oils, phenol formaldehyde resin, as well as the main structural materials.

There are existing problems with PVC. This may be separated out and sent to landfill, where there may be a problem with plasticizers. These are commonly phthalates, which have been identified as oestrogen-mimicking compounds, which may therefore have biological effects. They are persistent in the environment, and could leach out of the PVC over time. If PVC finds its way into the smelter, chlorine is produced. This has implications for corrosion, and emissions may be toxic, especially if reactions occur with complex organics to form dioxins. Replacement of PVC by a more recycling-friendly alternative would be desirable.

Inclusion of materials which either themselves, or as decomposition or reaction products, are extremely carcinogenic or toxic, is to be discouraged. Some polymers may react in recycling to form dioxins (see PVC above).

Coating the grids with polymeric materials by dip-coating has been tried [31]. This might make removal and treatment of the paste more difficult in some plants, depending on the physical nature of the coating.

The most likely change in separator material would be a move towards glass-mat separators in VRLA automotive batteries. Glass fibre is abrasive, is not recoverable, would

provide an additional maintenance overhead and would have a nuisance value [14].

## 6. Case materials, construction and design

The present material of choice is PP. Other case materials exist. These include co-polymers of polyethylene and PP, polyethylene reinforced with glass fibre, or with kaolin as a filler, acrylonitrile butadiene styrene (ABS), and polystyrole [31]. Foamed plastics, especially foamed polyethylene, have also been used. PP is an inspired choice for recycling, since it is possible to recover it comparatively easily during battery-breaking, and to clean it and process it without degradation to obtain a material that is acceptable for recycling into battery cases. Indeed, with sufficient care, it can reliably reach sufficient purity to be used in the manufacture of water pipes. Here though, just as with the choice of grid alloy, apparently minor decisions by the battery manufacturer can have unforeseen consequences for the recycler.

A problem which currently affects the acceptability of recycled PP polymer for the most demanding users is indirectly related to the colour of the case. Most battery cases are translucent white with top trays of more brightly coloured PP. This normally presents no problem whatsoever. Some manufacturers decide from time to time that all, or part, of the case should be yellow. These can be a thorn in the side later in the recycling chain, as the yellow colour is often provided by cadmium-based pigments. This then contaminates the bulk of the recovered PP, which may then fail acceptance criteria due to such cadmium contamination. The battery manufacturer may be tempted to say, 'well, pick out the yellow ones', but if scrap batteries are delivered in mixed loads to a large storage bay which has a throughput of 2000 tonnes per month or more, and which is kept tidy with the aid of heavy earth-moving machinery, hand-picking is not an acceptable option. The heart-felt plea of the recycler would be to find an alternative pigment, or an alternative colour if this is not possible.

If, as seems probable, VRLA batteries become common in automotive and EV applications, the choice of material and the strategy used to provide compression will be fundamental to the recyclability of a lead–acid battery. It seems to be possible by careful design, to provide adequate compression by judicious addition of strengthening ribs to a PP case [10,11]. This would provide no problems to recycling with current battery-breaking and separation technology.

Some workers in the field have advocated ABS for case construction in VRLA batteries due to its superior physical properties. The one attribute which seems to be rather lower than desired is impact resistance. This shortcoming, however, should not affect its performance in internal module cases for EV batteries. Should ABS, or a similar polymer, be adopted, recycling would be altogether more difficult. It should be possible to modify and tune hydrodynamic separation equipment to separate ABS from PP. The remaining problem is that unlike PP, there are many blends of ABS in use with different fillers and properties.

A random blend of ABS grades would be very difficult to sell, as the final properties could be disastrous, even when added to virgin terpolymer at the recommended maximum of 10% [42]. Even for single-grade regrind, commercial values are comparatively low. If more than one grade were to be adopted for use in batteries, separation of one grade from another would be difficult to justify economically and ABS cases would, in the short term, be burnt by many recyclers for their calorific value in smelting. In the longer term, it is possible that lead recyclers may have to consider alternative processes to the pyrometallurgical routes which are currently wide-spread. This would probably result in battery case materials going to landfill—not an environmentally sound approach.

If battery manufacturers must use ABS, industry-wide agreement on an optimum grade of ABS, with specified fillers should be an important goal. The optimum solution from the recycling perspective would be to use only PP for battery cases.

A far more difficult problem for recyclers would be adoption of integral steel-reinforcing elements, or even a steel case: a solution that some manufacturers have considered. This would be disastrous for recycling. No battery-breaking equipment now in use could deal with such a feedstock and any such machine which is designed for the purpose would be large, expensive, inefficient and be prone to excessive wear, breakdowns and maintenance. If such cases prove to be essential to achieve compression, a partial solution to the problem might be effected at the concept stage. A possible strategy might be to use hot-melt adhesives to assemble the reinforcing elements on the outside of the case, so that a hot tumble prior to battery-breaking could separate the steel from the battery. Another interesting possibility is that if the proposed internal pressurised bag system [43] is used to provide plate-group compression, it might be feasible to design the case so that it fragments cleanly on application of massive over-pressure to the bag, perhaps by compressed air to an external valve, releasing the contents cleanly.

Another possibility that has been discussed is to build a battery compartment into the car which allows compression to be applied. This neatly leaves the steel as part of the car, and would result in a battery which could be far less stiff than otherwise.

Flame retardants in plastics may cause environmental problems. Polybrominated biphenyls are extremely persistent in the environment and have been recently identified as having an environment impact. Flame-retardant systems should be considered from a recycling perspective to minimize any potential problems.

Recent developments in chemical markers called chromophores, added to plastics in ppm quantities, may allow plastics to be differentiated by fluorescence spectroscopy in the future. Current trials have succeeded in sorting three components a second with 100% accuracy [44]. An appealing thought is that if a battery case were identified as to the alloy system inside it, automatic sorting might be possible. This may be worth active investigation.

A final thought on design for recycling: mechanical battery-breakers are used by most recyclers, as this is the most effective technology currently available to dismember lead–acid batteries. These are expensive to buy, suffer from extreme wear, are subject to considerable damage if they ingest a piece of steel, or other hard material, and suffer from a lot of down-time and high maintenance bills. Is it feasible to design a battery case for disassembly, so that a battery may be easily separated into its component parts? Is it even possible to design battery cases which can be emptied and re-used? This way of thinking has been formalised as 'design for the environment (DfE)', which has been embraced by other industries; the battery industry should adopt it too.

Could it also be possible to reach agreement between car manufacturers and battery manufacturers on absolutely standard battery sizes with common terminations, as currently is the case for small primary cells? This might not have a major impact now, but there are many small ways in which it would benefit everyone in the future: the battery manufacturer and stockist would need a smaller stock-holding; the battery manufacturer would also have simplified production scheduling and component inventory; the recycler might be able to handle batteries with more finesse to recover materials more effectively; the car owner would stand a better chance of finding the correct replacement battery at the first port of call; the car manufacturer would be reducing costs in the recycling chain.

Such standardization is perhaps a counsel of perfection; it may almost be considered to be a flight of fancy. The fact that this is so, perhaps highlights how the battery industry is driven at each stage by absolute customer demand, not by informed, constructive, optimized design. If true standardization ever happens, it might be regarded as the acid test of communication, agreement and cooperation in the supply chain.

## 7. Discussion

The foregoing is not intended to be negative or Luddite in its message. If modifications to the materials, design, or construction of lead–acid batteries result in a product which is clearly better, more competitive, more cost-effective, more environmentally friendly, or which addresses new markets, then this product will and should happen.

Without good, competitive, constantly improving products, there will be no industry.

The thrust of the argument presented here is that significant developments with lead–acid batteries will occur in the near future. Some of these changes may influence the economics, nature, or environmental impact of recycling. Advance planning may be necessary in order to cope with the ramifications of these developments, especially for secondary smelters, where plant is very expensive and amortization must be over many years.

Currently, lead producers talk to battery manufactures, although often a comprehensive discussion of the recycling issues does not take place. Battery manufacturers talk to car manufacturers about current and future requirements—although communication here can evidently be less than perfect [45], but much of what is discussed will be regarded as commercially sensitive. In these discussions also, it is unlikely that issues surrounding recycling will be a major topic. Manufacturing decisions by car manufacturers may influence which of the many possible technical developments are actually implemented by the battery manufacturers. Some of these may affect the recycling behaviour of the battery.

It is not easy for lead producers faced with extensive work in the literature to second guess which developments will actually make it from the laboratory into the market place. It is also likely that optimization of any parameter not directly related to cost or performance will be quite low on the agenda in the debate between car and battery manufacturers.

The use of materials in lead–acid batteries that do not lend themselves easily to recycling is not new: Lyndon [1], in 1911, refers to a Worm grid, which contained 1.3 wt.% mercury, 2.2 wt.% antimony, remainder lead, and the Julien grid with 4.5 wt.% mercury and 3.5 wt.% antimony. He also mentions the use of asbestos fibre as a binder in paste. It is fortunate indeed that this combination did not find universal favour.

## 8. Concluding remarks

It is advocated that the following three strategies should be urgently considered to provide a more solid and reliable foundation for the battery industry, and for the lead industry as a whole.

(1) An informed and open three-way dialogue should be encouraged between car manufacturers, battery manufacturers, and lead producers. This would probably be more productive if implemented strictly between those parties in a particular supply chain, with confidentiality agreements in place where appropriate. The aim should be to identify the developments which are actually intended for production, with associated information on materials specifications where possible. Ramifications for all aspects of the life-cycle of the product should then be considered. It may

be that no-cost modifications to the intended product at this stage could have benefits outside the areas currently considered.

Car manufacturers, including industry leaders such as VAG and BMW, now consider recycling aspects of their product at the design stage, allowing this perspective to influence the choice of materials and to drive a process of design for disassembly. To argue for an extension of this process to cover bought-in items which are replaced several times during the life of a car should be knocking on an open door. It is likely that legislation will add further impetus to recycling.

(2) Life-cycle analysis (LCA) should be applied to batteries. This can be a complex, unrewarding and sometimes sterile exercise if approached in the wrong way. On the other hand, if used in a structured, focused manner, starting with a simple framework and building in complexity as required, valuable insights into the true costs, benefits and impacts of a product in its life from cradle to grave, or with a fully recyclable product such as the lead–acid battery, from cradle to cradle, may be gained.

Work is currently being sponsored in this area by Britannia and a recent paper [46] explains why this process is essential to the future of the whole industry. One of the authors, J.G.S. Robertson, has continued the work, which will be presented in a suitable forum in 1999.

LCA has been increasingly used to support one product or family of products against another. Lead suffers from a knee-jerk antipathy in many areas, including governments, regulators, pressure groups, and even in some areas, the general public. This technique can provide the logical, reasoned case for using lead, rather than an alternative technology.

(3) Where clear industry-wide indications exist, possible strategies should be discussed amongst all parties involved in the manufacturing/recycling loop and optimum solutions should be found. To return to the example of silver in battery alloys, the battery manufacturer will have to pay for its addition. If the chain operates as it does now, the recoverer/returner of the battery will see no extra for the battery for the silver content, the smelter/refiner will see a negative value for the silver due to the overall degradation of secondary lead, and the battery industry may find it difficult to source alloys requiring a low level of silver from secondary sources.

If batteries containing silver were readily identifiable, the option would exist at some point in the future to segregate those which contain silver from those which do not. This might allow economic recovery of the silver values from the segregated stream. For this to succeed, an agreed, standardized method of identification must be in place before any battery manufacturer launches a product of this nature. A suitable method of identification could be by colour, say a green stripe in the lid, or some other feature not currently used in a commercial design in Europe. This approach would be appropriate for any development where subsequent segregation would increase the economic value, minimize environmental impact, or both.

There is also a powerful argument for uniquely identifying batteries containing high-tin, silver-free alloys, as segregation from those using antimonial alloys allows the possibility of campaigning for different types to simplify recycling. This would maximize tin-recovery and minimize contamination of the tin by antimony.

Silver-bearing alloys are offered as an example: they might not be widely adopted at all. Nevertheless, the odds are that one or more of the developments that will gain favour at the turn of the century and beyond will have a potentially negative impact which might be avoided by industry-wide discussion at an early stage.

Given the current position in Britain with regard to transportation licences and other legislative issues coupled with the low value of scrap lead–acid batteries, an increasing number of traditional scrap merchants are no longer prepared to deal in these products. Any factor which reduces further the economic value of batteries at this point in the recycling chain is likely to reduce substantially the percentage of batteries recycled. To not recycle would be unacceptable to Europe, the British Government and many organizations and individuals. In this event, the options available would be to get out of the battery business, or to introduce a formal recycling scheme funded by a levy, possibly in the Swedish or Italian mould. If this analysis of the situation is accepted, industry-wide cooperation and discussion, combined with a pro-active approach to recycling must be an extremely attractive proposition.

A final thought: first, imagine a world 5 or 10 years hence, where lead–acid batteries are unidentified and where silver contamination has become a major problem. Due to this, and to other problems in recycling arising from unfriendly design and construction of lead–acid batteries, some secondary manufacturers are in danger of going out of business, and others are suffering. There is not a sufficient market for secondary lead with silver. Batteries for recycling have little monetary value and primary lead is cheaper to produce than secondary lead. Secondary refiners will not take material which they cannot sell, and the few lead producers who can remove silver from lead cannot afford to take the batteries, as the economics are so unfavourable. Legislation now in place requires each battery manufacturer to take back all the life-expired batteries which they have made and their sites are overflowing. Legislation also requires that all batteries are recovered and that it is the battery manufacturers' responsibility to either use recycled lead for their products, or ensure outlets elsewhere for any surplus. Finally, a recycler says that it will take the mongrel mountain of batteries, but will have to ask for, say, £60 per tonne (about £1.00 per battery), as a treatment charge to cover additional refining costs.

Now, imagine a world where batteries are clearly identified as to the alloy they contain, and lead–acid batteries are designed for recycling. For high-tin, silver-free batter-

ies, there is strong competition. For mixed batteries without silver, there is a healthy market. Secondary producers can produce recycled lead that is competitive in costs with primary lead. For batteries which contain silver, if the grids have sufficient in them (say 300 ppm), a recycler with a silver recovery plant may be able to cover costs on silver recovered and may not have to make a treatment charge. Recycling reaches almost 100%. Lead–acid batteries continue to have a competitive edge in the market place and regulators and legislators accept that it is a green technology.

Are these worlds works of fiction, or might one of them be a glimpse of the future?

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