

## X-RAY DIFFRACTION STUDIES OF BASIC LEAD SULPHATES

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### Introduction

Basic lead sulphates are produced during the mixing and curing of lead/acid battery pastes. The relative concentrations of the different basic sulphates strongly influence the properties of formed positive plates. In battery production, the goal is to obtain mechanically strong plates with good electrical properties. It is known that the presence of needle-like tetrabasic lead sulphate crystals in the positive active material improves the mechanical properties of the formed positive plates. On the other hand, the electrical formation of the positive plates is impeded by high concentrations of this basic lead sulphate. Quantitative X-ray powder diffraction (XRD) analyses of basic lead sulphates can be used as a powerful tool in determining a favourable compromise between the mechanical and the electrical properties of positive plates.

There is no known means of determining the relative concentrations of basic lead sulphates in positive active material by chemical methods; this is because the cured positive masses are mixtures of several lead compounds. By contrast, XRD methods have been successfully used for qualitative analyses of lead compounds in active materials, as well as in corrosion layers. In order to obtain semi-quantitative information about the phase composition of active masses, the relative intensities of X-ray diffraction peaks have been used [1].

The aim of the studies reported here is to clarify the suitability of X-ray powder diffractometry methods for quantitative analyses of basic lead sulphates. One crucial point concerning these analyses is to have acceptable standard materials. During this study, an investigation has been made of the production of monobasic ( $\text{PbO} \cdot \text{PbSO}_4 = 1\text{BS}$ ), tribasic ( $3\text{PbO} \cdot \text{PbSO}_4 \cdot n\text{H}_2\text{O} = 3\text{BS}$ ) and tetrabasic ( $4\text{PbO} \cdot \text{PbSO}_4 = 4\text{BS}$ ) lead sulphate. Attempts have been made to produce each basic lead sulphate in as pure a state as possible in order to use them as standard materials for quantitative XRD analyses. For the purposes of comparison, both paste and solution methods have been applied to synthesize the three basic lead sulphates [1-3]. Mill oxide from a battery factory and sulphuric acid (sp. gr. = 1.4) have been used as the raw materials in these syntheses.

## Experimental

The syntheses of basic lead sulphates were carried out in a simple laboratory mixer (beaker, mechanical stirrer, magnetic hotplate, cold water bath). Batches of 100 - 200 g of mill oxide were used in order to maintain effective mixing. The temperatures used in the synthesis and curing of 1BS, 3BS and 4BS were 30 °C, 30 °C and 80 °C, respectively. Electron micrographs were obtained on a JEOL 840A scanning electron microscope and powder diffraction patterns on a Siemens Diffrac 500 diffractometer. Wet chemical methods were used for routine analyses of active mass samples. A LECO SC-32 sulphur analyser was employed in chemical analyses of the synthesized products.

## Results and discussion

Electron micrographs showing two different morphologies existing in mill oxide are presented in Fig. 1. They show the presence of both a layered-crystalline and a coralloid modification of the raw material. Other properties of the mill oxide are given in Table 1.

There were no noticeable differences between 1BS formed by either the solution or the paste methods. On the basis of relative XRD intensities (Fig. 2), the paste method gave a slightly quicker reaction than the solution method. This may be due to the higher acid strength used in the former procedure. In addition, the diffraction patterns showed that the product from the solution method contained more 3BS after curing. Electron micrographs taken after 72 h curing (Fig. 3) revealed that 1BS crystals prepared by the paste method were smaller and more spherical than those produced by the solution procedure.

When comparing the formation of 3BS, it was found that a dramatic change in relative XRD intensities occurred in the solution method product

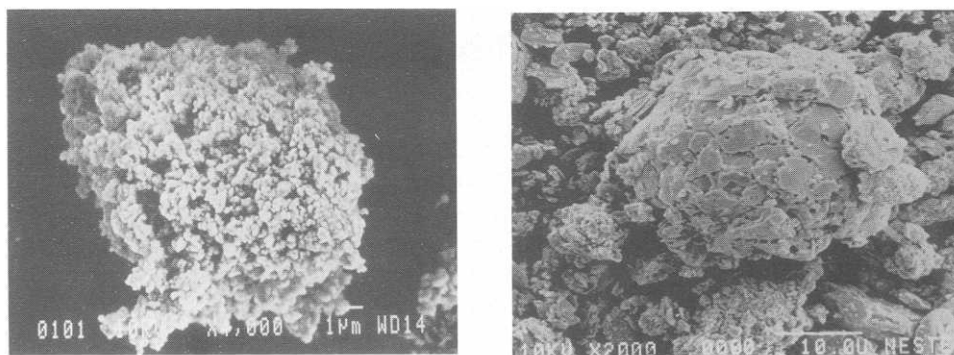


Fig. 1. Electron micrographs of mill oxide: (a) coralloid; (b) layered-crystalline modification.

TABLE 1

Properties of mill oxide used as raw material

PbO (wt.%)	Acid absorption (mg H <sub>2</sub> SO <sub>4</sub> g <sup>-1</sup> )	Scott density (g cm <sup>-3</sup> )	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Particle size distribution <sup>a</sup>	
79.4	244	2.1	3.5	> 20 μm	16.0 wt.%
				17 - 20 μm	0.5
				10 - 17 μm	1.6
				5 - 10 μm	10.5
				2 - 5 μm	13.5
				1 - 2 μm	14.9
				0.5 - 1 μm	23.1
				0.25 - 0.5 μm	22.9
> 0.25 μm	13.0				
				> 60 μm	60.0 wt.%

<sup>a</sup> Particles > 20 μm given as wt.%, other values given as % mass population.

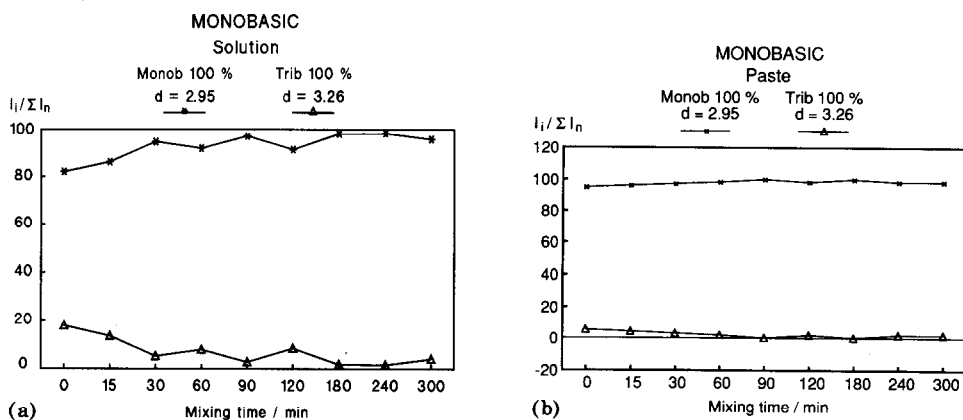
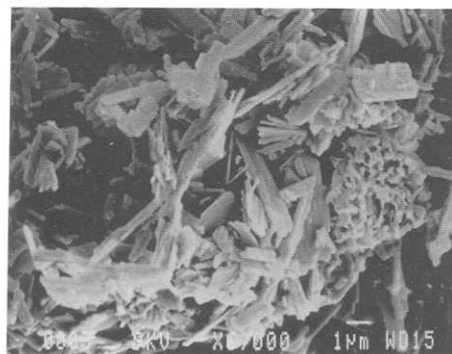
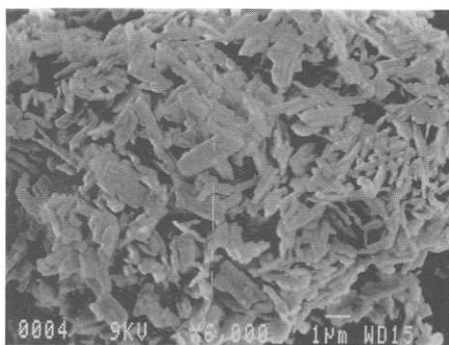


Fig. 2. Changes in phase composition of reaction mixtures of 1BS synthesis during mixing by: (a) solution method; (b) paste method.



(a)



(b)

Fig. 3. Electron micrographs of cured 1BS prepared by: (a) solution method; (b) paste method.

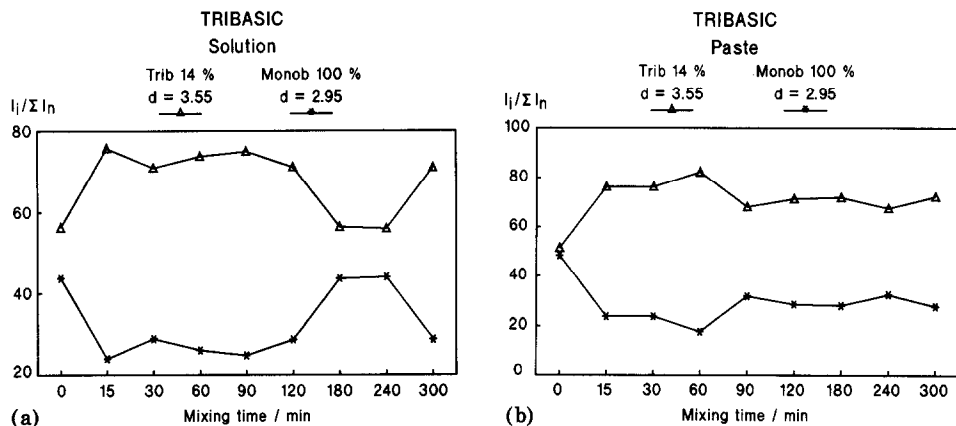
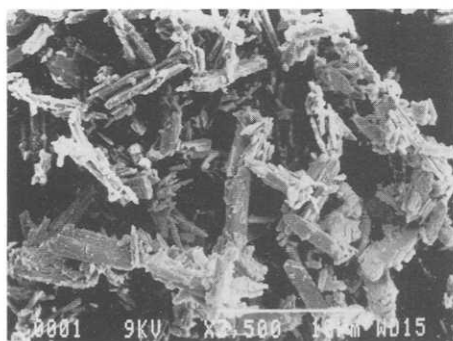


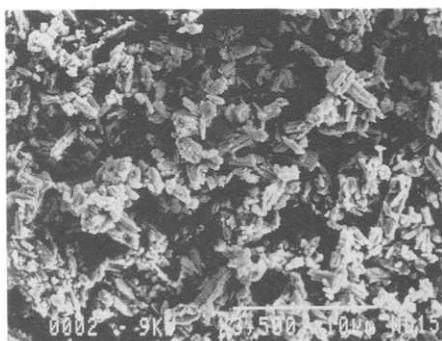
Fig. 4. Changes in phase composition of reaction mixtures of 3BS synthesis during mixing by: (a) solution method; (b) paste method.

after 2 h of mixing (Fig. 4). The relative intensity of 3BS dropped and that of 1BS increased. This change might be due to the breaking up of crystal agglomerates. According to wet-chemical analyses (Tables 2 and 3), the metallic lead content was higher in the solution method products. This observation was supported by XRD analyses carried out on the cured products: a clearly distinguishable diffraction peak for metallic lead was present only in the diffraction pattern for the solution method product. Electron micrographs of the cured products (Fig. 5) showed the 3BS crystals to be significantly larger when prepared by the solution method.

There were differences between the 4BS produced by the paste and solution methods (Fig. 6). First, production of 4BS after acid addition started earlier with the paste method. Second, the paste method reaction proceeded at a higher rate. Also, the relative XRD intensity of the 4BS peak reached a



(a)



(b)

Fig. 5. Electron micrographs of cured 3BS prepared by: (a) solution method; (b) paste method.

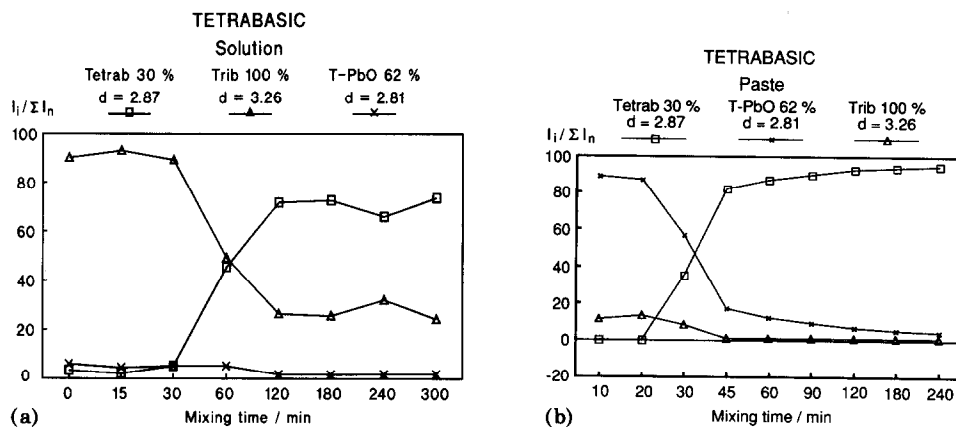


Fig. 6. Changes in phase composition of reaction mixtures of 4BS synthesis during mixing by: (a) solution method; (b) paste method.

TABLE 2

Results from chemical analyses of basic lead sulphates after an extended period of mixing  
Values given as wt.%.  
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Sample	Added $H_2SO_4$	Metallic Pb	Sulphate (wet chemical)	Sulphate (LECO SC-32)
1BS/solution	15.5	0.59	15.3	14.8
1BS/paste	16.6	0.16	17.0	16.2
3BS/solution	10.1	0.39	10.0	8.7
3BS/paste	10.1	0.30	9.3	8.4
4BS/solution	7.1	0.41	7.1	6.1
4BS/paste	7.1	0.31	7.1	6.7

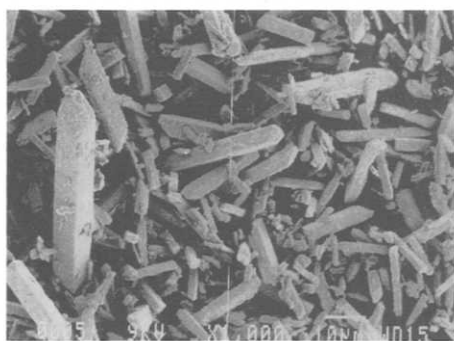
TABLE 3

Results from chemical analyses of basic lead sulphates after curing  
Values given as wt.%.

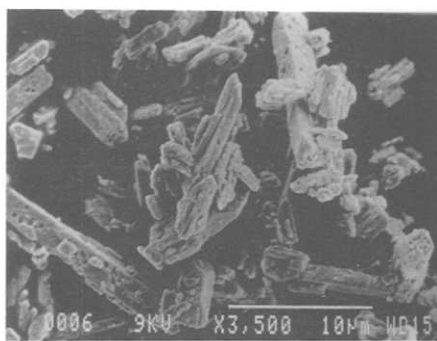
Sample	Added $H_2SO_4$	Metallic Pb	Sulphate (wet chemical)	Sulphate (LECO SC-32)
1BS/solution	15.5	0.54	15.2	14.7
1BS/paste	16.6	0.15	16.6	16.4
3BS/solution	10.1	0.38	10.0	8.8
3BS/paste	10.1	0.29	9.2	8.4
4BS/solution	7.1	0.39	7.0	6.2
4BS/paste	7.1	0.30	7.0	6.3

higher level in the paste method after completion of the reaction. Electron micrographs of cured 4BS (Fig. 7) showed the paste method product to be composed of crystal agglomerates. Small holes existed on the surfaces of individual crystals thus indicating that the crystals were porous. By contrast, 4BS crystals prepared by the solution method appeared more compact and were larger single crystals with approximately regular shapes.

In order to assess the effectiveness of the mixer and the applicability of the results obtained, XRD data for the production of 4BS (6 wt.%  $H_2SO_4$ ) in a pilot-scale mixer (Fig. 8) were compared with those collected in this study. It can be seen that the reaction proceeded at a higher rate in the pilot-scale mixer and the reaction was practically completed within 30 min of the acid addition.



(a)



(b)

Fig. 7. Electron micrographs of cured 4BS prepared by: (a) solution method; (b) paste method.

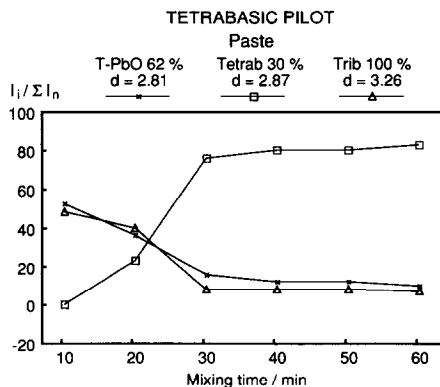


Fig. 8. Changes in phase composition of reaction mixtures of 4BS synthesis during mixing in a pilot-scale mixer.

## Conclusions

When producing basic sulphates for quantitative XRD analyses by paste and solution methods there are differences according to the method used, *e.g.*, in crystal sizes and shapes, in reaction rates, and in the compositions of the reaction mixtures. The results obtained to date are preliminary, and more thorough investigations are needed before reliable standard materials for quantitative XRD analyses can be produced. Also, it is very important to pay attention to the mode and parameters of the mixer in order to correlate the products of mixers of different type and scale. The use of a simple, but well controlled, laboratory mixer is, however, far more flexible for the preparation of standard materials required for X-ray analyses and method development.

## References

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- 2 J. Burbank, *J. Electrochem. Soc.*, 113 (1966) 10.
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