

Short Communication

Influence of calcium sulphate in the positive material on the discharge performance of lead/acid batteries

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Abstract

Calcium sulphate added to the positive material of flat or tubular plates of lead/acid batteries significantly improves performance at high rates of discharge, particularly at low temperatures. Calcium sulphate is added to the paste mix (flat plates) or blended with the precursor oxide (tubular plates). Cycle life is unaffected, as seen by the maintenance of the structural integrity of the plates. This finding is of practical significance to battery manufacturers.

Introduction

During the last several decades, attempts to improve the electrical performance of lead/acid batteries by introducing additives to the positive material have met with limited success. From available information, the composition of the positive material in commercial plates does not generally contain additives other than lead oxide, red lead, sulphuric acid, water and, perhaps, reinforcing fibres.

Tokunaga *et al* [1] have examined additives with a view to raising the discharge performance of positive plates without causing any deleterious effect on battery cycle life. Anisotropic graphite has been found to improve the utilization of the positive material. This behaviour has been attributed to an increase in porosity that is proportional to the quantity of graphite (0–3 wt %) in the positive mix. Graphite increases the thickness of the plate during service, thus reducing the shedding of the plates by compression.

Carbon black [2–4] has been tried with limited success. It is reported to affect the structure of the active material and to influence slightly the electrical performance [3].

The deleterious effect on battery life of adding barium sulphate to the positive plate is well known in commercial practice. Bode [5] has discussed the phenomenon, citing the work of Lorenz [5]. The latter noticed that the cycle life of batteries is reduced by 30–50% in the presence of 0.5 wt %

barium sulphate or strontium sulphate in the positive material Lorenz also reports that calcium sulphate is not isomorphous with lead sulphate and therefore has no deleterious effects on battery life Furthermore, calcium sulphate does not act as an inorganic expander

The present work shows that calcium sulphate, added to the positive mix, enhances battery performance, particularly at high rates of discharge Its influence at low discharge rates is marginal and is perhaps the reason why the effect has not been reported earlier

Experimental

Battery construction

The study was conducted on two types of automotive batteries one a conventional unit (12 V, 60 A h), the other a diesel electric locomotive starter battery (8 V, 450 A h) with tubular positives In the former case, calcium sulphate (Anhydrous, Reagent Grade) was added to the positive mass during the dry mixing before addition of water and acid For tubular plates, the calcium sulphate was dry-blended with the oxide before filling The concentration of calcium sulphate was either 0.25 or 2 wt % with regard to the weight of the oxide Details of the batteries (12 V 60 A h) are given in Table 1

In addition to the above, positive plates (previously formed, washed, and dried) were dipped in calcium nitrate solution and the excess nitrate allowed to drain The plates thus impregnated were subsequently dipped in dilute sulphuric acid in order to precipitate the calcium sulphate within the pores of the active material The plates were later washed free from acid and nitrate

The positive mixes made with calcium sulphate were pasted on commercially produced grids, the paste weights were controlled to within $\pm 5\%$ Plate curing and formation were carried out using standard practices Batteries were then assembled using commercial negative plates and sintered PVC separators The batteries, together with reference units containing no calcium sulphate, were subjected to an initial charge

TABLE 1
12 V, 60 A h test batteries

CaSO ₄ in positive mass (%)	Battery identification
0.25	A11, A12, A13
2.0	A21, A22, A23
0 (reference)	R11

Capacity tests

For automotive batteries, discharge performances were measured at the C/20 rate, and high-rate discharges at 0 and -15°C . The latter tests were carried out on a DIGATRON-HEW 2000 discharge tester.

The 8 V, 450 A h batteries with tubular positives were discharged at a current of 2300 A for a period of 15 s, followed by a rest period of 15 s. This constituted one discharge cycle.

Discussion

The results presented in Tables 2–6 and Figs 1–3 indicate that calcium sulphate incorporated into the positive mass at concentrations of 0.25–2 wt % increases the voltage at all discharge rates. The effect is more pronounced when the current is higher and the temperature is lower.

Ruetschi [6] has listed four different types of polarization that limit the discharge capacity of lead/acid batteries. These are charge transfer (activation), mass transfer (concentration); ohmic, and crystallization polarizations. Those relevant to the present study are crystallization polarization, and to some extent, concentration polarization. During discharge, supersaturation of lead sulphate occurs followed by nucleation and crystallization.

TABLE 2

Voltage (V) during discharge of 12 V, 60 A h batteries at 180 A at room temperature to end voltage of 8 V

Discharge duration		Battery identification ^a						
min	s	R11	A11	A12	A13	A21	A22	A23
0	05	10.69	10.65	10.63	10.67	10.64	10.64	10.72
0	30	10.64	10.72	10.66	10.71	10.71	10.71	10.73
1	00	10.58	10.69	10.62	10.68	10.69	10.69	10.70
1	30	10.51	10.63	10.58	10.63	10.64	10.64	10.65
2	00	10.43	10.57	10.53	10.57	10.59	10.58	10.59
2	30	10.33	10.51	10.46	10.51	10.52	10.52	10.53
3	00	10.24	10.43	10.39	10.43	10.45	10.46	10.45
3	30	10.14	10.34	10.32	10.35	10.39	10.39	10.37
4	00	10.03	10.26	10.23	10.27	10.30	10.30	10.27
4	30	9.91	10.16	10.14	10.18	10.21	10.22	10.20
5	00	9.77	10.05	10.03	10.09	10.12	10.12	10.11
5	30	9.62	9.94	9.91	9.99	10.02	10.02	10.01
6	00	9.43	9.79	9.77	9.87	9.95	9.91	9.89
6	30	9.18	9.60	9.59	9.73	9.78	9.77	9.75
7	00	8.75	9.33	9.27	9.55	9.61	9.61	9.58
7	30	8.52	8.52	8.59	9.29	9.39	9.37	9.34
8	00	—	—	—	8.71	8.98	8.93	8.86
Yield at end voltage (min s)		7'24"	7'39"	7'38"	8'11"	8'23"	8'23"	8'17"

^aSee Table 1

TABLE 3

Voltage (V) during discharge of 12 V, 60 A h batteries at 180 A at 0 °C to end voltage of 6 V

Discharge duration		Battery identification ^a						
min	s	R11	A11	A12	A13	A21	A22	A23
0	05	10 09	10 12	10 17	10 21	10 16	10 13	10 18
0	30	10 12	10 15	10 21	10 25	10 20	10 17	10 22
1	00	10 05	10 10	10 16	10 21	10 16	10 12	10 18
1	30	9 95	10 03	10 10	10 15	10 10	10 07	10 13
2	00	9 85	9 95	10 03	10 09	10 04	10 01	10 06
2	30	9 74	9 87	9 96	10 02	9 97	9 94	10 00
3	00	9 62	9 77	9 87	9 94	9 89	9 87	9 92
3	30	9 49	9 66	9 76	9 84	9 80	9 79	9 84
4	00	9 34	9 53	9 65	9 74	9 71	9 70	9 74
4	30	9 15	9 37	9 51	9 62	9 59	9 58	9 63
5	00	8 90	9 13	9 33	9 47	9 45	9 45	9 50
5	40	8 46	8 67	9 07	9 27	9 28	9 28	9 33
6	00	—	6 00	8 47	8 94	9 02	9 04	9 10
6	30	—	—	—	7 71	8 43	8 58	8 66
7	00	—	—	—	—	—	6 26	6 00
Yield at end voltage (min s)		5'45"	6'00"	6'20"	6'41"	6'54"	7'01"	7'00"

^aSee Table 1

TABLE 4

Voltage (V) during discharge of 12 V, 60 A h batteries at 300 A at -15 °C to end voltage of 6 V

Discharge duration		Battery identification ^a						
min	s	R11	A11	A12	A13	A21	A22	A23
0	05	8 07	8 29	8 45	8 32	8 34	8 29	8 30
0	30	7 90	8 01	8 26	8 07	8 15	8 04	8 06
1	00	7 55	7 74	8 02	7 81	7 93	7 82	7 81
1	30	6 70	7 35	7 75	7 52	7 72	7 54	7 58
2	00	—	6 21	7 16	6 91	7 32	6 96	7 17
2	30	—	—	—	—	6 57	—	—
Yield at end voltage (min s)		1'38"	2'03"	2'19"	2'15"	2'40"	2'17"	2'29"

^aSee Table 1

It is instructive to examine the extent to which calcium sulphate acts as nucleus for lead sulphate. First, calcium sulphate is not isomorphous with lead sulphate. Second, its solubility is several orders of magnitude higher than that of lead sulphate. The experimental results presented here confirm

TABLE 5

Duration of discharge of 12 V, 60 A h batteries at 3 A ($C/20$ rate) at room temperature to end voltage 10.5 V

Battery identification ^a	Discharge duration	
	h	min
R11	21	33
A11	22	44
A12	23	31
A13	23	18
A11	23	37
A12	23	22
A13	23	09

^aSee Table 1

TABLE 6

Effect of CaSO_4 on discharge capacities of 12 V, 60 A h batteries under different discharge conditions

Discharge condition	Battery identification ^a		Difference (%)
	R11	A22	
$C/20$ rate, room temp (3 A)	21'33"	23'22"	8.4
180 A at room temp	7'24"	8'23"	13.3
180 A at 0 °C	5'45"	7'23"	22.0
300 A at -15 °C	1'38"	2'17"	39.7

^aSee Table 1

that the voltage at the end of a 5 s discharge is practically unaffected by the presence of calcium sulphate. The *coup de fouet* effect still exists. The effect of calcium sulphate is seen only after the discharge has progressed to some extent. Only in the case of high-rate discharge at -15 °C are voltages higher in the first 5 s of discharge.

Change in porosity

Incorporation of carbon black in the positive material increases the porosity following oxidation and removal from the system. In the present study, experiments were conducted on plates dipped in a soluble calcium salt, followed by calcium sulphate precipitation within the active material. Although this treatment reduced the porosity by as much as 25%, an improvement in battery performance was obtained. It may be concluded, therefore, that the change in porosity is not responsible for the observed behaviour.

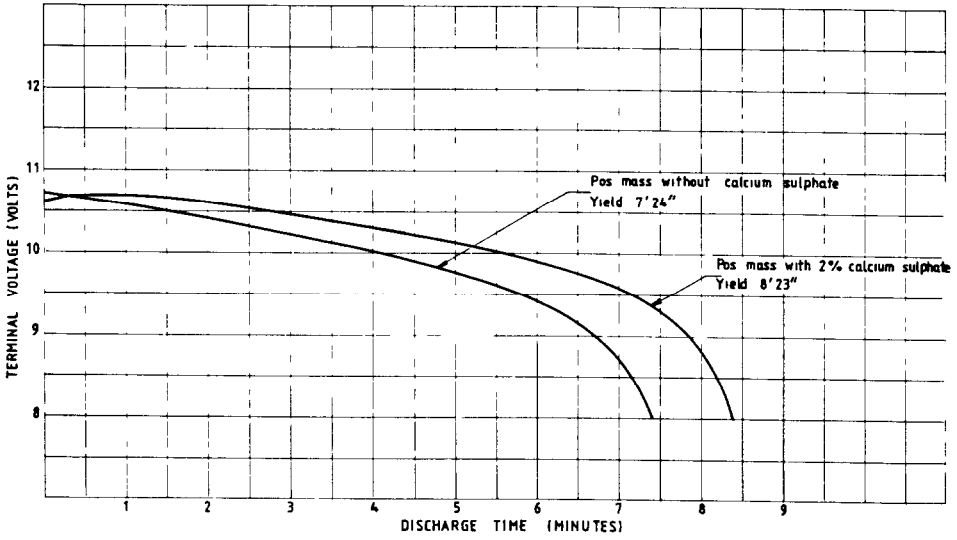


Fig 1 Voltages during high-rate discharge of a 12 V, 60 A h automotive battery at room temperature Discharge current 180 A, end voltage 8 V

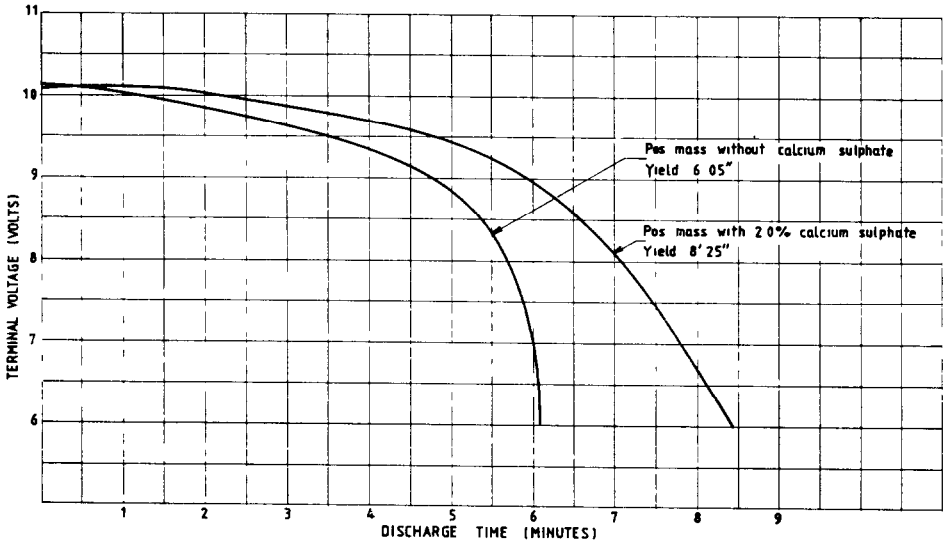


Fig 2 Voltages during high-rate discharge of 12 V, 60 A h automotive battery at 0 °C Discharge current 180 A, end voltage 6 V

Battery cycle life

Bode [5] found that calcium sulphate has no deleterious effect on the life of positive plates This is supported by the extensive use of lead-calcium alloys in maintenance-free batteries In these, the calcium leached from the grids has no deleterious effect on the integrity of the positive material Examination of cycled plates revealed that the slimy positive material normally

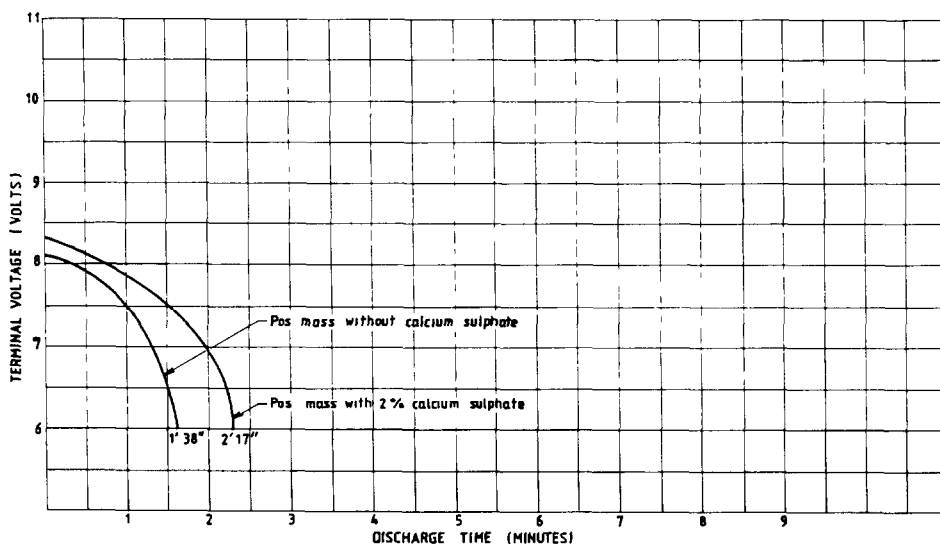


Fig 3 Voltage during high-rate discharge of a 12 V, 60 A h automotive battery at -15°C Discharge current 300 A, end voltage 6.0 V

witnessed on plates containing barium sulphate is totally absent in the presence of calcium sulphate. Thus, the action of these two sulphate species obviously proceeds via different mechanisms.

Barium sulphate encourages the lead sulphate to precipitate outside of the structural framework. On continued cycling, this results in the build-up of a non-conducting active material that eventually results in shedding and failure. At present, no unequivocal explanation can be given for the action of calcium sulphate and its beneficial influence on the positive active material.

References

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