Pergamon

Cement and Concrete Research 31 (2001) 1593–1599

CEMENT AND CONCRETE RESEARCH

Influence of MSFC-type dispersant composition on the performance of soluble anhydrite binders

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Received 17 February 2000; accepted 6 July 2001

Abstract

Synthetic soluble anhydrite binders, fluidized with melamine–sulfonate–formaldehyde condensates (MSFC), were investigated by rheological, calorimetric, mechanical and adsorption methods. The degree of sulfonation of the MSFC was found to be a key parameter in dictating its performance as a dispersant. A higher degree of sulfonation reduces the shear yield stress of the binder at early ages (20 min after mixing) but also reduces the subsequent rate of strength development. © 2001 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Natural and synthetic anhydrite binders, and products based on them, have been used in the building industry for a long time. The floor constructions of buildings are one of the most progressive fields of their application because the modified suspension with an anhydrite binder has so called self-levelling property even when water/binder ratio is very low. This technology is very effective. The self-levelling effect can be achieved only when melamine–formaldehyde polycondensate (dose of up to 1% of dry content from the mass of binder) and K_2SO_4 (dose of about 2%) are used. Any other type of organic additive has no equivalent effect on the rheological properties of anhydrite suspensions. The synthetic anhydrite is usually a waste product of the chemical industry. The production of hydrofluoric acid, for instance, is a source of a by-product mentioned as is evident from the following chemical reaction: $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$. The results [3–7] showed that relationships between chosen parameters of additives and properties of specimens with cement binders exist. The existence of similar relationships was presupposed also between parameters of polycondensates and modified specimens with anhydrite binders. The main aim of the tests was the study of interactions between organic and inorganic compounds of modified suspension. The results of the tests may contribute to the explanation of action principles of polycondensates and to the optimisation of their structural characteristics, synthesis and effectiveness.

2. Materials and methods

2.1. Anhydrite

Fresh synthetic anhydrite taken off from the plant of the producer, Spolchemia a.s. Ústí nad Labem, was used for the tests. Anhydrite was stored in hermetic plastic bags during the whole time of experiments. Its total X-ray photograph (apparatus Philips APD 15) is in Fig. 1. The composition of anhydrite is in listed Table 1. Very intensive diffractions of 0.350, 0.285, and 0.232 nm in Fig. 1 indicate that soluble anhydrite ($CaSO_4$ III) is the decisive compound in the specimen tested. The sample contains also a residual very small amount of CaF_2 further calcite and $Ca(OH)_2$ as diffractions of 0.316, 0.302, and 0.490 nm show.

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PII: S0008-8846(01)00609-3

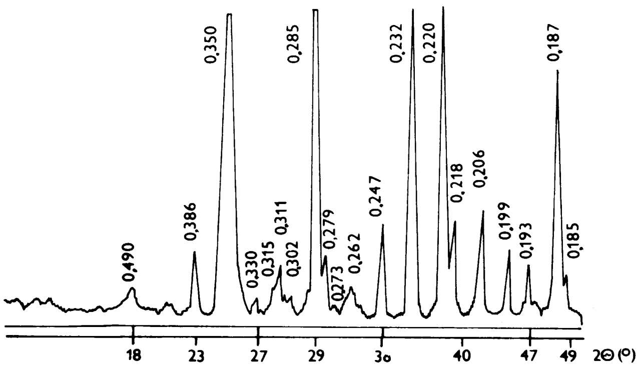

Fig. 1. Total X-ray photograph of anhydrite binder.

2.2. *Polycondensates*

Laboratory-made polycondensates, prepared according to the scheme in publication [1], were used for the tests. Their basic parameters are in listed Table 2. Dose of all polycondensates in all samples was 0.5% of dry content from mass of binder.

2.3. *Catalyst K_2SO_4 p.a.*

The dose of catalyst was uniformly 2% from the mass of binder in all specimens tested.

2.4. *Determination of SO_3Na content*

Using an ion exchanger, SO_3Na content was determined in all additives tested. The sulphogroup content was calculated from the determined amount of NaOH created by titration.

2.5. *Infrared spectra analysis*

The method is described in Ref. [1]. Determined absorbances of concentrates before sorption A_{c805} (triazine ring), A_{c1035} (sulphogroup), and sulphonation rate $\text{Sic} = A_{c1035}:A_{c805}$ are in listed Table 2. The same absorbances of unsorbed portion of polycondensates in the filtrates A_f after 20 min of interaction were determined. The absorbances of sorbed molecules A_s were calculated as follows: $A_{s1035} = A_{c1035} - A_{f1035}$ and $A_{s805} = A_{c805} - A_{f805}$. The rate of sulphonation of sorbed molecules is expressed as a ratio $\text{Sis} = A_{s1035}:A_{s805}$.

2.6. *Sorption*

Gel permeation chromatography (GPC) was used for the study of concentration changes in filtrates. The method of analysis is described in the article [1]. Sorption of organic molecules Sr (%) was calculated using following formula (Eq. (1)).

$$\text{Sr} = \frac{\text{Fc}-(\text{Fm}-\text{Ffa})}{\text{Fc}} \times 100 \qquad (1)$$

where Fc = area of total chromatograph of water solution of MF additive before sorption (cm^2); Ffa = area of total chromatograph of anhydrite binder's filtrate without additive after 20 min of interaction (cm^2); Fm = area of total chromatograph of filtrate suspension with anhydrite + additive after 20 min of interaction (cm^2).

2.7. *Heat evolution*

Heat evolution was tested using an isothermic calorimeter. Temperature during tests was constant at +20 °C.

2.8. *Rheological properties*

The principle of cone method is described in Ref. [2]. Limiting shear stress (Pa) of suspensions (water + additive + binder) was determined by this method. This method is suitable for testing of suspensions having plastic consistency.

Reproducible determination of rheological properties of modified anhydrite (or cement) suspensions having fluid consistency is a serious problem. Probably, the sedimentation of solid particles and activation of suspension makes it hard to achieve the steady-state and reproducible value of measured rheological characteristic. Modification of system (mainly of rotor) does not make it possible to express the rheological properties in standard units of viscosity. Therefore, the principle of standard Ford's method was used for the determination of fluidity of modified mortar suspensions having similar composition as in practice.

Natural sand (<0.5 mm, 67%; 0.5–2 mm, 33%) was used for the tests. The composition of mortar was: anhydrite 0.338 dm^3 (1000 g), sand 0.342 dm^3 (872 g), and water 0.320 dm^3. Dose of polycondensates was 0.5% dry content and K_2SO_4 2% from the mass of binder (both dissolved in the volume of mixing water). Compounds were mixed for 2 min in a laboratory mixer and, subsequently, the viscosity of suspension was tested. The suspension was repeatedly homogenised by hand before the determination of viscosity after 20 min. The criterion of viscosity was the time of outflow of modified suspension (500 ml) from the outlet (diameter 12 mm) of conic vessel.

2.9. *Compressive strength*

Cubes with 25-mm edges were prepared from suspensions having water/binder ratio = 0.31, polycondensates 0.5%, K_2SO_4 = 2%. The suspensions had fluid consistency. Specimens (4 × 4 × 16 cm) were prepared also from mortar

Table 1
Chemical composition of anhydrite

Ignition loss (%)		Compound (%)								
230 °C	600 °C	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
0.8	1.13	2.36	0.31	0.17	0.32	40.08	0.06	0.05	0.10	54.54

Table 2
Basic parameters of polycondensates (concentrates)

Sample	Sulphonation (min)	Concentration (%)	Sic (–)	SO_3Na (%)	CH_2O (%)	Ac805 (–)	Ac1035 (–)
MF 53*	60	19.78	1.803	16.00	0.99	0.260	0.468
MF 54	75	19.31	1.624	15.05	1.04	0.286	0.465
MF 55	90	19.65	1.850	11.76	0.82	0.228	0.422
MF 56	105	19.80	1.860	10.81	0.62	0.252	0.470
MF 57	120	19.34	2.000	9.22	0.52	0.233	0.468
MF 58*	45	19.41	1.829	19.74	1.17	0.242	0.433
MF 59*	60	19.38	0.958	12.50	0.72	0.289	0.277
MF 61	90	20.71	2.201	12.71	0.44	0.308	0.678
MF 62	75	20.45	2.160	10.63	0.45	0.229	0.495
MF 63	105	20.40	2.041	10.25	0.46	0.241	0.492
MF 64	120	20.04	1.927	12.95	0.51	0.261	0.503
MF 65*	45	20.24	2.000	16.67	0.79	0.273	0.546
MF 66*	60	19.95	1.513	10.90	0.50	0.261	0.395
MF 67*	45	20.02	1.298	15.90	0.82	0.325	0.422

after determination of its viscosity. The same tendency of relationship was obtained as in Fig. 2.

2.10. Regression analysis

The computer program Statgraphics 2 (Statistical Graphics, USA) was used. Coefficient of multiple determination Rd of relationships tested was determined in this way. Following limits were chosen for the judgement of Rd significance [8]: Rd < 30% — low or any relationship; Rd 30–60% — medium good relationship; Rd > 60% — very good relationship between tested variables exists.

3. Evaluation of results

3.1. Stability of polycondensates

Previously not included results showed that polycondensates change their parameters with time of storing. Mainly, increase in molar weight, viscosity and dispersivity was observed. The viscosity of cca 20% water solution of polycondensates (usual concentration of industrial products) prepared increases proportionally with increase in molar weight. Subsequent experiments showed that time of sulphonation is the most decisive parameter of synthesis influencing the changes in viscosity (and proportionally of molar weight) with time of storing. Those relationships valuable for all time of sulphonation used are presented in Fig. 3 for chosen polycondensates from Table 2 for illustration. The viscosity of specimens MF 53, MF 58 (time of sulphonation 45 and 60 min) is very high after 200 days of storing, and it was still increasing up to 1 year of storing. The viscosity of both polycondensates was not measurable by Ford's method after 360 days of storing (usual guarantee term of industrial products) because the specimens had gelatinous form. The viscosity of samples prepared with time of sulphonation of 75–120 min increases between 200 and 360 days only moderately, and all polycondensates remain fluid. All additives in Table 2 used for the preparation of tested suspensions were therefore stored after synth-

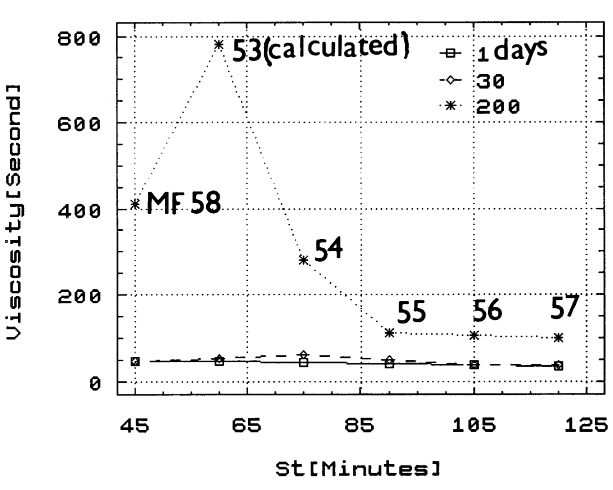

Fig. 2. Relationship between compressive strength of modified specimens after 24 h of hydration and sulphonation rate of polycondensates.

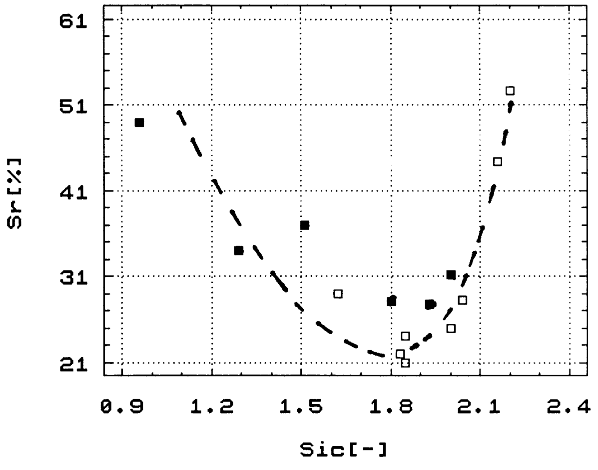

Fig. 3. Relationships between time of sulphonation and viscosity of polycondensates (Ford's method, outlet 2.5 mm) after different times of storing.

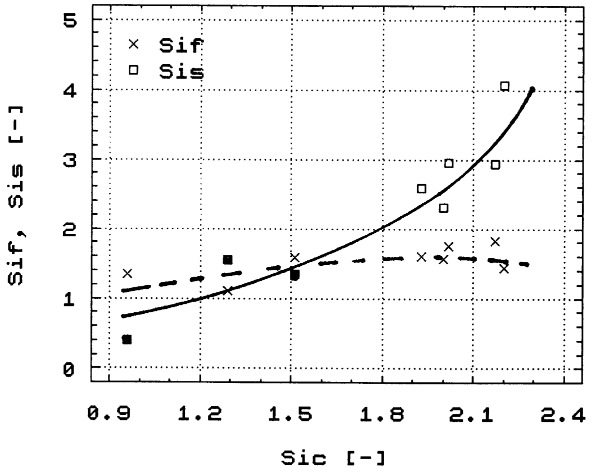

Fig. 4. Relationship between relative sorption Sr after 20 min and sulphonation rate of polycondensates Sic. □—time of sulphonation 75–120 min.

esis in a refrigerator (– 15 °C) during the whole time of the tests. Relationships between Sic of all polycondensates (Table 2) and parameters of modified specimens with anhydrite binder exist, as is demonstrated in Figs. 4 and 5. For the unfavourable viscosity changes, the attention was focused on the testing of polycondensates having long-term stability (sulphonation time 75–120 min—eight polycondensates). Those results are presented in Figs. 6–13.

3.2. Sorption affinity of polycondensates

Sorption of organic MF molecules is selective, and medium molar fractions are preferably sorbed out in the early stage of hydration according to our previous result [1]. The results in Fig. 3 show that a relationship between Sic (0.96–2.2) and sorption after 20 min exists. For stable polycondensates having sulphonation time of 75–120 min, a corresponding range of Sic values (1.624–2.2) exists.

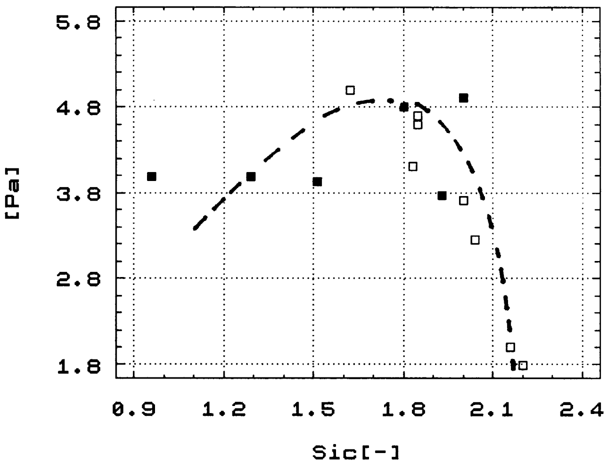

Fig. 5. Relationship between limiting shear stress of modified suspensions after 20 min of hydration and sulphonation rate Sic of polycondensates. Water/binder ratio = 0.25. □—time of sulphonation 75–120 minutes.

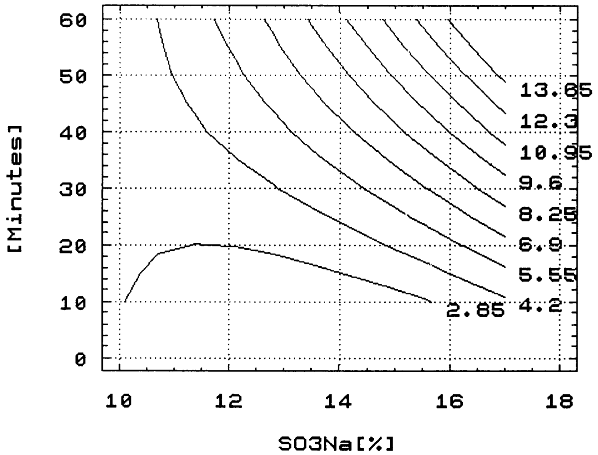

Fig. 6. Limiting shear stress (Pa—numbers in the figure) of modified anhydrite suspensions versus time of hydration and sulphogroup content in polycondensates used. Water/binder ratio = 0.25. Rd = 65.2%.

The sorption increases proportionally with the increase in Sic in this range.

The results in Fig. 4 indicate that the differences between sulphonation rate of sorbed Sis and unsorbed molecules of polycondensate-tested Sif markedly increase with the increase in Sic in the range about 1.6–2.2. The fractions of molecules having high content of sulphogroups are preferably sorbed out from the intergrain solution of modified suspensions.

3.3. Plastifying effectiveness of polycondensates

The limiting shear stress of modified suspensions decreases proportionally with the increase in Sic in the range 1.6–2.2 as is shown in Fig. 5. The similar tendency can be observed in Fig. 7 in the Sic range 1.6–2. The differences corresponding to Sic (2–2.2) in Figs. 5 and 7

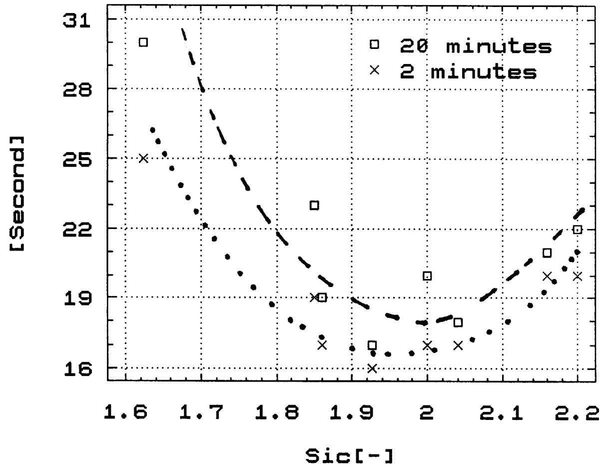

Fig. 7. Influence of sulphonation rate of polycondensates on the viscosity of modified mortars with anhydrite binder after 2 and 20 min of hydration. Water/binder ratio 0.32.

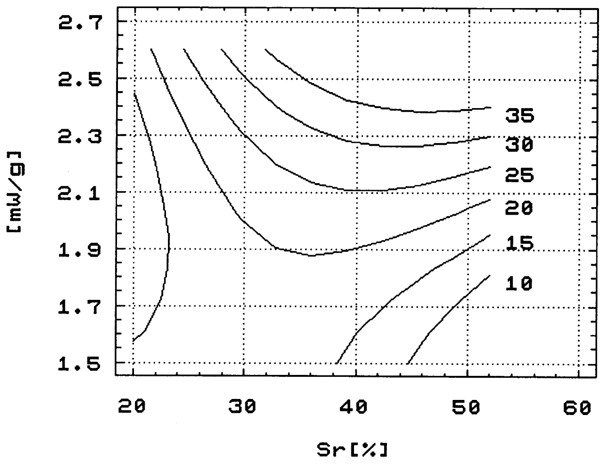

Fig. 8. Viscosity of modified mortars with anhydrite binder (s — numbers in the figure) versus relative sorption Sr and intensity of heat liberation after 20 min of hydration. Rd = 57.9%.

are probably due to the difference in composition of suspensions. The influence of polycondensates on the setting and deterioration of workability with time of hydration of modified suspensions is important for practice. Regression analysis of different variables showed that the highest value of the Rd coefficient was obtained when variables presented in Fig. 6 were tested. The results indicate that the increase of the SO_3Na group in polycondensates supports the creation of bases of solid structure and, therefore, it supports the increase of limiting shear stress in the early time of hydration. Polycondensates with the lowest content of the SO_3Na group have the lowest accelerating effect on setting of modified suspension up to 60 min of hydration and vice versa.

The rheological characteristic's changes of a suspension with anhydrite or cement binder after a certain time of early hydration depend on many variables. They may be, if some simplification is accepted, divided into two groups. The first group contains variables contributing to deterioration, and the second one contains variables supporting the improvement of viscosity or workability. Additives influence the proportions between those variables and therefore also the rheological characteristic changes. The heat liberation (mW/g, J/g) can be regarded as a measurable parameter representing and indicating the changes of proportions between free and bond water (physically or chemically) and also the rates of hydration and creation of solid structure and bonds between particles. The repulsive forces, under the same other conditions, grow proportionally with the increase in the sorbed amount of organic molecules on the surface of solid parti-

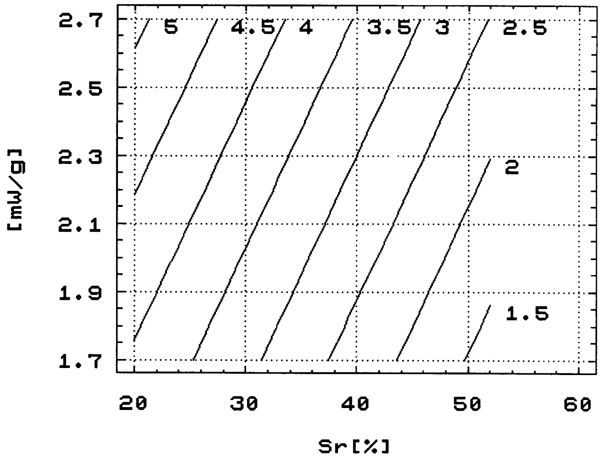

Fig. 9. Limiting shear stress of modified suspension (Pa — numbers in the figure) of anhydrite binder after 20 min of hydration versus sorption Sr and intensity of heat liberation. Rd = 83.36%.

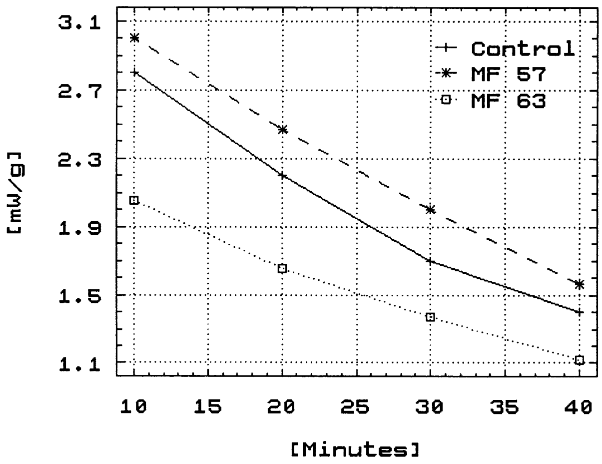

Fig. 10. Intensity of heat liberation of control and modified samples with two different polycondensates versus time of hydration.

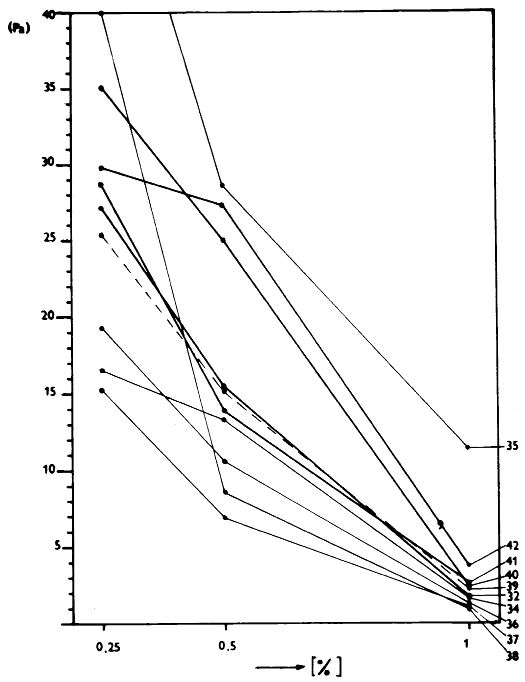

Fig. 11. Relationship between limiting shear stress of suspensions after 20 min of hydration and dose of different laboratory made polycondensates.

cles. More detailed information concerning that problem are in publication [7].

Regression analysis of variables Y = rheological characteristic, X_1 = sorption Sr, X_2 = intensity of heat evolution — all after 20 min of interaction — showed that very good correlation between tested variables exists. Results are in Figs. 8 and 9.

The courses of relationships differ, but they indicate the same tendency in both figures. The limiting shear stress and time of outflow of suspensions after 20 min tend to increase with the increase of heat liberation and tends to decrease with the increase of sorbed molecules on the surface of solid particles.

The results in Fig. 10 indicate that polycondensates may support the retardation or acceleration of the heat liberation in the early time of hydration and proportionally may influence the variables contributing to improvement or to deterioration of specimen's consistency. The specimens modified by MF 57 and MF 63 represent upper and lower limits of heat evolution. The determined values of specimens with remaining polycondensates from Table 2 change between those limits.

It seems that the plastifying effectiveness of a polycondensate depends on its influence on the proportions between repulsive forces and variables supporting the deterioration of consistency of modified suspension.

The results indicate that following different ways may be chosen for the increase in the plastifying effect of polycondensates.

(1) Production of polycondensates using optimal parameters of synthesis.

(2) Gradual increase of an additive's dose. The results in Fig. 11 show that the plastifying action of quite different laboratory made MF polycondensates depend substantially on their dose. Marked difference in limiting shear stress can be observed in the range 0–0.5% of dry content of polycondensates from the mass of binder. The differences are minimal when a dose of 1% is used (except sample 35). The increase in polycondensates' dose supports the sorption in accordance with Langmuir's law and the intensity of repulsive forces between solid particles on the one hand. The growing concentration of molecules on the surface of solid particles and in the intergrain solution retards the interaction of solid particles in the suspension and creation of bases of solid structure on the other hand. Both actions contribute to the decrease in friction forces and to the improvement of consistency.

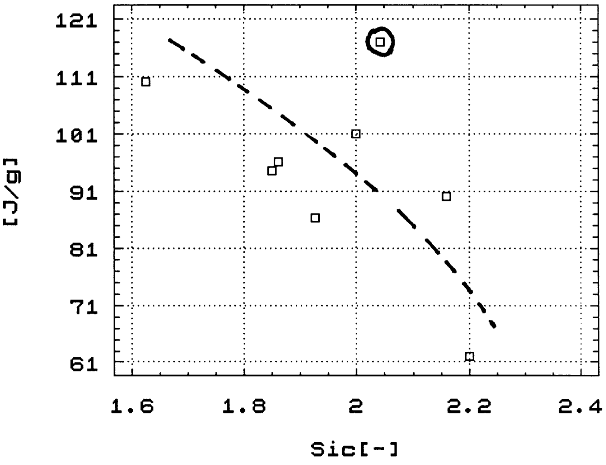

Fig. 12. Relationship between integral value of heat liberation after 24 h and sulphonation rate of polycondensates.

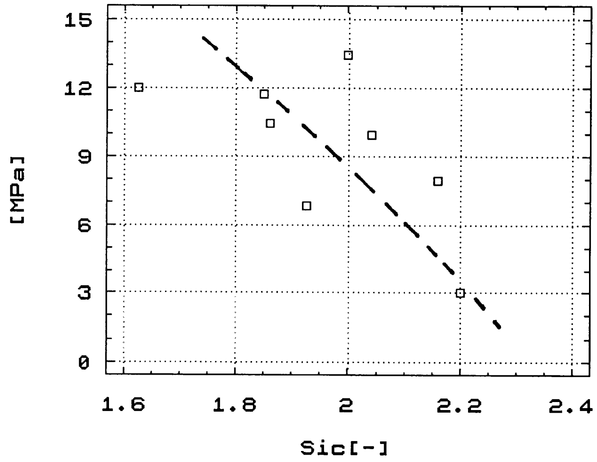

Fig. 13. Relationships between sulphonation rates of sorbed Sis and unsorbed organic molecules Sif in filtrate after 20 min of interaction and sulphonation rate of polycondensates. □ — time of sulphonation 75–120 min.

3.4. Heat liberation and the compressive strength

The results in Figs. 12 and 13 show that both parameters tend to decrease with increasing Sic value.

The results in Figs. 5, 7 and 13 show that the increase in Sic of polycondensates contributes to the improvement in their plastifying effectiveness but results in the decrease in compressive strength of modified specimens.

4. Conclusions

1. The degree of sulphonation of the melamine–sulfonate–formaldehyde condensates (MSFC) appears to be the most important parameter in determining its effectiveness as a dispersant in soluble anhydrite binder system.
2. The dispersant effect requires adsorption of the polymer into the surface of the binder phase. This can be increased either by changing the MSFC composition or by increasing the dosage.
3. The compressive strength at 24 h correlates with the total heat liberated.

4. The more highly sulfonated the MSFC, the more it reduces the rate of compressive strength development (at equal dosages).

Acknowledgments

This research was supported by grants 104/99/565 and 103/00/1185 from the Grant Agency of Czech Republic. The authors are grateful for the support.

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