

The influence of cement composition on superplasticizers' efficiency

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Abstract

Fundamental interactions between polymeric superplasticizers and cement are studied. Cements with different alite-, belite-, C₃A- and C₄AF-contents are used. The use of commercially available superplasticizers like melamine formaldehyde sulfite- (MFS) and β-naphthalene sulfonic acid formaldehyde-(NSF) resins is investigated. These superplasticizers (industrial products) are characterized by means of their molecular weights and polymeric radii, as well as by estimating the anionic charge density in water and in the cement filtrate of four CEM I cements. Application data of the eight cement-superplasticizer-combinations (heat flow calorimetry and mini-slump tests) are obtained and the surface chemistry of the superplasticizers with cement (zeta potentials and superplasticizer adsorption on cement) is studied.

Keywords: cement, superplasticizers, adsorption, zeta potential, charge density.

1. INTRODUCTION

The arising request for modern building materials that show better workability and durability can only be fulfilled by the application of different construction-chemical admixtures. Although some very good recipes have been developed e.g. for dry mix mortars, problems of compatibility between cement and organic admixtures have arisen. For this reason, the interaction of some superplasticizers on cement is studied. The results give some fundamental understanding in how far the cement industry can reduce the cement production and consequently the CO₂-emission which is of high environmental interest.

The relation between the C₃A content and naphthalene based-superplasticizers adsorption has been investigated by many researchers. It is clear that a large amount is adsorbed on C₃A of ordinary Portland cement [1]. The adsorption is also determined by the cement fineness [2]. It has been reported that hydration reactivity corresponds to high calcium aluminate contents [3, 4]. Generally, a certain amount of anionic superplasticizers are adsorbed on the surface of the cement grain or its hydrated phases to obtain a dispersing effect. The impact of these superplasticizers can be understood considering that polycondensates possess many –SO₃²⁻-groups and therefore a high negative charge. The grain surface will be also negatively charged, once these superplasticizers adsorb. Due to the repulsion forces between equal charges, a good dispersing effect is obtained and reagglomeration is avoided.

The information about variation in adsorption behavior of polycondensates with the different types of cements is very important for application to give an indication about the dosages necessary related to the type of cement. In extreme cases, adsorption can be as low as 10 % and no liquefaction of the cement paste is observed. This would confirm the cement “incompatibility” with polycondensate-superplasticizers and emphasize the need for intensive research in this area. Another important factor for this “incompatibility” can rely on the type and availability (solubility) of the sulfate carrier in the cement.

The aim of this research work is to establish fundamental interactions between polymeric superplasticizers and cement. For this purpose, cements with different alite-, belite-, C₃A- and C₄AF-contents are used. The use of commercially available superplasticizers like melamine formaldehyde sulfite- (MFS) and a β-naphthalene sulfonic acid formaldehyde-(NSF) resin and four CEM I (A-D) cements of different chemical composition is investigated. The adsorption behavior of the superplasticizer on cement is studied.

2. EXPERIMENTAL

The experiments are performed with aqueous suspensions of the different cements CEM I (A-D). Their medium particle size D_{50} is determined by using laser granulometry (Cilas 1064; Co. Cilas). The densities of these cements are established by a helium pycnometer.

The MFS- and NSF- resins are industrial products and are used without further purification. The solid content of the polymeric solutions are established by using an IR-balance. The characterization of the polymers is made by GPC, coupled with a refractive index and light scattering detector. This equipment permits calculation of molecular weights and radii of the polymers. Moreover polymer solutions with a concentration of 10 mg / mL (with respect to the polymeric solid content) are prepared. The solvent used is a 0.1 mol/L NaNO₃ solution; pH = 12.0; adjusted with NaOH). The column material (Co. Waters) used contained three columns consecutively connected (Ultrahydrogel 120, Ultrahydrogel 250, Ultrahydrogel 500). They cover a separation area of 5,000 – 400,000 Dalton. Each sample is injected with a syringe containing a forwarded spaced filter (0,2 μm) in a 2-mL-GPC-sample holder, out of which the GPC-apparatus injects 100 μL into the system. Therefore the polymeric solution needed for one run is 1.0 mg. The evaluation is carried out with the GPC-Software Astra 4,908 (Co. Wyatt Technologies). To calculate the averaged molecular weights, a 3rd order fit is used.

The anionic charges of the superplasticizers under investigation are measured by means of the particle charge detector PCD 03 pH (Co. Mütek). 100 mL standard solutions of polymeric concentration of 200 mg/L are used. The filtrates of cement pastes with a w/c-value necessary to produce a flow value of 18 ± 0.5 cm (mini-slump test) are used as a solvent for the polymers to measure the anionic charge in the pore solution. The charge density is determined by means of a titration experiment with the polymer poly-dadmac (0.001 N), a cationic polyelectrolyte.

Adsorption measurements are carried out at RT by determining the organic carbon content via High TOC II analyser (Elementar) of the centrifugate (20 min at 8500 rpm) previously produced from the cement pastes with polymeric admixtures.

The zeta potentials of the cement pastes with different amounts of polymers are measured using Model DT-1200 electroacoustic spectrometer (Dispersion Technology, Inc.). The following mixing procedure is used to prepare the cement pastes: cement is added to water (according to the necessary w/c-value) within 1 min. This paste is let sit for one more minute. Then, the mixture is vigorously stirred for 2 min in a casserole by using a spoon. The filtrate is taken for the measurement of the ionic background of the cement paste that is subtracted from the zeta potential values of the cement pastes containing the polymers.

To estimate the flow value, the superplasticizer dosages given in table 6 are poured into the mixing water in a porcelain casserole. After cement is added, the resulting paste is poured into a

VICAT-ring ($h = 40$ mm, $d_{\text{inner,above}} = 70$ mm, $d_{\text{inner,below}} = 80$ mm). After lifting up the VICAT-ring the diameter of the paste is determined.

3. RESULTS AND DISCUSSION

3.1 Characterization of the four types of cement

The analysis of the four types of cement is performed by using the Rietveld analysis- method. The results are listed in (table 1).

TABLE 1: Rietveld analysis of the cements CEM I (A-D).

Cement type Mineral Phase	CEM I (A)	CEM I (B)	CEM I (C)	CEM I (D)
Alite	67.3	60.1	69.8	61.0
Belite	10.9	22.4	6.9	22.0
C3A (cub.)	5.7	2.3	1.3	0.4
C3A (orth)	5.6	0.0	4.6	1.1
Na ₂ O	0.27	0.21	0.18	0.27
K ₂ O	0.67	0.63	0.72	1.27
C ₄ AF	1.7	12.2	6.8	14.0
Al ₂ O ₃	4.47	3.55	3.63	4.15
Fe ₂ O ₃	1.2	4.56	2.38	2.46
CaSO ₄ *2H ₂ O	0.1	2.5	0.1	1.1
CaSO ₄	2.5	0.0	2.4	0.0
CaO free	0.3	0.2	1.1	0.3
w/c	0.6	0.46	0.47	0.6

It can be seen that CEM I (C) has the highest alite content, while CEM I (B) & (D) comparably have the highest belite content. The highest C3A content, whether cubic or orthorhombic, is found for CEM I (A).

3.2 Characterization of the superplasticizers

The solid content determined by an IR-balance is found to be 38.71 % and 8.47 % for MFS- and NSF- resins, respectively. The pH-values of the polymeric solutions differed slightly from one another and found to be 8.47 in case of MFS-resin and 7.47 for the NSF-resin.

The GPC- analysis of the MFS-resin is listed in (table 2). Because the NSF-superplasticizer NSF-resin could not be analyzed chromatographically in aqueous medium because of adsorptive effects with the column material, a "batch"-measurement is carried out. The polymer samples of different concentrations are injected directly into the cell of the light scattering detector. Adsorptive Interactions of the polymers with the column are excluded. The "batch"-measurement gave the weight-average molecular weight M_w , the z-average radius of gyration Rg_z as well as the QELS (quasi elastic light scattering) – correlation function of the average hydrodynamic radius $Rh_{\text{(avg)}}$. Because of the absence of concentration information out of the refractive index detector, no values for M_n , M_z , Rg_n , Rg_w , Rh_n , Rh_z and polydispersity are obtained.

The "batch"-analysis via ZIMM-Plot is successful using double extrapolation. The first extrapolation occurs on the concentration zero. This is necessary to eliminate the intermolecular

interactions, because the scattered light intensity of a single molecule should be measured. The second extrapolation occurs on the scattering angle zero to eliminate the intramolecular influence. In the ZIMM-Plot all measured points are applied and connected to straight lines. From the slope of these straight lines the values of the 2nd virial coefficient A₂ and the z average radius of gyration R_{g_z} are obtained. With this information the weight-average molecular weight M_w of the NSF-resin could be deduced (table 3). It is clear that the molecular weights of the polycondensates are very high. The molecular weights and the polymeric radii lie within expectations [5].

TABLE 2: GPC-Analysis of MFS-resin and “batch” - analysis of the NSF-resin.

Property	MFS – resin	NSF – resin (“Batch”- analysis)
Molecular weight [g/mol] M _n	77670	
Molecular weight [g/mol] M _w	109800	193500 (4 %)
Poly-dispersity [M _w /M _n]	1.41	
R.M.S. Radius (R _g) [nm] R _{gn}	12.0	
R.M.S. Radius (R _g) [nm] R _{gw}	13.5	
R.M.S. Radius (R _g) [nm] R _{gz}	16.9	38.7 (8 %)
QELS Hydro dynamic Radius moment [nm] R _{hn}	7.5	
QELS Hydro dynamic Radius moment [nm] R _{hw}	8.4	
QELS Hydro dynamic Radius moment [nm] R _{hz}	10.7	
QELS Hydro dynamic Radius moment [nm] R _h (avg)	5.8	

According to the calculated Burchard-Parameter ($[R_{gz}/ R_{h(avg)}] = 2.56$) it is found that the MFS-resin in solution lies in form of steady chains.

3.3 Estimation of the specific anionic charge density

The results of the specific anionic charge density measurements are found in figure 1.

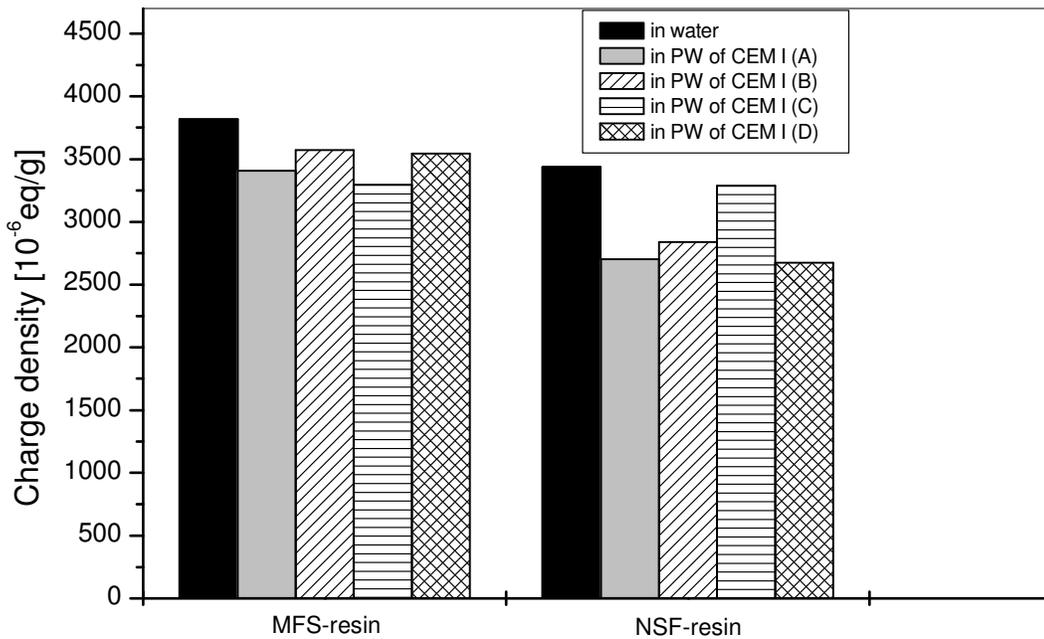


FIGURE 1: Anionic charge densities of the superplasticizers.

As expected, the polycondensates (MFS and NSF) show in salt free water as well as in the pore water of the four cements very high anionic charge densities.

While in water, the anionic charge density of the superplasticizers appear higher than in the different pore waters of the cements under investigation, due to the fact that pore water contains Ca^{2+} ions which form complexes with the superplasticizers. The two superplasticizers behave differently depending on the amount of free Ca^{2+} ions present in the pore solution and the affinity to form complexes with them.

3.4 Liquefying effect of the superplasticizers

The dosage (w.r.t cement) for each superplasticizer is estimated according to that necessary to produce a flow value of 26 ± 0.5 cm (mini-slump test). The blank value is a cement paste with a w/c-value for which the flow value is 18 ± 0.5 cm. By adding each superplasticizer, the dosage is adjusted so that a flow value of 26 ± 0.5 cm is obtained. The water content in the polymeric solutions is considered.

The dosages necessary to obtain a flow value of 26 ± 0.5 cm are similar for both polycondensates (table 6). Among all cements *CEM I (B)* is liquefied the best i.e. with the least dosage of superplasticizer, the best result is obtained. This is attributed to its low C_3A -content. Comparable behaviour is given by *CEM I (A)*.

The cements *CEM I (C)* and *CEM I (D)* need much higher dosages.

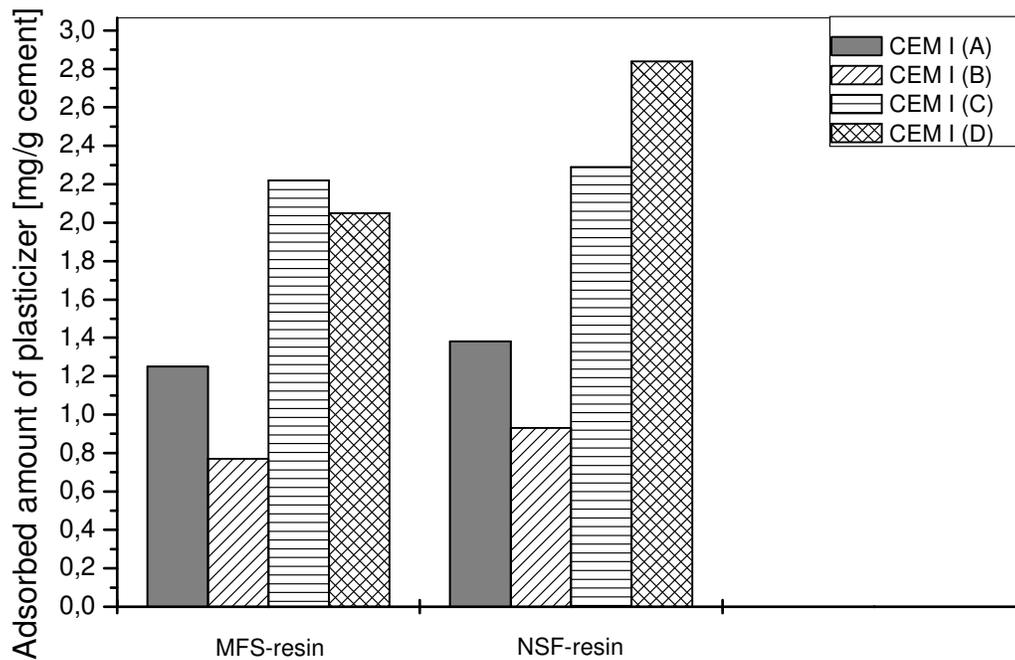
TABLE 3: Dosages of the superplasticizers necessary to obtain a flow value of 26 ± 0.5 cm.

Cement; w/c	MFS-resin	NSF-resin
CEM I (A); w/c = 0.6	0.15 %	0.15 %
CEM I (B); w/c = 0.46	0.12 %	0.1 %
CEM I (C); w/c = 0.47	0.25 %	0.25 %
CEM I (D); w/c = 0.6	0.25 %	0.25 %

This can be explained by the high sulfate content - especially the rapidly soluble sulfates like arcanite. The free sulfate adsorbs on the surface of cement hydration phases and prevents the superplasticizers to adsorb and function as liquefiers [6]. Another reason for the bad compatibility of the superplasticizer with cement is the free CaO content.

3.5 Estimation of the superplasticizers adsorption on cement

First, the TOC-content in the pore solution without superplasticizer is estimated as background. Then the superplasticizer dosages listed in table 3 are examined by adsorption measurements determining the TOC-content in the filtrate of non-adsorbed superplasticizer. Subtraction from starting dosages leads to the amount adsorbed. The results are shown in figure 2.



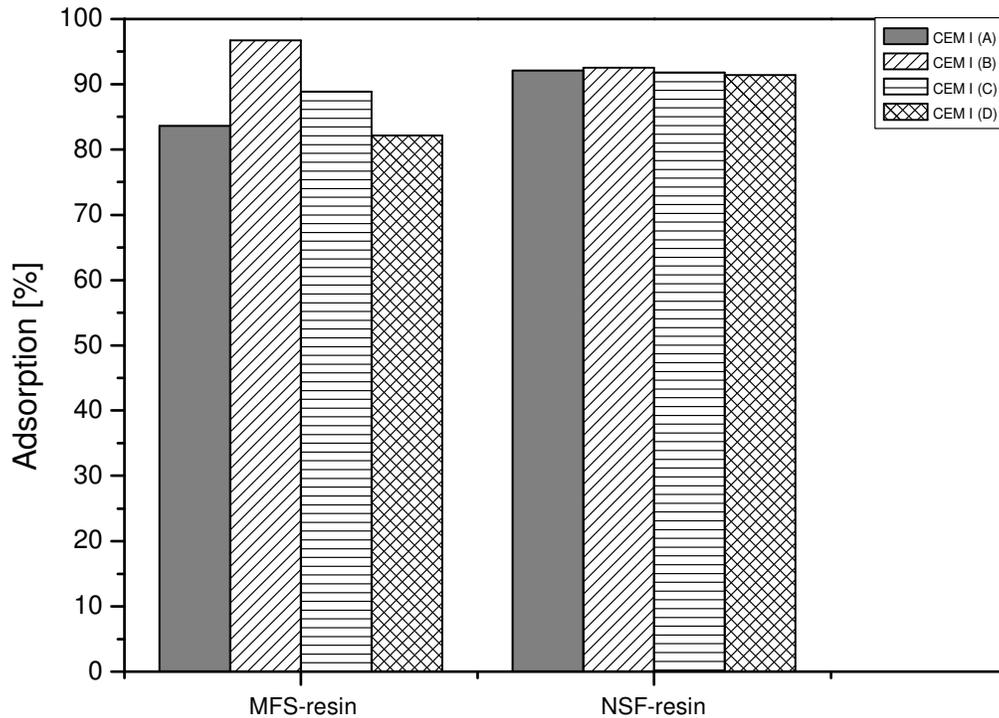


FIGURE 2: Adsorbed amount of superplasticizers in mg/g cement (above) and percent adsorption of the superplasticizers (below).

As expected, the C_3A -poor cement *CEM I (B)* adsorbed the least amount of superplasticizers, while *CEM I (C)* and *CEM I (D)* adsorbed the most. These results are consistent with the finding about dependence of adsorbed amount on the formation of ettringite [7]. In accordance with this, the high contents of sulfate and free CaO of *CEM I (C)* resulted in a high consumption of superplasticizers although it has a moderate C_3A -content.

Regarding the adsorbed amount of superplasticizers, the adsorption behaviors of MFS-resin und NSF-resin are very similar. The values of percental adsorption of these products indicated their limited function as superplasticizers (bad slump loss – behavior). These superplasticizers are good for precast concrete, because they show a high starting liquefaction of cement pastes with low dosages.

3.6 Zeta potential measurements

The zeta potentials are determined first without then with superplasticizer (figure 3) according to the dosages listed in table 3. The physical data needed to execute such experiments are given in as follows:

CEM I (B) - (D) have a density of 3.14 g/cm^3 , while CEM I (A)'s density is 3.12 g/cm^3 . The particle sizes $D_{50} [\mu\text{m}]$ of the CEM I (A) – (D) are 7.5, 11.28, 17.49 and 8.81, respectively.

The zeta potential of the cement pastes are -2.6 mV for CEM I (A), -8.3 mV for CEM I (B), -1.9 mV for CEM I (C) and -2.8 mV for CEM I (D) without superplasticizers addition (figure 3). The zeta potentials of the pure cements depend on their C_3A -content. Cements with higher C_3A - and sulfate contents can form higher amounts of ettringite during the hydration process which

shows a stronger positive zeta potential [8]. *CEM I (C)* has the least negative zeta potential of -1.9 mV. Apparently, this cement builds more ettringite due to its very high sulfate content than the *CEM I (A)*, which is richer in the C_3A -content. This effect is even more intensified due to the fact, that *CEM I (C)* possesses the biggest particle size. In the contrary to that, *CEM I (B)* shows a very negative zeta potential, because it can form less ettringite. Besides it has a higher content of silicates that produce a negative surface charge.

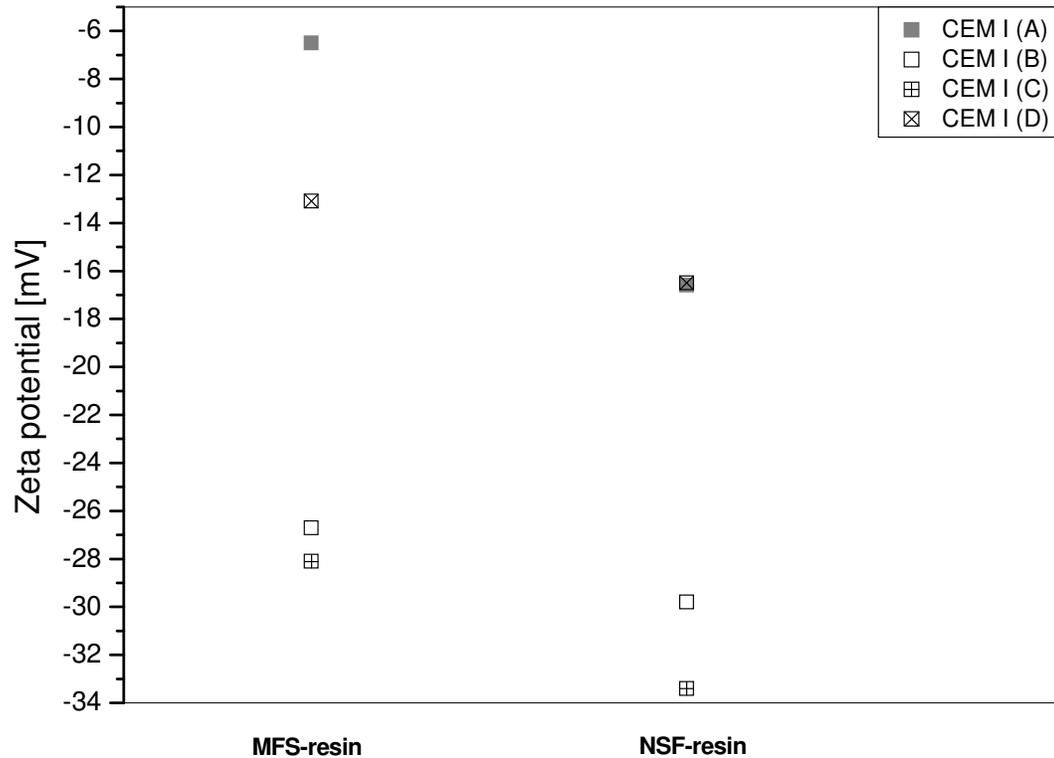


FIGURE 3: Zeta potentials of the superplasticizers on the four cements CEM I (A-D).

3.7 Heat flow calorimetry

For the evaluation of a probable retarding effect of superplasticizers, the samples are prepared according to the dosages listed in table 3 with the different types of cement. Regarding the data obtained from the heat flow calorimetry (figures 4 and 5), all cements are not retarded by the superplasticizers under investigation. Nevertheless, remarkable are the differences in the maximum heat of hydration of the pure cements. The results showed the coherence to the C_3A - and sulfate contents. Astonishing is the low heat of hydration of *CEM I (C)*. This can be attributed to the relatively big particle size of 17.49 μm .

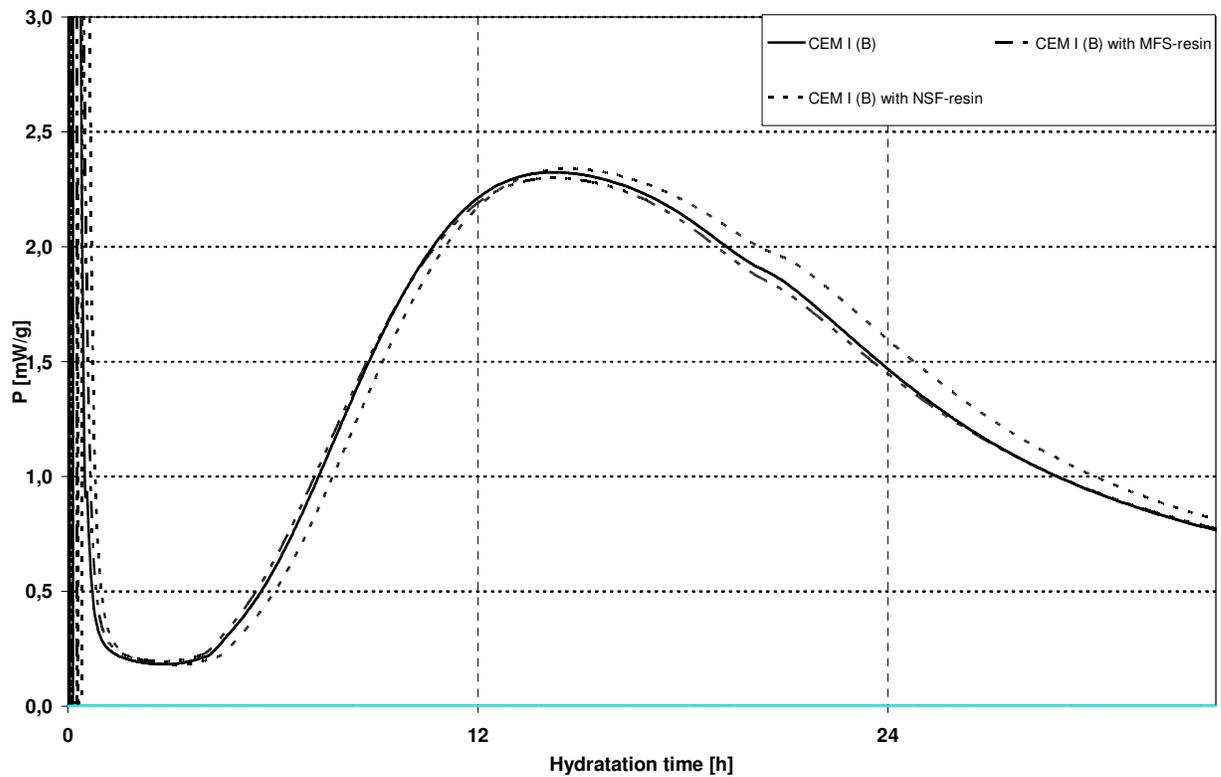
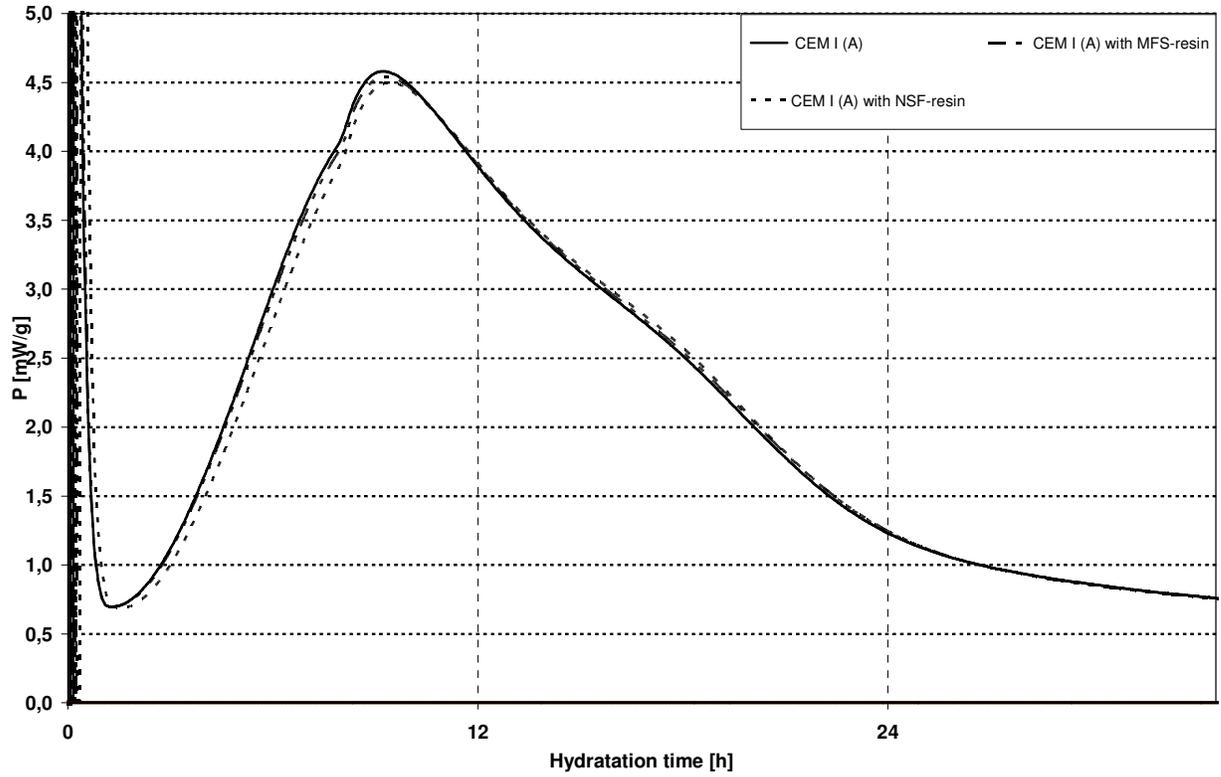


FIGURE 4: Heat flow calorimetry of the superplasticizers with CEM I (A) (above) and CEM I (B) (below).

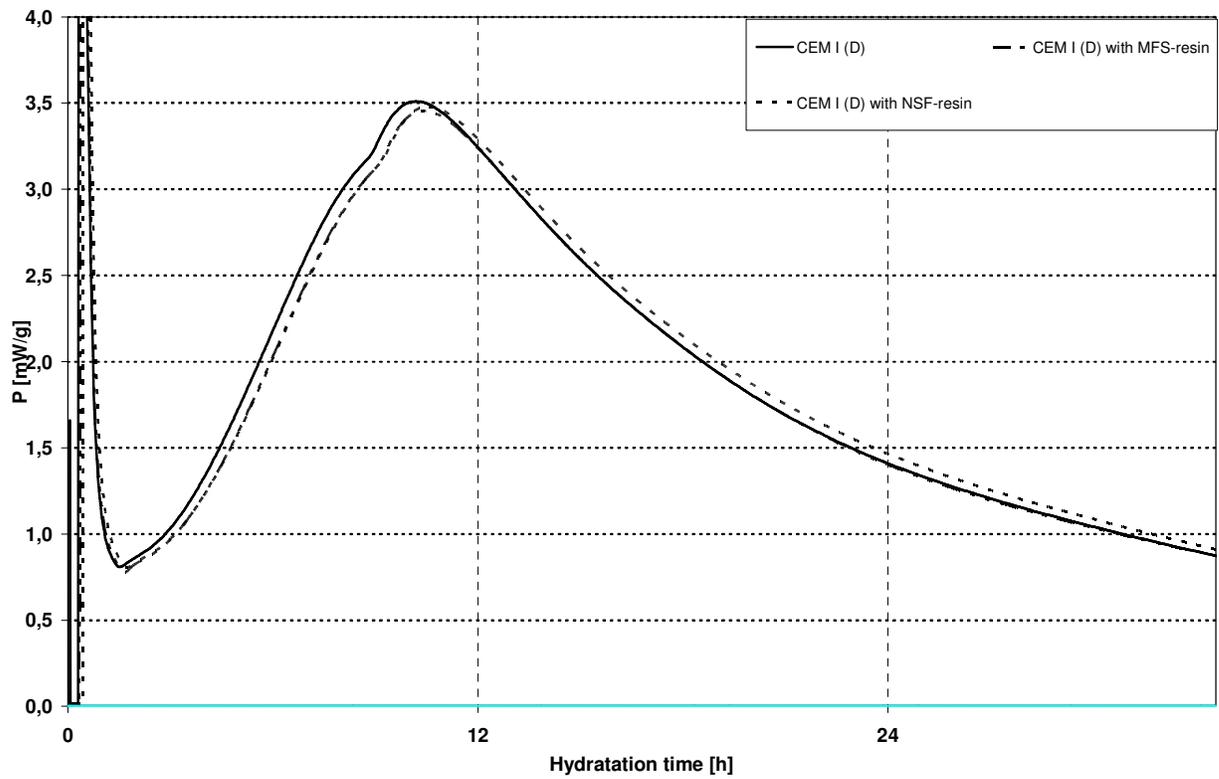
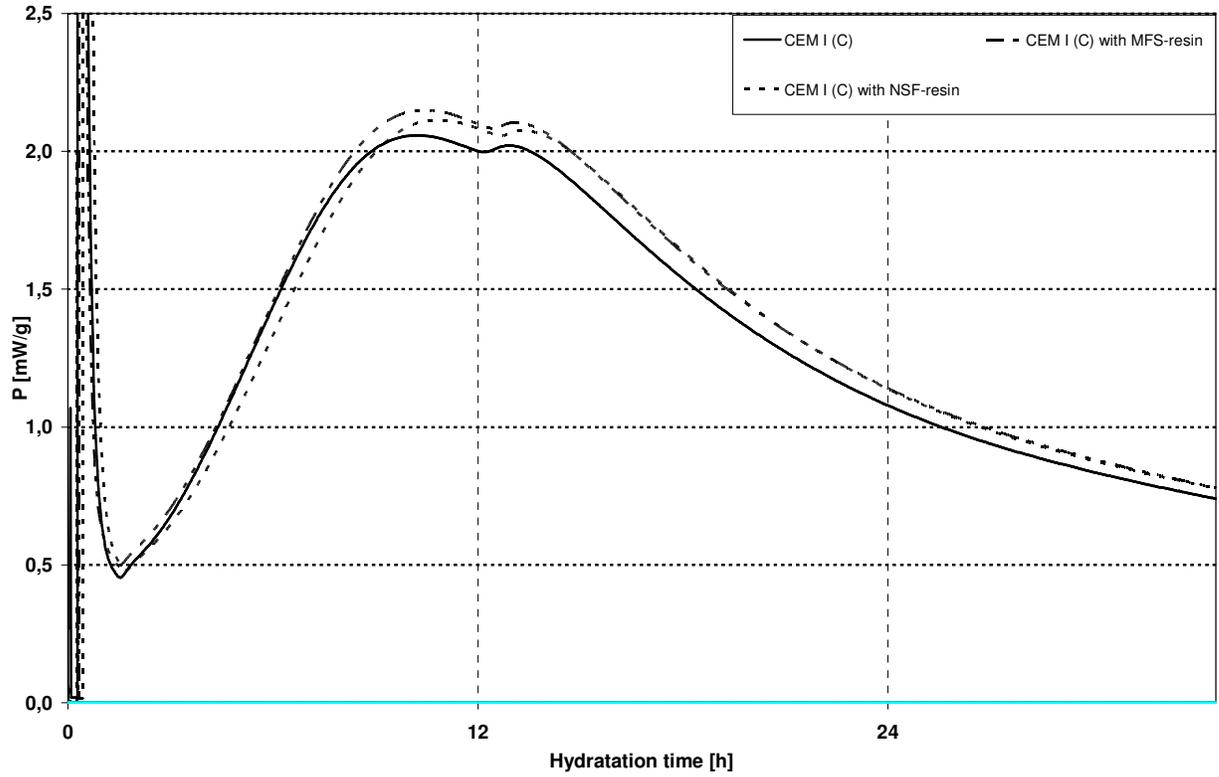


FIGURE 5: Heat flow calorimetry of the superplasticizers with CEM I (C) (above) and CEM I (D) (below).

4. CONCLUSION & FUTURE WORK

The interaction of two superplasticizers with four different types of cement is studied. Characterization of the polycondensates, MFS- and NSF-resins, showed that they have very high molecular weights. In solution, the MFS-resin lies as a steady chain according to the Burchard-Parameter. The adsorption behavior is affected by the anionic charge of the polymers in water and in the pore solutions of the four cements: The higher the anionic charge, the better the adsorption [9]. On the basis of low C_3A -content it is observed that *CEM I (B)* shows the best liquefying effect. The two cements *CEM I (C)* and *CEM I (D)* need higher dosages of superplasticizers to obtain the same result due to their high content of sulfate and free CaO. The adsorbed amounts of the superplasticizers in mg / g cement correlated with the dosages to obtain a flow value of 26 ± 0.5 cm. The C_3A -poor cement *CEM I (B)* adsorbed in all cases the least amount of superplasticizer. Regarding the heat flow values, no significant differences are observed for the cement combinations with superplasticizers. The results give an insight in how far the cement production (and consequently the CO_2 -emission) can be minimized by using admixtures which give good workability and compatibility which is of high environmental value.

5. REFERENCES

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