Impact of some parameters on rheological properties of cement paste in combination with PCE-based Plasticizers

Ameneh Schneider[1], Heinrich Bruckner[2]

[1] Smart Minerals GmbH, Vienna, Austria
[2] Vienna University of Technology, Vienna, Austria
Corresponding author: schneider@smartminerals.at

ABSTRACT

Four different Polycarboxylate ethers (PCE) known as superplasticizers were tested for their rheological performance in cement paste. The structure varies in the side chain and charge density of the molecules and the functional group. The investigations were focused on variation of some parameters (e.g. C_3A-conten and retarding agent) in cement type CEM I 42.5 R and their influences on the activity of PCE-based plasticizers. The rheological properties were measured using a rotation viscometer. Using a defined program, the rheological curves of the cement paste at defined physical condition were plotted to show the relationship between shear rate and yield. Saturation points (maximum PCE-concentration) of each PCE were determined. The plastic viscosity and the yield value were calculated for each cement variation and PCE-combination. The results show the differences in PCE activities. PCE2 with short side chain and low charge density reduces the viscosity and the yield value for all investigated cements at lower concentration; it, however, showed characteristic differences according to the cement composition. Cement with very low content of C_3A has higher viscosity but lower yield value as compared to cement with higher C_3A-content. All PCE showed different findings in connection with the C_3A-content. Our investigations clearly showed that the chemical characteristics of cement can modify the general statements about PCE-reactivity. The results underline the importance of rheological investigations in cement production concerning the reactivity of different PCE molecules. The Effect of temperature (summer, winter) is investigated as well.

Key Words: Rheology, Polycarboxlate ether, plastic viscosity, yield stress, temperature

1. INTRODUCTION – STATE OF THE ART

From the rheological point of view it is absolutely necessary to choose the right type and concentration of Polycaboxylate ether (PCE)-based super plasticizer for the cement and concrete technology according to the application. Rheological investigations are well known in the research field of construction materials. The potential of investigating the interaction between different raw materials is emphasised [1-3]. In literature [4-5] the adsorption capacity of PCE and thus their effect, which depends on the molecular structure of the PCE, are well described. Using Zeta Potential Rickert [6] and Hermann [7] investigate the mechanism of interaction between cement components like limestone and slag with PCE-molecules. It is known that the fluidity of cement increases by substitution of clinker through other granulates like limestone or blast furnace slag and consequently less concentration of PCE is needed. Main cement components and molecule structure of PCE affect the fluidity of the mixtures as well. A better workability of concrete was established by using CEM II or CEM III compared to CEM I. In 2008 the rheological properties of cement systems were investigated by using a rotating viscometer and it is presumed that the PCE-molecules adsorb predominantly on the clinker components and affect the first hydration products [8]. The importance of calculating

the yield stress and viscosity equation for different cementious construction materials is well described by Khayat et.al [9-10]. Controlling of sulphate ion concentration in aqueous phase, which has been known to affect the dispersing force of PECs, is well published in literature [11-13]. C_3A is the most reactive phase in the Portland cement clinker and is responsible for the stiffening of clinker or cement. The tricalciumaluminate is only slightly involved in the curing. By adding a sulphate as retarding agent to the cement mixture the tricalciumaluminate will react differently. Depending on the C_3A content, the fineness of the cement and the alkali content, there are certain optimum sulphate contents for each cement type. Because of the differences in solubility between hemihydrate (highly), gypsum (moderate) and anhydrite (poorly soluble), the nature of the sulphate-bearing compound added to the clinker is also of some importance. The retarding action of the sulphate agent on the C_3A is effected not only through the formation of ettringite, but also by the adsorption of sulphate ions on the particle surface, which is positively charged by the adsorption of calcium ions. The adsorption of sulphate ultimately leads to a reduction of the C_3A-solubility.
As mentioned above the sulphate concentration has a critical effect on the reactivity of PCE. The different composition of retarding agent was chosen by the cement producer and provided for this work.
The different issues of this investigation can be summarized as follows:

1. The scientific issue should define, if there are specific effects of clinker parameter (e.g. C_3A-content) on the PCE-effectiveness.
2. How important is the choice of sulphate-bearing compound in this field?
3. From the practical point of view, this knowledge should bring more understanding about the effect of specific and target variation in cement production on the rheological performance of cement paste.

2. EXPERIMENTAL DETAILS

2.1. Specimens selected

The unique feature of PCE offers the possibility to get tailor made synthesised products by matching the length of the side chain and variation of the density of charges as well as adding functional groups to the molecule structure. The following 4 PCE molecules were chosen by an admixture supplier in Austria.

- PCE-1: short side chain, high charge density.
- PCE-2: short side chain, low charge density.
- PCE-3: long side chain, low charge density.
- PCE-4: long side chain, active functional group.

These 4 PCE-compositions cover a very wide range of common plasticizers, which are used by concrete production in Europe.

All PCE samples were from one production charge and had a content of 30 percent.
All investigations were made on the cement type **CEM I 42.5 R**.
The variations of clinker parameters and sulphate retarding agent are shown in Tab.1:

	Variation A			Variable B	
Nr.	M 12/0254	M12/0255		M 12/0254	M 12/0253
Grain size					
Blaine [cm²/g]	5200	4980		5200	5370
RFA					
CaO %	61,04	60,99		61,04	60,00
SiO2 %	19,18	20,43		19,18	18,97
Al2O3 %	5,65	3,36		5,65	5,22
Fe2O3 %	2,78	5,50		2,78	2,72
SO3 %	3,61	3,31		3,61	3,55
MgO %	3,94	3,59		3,94	4,07
K2O %	1,12	0,77		1,12	1,12
Na2O %	0,40	0,28		0,40	0,39
RBA (Rietveld)					
C3S_Nishi_hkl %	57,62	63,71		57,62	54,39
C2S %	13,57	8,27		13,57	12,18
C3A %	**11,49**	**0,77**		11,49	10,24
CFAF %	6,84	16,04		6,84	5,59
Gypsum %	0,25	1,59		**0,25**	**1,64**
Anhydrite %	0,00	0,00		**0,00**	**2,55**
Hemihydrate %	4,36	3,59		**4,36**	**1,22**

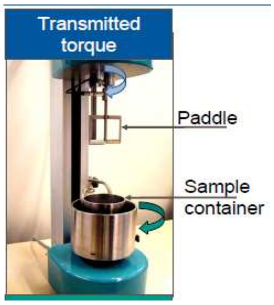
Tab. 1: Analysis data of cements

Important remark: For comparison of rheological properties of cement paste, the chosen cement should have the same range of grain size. Hence this parameter has most effect on the rheological parameter the big difference of grain size (± 300) by samples will overlap the effect of the clinker parameters, which are the matter of these investigations.

For two PCEs Molecules (PCE1 and PCE2) the effect of different temperatures was investigated as well. For summer temperature the rheological measurement were done at 35 °C and for winter temperature the measurement were repeated at 10 °C.

2.2 Rheological investigation

The rheological investigations were carried out on a rotation viscometer “Viskomat NT” (shown in Fig. 1), Many pre-tests were run for estimation of the best measurement parameter, e.g. operation mode, the water/cement ratio, mixing time, the measuring time and the reproducibility of the measurement. The results of these entire tests are summarised in Tab. 2.



Variation of parameter				
Type of blender	**Mortar blender**	Household blender		
Mixing time	**90 s**	120 s	150 s	180 s
W/C ratio	0,35	**0,4**	0,45	
Measuring time	**20 min**	45 min	60 min	
Shear profile	Ramp			
Repeatability	**± 3,2%**			

Fig. 1: Viskomat NT **Tab. 2: Parameter for measurements with Viskomat NT**

The measurement profile is shown in Fig. 2. With these parameters, the estimated values have shown a good reproducibility of ± 3,5 %.

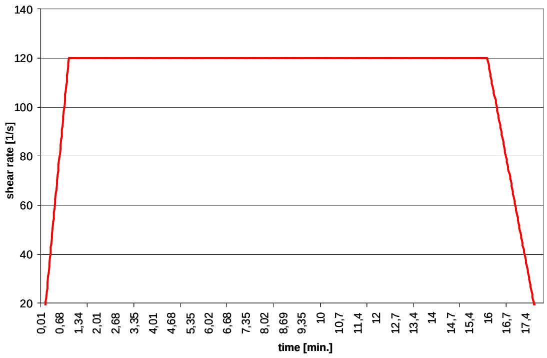


Fig. 2: **Measurement profile for Viskomat NT**

For estimating the saturation point for each PCE and cement the following measurement profile was developed and is shown in Fig. 3.
After running Viskomat at the shear rate of 120 1/s for 20 minutes the dosing of PCE starts. The Viskomat runs for 10 minutes with each concentration. The first dosage was 0,10 % and the end dose 0,35 % of cement content.

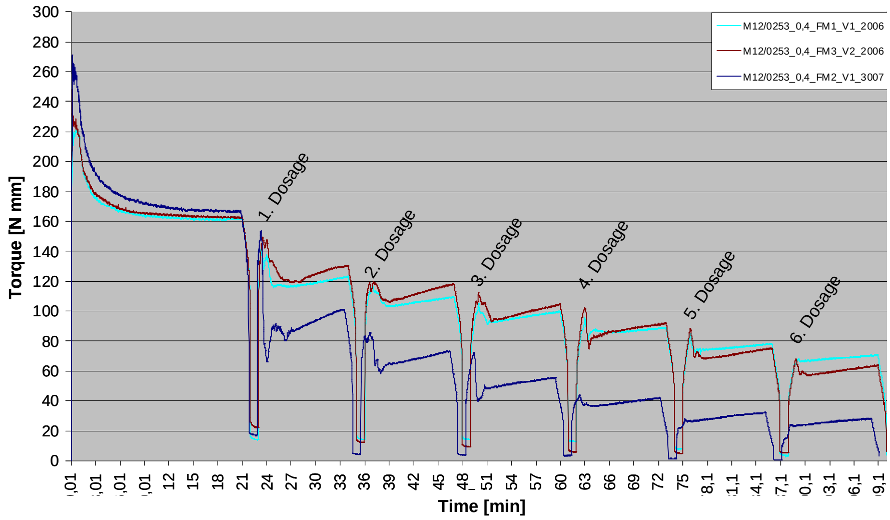


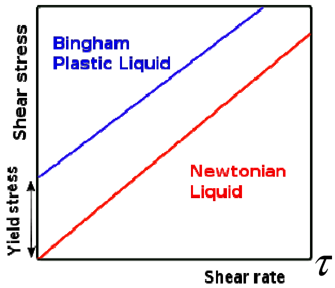
Fig. 3: Measurement profile for estimation of saturating point

2.3. Calculation of plastic viscosity and yield stress

It is known that the cement lime is not a Newtonian liquid and undergoes the rules of Bingham as shown in Fig. 4. Two material characteristics were calculated for each rheological measurement according to the Bingham Model:

A) Plastic viscosity: A property of fluids in motion, which is mainly determined by dynamic friction between moving elements

B) Yield stress: A property of the fluid at shear rate 0 and is mainly influenced by attractions and physical exchanges of two or more polymer chains in system → Variations of the first hydration products affect these forces in a cement based mixture and thus the cement paste.



$$\tau = \eta \times \gamma + \tau_0$$

Fig. 4: Bingham Model and formula

3. RESULTS AND DISCUSSION

3.1. C_3A-Content of clinker - Variation A

Figure 5 demonstrates the torque measurement with Viskomat NT for the two cements (type CEM I), one produced with clinker containing C_3A and one with C_3A-free clinker, without adding any PCE. As obvious in Fig. 5 the C_3A-content influences the rheological behaviour of cement paste. The cement containing C_3A in clinker has higher torque values (ca. 20%).

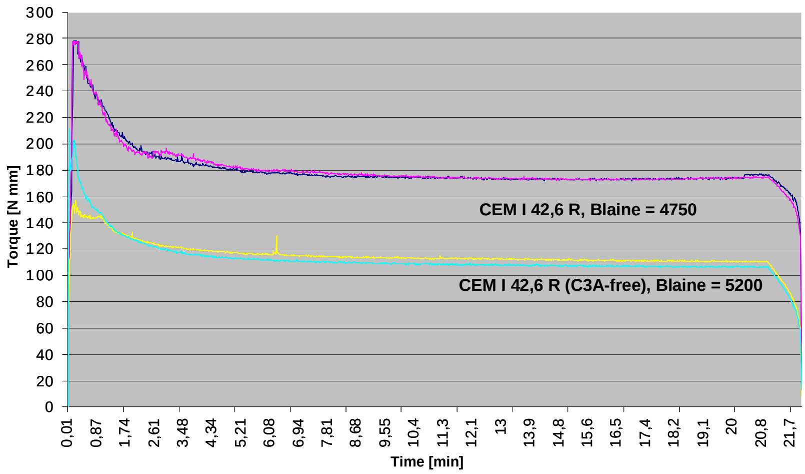


Fig. 5: Torque measurement at shear rate 120 1/S

Saturating points for all 4 PCE were estimated for these two cements. Starting from different torque values the behaviour of PCE was similar for both cements and is shown for C_3A-free cement in Fig. 6. PCE 2 is the most strong one and its saturating point is about 0,2 %. PCE 1 and 3 react similar and shown the same saturating point. PCE 4 is a special product with a strong stability and lower effect on fluidity. There was no saturating point for this product.

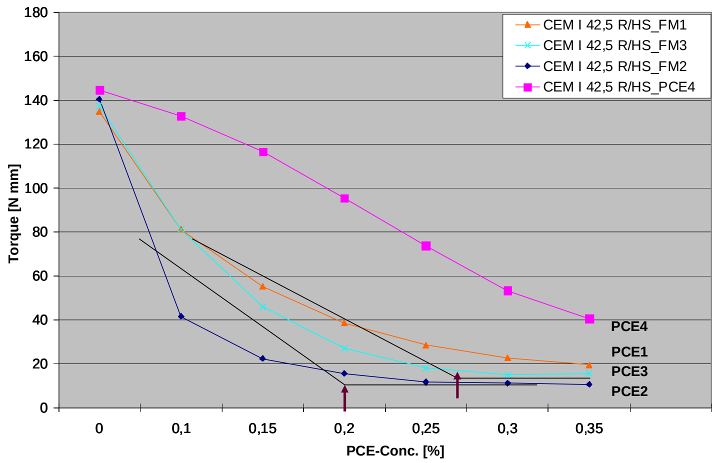


Fig. 6: **Estimation of saturating points for all PCE for C_3A-free cement**

As mentioned in 2.3 the two characteristic values of the cement paste (viscosity and the yield stress) were calculated for each rheological measurement at a concentration of 0,2 % PCE related to cement content. Fig. 7 demonstrates the different effects of PCE on these values for these two cements. The content of C_3A in clinker moderates the effect of PCE to some extent. The cement containing C_3A (blue points) has higher yield stress value and lower viscosity. In contrary the C_3A-free cement has lower yield stress but higher viscosity.

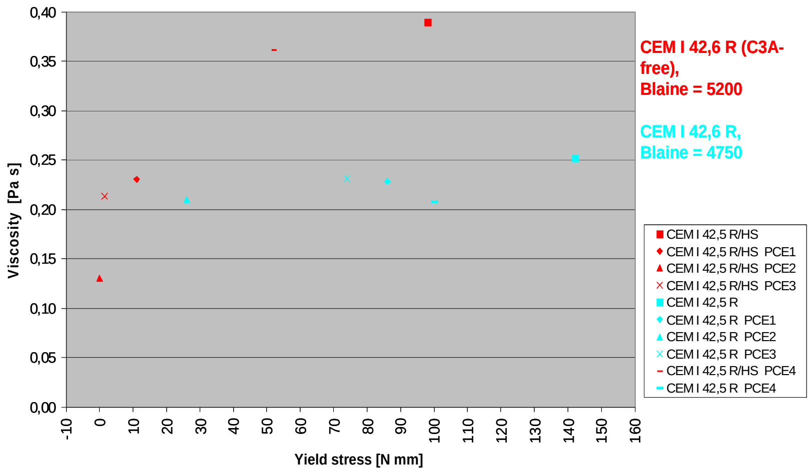


Fig. 7: Viscosity and yield stress with different PCEs

3.2. Composition of sulphate retarding agent - Variation B

Two samples with comparable C_3A-content and Blaine value were prepared with two different compositions of sulphate retarding agents. Hence during the production there is an uncontrolled conversion of semi-hydrate to anhydrite. These two cements were provided for these investigations by the cement producer. The curves in Fig. 8 show that this parameter affects the torque value as well but in lower extent than C_3A-content. Higher anhydrite-content reduce the torque value about 11%.

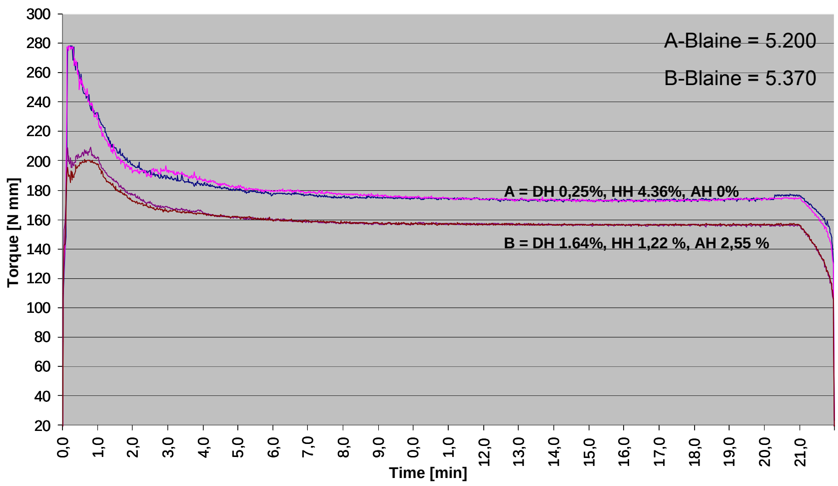


Fig. 8: Torque measurement at shear rate 120 1/S

Analogue to the first variation the two characteristic values of the cement paste were calculated for each rheological measurement at a concentration of 0,2 % PCE related to cement content. Adding Sulphate anhydrite changes obviously the initial values. PCEs change the yield stress and viscosity in a manner shown in Fig. 9 as expected. The different effect of PCE 4 is somehow unique for the cement with higher anhydrite content.

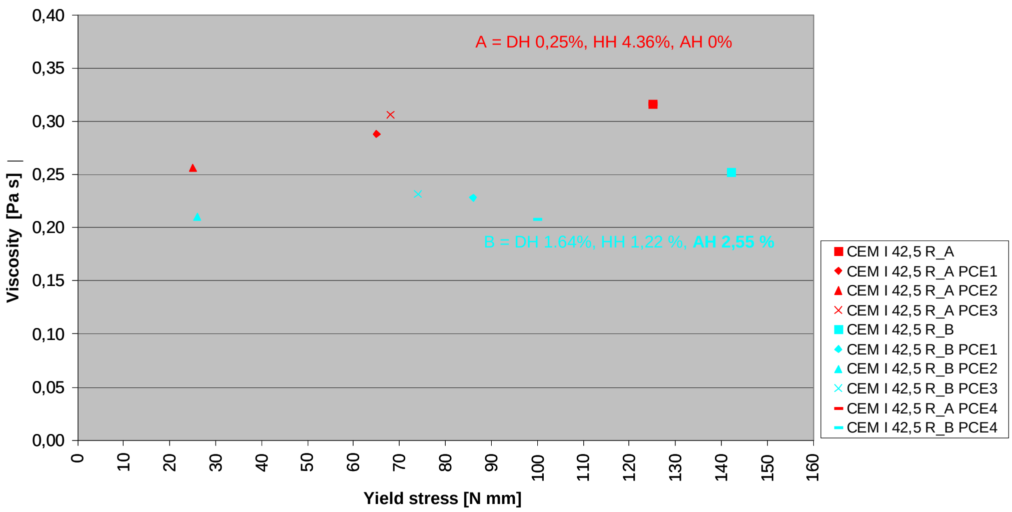


Fig. 9: Viscosity and yield stress with different PCEs

For investigation of relationship between the PCE adsorption behaviour on cement particles and paste fluidity the estimation of sulphate and other ions in pore solutions are crucial.
In this work the determining of sulphate concentrations from pore solution were carried after 15 minutes without adding PCE-solution. After adding PCE the sulphate concentrations were determined after 30, 60 and 90 Minutes. Fig. 10 shows the deviation of sulphate concentration during time for the cement number 254 containing C_3A and for number 255 declared as C_3A-free cement in combination with two different PCE-molecules.

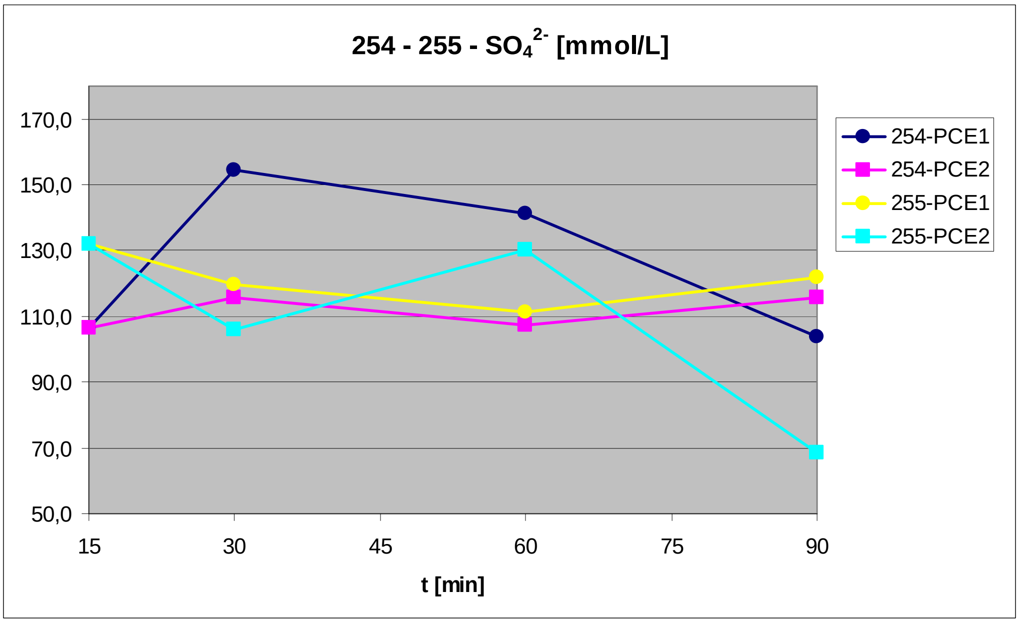


Fig. 10: changes of sulphate-conc. in pore solution by time

In case of C_3A-free the Sulphate concentration of pore solution developing more constantly with PCE 1 than in case of cement pastes with higher concentration of C_3A. For PCE2 the Sulphate concentration is more stable in presence of C_3A. The important time for this observation is from 15 to 60 minutes.

These results emphasise the known effect as described in literature, that the retarding action of sulphate agent on the C_3A is effected not only through the formation of ettringite, but also by the adsorption of sulphate ions on the particle surface, which is positively charged by the adsorption of calcium ions. The adsorption of sulphate ultimately is in completion with the PCE-molecules therefore there are big different between the developing of Sulphate concentration between PCE 1 and PCE 2 for the cement with different C_3A-content.

3.3. Variation of Temperature

It is known that the temperature affect the rheological properties of materials. Form the practical point of view (construction) we have chosen 35 °C for the summer time and 10 °C for winter time.

The saturating points were estimated in these two temperatures for PCE 1 and PCE 2 on cement type CEM I 42,5 R and are shown in Figure 11 and 12.

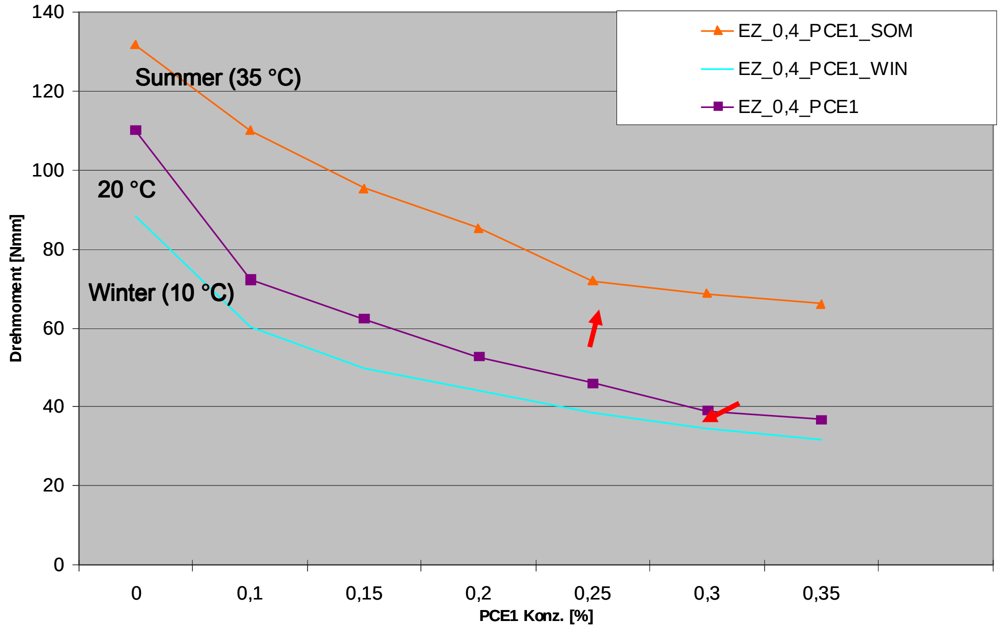


Fig. 11: saturating points for PCE 1

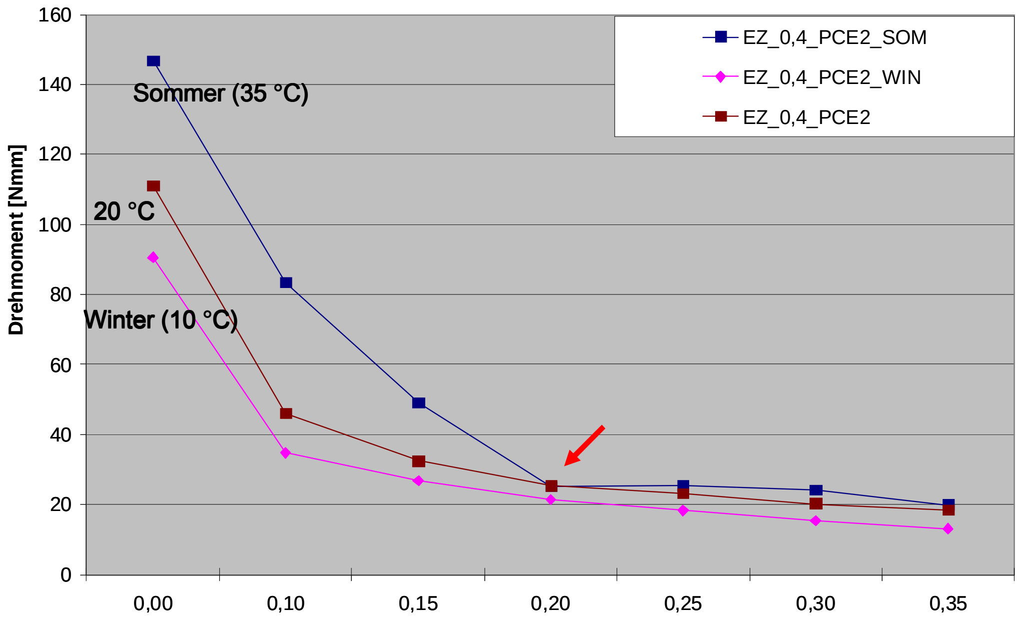


Fig. 12: saturating points for PCE 2

Obviously by using PCE 1 lower concentration is need at higher temperature in summer than in winter time. By using PCE 2 no effect of temperature is estimated.

CONCLUSIONS

This study showed that, in addition to the well known factors such as limestone and blast furnace slag content, fineness, sulphate retarding agent and C_3A-content affect the rheological performance of cement paste. Temperature during the construction time summer or winter have effect in some extends.

The rheometer is an appropriate instrument (tool) for

- Characterization or description of the flowability,
- Determining the yield stress values and viscosity of the cement pastes

- Comparison of the effect of different super plasticizers such as polycarboxylate ether-based (PCE) with different structures
- Determination of the most effective concentration of super plasticizers
- The combination of two or more factors of cement can be estimated by these kind of investigations as well

Rheological investigations are necessary for selection of the plasticizer for the best performance (fluidity and stability)

Outlook → transfer of the results on cement paste to mortar and concrete

REFERENCES

[1] O. Wallevik et al, Rheology as a tool in concrete science: the use of Rheolographs and workability boxes; Cement and Concrete Research 41, p.1279-1288 (2011).

[2] P. Coussot, Rheometry of Pastes, Suspensions and Granular Materials, John Wiley and Sons Inc., Hoboken, New Jersey. ISBN 0-471-65369-1, 291 pages.

[3] M. Greim, Rheological Measurement on Building Materials, a Comprehensive Research Program; Annual Transactions of The Nordic Rheology Society, Volume 5, 1997, Conference 1997, Reykjavik, August 6-9 (1997).

[4] J. Plank, B. Sachsenhauser, Experimental determination of the effective anionic charge density of polycarboxylate superplasticizers in cement pore solution; Cement and Concrete Research, 39 (1), p.1-5 (2009).

[5] R. Qianping et al, Effect of the length of the side chains of comb-like copolymer dispersants on dispersion and rheological properties of concentrated cement suspension; Journal of Colloid and Interface Science, 336, 624-633 (2009)

[6] J. Rickert, Zeta potential and rheology of cement pastes - influence of superplasticisers and of granulated blastfurnace slag and limestone; Beton, 60 (7-9), 315-320,363-365, (2010).

[7] J. Herrmann, J. Rickert, Influences of Slag of Limestone on the Performance of Superplasticizers, Tenth international conference on superplasticizers and other chemical admixtures (Prag 28.-31.10.2012). Farmington Hills: American Concrete Institute, ACI, 2012 (ACI Publication SP-288), S.317-328

[8] S. Hanehara, K. Yamada, Rheology and early age properties of cement systems; Cement and Concrete Research 21, 175-195 (2008).

[9] A.Yahai, K.H. Khayat, Application of rheological models to high-performance grouts containing supplementary cementious materials and viscosity enhancing admixture, Material and Strctures, Vol. 36, 402-412 (2003)

[10] J. Petit, E. K. Khayat, at alYield stress and viscosity equation for mortars and self-consolidating concrete, Cement and Concrete Research 37, 655-670 (2007)

[11] J. Plank, Dai Zhimin, et al, Fundamental mechanisms for polycarboxylate intercalation into C3A hydrate phases and the role of sulphate present in cement, Cement and Concrete Research 40 (2010)

[12] K. Yamada, S. Ogawa, S. Hanehara, Controlling of the adsorption and dispersing force of polycarboxylate-type super plasticizer by sulphate ion concentration in aqueous phase, Cement and Concrete Research 31, 357-383 (2001)

[13] A. Zingg, F. Winnefeld, et al, Adsorption of polyceletrolytes and its influence on the rheology, zeta potential, and microstructure of various cement and hydrate phases, Journal of Colloid and Interface Science 323, 301-312 (2008)