Efficiency of lignosulfonates and humic-related substances as expanders in negative electrodes of the lead/acid system

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Abstract

Organic expanders represent essential additives to the negative active material of lead/acid batteries, since they prevent the negative electrode from compaction during life cycling. Focussing on stability and efficiency of expanders, industrial lignosulfonates and humic substances from peat bogs, in comparison, were fractionated, chemically altered and analysed. With respect to a correlation of functional groups and expander action, these organic samples, fractions, and derivatives were assessed based on a cyclovoltammetric determination of expander performance. The majority of the humic material showed poorer aptitude than the commercially available lignosulfonate expanders. Improved performance was found for precursors of humic acids with a low molecular weight. The obtained results indicate the bonding mechanisms by functional groups like cation exchange, chelating, or formation of π–ϵ complexes do not seem to be significant. A good expander aptitude of some humic derivatives is attributed to their colloidal nature. It is assumed that the coagulation of colloids with low molecular weight is hindered, as these colloids form adsorbed surface films in the negative active material. The films cause an overpotential for the reduction of $PbSO_4$ resulting in fine-grained structures of the lead particles.

Introduction

A beneficial effect of 'wood' derivatives on the cycling performance of lead/acid batteries is known since the early days of battery development and production [1]. Although up to now, the influence of organic compounds, so-called expanders, on the negative active material's morphology still has been a subject of research.

Most contributions on the role of organic expanders in lead/acid batteries confirm the model of a mechanism, by which the expander is adsorbed in the negative electrode and affects the size and morphology of lead and lead sulfate crystals during cycling [2–6]. The reduction of $PbSO_4$ to Pb is hindered in the presence of an expander and requires a greater overpotential [7, 8]. According to Vetter [9] and based on the Stranski–Kossel theory of crystal growth, small crystallization overvoltages favour the formation of greater crystals, whereas at high overvoltages the occurrence of smaller crystals predominates. For a lead/acid negative electrode with expander, this effect on nucleation and growth rates results in a structure of fine-grained lead particles [8], an increased surface area [10], and thus, in a raised discharge capacity.

Although a lot of aspects of expander action are established state of knowledge, some problems are still unsolved. There are, e.g., deficiencies in understanding, why organic material can behave as a 'good' or 'poor' expander. Focus of this contribution is an evaluation of the expander's performance depending on its structural chemical composition. Lignosulfonate expanders and humic substances were fractionated, analysed, modified — e.g., by blocking of functional groups —, and cyclovoltammetric determinations were carried out with respect to activity, stability, and efficiency of the organic material.

Description of samples

Three commercially available expanders (LSE 1, LSE 2, LSE 3), two humic substances of natural origin (HM 1, HM 2), and an industrially produced synthetic humic acid (HA_{synth}) were chosen as original materials.

LSE 1, LSE 2, and LSE 3 represent typical lignosulfonate derivatives. HM 1 and HM 2 are both substances from a peat bog environment, where HM 2 characterizes a recent peat formation, while MH 1 is derived from a deposition of beginning early diagenesis. HA_{synth} is a humic acid of low molecular weight, obtained by oxidation of hydroquinone.

Fractionation

To yield organic substances of different chemical constitution, the original samples were subjected to a fractionation procedure. The materials were subsequently extracted by different solvents of increasing polarity: step 1, n-hexane; step 2, acetic acid ethyl ester (AEE); step 3, acetone; step 4, methanol; step 5, water, and step 6, 0.1 N NaOH.

For steps 1 to 5 Soxhlet extraction was applied, step 6 was carried out in suspension. The results of this extraction analysis are shown in Fig. 1.
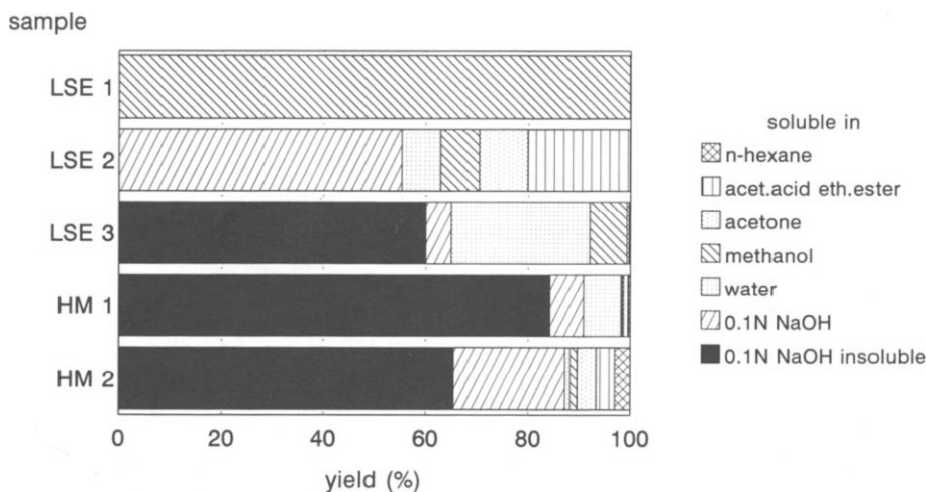

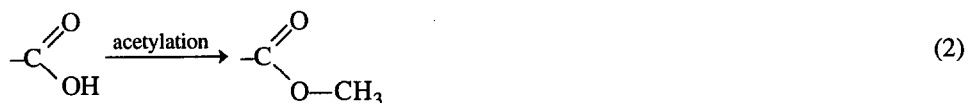Fig. 1. Fractionated extraction analysis.

LSE 1 is completely soluble in methanol, LSE 2 is completely dissolved after treatment with 0.1 N NaOH. LSE 3, HM 1 and HM 2 exhibit considerable amounts of alkali insoluble residues which, for the humic substances, can be attributed to humines and clay mineral complexes mainly.

Chemical analysis

The yielded extracts and residues of the fractionation steps were analysed for organic elements (C_{org}, H, S) and for acidic functional groups. Total acidity was determined by titration with $Ba(OH)_2$. The amount of –COOH was analysed using the calcium acetate method. Phenolic OH was calculated by the difference of both as described by Schnitzer and Khan [11].

Chemical alterations

To retain the main structures and to modify specifically the functional groups, selected fractions with 'good' expander performance were chemically altered by methylation, acetylation, and hydrogenation [12], according to following reactions:

$$-OH \xrightarrow{\text{methylation}} -OCH_3 \tag{1}$$

$$-C\overset{O}{\underset{OH}{\diagup\!\!\!\diagdown}} \xrightarrow{\text{acetylation}} -C\overset{O}{\underset{O-CH_3}{\diagup\!\!\!\diagdown}} \tag{2}$$

$$\overset{\diagdown}{\diagup}C=C\overset{\diagup}{\diagdown} \xrightarrow{\text{hydrogenation}} -\underset{H}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}- \tag{3a}$$

$$\overset{\diagdown}{\diagup}C=O \xrightarrow{\text{hydrogenation}} -\underset{H}{\overset{|}{C}}-OH \tag{3b}$$

Thus methylation blocks –OH groups converting them to ethers. Acetylation transfers carboxyl groups to esters. Hydrogenation affects double bonds resulting in a reduction of $\pi-\epsilon$ systems.

Electrochemical evaluation

Original samples, fractions, and modified substances were electrochemically assessed to investigate interrelations of structural composition and expander aptitude.

A good practicable voltamperometric method was chosen to evaluate the expander performance. The electrode used consisted of a lead filament sheathed by epoxy resin with an uncovered renewable surface of 1 mm^2. It was cycled in sulfuric acid (sp. gr. = 1.28). From the current–voltage curves obtained, the area of the lead oxidation peak was taken as the actual electrode's discharge capacity, whose course during cycling was recorded.
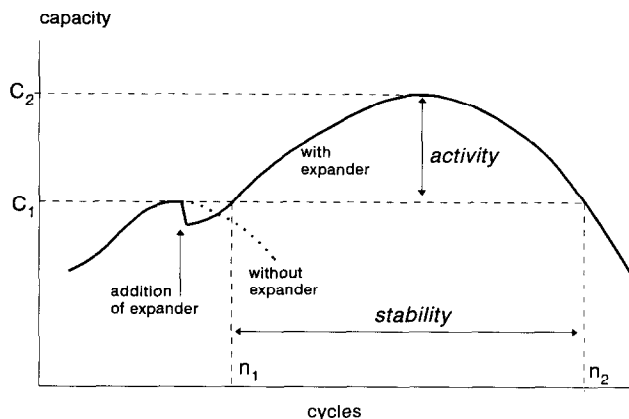
capacity

Fig. 2. Cycling procedure for expander evaluation (schematic).

Figure 2 shows the evaluating method for the expander performance. The lead electrode was cycled without expander until a porous surface structure was formed, corresponding to an increasing capacity until a maximum C_1 has been reached. Without the expander, the electrode's capacity decreased during further cycling. Addition of the expander in the range of the maximum C_1 showed a small drop, followed by a significant increase to a new maximum capacity C_2.

This relative capacity enhancement is proposed as expander 'activity':

$$A = (C_2 - C_1)/C_1 \tag{4}$$

The cycling period between cycles n_1 and n_2, at which the electrode capacity is above C_1, is called expander 'stability':

$$S = (n_2 - n_1)/1000 \tag{5}$$

The product of activity and stability is a suitable value to characterize the expander's overall performance, for which we use the term 'efficiency':

$$E = AS \tag{6}$$

These numerical criteria proved to be a practicable tool to distinguish organic matter concerning the utility as expander material.

Results and discussion

Figures 3 to 7 give a survey of the amount of functional acidic groups, expander activity and efficiency for the samples and fractions investigated.

Analysing the results, for expander LSE 1 (Fig. 3) the concentrations of –COOH (about 1.2 mequiv/g) and phenolic –OH (about 3 mequiv/g) in the methanol extract and in the extraction residues do not significantly differ from the values of the original materials. This is plausible since the amount of the methanol-soluble fraction is nearly 100% of the total sample and the extraction residues are very similar to the original material. Due to very small yields, the extracts of n-hexane to acetone were not analysed for acidity. The expander activity and efficiency are poor for the extracts
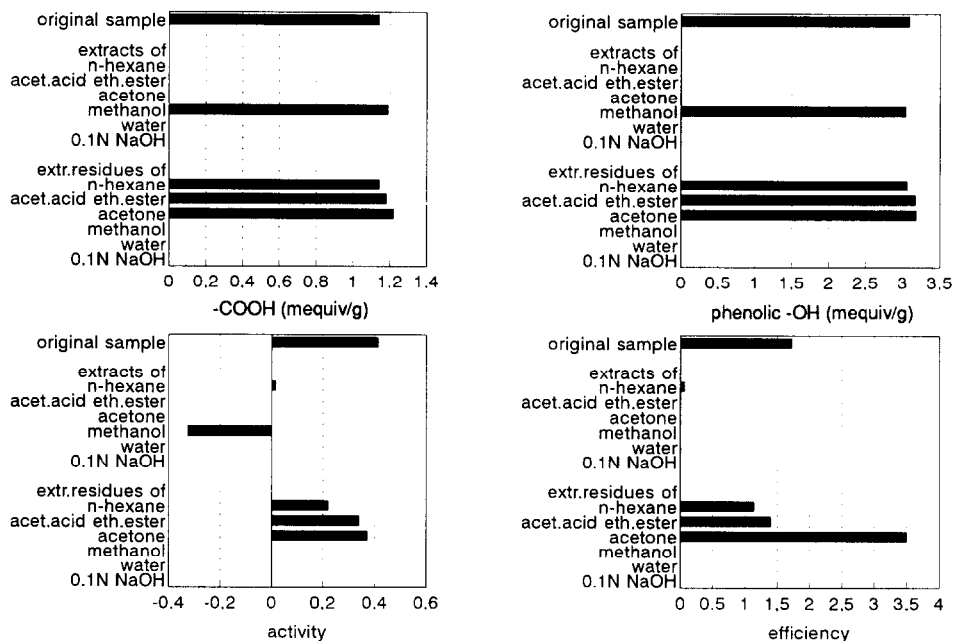
Fig. 3. Functional groups and expander performance of fractions of samples LSE 1.
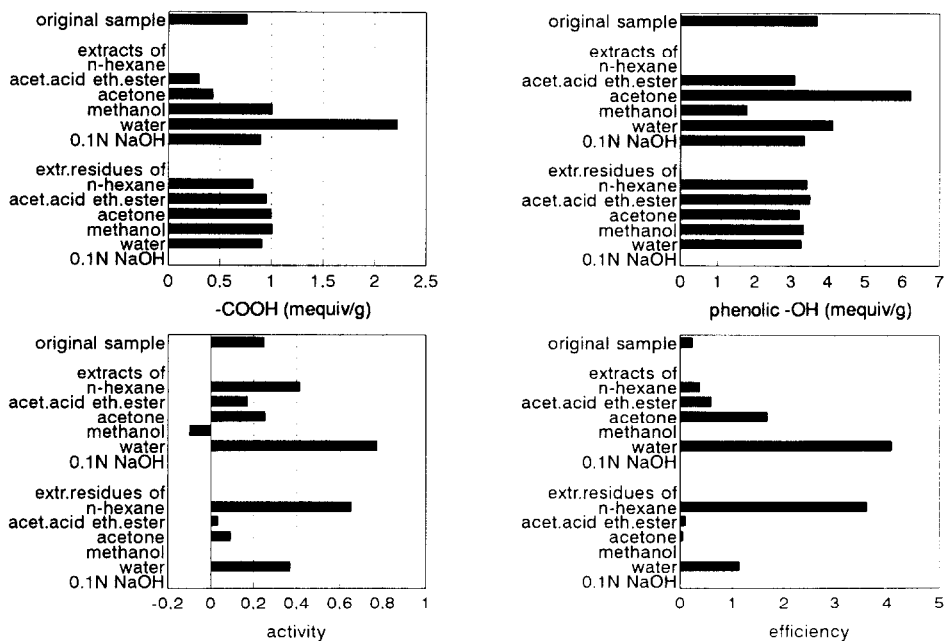

Fig. 4. Functional groups and expander performance of fractions of samples LSE 2.
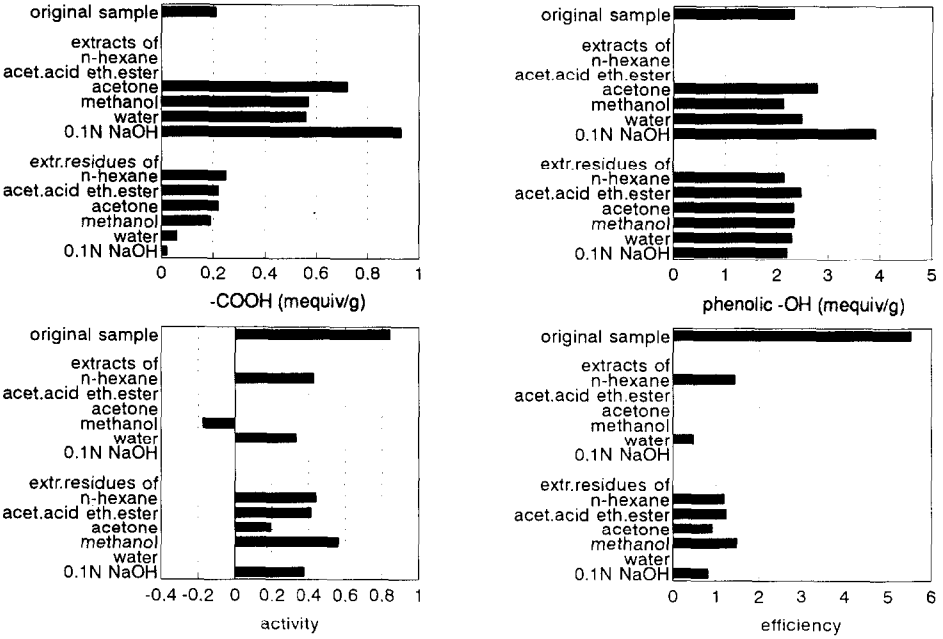
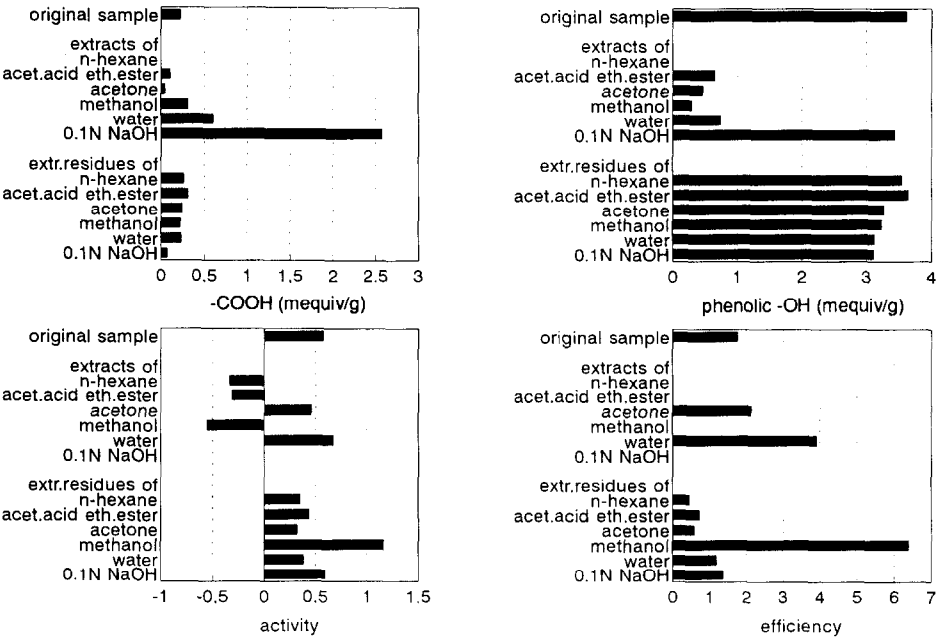Fig. 5. Functional groups and expander performance of fractions of samples LSE 3.

Fig. 6. Functional groups and expander performance of fractions of samples HM 1.
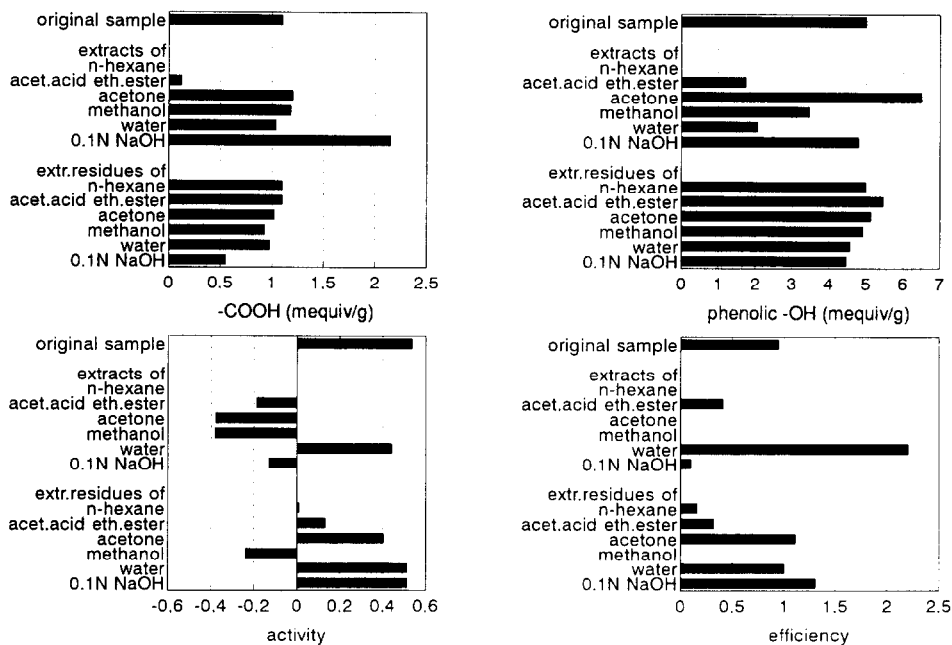
Fig. 7. Functional groups and expander performance of fractions of samples HM 2.

and better for the residues. A good performance is shown by the acetone extraction residue.

Compared with LSE 1 sample LS2 (Fig. 4) exhibits about the same amount of total acidity, but the contribution of low acidic groups is higher. Carboxyl is enriched in the water fraction, phenolic –OH in the acetone fraction. All residues are similar to the original samples. The best expander performance is found for the water fraction, which is high in –COOH.

LSE 3 (Fig. 5) shows little total acidity of about 2.5 mequiv/g. Enrichment of –COOH in the extracts (not determined for n-hexane and acetic acid ethyl ester (AEE) extracts) does not correspond to an enhanced expander performance. The original sample, by far, shows the best expander efficiency, which could not be improved by fractionation.

HM 1 (Fig. 6) is characterized by very little –COOH and small amounts of phenolic –OH. Fractionation leads to a distribution pattern, which is typical for humic material. Levels of –COOH in the extracts increase with increasing polarity of the extractants, and an enrichment occurs in the alkaline-soluble fraction. Expander activity and efficiency do not correlate with the amount of acidic groups. With the exception of the n-hexane, acetic acid ethyl ester, and methanol extracts, all fractions and residues show good expander performances. The best result is obtained for the residue after methanol extraction, which reveals the principal aptitude of humic substances as expander material.

HM 2 (Fig. 7) shows the highest amount in total acidity of all samples investigated with about 1.1 mequiv/g –COOH and 5 mequiv/g phenolic –OH. Carboxyl is typically enriched in the alkaline-soluble fraction. The best expander result is found for the

water fraction. A correlation between acidity and expander quality is not evident. The global expander performance is slightly poorer compared with the sample HM 1.

The results for all materials investigated show no correlation of functional acid groups and expander performance in their distribution patterns (Figs. 3–7), which means that a chemical bond of lead species to –COOH and phenolic –OH groups cannot be regarded as a significant mechanism for the expander action. Further possible mechanisms for chemical bonds of lead ions and organic expanders were investigated: samples and fractions with high expander efficiency were hydrogenated, acetylated, and methylated to block defined bonding sites. Figure 8 shows the effects of these alterations on the expander performance. The bars in the diagram represent the range of values found for five different preparations and cycling tests of the same sample, which indicates a sufficient reproducibility of the assessment procedure.

Hydrogenation of seven samples investigated shows nonuniform results. Deterioration of the expander performance occurs in two cases (HM 1 methanol residue, HA_{synth}), from which could be concluded that π electron systems or carbonyl groups of the humic material might take part in the chemical bond of lead species. On the other hand, expander activity and stability are not diminished for the majority of the samples and in one case (LSE 2) even an expander improvement is found. Consequently expander action cannot significantly be attributed to a bond of organic material and lead ions by either π complexes or carbonyl groups.

Acetylation, as well, shows deteriorations and improvements of the expander activity and efficiency. This once again demonstrates a missing correlation between –COOH groups and expander performance as already observed in the fractionation experiments. Carboxyl groups play an important role in the geochemical enrichment of metals by humic substances in natural occurrence, where they bind metal ions by cation exchange [11]. In the strong acidic environment of a lead/acid battery, carboxyl groups occur in 'H-form' and a bonding mechanism by ion exchange can obviously be excluded.

Methylation was carried out with a sample of synthetic humic acid (HA_{synth}). Since this transformation of –OH groups to –OCH$_3$ did not affect the expander action
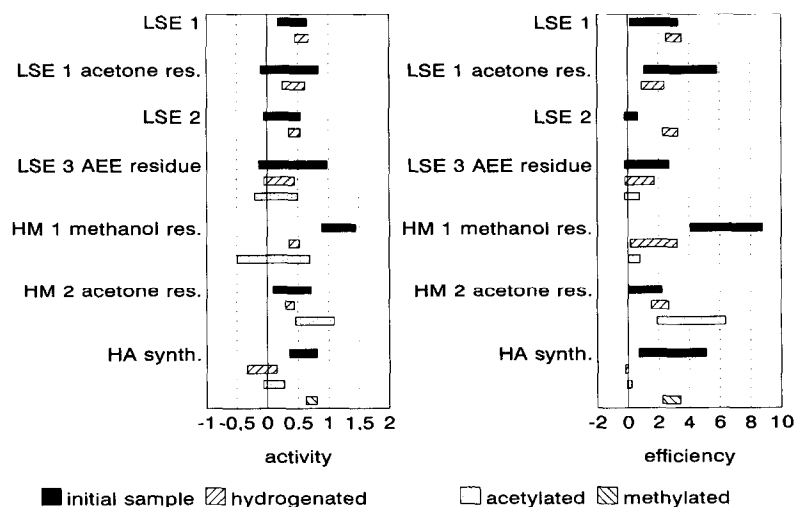

Fig. 8. Expander performance of chemically altered samples.

significantly, there is no evidence for –OH taking part in a chemical bond of lead species, e.g., by formation of chelates. The same result was obtained for phenolic –OH from the fractionation experiments.

Conclusions

Lignosulfonate expanders and humic substances have a complex and not a distinct reproducible chemical composition. From this point of view, it may be plausible that nonuniform substances may show nonuniform effects, regarding the expander aptitude of the different samples and fractions. Since macromolecular organic substances of natural origin typically exhibit a behaviour controlled by a lot of different parameters, it is possible that existing correlations can be superposed or even be suppressed by other interdependencies. With respect to this limitation, we conclude that the results of our experiments do not favour the assumption that strong chemical bonds between lead species and functional groups of the organic material are mainly responsible for the expander effect.

Obviously intermolecular interactions, which are weaker than chemical bonds, seem to be more important. Here the colloidal nature of humic-related material is considered to be relevant, although this aspect was not investigated in detail within our experiments.

Száva [13] pointed out the significance of a deflocculated, agglomerate-free structure of the negative paste that has to be provided by an expander film, covering the solid particles. Considering a classification of humic substances, humines, humic acids, and fulvic acids are distinguished based on their different solubilities in alkaline solutions and acids. Humines are insoluble in both acids and bases. Humic acids flocculate at pH values below about 4. Fulvic acids do not precipitate even in strong acidic solutions [11]. Furthermore, another hindrance for coagulation can occur, if the humic colloids, e.g., form surface films [12].

In our experiments, we found a good expander aptitude, especially for humic preparations, that showed enhanced solubility and low molecular weight, i.e., for substances similar to fulvic acids that are to be classified as 'humic acid precursors'. Therefore, we assume that low molecular units of expander colloids form coatings with a reduced tendency to associate, covering the surface of lead sulfate particles.

These postulated coating films are expected to cause a higher overpotential in the reduction of $PbSO_4$ to Pb [7, 8], resulting in the occurrence of small crystal sizes and porous electrode structures during cycling of lead/acid batteries.

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