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Relationships between the properties of ligninsulphonates and parameters of modified samples with cement binders Part III. Determination of sulphonated compounds content, characteristic of sulphonation, sorption studies

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Abstract

High- and low-molar fractions were separated from Mg^{++} sulphite waste liquor treated by fermentation. Additives were prepared by mixing the previously mentioned fractions in different ratios. Very good correlation between molar weight, content of ligninsulphonates in constant dose of additives, characteristic of sulphonation rate, and relative sorption of molecules were found.

Keywords: Adsorption; Admixture; Ligninsulphonates

1. Introduction

Relationships between molar parameters molar weight (Mw) and polydispersivity (Rp) of fractions prepared from Mg^{++} waste liquor and parameters of modified mortars were studied in Part II of this work [1]. It has been found that the Mw of additives dominantly influences the determined properties of tested samples [1,4]. Mw determined using liquid chromatography [2,3] depends mainly on the diameters of the molecules and on their outline characteristics. The proportional presence of molecules with different diameters, demonstrated by different molar mass corresponding to chromatographic peak can be determined by comparison of the peak areas under the chromatographic wave. The Mw parameter does not enable us to gain information concerning the structural characteristics of molecules influencing their affinity to solid particles (mainly those of cement). The knowledge of the parameters mentioned seems to be important for study of the principles of the action of the additives on the properties of modified samples with cement binders. The separation of fractions from waste liquor using ultrafiltration is insufficient, and the process is not quite reproducible because the higher-molar fractions usually contain a small residual amount of low-molar fractions. This is probably one of the reasons why molar parameters of certain fractions prepared repeatedly under the same other conditions may differ. Therefore, we prepared only two fractions containing high- and low-molar compounds of waste liquor. Various fractions (additives) were prepared by mixing them in different ratios. That method enabled us to avoid the errors that may occur by separately preparing a number of different fractions by ultrafiltration.

2. Methods

2.1. Materials

2.1.1. Additives

High- and low-molar fractions were separated by ultrafiltration from Mg^{++} waste liquor treated by fermentation. Various additives were prepared by mixing those fractions. The low- and high-molar fractions in the mixture (having constant dry content) were present as follows: Permeate: retentate = 100:0, 90:10, 80:20, 70:30, 60:40, 40:60, 20:80, 0:100 by weight of dry content. Mg^{++} waste liquor was also used for the tests.

2.1.2. Cement

The chemical composition of the industrial cement used is given in Table 1.

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Table 1
Chemical composition of ordinary Portland cement

Ign. loss	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
2.97%	20.25	3.47	5.19	0.40	62.08	1.69	0.79	0.42	2.71

Ign = ignition.

2.2. Methodology of the tests

2.2.1. Determination of sulphonation characteristic of additives

Equivalent mass (Mpe) parameter was used as a criterion of the sulphonation rate of the additives. It represents the average mass of a polymeric chain belonging to one sulphogroup. It can be calculated using Eq. (1):

$$\text{Mpe} = \frac{\text{Mw}}{k} \quad \text{or} \quad \text{Mpe} = \frac{m_a}{N_s} \tag{1}$$

where Mw is the molar mass of the additive (g/mole); k is a number of sulphogroups in one molecule; m_a is the mass of sulphonated compounds in additive (g/L); and N_s is the chemical equivalent (eq/L).

The content of ligninsulphonates in the samples tested had the same concentration and grew proportionally with increasing absorbance. Ligninsulphonates represent the decisive part of sulphonated compounds in the sample. Conductometric titration was used for the determination of dissociable (ionizable) groups. All $-OSO_2^-$ present were transformed to $-OSO_2H$ by HCl, which had a concentration of 1 eq/L. Content of HCl was subsequently determined by titration with NaOH, which also had a concentration of 1 eq/L. The titration curve shows two points of distinctive local changes. Part a (see Fig. 1) represents the process of neutralisation of free acid by NaOH. Part b represents the titration of all $-OSO_2$ H groups. The content of ligninsulphonates in the samples tested changed in relation to the absorbance A_c. The amount of sulphogroups in the tested sample grew proportionally with increasing consumption of NaOH. Therefore, the parameter N_s can be used as a characteristic expressing the sulphogroup content in the sample indirectly tested. The same concentration of additives (5 g/L) was used for determination of A_c and N_s parameters. Therefore, the parameters mentioned are compatible and can be used for multiple regression analysis.

2.2.2. Sorption characteristics

Sorption characteristics were determined by ultraviolet spectroscopy in the range of 195–330 nm (see Fig. 2). Cement (10 g) was mixed with 10 g of water solution of additive with a concentration of 5 g/L. The suspension was mixed and filtered for 25 min, and the filtrate was immediately analysed. The relative sorption S (%) was calculated using Eq. (2).

$$S = \frac{A_c - A_f}{A_c} \times 100 \tag{2}$$

The absorbance of additive-free cement filtrate A_2 was determined under otherwise the same conditions. Then A_f was calculated as the difference between the absorbance of filtrate with additive and cement after sorption A_1 and that of cement suspension without additive A_2. Sorption characteristic (Sr) represents a characteristic indirectly expressing the

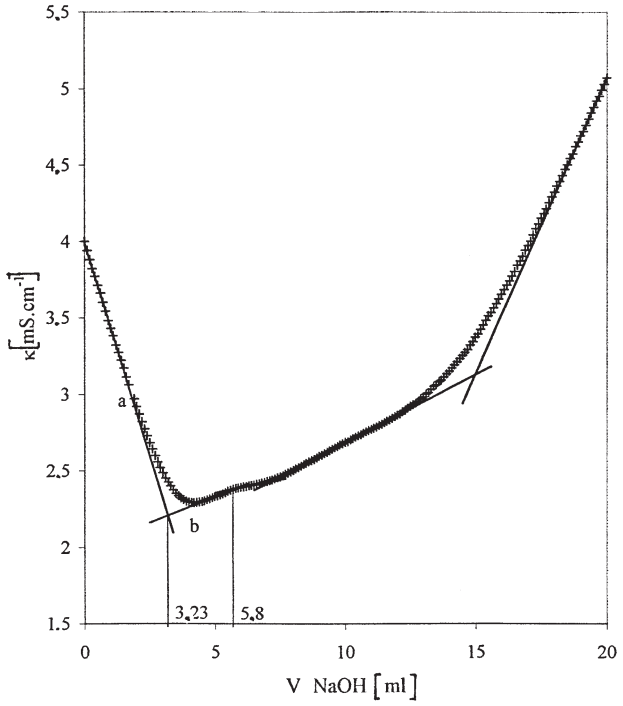

Fig. 1. Results of conductometric titration of permeate prepared from waste sulphite liquor.

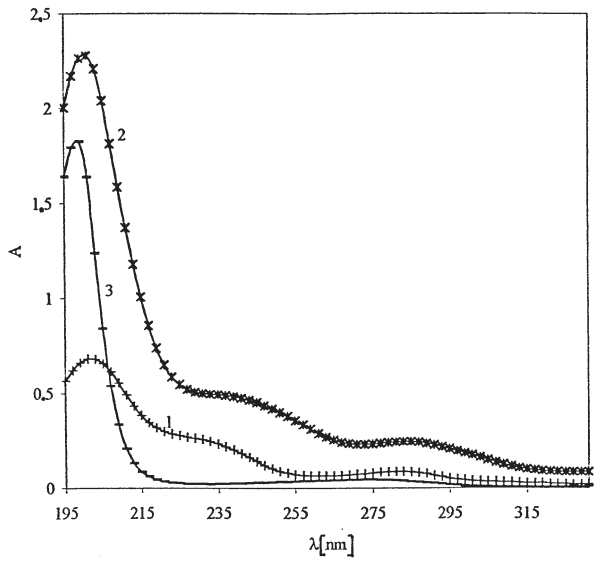

Fig. 2. Ultraviolet spectra of permeate: 0.5% concentration before sorption: (1) dilution 1:500, the same after sorption; (2) dilution 1:50, filtrate of cement without additive; (3) dilution 1:50.

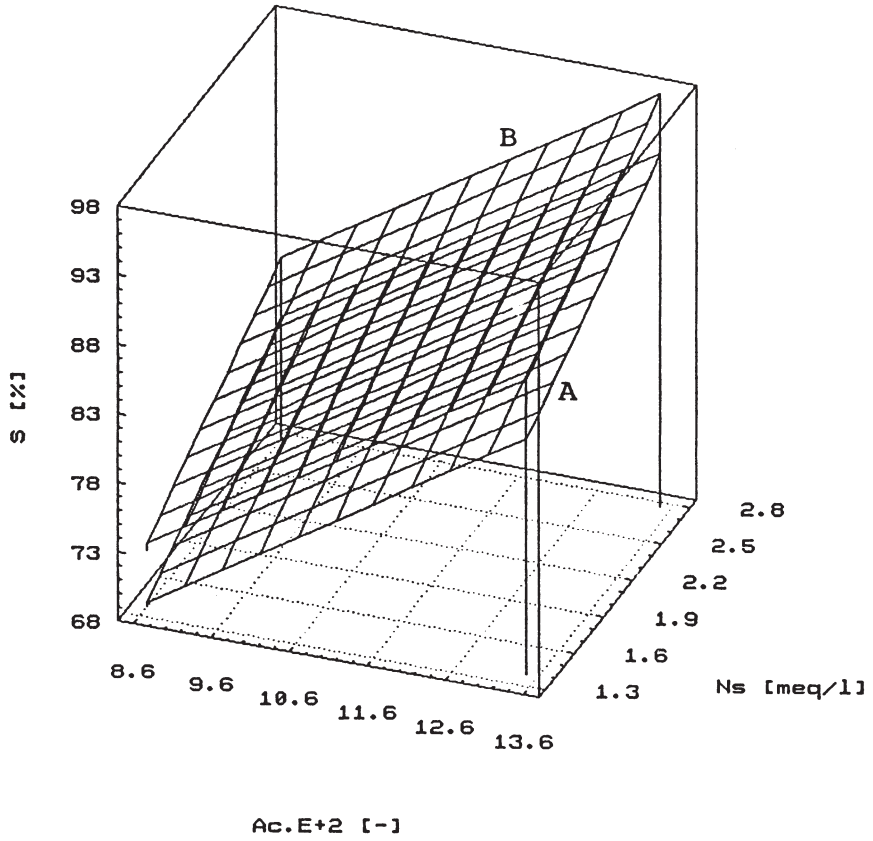

Fig. 3. Sorption S vs. absorbance Ac, sulphonation characteristics Ns and Mw of additives tested. A = permeate 1295 (g/mole); B = retenate 13,015 (g/mole).

sorbed amount of molecules on the surface of 1 g of cement tested and was calculated using Eq. (3):

$$\mathrm{Sr} = \frac{A_c - A_f}{m_c} \tag{3}$$

where A_c and A_f are absorbances of the sample before and after sorption (filtrate) (−), and m_c is the mass of cement used for sorption test (10 g).

2.2.3. Regression analysis

The relationship between the independent and dependent variables was tested using regression analysis (computer program Statgraphics 2). The independent variables chosen were: $X1$ = Mw, $X2 = A_c$, and $X3 = N_s$. Coefficient of determination R^2 (Rd) was used for judgment of significance of correlation between tested variables.

3. Results

Absorption spectra of chosen tested samples are presented in Fig. 2. The maximum of the absorption curve of the sample with ligninsulphonate can be observed at wave number 208 nm; the cement filtrate value is lower. The character and courses of curves before and after sorption do not differ from each other. Any other changes in characteristics of ligninsulphonates due to the interaction with cement particles cannot be deduced from these results.

Very good correlation between $X1$, $X2$, $X3$, and S exist because Rd = 98.06%. All variables not included in the analysis influence the dependent variable by approximately 2%. The significance level of the model fitting results showed that $X2$ has more significant influence on S changes than $X1$ and $X3$. The relationships in seen Fig. 3 were calculated separately for lower (A-permeate) and upper Mw values (B-retentate) from the tested range. The difference between relationships A and B in Fig. 3 indicates the contribution of Mw on S value changes. The relative sorption S increases with increasing Mw of additive tested. It also increases markedly with increasing concentration of ligninsulphonates in constant dose of additives (A_c) and with increasing sulphogroups content in it (N_s).

The results shown in Fig. 3 indicate that sorption of ligninsulphonate molecules is selective. The high-molar fractions, having a high content of sulphogroup, are sorbed out preferably from intergrain solution of cement suspension. This is in good accordance with our former observations [5,6]. It seems that the residual portion of aditive compounds that is not sorbed in intergrain solution is created

mainly by low-molar fractions of ligninsulphonates having a low sulphonation rate and with organic or inorganic compounds having low affinity to cement particles.

4. Conclusions

1. The method described seems to be suitable for determination of sulphonation characteristic of waste liquor and its fractions.
2. The relative sorption of ligninsulphonate molecules on the surface of cement particles increases with increasing Mw, concentration of ligninsulphonates (in constant dose of additive), and with increasing value of sulphonation character.
3. The results indicate that sorption of ligninsulphonate molecules is selective.

Acknowledgments

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References

[1] O. Stráněl, T. Sebök, Relationship between the properties of ligninsulphonates and parameters of modified samples with cement binders, Part II, Cem Concr Res 27 (1997) 185–191.
[2] O. Mikeš, Laboratory Chromatographic Methods (in Czech), State Publishing Company (SNTL), Prague, 1980.
[3] L. Mandík, L. Tuláková, GPC—Application on real systems, Research Report, VUSPL, Pardubice, 1974.
[4] T. Sebök, Study of sorption of ligninsulphonates on the limiting surface of cement particles and intergrain solution, Cem Concr Res 16 (1986) 275–282.
[5] T. Sebök, A. Tůmová, The effect of ligninsulphonate fractions on the properties of cement pastes, in: IVth Symposium Silichem, Brno, Czech Republic, 1983.