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Relationships between the properties of ligninsulphonates and parameters of modified samples with cement binders Part IV. Influence of sulphonated compounds and sulphonation characteristics on the properties of mortar samples

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Abstract

The influence of additives, prepared by mixing high and low molar fractions separated from Mg++ sulphite waste liquor, on properties of mortar samples was studied. Very good correlation among molar weight, content of sulphated compounds, characteristic of sulphonation rate of additives, and volume weight of fresh mortar (integral value of heat evolution) were found. The air-entraining action of additives influences the plasticity of mortar, volume weight, and compressive strength of modified samples after 3 and 28 days of hardening. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The following results are a continuation of previous work. Additives may influence the properties of modified samples in two main ways. They may influence the rate of hydration, sorption characteristics, rheological properties, and the creation of a solid structure of binder in the first period or in long terms of hydration [1–10]. They may also influence the composition of modified samples due to their water-reducing or air-entraining effectiveness [1,11]. Those two actions are decisive for overall influence of additive on the properties of mortar or concrete. Further publications present relationships among parameters of additives and those of modified samples [12–17]. These relationships seem to be valuable for the development of new additives, improvement of their structural parameters and effectiveness, and as an explanation of their principles of action. A considerable number of publications deal with the influence of commercial additives on parameters of samples with cement. Only a very few present similar relationships with laboratory-prepared additives. Relationships between molar parameters (mainly Mw) and parameters of modified samples are presented predominantly, as was the case of Part II of this article. The aim of the following tests is to broaden the knowledge in this field.

2. Materials and methods

2.1. Materials

2.1.1. Additives

The methods of preparation of additives and determination of their absorbance characteristics and sulphonation characteristic are described in Part III of the article [17]. Molar weight was determined using Gel Permeate Chromatography (GPC) analysis [12]. The dose of additives was uniformly 0.5% of their dry content from weight of cement in all specimens (Table 1).

2.1.2. Cement

Industrial ordinary Portland cement was used. The chemical composition of it is described in Part III [17].

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Table 1
Dependent and independent variables: Parameters of specimens tested

P:R (%)	*X*1, Mw (g/mole)	*X*2, Ac · E + 2 (-)	X3, Ns (meq/L)	Sr · E + 2 (-)	P (cm^2)	Vwm (kg/dm^3)	He (J/g)	Vw3 (kg/dm^3)	Vw28 (kg/dm^3)	Cs3 (Mpa)	Cs28 (Mpa)
100:0	1,295	8.61	2.76	6.57	201	2.031	127	2.071	2.119	25.03	40.23
90:10	2,470	9.19	2.72	7.23	187	2.003	125	2.027	2.079	22.16	37.94
80:20	3,645	9.50	2.62	7.57	181	1.959	132	1.986	2.054	22.84	35.78
70:30	4,800	9.66	2.51	7.81	189	1.951	134	1.962	2.029	19.94	32.08
60:40	5,977	10.15	2.49	8.30	197	1.925	137	1.936	2.018	17.15	28.66
40:60	8,270	11.00	2.03	9.26	205	1.892	138	1.929	1.980	15.95	26.97
20:80	10,55	12.09	1.82	10.41	221	1.873	139	1.918	1.989	14.47	23.60
0:100	13,015	13.46	1.38	11.93	244	1.862	140	1.899	1.945	13.54	17.94
Liquor	7,630	9.52	2.27	7.49	180	1.985	130	2.056	2.087	24.62	38.4
Control (without additives)					125	2.165	180	2.180	2.240	27.36	46.84
Rd (%)					91.0	91.9	79.2	87.4	89.2	90.1	96.0

P:R is ratio of dry contents of permeate and retentate in constant dose 0.5%.

2.1.3. Aggregate

Three fractions of quartz sand prescribed for determination of standard compressive strength of cement were used.

2.2. Methods

2.2.1. Heat evolution

An isothermal calorimeter was used for determination of integral values of heat evolution at +20°C.

2.2.2. Preparation of mortar samples

Sand (225 g) of each fraction I, II, and III was mixed with 200 g of cement. Water (110 mL) containing the dissolved additive was added to the homogenised dry components. The suspension was mixed by hand to avoid the extreme aeration due to intensive agitation, which occurs in the case of standard mixer use.

2.2.3. Rheological properties

The plasticity of mortar is expressed as an area of base of the mortar cone after 15 cycles of the compaction device. It was determined in accordance with the standard [18]. The rheological properties of mortars were tested 25 min after homogenisation of solid and liquid components of mortars.

2.2.4. Compressive strength

Compressive strength was determined using cubes with 40-mm edges, prepared, stored, and tested according to the standard [19].

2.2.5. Regression analysis

The computer program Statgraphics 2 was used. Independent variables chosen were: X1 = molar weight (Mw); X2 = absorbance (Ac), X3 = sulphonation characteristic (N_s) of additives. Dependent variables chosen were: He, integral value of heat evolution during 24 h; P, plasticity of fresh mortar; Cs3, Cs28, Vw3, Vw28, compressive strength and volume weight after 3 and 28 days of hardening; Vwm, volume weight of fresh mortar. Quadratic mathematical model of relationship (P vs. Sr and Vwm) was further analysed using a computer program for ridge analysis [20]. The results are shown in Fig. 1. The courses of variables *X*1, *X*2, and *Y* in Fig.1 depend on the change in the value of mediating factor *R*, which is a radius of *n*-dimensional ball whose magnitude can be expressed as shown in Eq. (1):

$$R^2 = \sum_{i=1}^{n} X_i \tag{1}$$

When, for instance, *R* = 8.4 (horizontal axis) is chosen, then corresponding coordinates of relationships shown in Fig. 1 are: X1 = 8, X2 = 1.97 kg/dm^3, and Y = 180 cm^2. That point is the local minimum of dependence Y = f(R). Corresponding coordinates of *X*1, *X*2 may be derived in a similar way for all values of *Y* in the range 180 to 248 cm^2.

The following limits were used for determination of each *Rd* coefficient significance (coefficient of multiple determination): *Rd* < 30, low or any correlation; Rd = 30 to 60%,

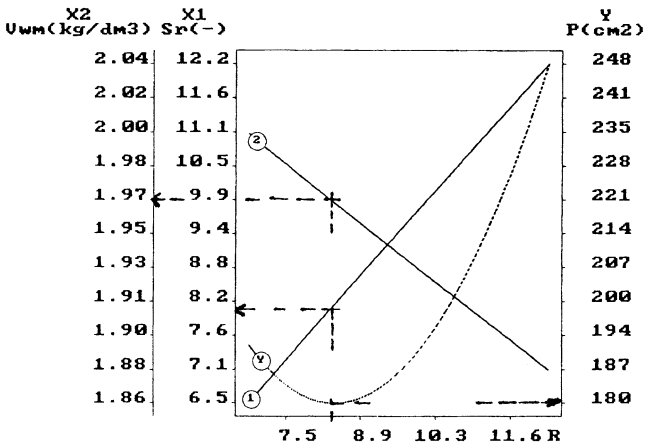

Fig. 1. Plasticity P (*Y*) versus sorption characteristic Sr (*X*1) and volume weight of fresh mortar Vwm (*X*2).

medium to good correlation; $Rd \geq 60$, very good correlation between analysed variables exists [21].

3. Results

Very good correlation between independent $X1$ (Mw), $X2$ (Ac), $X3$ (N_s), and all dependent variables exists as can be derived from Rd values in Table 1.

The results of regression analysis showed that plasticity P is influenced by Sr and Vwm changes by 98.67%. The courses of relationships mentioned are presented in Fig. 1. Sorption characteristic Sr ($X1$ axis, relationship 1) linearly increases and Vwm ($X2$ axis, relationship 2) linearly decreases in the whole range of defined values. The value of Y variable (axis Y on the right side) moderately decreases up to the local minimum of dependence. Then a rapid increase of Y can be observed in the range 180 to 248 cm^2. Corresponding coordinates of independent variables to maximal value of plasticity P = 248 cm^2 are: Sr = 12.2 (maximal value) and Vwm = 1.88 (minimal value). The results obtained indicate that an increasing amount of sorbed organic molecules of additives on the limiting surface of phases within the suspension increases the potential ξ and also increases proportionally the repulsive forces between fine solid particles and between the stabilised air pores. The air pores, having a spherical shape, are evenly distributed in the volume of the mortar. They are covered by a thin, smooth and cohesive film of water containing surface-active molecules. The film can be elastically deformed by the action of external forces without destruction in certain limits. An increase of sorption characteristic Sr (increase of potential ξ) and decrease of Vwm (due to increase of air content) cause the decrease of friction forces between the components of mortar. This is favourable for workability improvement.

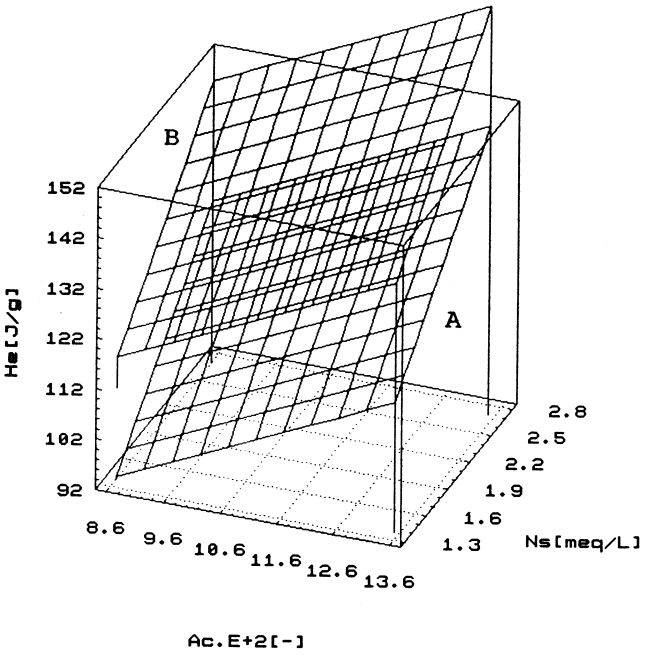

Fig. 2. Integral value of heat evolution (24 h) He vs. absorbance Ac, sulphonation characteristic N_s, and molar weight Mw of additives tested. (A) Mw = 1,295 (g/ mole); (B) Mw = 13,015 (g/mole).

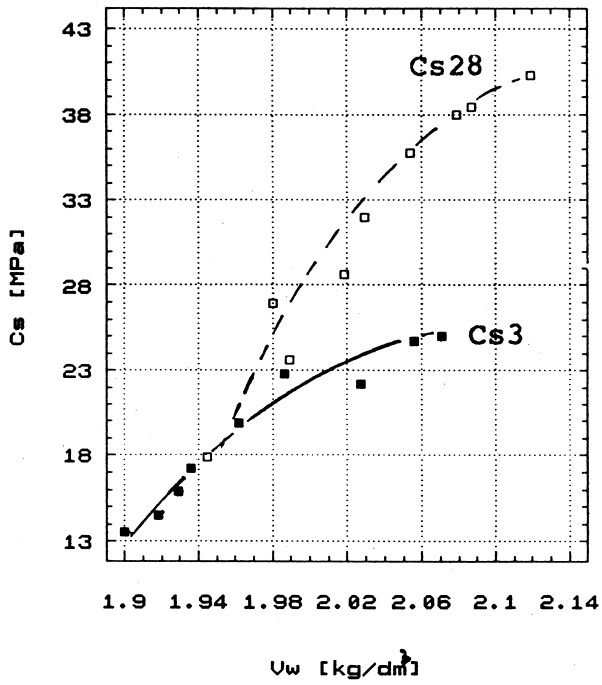

Fig. 3. Compressive strength Cs vs. volume weight of modified samples after 3 and 28 days of hardening.

All additives tested cause growth of air content in fresh mortar as can be derived from Vwm values in Table 1. Volume of air pores is not reduced significantly even after standard compaction of fresh mortar in the moulds.

The air-entraining action of additives tested grows with increases of Mw, Ac, and N_s variables. These results are in accordance with theory of surfactant action. It is known that the foaming power of liquid (water with surfactants) depends mainly on structural and molar parameters, rate of sulphonation of surfactants used, and on their concentration in liquid. The foaming power has a tendency to increase with a decrease in the liquid's surface tension. Ligninsulphonates are surfactants. The surface tension of mixing water also decreases with increasing content of ligninsulphonate fractions in constant dose of additive (here represented by Ac) and is influenced by the rate of their sulphonation (here represented by N_s). Increases of both variables have a tendency to support the air-entraining action of additives and stabilisation of air pores in mortar.

The heat evolution is retarded by the action of all additives tested in the chosen dose 0.5%. Retarding action of additives decreases with increasing Mw, Ac, and N_s parameters in Fig. 2. This effect may be caused by the variable content of minor low molar compounds (mainly reducing compounds and saccharides) in additives. Saccharides particularly have strong retarding action as was

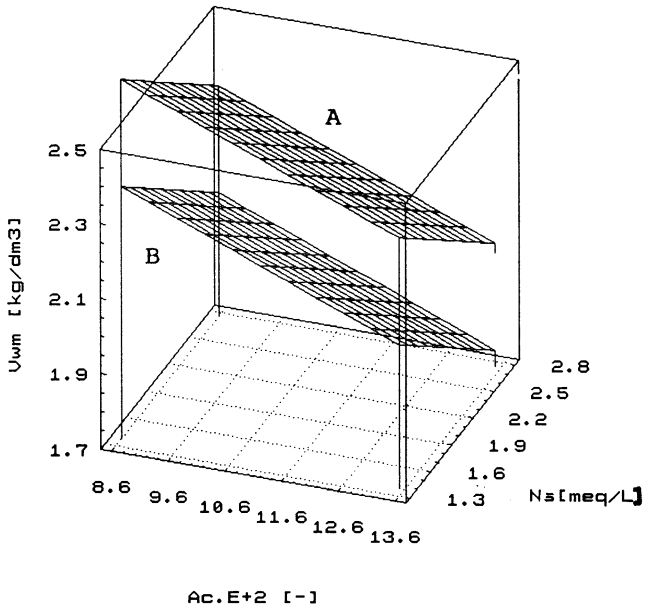

Fig. 4. Volume weight of fresh mortar Vwm vs. absorbance Ac, sulphonation characteristic N_s, and molar weight Mw of additives tested. (A) Mw = 1,295 (g/mole); (B) Mw = 13,015 (g/mole).

proven by number of published observations. The highest content of low molar compounds is in permeate and the lowest is in retentate. Therefore the retarding action of permeate is significantly higher, as can be derived from Fig. 2A and B.

The compressive strength of modified mortars or concrete depends on volume weight of samples. The change of air content in the samples manifests itself mainly by a change in their volume weight Vw. The results of regression analysis between Vw and Cs showed that Cs3 is influenced by Vw3 changes by about 92% and Vw28 influences the Cs28 changes by about 95%. Other parameters (variables) not included into regression analyses influence the compressive strength by about 8% (Cs3) and about 5% (Cs28). The relationships are shown in Fig. 3.

The results presented here not only confirm those in Part II of this work but also provide more detailed information concerning the mutual relationships between greater number of chosen parameters of laboratory-prepared ligninsulphonates and properties of modified samples.

4. Conclusions

1. Very good correlation between independent variables Mw, Ac, N_s, and dependent variables shown in Table 1 were found.
2. The rheological characteristic (plasticity) of modified mortars improves with increase of sorbed molecules on the limiting surface of phases and increase of air content in fresh mortar under the conditions of the tests.
3. The volume weight of mortar samples changes in reverse proportion to air content in the sample. Air-entraining action of additives increases with increase of Mw, Ac, and N_s of additives tested, as can be derived indirectly from the results in Fig. 4.
4. The retarding action of additives on heat evolution up to 24 h decreases with increase of Mw, Ac, and N_s parameters. Relationships (A, valid for Mw of permeate; B, valid for Mw of retentate) in Fig. 2 show that the retarding action of permeate is markedly higher.
5. Compressive strength depends mainly on the volume weight of samples tested.

The following conclusions can be assumed for optimal treatment of waste sulphite liquor for practical use: Retarding effect can be reduced by separation of low molar fractions, mainly saccharides. Minimal retarding action after 24 h have separated fractions with high molar weight and high sulphonation rate. These fractions have also higher plastifying and air-entraining effects. Higher air-entraining action is unfavourable for strength of modified samples. The volume of entrained air can be reduced by compaction of concrete mix in the mould or construction.

The results presented are valuable only for the materials used and for the conditions of the tests.

Acknowledgments

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