ABSTRACT
In the past, several publications have been dedicated
to the effect of polycarboxylate ethers in microsilica-
free low-cement castables. However, microsilica
containing high cement castables (HCC) can be
advantageous in application fields were high strength,
abrasion and thermal shock resistance is required. In
order to prevent penetration effects of the metal melts, a
low porosity of the castable material is necessary. This
can be achieved by reducing the water content in the
castable mix. In this context, the effect of
polycarboxylate ethers as deflocculants has been
investigated. It will be shown that they outperform
polycarboxylates and polyphosphates in terms of
workability and water reduction. Hence, they improve
the physical properties of the castable.

INTRODUCTION
In the industrial production of refractories, numerous
innovations took place in the last decades. In the 80’s,
sophisticated formulations have been developed, which
allowed to reduce the cement content to 5 %. This type
of refractories became known as low-cement castables
(LCC). The advantages of these refractories are the
significantly improved chemical and physical properties
due to the low water content. One further aspect was the
incorporation of microsilica in the formulations. The
effect of the ultrafine silica is twofold: on the one hand
it acts as microfiller and helps to adjust a grain size
distribution in the sub-micrometer level, and on the
other hand it provides special chemical properties to the
castable. But in order to achieve these improvements,
deflocculants had to be added and became an essential
part of the formulations. In the last decade, a new
generation of deflocculants – the so-called
polycarboxylate ethers – have been developed which
are not only very efficient in terms of water reduction
but also allow the adjustment of the setting of the
refractory material.

In the past, publications have been dedicated to the
effect of these polycarboxylate ethers in low cement
castables. It was shown that polycarboxylate ethers
outperform polycarboxylates in terms of dispersing
efficacy, plastification and capability of water reduction
[1-3]. However, it seems that deflocculated, microsilica
containing high cement castables (HCC) are gaining
more interest in the future, because this type of
castables can be advantageous in application fields
where high strength, abrasion and thermal shock
resistance in the temperature area up to 1300 °C is
required [4]. In this context, we have investigated the
effect of polycarboxylate ethers as deflocculants in
microsilica-containing high cement castables. The
efficacy of polycarboxylate ethers with different side
chain length are compared with commonly used
dispersants like polycarboxylates (PAA) and
polyphosphates (PMP).

TEST METHODS
A castable formulation based on Tabular Alumina
according to a proposal for classification of high
cement castables (CaO > 5.5 %; Microsilica < 2 % and
a deflocculant) [4] was used for a first approach. The
basic test recipe is shown in table 1. The spread of
the castables has been measured after lifting a cone (φbottom
= 100 mm, φtop = 70 mm, h = 50 mm) and vibrating for
20 sec. at 50 Hz. on a vibration table. Whenever the
castable showed self-flowing properties, the spread was
measured after the mix flowed freely for 2 minutes. For
each sample, measurements have been taken 10 min.,
30 min. and 60 min. after water addition. In order to
record the course of the temperature of the castable, a
thermocouple connected to a data logger was embedded
in a 500 g sample which was place in a dewar. The cold
crushing strength (CCS) was determined from specimen
of the dimensions 16 cm x 4 cm x 4 cm after storage at
20 °C and 60 % r.h. for 24 h.

In order to get a general overview of the efficacy of the
different types of dispersants, two commercially
available polycarboxylate ethers PCE 1 and PCE 2 [5]
as well as three new designed PCEs (experimental
products, designated as PCE 3, 4 and 5 resp.) have been
compared with a common polycrlylate and sodium
polyumphosphate. The three new designed
polycarboxylate ethers are of the same architecture,
they only distinguish in the length of the side chains
which increase in the sequence PCE 3 < PCE 4 < PCE
5. The dosage of each dispersant was 0.1 per cent by
weight of castable, while the water content of the mixes
dispersed with polyumphosphate and polycrlylate
have been increased in order to achieve an acceptable
initial flow.
Polycarboxylate ethers with long side chains are able to can be seen from figure 1b in more detail, polymetaphosphate show no or only minor self-flow. As with polycarboxylate ethers are in a range of 27 to 32 length). In contrast, the samples prepared with polycarboxylate ethers has been reduced from 6.5% (fig. 1) down to 5.8 per cent. For the mixes with polyacrylate and polyphosphate the amount of water had to be kept at 7% by weight of the castable.

**TEST RESULTS**

**Deflocculation of basic HCC**

The spread after vibration and the self-flow values of the castables prepared according to the test recipe shown in Table 1 are presented in figure 1a and 1b. Regarding the first graphics of the vibrational flow, all polycarboxylate ethers lead to castable mixes with an initial flow of 30 cm and more. Additionally, they maintain the workability over a time period of at least 60 minutes. The maximum decay of the spread is found for PCE 3, decreasing from 30 cm initial flow to 21 cm after 60 minutes. Comparing the values in more detail, it is noticeable that the spread of the castable increases by increasing the side chain length of the polycarboxylate ether, while the decay of flow over time decreases. However, the side chain length has a significant influence on the hydration of the cement. The shorter the side chain, the more retarded is the cement hydration. This is observed when recording the course of temperature over time of the castable samples. The maximum heat of hydration shifts from 12 h for PCE 5 to 48 h for PCE 4 and 95 h for PCE 3, respectively (in the sequence of decreasing side chain length). In contrast, the samples prepared with polyacrylate or polymetaphosphate exhibit also a “quick” hydration of the cement at 12 h. But a very important fact is, that the initial flow of the castable is inferior compared with those of the PCEs, even at a higher water content. Additionally, their working time is rather short. Already 30 minutes after mixing the castable does not show any vibrational flow. In order to prolong the working time, a retarding agent would have to be added which also would retard the hydration of the cement.

Following observation was made during this test series: only the castables prepared with polycarboxylate ethers showed to some extend self-flow properties (see fig. 1b). The initial flow values of each sample prepared with polycarboxylate ethers are in a range of 27 to 32 cm, while samples prepared with polyacrylate and polymetaphosphate show no or only minor self-flow. As can be seen from figure 1b in more detail, polycarboxylate ethers with long side chains are able to maintain the flowability over 30 and 60 minutes. Hence, it can be concluded that the improvement of the flow properties is a function of the side chain length.

A further very important observation was made during this basic screening of the different polymers. Although the spread of the castable samples is in an acceptable range, the mixes appeared to be “dry”. In order to improve the consistency of the castables, the test recipe was modified by partially substitution of the fines of the tabular alumina against reactive alumina (see Table 2). In order to study additionally the influence of the type of alumina, three test series with different types of reactive alumina have been conducted. The main focus of this investigation was on the hydration characteristics and the green strength development of the castables. In this context, the course of temperature of the castables has been recorded in order to get knowledge about retardation effects. Additionally, the cold crushing strength after storage at ambient temperature was determined. In the following test series, PCE 3 and PCE 4 have been omitted due to their strong retardive effect. On the other hand, the castables mixes deflocculated with polyacrylate and polymetaphosphate have been retarded by additionally dosing 0.05% per cent of citric acid. Due to the improved consistency – which is basically the effect of the alumina addition and a better particle size distribution – the amount of water of the mixes containing polycarboxylate ethers has been reduced from 6.5 % to 7.0%.

**Tab. 1. Basic HCC Test Recipe.**

<table>
<thead>
<tr>
<th>Tabular Alumina</th>
<th>wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 – 6 mm</td>
<td>25</td>
</tr>
<tr>
<td>1 – 3 mm</td>
<td>15</td>
</tr>
<tr>
<td>0.5 – 1 mm</td>
<td>11</td>
</tr>
<tr>
<td>0.2 – 0.6 mm</td>
<td>6</td>
</tr>
<tr>
<td>0 – 0.2 mm</td>
<td>12</td>
</tr>
<tr>
<td>0 – 0.045 mm</td>
<td>7</td>
</tr>
<tr>
<td>CAC</td>
<td>22</td>
</tr>
<tr>
<td>Microsilica</td>
<td>2</td>
</tr>
<tr>
<td>Dispersant b.w.c.</td>
<td>variable 0.1</td>
</tr>
</tbody>
</table>

![Fig. 1. Vibration flow and self-flow of basic HCC](image-url)
Tab. 2. Test Recipe with Reactive Alumina.

<table>
<thead>
<tr>
<th>Tabular Alumina</th>
<th>wt.-%</th>
</tr>
</thead>
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<tr>
<td>3 – 6 mm</td>
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<td>6</td>
</tr>
<tr>
<td>0 – 0.2 mm</td>
<td>7</td>
</tr>
<tr>
<td>0 – 0.045 mm</td>
<td>3</td>
</tr>
<tr>
<td>Reactive alumina variable</td>
<td>9</td>
</tr>
<tr>
<td>CAC Secar 71</td>
<td>22</td>
</tr>
<tr>
<td>Microsilica Elkor 971 U</td>
<td>2</td>
</tr>
<tr>
<td>Dispersant b.w.c. variable</td>
<td>0.1% (+0.05% citric acid for PAA and PMP)</td>
</tr>
</tbody>
</table>

Impact of reactive alumina

In general, the addition of reactive alumina helped to improve the flowability of the castable mix. The self-flow values of each series (see graphics 2, 3 and 4) are on a similar level as the spread after vibrating is. This is also observed for the mixes deflocculated with polyacrylic acid or polymetaphosphate, which is insofar remarkable, because in the alumina-free recipe a significant difference is observable for the latter castable mixes. The self-flow value (b) of each test series is shown in the graphics 2, 3 and 4 respectively.

Information concerning the influence of the modality of the reactive alumina on the flow properties of the castable mix can be gained comparing the corresponding mix designs within the series of the same deflocculant. With exception of PCE 2, only minor differences of the flow values are visible, indicating that the modality of the reactive alumina does not significantly influence the flow properties in general. This behaviour is attributed to the high cement content of the castable mix which contributes to great extent to the content of fines. The fact that the flow of the mixes prepared with polycarboxylate ether PCE 2 depend on the type of reactive alumina is most probably an effect based on molecular level. It may be that there are different interactions taking place between the deflocculant (architecture) and alumina. More specific investigation would be necessary to get more insight into this phenomenon. But this effect shall not be the focus here and therefore will not be discussed in more detail.

Influence of alumina on hydration

It is known that the specific properties of the reactive alumina have an influence on the cement hydration process [5, 6]. In this context, the influence of the alumina addition on the hydration process was studied by recording the course of the temperature of the castables and measuring the cold crushing strength. The course of the temperature, especially the point of time when the temperature rises to its maximum, reveals information concerning retardation effects. The cold crushing strength is associated with the hardening of the cement due to conversion of the cement clinker into its hydration products. To great extend, both processes are linked together, since (strong) retardation leads to a late hydration of the cement clinker. In figure 5 the point of time of the temperature maximum for each deflocculant and type of reactive alumina is shown. There are several interesting features observable: the castables prepared with PCE 2 and PCE 5 are the fastest mixes concerning the cement hydration. The type of alumina seems to have no influence. In contrast, the data of the castables prepared with PCE 1 show that in general the hydration process is retarded and that it depends on the reactive alumina used. It was found that the mix with monomodal alumina is the most retarded whereas the mix with multimodal alumina is the less retarded. But in general, the hydration process takes place at a later time for the series with PCE 1 as it does with PCE 2 and PCE 5. Regarding the values for the mixes prepared with polyacrylate and
polyphosphate, it is obvious that the combination of polyacrylate and citric acid is the most retardive mix design of all, even significantly more retardive than the combination of polymetaphosphate and citric acid. In both cases the alumina type has no significant influence on the hydration process.

![Graph 5: Time until max. heat of hydration (h)](image1)

**Cold Crushing Strength Development**

The values of the cold crushing strength are shown in figure 6. Regarding the mix with PCE 1 a strong influence of the alumina on the cold crushing strength is found. The drastic difference in cold crushing strength measured after 24 h between multimodal alumina containing mix and monomodal alumina containing mix corresponds with the shift of the temperature maxima observed. Interesting to mention is further that the cold crushing strength of the mix with PCE 5 is even higher as for the mix with PCE 2, although the temperature maximum occurs at the same time.

Due to the strong retardation effect of the combination polyacrylate and citric acid, the cold crushing strength is very low. In contrast, the mix design with polymetaphosphate is less retardive. The cold crushing strength is in the range of 80 N/mm², which is approximately at a 50 % level compared to those of the specimen prepared with PCE 5. But it has to be taken into account that the specimen prepared with PCE 5 are prepared with 17 % less water in the mix which leads to the increased green strength.

![Graph 6: Cold Crushing Strength Development](image2)

**SUMMARY**

This study has shown that in a basic high cement castable recipe, polycarboxylate ethers provide prolonged working time and improved flowability of the castable at lower water contents compared to mixes using polyacrylates or polyphosphates. The fact that self-flow properties can be achieved with polycarboxylate ethers shows that they are able to efficiently disperse fines efficiently also when microsilica is present.

It turned out that the addition of reactive alumina further helps to improve the plastification of the castables and this allows a further water reduction. The type of alumina had neither an influence on the flow properties nor on the hydration of the castable which was deflocculated with polycarboxylate ether PCE 5. According to the study conducted, PCE 5 seems to be efficient and rather resistant to changing reactive alumina types. This castable mix has the highest flow values, as well as the highest cold crushing strength.

**ACKNOWLEDGEMENT**

The author is grateful to Mr. Adolf Förberböck who carried out the numerous tests.

**REFERENCES**


[5] The polycarboxylate ethers are commercially available by BASF Construction Polymers GmbH, 83308 Trostberg, Germany. See also: www.construction-polymers.com
