INFLUENCE OF CEMENT PROPERTIES ON RHEOLOGY OF FRESH CEMENT MORTARS WITHOUT AND WITH SUPERPLASTICIZER

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Abstract

Sine qua non in workability of cement binder mixtures (mortars and fresh concretes) designing is the knowledge of the relationships between composition and constituents characteristics, and rheological parameters of mixture. Until recently the influence of cement properties on rheology of cement binder mixtures was considered to be of minor importance. At presents a number of research proves, that influence of cement properties on cement binder mixtures rheology may be significant.

The paper present results of investigation on influence of cement specific surface, C_3A, Na_2O_{eq} and SO_3 content in cement on rheological properties of mortars without and with different type superplasticizers addition. In order to obtain unequivocal relations, laboratory prepared cements were used. Rheology results have been evaluated according to the Bingham model. It was stated in literature that the relationships obtained for mortars can be used in controlling the workability of both mortars and fresh concrete.

It was determined that rheological properties of mortars depend successively on: C_3A content in cement, specific surface of cement, Na_2O_{eq} content in cement and interaction of these factors. No considerable influence of SO_3 content in cement on rheology of mortars was observed. The basic trends of influence of investigated cement properties on rheology of mortars are presented and discussed. The regression models of influence of cement properties on rheological parameters of mortars were developed. These models may be applied to choose appropriate cement or cement – superplasticizer from the workability point of view and what is more for designing workability of fresh cement binder mixtures.

Streszczenie

Warunkiem koniecznym do skutecznego kształtowaniu urabialności mieszanki na spoiwie cementowym (zaprawy lub mieszanki betonowej) jest określenie zależności pomiędzy charakterystykami jej składu i składników a jej parametrami reologicznymi. Wpływ właściwości cementu na reologię zapraw i mieszanek betonowych do niedawna traktowany był jako drugorzędny; szereg obecnie przeprowadzonych badań dowodzi jednak, że jest on bardzo znaczący.

W referacie przedstawiono badania wpływu powierzchni właściwej cementu oraz zawartości C_3A, Na_2O_e i SO_3 w cemencie na właściwości reologiczne zapraw bez i z dodatkiem superplastyfikatorów SNF, SMF i PE. W celu uzyskania jednoznacznych zależności zastosowano cementy przygotowane laboratoryjnie, w których zmieniano tylko badane właściwości. Wpływ cementu na właściwości reologiczne zapraw charakteryzowano poprzez zmiany parametrów reologicznych modelu Binghama - granicy płynięcia i lepkości plastycznej. Ponieważ, jak to wykazano w literaturze, wyniki uzyskane na zaprawach pozwalają na przewidywanie zmian właściwości reologicznych mieszanek betonowych, określone w referacie zależności mogą być wykorzystane do kształtowania urabialności tak zapraw, jak i mieszanek betonowych.

Ze względu na właściwości cementu parametry reologiczne mieszanek zależą przede wszystkim od zawartości C_3A w cemencie, a następnie od powierzchni właściwej cementu, zawartości Na_2O_e w cemencie oraz od interakcji tych czynników. W referacie omówiono ogólne tendencje wpływu tych właściwości cementu na parametry reologiczne zapraw. W badanym zakresie zmienności nie stwierdzono wpływu zawartości SO_3 w cemencie na właściwości reologiczne zapraw. Na podstawie analizy uzyskanych zależności opracowano modele regresyjne, opisujące wpływ właściwości cementu na parametry reologiczne zapraw. Modele te mogą być stosowane w praktyce do wyboru najlepszego ze względu na pożądane właściwości reologiczne mieszanki cementu oraz w projektowaniu urabialności mieszanek.

Keywords: **Cement; Mortar; Fresh Concrete; Rheology; Superplasticizer; Workability.**

1. INTRODUCTION

The definition of workability of cement binder mixtures, that is fresh mortars and concretes, should be considered in terms of the system's state (i.e., the composition of the mixture and the method of processing). This state is determined by the relationship between two factors: the rheological properties of a given cement binder mixture and the forces acting on it during processing [1]. The rheological properties are determined only by the mixture's composition. They characterize its stress – strain behavior. Therefore, workability of cement binder mixture is determined by the reaction of this mixture on the forces acting on it during transport and mechanical processing as the resistance of its structure to these forces [1]. Required workability can be achieved in two ways: rheological properties of mixture are adjusted to the given method and conditions of processing or method and conditions of processing are adjusted to given rheological properties of cement binder mixture. In practice the first method is used. Thus, sine qua non in workability of cement binder mixtures designing is the knowledge of the relationships between composition and constituents characteristics, and rheological parameters of mixture.

The most important factors influencing rheological properties of cement binder mixtures considered are: aggregate type and graining, volume part of cement paste in mixture, w/c ratio, presence, type and properties of admixtures, and laps of time from the end of mixing [1,2,3]. The influence of cement properties on rheology of fresh mortars and concretes was considered to be of minor importance and mainly connected with its water demandness resulting from specific surface area [1,3]. On the other hand, a number of research proves, that composition of cement, particularly C_3A, alkalis, and sulfate content, may also significantly change rheological properties of cement binder mixtures [1,4,5,6,7,8,9]. However, in literature still occurs the insufficiency of systematic researches enabling unequivocal determination of influence nature and assessment of significance of cement individual characteristics influence on mixture rheology, as well as influence of correlation between them. It is mainly because in most recent researches manufactured cements were used. Such cements differ from each other not only in investigated properties, but also in number of other properties. Such uncontrolled differences significantly influence relationships obtained in the researches.

It should be emphasized, that the possibility of making use of adjusting rheological properties of fresh cement binder mixtures of relation obtained in numerous investigations to cement influence on rheology of cement pastes is limited. Rheology of cement pastes and cement binder mixtures differ from each other, and nowadays are treated as separately developing fields of applied rheology [1,4,9,10,11,12]. It should be noted, that in literature related to cement paste there is also insufficiency of investigations making possible unequivocal definition of influence of cement properties on rheological properties of cement paste.

The paper presents results of investigation into influence of cement specific surface, C_3A, Na_2O_{eq} and SO_3 content in cement on rheological properties of mortars without and with different type superplasticizers addition. Superplasticizers were added in order to obtain higher flowability of mortars, while w/c ratio was kept constant. In order to obtain unequivocal relations, laboratory prepared cements were used. Composition and specific surface area of these cements were changed strictly according to assumed research plan, while other properties were kept constant. The influence of cement on rheology of cement binder mixtures was investigated using mortars. It was stated in [4,9,10,13] that the nature of rheological behavior of fresh mortar and concrete is similar, and that mortars can be considered to be a model concrete. The knowledge of influence of cement properties on mortars rheology may contribute to the understanding of rheological behaviour of fresh concrete, and also lead to the possibility of predicting the flow properties of the later from small scale tests on mortars. Thus, the results presented in the paper can be used in controlling the workability of both mortars and fresh concrete.

2. EXPERIMENT DETAILS

2.1. Rheological model and rheological parameters of fresh mortars measurements

It is well documented that fresh mortar behaves as Bingham material, whose properties can be expressed by two fundamental rheological parameters, the yield stress and the viscosity according the formula:

$$\tau = \tau_o + \eta_{pl}\,\dot{\gamma} \qquad (1)$$

where τ (Pa) is the shear stress at shear rate $\dot{\gamma}$ (1/s), τ_o (Pa) is the yield value and η_{pl} (Pa.s) is the plastic viscosity [1,4,7,10,13]. The physical interpretation of yield value is that of the stress needed to be applied to a material in order to start flowing. When the shear stress is higher then yield value, the mix flows and its flow resistance depends on plastic viscosity.

Rheological parameters of fresh mortar can be measured by applying a given shear rate and measuring the resulting shear stress. Because of the nature of rheological behaviour of mortar, the measurements should be taken at no less than two considerably different shear rates. The rheological parameters are determined by regression analysis according to the relation:

$$T = g + N h \quad (2)$$

where T is the shear resistance of a sample measured at rotation rate N and g (N.m) and h (N.m.s) are constants corresponding respectively to yield value τ_o and plastic viscosity η_{pl}. By suitable calibration of the rheometer, it is possible to express parameters g and h in fundamental units. According to [16], in the apparatus like used in this work, $\tau_o = 7.9$ g and $\eta_{pl} = 0.78\,h$, but all results are given below in terms of g and h. The principles of TPWT are presented in existing literature [1,4,17].

It should be underlined that rheological properties of cement pastes and cement binder mixtures (mortars and concretes) differ from each other. During the flow test cement paste reveals plastic characteristics with high degree of nonlinearity, and additionally with high ticsotropic effects [4,11,14,15]. As far as Bingham model is adequate to characterize rheological properties of fresh mortar and concrete, characterization of rheological properties of cement paste demands more complex models. It was demonstrated in [18,19] that rheological properties of cement paste are best described by the following models subsequently: Herschel-Bulkley model, Robertson-Stiff model and Ellis model. At the same time it was stated in [18,19] that Bingham model may be used for characterization of rheological properties of cement paste only in a very wide range.

2.2. Variables and research program

The variable and constant factors in research are presented in Table 1. The range of cement composition changes accepted in tests corresponds to variability of typical commercial cements [20]. The research program was planned in a manner making it possible to define, on the basis of analysis of variance (ANOVA), significance and hierarchy of significance of influence of cement properties on the rheological properties of mortars without and with superplasticizer. Research program is presented in Tables 2 and 3. Particular series of tests for individual blocks were performed on the basis of central composite 2^3 + star experiment design accepting polynomial of a second degree

Table 1.
Variable and constant factors in research

Factor		Levels of factor
Varaible factors	Cement specific surface Swc	320, 370, 420 m^2/kg
	C_3A content in cement	2, 7, 12%
	Na_2O_{eq} content in cement	0.3, 0.7, 1.1%
	SO_3 content in cement	2.5, 3.0, 3.5%
Constant factors	Sand type and cement to sand ratio	Mortar acc. PN EN 196 - 1 but of w/c = 0.55
	w/c ratio	w/c = 0,55
	Temperature	20°C

Table 2.
Research program

Block	w/c ratio	SP type and content [%]	S_{wc} [m^2/kg]	Cement composition [%]		
				C_3A	Na_2O_{eq}	SO_3
1	w/c = 0.55	-	320	2, 7, 12	0.3, 0.7, 1.1	2.5, 3.0, 3.5
2			370			
3			420			
4		PE - 1%	320			
5			370			
6			420			
8		SNF - 2%	370			
9		SMF - 2%	370			

Table 3. Research program for individual block according to Table 1

Number of test	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
C_3A content	2	2	2	2	2	2	2	7	7	7	7	7	2	2	2	2	2	2	2
Na_2O_{eq} content	0.3	0.3	0.3	0.7	1.1	1.1	1.1	0.3	0.7	0.7	0.7	1.1	0.3	0.3	0.3	0.7	1.1	1.1	1.1
SO_3 content	2.5	3	3.5	3	2.5	3	3.5	3	2.5	3	3.5	3	2.5	3	3.5	3	2.5	3	3.5

Table 4. Properties of laboratory prepared cements

Cement	Cement composition [%]											Cement specific surface $[m^2/kg]$
	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O_{eq}	SO_3	C_3S	C_2S	C_3A	C_4AF	
1	22.4	66.6	4.3	5.5	0.82	0.3 0.7 1.1	2.5 3.0 3.5	60	19	2	1	320 370 420
2	23.3	66.6	4.7	3.5	0.91	0.3 0.7 1.1	2.5 3.0 3.5	52	28	7	9	320 370 420
3	20.3	65.8	6.6	3.1	1.58	0.3 0.7	2.5 3.0 3.5	58	15	12	10	320 370 420
4	21.2	66.3	6.4	2.8	2.70	1.1	2.5 3.0 3.5	59	16	12	9	320 370 420

Table 5. Properties of cements used in control tests

Cement	Cement composition [%]											Cement specific surface $[m^2/kg]$
	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2Oe	SO_3	C_3S	C_2S	C_3A	C_4AF	
CEM I 32.5	19.50	61.5	5.80	2.80	1.37	0.83	2.7	60	19	11	9	329
CEM I 42.5	20.02	66.94	4.46	3.82	1.87	0.81	2.5	63	10	5	12	350
CEM I 42.5	20.38	64.06	4.77	2.50	2.14	1.10	2.5	60	13	8	8	379
CEM I 42.5	22.55	64.30	4.39	2.98	1.02	0.65	2.5	47	30	7	9	356
CEM I 42.5	21.61	64.41	4.46	2.24	1.25	0.40	3.1	55	21	9	7	383
CEM I 52.5	20.7	64.8	5.1	2.6	1.2	0.75	3.5	57	21	9	9	420

Table 6. Properties of superplasticizers

SP	Base component	Density $[g/cm^3]$	Concentration [%]
SNF	naphthalene sulphonate acid	1.09	26
SMF	melamine sulphonate acid	1.09	36
PE	polycarboxylate ether	1.09	17

Table 7. Composition of mortar (g/batch)

w/c	Cement	Sand	Water	SP type and content
0.55	450	1350	247.5	Acc. Table 2

with second order interactions as a response function. Such a program makes it possible to determine regression joining rheological parameters of fresh mortar with properties of cement – cement specific surface and C_3A, Na_2O_{eq} and SO_3 content in cement.

2.3. Materials and mixes

Cements of CEM I type, laboratory prepared by Mineral Building Materials Institute in Krakow were used for the investigations. Their main properties are presented in Table 4. Calcium sulphate in these cements was added in the form of gypsum. Commercial cements used for control tests are presented in Table 5. Properties of used superplasticizers are presented in Table 6. In order to eliminate influence of type and grading of sand on rheological properties of mortars the used sand was EN 196-1:1994 CEN model sand (2 mm max.). The mixture proportions of mortars were based on standard mortar proportioning according to EN 196-1:1994 but with w/c ratio changed to 0.55. The w/c ratio level was matched experimentally so that the specification of the influence of cements characteristics on mortar rheological parameters both with and without the superplasticizer. The necessity of the mortars of such high w/c ratio usage is the consequence of: measuring range of Viskomat PC rheometer, high sand to cement ratio in the standard mortar and high sand waterdemandness; the influence of last two effects on rheology of cement mixtures was thoroughly discussed in [9]. Mixture proportions are shown in Table 7.

Figure 1.
Viskomat PC and its measuring element

2.4. Mortar mixing and testing procedures

The mixer and mixing procedure were compliant with EN 196-1:1994; superplasticizers were added with water. After the end of mixing, the samples of mortars were transferred to Viskomat PC rheometer (Fig. 1) and tested according to the procedure shown in Fig. 2. This procedure roughly simulates the process of transport of concrete mix in a truck concrete mixer. Because the measurement at the constant velocity of the impeller rotation enables only the investigation of shear resistance (which at a given speed consists of yield value and plastic viscosity), at 10 and 60 minutes the rotation speed was changed from 120 to 20 1/min to define the rheological parameters from flow curves. The rate of sample segregation during measurement was checked testing differences in grading between upper, bottom, inner and outer parts of the sample. It was stated in [9] that differences in sample grading are in most cases lower then 5% and never exceed 10% when the shear resistance T of sample is higher then 10 N mm at rotation speed N = 60 1/min. Thus, basing on obtained results, it is possible to state that danger of segregation of mortar sample during the test is low. The correlation coefficients calculated from the flow curves used to determine rheological parameters of the mixes are in range of 0.95-0.99 with less than 5% failing below 0.90. The mean relative errors of parameters g and h determination are respectively 5.4% and 8.4%. They are in the same range as in other researches and prove that Bingham model is adequate to describe rheological properties of mortars. In the research range effects of segregation were not observed.

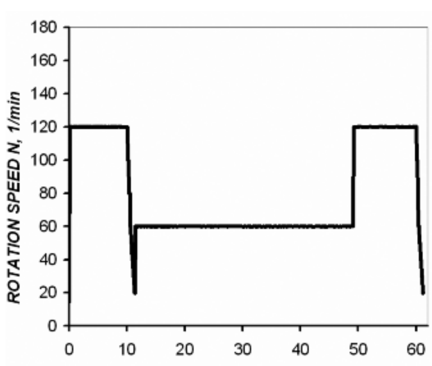

Figure 2.
Measurement of rheological parameters of mortars

- Start of measurement – speed 120 rev/min.
- Speed held constant for 10 min at 120 rev/min.
- Measurement of torque at decreasing speed 120-100-80-60-40-30-20 rev/min. Total test cycle time – 70 s.
- Speed held constant for 39 min at 60 rev/min.
- Increase of speed to 120 rev/min. Speed held constant for 10 min.
- Measurement of torque at decreasing speed 120-100-80-60-40-30-20 rev/min. Total test cycle time – 70 s.
- End of measurement. Total test cycle time – 3620 s.

3. THE INFLUENCE OF CEMENT PROPERTIES ON RHEOLOGICAL PARAMETERS OF MORTARS

The influence of cement specific surface and C_3A, Na_2O_{eq}, content on rheological properties of mortars are shown in Figures 3 and 4. The analysis of variance (ANOVA) of influence of these factors on rheological parameters of mortars are presented in Table 9.

On the ground of obtained results it is possible to state that yield value g and plastic viscosity h of mortars depend successively on C_3A content in cement,

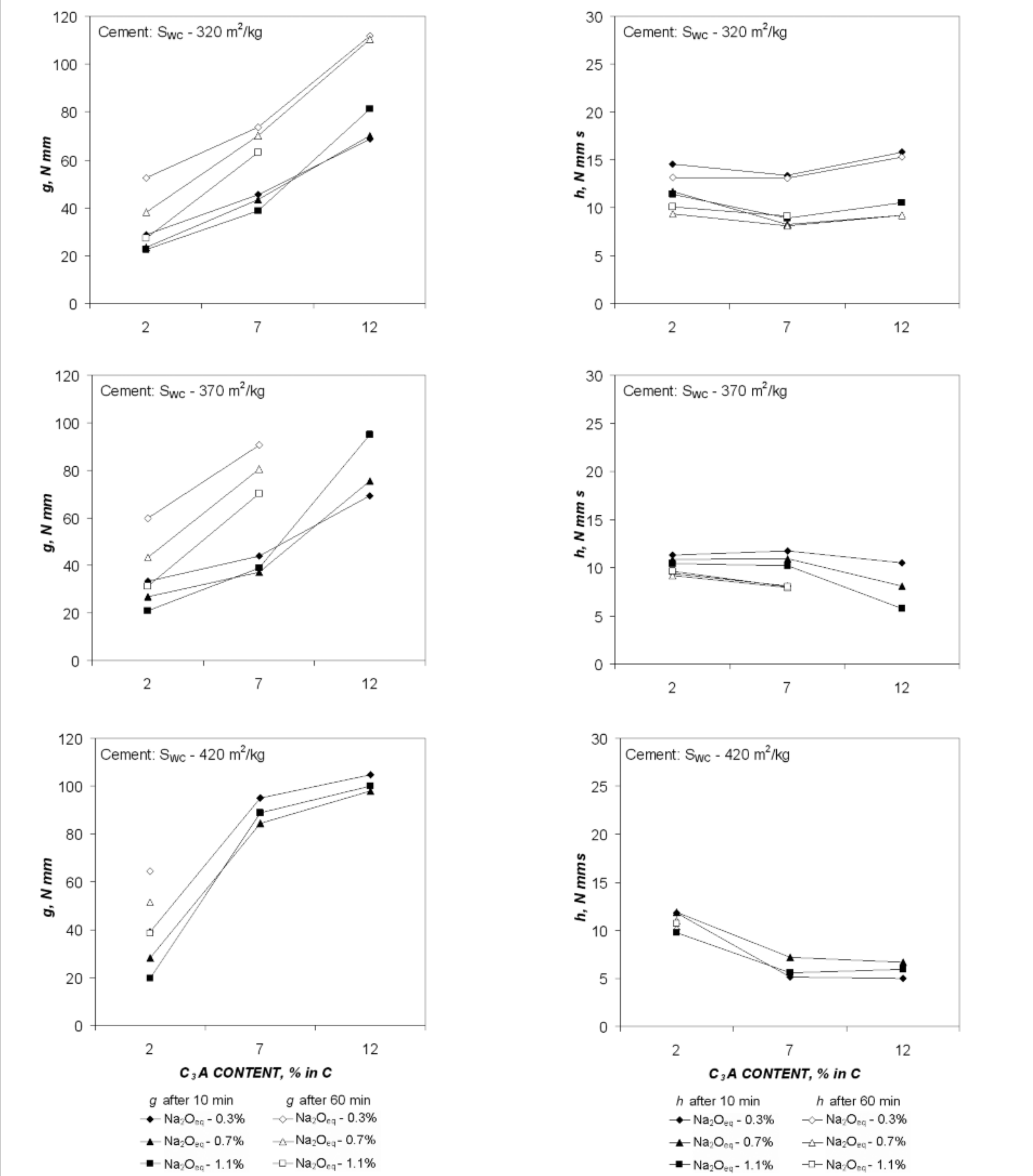

Figure 3.
The effect of cement specific surface S_{WC} and C_3A and Na_2O_{eq} content in cement on rheological parameters of mortars

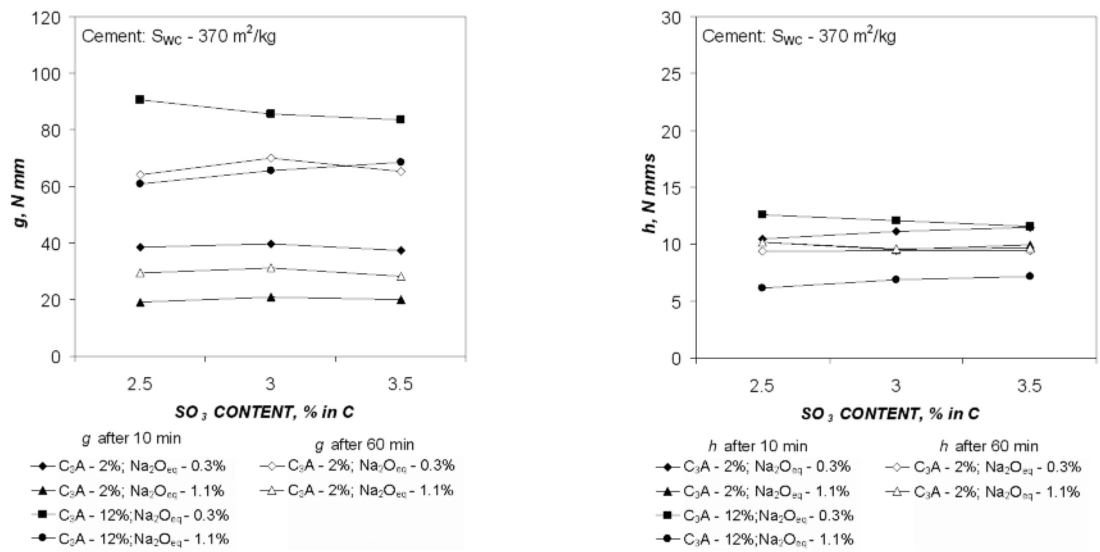

Figure 4.
The effect of SO_3 content in cement on rheological parameters of mortars

Table 8. Analysis of variance of influence of cement specific surface and C_3A. Na_2O_{eq} and SO_3 content in cement on rheological parameters of w/c = 0.55 mortars

Source of variation	g after 10 min		h after 10 min	
	F-ratio	Significance level	F-ratio	Significance level
A: Cement specific surface S_{wc}	15.021	0.000	26.838	0.000
B: C_3A content	187.591	0.000	8.077	0.001
C: Na_2O_{eq} content	0.421	0.660	3.004	0.061
D: SO_3 content	0.180	0.836	0.053	0.949
AB	9.412	0.000	7.654	0.000
AC	4.859	0.003	3.614	0.013
AD	0.413	0.798	0.689	0.604
BC	4.335	0.005	0.442	0.778
BD	0.509	0.730	0.717	0.586
CD	1.519	0.216	2.460	0.121

Table 9. Analysis of variance of influence of cement specific surface and C_3A. Na_2O_{eq} and SO_3 content in cement on rheological parameters of w/c = 0.55 mortars with PE superplasticizer

Source of variation	*g* after 10 min		*h* after 10 min	
	F-ratio	Significance level	F-ratio	Significance level
A: Cement specific surface Swc	0.324	0.725	1.452	0.246
B: C_3A content	176.353	0.000	10.169	0.000
C: Na_2O_{eq} content	3.275	0.048	0.741	0.483
D: SO_3 content	0.589	0.560	2.345	0.109
AB	6.798	0.000	6.452	0.000
AC	6.188	0.001	1.088	0.376
AD	0.285	0.886	1.058	0.390
BC	2.920	0.033	2.681	0.046
BD	0.400	0.807	1.784	0.152
CD	1.095	0.372	2.258	0.080

cement specific surface and interaction of these two factors. Influence of Na_2O_{eq} content in cement on both rheological parameters is generally weak, and appears mostly in case of cements of low cement specific surface and high C_3A content. It was found that the influence of SO_3 content in cement on rheological parameters of mortars is insignificant. The lack of influence of SO_3 on rheology of tested mortars does not mean that influence of SO_3 content is always insignificant. It means that when SO_3 content in cement is properly matched (in range from 2.5% to 3.5%), other characteristics of cement are decisive for rheological parameters of mortars. However, in case of cements of high C_3A content, changes in SO_3, content may cause clear variations in rheological parameters of mortars (Fig. 4).

Yield value g increases while plastic viscosity h of mortars decreases with increasing C_3A content in cement. Similar effect causes increasing cement specific surface. Range of changes of rheological parameters of mortars increases with increasing cement specific surface and C_3A content in cement. This effect clearly proves synergistic influence of cement specific surface and C_3A content in cement on rheological parameters of mortars.

Nature and range of influence of Na_2O_{eq} content in cement varies depending on C_3A content in cement and cement specific surface showing unequivocal tendencies. Nevertheless, in case of mortars with cements of S_{wc} = 320 and 370 m^2/kg decrease in Na_2O_{eq} in cement may cause significant, even double increase of plastic viscosity *h*.

Observed for mortars with S_{wc} = 370 and 420 m^2/kg cements rapid increase in shear resistance T with time made measurement of rheological parameters of these mortars after 60 min impossible. Thus, influence of cement properties on changes of rheological parameters with time was studied only for mortars with cements of S_{wc} = 320 m^2/kg. Increase in shear resistance T with time of these mortars is mainly the effect of increase in yield value *g* with time, because simultaneously occurring changes in plastic viscosity *h* are low and may be neglected. Range of yield value g increase with time increases two times with C_3A content in cement increasing from 2 to 12%. Influence of Na_2O_{eq} content in cement on changes in yield value g with time is usually insignificant. Only in case of mortars with cements containing 2% of C_3A increase in Na_2O_{eq} content in cement significantly, even three times, decreases range of yield value *g* increase with time.

4. THE INFLUENCE OF CEMENT PROPERTIES ON RHEOLOGICAL PARAMETERS OF MORTARS WITH SNF, SMF AND PE SUPERPLASTICIZERS

The influence of cement specific surface and C_3A, Na_2O_{eq}, content on rheological properties of superplasticized mortars is shown in Figures 5, 6, 7 and 8. The analysis of variance (ANOVA) of influence of these factors on rheological parameters of mortars with PE superplasticizer are presented in Table 10.

Superplasticizer addition decreases values of both rheological parameters of tested mortars. Effectiveness of PE type superplasticizer is clearly higher then of SNF and SMF type superplasticizers. It is worth noting, that effect of PE and SNF addition, expressed as relative decrease of yield value g, is the higher the higher content of C_3A in cement and cement specific surface is. It is also worth noting, that

Table 10.
Regression and correlation coefficients for equations (3) and (4) for mortars without and with superplasticizer PE

Series	g & h	G/H	A	B	C	D	AB	AC	AD	BC	BD	CD	AA	BB	CC	DD	R^2
w/c = 0.55 without SP	g_{10}	727.440	-5.627	3.527***	122.23	178.315	0.0007	-0.2861*	0.0043	0.478	-0.873	-6.322	0.0080	0.319	-9.278	-28.438	0.950
	h_{10}	-72.545	0.562***	-1.019*	-39.90***	3.655	-0.0041*	0.0624**	0.0035	0.088	0.266	2.644	-0.0008*	0.106	3.229	-1.405	0.865
w/c =0.55 SP PE	g_{10}	18.931	-0.587	7.086***	28.87	48.604	-0.0111	-0.1474	-0.0991	-1.298	0.637	10.125	0.0014	-0.010	-2.444	-3.384	0.939
	h_{10}	-26.860	0.038	-1.371	-0.98	20.414	0.0028*	-0.0123	-0.0057	0.165	-0.151	-0.213	0.0000	0.043	3.260	-2.834	0.820

*** - significance level = 0.001; ** - significance level = 0.01; * - significance level 0.05

yield value g of mortars with 7 and 12% C_3A cements and with SMF superplasticizer after already 10 min is higher than of analogous mortars without superplasticizer. Such an effect may be explained as a result of acceleration of cement hydration process in presence of SMF superplasticizer [21].

On the ground of obtained results it is possible to state that similarly as for mortars without superplasticizers, rheological parameters of mortars with superplasticizer depend mainly on C_3A content in cement, and next successively on interaction of C_3A content in cement and cement specific surface, and what is more also on Na_2O_{eq} content in cement. The influence of cement specific surface on rheological parameters of mortars with PE superplasticizer may be considered as less significant, while rheological parameters of mortars with SNF superplasticizer are strongly dependent on cement specific surface. Similarly as for mortars without superplasticizer, influence of SO_3 content in cement on rheological parameters of mortars is insignificant. Also in that case when the cements with high C_3A content are used, SO_3 content changes may cause variations in rheological parameters of mortars.

Yield value g of all superplasticized mortars increases with increasing C_3A content in cement. Such an influence is the higher the higher specific surface of cement is. Plastic viscosity h of PE mortars decreases with increasing C_3A content in cement, while of SNF and SMF mortars shows maximum when C_3A content in cement come to 7%. It is worthy noting, that yield value g of superplasticized mortars with 7 and 12% C_3A cement is higher than yield value g of mortars without superplasticizer with 2% C_3A cement. It shows that in the case of mixtures of high w/c ratio it is possible to obtain demanded flowability by appropriate selecting cement with lower C_3A content.

In general, the increase in specific surface of cement insignificantly influences rheological parameters of mortars with PE superplasticizer (however, similarly as for mortars without addition of superplasticizer yield value g shows tendency to increase and plastic viscosity h to decrease with increasing cement specific surface). In case of mortars with addition of SNF superplasticizer, the influence of cement specific surface depends on C_3A content. While cement specific surface increases yield value g of mortars with SNF superplasticizer increases (mortars with cements of 7 and 12% C_3A) or slightly decreases (mortars with cements of 2% C_3A). In the same time plastic viscosity h of SNF mortars always decreases with increasing specific surface of cement. The range of changes in rheological parameters of mortars due to variations in cement specific surface is clearly lower than that due to variations in C_3A content in cement.

Influence of Na_2O_{eq} content in cement on rheological parameters of SNF and SMF mortars is of extreme nature – minimum yield value g and maximum plastic viscosity h of these mortars are obtained when cements containing 0.7% Na_2O_{eq} are used. Simultaneously effectiveness of SNF and SMF superplasticizers is lowest when cements containing 1.1% Na_2O_{eq} are used. Content of Na_2O_{eq} in cement insignificantly influences plastic viscosity *h* of PE mortars, while yield value *g* of these mortars clearly depends on Na_2O_{eq} content in cement. Nature and range of the influence of Na_2O_{eq} content on yield value g is closely related to cement specific surface and C_3A content in cement. On the base of results obtained for w/c = 0.55 mortars it is difficult to define unequivocal trends. However, one may say that increasing Na_2O_{eq} content in cement causes drop in PE superplasticizer effectiveness and in consequence increase in yield value *g*.

Yield value *g* of superplasticized mortars increases with time, while plastic viscosity h increases (mortars with PE superplasticizer) or decreases (mortars with SMF and SNF superplasticizers). The range of changes of plastic viscosity h with time is generally low, and generally insignificantly influences changes of shear resistance T of mortars with time. Thus, the changes of rheological properties with time of superplasticized mortars are determined, similarly as of mortars without superplasticizer, by changes in yield value *g*.

Range of changes of *g* parameter with time depends on superplasticizer type, and next on C_3A and Na_2O_{eq} content in cement and cement specific surface. Increase of yield value *g* with time is lowest in case of mortars with PE superplasticizer and highest in case of mortars with SMF superplasticizer. Comparing the increase of yield value g with time of mortars without and with PE superplasticizer, one may say, that in case of superplasticized mortars the increase of yield value g with time is clearly lower. In case of SNF and SMF mortars the increase in yield value g may be even higher then in case of mortars without superplasticizer.

In case of superplasticized mortars with 2% C_3A cements changes of g parameter with time are insignificant. Increasing C_3A content in cement causes increase in range of changes of parameter g with time of superplasticized mortars. In case of PE mortars, the increasing content of Na_2O_{eq} in cement causes tendency to larger increase of *g* parameter with time. In case of SNF and SMF mortars the highest increase of g parameter with time is observed when cements of 0.3 % Na_2O_{eq} are used and lowest when cements of 0.7 % Na_2O_{eq} are used. Increasing specific surface of cement causes larger increase of

Table 11.
Regression and correlation coefficients for equations (3) and (4) for mortars without and with superplasticizer PE

Series	Swc [m²/kg]	*g* and *h* after 10 and 60 min	G/H	A	B	C	AB	AC	CB	AA	BB	CC	R^2
without SP w/c = 0.55	320	g_{10}	-49.07	0.87***	31.91**	39.92	-1.08	-0.27	-13.04	0.51**	-1.09	-4.44	0.990
		g_{60}	250.30	9.85**	1.43	-158.70	6.11	-1.47	-17.41	-0.17	0.69	31.06	0.988
		h_{10}	60.54	-1.26	-31.08**	-22.38	-0.60	0.24	1.86	0.06	16.20	3.18	0.938
		h_{60}	-49.50	-1.26	-54.06	54.96	-1.26	0.18	6.66	0.06	26.304	-10.38	0.897
	370	g_{10}	273.1	-3.16***	-113.00	-138.00	3.28	-0.25	4.44	0.51*	49.00	22.85	0.975
		h_{10}	-2.94	0.00	-23.52	14.76	0.48	0.00	7.68	0.00	0.24	-3.30	0.880
	420	g_{10}	117.5	24.05***	-90.80	-67.89	2.04	-1.47	-12.17	-1.00**	72.36	13.33	0.996
		h_{10}	46.86	-4.56	-31.08	-10.74	1.44*	0.54	10.98	0.12	-6.54	0.24	0.877
SP PE w/c =0.55	320	g_{10}	-32.34	6.27***	-16.22***	22.09	-2.80***	0.17	-1.56	-0.12*	18.37	-3.47	0.992
		g_{60}	14.94	10.08**	-39.56	-6.92	-3.49*	-0.46	2.95	0.04	24.36	0.85	0.990
		h_{10}	-24.48	-1.14*	0.48	23.28	0.72*	0.00	-0.96	0.06	-0.12	-3.78	0.891
		h_{60}	32.64	-0.90***	0.12	-16.20	-0.06**	0.12	-2.28	0.06**	6.18***	2.88	0.999
	370	g_{10}	168.9	-4.45**	-122.10	-77.37	4.64	1.13	22.35	0.17	27.23	9.48	0.900
		h_{10}	-43.74	0.66	-15.90	37.68	-0.30	-0.60	5.40	0.06*	1.08	-6.60	0.897
	420	g_{10}	123.5	12.79***	-83.67	-78.87	-1.046	0.104	9.300	-0.623*	37.53	12.36	0.924
		h_{10}	17.58	0.06**	15.18	-11.58	0.30	0.06	-3.30	-0.06	-4.80	2.34	0.907
SP SNF w/c =0.55	370	g_{10}	219.0	-4.01***	-97.92*	-119.20	1.87	0.68	-0.23	0.42	63.66	19.18	0.925
		g_{60}	121.0	24.98**	-17.83*	-101.60	-10.22	-0.14	13.23	-0.66	-3.66	15.84	0.977
		h_{10}	-37.80	1.50*	21.72	24.78	-0.48	0.12	1.38	-0.12*	-17.40*	-4.26	0.927
		h_{60}	-16.02	-0.66	28.44**	11.46	1.44*	-0.24	-2.46	0.06	-15.72*	-1.68	0.965
SP SMF w/c =0.55	370	g_{10}	341.9	6.27***	-135.9	-211.3	6.81*	-0.68	10.70	-0.04	55.57	34.62	0.933
		h_{10}	-26.52	0.84**	28.08	16.92	-0.66	-0.36	-3.84	-0.12*	-8.52	-2.70	0.900

*** - significance level = 0.001; ** - significance level = 0.01; * - significance level 0.05

yield value g with time of superplasticized mortars. However, the influence of cement specific surface is clearly lower than influence of C_3A and Na_2O_{eq} content in cement.

5. PROPERTIES OF CEMENT AND RHEOLOGICAL PROPERTIES OF MORTARS – REGRESSION RELATIONS

The analysis of experimental data enables the regression relations joining the properties of cement - cement specific surface and C_3A, Na_2O_{eq} and SO_3 content in cement – with rheological parameters of mortars with and without superplasticizer. They are as follow:

$$g = G + AU_1 + BU_2 + CU_3 + DU_4 + ABU_1U_2 + ACU_1U_3 + ADU_1U_4 + BCU_2U_3 + BDU_2U_4 + CDU_3U_4 + AAU_1^2 + BBU_2^2 + CCU_3^2 + DDU_4^2 \quad (3)$$

$$h = H + AU_1 + BU_2 + CU_3 + DU_4 + ABU_1U_2 + ACU_1U_3 + ADU_1U_4 + BCU_2U_3 + BDU_2U_4 + CDU_3U_4 + AAU_1^2 + BBU_2^2 + CCU_3^2 + DDU_4^2 \quad (4)$$

where: U_1 – cement specific surface S_{wc}, [m^2/kg]; U_2 – C_3A content in cement, [%]; U_3 - Na_2O_{eq} content in cement, [%]; U_4 – SO_3 content in cement, [%]; *G, H, A, B, C, D, AB, AC, AD, BC, BD, CD, AA, BB, CC, DD* – material constants depending on mortar constituents properties and time passing from the end of mixing. In the equations (3) and (4), like in equations (5) and (6) mentioned below, SO_3 content in cement was also taken into consideration. It was done, because the influence of SO_3 content in cement in extreme points of factorial space may be significant, thus omission of that factor may reduce accuracy of calculation of rheological parameters. Values of material constants for tested mortars together with significance levels and coefficients R^2 are presented in Table 11. The relationship between calculated and measured values of rheological parameters of mortars according to equations (3) and (4) are presented in Fig. 10.

Equations (3) and (4) take into consideration influence of cement specific surface. However, in practice cement specific surface is closely related to the grade of cement, which in turn is specified by strength demands of concrete. Due to this, in most cases factor of cement specific surface may be treated as constant from the point of view of demanded rheological properties of mixture.

In that case the regression relations joining the composition of cement – C_3A, Na_2O_e and SO_3 of cement of given specific surface S_{wc} = 320. 370 and 420 m^2/kg (cements of grade 32.5, 42.5 and 52.5 respectively) with rheological parameters of mortars with and without superplasticizer are as follow:

$$g = G + AU_1 + BU_2 + CU_3 + ABU_1U_2 + ACU_1U_3 + BCU_2U_3 + AAU_1^2 + BBU_2^2 + CCU_3^2 \quad (5)$$

$$h = H + AU_1 + BU_2 + CU_3 + ABU_1U_2 + ACU_1U_3 + BCU_2U_3 + AAU_1^2 + BBU_2^2 + CCU_3^2 \quad (6)$$

where: U_1 - cement specific surface Swc, [m^2/kg]; U_2 – C_3A content in cement, [%]; U_3 – Na_2O_{eq} content in cement, [%]; U_4 – SO_3 content in cement, [%]; *G, H, A, B, C, D, AB, AC, AD, BC, BD, CD, AA, BB, CC, DD* – material constants depending on mortar constituents properties and time passing from the end of mixing. Values of material constants for tested mortars together with significance levels and coefficients R^2 are presented in Table 12. The relationship between calculated and measured values of rheological parameters of mortars according to equations (5) and (6) are presented in Fig. 11.

Obtained high correlation coefficients and relatively small values of deviation of rheological parameters calculated from those measured in control tests (made using commercial cements of properties presented in Table 5), prove that functions (3) (4) and (5) (6) describe well the relation of cement properties and rheological parameters of fresh mortars. These equations may be helpful in preliminary selection of cement and cement – superplasticizer system optimal from workability demands point of view. They may be also used for anticipation of direction and range of changes of rheological parameters of cement binder mixtures, and in consequence, may be used for workability control especially when properties of used cement undergo changes. It should be noted that equations (5) (6) give better conformity of calculated and measured results. Thus, when the cement specific surface is determined, these equation should be used instead of equations (3) (4).

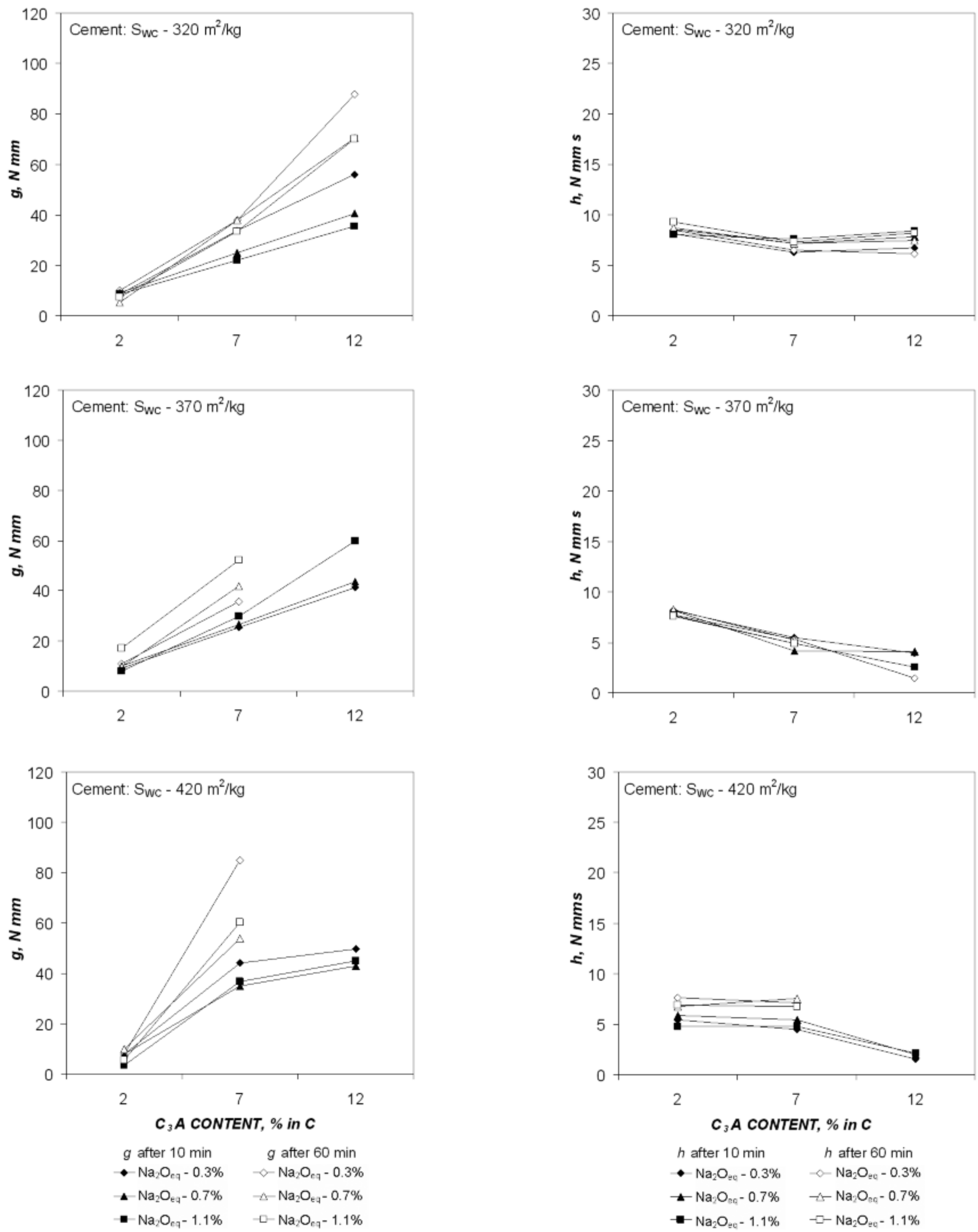

Figure 5.
The effect of cement specific surface S_{wc} and C_3A and Na_2O_{eq} content in cement on rheological parameters of mortars with PE superplasticizer

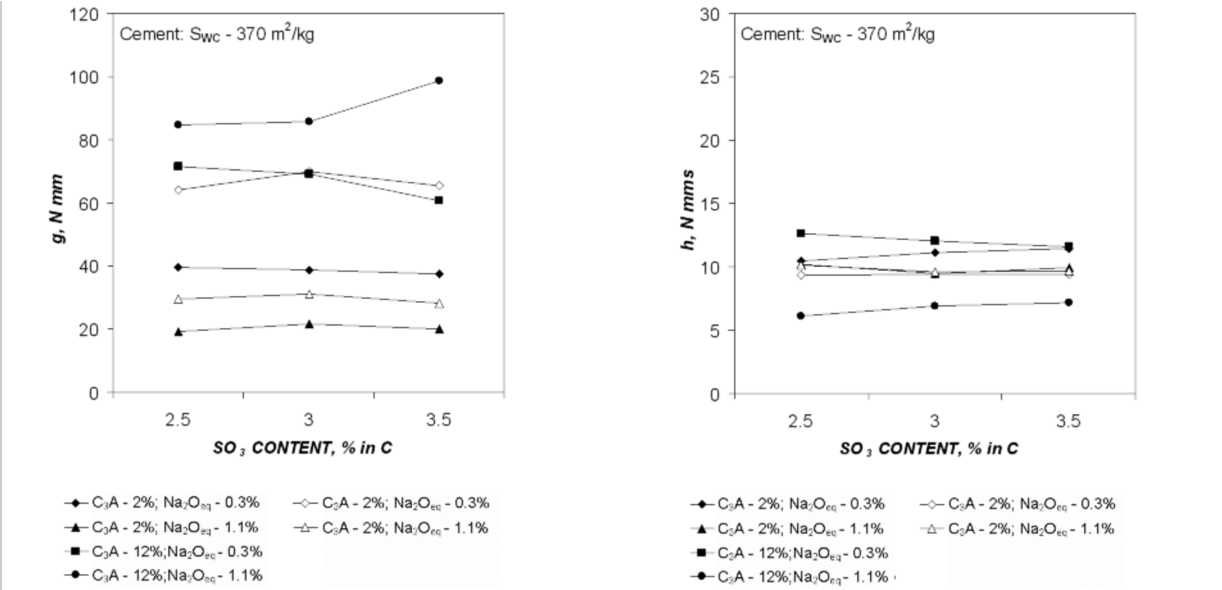

Figure 6.
The effect of SO_3 content in cement on rheological parameters of mortars with PE superplasticizer

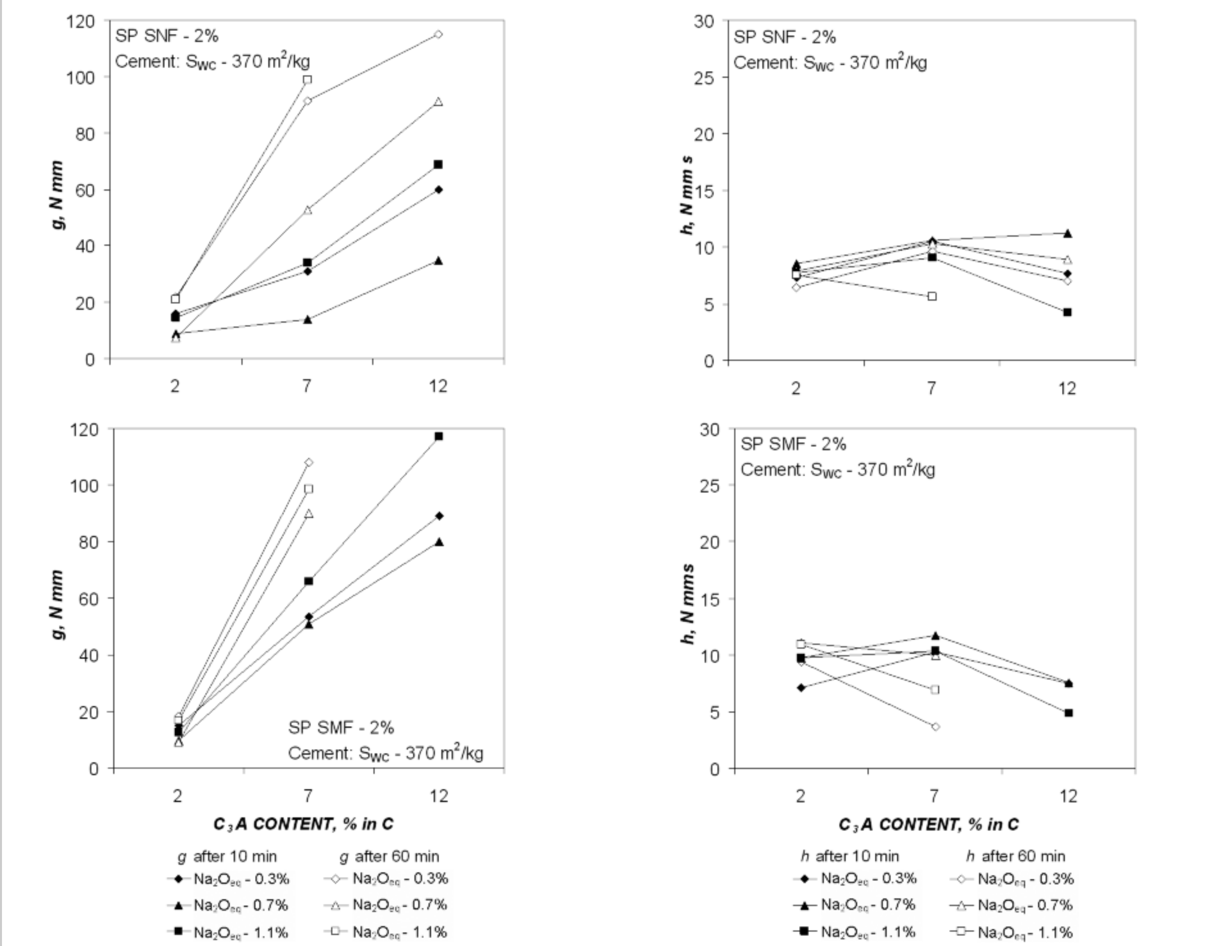

Figure 7.
The effect of C_3A and Na_2O_{eq} content in cement on rheological parameters of mortars with SNF and SMF superplasticizers

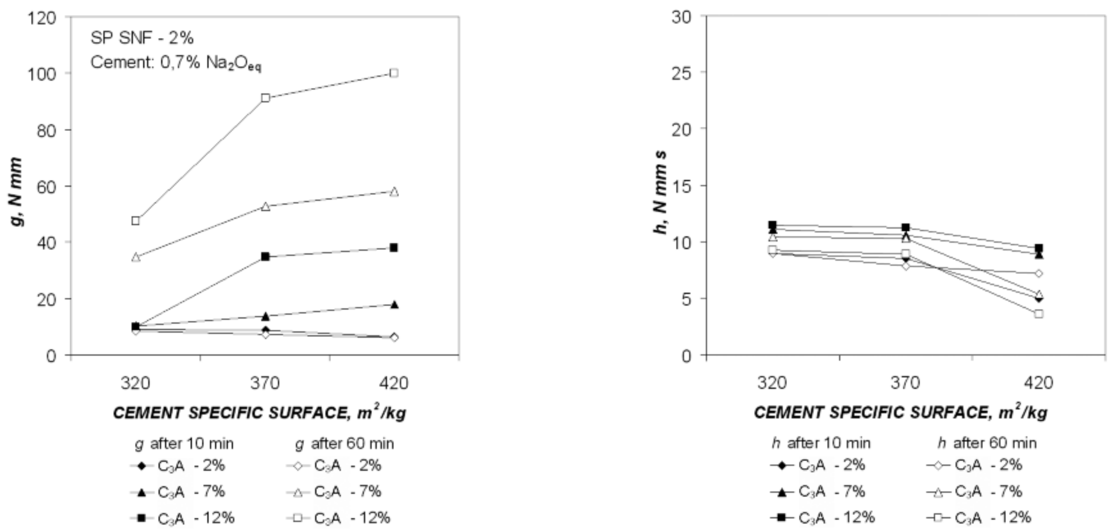

Figure 8.
The effect of cement specific surface S_{WC} and C_3A content in cement on rheological properties of mortars with SNF superplasticizer

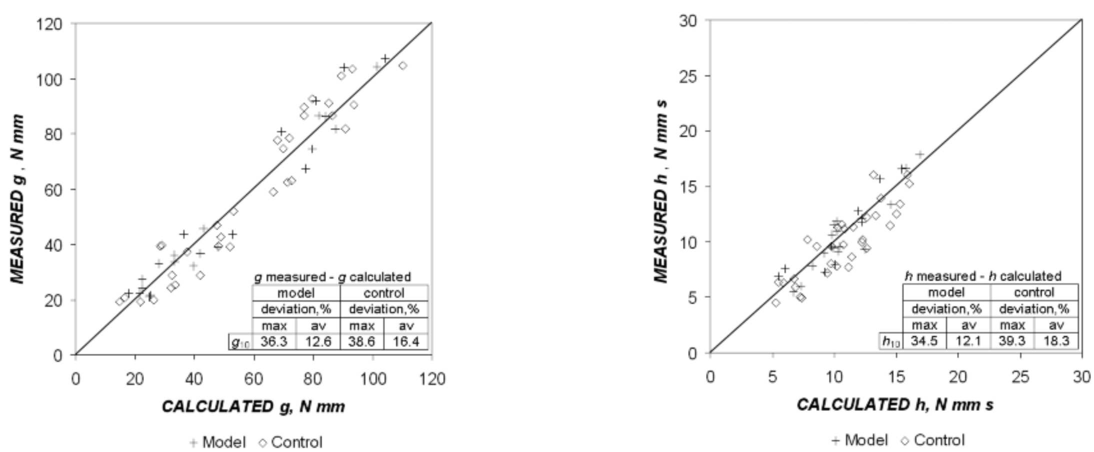

Figure 9.
The relationship between predicted and measured values of rheological parameters after 10 min for mortars without superplasticizer according to equations (3) and (4)

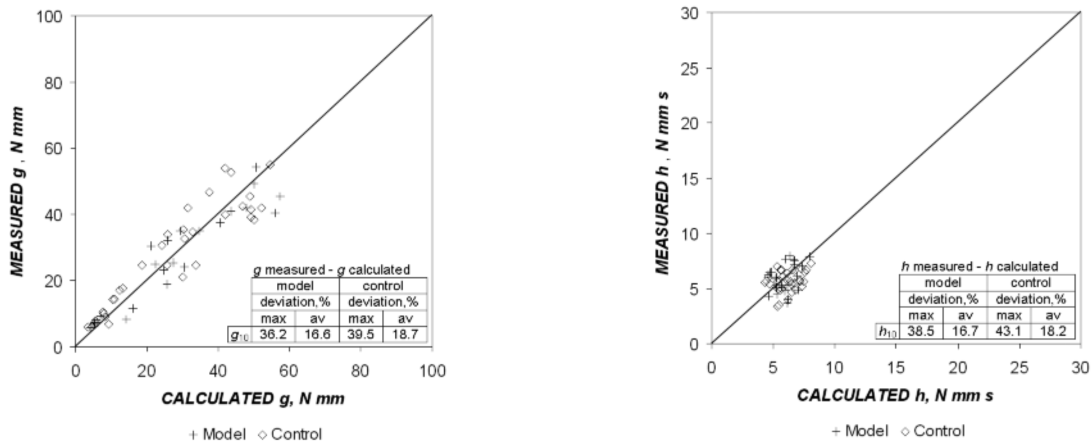

Figure 10.
The relationship between predicted and measured values of rheological parameters after 10 min for mortars with PE superplasticizer according to equations (3) and (4)

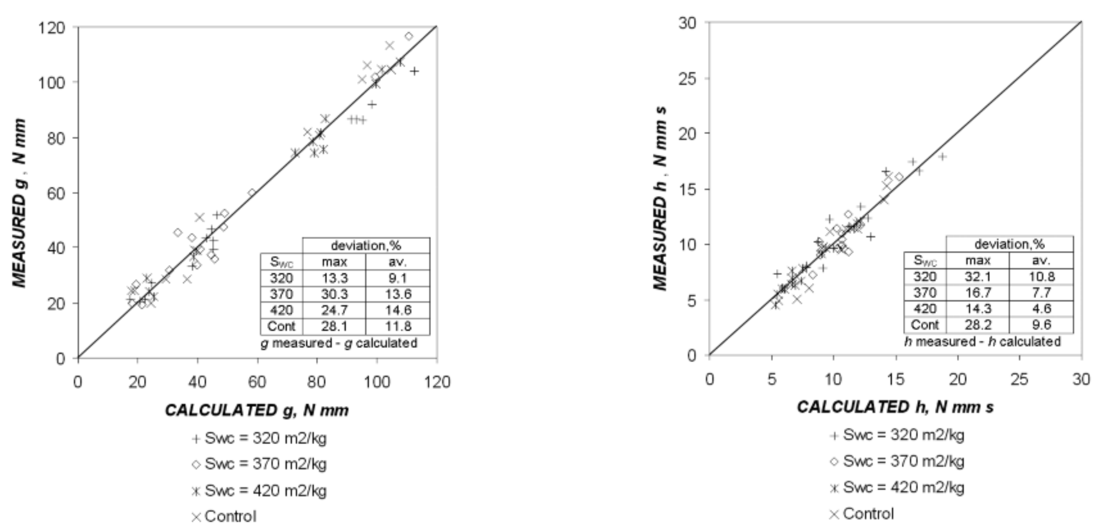

Figure 11.
The relationship between predicted and measured values of rheological parameters after 10 min for mortars without superplasticizer according to equations (5) and (6)

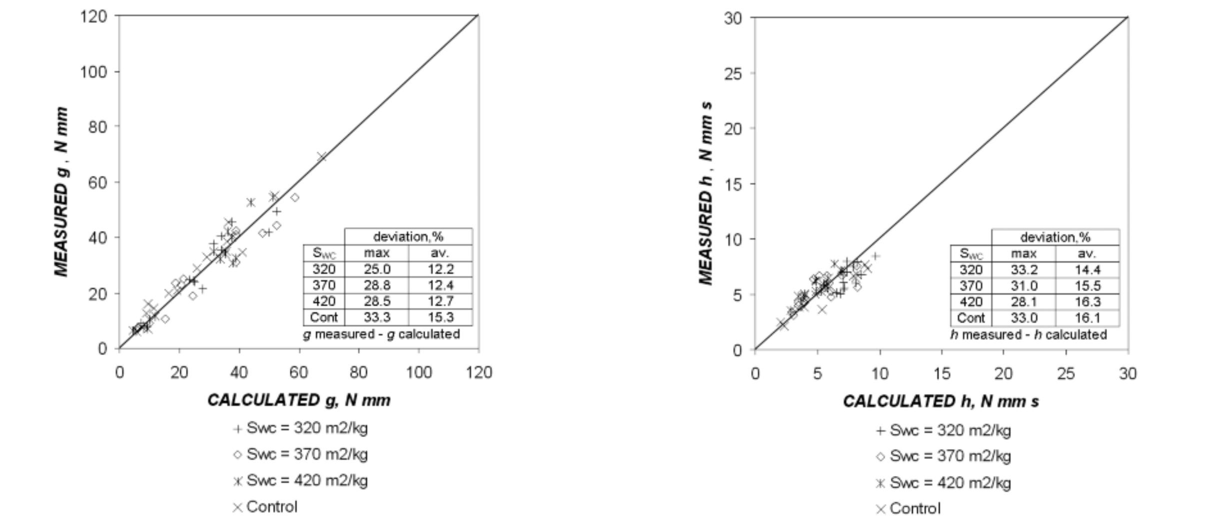

Figure 12.
The relationship between predicted and measured values of rheological parameters after 10 min for mortars with PE superplasticizer according to equations (5) and (6)

6. CONCLUSIONS

From amongst the factors related to the properties of cement, the highest influence on rheological parameters of mortars have C_3A content in the cement, and next, successively, cement specific surface, Na_2O_{eq} contents in the cement (first of all for superplasticized mortars) and interaction of these factors. In tested range of variability of cement properties no considerable influence of SO_3 content in cement on rheological properties of mortars or superplasticizer action effects were observed.

As a result of increased C_3A content in the cement yield value g of mortars intensively increases while plastic viscosity h slightly decreases. Range of changes of these parameters with time increases as a result of increasing C_3A contents in the cement (especially of yield value *g*). The intensity of C_3A influence increases with increasing cement specific surface.

Increasing cement specific surface of low C_3A content results in insignificant reduction, and in case of cements of high C_3A content in the increase of yield value g of mortars. Plastic viscosity h of these mortars decreases with increasing cement specific surface. Superplasticizer action effects decay faster when cement specific surface and C_3A content increases.

The effectiveness of SNF and SMF superplasticizers is greatest when cements containing 0.7% Na_2O_{eq} are used. Performance of PE superplasticizer increases when Na_2O_e content in cement decreases. Such mortars are characterized by the lowest yield value g and the lowest yield value g changes with time. The influence of Na_2O_{eq} content in cement on rheological parameters of mortars increases with increasing C_3A content in cement.

Due to wide range of factorial space in which the equations (3) (4) and (4) (5) were created, they show utilization possibilities and may be applied to choose the appropriate cement or cement – superplasticizer from the workability point of view and what is more for designing and controlling workability of fresh cement binder mixtures.

Hydration process of cements and mechanism of superplasticizers action were not the subject of presented investigation. However, obtained results stay in good correlation with relevant existing data. Increasing specific surface of cement and increasing content of C_3A in cement cause increase of hydration products mass, decrease in free water content in mixture, increase in rate of superplasticizer adsorption on cement and decrease of content of free superplasticizer in mixture [15,21,22]. These effects correspond well with, observed in the research, the nature of influence of cement specific surface and C_3A content in cement on yield value g and plastic viscosity h of mortars. The decrease in plastic viscosity h caused by increase of cement specific surface may be explained as a result of decrease in diameter of cement grains. Nature of influence of Na_2O_{eq} content in cement on SNF and SMF mixtures rheology correspond well with effects described in [22,23]. When SNF and SMF superplasticizers are added to mixture with low alkalis cement, then more of its polymers are adsorbed on aluminate phases and locked into hydration products. Such effect reduces effectiveness of SNF and SMF superplasticizers. On the other hand, when alkalis content in cement is high, amount of sulfate ions in solution increases, what increases ionic strength of solution and causes reduction of mixture flowability. Thus, there is optimal alkalis content in cement, when SNF and SMF superplasticizers efficiency is highest. According to [23] this optimal alkalis content is 0.5-0.8%, which stays in good correlation with the results presented in section 4. Performance of PE superplasticizer decreased when Na_2O_{eq} content in cement increased. It can be explained well by the effect described in [24,25] – conformation of polymers enclosed in PE superplasticizer considerably changes (the spread of polymer decreases) due to increase of SO_4^{2-} ions concentration in presence of high alkali content. In consequence the steric effect is weakened, effectiveness of PE superplasticizer reduced and fluidity (mainly yield value g) of mixture decreased.

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