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RELATIONSHIPS BETWEEN THE PROPERTIES OF LIGNINSULPHONATES AND PARAMETERS OF MODIFIED SAMPLES WITH CEMENT BINDERS
Part I. Characterizing ligninsulphonates and studying their sorption properties

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ABSTRACT

The effects of molar parameters of ligninsulphonates on their interaction with the cement binder were observed. It has been proved that the sorption of polydispersed ligninsulphonates depends primarily on their molar mass and that on the surface of the cement particles, fractions with higher molar mass are bonded in the first place. The cement types and properties also have certain effects on the sorption behaviour of ligninsulphonates. © *1997 Elsevier Science Ltd*

Introduction

In contact of plasticizing additives with components of the concrete mixture there is an interaction of their effective components with the surface of solid particles of the suspension, especially with that of cement. As a result, there is a considerable influence on the rheological properties of suspensions, the hydration kinetics, and the formation of solid structure of the cement binder.

The nature and mechanism of the action of plasticizing additives have not yet been explained in a satisfactory way (1-9). It is evident at the same time that knowledge of the nature of these processes can contribute significantly to the development of new plasticizing additives and/or to the optimization of the treatment of materials manifesting such behaviour, e.g. very cheap ligninsulphonates. Sulphite liquors are waste products and represent a very complicated mixture of organic and inorganic materials. A major component is formed by ligninsulphonate acid salts showing considerable distribution of the molar mass especially.

In order to improve their utility characteristics it appears to be useful to determine the effects of their molar parameters on the interaction with the cement binder and/or to minimize the negative effects of some probably low-molecular accompanying materials.

Experimental Part

Materials and Testing Methods Used. For GPC study of molar parameters of the tested ligninsulphonate fractions and their sorption characteristics the following instruments were used: liquid chromatograph model SP 8000, Spectra-Physics Ass.; differential refractometer, R 401 Waters Ass., UV/VIS model detector LCD 2040, Ecom; fluorescent detector, model 8200, Knauer; carbon analyser model 915, Beckmann; spectrophotometer Specord M42, Carl Zeiss.

GPC analysis was made on chromatographic columns VIT-X which are of porous deactivated glass supplied by Perkin-Elmer company.

For calibration of the GPC system dextran standards (Pharmacia Fine Chemicals, Uppsala) and ß-naphtalene sulphonate were used. NaCl water solution of 0.25 M was used as eluent.

For testing the rheological properties of cement pastes was used rotary viscomerer Rheotest 2 , Prufgerate-Werk, Dresden.

For testing of the development hydration heat was used isothermal calorimeterVUPS 2 developed at Building Research Institution Prague.

Cements. Four types of cements made in laboratory by grinding clinkers from four cement works with gypsum in a mass ratio 95:5 was used for the experiments. The properties of industrial cements used are described in the further parts of the article. Basic characteristics of the cements are given in Tabs. 1 and 2.

Additives. For tests, basic sulphite waste liquors were used, namely, from paper mills Biocel a.s. Paskov, and Jihočeské papírny a.s., Větřní. With regard to the aims of the tests, the waste liquors were treated by fractionation-membrane separation as well as chemically, biologically.

Filtrates. The water solution of an additive in chosen concentration was mixed with cement in a mass ratio 1:1. The suspension, developed in this way, was homogenized in a shaking machine for 20 minutes and after that immediately filtered through nitrocellulose membrane filter Sympor 5 (pore size 600 ± 100 nm). The filtrate was then analysed immediately.

TABLE I

Mineralogical composition of clinkers, determined by optical method

Component	B.Bystrica - B	Štramberk - S	Čížkovice - C	Maloměřice - M
C_3S	68.04	51.85	55.43	66.42
C_2S	10.19	22.11	21.07	13.41
C_3A	9.67	11.71	14.05	6.72
C_4AF	9.55	11.44	6.66	12.42
Free CaO	1.35	2.89	1.78	0.95

TABLE 2

Basic Standard Properties of Laboratory-Made Cements

Cement	Specific Surface m^2/kg^{-1}	Standard Density %	Setting, hrs:mins		Compression Strength MPa Days			
			Start	Time	1	3	7	28
B	299.9	25.50	2:35	3:25	12.0	26.5	39.3	52.1
S	303.6	24.75	2:00	2:55	12.9	27.5	34.9	51.0
C	302.2	26.00	2:05	3:05	17.4	30.3	38.0	50.5
M	304.1	26.75	2:25	4:10	8.5	22.8	33.4	46.2

Preparation of Specimens with Cement Binder. Specimens of mortars both with additives and without them were made by mixing the cement with the finest standard sand in a ratio 1:1 of mass portions with w/c = 0.45. From the pastes prepared in this way cubes were made according to the method (Slovac Academy of Science prescription, Bratislava 1962) for testing of cements and mortars properties, with edges of 20 mm for tests of the compression strength. After 24 hours following the preparation the specimens were placed in water till the time of the tests.

Specimens of concrete mixtures and concrete both with and without additives were made, placed under water and tested (10).

Rheological Properties of Cement Pastes. The properties were tested using a rotary viscometer Rheotest and a plastic meter of an entirely new structure described in the literature (7).

Development of Hydration Heat. The development of hydration heat was observed using an isothermal calorimeter facilitating the evaluation of integral value of the hydration heat (HT) development and that of immediate intensity of the HT development.

Results and Discussion

For a detailed study of the effects of molar parameters of ligninsulphonates on their interaction with the surface of the cement in liquid phase, four fractions of the sulphite waste liquor, based on magnesium ligninsulphonate, were prepared by ultrafiltration.

GPC study has proved that these ligninsulphonates are typical polyelectrolytes, for which it means in general that the shape and size of the macromolecular ball are essentially dependent on quantities such as the polyelectrolyte concentration proper and the ionic strength of solution. As GPC uses the very outline size and shape of the macromolecular ball to determine the molar mass, it is a suitable method in the study of this kind. In increasing the ionic strength of solution by adding an electroneutral salt (NaCl) above a certain critical value (0.25 mol/l) the expansion of ligninsulphonate macromolecules was prevented, and these polyelectrolytes could be characterised, with regard to the outline size, also using polysaccharides as standards.

TABLE 3

GPC Determination of Molar Mass of the Magnesium Ligninsulphonate Fractions

Marking of the Fraction/Specimen	Mw g/mol	Mn g/mol	Rp
1	1 247	344	3.622
2	2 637	491	5.372
3	3 813	411	9.269
4	11 940	504	23.690

Note: Mw is mass average of molar masses
Mn is numerical average of molar masses
Rp is polydispersivity (Mw/Mn)

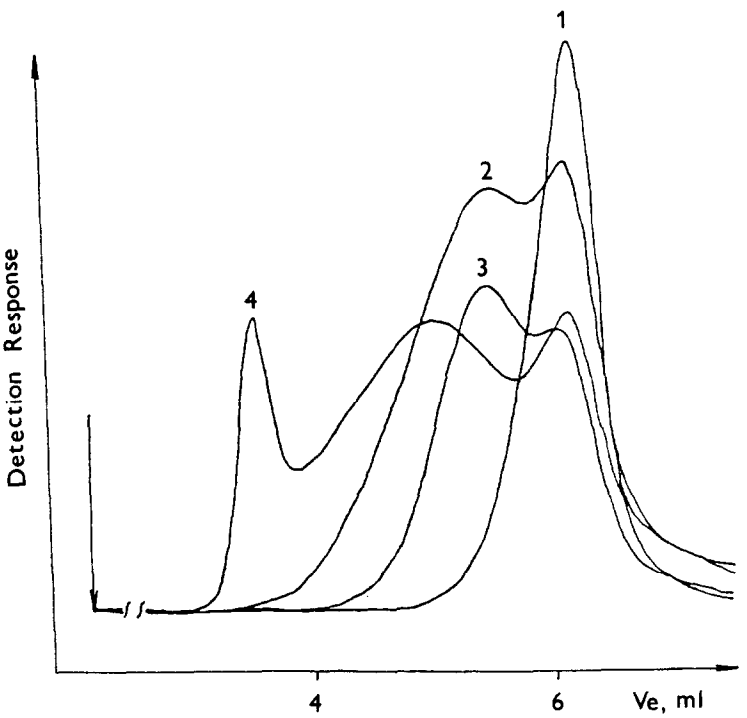

FIG. 1.
GPC chromatograms of ligninsulphonates fractions (1-4). Conditions: column, VIT-X 328, flow rate 22 ml/h, solvent, 0.25 M NaCl in water, RI detection. Ve-elution volume.

TABLE 4

Results of GPC Determination of M_{peak} Change in Interaction of Ligninsulphonates with Cement

Specimen No.	GPC - Detection UV-254		GPC - Fluorescent Detection	
	Before Interaction M_{peak} g/mol	After Interaction M_{peak} g/mol	Before Interaction M_{peak} g/mol	After Interaction M_{peak} g/mol
1	1 288	759	1 122	759
2	3 236	1 820	2 454	1 479
3	3 236	1 698	3 236	1 585
4, 1st wave	6 456	851	6 456	1 122
4, 2nd wave	38 904	-	28 840	-

M_{peak} is molar mass corresponding to chromatographic peak

The results of GPC determination of the molar mass of functionalized magnesium ligninsulphonate under such conditions are summarized in Tab. 3.

Chromatograms are summarized in Fig. 1, i.e. using a universal refractometric detection (RI). The fraction with the lowest molar mass according to ultrafiltration shows one wave (specimen no.1), fractions 2 and 3 two waves, and specimen no. 4 three waves. At the same time the value of Rp increases.

For studying the interaction of ligninsulphonates with cements GPC analysis, UV spectroscopy, and TOC analysis were used.

TABLE 5

Results of Determination of the Sorption of Ligninsulphonates in Cement

Specimen	Absorbed Amount of Ligninsulphonates (Mass %) According to Methods			
	GPC - Detection UV 254 nm	GPC - Detection Fluorescent	UV (240 nm) Spectroscopy	TOC
1	14.2	52.0	22.3	37.3
2	40.1	72.0	42.9	49.1
3	62.3	84.0	55.5	61.3
4	84.0	92.0	73.6	77.5

In GPC study of the interaction a preferential bonding of higher-molecular ligninsulphonate fractions to cement was registered. Keeping in view of fact that the universal RI detection cannot be used due to the interference of substances leached from cement, we can provide documentary evidence for this claim by the changes of M_{peak} of ligninsulphonates before and after the interaction, determined by sensitive and selective UV-254 detections and/or by fluorescent detection. The results are given in Tab. 4.

It is evident from the results that in the first place, higher-molar fractions of polydispersed ligninsulphonates are bound. Fractions with the highest molar mass in specimen 4 disappear entirely and with the other fractions a noticeable shift occurs in M_{peak} after the interaction in all the specimens (1 to 4) towards lower values.

Certain differences in M_{peak} determined by UV-254 and fluorescent detections are caused by their different sensitivity of detection to polydispersed ligninsulphonates.

These conclusions are in a very good conformity with the results gained in determining the volume of ligninsulphonate bound to cement.

These results also confirm a preferential binding of higher-molecular fractions of ligninsulphonates to cement regardless of the method of determination (Table 5).

As regards certain differences in values of the bound amount determined by different methods, these differences result from the polydispersed character of individual specimens and from the different sensitivity of methods to individual functional groups of ligninsulphonates. It shows itself especially with fluorescent and UV detections, when e.g. the fluorescent detection prefers rigid, e.g. polycondensed aromatic groups and the like. Determining the total organic carbon (TOC), on the other hand, monitors the overall sorption of organic materials regardless of their structure, and therefore a comparison of these results with those of selective methods is very valuable.

Conclusions

Using GPC method, molar parameters of ligninsulphonate fractions prepared by ultrafiltration were determined.

Ligninsulphonates show typical polyelectrolyte properties and considerable polydispersiveness of molar masses.

Sorption of ligninsulphonates to cements is selective. Preferentially, it is the fractions with higher molar mass that are bound to the surface of cement from the intergrain solution.

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