RECENT DEVELOPMENT IN USE OF SPHERICAL PARTICLES IN NCC

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ABSTRACT

No-cement castables have the last few years become increasingly popular, particularly since the introduction of SioxX-Zero® (microsilica-gel bond) and DAReS (Dry Advanced Refractory System) binder technologies. In parallel with the development of these binder systems, development of highly specialized raw materials have progressed, and the current paper focuses on the use of spherical alumina for no-cement applications in general, and silica-free corundum-spinel systems in particular.

INTRODUCTION AND BACKGROUND:

"The rheology of a castable has been demonstrated to be influenced by the particle size distribution of the mix, so that in practice, self-flowing or vibratables can readily be designed based on their total PSD[1]. Self-flow is facilitated if the particle size distribution contains an increased amount of fine particles."

This is taken from the "Introduction and Background" of a presentation by B. Myhre at the ALAFAR meeting in 2012[2] that for the first time presented use of spherical, sub-micron alumina particles. The focus was on the dilatancy that is experienced with silica-free alumina castables. It was demonstrated that dilatancy could be avoided if spherical sub-micron particles were used as superfines.

The shape of the ultrafine particles was found to have a decisive influence on the tendency to dilatancy. A spherical shape as represented by microsilica and spherical microalumina (from here on denominated as "microalumina") almost eliminated dilatancy, whereas plate-like elementary particles as seen in reactive alumina seemed to promote dilatancy. This effect was particularly obvious with narrow PSD of the reactive alumina.

The paper from ALAFAR 2012 focused on sub-micron alumina in castable mixes containing among others calcined alumina. Later, a coarser grade of spherical alumina has become commercially available. This alumina has roughly the same size as calcined alumina and is sold by the trade-name AloxX-spheres by Elkem (from here on called Spherical alumina). At Unitecr in 2015[3] its flow enhancing properties was demonstrated, producing castables that could easily be placed with water levels of 2.7%.

Both Microalumina and Spherical alumina is today available; Microalumina is essentially sub-micron, extending from normally 0.01 to 1 micron Coarser sizes roughly 100-times larger, from 1 to 100 micron, are covered by the Spherical alumina. The sub-micron sizes have been shown to reduce or remove dilatancy that can be a problem in microsilica-free alumina caststables, the coarser ones have been shown to have several beneficial properties, improved flow is perhaps the most obvious. Positive effects as binder systems have also been reported[4] even though the exact mechanism behind is not fully understood.

CHARACTERISATION

Microalumina:

Fig. 1 and 2 shows TEM microsgraphs of Microalumina and for comparison also one of Microsilica 971 at approximately the same magnification. The similarity is striking and based on these TEM micrographs alone it is difficult to differentiate between the two microfine powders. It is possible however - at higher magnification (HRTEM), where it becomes clear that the microalumina has a stepped surface while the microsilica has not. This is a clear indication that the microalumina is crystalline while the microsilica is amorphous.

To our fascination, we found that looking closer at the microalumina crystallites (Fig. 3 and 4), it was found that most crystals are twinned, but many are monocrystals. Spherical monocrystals! Some of them show tendencies to faceting and the curved surfaces are created by steps in the crystal lattice.

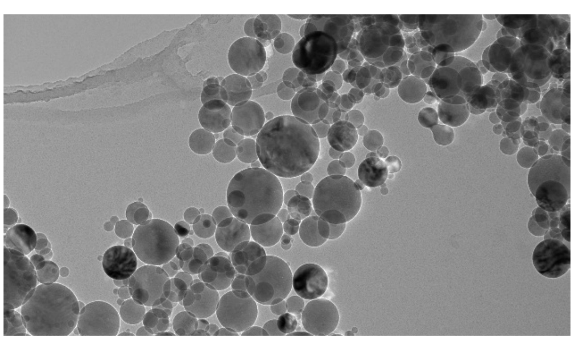


Fig. 1: Microalumina TEM micrograph

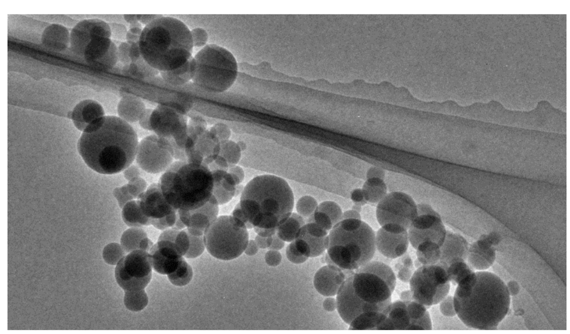


Fig. 2: Microsilica 971, TEM micrograph

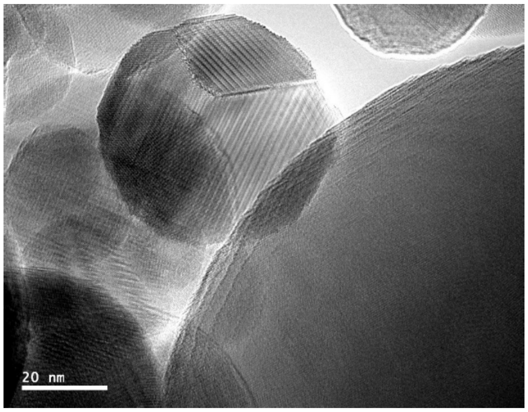


Fig. 3: Microalumina close-up. Most of the crystals are twinned, showing mirror planes as interfaces between the twin domains. Faceted small crystal.

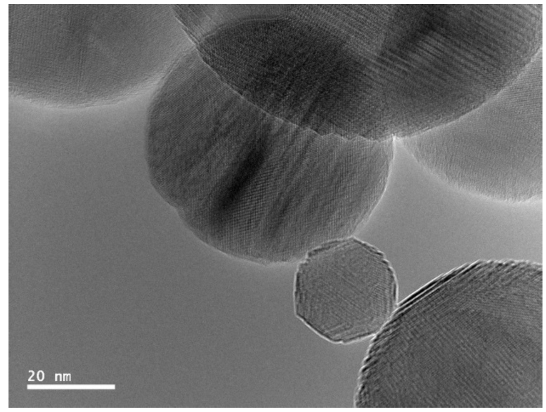


Fig. 4: Microalumina close-up: At a closer view some of the "spherical" crystals show the beginning of faceting.
The curved surfaces show small steps.

XRD of Microalumina:

The exact structure is so far unknown, but the specific gravity has been found (He-pycnometer) to be approximately 3.59 g/cm^3. Somewhat surprisingly, neither alpha-alumina (the thermodynamically stable) nor the most common metastable gamma-alumina match the XRD powder patterns. Alpha-alumina cannot be identified and only some of the reflections are in agreement with the gamma-phase

There are indications, that the metastable delta*-alumina is present in the material.

Common for all the matches are lattice parameters of approx. 800 pm and an orthogonal crystal system.

From high-resolution TEM nearly tetragonal projections with distances of approx. 800 pm are found.

Spherical alumina:

Spherical alumina is produced in several size classes, but mostly in sizes similar to calcined alumina. This means that the size of a typical Spherical alumina sphere is 10-100 times bigger than the particles of Microalumina. Fig. 5 and 6 are PSD of Microalumina and Spherical alumina respectively. The spheres are compact and the crystallographic make-up of spherical alumina is alpha-alumina, or corundum, with a SG of approximately 3.9g/cc.

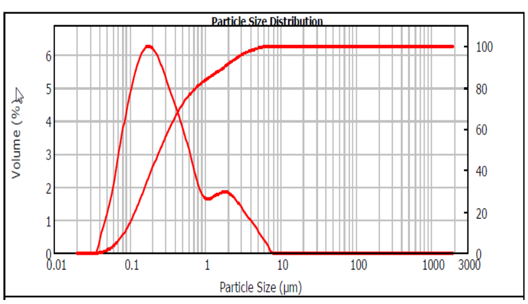


Fig. 5: Typical PSD of Microalumina.

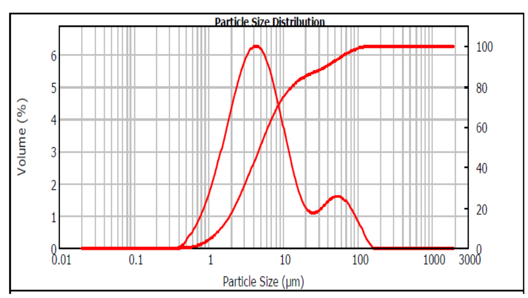


Fig. 6: Typical PSD of Spherical alumina

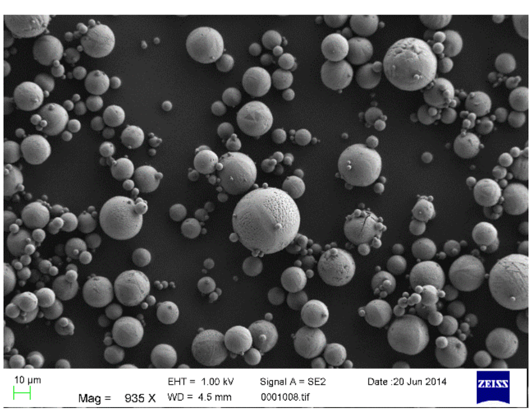


Fig. 7: Spherical alumina. This alumina quality contains both small and larger spheres

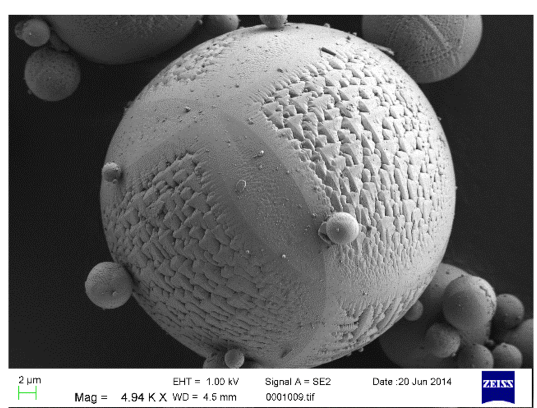


Fig. 8: Spherical alumina close-up of the textured surface often found on the coarser spheres

EXPERIMENTAL RESULTS AND DISCUSSION:

The foremost ambition of this investigation was to make silica-free NCC corundum-spinel castables using the spherical microparticles described above. It had earlier been found (proprietary results) that spherical alumina could have some interesting strength improving properties in alumina castables with SiC, particularly under reducing conditions, Fig. 9 shows the effect of replacement of up to 3% reactive alumina by spherical alumina (A1-3) fired under reducing conditions.

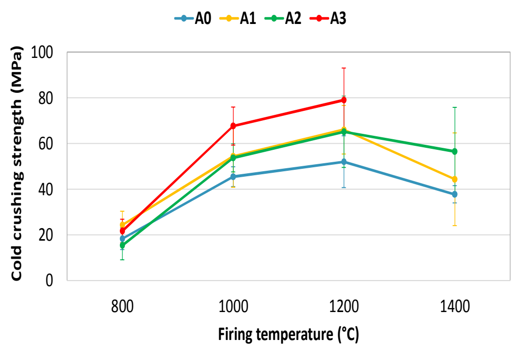
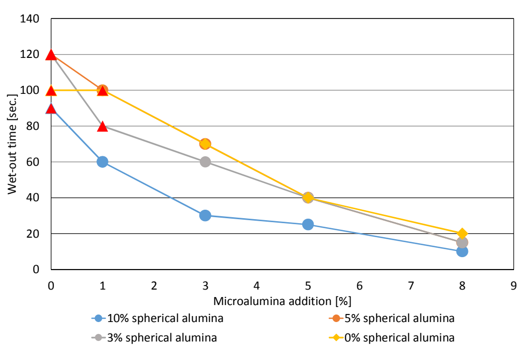


Fig. 9: CCS as a function of firing temperature. SiC containing castable where reactive alumina has been replaced by spherical alumina. (A1= 1% reactive replaced by spherical alumina, etc.)

Based on Elkems experience on microsilica-gel bond and MgO–SiO_2 castables, it was decided to try to make silica-free corundum-spinel castables using MgO in combination with fine aluminas as binder. Castables were based on Tabular alumina aggregates with calcined alumina being successively replaced by spherical alumina and similarly, reactive alumina being replaced by microalumina. These replacements had similar PSD so that the composite PSD was maintained. The PSD followed an Andreassen distribution with a q-value of approximately 0.25. 4.09% water was used for casting.

Tab. 1: Castable composition for making NCC Corundum-spinel castables

MgO(325mesh)	3
Additives	1
Tabular alumina	79
reactive alumina	8-0
calcined alumina	10-0
microalumina	0-8
spherical alumina	0-10
water	4.09



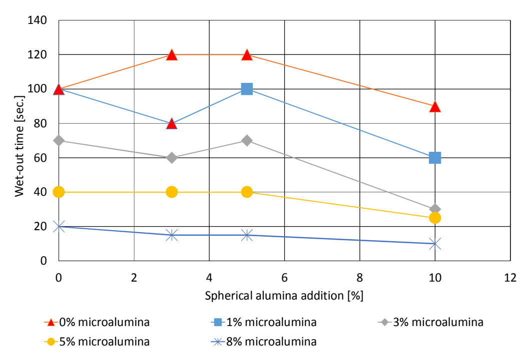


Fig. 10: Wet-out time for the corundum-spinel castables as a function of content of spherical particles. Microalumina to the left and spherical alumina to the right. There is a profound effect on wet-out by replacing reactive alumina with microalumina. Also dilatancy is influenced heavily. Results indicated by a red triangle are indicative of casting difficulties, like dilatancy. Hence the present castables without microalumina additions (those indicated with red triangles) can in practise not be made at the current water addition level.

It was quickly discovered that unless microalumina was added in the recipe, dilatancy should be expected. In Fig. 10, these dilatant castable mixes are indicated by a red triangle. In Fig. 11 the self-flow, green strength and 1200°C Hot-MOR is shown, also here a red triangle indicates dilatancy. It was found (Fig. 10) that microalumina addition could reduce the wet-out time significantly. Not unexpectedly also flow was positively influenced (Fig. 11), but in this case perhaps to a lesser degree than has been seen before (ref: 2,3). All castables were allowed to cure at >95% RH and 22°C+/-2 for 24 hours before demoulding and green-strength measurement.

The green-strength is unfortunately somewhat on the low side but is improved if spherical alumina is added above 5%. At 1200°C, the improved reactivity of the microalumina as compared to reactive alumina is shown as an increase in Hot-MOR, an effect probably attributable to the meta-stable crystal structure of the microalumina. Another possible use could be in bricks. The increased reactivity as compared to reactive alumina has been found capable of reducing firing temperature in alumina brick by 50-100°C (1-2% microalumina, proprietary information, details lacking). With spherical alumina a somewhat lower Hot-MOR is often measured, this is believed to be connected to micro-crack generation that is considered to give improved thermal behaviour. This has been seen for compositions used in steel-making applications (proprietary), but is neither well understood nor documented.

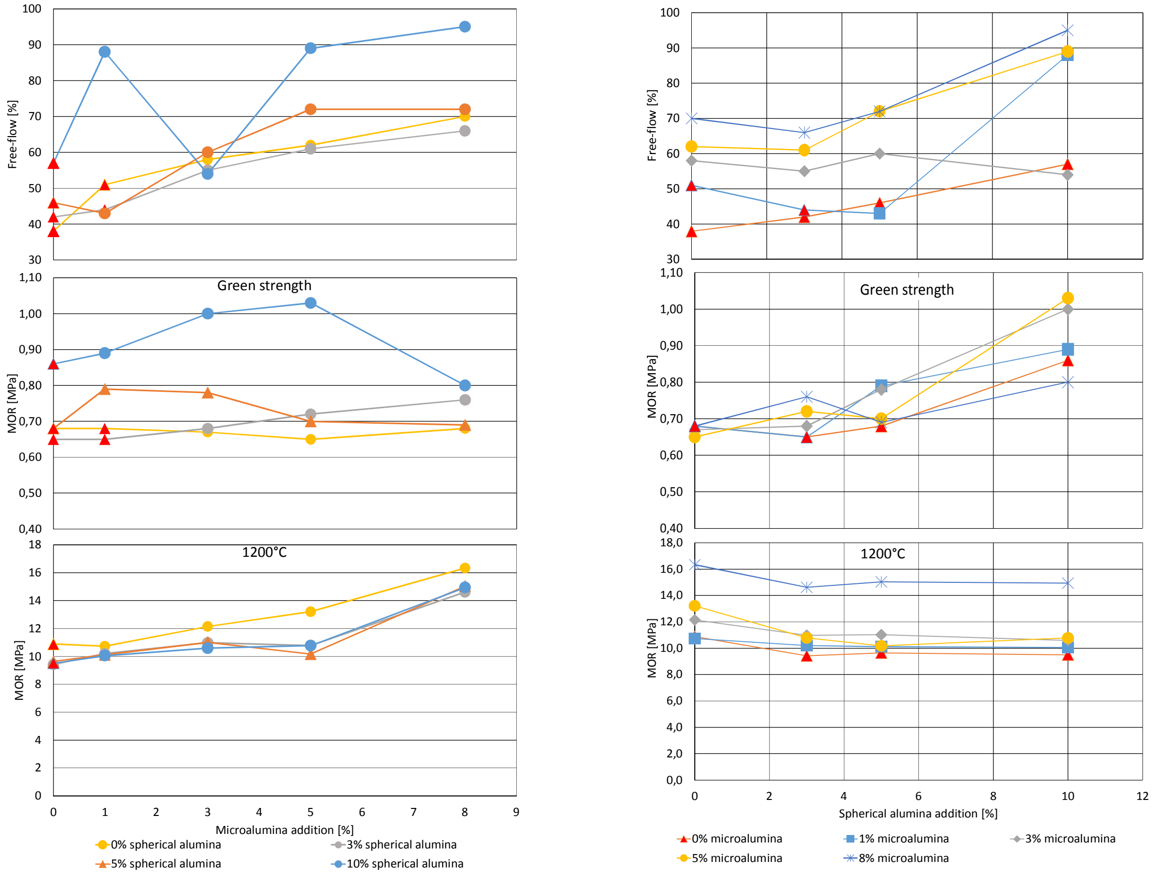


Fig. 11: Flow, green-strength (MOR) and Hot-MOR after 24hours firing at 1200°C of the NCC corundum-spinel castables, showing the effect of spherical particles on self-flow, the improvement of the green strength by spherical alumina and the improved reactivity (sinterability) at 1200°C caused by the replacement of reactive alumina by microalumina.

CONCLUSION:

Microalumina and spherical alumina are two types of spherical alumina particles that have particle size distributions matching reactive and calcined alumina. The particles are spherical and are easy to disperse. Experience has shown that the rheological behaviour of silica-free castable can be improved, not only by reducing dilatancy, but also by shortening the wet-out time of the castables. Due to the meta-stable crystallography of the microalumina, increased reactivity is also expected, and found. At 1200°C the hot-MOR increases with microalumina content, which can be attributed to increased reactivity (sinterability) as compared to reactive alumina (sub-micron).

Spherical alumina has a good flow enhancing effect, increasing self-flow significantly in some cases. Also the green-strength was considerably improved by increased additions of spherical alumina, an effect that may be connected to the improved flow. However, as other sources also indicate improvement at higher temperatures it is fair to say that we do not understand the full effect of these spherical particles and their role in castables.

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