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ORIGINAL PAPER

A new look at determining acid absorption of lead oxide used in the manufacturing of Pb-acid batteries

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Abstract Acid absorption is a routine analytical method used in the manufacturing of lead oxide, that is, then further used to manufacture Pb-acid battery electrodes. This study had a new look at the definition of acid absorption being an indication of the acid reactivity of the oxide forming certain lead sulphate-related phases. Quantitative powder X-ray diffraction analysis of the acid reaction products showed there were significant differences in the phases formed that could be related to the amount of acid used in the acid absorption test. The study also showed that there were significant changes in the surface area of the oxides once they had reacted with the acid, where a traditionally slow reacting oxide such as β-PbO would show the greatest increase in material surface area once reacted with the acid. The accuracy of the method used by various laboratories was also studied by comparing the results obtained from two different methods and from three different laboratories. The results showed that there were significant differences between the reported values, and that one should with caution compare acid absorption numbers obtained from different laboratories.

Keywords Acid absorption · Lead oxide · Lead acid battery

1 Introduction

In the manufacturing of lead acid batteries, a number of analytical techniques are used on a routine basis to determine the quality of the raw materials. Besides measuring the quality of the material in terms of the levels of impurities such as unwanted trace metals, other important factors that often determine the manufacturing quality are the consistency and reproducibility of certain physical and chemical properties of a particular starting material used within predetermined set of parameters. For example, in the manufacturing of the lead oxide powder, routine methods used include the determination of the free Pb, apparent density and acid absorption. Acid absorption is understood as a property that relates to the paste mixing of the oxide before it is processed further to make pasted and cured electrodes. The measured results give an indication of the paste's preparation ability and can influence the quality of the cured plate and finally the formed electrode's characteristics. The test is described as a measure of the wetted surface of the oxide and gives an indication of the reactivity of the material with sulphuric acid [1–8].

The term absorption in chemistry is understood as a substance (gas or liquid) that diffuses into a matrix bulk (liquid or solid) to form a solution. On the other hand, adsorption is a process that occurs when a gas or liquid accumulates on the surface of a solid or a liquid (adsorbent), initially forming a film of molecules or atoms. A common example is the measure of surface area and porosity by nitrogen gas adsorption in BET surface area analysis. The term wettability in chemistry relates to the interface formed between a solid and a liquid. The degree of wetting is related to the surface tension of the liquid and depends on the contact angle that can be measured to give an indication of the wetting ability of the surface by the

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liquid. The acid "wetting" the glass matt separators used in Valve Regulated Lead Acid (VRLA) type batteries can be seen as a typical example, where the liquid adsorbs onto the solid glass fibre surface. The liquid can also desorb from the solid surface thereby separating the two phases from each other without having undergone any chemical reaction or change. In referring to the measure of acid absorption by the oxide as a measure of the wetting ability is not strictly correct, where it will be shown that a chemical reaction occurs between the acid and the oxide and one cannot simply "un-wet" the material to obtain the original starting material without having to undergo another chemical reaction.

The understanding of measuring the acid absorption of lead oxide should rather be seen as an indication of the reactivity of the lead oxide where the material undergoes a chemical change. The reactivity of the acid with the oxide does give an indication of the surface area available for reaction, but not in terms of just a larger available surface area allowing for more absorption of the acid onto the surface of the oxide, but rather in terms of a different reaction products forming.

The general method in literature for determining acid absorption is described by adding a known amount of manufactured lead oxide (usually 50 g) to a solution of sulphuric acid (100 mL 1.10 SG) at 25 °C [1, 2, 4]. Heubach [3] specified the temperature of the analysis to be 32 °C. The solution is thoroughly mixed and a filtered portion of the remaining acid is titrated with a 1 M NaOH solution. The value is then compared to the titrated blank result and reported as (mg H_2SO_4)/(g of manufactured oxide). Note that the amount of manufactured oxide also known as grey oxide would be a mixture of the two possible oxide phases (α-PbO and β-PbO) and free Pb in various proportions. It is known that the free Pb content of the grey oxide can change significantly with time, especially for oxides obtained from the Ball mill processes [9]. Noticeably, both the free Pb and acid absorption values are reported on a laboratory report sheet and their determination are usually done simultaneously on a batch of grey oxide received from the manufacturing facility.

A problem arises when a comparison is done on results obtained from different laboratories with different methods and possibly on oxide obtained from different processes such as the Barton Pot or Ball mill. This was shown in the study done by Hardy and Marx [8], where considerable variation between three methods over the range of oxides analysed was reported. The authors did not describe the methods used, but by doing a simple ANOVA 2 statistical test of their results, one could show that there were significant differences between the three sets of methods used for determining acid absorption. The authors also suggested a worthwhile aim was to agree on an international standard. Again, the variation between acid absorption techniques for different manufacturing facilities might not be essential, where the importance of the precision of one technique used within one facility is maintained. However, one must be careful when comparing acid absorption results across different manufacturers using slightly different methods on the basis of the reported values only. One should also consider the type of lead oxide manufactured with its free Pb, oxide phase composition and the final reaction product of the acid absorption test.

This study looked at the use of the term acid absorption as the reactivity of the Pb oxide with the acid rather than its wetting ability and will be referred to as "acid reactivity" in the "Results and discussion". The resulting product of the acid reacting with the oxide would give an indication of the type of oxide and the influence of the free Pb in the calculations of the final reported results. An attempt is made at possibly standardizing the method to give a clearer meaning of the actual reported value across various manufacturing facilities where even though the material might be made by different processes giving very different values, the chemistry behind each of the reactions would not necessarily indicate that one oxide process is better than another in terms of the acid absorption number, but rather that the resulting chemical reaction products have unique properties and are different within its specific manufacturing environment.

2 Experimental

Manufactured grey oxide was obtained from both the Ball Mill (BM) and Barton Pot (BP) processes. Seven set of samples from different batches were obtained for each oxide type. A commercial oxide was also obtained from Aldrich and identified as pure β-PbO by powder X-ray diffraction (PXRD).

Particle size analysis of the oxides was done by laser diffraction on a Malvern Mastersizer S and the results reported as the particle volume mean diameter $D(4,3)$. The BET surface area of the oxides was done by measuring the nitrogen adsorption on a Micromeretics Gemini.

Two acid absorption (reactivity) methods were used and are described as the low temperature (LT) and high temperature (HT) method, respectively.

The LT method was done at 25 °C. 50 g of the manufactured grey oxide was added to a 500 mL flask to which was added 100 mL of sulphuric acid that had an SG of 1.100. The content was vigorously stirred on a magnetic stirrer for 10 min after which the content was allowed to settle for about 5 min. The clear liquid was decanted through a dry filter paper after which 25 mL of the filtrate was then titrated with a 1 M solution of NaOH. A similar 25 mL blank of the original acid solution was also titrated with the 1 M NaOH and the difference in concentration was then an indication of the degree of acid reactivity (absorption). The difference in the acid concentrations was then used to determine the mass (mg) of H_2SO_4 per gram of grey oxide (50 g).

The HT method was done between 32 and 34 °C by adding 35 g of the manufactured lead oxide excluding the mass contribution of the free Pb. Hence, the final mass of the grey oxide amount weighed included the mass contribution of the free Pb for a particular sample. The sample was added to a 500 mL flask to which was added 100 mL of sulphuric acid that had an SG of 1.100. The content was vigorously stirred on a magnetic stirrer for 10 min after which the content was allowed to settle for about 5 min. The clear liquid was decanted through a dry filter paper after which 25 mL of the filtrate was then titrated with a 1 M solution of NaOH. A similar 25 mL blank of the original acid solution was also titrated with the 1 M NaOH and the difference in concentration was then an indication of the degree of reactivity (absorption). The titrations were done at room temperature. The difference in the acid concentrations was then used to determine the mass (mg) of H_2SO_4 per gram of grey oxide used (35 g oxide + x g free Pb).

The free Pb in the oxides was determined gravimetrically by adding 60 mL of a solution of 5% acetic acid to an accurately weighted oxide sample (about 2.5 g). The solution was boiled on a hot plate for about 10 min until it turned clear. The remaining free Pb residue was washed with excess water and dried at 120 °C until all the moisture was removed. The remaining residual Pb was then weighted and compared to the starting mass of the oxide sample.

The free Pb that remained in the acid reaction product was done by considering the whole reaction mixture that was filtered from the analyte. The sample material on the filter paper was rinsed with deionized water until neutral and transferred carefully into a beaker ensuring that all of it was rinsed from the paper. About 180 mL of a 5% solution of acetic acid was added to the mixture. This was followed by about 40 mL of a solution of ammonia followed by 40 mL of concentrated acetic acid. The solution was allowed to boil until clear, where only the free Pb remained as a residue. The residual free Pb was rinsed a few times with water, dried and weighed. The amount of dry free Pb was then compared to the original amount of free Pb present in the oxide sample used for the acid absorption test. This was determined by the free Pb method in the oxide described previously. Hence, this would then give an indication of the amount of un-reacted free Pb remaining after the acid absorption test.

The phase composition of the original oxides and the acid reaction products were done by powder X-ray diffraction analysis (PXRD) on a Bruker D8 Advance using Cu radiation. The scan range was 5–70 2Θ at 0.02° step^{-1}. The quantification was done by using commercial software (Topas) that uses the method of Rietveld structural refinement of the solid phases [10]. The crystal structural information for the phases of interest was obtained from the literature and used in the refinement model accordingly [11–15].

3 Results and discussion

The PXRD phase composition analysis of the seven Barton Pot and seven Ball mill oxides showed that the Ball mill oxide contained only the α-PbO phase (Table 1). The Barton Pot oxides samples contained small amounts of the β-PbO phase and were quantified by using full pattern Rietveld refinement using Topas [10]. The percentage of the Pb phase determined by PXRD is usually lower than the free Pb determined by wet chemical methods and is not shown in the results. This can primarily be ascribed to the strong X-ray absorption of the Pb in the oxide that usually coats the free Pb particles.

The results also show the comparative acid reactivity study of the various oxides using the two analytical methods (LT and HT) from one laboratory (Table 1). Doing a statistical paired two t test on the two set of experimental results, and having a null hypothesis that assumes there are no differences between the two methods [16]. For a two-tailed test of the LT and HT set of results, with 13 df, the accepted critical statistical value for t at 95% confidence levels is 2.16. The t value determined for these acid reactivity results gave a t value of 2.07, which is close to the 95% confidence level. This shows that the null hypothesis can still be considered as valid and that there are no differences between the results obtained from the two methods done in one laboratory but with caution, since the obtained t value for the set of results are close to the critical value. However, the results of the seven Ball mill oxides obtained from two other Pb-acid battery laboratories (Table 1), showed that there were significant differences between them and that they could not be considered as being the same. For the seven samples with 6 df the accepted critical t value at 95% confidence levels is 2.45. The t value determined for them was 8.37, implying that they are significantly different.

This supports the results that were reported by Hardy and Marx [8] that also showed variation in acid absorption (reactivity) values of the same material obtained from different laboratories. Laboratories usually adapt their methods to suite their particular manufacturing processes and would look at the consistency of results from their

Table 1 Acid reactivity and free Pb of 14 set of lead oxide manufactured by the Ball mill (BM) and Barton Pot (BP) process

Sample	Free Pb (%)[a]	β-PbO XRD (%)	HT acid reactivity (mg H_2SO_4 g^{-1})	LT acid reactivity (mg H_2SO_4 g^{-1})	LAB 1 acid reactivity (mg H_2SO_4 g^{-1})	LAB 2 acid reactivity (mg H_2SO_4 g^{-1})
BM1	23.71	0	308.1	272.3	263	284
BM2	22.01	0	307.5	278.9	247	267
BM3	22.60	0	305.9	277.3	268	300
BM4	18.35	0	286.5	286.1	252	290
BM5	16.73	0	276.4	284.4	257	303
BM6	13.88	0	280.5	286.8	257	286
BM7	24.06	0	294.7	303.2	268	301
BP1	10.77	7.14	174.9	188.9		
BP2	20.02	2.95	201.2	185.7		
BP3	20.94	9.44	208.5	183.7		
BP4	18.05	8.51	185.9	168.3		
BP5	13.07	4.45	165.7	157.6		
BP6	23.20	3.30	173.2	166.7		
BP7	18.70	3.08	173.3	173.1		

[a] Free Pb determined within a day of receiving the oxide sample

specified methods as a quality control, rather than comparing values that come from other laboratories, especially from other types of oxide manufacturing processes.

It is well known that the surface area of the Ball mill lead oxide is considerably larger than the lead oxide obtained from the Barton Pot process [1–4]. These differences can be seen in Table 2 for the 14 samples considered in this study. Of interest were the phase compositions and the change in surface area of the material once it had undergone the acid reactivity analysis. PXRD phase composition analysis showed that the product of the Ball mill oxide comprises of almost 50% mixture of $PbSO_4$ and $PbO{\cdot}PbSO_4$ (T1) with no remaining PbO (Fig. 1). On the other hand, the PXRD phase composition of the Barton Pot acid reaction product showed it to contain considerably more of the T1 phase than $PbSO_4$ (Fig. 2).

Table 2 The phase composition and change in BET surface area of the acid reaction product for the different manufactured lead oxide

Sample	BET surface area oxide (m^2 g^{-1})	BET surface area after HT acid reactivity product (m^2 g^{-1})	XRD phase composition after acid reactivity	
			T1 (%)	$PbSO_4$ (%)
BM1	1.014	1.853	47.89	52.11
BM2	1.163	2.071	49.42	50.58
BM3	1.099	1.389	53.24	46.76
BM4	1.323	1.494	46.10	53.90
BM5	1.306	1.723	50.34	49.66
BM6	1.522	2.070	46.95	53.05
BM7	1.451	1.938	33.58	66.42
BP1	0.189	1.970	97.16	2.84
BP2	0.294	1.994	83.84	16.16
BP3	0.323	2.657	89.01	10.99
BP4	0.228	1.355	96.25	3.75
BP5	0.197	1.536	99.04	0.96
BP6	0.233	2.155	94.62	5.38
BP7	0.255	1.162	90.65	9.35

The determination of the free Pb that remained after the acid reactivity by PXRD was not possible since the diffracted peak positions for Pb corresponded to the strong peaks of $PbO{\cdot}PbSO_4$ (T1) (Fig. 3). The results show that the (111), (002) and (022) peaks for Pb strongly overlap with the (020), $(5\bar{1}1)$and $(3\bar{3}1)$peaks of T1, respectively, and cannot be used to accurately quantify Pb by Rietveld refinement of the diffraction pattern. Hence all XRD results reported exclude the portion of the remaining free Pb. The free Pb content of some of the samples was determined by wet chemical methods (Table 3). Analysis was done on four new Barton Pot oxides that had reasonably high free Pb in the oxide. The results showed that approximately 2.7% of free Pb that is based on the initial oxide mass remained in the acid reaction product.

In addition, the acid reactivity analysis and the change in surface area of a commercial β-PbO sample were done in duplicate (Table 4). The PXRD phase composition of the acid reaction product showed surprisingly no $PbSO_4$ and only the presence of T1 and $3(PbO){\cdot}PbSO_4{\cdot}H_2O$ (T3), which is usually found in cured electrodes (Fig. 4). A small amount of un-reacted β-PbO remained in the mixture. Notably, the acid reactivity number when using the LT method was considerably smaller when compared to the other two types of manufactured lead oxides studied.

Fig. 1 Quantitative PXRD of an acid reaction product from the Ball mill oxide that gave an acid reactivity of 278.9 mg g^{-1} grey oxide (LT method)

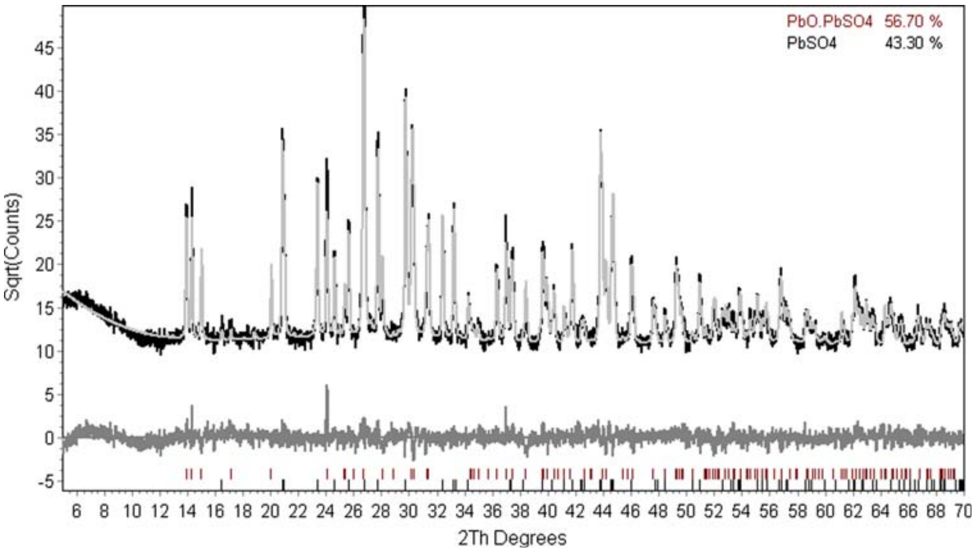

Fig. 2 Quantitative PXRD of an acid reaction product from the Barton Pot oxide that gave an acid reactivity of 188.9 mg g^{-1} grey oxide (LT method)

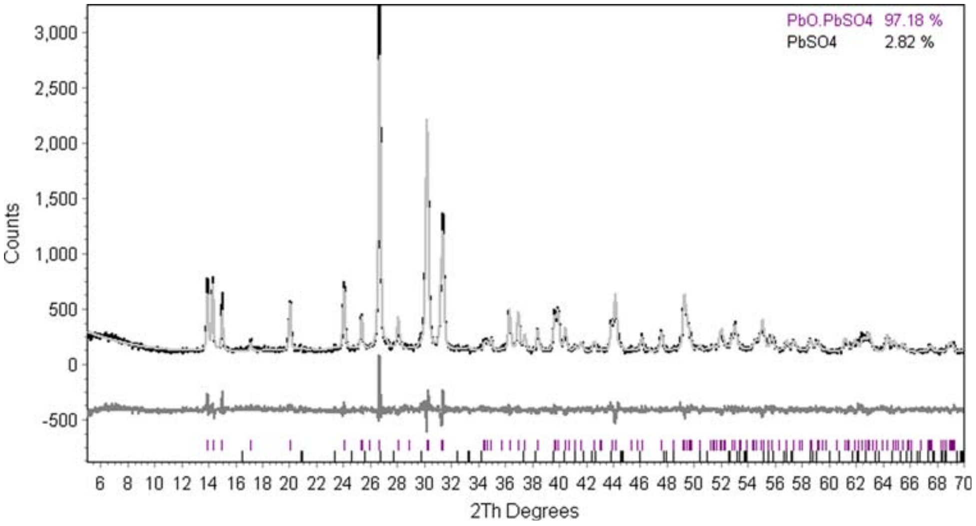

Fig. 3 Magnification of the diffraction pattern of the acid reaction product containing both the PbO·PbSO$_4$ and Pb showing the overlap of the Pb peaks. The wet chemical method of this particular samples showed it still contained about 2% free Pb

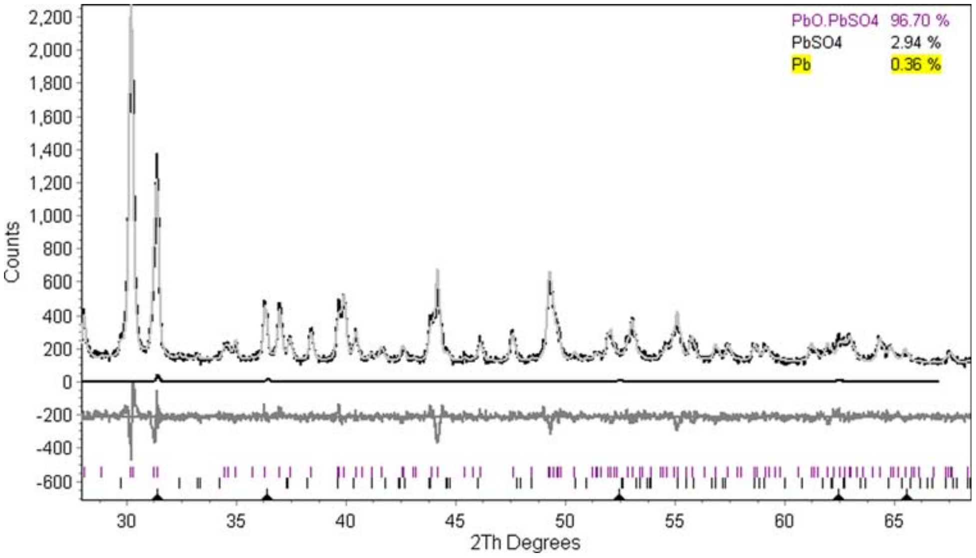

Table 3 Loss in free Pb of Barton Pot oxide samples that were analysed by the LT acid reactivity method

Sample	Free Pb in oxide (%)	Loss in free Pb (%)	Free Pb remaining in sample based on the initial oxide sample (%)
BP8	24.06	88.98	2.65
BP9	27.61	88.94	3.05
BP10	21.70	87.69	2.67
BP11	21.38	87.91	2.58

The total sulphate content (%) of the acid reaction products can be determined by considering the PXRD phase composition and then compare it to the sulphate measured by the acid reactivity test (Fig. 5). The results in the figure include additional samples that were analysed and are not shown in Table 1. The results show that there was a good correlation between the sulphate determined by PXRD and that by the acid reactivity method. Notably, the results of the three types of PbO are grouped together with the Ball mill acid reaction products having a higher sulphate content than the Barton Pot and commercial PbO. The best fit straight line through all the results show a *y*-axis intercept of about 7%, which implies that on average the results from the PXRD are 7% higher in sulphate than the value determined by the wet chemical method. This difference could be due to the assumption made by the PXRD quantification method of perfect crystal structures of the identified phases and that all possible crystal defects and some minor sulphate phases that lack structural consistency are not considered. The sulphate content that is determined from the acid reactivity number does not take into consideration the effect of the free Pb, and that not all the material had possibly reacted with the acid, as was shown with the commercial PbO sample, where some *β*-PbO remained. This implies that the acid absorption (reactivity) of the oxide is a measure of the resulting acid reaction product and not necessarily a measure if its wettability or ability to react.

The results of the surface area analysis showed that there were considerable differences between the oxide and the final acid reaction products for the different oxide types (Fig. 6). The surface areas of the acid reaction products that came from the manufactured Barton Pot and Ball mill processes had relatively similar surface areas, even though, the Ball mill oxide had a significantly larger surface area than the Barton Pot oxide. In comparison, the surface area of the reaction product from the *β*-PbO oxide which contained a large amount of T3 had a considerably higher surface area. However, the commercial *β*-PbO had a very

Table 4 Surface area, LT acid reactivity analysis and PXRD phase composition of commercial *β*-PbO

Sample	BET surface area oxide ($m^2\,g^{-1}$)	BET surface area HT acid reactivity product ($m^2\,g^{-1}$)	LT acid reactivity (mg H_2SO_4 g^{-1})	XRD phase after acid reactivity		
				T1 (%)	T3 (%)	*β*-PbO (%)
1. *β*-PbO	0.0406	4.4285	100.9	62.23	36.57	1.21
2. *β*-PbO	0.0392	4.2433	102.9	71.45	27.00	1.55

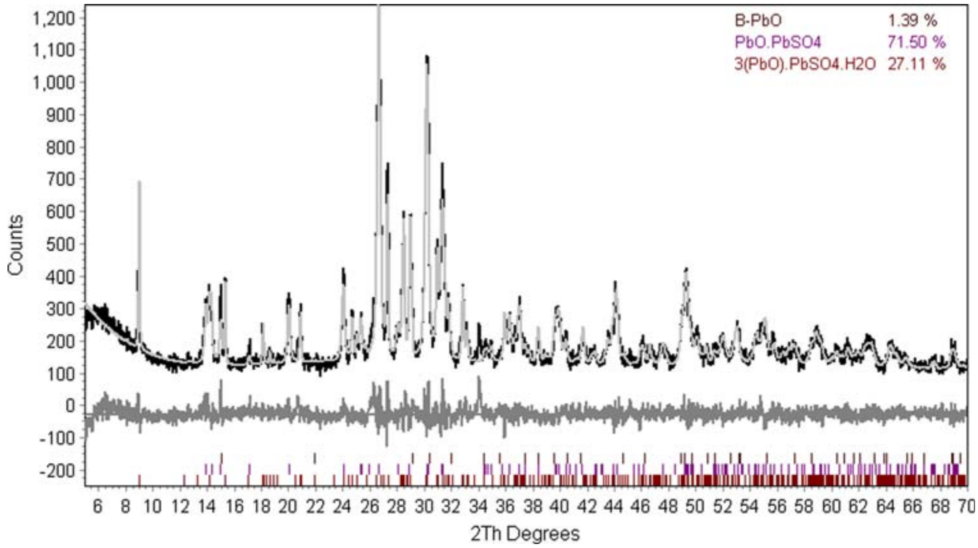

Fig. 4 Quantitative PXRD of the acid reaction product from commercial *β*-PbO that gave an acid reactivity of 100.9 mg g^{-1} oxide (LT method)

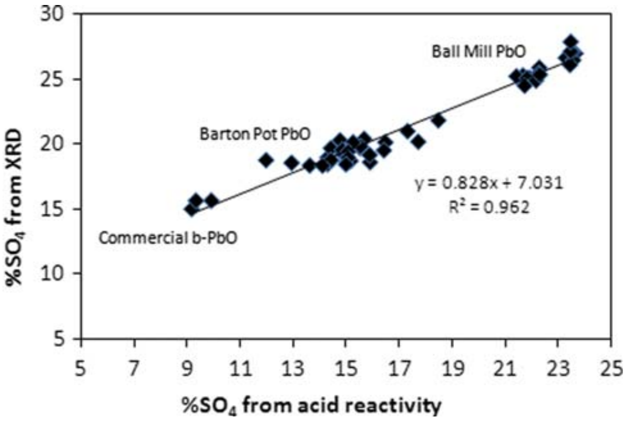

Fig. 5 A comparison of the sulphate content of samples analysed by the quantitative PXRD and the acid reactivity method

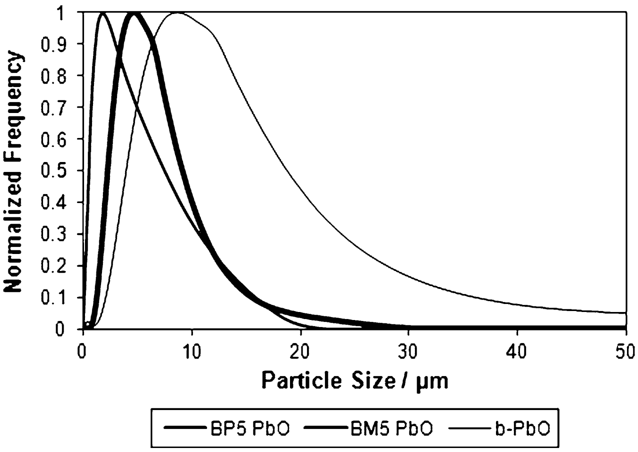

Fig. 7 Normalized frequency particle size distribution of the three different lead oxides

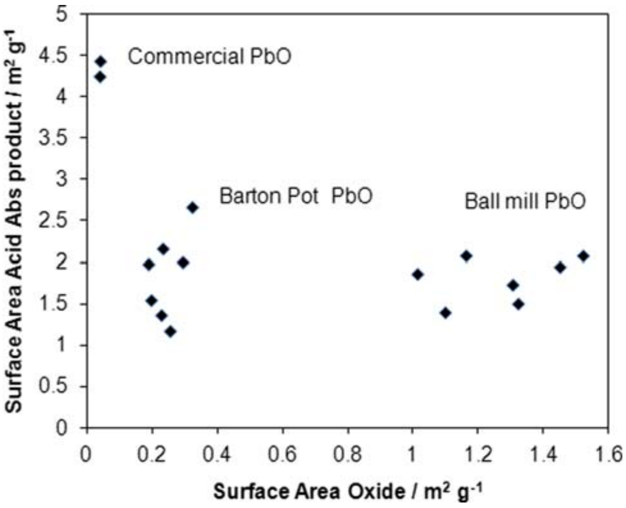

Fig. 6 The difference in surface area of the acid reaction products and their PbO types

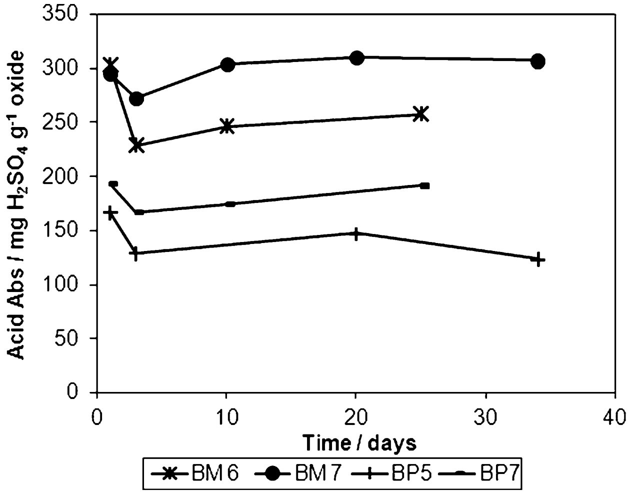

Fig. 8 Acid reactivity (absorption) of Barton Pot and Ball mill oxides with time

small surface area when compared to the other two oxide types. These variations in surface area of the different oxides could be explained by the difference in particle size and by the manufacturing processes, where the Ball mill process produces a finer flatter plate like particle when compared to the Barton Pot oxide [1].

The normalized particle size distributions of the three lead oxide types are shown in Fig. 7. The average volume mean particle size *D*(4,3) for the seven Ball mill lead oxide in Table 1 was determined to be 3.4 µm and for the seven Barton Pot lead oxides as 5.1 µm, respectively. Whereas the *D*(4,3) for the commercial β-PbO was 10.6 µm. This is larger than the other two oxides and can partly explain why some un-reacted β-PbO remained in the acid reaction product (Fig. 4). In the acid, the larger oxide particles would only form the reaction product on their outside surface, leaving some of the inner part un-reacted.

The study of also confirmed the fact that the free Pb of the manufactured lead oxide change with time [9]. By doing the LT acid reactivity analysis of the oxides with time, the results on average showed little or no change in the acid reactivity number whereas the amount of free Pb in the oxide decreased with time (Figs. 8, 9). This implies that there is no direct relationship between the acid absorption (reactivity) number of a manufactured lead oxide and the free Pb and that the two analytical results imply different oxide properties for the paste and curing processes.

4 Conclusion

The perception of the acid absorption analytical testing in the lead-acid battery industry was that the number relates to the particle size of the oxide in that a material with a

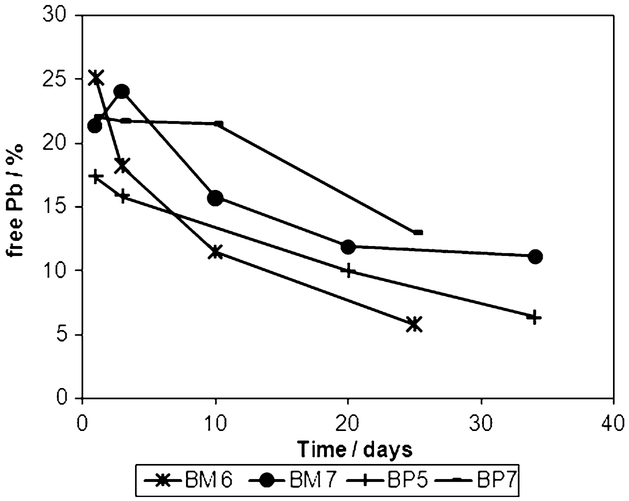

Fig. 9 Free Pb change of Barton Pot and Ball mill oxides with time

smaller mean particle diameter would have a larger surface area and hence a higher acid absorption value. It was argued that this was a measure of the lead oxide's "wettability" and would be an indication of the quality of the oxide thereby influencing the way the electrode paste is made and subsequently influence the product characteristics in the cured and formed electrode. This study showed that there are considerable differences in the methods used in determining the acid absorption of manufactured oxide and that no direct comparisons between reported values from different laboratories could be made unless the technique is standardized. Rather, of importance in its use is the consistency with which an analysis is used as a quality control method and that an understating is achieved of what exactly the reported value means for the intended application.

In part, the acid absorption number does relate to the reactivity of the oxide, but rather to the formation of the type of reaction product. This study showed that the acid absorption is a measure of a particular oxide reacting with the acid resulting in a mixture of T1 and $PbSO_4$. Depending on the reactivity of the oxide, where the Ball mill oxide is considered to be more reactive, the final acid reaction product would contain more $PbSO_4$ than the T1 phase. This reactivity is determined by the oxide's particle size, available surface area and shape. Hence kinetically, it seemed that the $PbSO_4$ phase would form preferably quicker with the finer high surface area oxide particles. The reaction mechanism between the oxide and the acid is in an excess acid environment and would favour the reaction product of $PbSO_4$ [17]. With time, as all the finer particles are consumed, the larger particles with a lower surface area seem to preferentially form the T1 phase. This can in some way be related to the curing process described by Dimitrov et al. [17], where an acid to oxide ratio of 75% would preferably form the T1 phase. This is evident with the Barton Pot oxides that have larger more spherical shaped particles where the acid reaction product consists mainly of the T1 phase. The final surface areas of the acid reaction product of the two manufactured oxides were almost the same over the range of samples studied.

The effect of the surface area, particle size and oxide type on the acid reactivity was even more evident in that the reaction product of the commercial β-PbO showed no $PbSO_4$ and only a mixture of T1 and T3 phases. It is known that the β-PbO is often not preferred in the manufacturing industry due to its lower reactivity. This lower reactivity can be seen in that the reaction product forms the T3 that is often associated with the slow kinetic reactions that occur in the curing process [17]. However, a surprising result of the reaction product was the higher surface area when compared to the reaction products that came from the two manufactured oxides.

Hence, one should not only look at the acid absorption as a definitive measure of a better or worse manufactured oxide, but rather as a measure of the oxides' acid reactivity resulting in a mixture of phases under certain conditions. The implications of the rates of forming these mixed phases and their types should then be understood in terms of the next manufacturing step of preparing a paste, followed by the curing process. The range of allowed acid reactivity (absorption) number decided on by a particular manufacturing facility using their particular method can be optimized to give the most desirable products that relate to the final cured and formed electrode. In addition, the role of the free Pb should not necessarily be linked to the acid absorption number and rather be treated as a separate parameter that has unique properties and implications of the manufacturing procedure and paste preparation.

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