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Multivariate analysis for characterization of expanders

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Abstract

Eight lignin products have been characterized with regard to chemical composition, physical properties and function as battery expanders. Altogether, 128 different parameters have been measured for each of the expanders. The Principal Component Analysis method has been used to analyze the correlations between these parameters. Several possible correlations between lignin properties and effectiveness in batteries were found. The type of lignin seems to be a very important factor and few correlations hold across different types of lignin. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Expanders; Lignosulphonates; Stability of lignosulphonates; Battery performance; Lignin structure–battery parameters relationship

1. Background

Organic expanders are a necessary component of the negative active mass in lead acid batteries [1]. Lignosulphonates have proven to be very well-suited as organic expanders. Although lignosulphonates have been used for more than 50 years, the relationship between the structure of the organic expander and the performance in lead acid batteries is still largely unknown.

Lignin is a natural polymer encrusting cellulose fibers in wood. In wood, the lignin forms a three-dimensional net work. The monomers in lignin are 2-methoxy-4-propyl-phenol (guajacol) in soft wood and a mixture of 2-methoxy-4-propyl-phenol (guajacol) and 1,5-dimethoxy-4-propyl-phenol (syringol) in hardwood. The lignin monomers are polymerized via a free radical mechanism, and there are at least 10 different linkages between monomer units. During the pulping process some of the ether bonds are broken, the lignin fragments are solubilized by two processes.

During Kraft pulping, strong alkali and a sodium sulphide catalyst are used to break down the lignin in wood. The ionization of phenolic groups at high pH is enough to solubilize the so-called Kraft lignin. During this process, some of the methoxy groups may also be cleaved to form catechol hydroxyl groups. The propyl chain is also extensively modified. The lignin resulting from the Kraft process is often depicted as relatively thin sheets. Kraft lignins can be recovered from the pulping liquor by lowering the pH. Kraft lignins are often sulphomethylated to increase their solubility.

During sulphite pulping, calcium bisulphite is used under strongly acidic conditions to fragment the lignin, and to sulphonate the lignin fragments to lignosulphonates. Due to the sulphonic acid groups lignosulphonates are soluble over a wide pH range. During the sulphite cook less ether bonds are split than during the Kraft process and there will also be some condensation of the lignin fragments especially towards the end of the sulphite cook. The molecular weight for lignosulphonates is much higher than for Kraft lignin, and the molecules can be described as microgels or highly branched polymers. Lignosulphonates are further processed into a number of products.

When the extensive lignin polymer is broken down during the pulping processes, polymer fragments with a wide range of molecular weights are created. The molecular weights can be characterized by different molecular weight averages.

The relationship between the composition and structure of the expander, and the electrical performance in batteries

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is complicated. There is a complex interplay between different properties of the expander and the performance. Literature data illustrating this relationship are presented in Table 1.

Ritchie [2], and Hayashi and Namura [3] both used simple, low molecular weight (LMW), single compounds. Both used the capacity as their measure of performance. In Ritchie's work most of the compounds only contained one functional group. With sulphonic acids, he noted a large difference between those compounds only containing the acid group and those containing both sulphonic acid and phenolic groups. The first has no effect initially and has a detrimental effect on cycle life. The second group has a positive effect initially, and retains this positive effect upon cycling. Hayashi and Namura mostly use compounds with several different functional groups. Their results are thus a little harder to interpret in terms of functional group contributions, but might also be more representative of the lignins which contain several different functional groups together in the same molecule.

Von Borstel et al. [4] looked at three lignosulphonates and two humic acids, each of which where split into six extracts and five extraction residues. Some of them were also further chemically modified. Their conclusion is that neither the carboxylic acid nor the phenolic hydroxyl bear any simple relationship to the performance as expanders. They also noted that in some instances, the fractions with more carboxylic acids improved the performance, while in others they did not.

Pavlov et al. [5] used several organic expanders. Most of those were already used commercially in battery manufacturing. They all contained several functional groups and the results are thus harder to interpret and draw conclusions from. On the other hand, the structures are more realistic in terms of the combinations of several groups. The only important functional group seems to be the catechol group.

Zachlin [6] also studied different lignins. He found very little variations between the different lignins with respect to initial performance and the warm capacity during cycle life studies. Charge acceptance and cold cranking capacity during cycling varied between the different lignins, with hardwood giving poorer results than softwood.

There are also some discrepancies in the results from the literature; benzoic acid gives good results for Ritchie [2], while Hayashi and Namura [3] obtain poor results. This could be due to antagonistic effects from other groups in the latter study. Ritchie's work also shows different effects of the sulphonic acid group whether or not the hydroxyl group is present.

Both Zachlin's and Ritchie's works clearly show that the effect of a given functional group or expander might be different for cycle life and initial performance. In other words, the correlation between the functional groups and properties should be investigated for each property of the battery, as well as, for each functional group.

Due to the way lignins are prepared, there are also often correlations between the amounts of different functional groups. Demethoxylation to lower the amount of methoxyl groups, will also increase the amount of hydroxyl groups. Oxidation to increase the amount of carboxylic acid groups, will usually also give a degradation of the lignin, and thus lower molecular weight.

The large number of possible correlations between battery performance and functional groups, together with the correlations between some of the properties of the lignins, is the kind of problem which is well-suited for a multivariate analysis [7,8]. In this study, we will describe a first attempt on a multivariate analysis of the expander characteristics and performance. In this work, we will mostly concentrate on the parameters that influence the lifetime of the batteries. Over the last decade, the cycle life of lead acid batteries has increased by an order of magnitude. This puts new, stringent demands also on the expander. It is thus of interest to better understand its function.

The parameters used in this study can broadly be divided into five types; the constitution of the lignins, the contaminants in the lignins, the initial electrical performance of the cells, the cycle life of the cells, and properties of the lignins. The last includes properties like surface tension which will depend on the lignin used, but also to a large extent on the exact experimental parameters, e.g.,

Table 1
A summary of earlier work on the relationship between functional groups and expander performances. ''+'', ''−'', and ''0'' indicate positive, negative and no correlations, respectively

Reference	Functionality								
	Ar–COOH	R–COOH	–CHO	> C=O	Ar–OH	Ar–$(OH)_2$	Ar–OH, –OMe	–OMe	$-SO_3H$
Ritchie initial [2]	+	0	0	0	0	+			0[a] +[b]
Ritchie cycle [2]	0/−	+	−	0	+	+			−[a] +[b]
Hayashi and Namura [3]	−	0/−	0/−		−	+	+		
Von Borstel et al. [4]	0[c]	0[c]			0			0	
Pavlov et al. [5]						+			

[a] Only $-SO_3H$ groups.
[b] $-SO_3H$ and –OH groups together.
[c] Not distinguished between aromatic and aliphatic acids.

temperature, concentration, and pH. It is hoped that the last group will contain useful screening parameters, and, in fact, several of them have been suggested previously.

2. Experimental

2.1. Samples

The lignin expanders were made by LignoTech Research Laboratory. The samples were chosen to span a wide range in molecular weights, degree of sulphonation, and other functional groups.

UP-416 is a purified softwood Kraft lignin. UP-393 is a softwood Kraft lignin sulphonated via a proprietary process. The sulphonic acid groups are introduced in the side chains, while most sulphomethylated lignins will have the sulphonic acid groups in the ring. UP-417 is a purified, softwood sodium lignosulphonate UP-413, and UP-414 are desulphonated, high molecular weight (HMW) sodium lignosulphonates made from softwood. Vanisperse A is a purified, oxidized, softwood sodium lignosulphonate with LMW. M and D are purified, oxidized, hardwood sodium lignosulphonates with LMW.

2.2. Electrical testing

The electrical tests were performed at CLEPS. The negative plates were produced using leady oxide (PbO/Pb = 0.73/0.23), H_2SO_4 s.g. 1.4 (H_2SO_4/LO = 4.5%), the expanders under investigation in the different concentrations plus 0.8% $BaSO_4$, 0.2% carbon black and H_2O. The pastes were pasted over SLI grids cast of Pb–1.8% Sb–0.1% As–0.2% Sn alloy. After curing and formation, the plates were dried in a nitrogen atmosphere.

The expanders were tested in varying concentrations from 0.1% to 0.4%. Batteries (12 V/42 A h) were assembled with cells containing four negative and five positive plates. The battery performance parameters were limited by the negative plates. In all tests, the behaviour of the negative plate potential was followed. Polyethylene gauntlet separators (Daramic, Germany) were used. All batteries were of the flooded type with H_2SO_4 s.g. 1.28.

All batteries were set to tests following the DIN 43539-2 test protocol for SLI batteries. Two batteries of each type were tested, one of them being set to initial performance and cycle life tests, and the other one to self-discharge and charge acceptance tests. The details can be found in an accompanying paper in this issue [9].

The cycle life tests were performed at 40°C. One 1-week cycle comprised 10 charge–discharge cycles followed by 65 h of rest on open circuit at 40°C and then a CCA test. We used the values for each of the cycles as input to the multivariate analysis.

2.3. Chemical characterization

Expanders were characterised by the amount of functional groups and their molecular weight. The amount of functional groups are given as weight percentages and lignin dry weight.

Carboxylic acids groups were determined by conductiometric titration by titration against 0.05 M NaOH [10]. A 150-mg sample was dissolved in 250 ml water. 10% sulphuric acid was added to a reading of 500–600 μS/cm. The conductivity was measured with a Orion mod 150 conductometer using a Orion CDC 012210 electrode. The NaOH was added in small increments and the conductivity measured after each addition. The conductivity vs. added NaOH volume will show a rapid decrease, a slow increase, and finally a rapid increase. The weak acids correspond to the volume corresponding to the slow increase. The standard deviation of the method is 0.2%.

Methoxyl groups were determined by a modified Zeisel procedure. The lignins were treated with hydrogen iodide to release methyl iodide. The methyl iodide was converted to methyl bromide and iodic acid. The iodic acid was reduced to iodine, and the iodine titrated with sodium thiosulphate [11]. The standard deviation of the method is 0.3%.

The phenolic hydroxyl groups were determined by a UV absorption method, looking at the difference in the UV spectra at high (>11) and low (2.0–2.2) pH. The pH was adjusted by 5 M NaOH or 5 M HCl. The standard deviation is 0.04%.

Lignins have an absorbance maximum at 270–280 nm at low pH (2.0–2.2). K_{solid} is the absorbance maximum for a 500 ppm solution of the lignin. UV spectra were recorded on a Perkin-Elmer Lambda 2S UV–Visible spectrophotometer. Distilled water was used as the reference. The standard deviation is 0.04%.

Inorganic sulphur was determined by precipitation with barium chloride to measure the amount of insoluble barium sulphate. Total sulphur was determined by oxidation of the sample with perchloric acid to convert all sulphur into sulphate and then precipitating with barium chloride. Organic sulphur is taken as the difference between the total sulphur and the inorganic sulphur [12]. The standard deviations in the determination of sulphur is 0.1% for inorganic sulphur, and 0.3% for total and organic sulphur.

Molecular weights were determined on a Jordi Glucose DVB 10,000 Å column. The mobile phase consisted of 10% DMSO in water buffered to 10.5 with a sodium hydrogen phosphate buffer and 0.1% SDS added. A Spectra System AS3500 sample, P4000 pump, and UV2000 detector were used.The software allows the calculation of different molecular weight averages (M_n, M_w, M_z, and M_{z+1}) as well as polydispersity. M_n and M_w are easily available via several different experimental techniques as they are directly related to physical properties of the solution in simple ways. M_z and M_{z+1} give important

information about the asymmetry or skewedness of the distribution.

The molecular weights are given relative to two in-house standards with M_w of 68,000 and 8300 Da, respectively. The relative values of the different lignins are accurate to ± 1000, while the absolute values depend on the accuracy of the standards. For the purpose of this study, the absolute molecular weights are of less importance.

The content of different metal ions were determined by inductively coupled plasma (ICP) ion chromatography on a Thermo Jarrel AS IRS Advantage. The samples were digested in nitric acid. Only metals that were present at levels above the limit of quantification (LOQ), for most of the samples were included in the multivariate analysis. The LOQ is defined as the concentration where the experimental uncertainty is equal to 30% of the value.

2.4. Characterisation of lignin properties

The lignins were further characterized by some physical properties. These depend both on the lignin investigated and on the exact experimental conditions.

The surface tension was determined by a Cenco de Noüy tensiometer with a platinum ring. The solutions used were 0.1% lignin in a phosphate buffer at pH 7. The temperature was 23°C during the measurement. The values are the average of three measurements. The experimental uncertainty is less than 0.2%. This will be a measure of the surface activity of the lignins.

Adsorption to lead, lead(II)oxide, and barium sulphate were investigated by looking at the molecular weight of the non-adsorbed fraction. Some preliminary work was done to determine the best lignin concentration to use. For lead and lead(II)oxide, 5000 ppm lignin solutions were used for barium sulphate 200 ppm lignin solution. The equilibrium time was 17 h in all studies. To quantify the adsorption we calculated a removal coefficient (RC):

$$\mathrm{RC} = \left(M_{\mathrm{w}}^{\mathrm{ref}} - M_{\mathrm{w}}^{\mathrm{ads}}\right)/M_{\mathrm{w}}^{\mathrm{ref}},$$

where M_w are the weight average molecular weight and the superscripts ref and ads refer to the sample before and after the adsorption. The difference in adsorbed amount that was found between barium sulphate and lead is similar to the difference found earlier between lead sulphate and lead [13]. Adsorption to the active surfaces is an important step in the lignins function as expanders. The RC is probably a better measure of the absorption for lead and lead(II)oxide where the lignin is cleanly removed from the HMW end, than it is for barium sulphate where the adsorption process is much more difficult.

The precipitation pH was determined by dissolving the lignins in water and adding sulphuric acid until a precipitate or cloudy solution formed. Solutions with lignin in 6% sulphuric acid were filtered and the molecular weight determined for the soluble fraction in this acid.

The high temperature stability was determined in a solution of 4.16 g lead oxide, 17.17 g sodium sulphate and 14.95 g 36% sulphuric acid diluted to 1.000 l. The pH of this solution was 1.88. About 1.0 g of each of the lignins were dissolved in 20 ml of this solution and heated to 65–70°C for 5 days. The samples were filtered off, dried and weighted. The percentage insoluble material was calculated. This will give a measure of the survival of the lignins in a battery environment.

Screening tests with H_2 and O_2 were performed at CLEPS as described earlier [5]. A larger number of lignins were tested before the selection for this study.

2.5. PCA analysis

The PCA analysis was performed by the BACCOS software v. 3.0. One advantageous feature of this software is that we can use the full data set for the PCA, while some of the data can be left out of the plots to make them clearer. Neither of the plots in this paper will thus show all the measurements performed, although they are included in the calculations. The parameters measured and their codes in the plots are given in Appendix A.

3. Results and discussion

3.1. Chemical composition and molecular weight of the expanders

Table 2 presents the most important analytical data for the expanders investigated.

The expanders belonging to this group differ substantially in chemical composition. This will inevitably affect the properties of the lignins and hence, the parameters of the negative plates prepared with these expanders.

3.2. Principal component analysis

This method provides a complete picture of the correlations between the chemical composition and physical properties of the expanders, and the battery performance parameters.

We have 128 measurements for each of the eight expanders. Several of these measurements are highly correlated. There are 16,256 possible correlations between our different observations if just pairwise correlations are considered, in addition, there will of course be more complex relationships where one property might depend on several others. Moreover, all the measurements will contain larger or smaller measurement errors, which will complicate the interpretation of the measurements. Several chemometric software packages are developed to handle this type of problem. In this work, we will use the chemometric tool for data description, or explorative data structure modelling [7]. A brief description of the method will be provided.

Table 2
Some selected properties of the expanders investigated

Property	393	414	VS A	416	413	M	D	417
Methoxyl, % w/w	9.4	10.5	12.3	11.2	10.0			8.3
Phenolic OH, % w/w	2.01	2.02	1.61	0.78	1.76	2.70	2.40	1.56
Inorganic S, % w/w	0.50	0.52	0.47	0.43	0.23	0.34	0.54	0.76
Organic S, % w/w	1.4	5.5	2.5	1.1	4.9	2.5	3.4	6.2
Total S, % w/w	1.9	6.0	3.0	1.5	6.1	2.8	3.9	7.0
Carboxylic acid, % w/w	12.62	6.66	11.20	11.79	8.96	8.61	8.37	8.15
K_{solid}	19.94	15.31	n.a.	16.03	13.60	22.60	18.10	9.61
M_n (kDa)	3.62	6.37	5.01	2.08	6.84	4.61	4.14	7.17
M_w (kDa)	25.6	78.0	15.6	24.8	81.0	29.7	23.2	50.9
M_z (kDa)	114.9	343.5	30.5	122.4	332.8	69.4	62.6	232.7
M_{z+1} (kDa)	394.8	608.0	50.3	334.2	593.6	118.6	133.0	502.1
Polydispersity	7.08	12.38	3.11	11.96	11.84	6.43	5.61	7.10

The data is plotted in a multi-dimensional space. For our 128 measurements, a 128 dimensional space is used. The samples will be scattered in this space. By ordinary linear algebra, a new vector is found that describes as much of the difference between the samples as possible. This is called principal component no. 1, or PC_1 for short. The samples will be scattered around this vector. They can all be projected unto PC_1 to give then a coordinate along this axis. PC_1 is usually not enough to explain all the variations among the samples. PC_2 is constructed with two constraints. It should be perpendicular to PC_1, and it should explain as much as possible of the remaining differences. Further principal components can be constructed with the constraints that they should be perpendicular to the previous PCs, and that they should explain as much as possible of the variations in the data. Additional PCs are constructed until the structure of the data is explained, while the noise (or experimental uncertainties) should not be modelled. There are different tests, which tell when a sufficient number of PCs are included. The construction of PCs removes all covariance between different variables, and reduces the number of variables needed to model any response.

The cost is that the PCs have no direct physical meaning. They will be abstract entities with contribution from many, or all, of the variables. This can make a direct visualization or interpretation more difficult. Loading plots are useful tools that bridge the gap between the physical measured values and the abstract principal component space. They can be thought of as projections of the unit vectors of the original space on to the new principal component space. Variables that appear close together in a loading plot will be highly correlated, if they appear on top of each other, the correlation is perfect. Variables that appear at opposite sides of the origin in a loading plot will be negatively correlated. Variables that appear far apart are uncorrelated. The loading plots will thus give a quick, easy and graphical way to investigate all the 16,256 possible

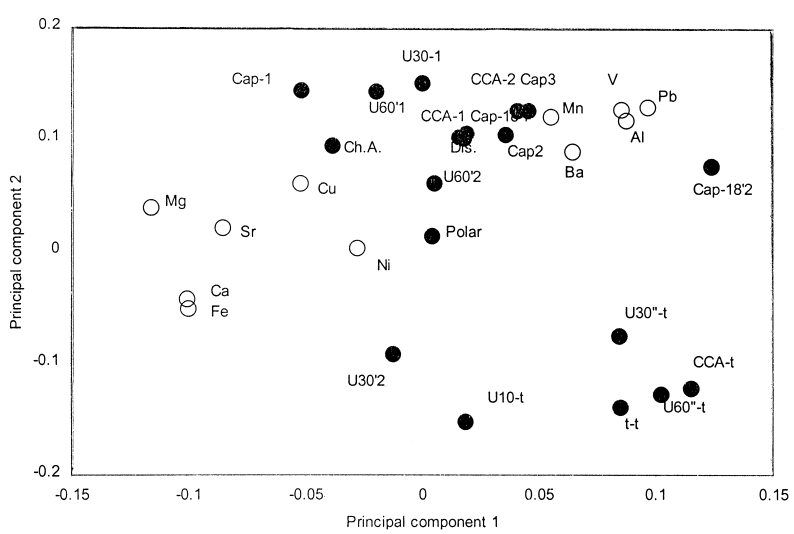

Fig. 1. A loadings plot of the electrical data and metallic impurities projected onto principal components 1 and 2. The meaning of the symbols are as given in Appendix A.

correlations at a glance. Loading plots are usually presented as two-dimensional plots. This will be a window into the PC space. Obviously, points that appear close together in a two-dimensional plot might appear far apart along the third dimension. All the plots in this work are thus shown in two different projections.

The data for eight expanders were used for this study. From the 128 measurements and characteristics on each expander, it was found that three PCs were sufficient to explain most of the variation in the data. For the plot used in this work, the values for the optimum concentrations are shown. We also did the same investigation with 0.2% of all the expanders and there were no significant differences in the results between the two investigation.

First, the correlation between the metal impurities in the expanders and battery performance was considered. Figs. 1 and 2 present loading plots, showing all the metals contained in the expanders, together with the electrical performances of the cells with the different expanders. Parameters that appear close in the plots are highly correlated, while those that are at opposite sides of the origin are negatively correlated. From Fig. 1, it might appear that copper contained in the expanders has a positive influence on the charge acceptance of the batteries, while aluminium, barium and vanadium appear to have a positive influence on the initial capacity. Fig. 1 is one look into the principle component space and when we look at Fig. 2, which is another projection of the principle component space, most of these correlations disappear. There still seems to be a positive correlation between copper content and the charge acceptance, but this may be an artifact as the level of metals is low in all the expanders tested. The content of metal impurities in the paste used for preparation of the negative plates is within the range 0.1–0.4%. This indicates that the metal content in the plates is reduced further by two to three orders of magnitude, i.e., it becomes negligibly small and would have but a very weak effect on the performance of the plates. The small variations in metal levels do not influence the properties much compared to the much larger variations in other properties.

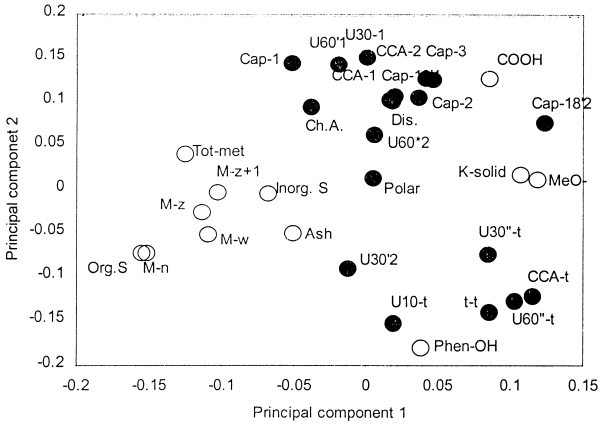

Fig. 3. A loadings plot of the electrical data and analytical data for the lignins projected onto principal components 1 and 2. The meaning of the symbols are as given in Appendix A.

The data in Figs. 1 and 2 show that any results found in the rest of the study are not due to contamination of the expanders. As the metals appear to be unimportant, a new multivariate analysis was performed without the metal data. This did not improve the model or change the conclusions in any way.

Next, we investigated the correlation between expander chemical composition and battery performance. Figs. 3 and 4 show the analytical data for the expanders together with their electrical performance. Phenolic OH seems to be related to a long cycle life. Carboxylic acid is positively correlated with the initial performance. The content of carboxylic acids also varies with the type of lignin, this variation could thus as well be related to the different types of lignin used. Organic sulphur and the higher moments of the molecular weights (M_w, M_z and M_{z+1}) are negatively correlated with the initial performances. The organic sulphur content and molecular weight are well-correlated. For molecular weight, we see the two groups with

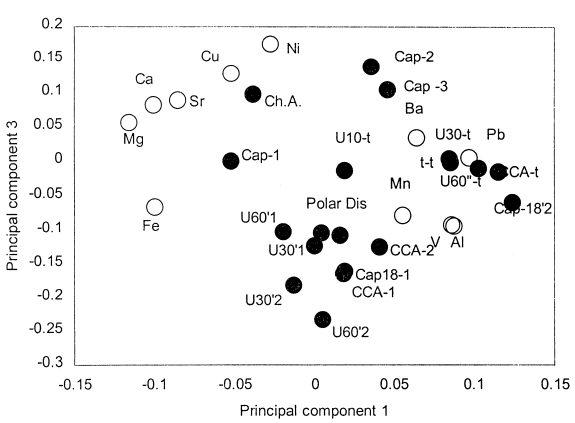

Fig. 2. A loadings plot of the electrical data and metallic contaminations projected onto principal components 1 and 3. The meaning of the symbols are as given in Appendix A.

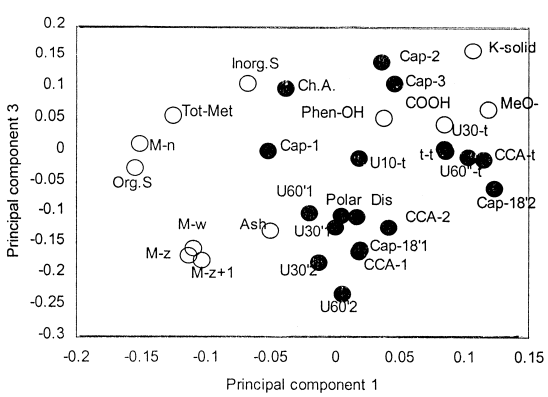

Fig. 4. A loadings plot of the electrical data and analytical data for the lignins projected onto principal components 1 and 3. The meaning of the symbols are as given in Appendix A.

HMW lignosulphonates being poorer than the LMW compounds. But within each group, the initial cold cranking capacity actually increases with increasing M_w. This makes the data hard to interpret. These possible correlations are investigated further in an accompanying paper [9]. That there are few correlations between cycle lifetime and functional groups is not surprising. None of the groups investigated are labile, they will thus not destabilize the polymer. The stability of the polymers is thus more dependent on the total structure, which is not well-described by the amount of functional groups. Neither are the changes that occur with time well-predicted by the functional groups. The initial performance is easier to correlate with the composition of the expanders. Much of the initial performance can be related to surface activity, which depends on the structure of the polymers. Particularly, the ionic groups and hydrophobic groups are important in this respect.

Figs. 5 and 6 show the correlations between the properties of the lignins and the electrical performances. Precipitation pH, adsorption to lead, and initial pore volumes are all closely related and related to the initial capacity. The surface tension is inversely related to all these properties. The data for precipitation pH is highly skewed by the pure Kraft lignin UP-416 giving both an extremely high precipitation pH, and a good initial performance. A more detailed look at the data shows that within each type of lignin, the initial capacity increases with decreased precipitation pH, while the overall trend is the opposite. The type of lignin is clearly more important than the precipitation pH. For the adsorption to lead, initial pore volume and surface tension the stories are the same. Although there are general trends, none of them are found for the individual groups of lignins.

3.3. Expander stability and its correlation to battery cycle life performance

The stability test measures the insoluble residue of the lignins (in %) after heating them at 60°C in sulphuric acid.

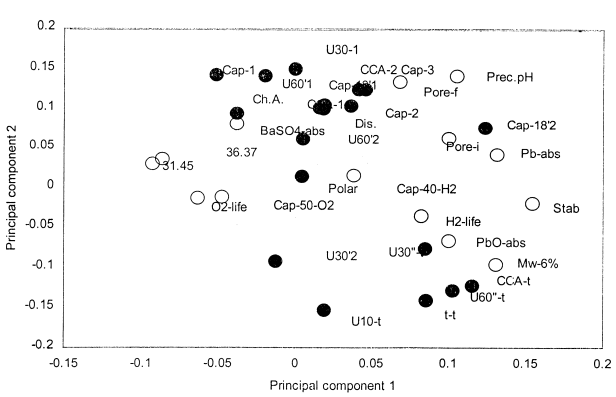

Fig. 5. A loadings plot of the electrical data and performance data for the lignins projected onto principal components 1 and 2. The meaning of the symbols are as given in Appendix A.

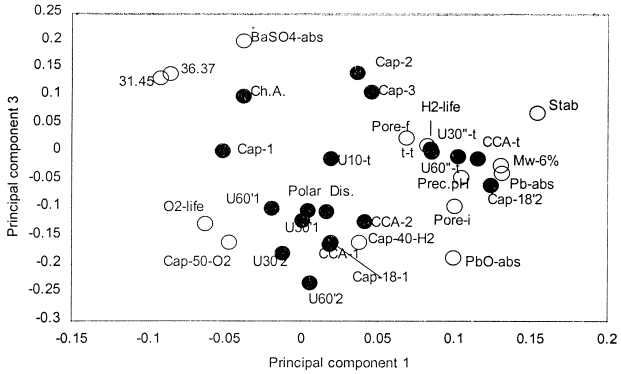

Fig. 6. A loadings plot of the electrical data and performance data for the lignins projected onto principal components 1 and 3. The meaning of the symbols are as given in Appendix A.

The solubility of the lignins depends on the degree of sulphonation. On grounds of the data in Table 2 the lignins under test can be divided in two groups:

(a) HMW, including UP-414, UP-413 and UP-417, which are highly sulphonated and hence, would be readily soluble;

(b) LMW, including VS-A, UP-393, M, D and UP-416, which have a low degree of sulphonation and consequently, would be less soluble.

Fig. 7 shows the correlation between expander stability and battery cycle life expressed in DIN week cycles until reaching the limit values for: (a) voltage at the 60th second of CCA discharge, and (b) capacity at CCA discharge with $I = 5\ C_{20}$ A at -18°C. The primary data on the cycle life of batteries with different expanders is presented in Ref. [9].

The following conclusions can be drawn from Fig. 7.

(a) Expanders can be classified in two groups according to their stability, which correspond to the HMW and LMW classification of the lignins.

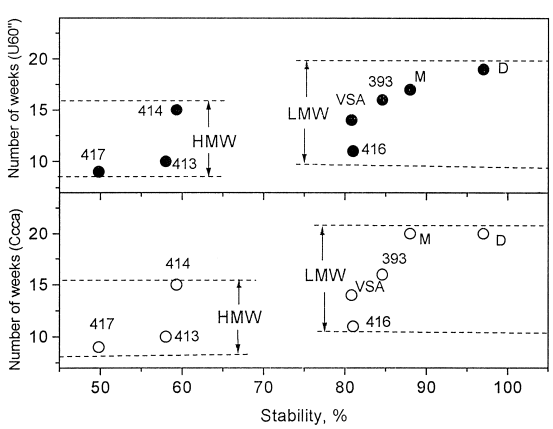

Fig. 7. Relationship between stability of expanders (%) and battery cycle life. LMW = low molecular weight and low sulphur, HMW = high molecular weight and high sulphur expanders.

This differentiation is probably due to the different structure of the polymers for the two groups. The LMW expanders have 2 weeks longer cycle life than the HMW lignins.

(b) Within each of the groups, the cycle life increases with an increase of expander stability (i.e., increase in the insoluble residue after heating in H_2SO_4 solution). This indicates that the battery cycle life is influenced by that part of the expander that remains unattacked by the H_2SO_4 at high temperatures.

No linear dependence has been found between the number of week cycles and the sulphur content nor the molecular weight of the lignins.

The stability of the lignins under hydrogen attack seems to give the best indication for the cycle life of the cells. A detailed description of the method used to determine the expander stability on H_2 attack is given in Ref. [5]. Fig. 8 illustrates the correlation between the number of week cycles until reaching the limit values for the voltage at the 60th second of CCA discharge with $I = 5\ C_{20}$ A at -18°C and for the CCA capacity. Except for the battery with VS-A, the tendency for all other expanders seems to be that the battery cycle life increases with increase in expander stability on H_2 attack.

As can be seen from Fig. 8, there is no linear dependence between the above parameters. There are also 20% variations in the number of week cycles of batteries even if cells with the same expanders gave the same lifetime under hydrogen attack. All accelerated testing stresses the batteries more than normal use to affect a faster breakdown. A major problem in all accelerated testing is that mechanisms that are unimportant in normal use can be very important during more extreme conditions. The relationship between the lifetime under hydrogen attack and the cycle life of the batteries under the DIN-43539-2 test gives strong hints about the important mechanism for expander break down.

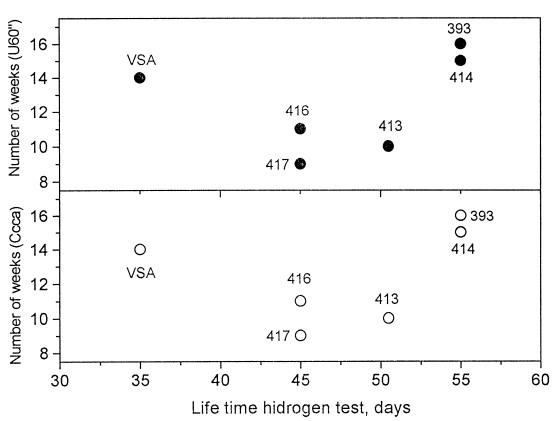

Fig. 8. The relationship between the lifetime under hydrogen gas attack, and cycle life according to DIN 43539-2. End points for DIN 43539-2 test given for: (a) 30 s discharge voltage (open circles); (b) cold cranking capacity (squares).

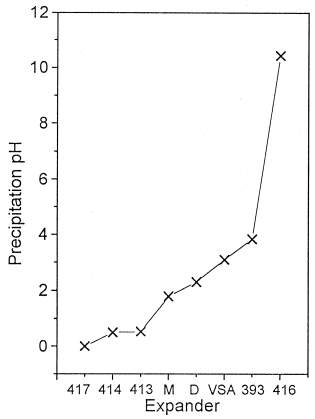

Fig. 9. Precipitation pH data for the expanders under test.

3.4. Precipitation pH of the expanders under test

Fig. 9 presents the data for the precipitation pH obtained for the different expanders. As evident from the figure, only expander UP-416 precipitates in weak alkaline solutions. Expanders UP-417, UP-414 and UP-413 precipitate at pH values ranging from 1.5 to 4.0. The latter expanders have the most pronounced positive effect on the overall performance and the cycle life of the batteries [9].

In Fig. 10, the relationship between the precipitation pH and the initial capacity is shown. It follows from this figure that Kraft lignins (UP-416, UP-393) give nearly the same good initial capacity irrespective of their precipitation pH, while the lignosulphonates (UP-413, UP-414, VS-A) have widely varying initial capacity with nearly the same precipitation pH values. The hardwood oxylignins (M,D) both have similar precipitation pH and similar initial capacity. The precipitation pH is clearly not useful in predicting the performance of the expanders.

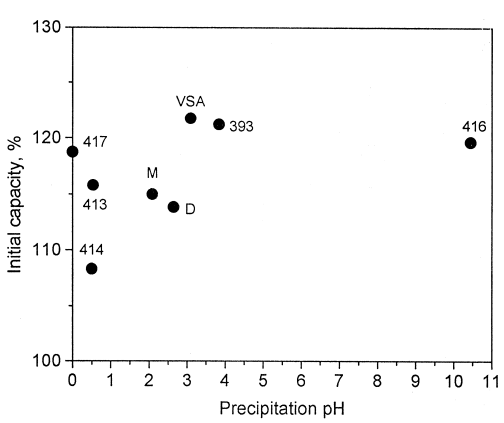

Fig. 10. Relationship between the initial capacity of the batteries and the precipitation pH of the expanders.

4. Conclusions

Through Principal Component Analysis, some correlations have been found between battery parameters and the structure and properties of the lignins. The type of lignin should be accounted for when considering the above correlations. Only few correlations hold across different types of lignins. Within each of the groups of expanders, i.e., with high or low molecular weight, a decrease in solubility of the lignins leads to an increase in battery cycle life.

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Appendix A

The properties and performances used in this multivariate analysis of eight expanders. The symbols in parenthesis are of little importance and not actually shown in the figures.

Constitution of the lignin

K-solid	K_{solid}
Phen-OH	% Phenolic OH
COOH	% Carboxylic acid
MeO–	% Methoxyl
Org-S	% Organically bound sulphur
Inorg-S	% Inorganic sulphur
M-*n*	Number average molecular weight $M_n = (\sum_i n_i M_i)/(\sum_i n_i)$; where n_I is the number of species having the molecular weight M_i
M-*w*	Weight average molecular weight $M_w = (\sum_i n_i M_i^2)/(\sum_i n_i M_i)$
M-*z*	*z*-average molecular weight $M_z = (\sum_i n_i M_i^3)/(\sum_i n_i M_i^2)$
M-*z* + 1	$z+1$-average molecular weight $M_{z+1} = (\sum_i n_i M_i^4)/(\sum_i n_i M_i^3)$
(Poly)	Polydispersity (M_w/M_n)
(HW)	Category variable, hardwood
(SW)	Category variable, softwood
(KL)	Category variable, Kraft lignin
(LS)	Category variable, lignosulphonate
(Oxy)	Category variable, oxylignin

Contamination of the lignin

Ash	Ash content
Al–Zn	All the metals are given by their IUPAC symbols
Tot-met	Total metal content

Initial electrical performance

Cap-1	
Cap-2	
Cap-3	Capacity in 1st, 2nd, 3rd cycle of DIN 43539-2 test
Cap-18′1	
Cap-18′2	Cold cranking capacity in 1st and 2nd cycle of DIN 43539-2 test
CCA-1	
CCA-2	Time to 6 V at −18°C, 1st and 2nd cycle
Polar	Polarisation from screening test
Ch.A.	Charge acceptance
S.Dis.	Self discharge
*U*30″-1	
*U*30″-2	Voltage after 30 s discharge, 1st and 2nd cycle
*U*60″-1	
*U*60″-2	Voltage after 60 s discharge, 1st and 2nd cycle

Cycle life

(*U*-*n*)	Voltage at week cycle *n*
(*U*30″-*n*)	Voltage after 30 s discharge at week cycle *n*
(*U*60″-*n*)	Voltage after 60 s discharge at week cycle *n*
(*t*-*n*)	Time to 6 V during discharge at week cycle *n*
(*C*-*n*)	Cold cranking capacity at week cycle *n*
*U*10-*t*	Number of cycles to fall below 10 V
*U*30″-*t*	Number of cycles before failing the DIN 43539-2 test for 30 s voltage
*U*60″-*t*	Number of cycles before failing the DIN 43539-2 test for 60 s voltage
t-*t*	Number of cycles before failing the DIN 43539-2 test for seconds to 6 V
CCA-*t*	Number of cycles before failing the DIN 43539-2 test for cold cranking capacity

Properties of the lignin

Pore-i	Specific pore volume the lead active mass before the test
Pore-f	Specific pore volume the lead active mass after the test
31.45	X-ray intensity of the characteristic diffraction line for lead with $2\theta = 31.45°$
36.37	X-ray intensity of the characteristic diffraction line for lead with $2\theta = 36.37°$
Prec.pH	Precipitation pH
Stab	Stability of expander
H2-life	Days to survive H_2-test
O2-life	Days to survive O_2-test
Cap-50-O2	Capacity of day 50 of O_2-test

Cap-40-H2	Capacity of day 40 of H_2-test
BaSO4-abs	RC for barium sulphate
PbO-abs	RC for lead(II)oxide
Pb-abs	RC for lead
Surf	Surface tension at 0.1% TS and pH 7
Mw-6%	M_w for soluble fraction in 6% sulphuric acid

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