

Use of secondary lead for new generations of lead/acid batteries

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Abstract

Secondary lead will become more and more the main source of raw material for battery producers. The final objective of this study is to define maximum levels of impurities compatible with the use of secondary lead for oxide production for maintenance-free automotive batteries. Today, statistical investigations show that the quality of secondary lead can vary with the smelter, and can be adjusted in certain cases, but it is necessary to evaluate more accurately the effect of each harmful impurity (alone or in combination). Impurities affect principally the self-discharge of batteries. Addition of impurities to the electrolyte has been proved to give non-realistic values of their real influence in batteries. In order to obtain accurate results of the effect of impurities at various levels, syntheses of Barton or mill oxides containing Bi or Ag added to lead of high purity have been undertaken. It has been clearly shown that levels up to 200 ppm Bi or 40 ppm Ag can be admitted without significant differences in the performances of automotive batteries.

Introduction

Within the next ten years, the percentage of recycled lead/acid batteries should increase to almost 100%, with respect to the modifications of regulations. As a consequence, secondary smelters will become the major source of lead for battery producers. On the other hand, it is foreseen that automotive batteries will require an increasingly reduced water consumption, or will even be valve-regulated and designed for gas recombination. These trends require purer oxides. What must be the quality of secondary lead required for such new generations of maintenance-free or valve-regulated batteries is an important question both for battery manufacturers and for lead producers.

In the framework of a three-year EEC programme, a team of six research laboratories of European lead producers, battery manufacturers and universities has studied the effect of some impurities that are normally present in secondary lead. Some of the results are presented below. The original feature of the approach consisted of starting from pure-lead metal doped by the specific element, oxidizing the metal into leady

oxide on an industrial scale, pasting grids, and finally performing comparative tests in batteries.

Lead for battery applications and requirements of battery manufacturers

The lead producers' point of view

As reported by Pugh [1], the consumption of lead in recycleable uses has already increased to 80% of its total consumption in 1990. It is expected that this level will reach 90% in the year 2000, under the pressure of more stringent regulations of Western governments. Among these uses, lead/acid batteries represent the main consumption. Today, up to 70% of total Western-world lead production is devoted to this use. The proportion is expected to increase to up to 75%. Accordingly, in the near future, secondary production can be expected to become the main supply of lead to battery manufacturers. Primary production will be considered as a second-order capacity.

With respect to the impurity content of secondary lead, the questions that must be considered are: the nature of elements, the methods of analyses, and the level of concentrations.

To find out what possible traces and accompanying elements are to be encountered within secondary lead, five batches of lead were carefully screened with trace-analytical methods that included: optical emission spectroscopy, excitation by spark or inductively-coupled plasma, and atomic absorption spectrometry.

It emerged that only the elements Ag, Bi, Cu, Ni and Tl occurred in concentrations above the limits of detection of the respective analytical procedures (Table 1, detected elements are underlined).

Sampling campaigns were undertaken in four plants, in order to determine exactly the level of these five impurities present in various lead batches. The actual concentration of these elements has been evaluated statistically. The results are given in Figs. 1 to 5. From these data, the percentages of batches with defined maximum Ag, Bi, Cu,

TABLE 1

Detection (ppm) of trace and accompanying elements in secondary soft lead^a

<u>Ag</u> > 0.06	Fe < 0.3	Pd < 1
Al < 1	Ga < 0.4	Sb < 5
As < 5	Ge < 0.2	Se < 4
Au < 0.5	Hg < 1	Sn < 5
Ba < 3	In < 1	Sr < 0.5
Be < 0.01	K < 10	Te < 2
<u>Bi</u> > 0.1	Li < 0.5	Ti < 0.2
Ca < 0.3	Mg < 0.1	<u>Tl</u> > 2
Cd < 0.3	Mn < 0.1	V < 0.2
Co < 1	Mo < 2	Zn < 0.3
Cr < 0.2	Na < 0.5	
<u>Cu</u> > 0.02	<u>Ni</u> > 0.02	

^aThe compilation states, in alphabetical order, whether the concentration of a specific element in ppm is above or below its limit of detection (referred to the respective analytical procedure applied).

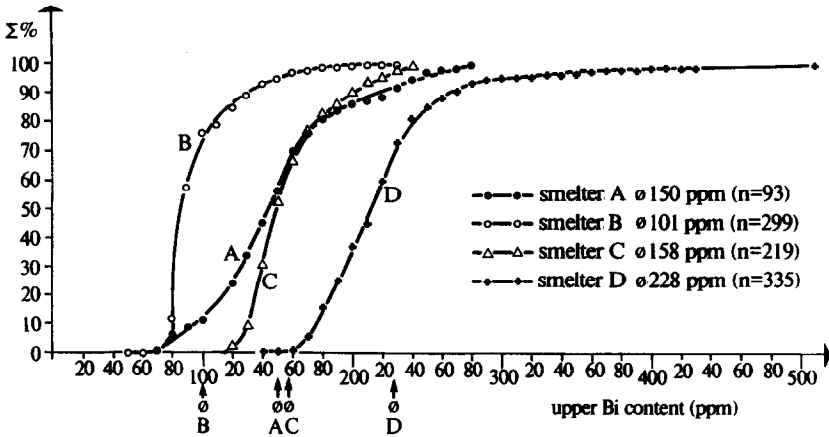


Fig. 1. Statistical data on bismuth content in secondary lead; percentages of batches with defined upper limit of bismuth content in soft lead of four secondary smelters.

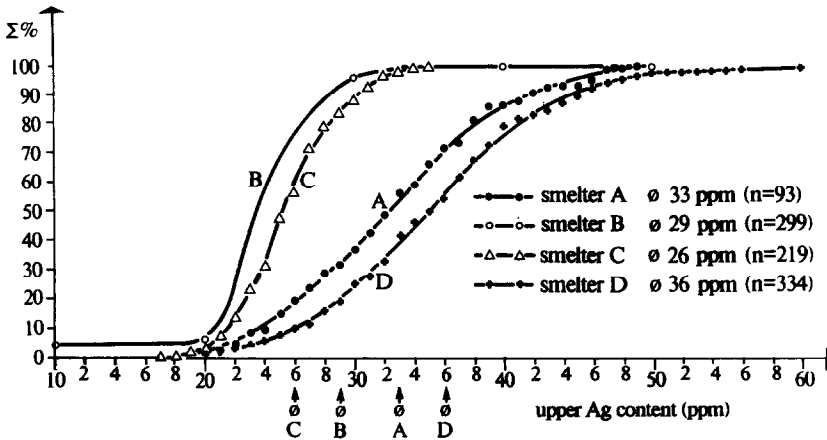


Fig. 2. Statistical data on silver content in secondary lead; percentages of batches with defined upper limit of silver content in soft lead of four secondary smelters.

Ni or Tl contents, respectively, can be taken for the given smelters. The latter are indicated as A, B, C and D. The maximum contents are given by the abscissa and their respective percentages of batches are indicated by the ordinate. The diagrams also contain the respective mean values and numbers of batches (n) considered.

As is obvious from the obtained information, the levels of accompanying elements can vary considerably from smelter to smelter. The reason may, on one hand, stem from different separation and refining technologies. On the other hand, differences in mixing of the raw materials may also be a possible explanation. Besides spent batteries, the raw-material mixes may have also contained scrap from cable sheaths, construction materials, semis, linings and the like, as well as drosses, ashes, flue dusts, etc. Furthermore, the possibility of contamination must be considered, e.g., through

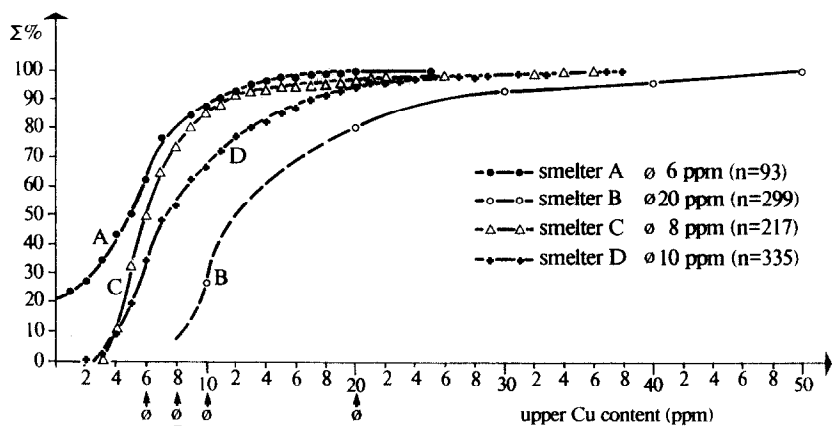


Fig. 3. Statistical data on copper content in secondary lead; percentages of batches with defined upper limit of copper content in soft lead of four secondary smelters.

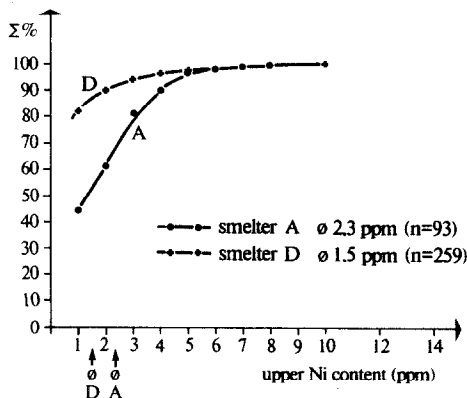


Fig. 4. Statistical data on nickel content in secondary lead; percentages of batches with defined upper limit of nickel content in soft lead of two secondary smelters.

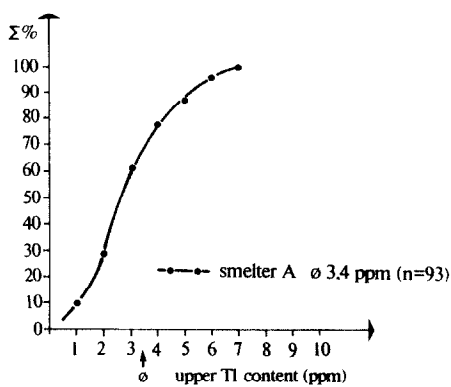


Fig. 5. Statistical data on thallium content in secondary lead; percentages of batches with defined upper limit of thallium content in soft lead of one secondary smelter.

stray Ni/Cd batteries, etc. Finally, among the five elements, the concentrations of Ag and Bi are, and this is only for economic reasons, typically higher in secondary lead than in primary lead.

Battery manufacturers' point of view

In the meantime, the requirements for a completely maintenance-free battery, and the increasing use of sealed batteries, has resulted in battery manufacturers increasing their demands for purer primary lead. In order to compare the typical composition of a secondary lead with the request of the battery industry, a broad set of specifications for oxide and lead-calcium alloys was collected (see Table 2).

TABLE 2
Permissible trace elements (wt.%) in lead for oxide manufacture. Individual manufacturers indicated by letters

Element	A	B	C	D	E	F	G	H	J	A1	A2	A3
Pb	99.97	99.99	99.97	99.99	99.99?	99.97	99.95	99.99	99.99	99.97	99.97	99.96
Ag	0.005	0.001	0.005	0.0019	0.001	0.005	0.006 0.002	0.002	0.002	0.001	0.001	0.001
Al												
As	0.001	0.0005	0.001	0.0019	0.001	0.002	0.0005	0.001	0.002	0.0005	0.0005	0.0005
Bi	0.03	0.003	0.03	0.01	0.024	0.024	0.025	0.003	0.005	0.025	0.025	0.025
Ca				0.0008								
Cd		0.0005	0.001		0.001	0.001	0.0015	0.0005		0.0003		
Co							0.0005					
Cr			0.0005				0.002	0.0001				
Cu	0.003	0.001	0.003	0.0008	0.001	0.005	0.003	0.003	0.002	0.0003	0.0003	0.001
Fe	0.005	0.002	0.005	0.003	0.001	0.004	0.001	0.005	0.002	0.0005	0.0004	0.0004
Mn	0.0005		0.0005	0.001			0.005	0.001	0.002			
Mo							0.002					
Ni	0.001		0.001	0.0008	0.001	0.003	0.001					
Pt				absent								
S			0.001					0.0005				
Sb	0.005	0.001	0.005	0.0019	0.002	0.001	0.0005	0.005	0.005	0.0025 ^a	0.0025 ^a	0.0025 ^a
Si								0.005				
Sn	0.001	0.0005	0.001	0.0019	0.001	0.001	0.001	0.001	0.005	0.0005		
Te	0.0005	0.0005		0.0008			0.0005					
Th				0.0008								
Tl												
V							0.002					
Zn		0.0005	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.0005	0.0006	0.0005
Cl	0.001		0.001					0.001				

^aConcentration range stated for antimony 15–25 ppm.

Among existing specifications for lead oxide, or for lead-calcium alloy production, some can be met only with primary lead, others easily with good quality secondary lead, while a third group requires secondary lead provided special batches with appropriate compositions are chosen carefully at the smelter. The main problems, whether technically justified or not, are Ag and Bi. Cu can also be a critical element for certain smelters. Other elements such as As, Cd, Fe, Ni, Sb, Sn, Te and Zn, or even such exotic ones as Co, Cr, Mn or V, that are sometimes specified by battery manufacturers at very low maximum levels, should not pose any particular problems for good secondary smelters.

Differences occurring from the use of lead with impurities in batteries: lead oxidation

Oxidation tendency is an important processing property of lead melts in two aspects. In addition to other factors, it determines whether a lead (or lead alloy) melt is susceptible to metal losses and processing disturbances through excessive drossing and, conversely, it is a crucial factor in oxide production in a Barton pot. It is known that the oxidation tendency of a melt is strongly effected by its content of trace and alloying elements.

Influence of trace elements on the oxidation tendency of lead melts at 400 °C

An interference colour test method has been used to analyse the effect of 28 potential trace elements on the oxidation tendency of lead melts. A very pure electrolytically-refined primary lead has been chosen as a baseline material (see composition, Table 3).

The addition of the foreign elements has been effected at different concentrations. A classification has been achieved between elements strongly accelerating (such as Sb, Ca, Co), moderately accelerating (such as Ni, Se, Te) or retarding the oxidation tendency (Sn, for example). According to the oxidation diagrams, (Figs. 1 to 5), it can be clearly seen that the effect of Ag, Bi and Cu on the oxidation tendency of lead melts at 400 °C is negligible, at least in the concentration range in which primary lead differs from secondary lead. It must be noted that Ca increases the oxidation tendency dramatically. Results are detailed hereafter in Table 4.

Influence of trace elements on lead oxide production in a Barton pot

Five batches of lead oxides with special compositions were produced in the Metaleurop plant at Rieux (France) in order to evaluate the effect of impurities on

TABLE 3

Composition of base lead (99.995 wt.%). Values, in ppm, obtained by trace analytical methods^a

Ag = 4.57	Co < 0.01	Pd < 0.1
As < 0.04	Cu = 0.4	Sb < 0.05
Bi = 13.9	Fe = 0.16	Se = 0.02
Ca < 0.01	Mn < 0.02	Te < 0.1
Fe = 0.16	Ni < 0.02	Tl = 6.07
		Zn = 0.09

^aMean values for two samples.

TABLE 4

Summary of the results of the interference colour tests

Trace element	Investigated range of concentration (ppm)	Oxidation tendency of lead melts
Li	2.0-13.0	strongly accelerating
Co	2.0-3.0	strongly accelerating
Ba	6.0	strongly accelerating
K	< 50	strongly accelerating
Sr	13.0-380.0	strongly accelerating
Zn	0.09-4.0	no effect
	4.0-69.0	strongly accelerating
Mg	3.0-4.0	retarding
	4.0-39.0	strongly accelerating
Ca	5.0-86.0	strongly accelerating
Ce	< 6.0	retarding
	6.0-130.0	strongly accelerating
Sb	1.0-25.0	strongly accelerating
	0.3-30.0	strongly accelerating
As	< 1	strongly accelerating
	2.0-50.0	moderately accelerating
Na	1.0-5.0	strongly accelerating
Ni	3.0-49.0	moderately accelerating
Pt	5.7-55.0	moderately accelerating
Se	4.0-80.0	moderately accelerating
Hg	5.0-61.0	moderately accelerating
Te	5.0-65.0	moderately accelerating
S	3.0-17.0	moderately accelerating
Tl	6.0-340.0	weakly accelerating
Cd	0.45-74.0	weakly accelerating
Pd	4.6-44.0	weakly accelerating
Mn	2.0-4.0	weakly accelerating
Cu	0.39-92.0	weakly accelerating
Ag	4.56-61.0	weakly accelerating
Bi	13.6-340.0	
Cr	4.0-10.0	retarding
La	37.0-230.0	retarding
Sn	< 5.0-5.8	
Al	4	hindering

the oxidation process, and also to perform battery tests with industrial oxides. Four lead qualities were chosen: (i) very pure electrorefined lead (batch 1); (ii) primary lead (batch 2); (iii) secondary lead (batch 3); and (iv) primary lead doped with bismuth up to 500 ppm (batch 4).

The oxides were prepared in a P20 reactor. A minimum of 10 tonnes of oxide was produced, to have stabilized parameters of production. The different adjustments of the P20 reactor give rise different production rates (Table 5). Concentrations of impurities of the oxides are given in Table 6. Oxides were used for battery manufacturing (see below).

TABLE 5

Production of lead oxide in P20 reactor

Lead origin	Oxide production rate (kg h ⁻¹)	Lead content (%)
Electrorefined lead	735	30
Primary lead	826	30.6
Secondary lead	734	30.6
Primary lead doped with bismuth	915	26.5

TABLE 6

Concentrations of trace elements in Metaleurop oxides (ppm)

	Pure Pb batch no 1	Primary Pb batch no 2	Secondary Pb batch no 3	Primary Pb and Bi batch no 4
Ag	3	3	21	3
Al	0.2	0.2	0.2	0.4
Bi	24	130	151	430
Ca	0.6	0.5	0.5	2
Cd	0.3	0.1	0.1	0.24
Cu	0.1	0.8	5	1.3
Fe	1	1	1	3
Mg	0.2	0.2	0.2	0.4
Mn				
Ni	<0.05	0.05	0.3	<0.05
Sb				
Se				
Sn	<0.03	<0.03	<0.03	0.2
Te	<0.1	<0.1	2.4	<0.1
Tl	6	2	3	2
Zn	0.1	0.1	0.1	0.6

It appears that the oxidation rate is particularly high with a high bismuth content. Though this difference leads to the need for a new set of parameters for running the oxidation, the main advantage is the ability to produce Barton-pot oxides with approximately the same characteristics (α/β PbO ratio, mean grain diameter, surface area) from lead of different origins.

Differences in battery performance due to the use of lead with impurities

The effect of metallic impurities that are likely to be present in lead has been examined by battery manufacturers in various ways and situations (e.g., in terms of self-discharge, water consumption, cycle life, resistance to corrosion). The majority of studies deals with the influence of impurities added to the electrolyte [2-6]. The effects are usually measured by cyclic voltammetry of small lead electrodes, or by examining the gas evolution characteristics of pasted plates. Though it is qualitatively interesting to test differences between impurities, these tests remain questionable with regard to

evaluating accurately the level of each impurity that is harmful to batteries, since they emphasize phenomena that are related to surface adsorption.

Other studies have been more directly related to investigating plates that contain impurities in the active materials themselves [7, 8]. The interesting study of Culpin *et al.* [8] has demonstrated the large differences that the use of primary or secondary lead exert on the gassing properties of negative plates. It was not possible, however, to correlate the results to analyses of the impurity contents, probably because of difficulties in determining accurately the amounts of very active minor elements.

None of the studies is really able to give quantitative results on the level of impurities that can be tolerated in secondary lead, or on the combined effect of various elements.

Tests in batteries: methodology

In the first stage of the work reported here, a review was made of the points of specifications of automotive batteries that are sensitive to the use of primary or secondary lead. This involved a comparison of the performances with different types of lead. The following characteristics were measured:

- low-rate capacity
- high-rate characteristics at $-18\text{ }^{\circ}\text{C}$
- charge profiles
- self-discharge
- capacity decay on cycling (discharge: constant current 1 h at $0.1\text{ C}/20$, charge 5 h at the same rate)

Since the self-discharge of batteries has been proven to be the parameter that is most sensitive to the use of secondary lead, it was decided to screen impurities only from this view point.

Tests with additions of impurities to the electrolyte of batteries were achieved, but the results were not satisfactory. For example, although differences in overvoltage were noticed (in agreement with well-known previous results in the literature), no clear correlation could be established with the self-discharge rates of the batteries. This is the reason why, in parallel, several tonnes of oxides with known amounts of Bi or Ag (impurities with the higher content in secondary lead) were prepared from very pure lead that contained the requisite amounts of Bi or Ag. Plates pasted from those oxides were tested in batteries. Two types of element were assembled and corresponded to positive- or negative-plate limitation. Measurement of self-discharge was made according to the following procedure:

- assembly of batteries with plates using lead-calcium-tin alloy
- formation of the batteries (2 V elements), followed by measurement of initial high-rate capacity (30 A dm^{-2} ; $-18\text{ }^{\circ}\text{C}$)
- storage at $40\text{ }^{\circ}\text{C}$ (8 weeks)
- measurement of high-rate discharge residual capacity (same conditions)

Preliminary tests made according to specifications for automotive batteries: comparison of primary and secondary lead

Primary and secondary lead from Metaleurop (for analysis, see Table 6), and two further oxides from CEAC plants were pasted on lead-calcium-tin grids. Tests were performed with the methodology described above.

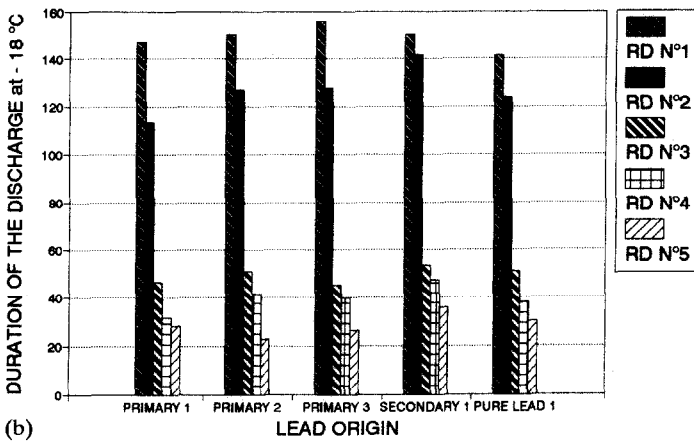
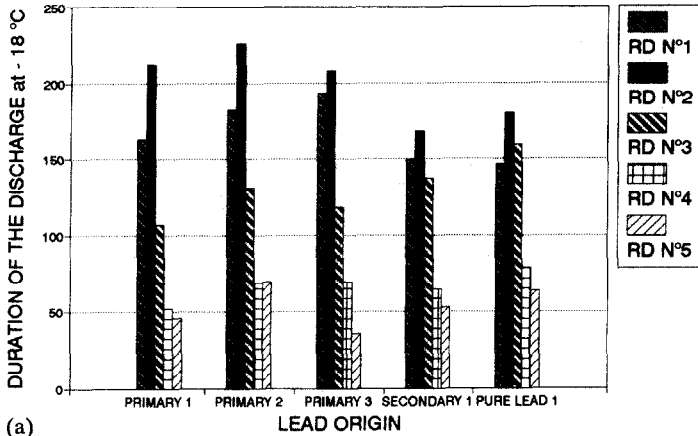
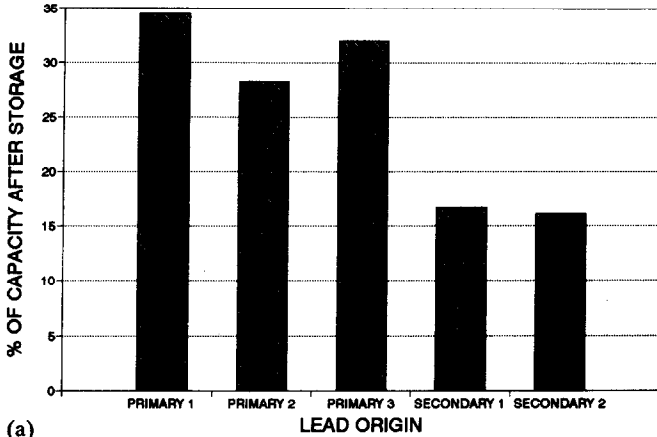


Fig. 6. High-rate discharge performance of batteries with primary or secondary lead. RD nos. 1 to 5 correspond to different cycles of rapid discharge: (a) batteries with positive-plate limitation; (b) batteries with negative-plate limitation.

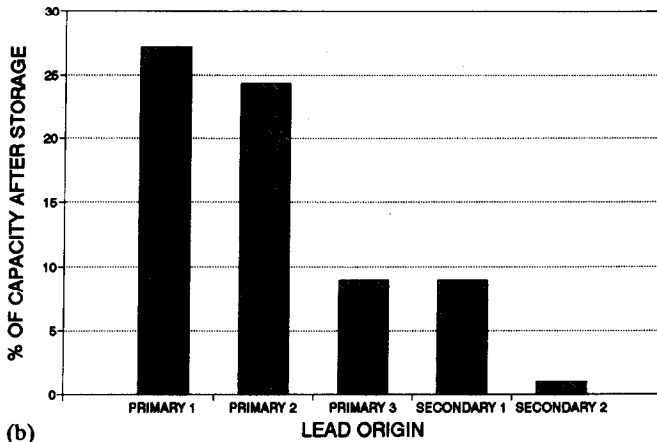
The fast-discharge capacities are given in Fig. 6. No significant differences were found between the oxides. By contrast, large differences were observed for the self-discharge characteristics (Fig. 7). The variations existed between primary and secondary lead, as well as between different primary leads.

Influence of the addition of bismuth to pure lead

Bismuth is not known to be particularly detrimental to the self-discharge reactions in lead/acid batteries. The only drawback that is often mentioned is the decrease in cycle life of some cells containing high levels of bismuth and used in deep-cycling applications. No influence of bismuth in the lead samples on cycle performance has



(a)



(b)

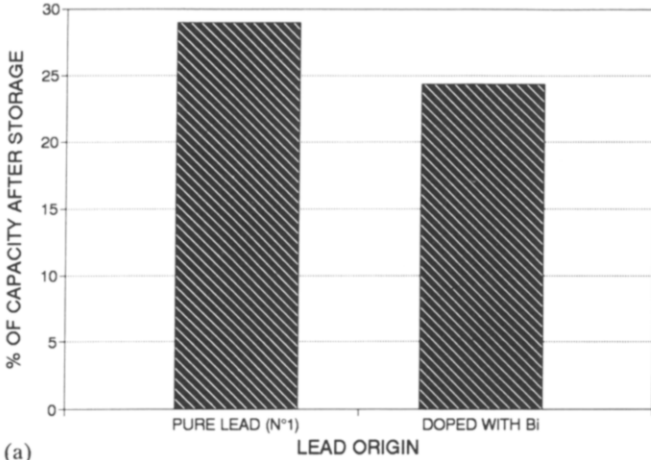
Fig. 7. Self-discharge performance of batteries with primary or secondary lead: (a) batteries with positive-plate limitation; (b) batteries with negative-plate limitation.

been noticed under the conditions of cycling used above (which correspond to automotive applications; this test does not confirm, of course, that no influence exists under deep-cycling service. This point was not examined as such duty is not relevant to automotive batteries).

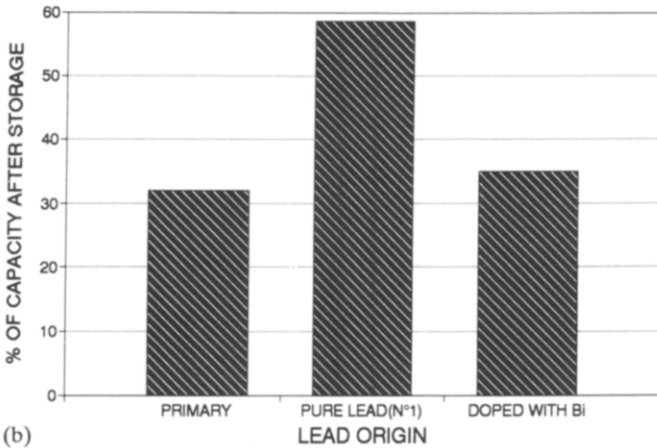
To verify the absence of influence on self-discharge, an alloy containing more than 400 ppm Bi was prepared. The complete analysis of the alloy has been given in Table 6, and the results of self-discharge measurements are presented in Fig. 8. No influence of Bi on self-discharge is observed.

Influence of the addition of silver to pure lead

Samples of lead of the same high purity (Britannia) were doped with silver, in order to obtain samples with roughly 5, 40 and 100 ppm Ag. The first sample with



(a)



(b)

Fig. 8. Self-discharge performance of batteries containing lead with 430 ppm bismuth: (a) batteries with positive-plate limitation; (b) batteries with negative-plate limitation.

5 ppm was, in fact, pure lead without the need for Ag addition. Oxides were made using the mill technology at the Cookson plant.

The influence of the amount of Ag on self-discharge of batteries was tested according to the method described above. Results of the test are given in Fig. 9. This shows a limited influence of Ag when added as a single element to the alloy. After an 8-week storage at 40 °C, the loss of capacity of batteries with 100 ppm Ag in the oxide, compared with batteries using pure lead, is only 5% for batteries limited by the positive plate, and 10% for batteries limited by the negative electrode. With 40 ppm Ag, the difference in capacities between batteries with or without Ag is lower than 3%, and is considered to be non significant.

These results must be compared with those from cyclic voltammetric experiments that are given in Table 7. In this Table are expressed the ratio of currents measured at constant voltage (versus a Hg/Hg₂SO₄ reference electrode), with or without the addition of impurities to the electrolyte. Compared with other impurities, Ag is expected

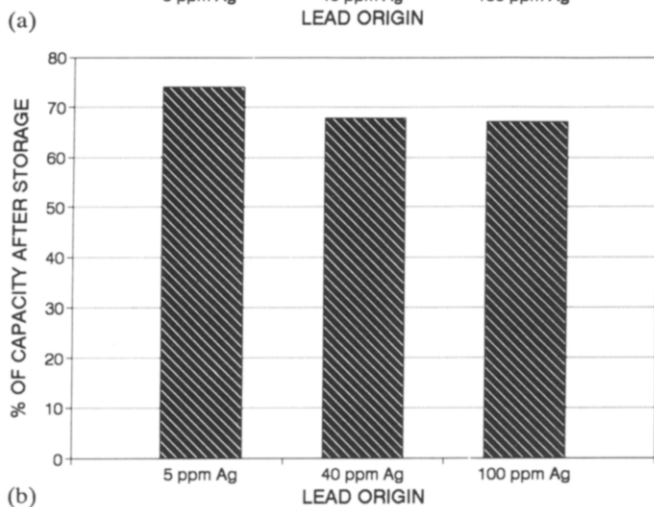
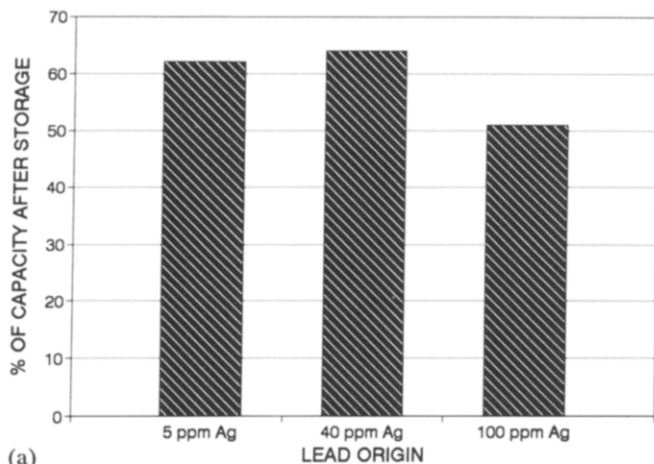


Fig. 9. Self-discharge performance of batteries with different amounts of silver in the oxide: (a) batteries with positive-plate limitation; (b) batteries with negative-plate limitation.

to present a tremendous increase in gassing at both electrodes and, consequently, a high self-discharge. This Table of comparison points out the limited value of cyclic voltammetry to predict results in batteries when accurate results, and not only tendencies, are required.

Conclusions

This study has shown that the high self-discharge obtained with certain samples of secondary lead does not originate from the major impurities present, i.e., Ag and Bi. A relatively high amount of Ag can be tolerated. Further work is in progress to examine the effects of other metallic impurities (Ni, Te) and of coupled additives (Bi plus Ag in the same alloy).

TABLE 7

Influence of impurities on oxygen and hydrogen overvoltage as measured by cyclic voltammetry. The Table gives the ratios expressed in percentage between currents measured at fixed voltage vs. a Hg/Hg₂SO₄ reference electrode during cycle no. 1 after impurity addition to the electrolyte, and the cycle immediately before the addition

Impurity	Positive electrode (%)	Negative electrode (%)
Ag	600	180
Bi	118	90
Cd	100	100
Co	560	100
Cu	100	120
Fe	100	100
Mn	180	100
Ni	100	112
Se	128	118
Te	158	152
Zn	100	100

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