

# VALUE ENHANCEMENT FOR REFRACTORY CASTABLES BY DEFLOCCULANTS BASED ON COMB POLYMER TECHNOLOGY

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## ABSTRACT

The paper presents Polycarboxylate ethers (PCE) with comb polymer structure, the new generation of dispersants for refractory castables, in respect of chemical structure and mode of action. The molecular design of the Polycarboxylate ethers is crucial for their performance, but the comb polymer architecture can be tailor-made in a very broad range for various refractory materials and requirements. The investigations focus also on the understanding of polymer interaction with refractory materials.

Polycarboxylate ethers add remarkable value to the refractory industry as these advanced polymers supports the trend from shaped to unshaped refractory products. Successful production and installation of self-flow castables at low water contents is enabled by the application the latest Polycarboxylate ether technology.

The benefits of the comb polymer deflocculants are twofold by influencing positively both fresh and hardened properties of refractory castables. Hence, these polymers contribute sustainable in the further improvement of refractory materials and future installation technology.

## INTRODUCTION

The industrial production of refractory castables started almost 75 years ago in the United States and later on in Japan. The use of refractory castables was continuously expanded and the chemical and physical properties improved. In the beginning, this was only possible with the extension and improvement of the Calcium Aluminate Cements (CAC). But a real push of innovation of refractory castables took place in the mid 80's, when castables were produced with sophisticated formulations, which outperformed even refractory bricks in many applications. The technology which allowed such concretes to be developed, was dependent on two main factors: a) the theories of particle packing and optimised granulometry and b) the availability of ultrafine silicas (silica fumes) and aluminas [1].

The availability of the ultrafine fillers allowed the formulation of continuous gradings down to sub-micrometer levels, and as consequence, it was possible to formulate refractory castables with very low alumina cement contents in resulting in low-cement (LCC) respectively in ultra-low cement castables. (ULCC). The latest technology has concentrated on the optimization of the rheological properties of the castables enabling the applicators to install the refractory material without mechanical vibration. These are known as self-flow castables (SFC) pushing the development of monolithic refractories remarkable. There are basically two categories of refractories in terms of form type namely bricks (shaped) and monolithics (unshaped). The bricks was the largest refractories segment in 2013 globally by form type, however, the monolithic segment is expected to grow by annually of 3,9% through 2020. [2] In total the global refractory market is growing steadily, holding immense business potential with the rapid pace of innovation and wider acceptance. The growth and wider acceptance of refractories won't have been possible without the latest developments of newly developed additives based on Polycarboxylate ether technology (PCE) which contribute essentially to the further penetration for the above mentioned types of self flow castable.

The success factors of this development is e.g. faster installation and less mixing water to produce a flow castables resulting in a lower porosity of the castables while increasing the density and strength. All in all these properties gives a longer durability and cost savings for the refractory applicators.

Nowadays self flow castables are getting more and more highly sophisticated formulations and the proper dispersants play a key role within the refractory mix. In order to fulfill the requirements of the different type of castables, specific dispersants are under development. In this article, the structure of different dispersants is presented and the effect of comb polymer dispersants in castables is discussed.

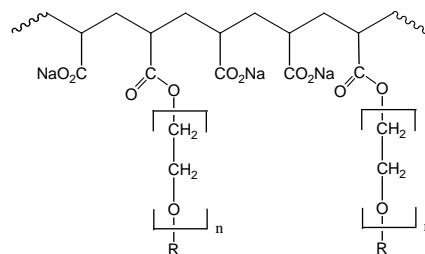
## COMB POLYMER DISPERSANTS

Comb polymer dispersants are indispensable additives in modern high performance and low-moisture castables. Conventional dispersants are e.g. the inorganic sodium trimetaphosphate (NaTPP) and the organic tri-sodium citrate (Na-CT).

The fluidifying effect of both NaTPP and Na-CT is very weak regarding calcium aluminate cements and is a result of the slow down of ion dissolution of the cement clinker. [3] A disadvantage of these additives is also that an overdose leads to a degradation of flow properties. Furthermore, both dispersants, especially tripolyphosphate, are set retarders which can cause difficulties in demolding in certain cases. Another drawback for this kind of chemistry is, the products can't be chemically modified in order to optimize and adopt their properties for the latest demands and trends in the refractory industry.

The primary role of additives in dispersed castable systems is to provide sufficient flow for placing the refractory concrete at low water additions, necessary to achieve low porosity, high strength and long durability. This can be achieved by polymeric dispersants tailor-made for the dispersion of the refractory materials. The PCE chemistry allows almost endless possibilities to tailor the polymer architecture for optimum performances.

The new molecules consist of a carbon-carbon backbone having anionic carboxylic groups responsible for electrostatic interaction. Additionally the molecules have included water soluble nonionic polyether side chains which are responsible for sterical interaction. The introduction of the first polycarboxylate ether polymer into the refractory market was in 1996. A model of the molecular design for PCE is shown in figure. 1



Polycarboxylate ether, Na-salt

Fig. 1: Schematic representation of PCE

If the PCE molecule is sufficiently stretched in the aqueous environment, the backbone of the polymer can rotate freely around the C-C bonds and the entire molecule forms a trunk like conformation with the charged backbone in the center, whereas the side chains themselves are more or less helically looped. For the PCEs used in refractory applications, the main chain length is usually in the nanoscale range of 3 to 20 nm, and the side chain length from 3 to 40 nm, respectively. The shape of some dispersants is illustrated in figure 2.

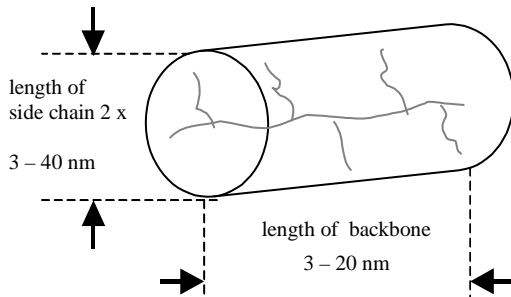


Fig. 2: Schematic shape of PCE

Depending on the chemical structure, polycarboxylate ethers can influence the flowability of the refractory concrete and hydration process of the calcium aluminate cement. Depending on the size of the polycarboxylate ether it can retard the cement hydration process, which gives a prolonged workability of the refractory material at elevated temperatures, or accelerate the development of the green strength which is desired by the production of precast elements.

#### DISPERSING MECHANISM

PCE's backbone, which is negatively charged, permits the adsorption on the positively charged colloidal particles. As a consequence of PCE adsorption, the zeta potential of the suspended particles changes, due to the adsorption of the COO<sup>-</sup> groups on the colloid surface. This displacement of the polymer on the particle surface ensures to the side chains the possibility to exert repulsion forces, which disperse the particles of the suspension and avoid friction. These forces can be directly detected by the use of the atomic force microscopy (AFM), working with model substances in liquid environment. [4]

The mechanism of the mode of action can be explained as follows. As indicated in figure 1, the Polycarboxylate ether adopts a trunk shaped conformation. The carboxylate groups are positioned along the longitudinal axis and hence, in the center. When the dispersant with the negatively charged anchor groups approach to the cement surface, the whole molecule has to change its conformation in that way that the side chains orientated to the cement surface turn away and stretch into the aqueous phase. From the illustration in figure 3, it can be concluded that occupation of sites on the cement surface is less for a polymer with longer side chains as for a macromolecule with shorter ones. The surface coverage influences the hydration of the calcium aluminate cement by changing the dissolution and the nucleation processes. [5] Thereby, the course of the electric conductivity of a cement paste was recorded.

As consequence, the Polycarboxylate ether with the longer side chains provides on the one hand excellent separation of the particles but on the other hand allows water to penetrate more easily into the polymer layer around the cement grain. Thus leads to a shorter dissolution period and the cement hydration can start earlier resulting in faster setting and better early strength development.

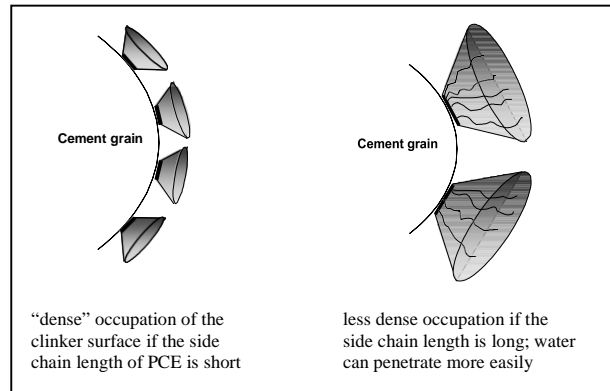


Fig. 3: Model of adsorption of PCEs on a cement surface

It turned out that this type of additives are not only effective dispersants for Calcium Aluminate cement but also for the very fine reactive or calcined aluminates used in the binder matrix. Other experiments, however, revealed that Polycarboxylate ethers could not always display their efficacy in castable formulations which contain silica fume. [3] The addition of even small amounts of microsilica can improve the flow properties of a castable. The dense particle packing achieved by microsilica additions will minimise the amount of water needed for casting. This gives low porosity and high strength properties in the fired product. But the silica surface exposes a high density of silanol groups (-Si-OH) towards the aqueous phase. These groups can be ionized to form negatively charged -Si-O<sup>-</sup> groups, and at low pH also positively charged -SiOH<sub>2</sub><sup>+</sup> groups can be formed. At pH values > 2 silica is (partially) negatively charged, whereby the charge density is a function of the pH. At a pH value of 8-8.5 both charged -Si-O<sup>-</sup> and non-charged -Si-OH groups are present on the silica surface which can interact with Polycarboxylate ethers. Often refractory producers consider microsilica as an inert towards Polycarboxylate ethers and believe only calcium aluminate cement affects the performance of the polymeric comb polymers because of its perceived role as a filler only.

In order to get a more fundamental understanding of the behavior of polycarboxylate ethers in such mix designs, some investigations for microsilica containing binder systems have been carried out. Here we want to report on the outcome of this study investigating two different types of microsilica.

#### EXPERIMENTAL PART

Aqueous microsilica slurries as well as blends of microsilica with calcium aluminate cement were investigated by measuring fresh properties e.g flowability. Mixing time was 1 min with a hand mixer. The test systems are shown in Table 1 and 2.

Tab. 1. Microsilica slurries

Microsilica	SiO <sub>2</sub> > 96%	50.0	%
Water : MS ratio		1 : 1	
Dispersant	PCE	0,05	%

Tab. 2. Microsilica – CAC blend

Microsilica	SiO <sub>2</sub> > 96%	50.0	%
CAC	70 % Al <sub>2</sub> O <sub>3</sub>	50.0	%
Water : MS+CAC Ratio		1 : 1	
Dispersant	PCE	0,05	%

In order to determine the impact of the microsilica type two different qualities from different sources were used. The typical analytical data are summarized in Tab 3.

Tab. 3. Microsilica – Typical Analytical data

	MS Type A	MS Type B	
SiO <sub>2</sub>	98	96	%
C (free)	0.5	0.7	%
Fe <sub>2</sub> O <sub>3</sub>	0.01	0.05	%
Al <sub>2</sub> O <sub>3</sub>	0.2	0.2	%
CaO	0.2	0.3	%
MgO	0.1	0.25	%
K <sub>2</sub> O	0.2	0.5	%
Na <sub>2</sub> O	0.15	0.08	%
LOI	0.5	1.2	%
Coarse Particels >45µm	0.2	1.5	%
pH value	6.8	7.5	%
Bulk Density	300	200	Kg/m <sup>3</sup>
Specific surface (BET)	21	20	m <sup>2</sup> /g

The microsilica slurries properties were evaluated by measuring the flowability with a truncated cone with the dimension of 5 cm in height and 3 cm inner diameter. The rheological properties were determined by Brookfield rheometer.

Also low-cement castables according to the guide recipe given in Table 4 have been prepared by mixing all dry ingredients in a Hobart mixer for one minute. After water addition, mixing was continued for additional four minutes. Immediately after mixing the prepared castable was placed into a stainless steel cone ( $\phi_{\text{bottom}} = 100 \text{ mm}$ ,  $\phi_{\text{top}} = 70 \text{ mm}$ ,  $h = 50 \text{ mm}$ ). The cones were lifted 10 min., 30 min., and 60 min. after water addition. The castable was allowed to flow freely for two minutes. Then two perpendicular diameter measurements  $d_1$  and  $d_2$  were taken and the average value  $d$  was used to calculate the flow value FV as a percentage, according to the following equation:

$$\text{Flow value (FV) [\%]} = \frac{d \text{ (mm)} - 100 \text{ mm}}{100 \text{ mm}} \times 100$$

Tab. 4. Basic LCC test recipe

Tabular Alumina	1 - 3 mm	29.0	%
	0.5 - 1 mm	22.0	%
	0.2 - 0.6 mm	6.0	%
	0 - 0.2 mm	21.0	%
Calcined Alumina	multi-modal	10.0	%
Microsilica	SiO <sub>2</sub> > 96%	5.0	%
CAC	70 % Al <sub>2</sub> O <sub>3</sub>	5.0	%
Dispersant b.w.c.	PCE	0.1	%
Water b.w.c.		5.3	%

b.w.c.: by weight of castable

The Polycarboxylate ethers applied in this study are graft polymers of polyglycol side chains with different molecular weight on an anionic C-C backbone. The side chain varied from very short, medium and to long side chain length.

## RESULTS AND DISCUSSION

The first investigations for the pure aqueous microsilica slurry revealed for both types an incompatibility depending on the

molecular weight of the applied additive. This phenomena was not only observed for the polyethylene glycols with varying molecular weights as shown in Figure 4, but also for the different Polycarboxylate ether dispersants as depicted in Figure 5. For Microsilica type A the thickening effect overserved in the screening starts already with medium molecular weight polyethylene glycol (PEG 2000) whereas for MS type B only high molecular weight polyethylene glycol (PEG 6000) causes no flowability.

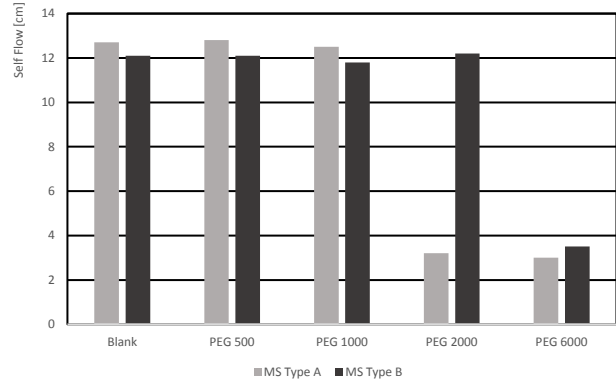


Fig. 4: Flow values of MS slurries with different PEGs – Dosage 0.05%, pH 7.0 – 8.0, Temp. 20°C

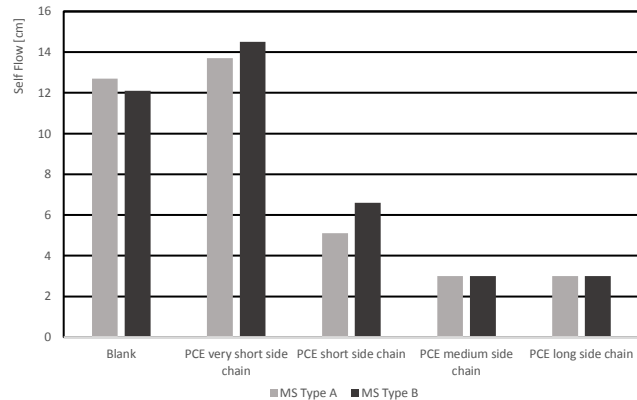


Fig. 5: Flow values of MS slurries with different PCEs – Dosage 0.05%, pH 7.0 – 8.0, Temp. 20°C

Both graphs clearly show if the non-ionic polyethylene glycols and the Polycarboxylate ethers exceed a certain threshold of molecular weight a thickening effect is observed. The negatively charged Polycarboxylate ethers act only with very short side chains as dispersing agents. The flocculating effect occurs already with short side Polycarboxylate ethers which wasn't expected based on the findings for the pure microsilica slurries.

The experiment indicates a higher adsorption rate for the Polycarboxylate ethers leading to a bridging and thickening effect resulting in high viscosity and no flow even for short side chain dispersants. The adsorption characteristic of Polycarboxylate ethers depends on their individual structures like charge density and length of side chains. These effects are discussed in more detail elsewhere. [6]

The surface of the main component in Calcium Aluminate Cement is mono-calcium-aluminate (CA) which is positively charged. Hence, the negatively charged Polycarboxylate ethers adsorb in considerable amounts on the cement particle and should less interact with the microsilica particles. The results are depicted in Fig. 6.

When placed in contact with water the hydration of CA is characterized by rapid dissolution of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  followed by a rapid precipitation of hydration products. These cationic salts interact with the negatively charged  $-\text{Si}-\text{O}^-$  groups on the silica surface causing a flocculation especially for MS Type B where the measured pH value was at approx. 12. The combination of MS Type A and CAC was only at a pH value of approx. 8 meaning the microsilica surface carried less negative groups hence also less interaction with the cationic groups. It was expected the CAC share in the blend would compensate the incompatibility of the long side chain dispersants, but this wasn't the case. The experimental result emphasises the theory of the network formation for PCEs when higher proportions of microsilica are in the mix.

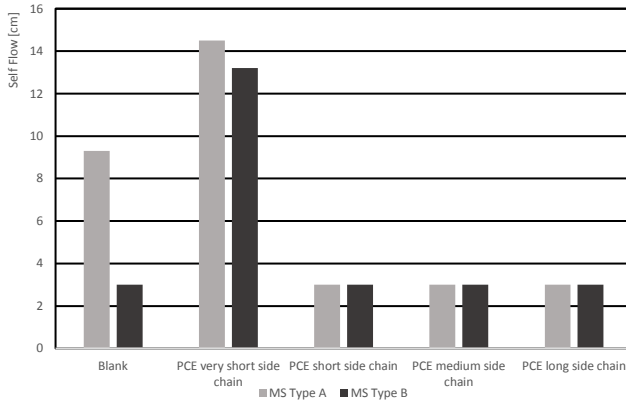


Fig. 6: Flow values of MS-CAC slurries with different PCEs – Dosage 0.05%, Temp. 20°C

For verification of the findings in the aforementioned recipes the different PCEs were screened in a LCC castable and the results are summarized in Fig 7 and Fig 8. The LCC recipe with MS Type A could only be plasticized with the PCE with the very short side chain whereas in the second test recipe with MS Type B the dispersant with the long side chain gave the highest self-flow values. These very interesting results are evidences that the type of microsilica has a very strong impact on the performance of Polycarboxylate ether. An assumption for the very different performance is the release of varying amounts of ions into the pore solution and influencing the hydration kinetics between CAC and MS Type A and MS Type B in a different way. The negatively charged Polycarboxylate ethers can be very sensitive towards the type and concentration of the multivalent ions. The multivalent ions can shield the negative charge either on the microsilica surface or in the polymer affecting a change of the dispersant confirmation.

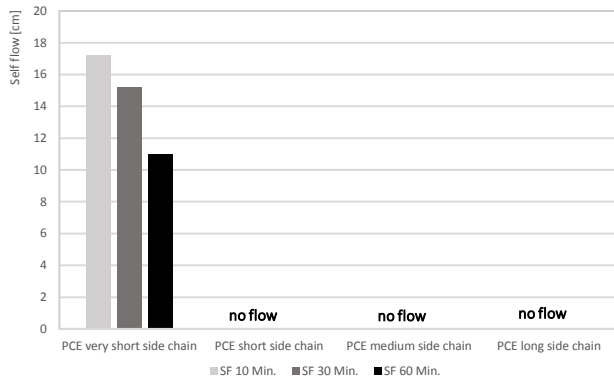


Fig. 7: Flow values of LCC containing MS Type A with different PCEs – Dosage 0.05%, pH 7.0 – 8.0, Temp. 20°C

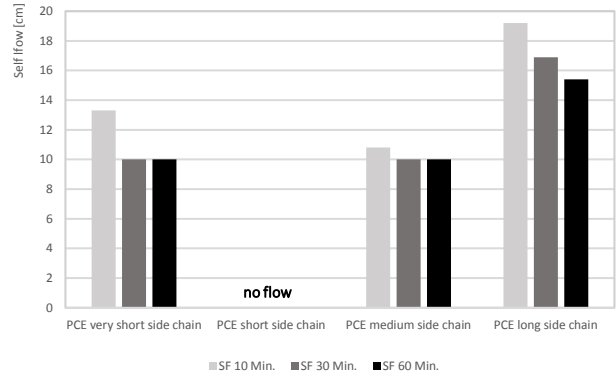


Fig. 8: Flow values of LCC containing MS Type B with different PCEs – Dosage 0.05%, pH 7.0 – 8.0, Temp. 20°C

## SUMMARY AND OUTLOOK

Polycarboxylate ether adsorb via different mechanisms on microsilica and calcium aluminate cement particles. Due to the opposite surface charges of microsilica and calcium aluminate cement both substrates undergo strong interaction with each other and compete also in the adsorption of Polycarboxylate ether molecules. Depending on the type and composition of the microsilica different Polycarboxylate ethers are needed to give the best performance. The polymer synthesis is very versatile and therefore it's possible to synthesis tailor made Polycarboxylate ethers with unique properties and good compatibility for the different refractory raw materials enabling the development of castables with specific requirements or make new raw materials applicable which wasn't possible with the conventional dispersants till now.

In the future further basic investigations are needed in order to get a better and deeper understanding for the interactions of polymers and surface active refractory raw materials. The focus will be on the interdisciplinary combination of polymer chemistry, mineralogy, polymer structure and property resp. performance relationship for advanced refractory systems.

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