

Effects of cobalt in lead/acid batteries

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Abstract

The effects of cobalt additions (0.1–1 g/l) to the electrolyte have been studied by anodic corrosion tests on sheets of various alloys, and by continuous charge, cycling and charge retention tests on thick plate automotive-type of batteries. Positive grid corrosion decreases with increase in cobalt concentration but the effect is less marked for alloys with high intrinsic corrosion resistance. Cobalt oxidizes some types of separator even at a relatively low concentration. The top-of-charge voltage is reduced by the presence of cobalt, the effect occurring mainly at the positive plate. Cobalt causes increased open-circuit losses but the effect is fairly small at low concentrations (0.1–0.15 g/l).

Keywords: Lead/acid batteries; Cobalt; Open-circuit voltage

1. Introduction

It has long been known that cobalt has an effect on the corrosion of lead and lead alloys. In 1938, Rey and co-workers [1,2] reported that the addition of cobalt sulfate to the electrolyte in the electrolytic production of zinc reduced the corrosion of the lead anodes. Later experiments by Koenig et al. [3] confirmed that the formation of lead dioxide on the lead anode was retarded. In 1953, a patent [4] was granted for the use of a corrosion-resistant lead alloy containing cobalt (and other elements) in the electrodeposition of zinc from zinc sulfate solutions. However, it is very difficult to produce Pb–Co alloys with reproducible results. In electrochemical processes, it is far easier to add cobalt to the electrolyte rather than to make Pb–Co electrodes.

The first studies of the effect of cobalt additions to lead/acid batteries were made in the USA by Vinal et al. [5], and in the former USSR by Krivolapova and Kabanov [6,7]. The results of their experiments showed that the presence of cobalt reduced the corrosion of the positive grid, but it had a destructive effect on the wood separators used in batteries at that time. Later work by Razina and Kozlovsky [8,9] confirmed that corrosion of the grid was reduced in the presence of cobalt.

Since this early work, although several studies of the effect of cobalt in batteries have been carried out by various battery manufacturers, few results have been published. However, in 1979, Galgali et al. [10] reported that the presence of cobalt was beneficial for grids in overcharge condition but Berndt [11] cautioned against its use as the corrosion advantage was

outweighed by the oxidation of the separator and the increased hydrogen evolution associated with cobalt.

The present paper reports results of anodic corrosion tests on various alloys and also battery tests carried out in the laboratory with various additions of cobalt to the electrolyte; it gives an overall assessment of the benefits of such additions.

2. Experimental

2.1. Anodic corrosion tests

The compositions of the four alloys tested were:

1. Pb–11%Sb–0.15%As–0.1%Sn
2. Pb–3%Sb–1.5%Sn–0.04%Se
3. Pb–0.07%Ca
4. Pb–0.07%Ca–0.5%Sn–0.25%Ag

Test specimens were spade-shaped slabs which were cast in a mould with a light dressing of cork dust. The rectangular plate portion had dimensions 38 mm × 25 mm and a thickness of 2.5 mm, and the shank had a diameter of 4.8 mm with a length of 76 mm. Corrosion tests were carried out in small glass containers with rubber stoppers. The test specimen, to be used as an anode, was carried (by its shank) in a central hole drilled in the stopper. Counter electrodes of the same shape were cut from pure lead and also carried in the stopper, so that they were parallel to the test specimen and a short distance from it. The stopper also carried a short glass tube for the escape of gas. A stop-off bitumastic anti-sulfuric acid paint was applied to the shanks of the specimens and also to

the top and bottom of the spade to give an accurate 25 mm × 25 mm area for test.

The sulfuric acid electrolyte had a sp. gr. of 1.250 (± 0.002). Tests were carried out with the addition of cobalt: 0, 0.1, 0.25 and 0.5 g/l. In the case of the high antimonial alloy, additional tests were carried out with cobalt contents between 0 and 0.1 g/l. Anodic corrosion tests were carried out in triplicate at a constant current of 3.1 mA/cm² for 400 h.

After testing, the samples were immediately removed and washed in water and then in alcohol to ensure rapid drying. Trichloroethylene was used to remove the paint and the corrosion product was stripped by immersion in hot glycerol (to reduce the lead dioxide to lead monoxide) followed by immersion in hot 50% aqueous ammonium acetate (to dissolve the lead monoxide) for up to 10 min. The samples were then dried.

The amount of corrosion was assessed by weighing the samples before and after test and determining the weight loss.

2.2. Cell tests

Three-cell batteries were assembled using 13 plate cells with automotive-type of plates. In order to ensure that the batteries would not suffer from premature capacity loss, the positive grids were relatively thick (2.2 mm) and a Pb–11% Sb alloy was used. Both continuous charge and cycle tests were carried out on batteries containing electrolyte with additions of up to 1 g/l cobalt.

The effect of cobalt on the corrosion of the positive grid was determined by continuous charge tests at 6 A for 2000 h with batteries containing microporous poly(vinyl chloride) (PVC) separators. After testing, the thickness, height and width of the positive grids were measured to assess the degree of corrosion and grid growth. Sample grids were also weighed after removal of the corrosion product to determine the weight loss.

In order to assess the effect of cobalt on separator degradation continuous charge tests were also carried out on batteries assembled with various separators: paper, microporous PVC, microporous rubber and microporous polystyrene. In some cases, a glass wool mat was used between the main separator and the positive plate. After 1000 h continuous charge, the batteries were dismantled and, after carefully washing and drying the separators, the weight loss of the separators was determined. Batteries with some of the separators were allowed to continue the test up to 2000 h.

Batteries (assembled with microporous PVC separators) were also cycled to a 8 h/10 h schedule, discharging to 80% of the 10 h capacity and returning 100% of the 10 h capacity during recharge. Actual capacities were determined at every tenth cycle. At the end of test, the strength of the positive plate, and the condition and amount of shedding of the positive active material were assessed.

The effect of cobalt on the open-circuit voltage loss was also determined by a cycling test to the 8 h/10 h schedule,

with 14 days open circuit every 20 cycles. The fall in electrolyte density and the loss in capacity after the open-circuit period were determined.

3. Results

3.1. Anodic corrosion

The results of the anodic corrosion tests on the four alloys are given in Fig. 1 where the weight loss versus cobalt content in the electrolyte curve is given.

A cobalt addition resulted in a reduced corrosion rate in all cases. The effect was most marked for Pb–Sb alloys. The anodic weight loss of the Pb–11% Sb alloy was decreased by 35% with a 0.1 g/l cobalt addition and 70% by a 0.5 g/l addition. In the case of the low antimony alloy (3%), an addition of 0.1 g/l cobalt decreased the weight loss by more than 50% and higher additions resulted in further smaller decreases.

Cobalt also reduced the corrosion rate of non-antimonial alloys. An addition of 0.1 g/l cobalt caused a 70% decrease in weight loss of the Pb–Ca alloy but further additions of cobalt had only small effects. Cobalt had the least effect on the corrosion-resistant Pb–Ca–Sn–Ag alloy. A 0.1% addition caused a reduction in weight loss of 40% but no further reductions were obtained when the cobalt content was increased to 0.5 g/l.

3.2. Cell performance

The effect of cobalt on the positive grid corrosion in actual batteries after 2000 h continuous charge is shown in Fig. 2, where the percentage weight loss is given as a function of cobalt addition, and in Table 1 where the amount of grid growth and the remaining grid thickness are recorded.

After 2000 h continuous charge, the positive active material was firm and in good condition in all cases. The negative plates in the cells containing up to 0.5 g/l cobalt were also in good condition but there was some over-expansion of

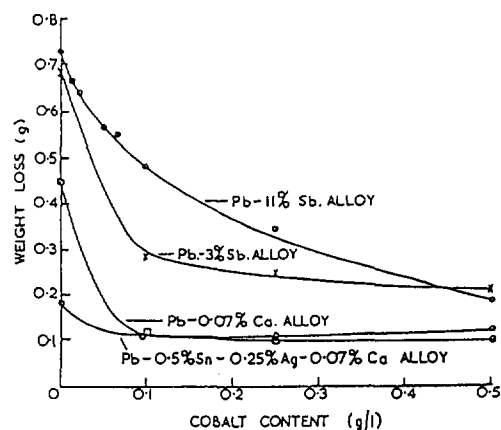


Fig. 1. Effect of cobalt on corrosion of lead alloys.

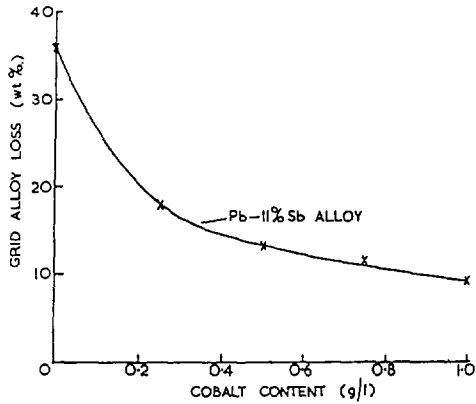


Fig. 2. Effect of cobalt on grid corrosion after 2000 h continuous charge.

Table 1
Grid corrosion and growth after 2000h continuous charge

Cobalt concentration (g/l)	Grid thickness (mm)	Grid growth	
		Height (mm)	Width (mm)
0	1.4	6.8	4.0
0.25	1.8	5.3	4.8
0.50	1.9	3.8	3.8
0.75	1.95	3.0	4.0
1.00	2.0	1.8	2.8

the negative active material in the cells containing 0.75 and 1.0 g/l cobalt, respectively.

The top-of-charge voltage of the batteries, and the positive and negative potentials with respect to a cadmium electrode are given in Table 2.

With increase in cobalt content up to 0.5 g/l, there was a progressive decrease in top-of-charge voltage but higher amounts of cobalt had little further effect. The individual electrode potentials show that the main decrease occurred at the positive electrode.

The results of the continuous charge test (1000 h) on batteries containing various separators are shown in Fig. 3, where the weight loss of the separators versus cobalt content after test is plotted. All the separators were attacked in the presence of cobalt, with the exception of microporous polystyrene where no significant effect was observed. In general, the weight loss increased with increasing amount of cobalt

Table 2
Effect of cobalt on top-of-charge voltage

Cobalt concentration (g/l)	Cell voltage (V)	Plate potential reference cadmium (V)	
		Positive	Negative
0	2.61	2.51	-0.10
0.1	2.55	2.45	-0.10
0.25	2.52	2.44	-0.08
0.5	2.50	2.42	-0.08
0.75	2.50	2.42	-0.08
1.0	2.50	2.40	-0.10

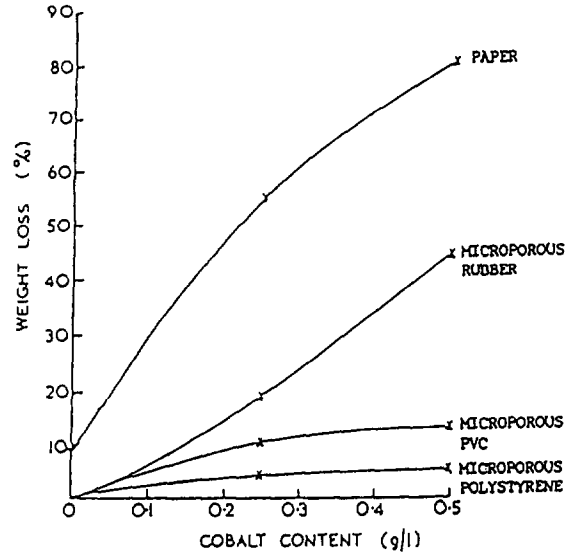


Fig. 3. Effect of cobalt on separators after 1000 h continuous charge.

additions. The paper (cellulose) separator showed the greatest deterioration and batteries containing both 0.25 and 0.5 g/l cobalt were failing after 1000 h. The battery with microporous rubber separators and 0.5 g/l cobalt addition was also failing after 1000 h but a similar battery containing only 0.25 g/l cobalt completed 2000 h test. Batteries containing microporous PVC and 0.5 g/l cobalt completed 2000 h continuous charge and were still operating efficiently at the end of the test, although they were found to be mechanically weak on dismantling the battery.

Where glass wool mats were used between the separator and the positive plate, the resin binder of the glass wool was attacked and removed in the presence of cobalt but this did not appear to affect the performance of the glass wool as an active material retainer.

When glass wool was used, the attack on the separator was reduced in all cases, the weight loss of a paper separator being decreased by about 50% and that of a microporous PVC separator by about 30%.

The results of cycling tests (8 h/10 h) on batteries containing microporous PVC separators and up to 1 g/l cobalt are given in Table 3.

Batteries containing from 0.075 to 0.25 g/l cobalt completed 210 cycles whereas those containing 0.5 to 1 g/l cobalt

Table 3
Effect of cobalt on cycle life

Cobalt concentration (g/l)	Duration (cycles)	Mud weight (g)
0	180	240
0.075	210	310
0.15	210	300
0.25	210	290
0.5	180	230
0.75	180	200
1.0	180	214

completed only 180 cycles, similar to an uncontaminated battery.

After testing, the positive active material in all cases was soft and shedding had occurred with the mud spaces virtually full in all the batteries. The positive grids from batteries containing 0.25 g/l cobalt or more were strong but below this concentration the mesh of the positive grids was weak and beginning to break up. The negative plates in all the batteries were in good condition with even expansion of the active material.

The effect of charge and discharge on the cobalt concentration remaining in the electrolyte for a battery with an initial concentration of 0.4 g/l is shown in Fig. 4. During the charge period, over 80% of the cobalt is removed from the electrolyte and absorbed in the plates with subsequent release into the electrolyte again during the discharge period.

The results of the open-circuit loss tests (14 days) at various stages during cycling of batteries containing microporous PVC and from 0 to 1 g/l cobalt are shown in Table 4. The fall in density and the loss in capacity increased with increasing cobalt content and increasing age (number of cycles).

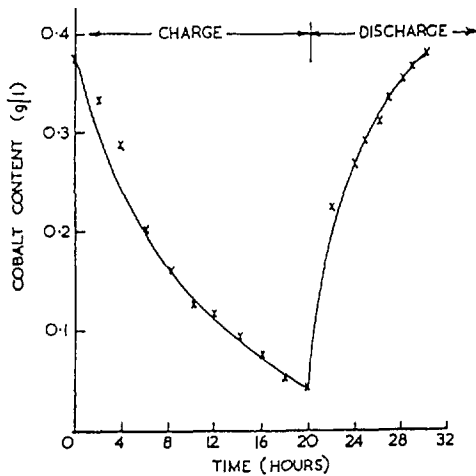


Fig. 4. Cobalt content in electrolyte during charge and discharge.

Table 4
Effect of cobalt on open-circuit loss

Cobalt concentration (g/l)	No. of cycles	Density fall (points)	Capacity loss (%)
0	0	4	0.8
	22	6	2.9
	42	10	4.4
0.25	0	10	1.5
	22	12	5.5
	42	14	5.0
0.5	0	14	3.9
	22	16	6.0
	42	20	7.3
0.75	0	19	8.5
	22	31	11.5
	42	40	13.0

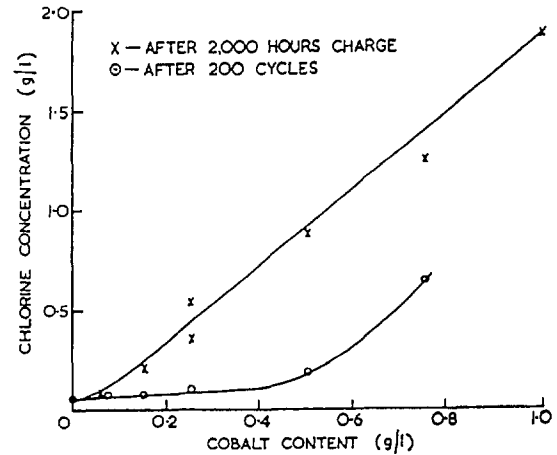


Fig. 5. Effect of cobalt on chlorine content in cells with PVC separators.

Fig. 5 shows the chlorine content in the batteries assembled with PVC separators after continuous charge and after cycling, caused by the attack on the microporous PVC separator by the cobalt. With increasing cobalt content the chlorine content increased, the effect in general being more marked during the continuous charge test than the cycling test.

4. Discussion

The results of both anodic corrosion tests and battery tests confirm that there is a progressive decrease in corrosion rate with increase in cobalt content for Pb-Sb alloys. Alloys containing calcium (especially the intrinsically corrosion resistant Pb-Ca-Sn-Ag alloy) show a less marked effect. For these alloys, there is a significant effect with cobalt additions up to 0.1-0.2 g/l but there appears to be little point in adding higher amounts. It is also interesting that the laboratory corrosion tests on slabs indicate that a Pb-Ca alloy with about 0.1 g/l cobalt in the electrolyte has an equivalent performance to the highly corrosion-resistant Pb-Ca-Sn-Ag alloy in normal electrolyte.

The decrease in cobalt content in the electrolyte during charge and the lower positive plate potential indicate absorption of cobalt on the positive plate, as proposed by Krivolapova and Kabanov [12], causing the formation of a more adherent and less porous lead dioxide corrosion product on the grid. This may be the α -form as suggested by Kabanov and co-workers [13-15]. The lead dioxide structure consists basically of octahedra formed by close-packed layers of oxygen atoms, with lead ions at the centres of half the available octahedra. In β -lead dioxide, the lead ions are packed to give straight chains of octahedra whilst, in the α -modification, there are zig-zag chains. The adsorption of the large sulfuric acid anion will promote the formation of straight chains [16] and β -lead dioxide is therefore normally formed in sulfuric acid. The cobalt probably interferes with the acid anion adsorption and thus allows the α -modification to be formed. The less porous and more adherent nature of this form of

corrosion product impedes further corrosion, causing a retardation in the corrosion rate.

One of the disadvantages of cobalt is the separator oxidation and, of the separators tested, only polystyrene was virtually unaffected. Microporous PVC separators can withstand 2000 h overcharge but oxidation does take place, releasing chlorine into the electrolyte. After 2000 h continuous charge, the presence of 0.15 g/l cobalt resulted in a chlorine content of 0.2 g/l, but much lower levels were obtained during the cycling tests. Obviously, if it is intended to use cobalt in a battery electrolyte, particular attention should be paid to the choice of separator.

The other serious disadvantage of cobalt is the resulting higher self-discharge rate. However, at a cobalt level of up to 0.25 g/l, the increase is not dramatic.

The best cycle life was obtained from batteries with 0.075–0.25 g/l cobalt. However, all the batteries failed by shedding of active material and the mud spaces were full. The potential beneficial effects of cobalt were obviously masked by this type of failure.

5. Conclusions

1. An addition of 0.1–0.15 g/l cobalt results in a significant increase in corrosion resistance of the positive grid. This is true for both Pb–Sb and Pb–Ca alloys.

2. Cobalt attacks many separators but, at a level of up to 0.1 g/l, the effect can be minimised. If cobalt is used, the choice of separator is important.

3. Cobalt causes increased self-discharge but the increase is relatively small even at a level of 0.25 g/l.

4. Cobalt has little effect on softening and shedding of active material during cycling.

5. An addition of 0.1–0.15 g/l cobalt would be beneficial for flooded batteries operating mainly under overcharge conditions, providing the separator is carefully chosen.

6. An addition of 0.1–0.15 g/l cobalt would reduce the grid corrosion of cycling batteries but would have little effect on life if the cause of failure was shedding of active material.

7. The effect of cobalt on the characteristics of maintenance-free VRLA cells would have to be carefully studied before considering its use in this design.

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