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Relationships between the properties of ligninsulphonates and parameters of modified samples with cement binders. Part II. Study of relationships between molar parameters of ligninsulphonates and characteristics of the samples tested

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Abstract

The relationships between molar parameters of Mg^{++} ligninsulphonate fractions and sorption characteristics, properties of modified cement suspensions, and hardened mortar samples were studied. It has been found that the molar weight of fractions has a significant influence on the sorbed amount of molecules of additives, heat evolution, plasticity, volume weight, and compressive strength of the samples with the cement used. The sorption characteristics depend also on the method used for determination.

Keywords: Admixture; Adsorption; Hydration; Rheology; Compressive strength

The sorption of ligninsulphonate additives on the surface of solid particles in cement suspension is selective according to the results published in Part I of this article [1]. The sorption characteristics influence the water-reducing effectiveness of additives. The potential-zeta of fine particles in cement suspensions is increasing because of the sorption of molecules of additive on their surfaces. The repulsive forces between the particles, having the same charge, increase as a result of potential-zeta growth. The friction forces in suspension with cement binder decrease because of the phenomenon mentioned. That complex problem has been studied by many authors. The main results of authors referred [2–11] can be briefly summarized as follows:

The potential-zeta of fine particles of C_3S, beta-C_2S, hydrated C_3A, quartz, Al_2O_3, flying ash, and wollastonite is negative in pure water [5,6,8]. The same potential of C_4AF, unhydrated C_3A, and $Ca(OH)_2$ is positive [5,9]. The potential-zeta of the particles is negative when molecules of plastifying additives are present in the suspension. The repulsive forces in the case of the cement particles outweigh the attractive ones only when their potential-zeta is greater than −35 mV [9]. The molar weight of additive may influence the value of potential-zeta [10] and properties of modified samples with cement binder [11]. Ligninsulphonates have the most favourable dispersing effect when their molar weight changes in the range of 5,000–25,000 g/mol. The sulphogroup content in the molecules is very important; the most favourable dispersing effect has been found when their content is 14–15% by weight of ligninsulphonates.

1. Materials and methods

1.1. Additives

Mg^{++} sulphite waste liquor was used. The content of chief compounds in dry of tested liquor was as follows: 60.27% ligninsulphonates, 7.01% pentosans, 11.80% reducing compounds, and 11.36% monosaccharides.

Permeates and retentates (fractions), differing from each other in molar parameters, were prepared by ultrafiltration of Mg^{++} sulphite waste liquor.

The dose of additives in all samples was 0.5% dry by the weight of cement.

1.2. Cement

Laboratory-made cement was used. The mineralogical composition of the clinker from cement work Čížkovice

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Table 1
Setting of samples with fractions tested

Mw (g/mol)	Time of setting (hours, minutes)	
	Initial	Final
Control	02,10	03,40
1,247	01,45	04,35
2,637	04,31	05,50
3,813	05,30	06,45
11,940	06,05	07,55

and other parameters of the cement used are described in the Part I of this article [1].

1.3. Plasticity

Plasticity is expressed as the area of the base of the cone of mortar sample after 15 cycles of the compaction apparatus, according to the standard ČSN 722441–Determination of the Plasticity of Mortar.

1.4. Sorption, heat evolution, and compressive strength

These methods are described in Part I of this article [1].

1.5. Time of setting

The time of setting was determined using Vicat's method in accordance with the standard ČSN 722115. The results are in Table 1.

2. Evaluation of results

The relationships between the independent and dependent variables were tested using regression analysis (computer program Statgraphics 2). Variables tested are in Table 2. The designation of symbols is: X_1 = average of molar masses, X_2 = polydispersivity of Mg^{++} sulphite waste liquor and its fractions, Y_1 = relative sorption S_{UV} (UV spectroscopy), Y_2 = relative sorption S_{TOC} (TOC analysis). Y_1 and Y_2 were both calculated using Eq. (1)

$$S = \frac{A_b - A_a}{A_b} \times 100 \quad (1)$$

just in the term of the 20 minutes of interaction. Y_3 to Y_6 were calculated using Eq. (2)

$$P_p, H_p, V_p, C_{p28} = \frac{P_a}{P_o}. \quad (2)$$

Results are shown in Figs. 1, 2, 3, and 4.

A_b and A_a are the concentrations of additive in the liquid phase before and in the filtrate after sorption (mg/g), respectively. P_p, H_p, V_p, and C_{p28} are the ratios of plasticity, integral value of heat liberation (24 h), volume weight, and compressive strength (28 days), respectively. P_a and P_o are determined parameters of the samples with and without additives, respectively.

The method of expression of the Y variables, Y_i, enables us to avoid problems with slight changes of cement properties during several months of proper storing. It protects against the action of moisture and CO_2 and also makes it possible to include the measured values of the control samples without additives into the regression analysis.

The aim of the test was to find out the relationships between the molar parameters Mw and Rp of the tested additives and the dependent variables in Table 2. The characteristics of regression analysis showed that the Mw parameter has a decisive influence on changes in the Y_i variables. That is why only simple regression between the variables mentioned was included in this article. The coefficients of simple correlation, Rk, are in Table 2.

3. Conclusions

1. A very good correlation between the tested variables exists, as Table 2 shows. The sorbed amount of ligninsulphonates grows with increasing Mw (Figure 1). The measured values of sorbed amounts depend on the method used because they have different sensitivities of indication to the individual compounds in the

Table 2
Basic parameters of variables tested

Fraction	X_1 Mw (g/mol)	X_2 Rp (−)	Y_1 S_{UV} (%)	Y_2 S_{TOC} (%)	Y_3 P_p (−)	Y_4 H_p (−)	Y_5 V_p (−)	Y_6 C_{p28} (−)
1	1,247	3.62	22.3	37.3	0.815	0.557	0.997	1.22
2	2,637	5.37	42.9	49.1	1.068	0.658	0.969	1.10
3	3,813	9.26	55.5	61.3	1.188	0.690	0.950	1.16
4	11,940	23.70	73.6	77.5	1.282	0.765	0.947	0.86
5	1,938	6.80	23.2	40.0	0.982	0.612	0.982	1.15
6	10,950	15.01	66.2	76.7	1.260	0.750	0.949	0.84
7	12,140	13.98	81.8	80.0	1.260	0.793	0.947	0.80
Waste liquor	8,569	18.49	54.8	56.0	1.310	0.830	0.949	1.03
Control	—	—	—	—	117 cm^2	180 $J.g^{-1}$	2.27 $kg.dm^{-3}$	47.0 MPa
Rk–X_1, Y_i	—	—	—	—	0.9329	0.9417	0.9390	0.9451

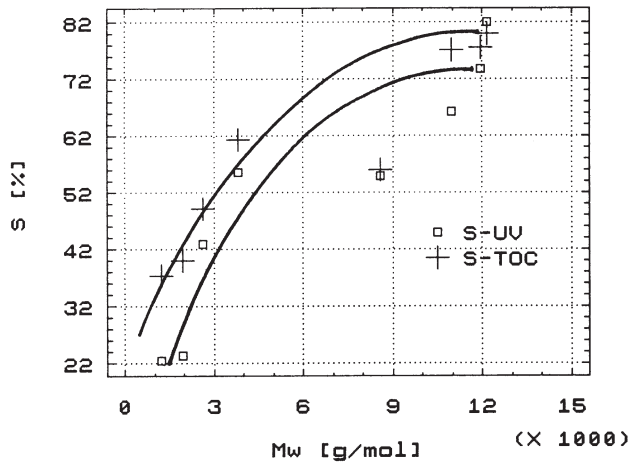

Fig. 1. Influence of Mw on sorption characteristics.

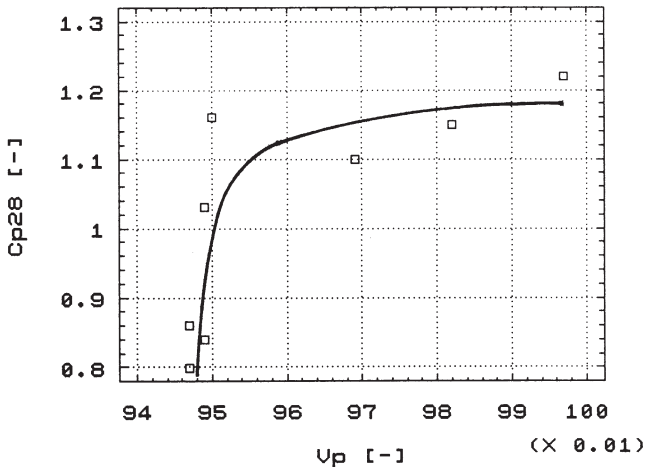

Fig. 4. Relationship between Vp and Cp28.

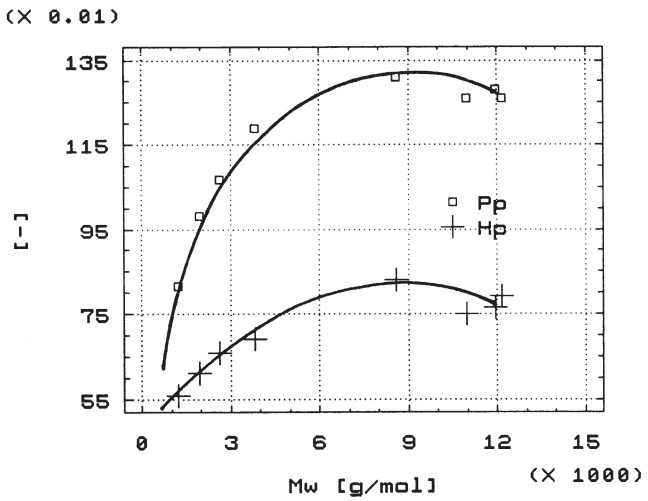

Fig. 2. Influence of Mw on Pp and Hp.

samples. The TOC analysis indicates the concentration changes of ligninsulphonates, and low molar organic compounds with bond carbon in molecules (for instance saccharides) in the sample regardless of their molar weight. That is why the measured values of sorption (TOC) are higher in the case of permeates than those measured by UV spectroscopy.

2. The changes in heat evolution of modified samples indicate the influence of additives on the hydration and creation of the base of solid structure of the sample. The H_p values decrease with decreasing Mw values, as is evident from the results in Fig. 2. All tested additives cause measurable retardation of the heat evolution after 24 hours of hydration.
3. All tested additives having Mw over ~2,000 g/mol improve the plasticity of modified mortars in comparison with that of control. The Pp values increase with increasing Mw (Fig. 2).

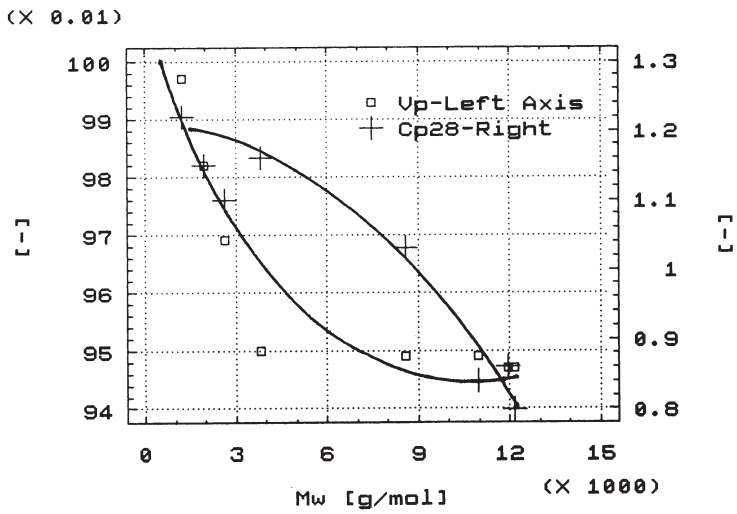

Fig. 3. Influence of Mw on Vp and Cp28.

4. All fractions cause an increase in the air content of tested suspensions. This manifests itself by the decreasing V_p and C_{p28} values of the samples tested with increasing Mw (Fig. 3), even after compaction.
5. It seems that the volume weight influences the compressive strength of samples with additives, as shown in Fig. 4.

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