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A contribution to the explanation of the action principles of organic plasticizers

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Abstract

Suspensions of laboratory cement modified with 0.25% to 1.5% of MSFC-type dispersant were prepared. The sorption of organic molecules, viscosity and integral value of heat liberation after 5, 10 and 20 min were determined. Regression analysis showed that the viscosity changes of suspension are influenced by about 86% by the changes of sorption and heat liberation.

Keywords: Calorimetry; Rheology; Adsorption; Admixture

1. Introduction

The effectiveness of plasticizers on the rheological parameters of concrete mixes is tested according to the standard specifications of industrial countries, up to 30 min. This time seems to be sufficient for the filling of moulds and compaction of mixes in practice. Therefore, our experiments were focused to this time period.

The rheological properties of cement suspensions and the influence of dispersants on them have been studied by a number of authors (for instance, [1–13]) for a long time. Therefore, many questions remain without explanation. The substantial results can be shortly assumed as follows.

The water/cement ratio, derived parameter-hydraulic radius, dose of dispersants in a mix and parameters of cement and additives influence the viscosity of suspensions predominantly. Changes of the potential ζ of cement particles are influenced by the concentration and parameters of additives. But a commonly accepted relationship between the potential ζ of cement particles and rheological parameters of modified suspensions has not been found.

The intensity of steric repulsive forces between the charged particles depends on the structure and other parameters of sorbed organic molecules and on their concentration on the surface of cement particles. But relationships between the potential ζ, magnitude of those forces and viscosity of modified suspensions have not been published.

2. Experimental part

2.1. Cement

The mineralogical composition of the clinker, determined by optical microscopy [14], was the following (%): C_3S=65.3, C_2 S=8.7, C_3A=9.1, C_4 AF=16.8 and porosity 3.71%.

Clinker +5% gypsum was ground in a laboratory ball mill. The specific surface of the cement was BET=1.8 m^2/g and Blaine=0.536 m^2/g. Density was 3.104 g/cm^3.

2.2. Additive

The results published [15] indicated that the molar weight of MSFC-type dispersants changes with the time

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of storing. Therefore, the powder form of additive Melment F10X was used for the tests. Fresh solutions of additive were prepared 24 h before the preparation of suspensions. The dose of additive is expressed in percent of dry content from the mass of cement.

2.3. Determination of viscosity

A number of preliminary tests were carried out for the determination of optimal conditions for the tests. The following parameters seemed to be optimal for the best reproducibility of results: water+additive, cement ratio was 0.5. The cement and the solution of additive were homogenized by hand 10 s. Then, the suspension was homogenized using a propeller agitator (400 rotation/min) during 15 s. The suspension was homogenized by hand again before the determination of viscosity after 5 min. Rotary viscometer Rheotest RV (Prüfgerete Werk, Medingen), cone-plate system was used for the tests. The vertex angle of the cone was 150°, D=48.3 s^{-1}. The temperature of the compounds and environment during measurements was constant at 20±0.5 °C (Table 1).

Table 1
Variations of determinations of the cone–plate system used

Number	After 5 min (mPa s)	After 10 min (mPa s)	After 20 min (mPa s)
1	364	408	504
2	330	432	520
3	336	480	510
4	320	412	507
5	305	440	525
6	318	430	512
Average	329	433	513

Additive=0%.

2.4. Calorimetry

The integral value of heat liberation was determined by a calorimeter in isothermal conditions t=+20 °C. The composition of suspensions was the same as for the determination of viscosity.

2.5. Sorption

It was found that the peak of 217 nm from the total UV spectra of additive (apparatus Cecil CE 3041) was optimal for sorption studies. It is distinctive and does not coincide with that of filtrate of cement. Solutions having different concentrations of MSFC additive (concentrates) were analyzed by the method of UV spectra analysis. A linear relationship between the concentration of solutions and the absorbencies was found.

Afterwards, 100 g of cement was mixed with 100 g of a solution additive. The suspension was filtered (glass porous filter pores 0.7–1.3 μm, vacuum filtration) after a chosen time, and the filtrate was subsequently analyzed. The sorbed amount of organic molecules S_r (mg/g) was calculated from formula:

$$S_r = \frac{(C_{rc} - C_{rf})V}{m} \qquad (1)$$

where C_{rc} and C_{rf}—the concentration of the additive before (concentrate) and after sorption, respectively (mg/l); V—the volume of the MSFC solution used for sorption (l); and m—the mass of cement (g).

2.6. Regression analysis

The computer program Statgraphics 7 (Statistical Graphics, USA) was used. For the significance of R^2 (coefficient of multiple determination), the following limits were used [16]: R^2 ≤30%—bad or any correlation; 30–60%—medium correlation; and >60%—very good correlation between tested variables exists.

3. Evaluation of results

Results in Fig. 1 and Table 2 indicate that the sorption-active fractions of organic molecules are sorbed out up to 5 min. Changes of sorption between 5 and 20 min are minimal. It seems that differences are in the limits of the method's reproducibility. The course of relationship in Fig. 1 is linear up to about 0.75%. Further changes of sorption are lower.

Our conception presented is based on the presupposition that changes of the rheological parameters of modified cement suspension depends mainly on the proportional influence of additive on the repulsive forces between the charged particles and on the increase of cohesive forces (hydrates and bonds) between them. The final influence of an additive on the rheological characteristics of suspension depends on the proportional action of those forces. Therefore, the sorption and the integral value of heat liberation were chosen as certain comprehensive parameters (or representatives) of those opposite effects.

We presuppose that the magnitude of all defined, and also of undefined, repulsive forces acting due to the presence of sorbed organic molecules on the surface of solid particles changes proportionally with the sorption characteristic S_r in Fig. 1.

The integral value of heat liberation represents a number of simultaneous partial processes, which are influenced by the organic additives. The changes of proportions between the bound and free water in the hydrating suspension due to the wetting of surfaces, hydration and the creation of new formations are decisive, according our presuppositions.

It is known that the heat liberation of certain cement is a function of time of hydration and can be influenced by additives. Therefore, a regression analysis between the integral value of heat liberation (dependent variable Y) after 5, 10 and 20 min (independent variable X_1) of the control

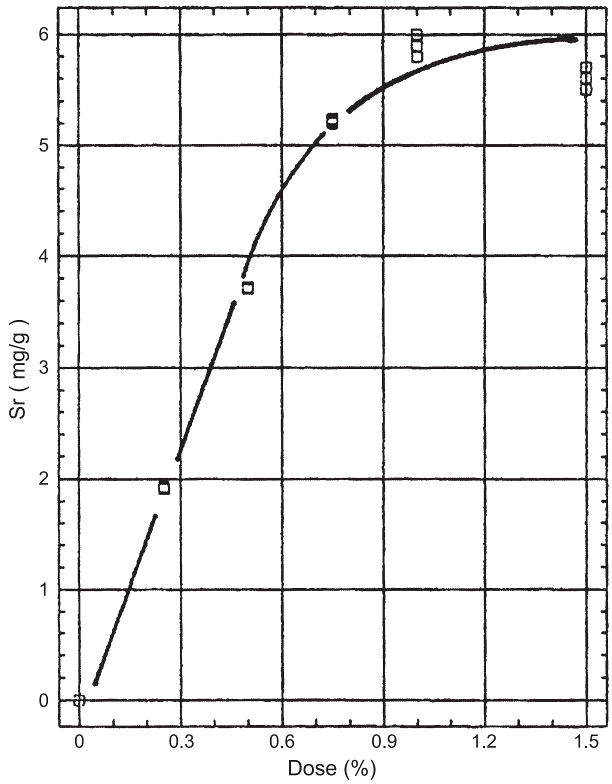

Fig. 1. Relationship between the sorption characteristic S_r, after 5, 10 and 20 min, and the dose of additive.

and modified suspensions and the sorbed amount of organic molecules, S_r (X_2), was carried out. Very good correlation (R^2=95.81%) between the tested variables was found. The courses of lines of relationship in the contour presentation in Fig. 2 show that heat liberation significantly decreases with the increase of S_r value and increases with the time of

Table 2
Basic parameters of suspensions—parameters of regression analyses

Additive (%)	Interaction (min)	Sorption (%)	S_r (mg/g)	Heat liberation (J/g)	Viscosity (mPa s)
0	5	0	0	14.2	329
	10	0	0	14.7	433
	20	0	0	15.2	513
0.25	5		1.91	11.4	192
	10	85	1.92	13.3	288
	20		1.93	14.4	470
0.50	5		3.70	7.1	72
	10	81	3.72	12.3	158
	20		3.74	14.2	322
0.75	5		5.20	6.6	34
	10	76	5.22	11.4	120
	20		5.24	13.7	240
1.00	5		5.80	5.2	29
	10	63	5.90	9.5	72
	20		6.00	13.3	144
1.50	5		5.50	4.9	24
	10	41	5.60	9.0	48
	20		5.70	12.8	120

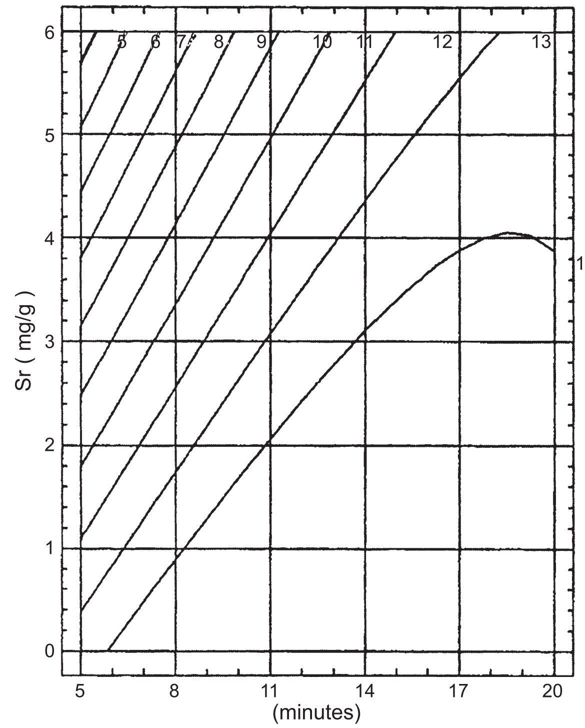

Fig. 2. Influence of sorption S_r and time of hydration on the integral value of heat liberation of modified suspensions (J/g: numbers at lines).

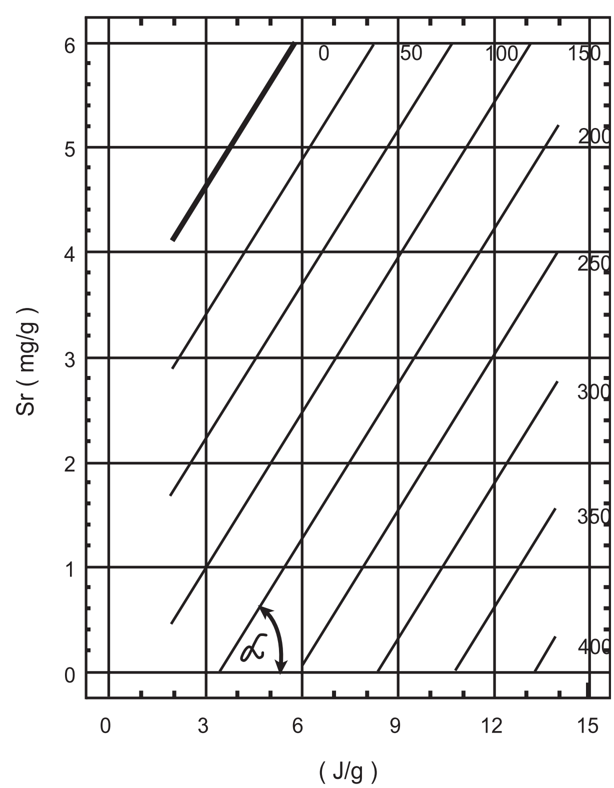

Fig. 3. Influence of sorption S_r and integral value of heat liberation on the viscosity of suspensions (Pa s: numbers at lines).

hydration. The influence of additive tested on the heat liberation is significant.

Very bad or any correlation between the S_r value and the viscosity of suspensions (Table 2) was found. It means that other important variable or variables were not included.

A very good correlation (R^2=86.04%) between the viscosity (dependent variable) and the independent variables—integral value of heat liberation and sorption S_r (after the same time of hydration)—was found when the linear model was used. Those results indicate that chosen independent variables influence the viscosity changes decisively. All other variables not included influence the viscosity by about 14%. The relationship is shown in (Fig. 3). The courses of lines indicate that viscosity decreases with the increase of sorbed amount of organic molecules and increases with the growth of heat liberation. We presuppose that this relationship can be derived for any modified suspensions in general. The changing proportions between the repulsive or cohesive forces due to the action of an additive (as are defined above) will result in the slope of lines (angle α). The following conclusions can be derived for the synthesis of an "ideal" plasticizer:

- The kinetic of sorption should be extremely rapid, and the maximal portion of dissolved molecules should be sorbed out as rapid as possible. The parameters of molecules should be influenced by the parameters of synthesis to reach maximal repulsive forces between the charged fine particles of suspension.
- The contribution of sorbed and unsorbed molecules to the retardation of hydration processes and heat evolution should be as high as possible up to 30 min. Afterwards, the retarding action should be minimal or any.

4. Conclusions

4.1 A very good relationship between the viscosity of modified suspensions, integral value of heat liberation and sorbed amount of organic molecules on the surface of cement particles was found.

4.2 The increase of sorption characteristic contributes to the improvement and that of heat liberation contributes to the deterioration of viscosity.

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