DEFLOCCULATED MICRO SILICA CONTAINING CASTABLES: MORE ROBUST AND EASY TO USE WITH A NEW CALCIUM ALUMINATE BINDER

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ABSTRACT

The performance of microsilica containing deflocculated concretes as ultra low, low, and medium cement castables (ULCC, LCC, MCC) relies to a large extent on a precise dosage and homogeneous distribution of a small amount of a deflocculating additive. Interaction between high purity 70% calcium aluminate cement (CAC) and silica fume (as called microsilica), the fines of natural aggregates and the deflocculant occur with effects for castable setting. Set times can become unpredictable when lot to lot variations for example in medium quality microsilicas occur, different fines of natural aggregates are used or the casting is done at low ambient temperatures. Each wet mixing system requires slightly different water additions which impacts as well castable properties. To better master the complex raw material interactions and to make deflocculated microsilica castables more robust a new 84% calcium aluminate binder has been developed, SECAR Xeniom™. It contains a buffering system to reduce the variability induced by many formulation components especially those of silica fumes and also of different types of aggregates-fines like fireclay, andalusite and bauxite. At the same time the ambient temperature sensitivity is reduced so that even andalusite based LCC’s, known for their delayed setting at low temperatures, have a homogeneous and fast set. The new binder with its integrated fast deflocculating system is more robust to use with different kind of industrial intensive wet mixing systems compared to a reference system based on a 70% CAC and TPP as deflocculant. And already simple concrete mixers can activate the deflocculating system inside this new calcium aluminate binder. Nevertheless water addition and mixing time have to be increased compared to intensive mixers, but high strength levels of more than 130 MPa after drying are still achievable with this new binder SECAR Xeniom™.
Introduction

Deflocculated silica fume containing castable can replace refractory bricks in many applications, helping reducing the global operation costs, increasing availability and capacity of furnaces. In the iron and steel production they are present for example in blast furnace troughs, tundish permanent linings, and in reheating furnaces. Well known for their low porosity and very small pore size diameters due to the filling effect of the spherical fume silica, they expose very high abrasion and thermal shock resistance especially in the medium application temperature range up to 1600°C.

High purity 70% calcium aluminate cement is typically used to formulate a wide range of these sophisticated formulations. This high purity CAC doesn’t perturb the rheology but securing a controlled solidification of the concrete for a given mix of raw materials especially when high purity microsilicas are used. Medium purity and more variable silica fumes are more difficult to use if a stable rheology and a repeatable castable set time is required, although their purity would be sufficient with respect to the targeted application temperature. Other formulation components like fines of natural raw materials as andalusite and bauxite are also not inert to calcium aluminate hydration. Ambient temperature has a strong impact on castable set time. All together the deflocculated cement reduced systems, although made with high purity calcium aluminate cement and high purity microsilica, are much more sensitive to small changes in the system than conventional castables.

Formulating deflocculated low cement castables is not a very difficult objective, but formulating in a way that performance of the concrete remains along the year in the targeted quality range is not an easy job to do in front of a fast changing international raw material market. Complex interactions between calcium aluminate binder, admixture system, filler and aggregates have to be taken into account when raw materials have to be changed and when raw materials with higher intrinsic variability are used. One has to take into account many factors which can have a strong impact on the final performance of these sensitive concrete systems when they come out of the laboratory into the real industrial environment:

- Quality variation of raw materials like silica fumes and fines of natural raw materials
- Dosing small amounts of powder additives during dry mixing process
- Quality of concrete mixer and mixing time
- Dosage of mixing water
- Ambient temperature during castable installation.

Problems that occur during dry-mix production and the installation of the cement reduced castables due to the variables in the system are causing reduced life time during their final application at high temperatures.
2 Mechanisms of interactions

The basis for the development of this new binder system was the analyses of the underlying mechanisms which can perturb the quality of traditional silica fume containing low cement systems. To better understand the impact of the silica fume quality on the hydration of high purity calcium aluminate cement with 70% Al₂O₃ a detailed chemical analysis has been conducted. In pure calcium aluminate/water pastes the cement hydration happens in mainly 3 steps:

- Dissolution of CaO and Al₂O₃ from the calcium aluminate phases in the mixing water
- Saturation of the aqueous solution with lime and alumina
- Precipitation of calcium aluminate hydrates from the aqueous solution

In deflocculated systems the initial setting (also called working time) is strongly influenced by the interaction between the deflocculant, the microsilica filler and the calcium aluminate cement. As an example the interaction between sodium tripolyphosphate and calcium aluminate in a silica fume containing castable has been studied [1]. Figure 1 shows the evolution of the ionic concentration in the pore solution of the concrete during the early phase after mixing with water.

As can be seen, calcium and aluminium ion concentration only slowly increases over time while Na-TPP with its high solubility brings sodium and phosphate nearly instantaneously into solution. But soon after mixing with water, the concentration of phosphate starts to diminish. On the other hand calcium increases, but less fast than the increase of aluminium. From that it can be concluded that a first interaction between calcium and phosphate occurs which even accelerates after about 60 to 90 minutes. After nearly 2 hours, all phosphate and nearly all calcium have been consumed. The concentration of aluminium reaches more than 40 mmol/l, compared to that a pure mix of only SECAR® 71 with water would create a concentration of aluminium and calcium of only about 20 mmol/l for both species [2].

The phosphate interacts with the calcium to form less soluble calcium phosphates. While the formation of solid calcium phosphate occurs the rheology of the castable changes till the concrete doesn't flow anymore under vibration (working time) which was the case after 120 minutes in this model system. The flow decay can be caused by different aspects:

- Formation of solid calcium phosphates which creates a first loose bridging inside the matrix
- Reduction of available amount of deflocculant due to reaction of phosphate with calcium
- First formation of calcium aluminate and alumina hydrate gels

The massive calcium aluminate hydration which causes the strength ramp-up occurs in this system significantly after the moment at which the castable is not anymore vibratable. The massive cement hydration can easily be followed by the heat development in the LCC or by an ultrasonic test method [5] if the heat of hydration is very low as in ULCC's. The dosage rate of the deflocculant like Na-TPP has a strong impact on the flow decay and the working time.
Fig. 1: Pore solution chemistry evolution in a silica fume containing castable with SECAR 71 and Na-TPP

With higher dosage (0.15%) the flow decays fast and working time is less than 80 minutes only while with a low concentration (0.03%) a more stable flow during the first 60 minutes and a longer working time can be achieved. But at low TPP dosage the castable becomes more sensitive to ambient temperature and to the accuracy of the dosage [3].

Beside the interaction between Na-TPP and calcium aluminate another mechanism has a strong influence on the system. Silica fumes can contain a small but, with respect to calcium aluminate cement dissolution and precipitation, a significant amount of soluble species [4]. Amongst these species sulphates, phosphates and chlorines of magnesium, calcium, potassium and sodium are the most typical.

But different from the well defined Na-TPP/CAC system the concentration of the soluble compounds of silica fumes that are by-products from ferrosilicon, silicon or the zirconium industry can vary from one lot to another and from one product to the next. Fig. 2 shows for example the lot to lot variation of minor elements like CaO, MgO, K2O and P2O5 in a 95%-SiO2 containing microsilica. As a consequence of the variable concentration in the silica fume lots, the working time of a deflocculated castable (see LCC2 in table 2) changes from 70 over 115 to 55 minutes from lot A over B to lot C of the 95% silica fume (Fig. 3). This makes castable adjusting in an industrial day-to-day business difficult since not only the concentration but as well the ratios of the soluble trace elements vary to a large extent. A chemical analysis by X-ray fluorescence doesn't differentiate between water soluble and non-soluble species and more extensive test methods would need to be applied to analyse the water soluble elements of microsilicas.
A new calcium aluminate binder with a buffering effect

A new binder, SECAR Xeniom™, has been developed to reduce the system-intrinsic variability and to increase the robustness of deflocculated silica fume containing castables. In order to achieve this improved robustness level a special buffering system has been employed in the binder. It contains as well an adapted deflocculation system which fits on one hand to the buffer and on the other hand to a wide range of silica fumes and fines of natural and synthetic raw materials. The model formulation LCC1 (Tab.2) is based on this new binder system and will be compared with a classical LCC-system which is based on calcium aluminate cement with 70% Al₂O₃, SECAR 71. In this case sodium tri-polyphosphate has been chosen as deflocculant (LCC2).

The new binder SECAR Xeniom™ enables formulating deflocculated castables:

- without addition of further deflocculants
- with a higher robustness to lot-to-lot variations of silica fumes
- with a large range of microsilicas with more than 92% SiO₂ (+ZrO₂)
- that are easily be switchable from one aggregate to another (e.g. bauxite vs. andalusite or fireclay etc) without significant changes in hardening
- with a homogeneously hardening of the full monolithic body even at low ambient temperatures and with andalusite in the mix.
- that are easily and fast to mix with water so that a wide range of concrete mixers can be used

The basic characteristics of this new binder system SECAR Xeniom™, a calcium aluminate binder with about 84% Al₂O₃, are shown in the table 1 in comparison to the reference calcium aluminate cement SECAR® 71 with 70% Al₂O₃.

Experimental results

The results of this investigation are based on a comparison of these two calcium aluminate binders in silica fume containing model formulations (Tab.2). The reference LCC2 contains 5% SECAR® 71, 5% calcined alumina and sodium tri-polyphosphate (TPP) as deflocculant. To make the comparison at constant castable chemistry, 5% SECAR® 71 and 5% calcined alumina have been replaced by 10% SECAR Xeniom™. Since SECAR Xeniom™ contains already a deflocculation system it was not necessary to add TPP in case of LCC1. In order to evaluate the robustness of this new binder system different aggregates and silica fumes have been tested in the two model recipes. The amount of silica fume has been fixed at 5% in all cases and the amount of aggregates at 85%. The aggregates comprise the fractions 0-0,09mm, 0-1mm, 1-3mm and 3-5 resp. 3-6 mm with similar overall grain size distributions for the formulation with different aggregate types. Rheology, castable setting and strength development have been measured using the classical methods as described by [5]. The water addition has been adapted to reach similar initial flow values on a vibration table for the different mixes.

Fig. 2: Minor elements concentration in 3 lots of a 95% silica fume
Fig. 3: Working time of the bauxite based LCC1 and LCC2 with different lots of 95% silica fume

Tab. 1: Characteristics of the calcium aluminate binders SECAR Xeniom™ and SECAR® 71

<table>
<thead>
<tr>
<th></th>
<th>SECAR Xeniom™</th>
<th>SECAR 71</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main field of application</td>
<td>Silica fume containing ULCC, LCC, MCC</td>
<td>All types of deflocculated and non-deflocculated castables</td>
</tr>
<tr>
<td>Al2O3 %</td>
<td>82-85</td>
<td>68.7-70.5</td>
</tr>
<tr>
<td>CaO %</td>
<td>14-16</td>
<td>28.5 – 30.5</td>
</tr>
<tr>
<td>Blaine cm²/g</td>
<td>&gt;10000</td>
<td>3800-4400</td>
</tr>
<tr>
<td>BET m²/g</td>
<td>5-8</td>
<td>1</td>
</tr>
<tr>
<td>Main mineral phases</td>
<td>CA, CA₂, A</td>
<td>CA, CA₂</td>
</tr>
<tr>
<td>Castable deflocculation system</td>
<td>Integrated</td>
<td>Not integrated</td>
</tr>
<tr>
<td>Buffering system against raw material and ambient temperature variability</td>
<td>Integrated</td>
<td>Not integrated</td>
</tr>
</tbody>
</table>

Impact of different lots of a 95%-SiO₂ containing silica fume:
As mentioned before, silica fumes have a strong impact on castable set time. The buffering system employed in the new binder allows smoothing of the lot-to-lot variation of microsilicas with respect to castable working time. Figure 3 gives an example for 3 lots of the 95% silica fume. The bauxite based LCC1 with the new binder creates with all 3 lots of silica fume almost identical working times while with the reference system LCC2 significant variations are observable.

Compatibility to silica fumes of different purity:
The new binder doesn’t only buffer the lot-to-lot variations of microsilicas. Figure 4 shows results for undensified silica fumes of different purities in the bauxite based LCC1 and LCC2. Here the reference system LCC2 has been formulated in one case with Na-TPP (0.08%) and in another with a combination of 0.1% polyacrylate (PA) and 0.02% citric acid (CA) instead of Na-TPP. Both reference systems show a high sensitivity to the different silica fume products. The PA/CA-system seems to be even more critical than the Na-TPP system. Opposite to this behaviour, LCC1 with the new binder system and its integrated buffering and deflocculating effect shows very stable behaviour in combination with all 5 microsilica products.

Tab. 2: Model formulations with equal castable chemistry but 2 different binder systems

<table>
<thead>
<tr>
<th>Aggregates</th>
<th>LCC1</th>
<th>LCC2</th>
</tr>
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<tbody>
<tr>
<td>0-6 mm</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Silica fume</td>
<td>≥93% (SiO₂+ZrO₂)</td>
<td>5</td>
</tr>
<tr>
<td>New binder SECAR Xeniom™</td>
<td>84% Al₂O₃</td>
<td>10</td>
</tr>
<tr>
<td>Reference LCC binder SECAR® 71</td>
<td>70% Al₂O₃</td>
<td>-</td>
</tr>
<tr>
<td>Calcined Alumina AC44B4</td>
<td>d₅₀=4 µm</td>
<td>-</td>
</tr>
<tr>
<td>Na-TPP powder</td>
<td>0.08</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig 4: Working time of the bauxite based LCC1 and LCC2 with silica fumes of different purity.

Impact of aggregate type on castable working time:
Figure 5 summarizes the effect of the aggregate type on the working time. A 97% silica containing microsilica has been used in this case for all mixes. The concretes with tabular alumina and bauxite give similar working times in the reference LCC2, while it is much longer when andalusite is used and shorter for the 60% and 45% fireclays. If the castables are formulated with SECAR Xeniom™ as binder (LCC1) they have a very similar working time independently of the aggregate type. This makes modifications of castables for example a switch from bauxite to andalusite or combinations of both much easier and allows a modular formulation and production concept.

Fig 5: Working time of LCC1 and LCC2 with different types of aggregates

Impact of mixer type on LCC performance:
Controlled laboratory conditions and sophisticated equipment like intensive mixers are the basis to describe the performance profile of a castable. But in real industrial life many different types of mixers are in use to mix the concrete with water. Therefore it is important to know how sensitive a castable reacts to these different machines and if the castable specification defined in the laboratory can be realised under industrial conditions. Although it is not recommended to use simple non-intensive concrete mixers for deflocculated castables, one can still find cases where at least small amounts of a castable have to be mixed in a normal concrete mixer due to non-availability of high-energy mixers. Industrial trials have been conducted with bauxite based LCC1 and LCC2 in different machines as shown in the Fig. 8 below. It was studied how different mixer influence the water demand and performance. The amount of water was adjusted by a professional installation supervisor to an amount which gives a “visible” correct castable consistency (ball in hand test).
In the laboratory mixer (A) batches of up to 20 kg of concrete have been mixed with water. The industrial high energy batch mixer (B) has been used to mix 150 kg of castable. In the mixing/pumping unit (C) batches of 800 kg have been prepared. The mixing time in these batch mixers was 4 minutes. The screw-type mixer (D) is a mixing equipment with a continuous throughput of about 6-8 t/h. Blocks have been cast from which samples have been cut for strength and abrasion measurements and determination of refractory properties like hot modulus of rupture and refractory under load.

For these mixing trials, LCC1 and LCC2 have been chosen in combination with bauxite as aggregates and the 95% silica fume. While the reference LCC2 exposed very high strength when the intensive laboratory mixer was used, the industrial intensive mixing gave lower strength results (Fig. 9). With the continuous mixer it was more difficult to adjust the right amount of water in case of LCC2. Here the deflocculation and wet out takes more time than the time for the castable to pass through the mixing screw.

LCC1 gave a very homogeneous mixing result over all types of mixers including the continuous mixer. As a result a more stable strength development independently of the type of mixer could be achieved. Furthermore the strengths of the industrial mixes were in all cases of LCC1 slightly higher than from the laboratory mixing. This gives some extra security when the product is scaled up from the laboratory to the industrial level. With LCC2 the laboratory results are more difficult to replicate on the industrial scale.
In addition to these high energy mixing trials some further tests have been conducted in a classical low energy concrete mixer (E). Batches of 75 kg have been mixed in this case. Different from the previous mixes in this case the formulation LCC2 was made with 7% SECAR® 71, 7% reactive alumina and 0.12% NaTPP which have been replaced in LCC1 by 14% SECAR Xeniom™. Both formulations contain 5% of the 95% silica fume. With this type of simple mixer it is essential to mix at least 10 minutes and not to add too much water too early since the des-agglomeration and de-flocculation needs more time due to the low energetic mixing. Respecting this, and accepting an increase in total water addition of about 2% compared to intensive mixers, a reasonable mixing result and strength level can still be achieved as can be seen in Fig.10. LCC1 with SECAR Xeniom™ reaches despite a slightly higher water addition a significantly higher modulus of rupture and a cold crushing strength after drying at 110°C of more than 130 MPa.

![Graph](image)

**Fig.10:** Cold modulus of rupture and cold crushing strength of bauxite mixes LCC1 (14% SECAR Xeniom™) and LCC2 (7% SECAR® 71, 7% reactive alumina, 0.12% TPP) prepared in a low energetic concrete mixer

**Impact of ambient temperature on LCC performance:**

Another difficulty of LCC and ULCC compared to conventional castable is their slow strength formation at low ambient temperatures. Fig. 6 is an example for an andalusite based formulation. In this case the amount of TPP in the reference formulation LCC2 has been increased already to 0.15% to compensate the retarding effect of andalusite. But working time at 10°C is still more than 12h and strength after 24h is just sufficient to start de-moulding carefully. Formulating the andalusite LCC with SECAR Xeniom™ makes it more robust to the impact of ambient temperature.
At 10°C the working time can be achieved in a normal day shift and the strength acquisition is fast enough to de-mould the monolith already after 12h hours. In Fig. 7 the strength acquisition as function of ambient temperatures are indicated. For the andalusite-based LCC-reference (5% SECAR® 71 and 0,15% TPP) a significant delay of strength formation occurs at 10°C. In case of LCC1 with SECAR® Xeniom the differences in strength formation between 10°C and 20°C are minimised.

Fig. 6: Working time for Andalusite based LCC’s as function of ambient temperature

Fig. 7: Early strength development in andalusite LCC as function of ambient temperature

Abrasion resistance, refractoriness under load and hot modulus of rupture
Samples from the intensive batch mixer trials with LCC1 (10% SECAR® Xeniom™) and LCC2 (5% SECAR® 71, 5% calcined alumina, 0,08% TPP) have been used to measure abrasion resistance (ASTM C 704) after heat treatment at 800°C. Both, LCC1 and LCC2 have excellent abrasion resistance, with both, the 97% and the 95% silica fume. Values of less than 4 cm³ volume loss could be achieved with the new binder. The refractory under load (Fig 11) is almost identical for LCC1 and LCC2. In this case tabular alumina was used as aggregate in combination with the 97% silica fume. Samples have been dried only at 110°C prior to the test. A difference can be found when the 97% silica fume is replaced by the 95% microsilica. In the temperature range of 800 to 1000°C some intermediate liquid formation occurs before re-crystallisation in new phases re-strengthens the monolith before it finally softens above 1350°C in a similar way with both silica fumes. The softening between 800 and 1000°C occurs only during the first heat-up and is not reversible and therefore not critical for the 95% silica fume. The hot modulus of rupture at 1350°C of pre-dried (110°C) and of pre-fired samples (1350°C) has been measured with the same tabular alumina and 97% silica fume based concretes. LCC1 with the new binder SECAR® Xeniom™ gives in both cases higher values than LCC2 (Fig 12).
5 Summary

A new calcium aluminate binder, SECAR Xeniom™, with an Al₂O₃ content of 84% has been developed to increase the robustness of microsilica containing concretes. The integrated buffering and deflocculation system allows formulating with a wide range of refractory aggregates as bauxite, andalusite or fireclay without a negative impact on the cement hydration when switching from one aggregate to another. It makes the system less sensitive to the impurities that can occur in silica fumes. At the same time the new binder makes the formulation more robust to ambient temperatures variations, as can be seen for example with the andalusite based LCC at low temperatures, where strength acquisition is faster than in the reference system. An easy transfer from the laboratory to the industrial reality is possible since the binder gives equally good mixing results over a large range of high-energetic concrete mixers. All together a more reliable castable performance can be achieved with this new binder thanks to the special buffering effect combined with the integrated deflocculation system and the selected calcium aluminate composition of SECAR Xeniom™.

7 References