Investigation on soaking and formation of lead/acid battery plates with different mass structure

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Abstract

The influence of paste density and curing temperature on soaking and formation was investigated by different analytical methods including X-ray, porosimetry, BET and SEM. The soaking was carried out in sulfuric acid with different gravity and the time was varied between 0.5 and 24 h. Plates cured at high temperature resulting in mainly tetrabasic lead sulfate (4BS) behave markedly different to those cured at low temperature having only tribasic lead sulfate (3BS). The behaviour of plates cured at medium temperature resulting in a mix of both 4BS and 3BS was between the two extremes. There was also some influence of the paste density but smaller than the effect of different curing conditions. The results can be explained by considering the different mass structure and pore size distribution of the respective plate version. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

The manufacturing process of lead/acid batteries involves many variables that can have a strong influence on performance and life cycle of lead/acid batteries [1,2]. This is especially true for the valve-regulated design which requires a manufacturing process that has to be more precisely controlled than that employed for flooded batteries. Process deviations that are without, or of only minor importance for flooded cells can have tremendous consequences for valve-regulated batteries. Many studies on that subject have been published in recent years; some examples are given in Refs. [3–6].

The life cycle of valve-regulated lead/acid batteries having virtually no antimony in the grids is often limited by a capacity loss of the positive plate. Some decades ago, when lead/acid batteries with positive lead–calcium grids without antimony had first been placed on the market, there was a major disaster in terms of a very poor life cycle. Investigation of this phenomenon revealed that the

cause of the failure was the formation of a barrier layer of lead sulfate between the positive grid and the active material. Since this occurred more easily when antimony was excluded from the battery, it was called the ''antimony-free effect''. The influence of grid alloy composition on the behaviour of the positive mass during charging and discharging has been the subject of many investigations [7–13]. An important result of these studies was the discovery that a lack of antimony has not only an effect on the grid/positive mass interface, but also on the whole crystalline structure of the positive active mass [10] and on the so-called mass softening process. Nowadays, effects that are promoted by using grids without antimony are collectively termed premature capacity loss (PCL) [11].

In electric vehicle service, high pulses of discharge current are required which place an extreme load on the battery. Accordingly, the phenomenon of softening of the positive mass has often limited the lifetime of the batteries [5,14]. At present, it appears that softening is a more severe problem than the development of barrier layers. As a result of many research activities in the past, it seems that barrier layers no longer have a marked effect on the life of valve-regulated lead/acid batteries, even when the batteries are used in heavy cycling applications. This is contrary to the generally held belief that lead/acid batter-

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ies without antimony principally fail through the formation of lead sulfate barrier layers at the positive grid/mass interface.

Softening means a loss of contact between PbO_2-particles and a change of structure of the positive mass and has been the subject of many investigations during the last few years [10,15–18]. Several theories have been formulated to provide an explanation for that degradation of the positive mass [15–24] but up to now it is not really clear which parameters are the most important in avoiding softening, or at least in slowing down the softening process.

Although there are several parameters that strongly influence the speed of softening, it seems that processing of the positive plate such as pasting, curing, soaking and formation has one of the most important influence. There are many papers published about soaking and the influence of soaking time, sulfuric acid concentration and amount of electrolyte on the behaviour of the plates during the formation process. A summary of earlier work on that subject can be found in Refs. [1,2]. There is a substantial effect of the sulfuric acid concentration especially with regard to the occurrence of alkaline regions in some inner parts of the plate [25]. The paste density and the paste composition has also a marked influence on the progress of sulfation [26]. It was pointed out that depending on paste composition and soaking there is a different pH in the inner part of the mass in comparison to the outer part and this has a marked influence on the ratio of the two lead dioxide modifications α/β-PbO_2.

There were studies about the soaking/formation process with regard to porosity and volume changes [27]. It was pointed out that the structure of the formed mass is highly influenced by the concentration and flow of ions in the pores [28]. The influence of acid concentration was also discussed [29]. Recently, a paper has been published considering the effect of local decrease of acid concentration in the pores [30].

There was a general overview on technical problems of the soaking and formation process [31]. A theoretical study gave some mathematical equations for mass transport during formation [32]. Some investigations were made on soaking/formation with regard to find optimal process conditions [33]. There was a study about the influence of a long or a short soaking time on the formation process in combination with pulse current formation of tetrabasic lead sulfate plates [34]. It was pointed out that the duration of the soaking treatment influences markedly the mechanism of the formation process.

Some earlier studies about this subject with regard to formation of tetrabasic lead sulfate (4BS) are given in Refs. [35–37]. The use of a relatively low specific gravity of the electrolyte was proposed [38] to overcome problems of 4BS formation and to get a good oxidation efficiency. Some more studies about the mechanism of soaking/formation especially with regard to 4BS was published some years ago [39]. Recently, a paper has been published about

an improvement of the positive electrode efficiency by using cured mass with relatively small 4BS crystals [40,41]. The behaviour of such a mass on formation was studied in detail.

The objective of our work was to investigate in detail the soaking and formation process and to find out the influence of paste density and curing temperature on these processes with regard to a better understanding about the effect of the initial mass structure on the softening process.

2. Pasting and curing

The grids with a height of 119 mm, a width of 112 mm and a thickness of 2.5 mm were gravity cast by using a lead/calcium/tin alloy (0.087% Ca and 0.98% Sn). The lead oxide was from a conventional ball mill of the Sovema type and had a free lead content of 27%, an acid absorption of 255 mg/g and a specific surface (BET) of 1.98 m^2/g. A 10-kg laboratory mixing machine from Eirich was used for the paste preparation. The paste recipe and the mixing procedure was:

lead oxide	10.2 kg	lead oxide mixing	1.5 min
fibres	4.0 g	water and fibres addition	0.5 min
water	1.43 kg	first mixing	5.0 min
sulfuric acid (1.40 g/cm^3)	1.23 kg	sulfuric acid addition	9.0 min
		second mixing	15.0 min

The addition of 1.43 kg water gave 4.0 g/cm^3 paste density. For getting a higher or lower paste density, the amount of water was slightly modified. The total mixing time was 31 min. Cooling by air was used to keep the paste temperature below 70°C. After the density and penetration control, the grids were pasted by hand. The paste weight was 137 g/plate in case of 4.0 g/cm^3 paste density and slightly modified at higher or lower paste density in order to have the same amount of lead in all plates. The plate thickness was around 2.8 mm.

For curing and drying, a laboratory curing chamber was used where temperature and humidity could be controlled precisely. The plates were placed vertically in a special rack in which they could be kept on the same distance of about 1 mm. Some of the plates were equipped with temperature probes so that the mass temperature could be measured during the whole curing and drying process. These temperature measurements showed the three typical stages of the curing process. During the first stage, the temperature of the mass was close to the air temperature of the curing chamber. After a time period of about 4–6 h, the plates had lost so much water that oxidation of the free

Table 1
Characteristic data of the cured plates

Paste density (g/cm^3)	Curing temperature	Crystal size	3BS (%)	4BS (%)	Porosity (%)	Pore diameters (μm)	BET (m^2/g)
3.8	high	large	0	81	54	11	0.3
4.0	high	large	3	81	53	9	0.4
4.3	high	large	0	81	49	6	0.4
3.8	low	small	50	0	51	0.6	1.2
4.0	low	small	52	0	48	0.5	1.3
4.3	low	small	41	0	46	0.4	1.2
3.8	medium	large/small	38	28	51	0.8	1.0
4.0	medium	large/small	28	33	49	0.7	0.9
4.3	medium	large/small	30	37	48	0.8	0.9

lead could start. This second stage was noticed clearly by a temperature increase of the mass by some degrees centigrade. Some hours later, most of the free lead had been oxidized and then there was the third stage where the plate temperature returned to the air temperature of the curing chamber while decrease of moisture still continued.

The humidity was about 95% during curing and about 30% during drying. The drying temperature was 50°C. In order to get tribasic lead sulfate (3BS), tetrabasic lead sulfate (4BS) or a mixture of 3BS/4BS there were three different temperatures during curing: 50°C, 70°C or 80°C. After drying, the plates were investigated by X-ray diffraction which confirmed that, as it was planned, low temperature curing (50°C) gave only 3BS and high temperature curing (80°C) gave only 4BS. Curing at medium temperature (70°C) gave indeed a mixture of 3BS and 4BS. Investigation by SEM showed rather large crystals after high temperature curing and much smaller crystals after low temperature curing. The BET-surface and the medium pore size was also measured and the results fit well to the SEM pictures. A summary of all results is given in Table 1.

3. Soaking

3.1. Process

There was an investigation of the soaking process in sulfuric acid with different specific gravity of 1.06, 1.12 or 1.20. This investigation should give some information about the behaviour of the different versions of the cured mass and about the changes in composition of the mass during soaking which is virtually always the standard process before formation starts.

Single cured plates were put into containers filled with 150 ml sulfuric acid at a temperature of 20°C. The plates were kept in sulfuric acid for different time periods (0.5, 2, 5 or 24 h). Then they were taken out and, after washing and drying, investigated by different analytical methods including X-ray, porosimetry, BET and SEM.
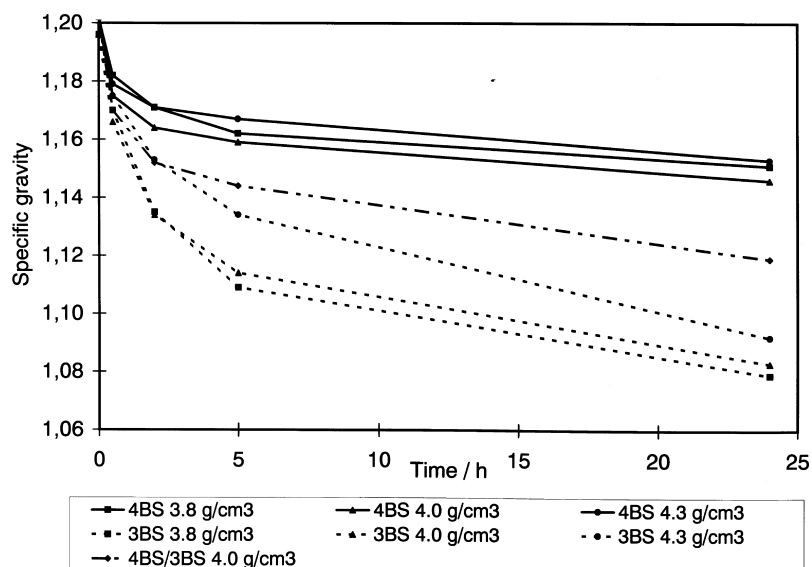

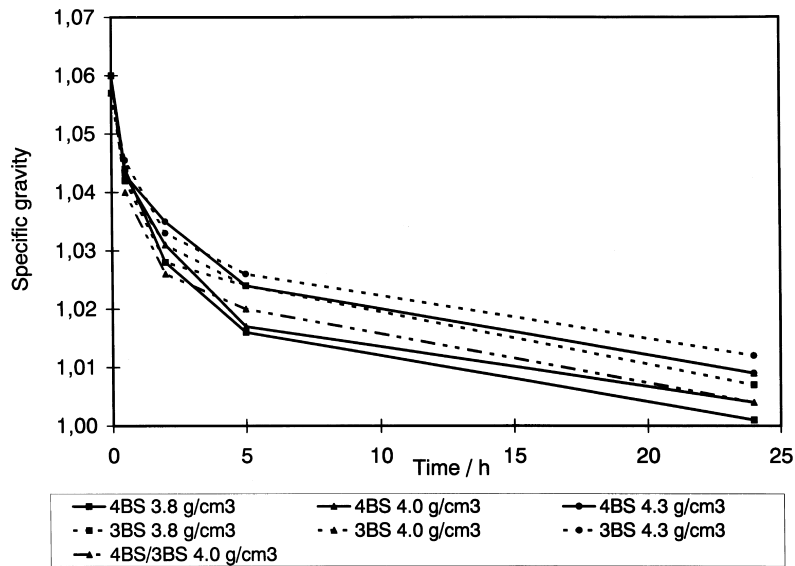Fig. 1. Decrease of the specific gravity during soaking starting with 1.20.

Fig. 2. Decrease of the specific gravity during soaking starting with 1.06.

The progress of sulfation of the plates could be measured by the change of the specific gravity of the sulfuric acid in the container. The decrease of the specific gravity during soaking is shown in Fig. 1 when soaking started with 1.20 specific gravity and in Fig. 2 when soaking started with 1.06 specific gravity. Both figures show the results of soaking with plates cured at high temperature (4BS mass structure) and made from 3.8, 4.0 or 4.3 g/cm^3 paste, plates cured at low temperature (3BS mass structure) and made from 3.8, 4.0 or 4.3 g/cm^3 paste, and plates cured at medium temperature (4BS/3BS mix) and made from 4.0 g/cm^3 paste.

It can be seen that, as expected, the specific gravity decreases due to the consumption of sulfuric acid by a sulfation of the cured mass. With sulfuric acid of 1.20

specific gravity there was still a marked amount of acid available even after 24 h soaking, whereas with sulfuric acid of 1.06 specific gravity most of the acid disappeared after some hours of soaking. That is a general difference when starting with a specific gravity of 1.20, a value in a range typical for container formation, or starting with a specific gravity of 1.06, a value in a range typical for tank formation. The ratio of 150 ml acid per plate with about 120 g cured mass is typical for container formation. For tank formation, there is often more acid available but in order to compare the results of our experiments we used the same amount of acid also in case of 1.06 specific gravity.

With a specific gravity of 1.20 (Fig. 1), there was a marked influence of the curing temperature. Low tempera-
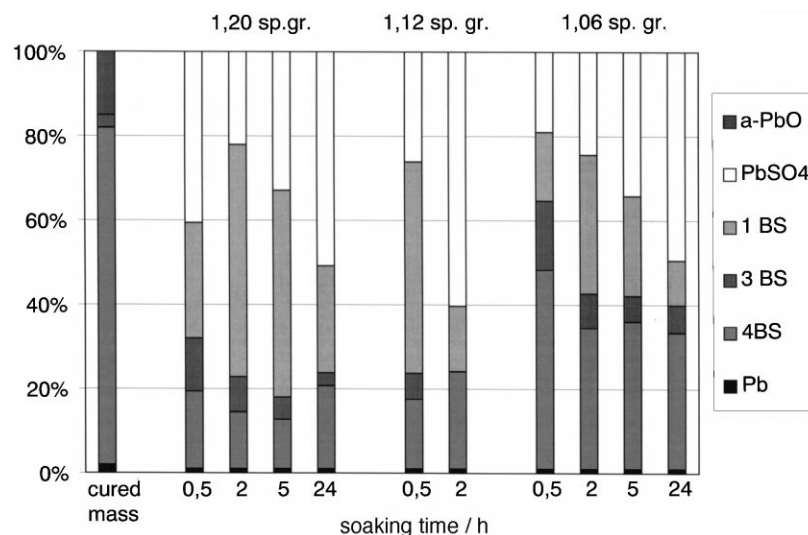

Fig. 3. X-ray investigation after different soaking time of 4BS mass from 4.0 g/cm^3 paste.
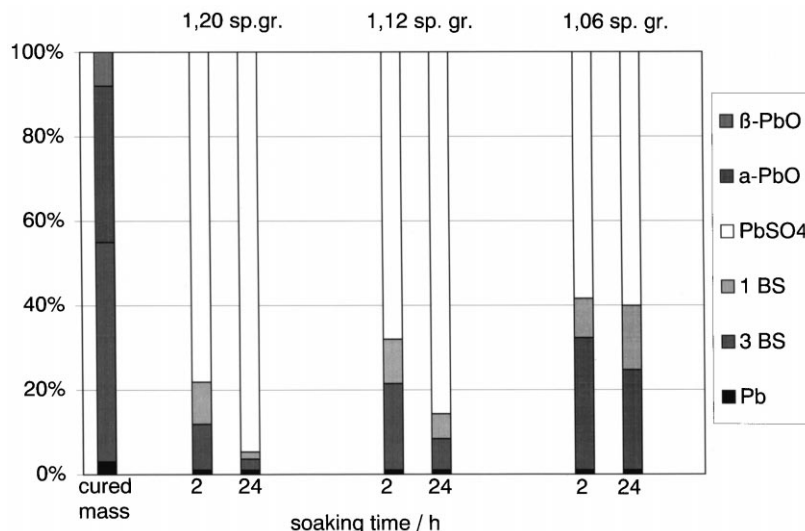
Fig. 4. X-ray investigation after different soaking time of 3BS mass from 4.0 g/cm³ paste.

ture curing, this means 3BS mass structure, gave a sharp decrease of the specific gravity to 1.13 within 2 h and after 24 h it was down to about 1.09. High temperature curing, this means 4BS mass structure, gave a much slower decrease to 1.17 within 2 h resulting in 1.16 after 24 h. The mix 3BS/4BS behaved within these two extremes. There was a decrease of the specific gravity to 1.15 within 2 h and after 24 h it was 1.13. In case of 3BS, there was also an influence of the paste density and 3.8 gave the highest and 4.3 the lowest consumption of sulfuric acid. There is no clear relationship in case of 4BS.

With a specific gravity of 1.06 (Fig. 2), there was much less difference in the behaviour of the different curing variants. After 2 h, it was between 1.04 and 1.03 and, after 24 h, it was between 1.01 and 1.00. There is again the relationship that a lower paste density gives a higher consumption of sulfuric acid.

The behaviour of the different curing variants in sulfuric acid with a specific gravity of 1.20 can be explained by considering the finer crystalline structure of 3BS in comparison with 4BS which allows a better and faster reaction of the sulfuric acid with the lead oxide as long as enough acid is available. In the case of 1.06 specific gravity, there is a marked lack of electrolyte which becomes the limiting factor.

3.2. X-ray

Figs. 3–6 give the results of X-ray investigation on the cured plates before and after some time of soaking. The results on the mass made from 4.0 g/cm³ paste and cured at high temperature is shown in Fig. 3. It gives the X-ray mass composition after soaking over 0.5–24 h in sulfuric acid with a specific gravity of 1.20, 1.12 or 1.06. There is
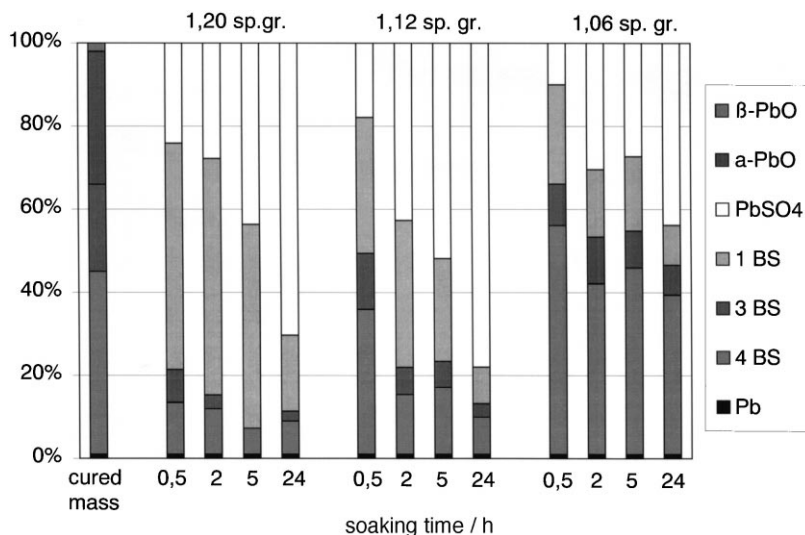

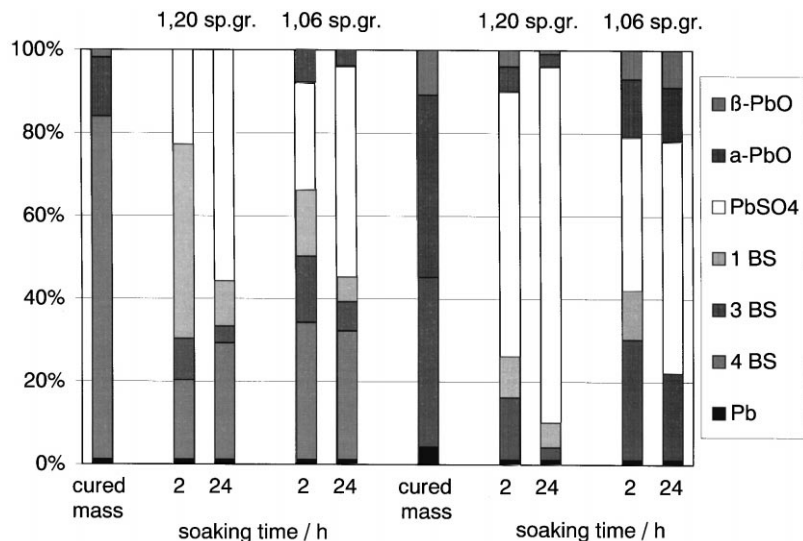Fig. 5. X-ray investigation after different soaking time of 3BS/4BS mix mass from 4.0 g/cm³ paste.

Fig. 6. X-ray investigation after different soaking time of 4BS mass and 3BS from 4.3 g/cm³ paste.

also the result of the cured plate before soaking where 80% 4BS was found.

In the case of 1.20 specific gravity, most of the 4BS disappeared in the beginning of soaking within 0.5 h and was obviously transferred to lead sulfate but also to a marked amount of monobasic lead sulfate and to some 3BS. In some cases, the amount of monobasic lead sulfate was even higher than that of lead sulfate. It seems that most of the reaction happened within 0.5 h and there was less progress during the next hours. That fits well to the results of acid consumption shown in Fig. 1. After 24 h, there was about 50% lead sulfate and about 20% monobasic lead sulfate and still about 20% 4BS.

There is a different situation with 1.06 specific gravity. After 0.5 h, much less mass had reacted with sulfuric acid. There was still about 50% 4BS. At this low specific gravity, the mass reacted much more slowly and there was some progress over all the soaking time. This behaviour fits well to the decrease of acid density shown in Fig. 2. After 24 h, there was still about 35% 4BS. The results at a specific gravity of 1.12 fit well to those at 1.20 or 1.06. In all cases, there was all the time a rather high amount of monobasic lead sulfate which was not there before soaking. There was also some more 3BS than in the cured stage. It seems that even after 24 h the amount of lead sulfate could not increase to more than about 50% even at a specific gravity of 1.20 where there was enough acid available. Probably, this means that the acid cannot penetrate the lead sulfate layer to react with the monobasic lead sulfate beneath that layer.

The soaking behaviour of 3BS plates made from 4.0 g/cm³ paste was quite different (Fig. 4). The cured mass had about 50% 3BS and about 40% α-PbO, but also some β-PbO. Even after 0.5 h, there was a marked amount of lead sulfate especially in the case of 1.20 specific gravity where nearly 80% lead sulfate was found. After 24 h, the

mass was nearly completely sulfated in the case of 1.20 specific gravity whereas it was only 65% in the case of 1.06 specific gravity. This lower amount can be explained by a lack of sulfuric acid inside the plate as already discussed. Again soaking at 1.12 specific gravity gave results somewhat in the middle between those at 1.20 and 1.06. There was also some monobasic lead sulfate in the soaked mass but less than in the case of 4BS samples. The main product was clearly lead sulfate.

This means that with 3BS there is a relatively fast reaction to lead sulfate while 4BS reacts first mainly to monobasic lead sulfate and afterwards some of it much more slowly to lead sulfate. A comparison of the results of soaking of 3BS and 4BS samples in 1.06 specific gravity after 24 h shows nearly the same amount of lead sulfate confirming the assumption made before that the acid availability is limiting the sulfation process at low specific gravity.

The behaviour of plates cured at medium temperature is given in Fig. 5. The cured mass had about 40% 4BS and 20% 3BS. The progress of sulfation was between that of 3BS and 4BS. Similarly to the 4BS plates, there was much monobasic lead sulfate. At 1.20 specific gravity about 70% lead sulfate was formed after 24 h and there were only a few percent 4BS and 3BS. Again, the results at 1.12 specific gravity were between those at 1.20 and 1.06.

Results from soaking of plates made from 4.3 g/cm³ paste and cured at high or low temperature are given in Fig. 6. The mass cured at high temperature had about 80% 4BS and the mass cured at low temperature had about 40% 3BS and no 4BS. In principle, the behaviour of these samples was the same as for 4.0 paste density. Again, there was a marked amount of monobasic lead sulfate especially in case of 4BS plates. In case of 3BS, the sulfation seems to be slightly lower in comparison with 4.0 paste density. Another difference with 3BS plates is the occurrence of
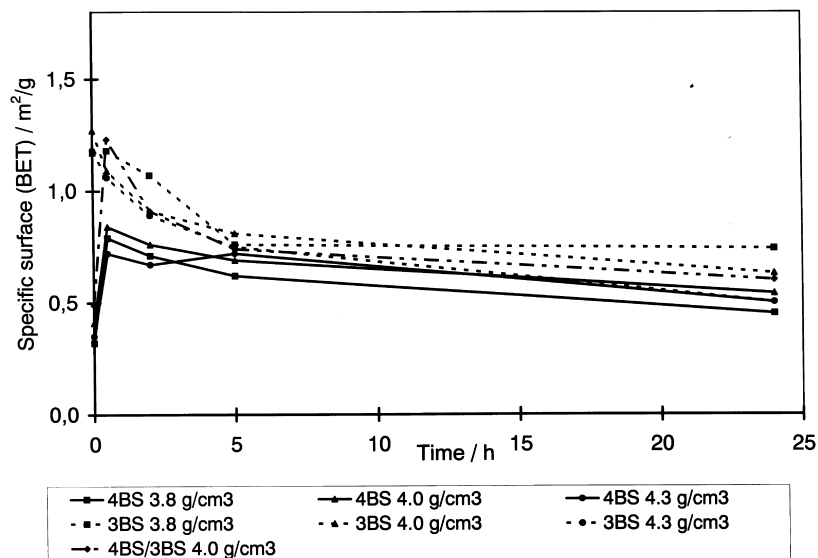
Fig. 7. Change of the BET surface during soaking in 1.20 specific gravity.

some PbO during soaking especially at 1.06 specific gravity. This was never found with samples made from 4.0 paste density.

3.3. BET

Figs. 7 and 8 give the results of BET measurements. Fig. 7 shows the change of the specific surface of the mass at different stages of the soaking process in sulfuric acid of 1.20 specific gravity. 3BS samples which had a relatively high specific surface after curing (more than 1 m^2/g) had a loss of the specific surface from the beginning of soaking resulting eventually to about 0.7 m^2/g. There was an influence of the paste density and 3.8 gave the highest and 4.3 the lowest value.

4BS which had a relatively low specific surface after curing (about 0.4 m^2/g) showed within 0.5 h of soaking a sharp increase to about 0.8 m^2/g and afterwards a slow decrease to values around 0.5 m^2/g after 24 h which were not much below those of the 3BS samples. The 3BS/4BS mix had a very sharp increase of the specific surface from about 0.5 to more than 1 m^2/g within 0.5 h soaking and afterwards it behaved similar to the 3BS samples.

The change of the specific surface of the mass at different stages of the soaking process in sulfuric acid of 1.06 specific gravity is given in Fig. 8. With 3BS plates, the specific surface did not change much over the whole soaking time except of one 3BS sample with a temporary increase in the early stage of soaking. The change of the specific surface of the 4BS plates was not much different
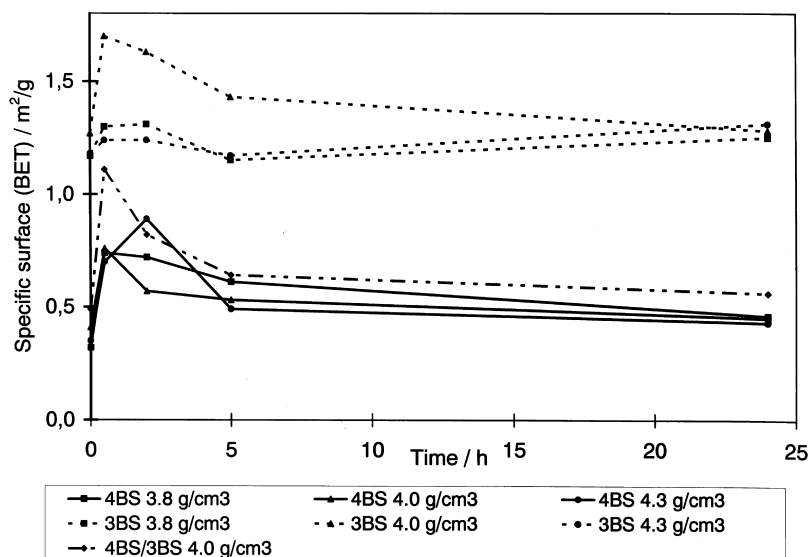

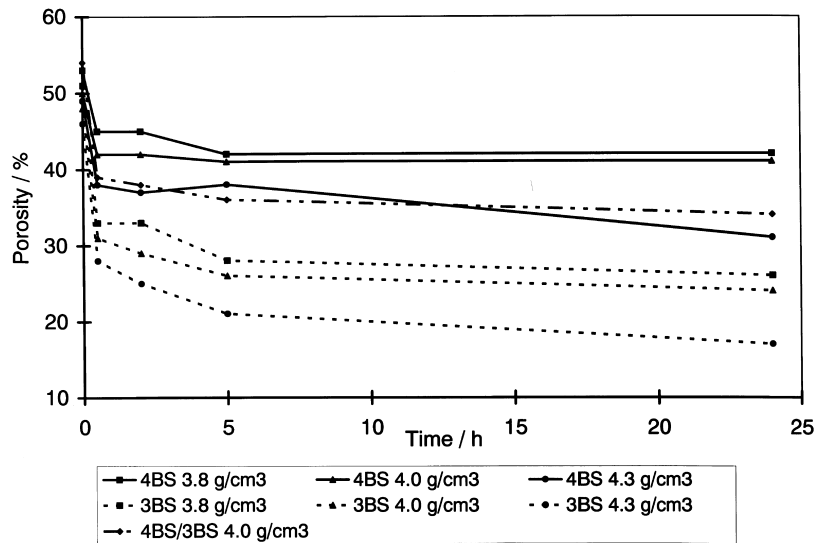Fig. 8. Change of the BET surface during soaking in 1.06 specific gravity.

Fig. 9. Decrease of the mass porosity during soaking in 1.20 specific gravity.

to the results with 1.20 specific gravity. The 3BS/4BS mix behaved similar to the 4BS samples. In all cases, there was no clear influence of the paste density.

It is remarkable that with 1.20 specific gravity, where there was much more sulfation of the 3BS plates, the specific surfaces of all the soaked samples were quite similar. On the other hand with 1.06 specific gravity, where both 3BS and 4BS had virtually the same degree of sulfation, there was a marked difference between these two curing versions. This means, as long as there is not much sulfation of 3BS samples due to a lack of sulfuric acid, 3BS keeps the high specific surface whereas a nearly complete sulfation at higher specific gravity reduces the specific surface of 3BS samples to values similar to those of 4BS plates. It is interesting that 4BS and also the 3BS/4BS mix had always a temporary increase of specific surface in the early stage of soaking.

3.4. Porosity, pore size distribution and medium pore diameter

The porosity which was around 50% at the cured stage decreased during soaking due to the sulfation of the mass. In the case of much sulfation (3BS in 1.20 specific gravity), there was a decrease of the porosity to very low values of about 25% which can be seen in Fig. 9. The 4BS plates and also the 3BS/4BS mix had only a relatively small reduction of porosity values to around 40%. The different paste density gave already a difference of the porosity of the cured samples and these differences could also be seen after the soaking process.

The results with 1.06 specific gravity are given in Fig. 10. With this low specific gravity, the degree of sulfation was similar in all cases and consequently the porosity changed very little. Anyway, 3BS had a slightly lower
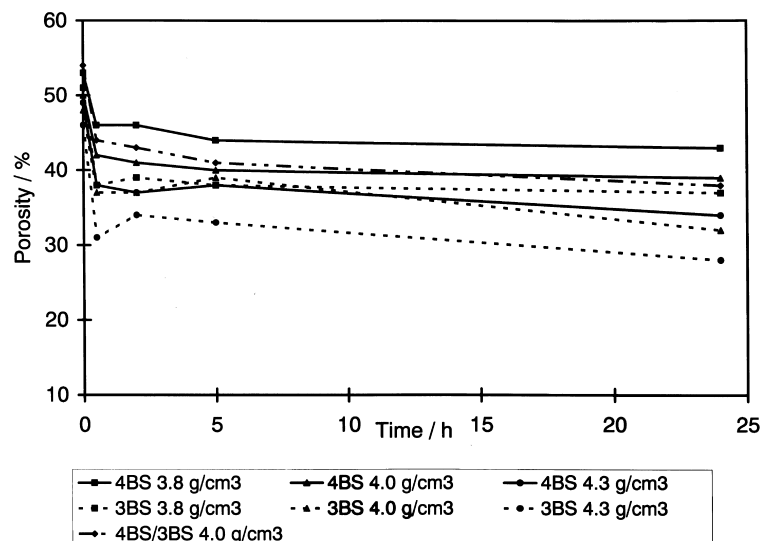

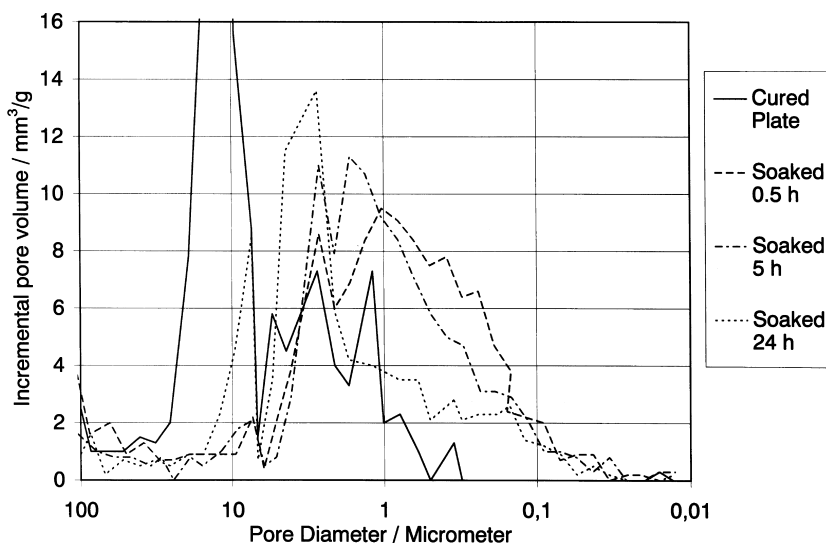Fig. 10. Decrease of the mass porosity during soaking in 1.06 specific gravity.

Fig. 11. Change of the pore size distribution of 4BS during soaking in 1.20 specific gravity.

porosity in the end but there was a more distinct influence of the paste density which gave the different starting values of the porosity.

Figs. 11 and 12 show the pore size distribution of the cured and soaked plates. The change of pore size distribution during soaking in 1.20 specific gravity is given in Fig. 11 for a 4BS sample and in Fig. 12 for a 3BS sample. The cured 3BS mass had most of the pores within the range of 0.1–1 μm and due to sulfation and reduction of porosity there was a shift to lower values during soaking. Most of the pores had then a size much smaller than 1 μm and there were also some below 0.1 μm. This shift to lower values was essentially within 0.5 h of soaking and afterwards it virtually did not change further.

On the contrary, 4BS changed the pore size distribution significantly over the whole soaking time. The cured 4BS mass had most of the pores around and markedly above 10 μm. In the early stage of soaking, there was a drastic shift to much lower values in the range of some micrometers down to 0.1 μm. With longer soaking time, the pore sizes increased again and most of the pores below 1 μm disappeared. This means there was a shift back to larger pores. This result fits well to the sharp increase of the BET surface of the 4BS samples to a maximal value after 0.5 h soaking shown in Figs. 7 and 8 as already discussed.

Figs. 13 and 14 give the change of the medium pore diameter during soaking. The medium pore diameter during soaking with 1.20 specific gravity is shown in Fig. 13. With 4BS plates, there was a sharp decrease of the pore diameter in the early stage of the soaking process to values markedly below 1 μm but then the pore diameter increased steadily back to higher values. 3BS had a relatively low medium pore diameter which became slightly lower in the early stage of soaking and then it was relatively constant.
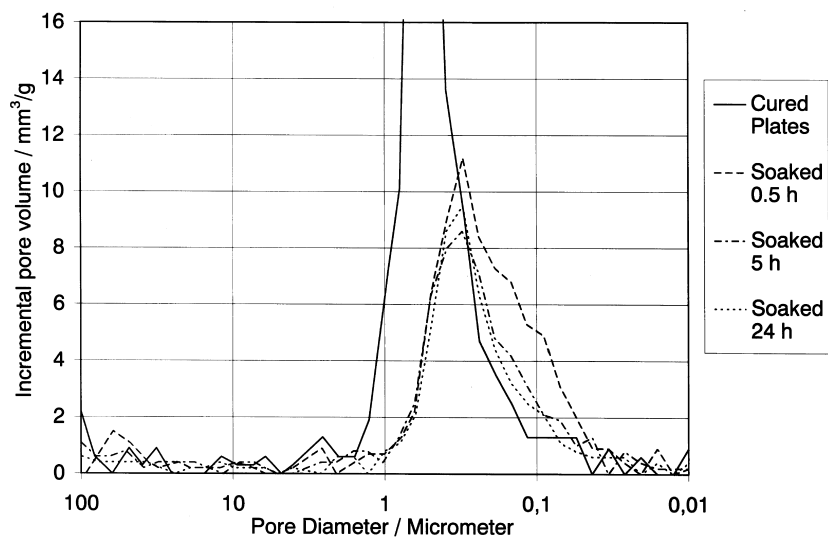

Fig. 12. Change of the pore size distribution of 3BS during soaking in 1.20 specific gravity.
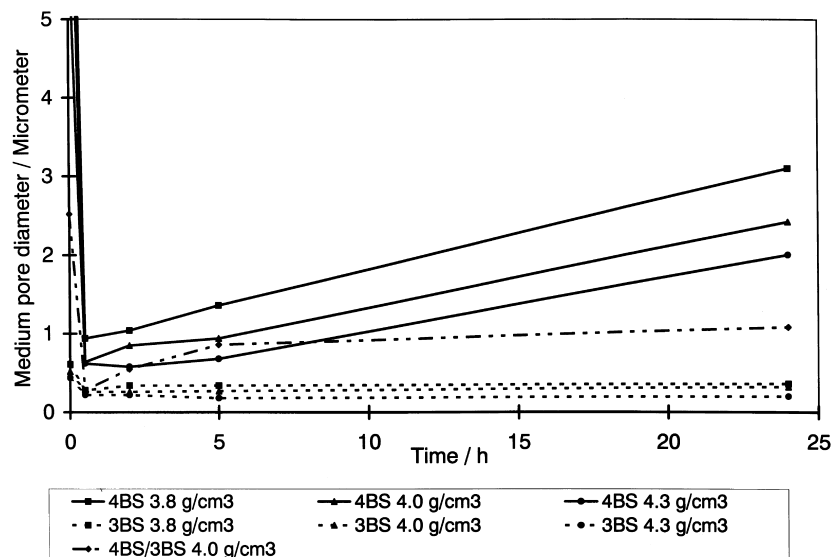
Fig. 13. Change of the median pore diameter during soaking in 1.20 specific gravity.

As for many other parameters, the mixture of 3BS and 4BS behaved between the two extremes of only 3BS or 4BS.

Soaking with 1.06 specific gravity gave only small changes of the medium pore diameter for 3BS plates as can be seen in Fig. 14. The change of the pore diameter of 4BS plates during soaking with 1.06 specific gravity was quite similar to the change with 1.20. As a whole, the change of the medium pore diameter fits well to the change of the BET surface given in Figs. 7 and 8.

3.5. Microscopic investigations

3BS and 4BS mass after 5 h soaking with 1.20 specific gravity was investigated by SEM. Fig. 15 shows with a magnitude of 1000 as an overview, the typical structure of 4BS mass. Additionally, with a magnitude of 10 000, there is a cross-section of one 4BS crystal. This crystal has still a core of material which had no reaction with sulfuric acid but there was a high degree of reaction within a surface region with a depth of about 1 μm. Fig. 16 shows with a magnitude of 1000 and 10 000 many small, formerly 3BS, crystals which had obviously nearly completely reacted to lead sulfate. Both pictures give typical regions of the soaked 3BS or 4BS material and fit well to the results of X-ray investigation shown in Figs. 3–6.

The sulfation during soaking was also investigated by cross-sections of the plate. The view by a light microscope on such cross-sections at different stages of the soaking process showed how the sulfation proceeds during soaking. There were cross-sections after 0.5, 2, 5 and 24 h. Soaking
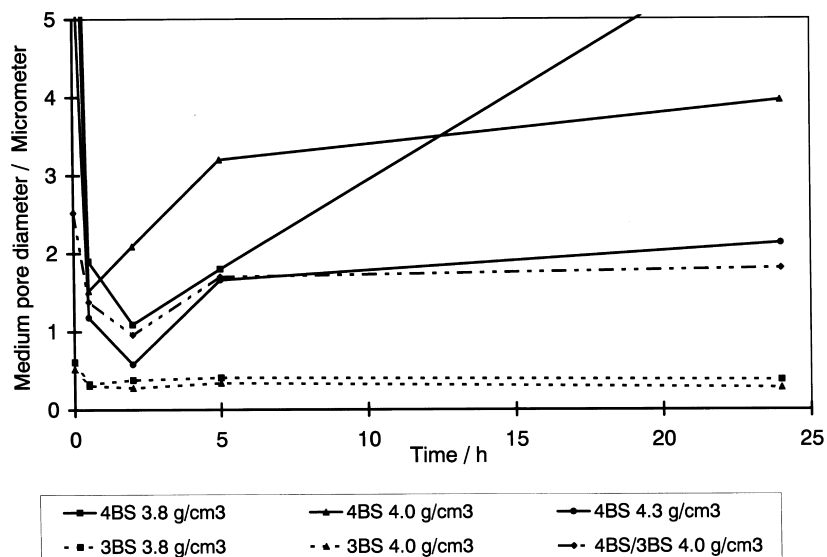

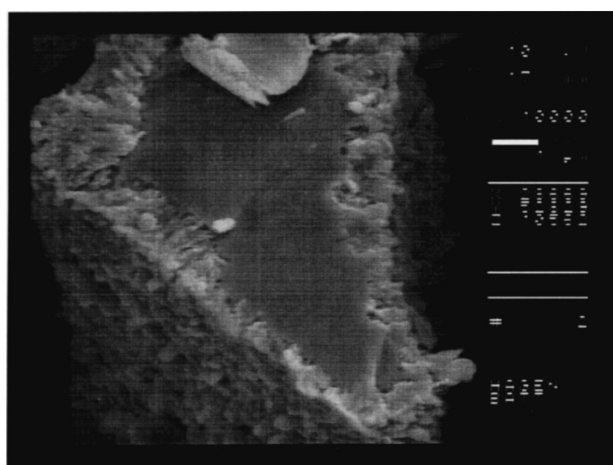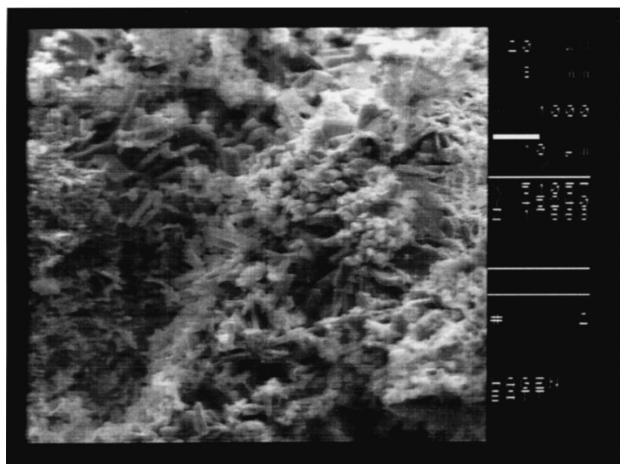Fig. 14. Change of the median pore diameter during soaking in 1.06 specific gravity.

Fig. 15. SEM picture of mass cured at high temperature (80°C) after 5 h soaking in 1.20 specific gravity.

with 1.06 specific gravity made the mass divide into two parts. There was an inner part with a dark yellow colour and an outer layer with an grey colour. With longer soaking time, the yellow inner part became smaller and was steadily replaced by the grey material but even after 24 h soaking there was still a yellow zone in the middle of the mass although it was then rather thin. The dark yellow colour represents lead oxide whereas the grey colour was caused by the sulfated part of the mass. The increase of the grey zone shows therefore the advance of the sulfation. This increase of the grey zone was not much different between 3BS and 4BS samples although in case of 3BS the mass seems to be a more uniform mixture of grey and yellow particles rather than a clear layer structure.

Soaking with 1.20 specific gravity gave a nearly completely grey coloured mass even after 0.5 h soaking. Thus, there was no clear difference in appearance between the outer and the inner part of the samples. Sometimes, there were some yellow islands within the grey mass especially in the early stage of soaking. These results show that soaking with 1.06 specific gravity leaves some regions of the mass on a high pH level when formation starts, whereas

after a soaking process with 1.20, formation starts with a much lower pH.

Of course, plate thickness is another important parameter and our results about soaking are only valid for a plate thickness of about 2.8 mm as all our tests were carried out with plates having this thickness. It can be expected that sulfation will be much faster in case of rather thin plates whereas plates thicker than 3 mm will react slower.

4. Formation

The positive plates were formed in tanks with sulfuric acid (325 ml per positive plate, specific gravity 1.06). The soaking time before the start of the electric program was mostly 2 h except for a few formations where 0.5 h or 5 h were used. After formation the specific gravity was between 1.086 and 1.098. Three different formation programs (current per plate) were used:
1. Constant current formation $I = 1.5$ A for 43 h.
2. Formation with constant current $I = 1.9$ A for 24 h followed by a discharge step with 1.5 A for 4 h (-6 Ah) and a further charge step with 1.23 A for 24 h.
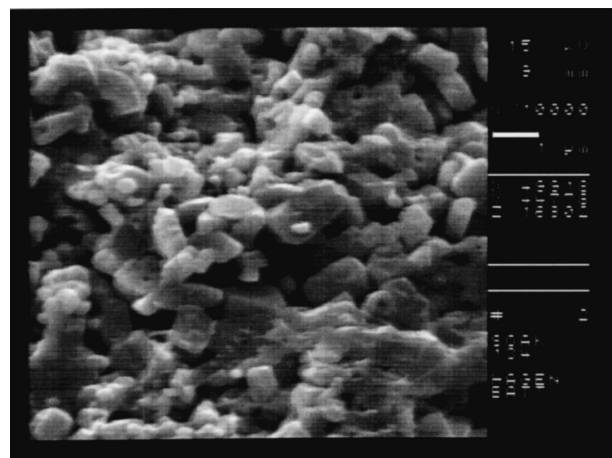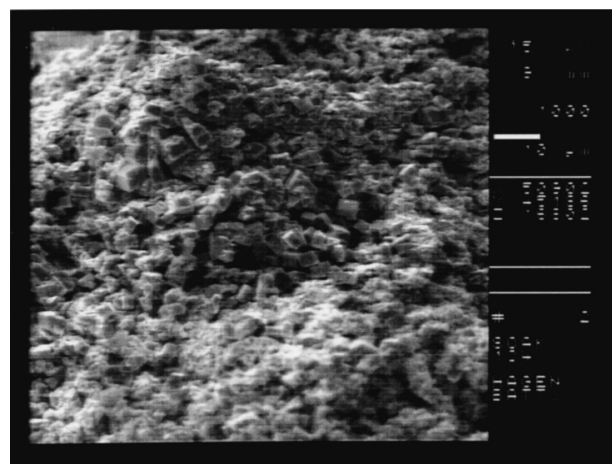

Fig. 16. SEM picture of mass cured at low temperature (50°C) after 5 h soaking in 1.20 specific gravity.

3. Pulse formation for 43 h (10 s pulse $I = 3$ A/10 s rest $I = 0$).

The total charge amount was always 64 Ah. Considering the cured mass weight of 125 g, this was more than twice the charge which is theoretically necessary to form 100% PbO_2. This overcharge factor gives in general a well formed mass although the plates with a high content of 4BS are expected to have a rather low initial capacity which increases normally within some cycles and can be brought finally to nearly the same level as the capacity of 3BS plates.

In some cases, the positive plate potential was measured during formation by using a saturated mercury/mercurous sulfate reference electrode ($+650$ mV vs. SHE). Fig. 17 gives the change of the positive plate potential during constant current formation for six different types of plates. In the beginning of formation, the positive potential was relatively high but then it decreased quite fast. In the second stage of formation, nearly the whole current was used for mass formation. Gassing was rather low and therefore the positive potential was low too. In the third stage, the portion of current which could no longer be used for mass formation increased steadily and gassing, this means oxygen evolution, was enhanced together with an increase of the potential. Although this was valid in general for all six different plate types some differences in the behaviour can be seen clearly from the curves in Fig. 17.

In the beginning of formation, 4BS plates were the first where the positive potential dropped followed by the 3BS/4BS mix whereas 3BS needed the longest time to reach a lower level of the positive potential. The minimum of the potential was the lowest for 4BS and was reached after about 2 h formation time, whereas 3BS reached a minimum after about 8 h but on a level higher than 4BS. The behaviour of plates with 3BS/4BS mix was between

Table 2
Initial capacity of positive plates after constant current formation

	3BS-4.0	3BS-4.3	3BS/ 4BS-4.0	3BS/ 4BS-4.3	4BS-4.0	4BS-4.3
1. C5/Ah	14.2	14.1	12.9	12.7	7.6	6.8
2. C5/Ah	14.2	14.2	14.4	14.5	11.7	10.8
8. C5/Ah	14.3	14.3	14.6	14.8	14.7	14.0

that of 3BS and 4BS. There was also some influence of the paste density.

An explanation for the different behaviour of the six plate types during formation can be given by considering that the formation process starts at the grid surface and then spreads into the cured material preferentially along the surface of the crystalline network. It can be expected that this process takes place faster with tetrabasic lead sulfate than with tribasic lead sulfate according to the different shape and size of the crystals. Besides, the different soaking behaviour could also have an influence. After 2 h soaking with 1.06 specific gravity 3BS plates had about 60% lead sulfate so that many of the even before rather small pores became now so small that ionic migration was hindered much more in comparison to the larger pores of 4BS plates.

After formation, the plates were washed and dried and some of them were taken for analysis. Other plates were used for capacity tests (C5) in sulfuric acid of 1.30 specific gravity. Table 2 gives the results of six different plate versions after constant current formation. The first C5 showed the expected differences, as 4BS gave only about 7 Ah whereas 3BS gave about 14 Ah. However, after some more capacity tests, the differences became much smaller. At the eighth discharge, there was no longer any marked difference between 3BS and 4BS. Plates formed from a
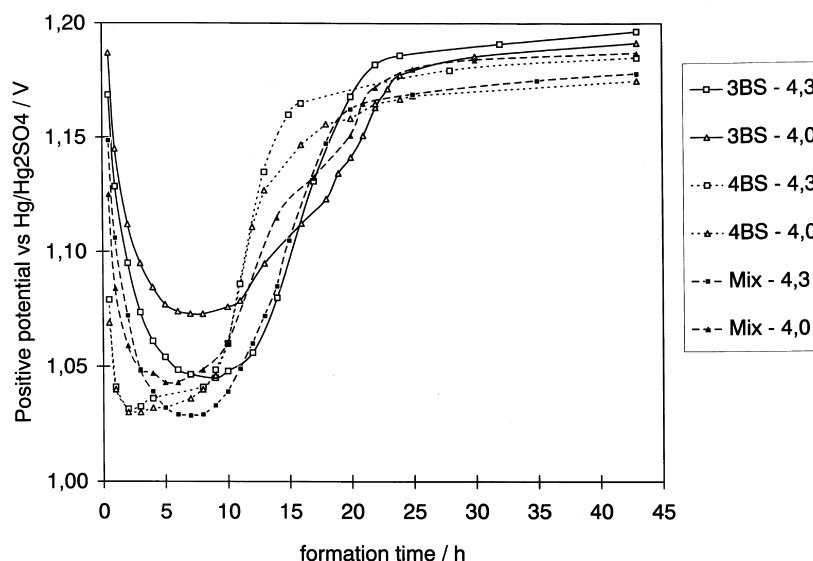

Fig. 17. Positive electrode potential during constant current formation of six different types of cured mass.
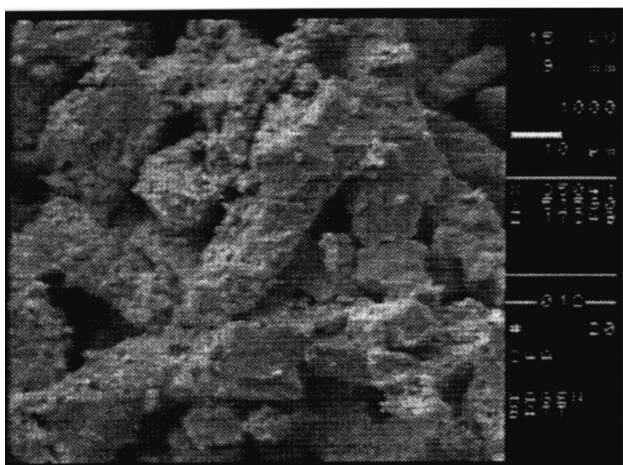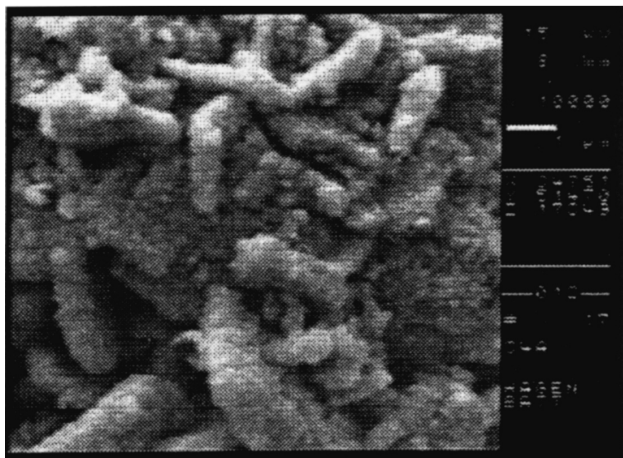
Fig. 18. SEM picture of mass cured at high temperature (80°C) after constant current formation.

mix of 3BS/4BS reached the higher capacity level of 3BS plates already at the third discharge. The difference in the PbO_2 content of the mass just after formation (slightly above 90% in case of 3BS, below 90% in case of a 3BS/4BS mix and sometimes even below 80% in case of 4BS) fits well to the electric behaviour of the plates.

There was a marked influence of the formation program on the initial capacity. The best results were given by a constant current charge with a discharge step for 4 h where even with 4BS the initial capacity (13 Ah) was on a relatively high level. With 3BS up to 15 Ah were found. Pulse formation gave also better results than constant current formation (about 11 Ah with 4BS and about 14 Ah with 3BS). Therefore, with regard to the initial capacity, the conclusion can be made that a formation with a discharge step or a pulse formation is a good way to overcome the problem of worse formation capability of high temperature cured mass.

The mass structure after formation was investigated by SEM. Positive mass formed from 4BS had still the typical network structure of tetrabasic lead sulfate with rather large crystals which act like a skeleton for the positive

active mass (Fig. 18). The pictures of positive mass formed from 3BS show a well formed mass with the typical structure of β-PbO_2 forming a network of agglomerates of rather small PbO_2 particles (Fig. 19).

X-ray investigation after formation showed that the formed positive mass had much more β- than α-PbO_2. In some cases, there was a small amount of α-PbO_2 but always less than 10% whereas in other plates there was no α-PbO_2 within the detectable limits of X-ray analysis. There was no clear relationship of the amount of α-PbO_2 to the formation program or the curing temperature. By investigating the influence of soaking with a low specific gravity (1.06), a trend was found to have more α-PbO_2 in case of a short soaking time (0.5 h) but the amount of α-PbO_2 was never more than 10%.

In order to achieve some information about the influence of plate thickness, additional experiments were made with thicker positive plates. This investigation showed that indeed with an about 1 mm thicker plate (3.7 mm) the inner part of the mass was not much sulfated even after some hours of soaking, and therefore it can be expected that the thicker plate had a marked portion of alkaline
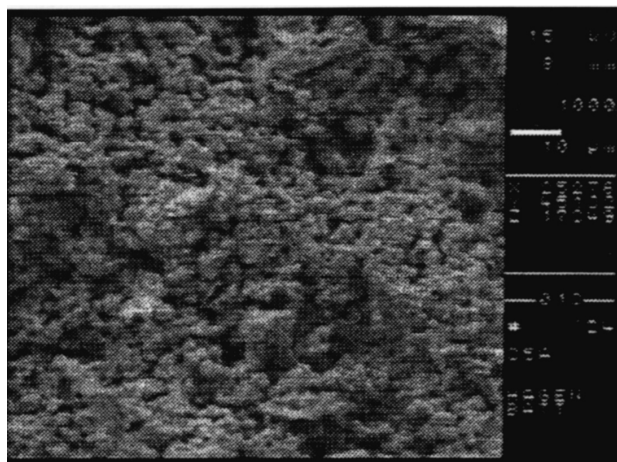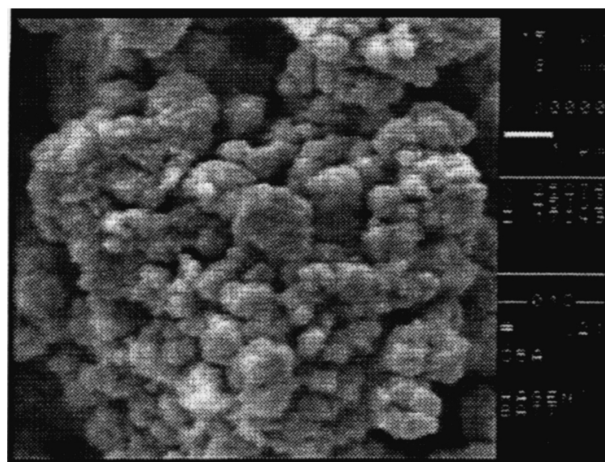

Fig. 19. SEM picture of mass cured at low temperature (50°C) after constant current formation.

material in the inner part of the mass when formation started. Two tests were carried out, one with 3BS plates and a second one with 3BS/4BS plates both made from 4.3 g/cm^3 paste. The specific gravity was 1.06 and the soaking time was 2 h.

After a standard formation with constant current, the X-ray investigation gave 36% α-PbO$_2$ in the case of 3BS plates and 23% α-PbO$_2$ in the case of 3BS/4BS plates. This was the result of the total amount of the mass. A more detailed X-ray investigation by dividing the total mass into two halves, one from the inner part and one from the outer part of the plate, gave more than 50% α-PbO$_2$ in the inner part and virtually no α-PbO$_2$ in the outer part. This result shows clearly how much the plate thickness influences the pH in the inner part of the mass in the beginning of formation and therefore also the amount of α-PbO$_2$ in the formed mass.

5. Conclusion

The curing process gives the crystalline structure of the mass and this first structure acts like a skeleton for the active mass. The soaking/formation process makes then the microcrystalline structure. The behaviour of the mass during soaking and formation is strongly influenced by curing and slightly by the paste density and therefore the processing of unformed plates does also influence substantially the microcrystalline structure of the formed mass. Plate thickness is another important parameter and our results on soaking are only valid for a plate thickness of 2.8 mm as all our tests were carried out with plates having this thickness.

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