

Rheology of High Performance Alumina and Spinel Castables

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The article provides a basic understanding of the impact of the matrix components on the rheology of castables with special focus on high performance alumina and spinel castables. A broad particle size distribution of the matrix fines helps to achieve optimised packing and therefore a high solids content with low viscosity of the suspension. As solids content increases the amount of water is consequently reduced. Additives are required to counterbalance agglomeration of the particles in a suspension.

1 Introduction

Cement-based refractory mixes are used in a widespread range of applications and their share is still growing when compared to the total of refractory products. The satisfactory performance in use of castables is strongly dependent on their good workability for transport and casting. Poor flowability is often solved on site by high water additions. This, however, has a negative influence upon the desired properties.

The developer of a refractory castable has to know the product properties he would like to achieve in the final application. This is taken into consideration when formulating to achieve good flowability. For example, this might be a matrix of a high alumina castable designed with high microsilica content to achieve mullite formation or a spinel containing castable for steel ladles where the use of reactive alumina is the only way to achieve high performance castables.

The intention of this paper is not to suggest reactive alumina as the only solution for the design of high performance castables with good flowability. The focus is much more to provide a basic understanding of the impact of the matrix components on the rheology of castables with special focus on high performance alumina and spinel castables.

2 Rheology of suspensions

2.1 Impact of solid content, particle size and particle size distribution

Refractory castables are composite materials with aggregates, matrix fines, cement and water as the main components. They can be considered as concentrated suspensions of solid particles (aggregates) in a viscous liquid (matrix paste). The matrix is not a homogeneous fluid and is itself composed of particles in a liquid (water).

The rheological behaviour of a suspension is defined by the viscosity as a measure of the internal friction between the particles dispersed. External forces (mixing, pumping) influence the flow behaviour of a suspension and different flow behaviours can be found (Fig. 1):

- **Newtonian:** Viscosity remains constant while shear rate increases.
- **Shear-thinning:** Viscosity decreases with increasing shear rate. As shear is applied, the structure of the material breaks down and it flows more readily.
- **Shear-thickening (dilatant):** The viscosity increases with increasing shear rates.

The viscosity of a suspension is influenced by the volume fraction of the solid particles, the particle size and the particle size distribution. Many models exist to describe the relationship between viscosity and solids content. The equation developed by *Krieger and Dougherty* is the most commonly used [2, 3].

$$\frac{\eta}{\eta_{\text{medium}}} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$

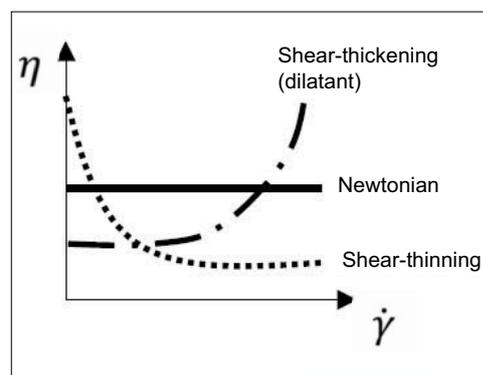


Fig. 1 Flow behaviours of suspensions [1]; viscosity as function of the shear rate

η is the viscosity of the suspension, η_{medium} is the viscosity of the base medium, ϕ is the volume fraction of solids in the suspension, ϕ_{medium} is the maximum volume fraction of solids in the suspension and $[\eta]$ is the intrinsic viscosity of the medium, which is 2,5 for spheres.

According to this correlation the viscosity of a suspension increases with increasing solids content (Fig. 2).

This can be explained by the fact that with higher packing of the particles in the system it becomes more difficult for them to move freely. The interaction between the particles increases and therefore the viscosity rises.

The volume fraction of solid particles also affects the nature of the relationship between shear rate and viscosity for the system. At low solids content the suspension exhibits close to

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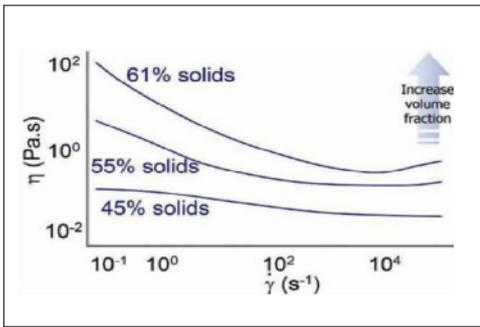


Fig. 2 Viscosity as a function of shear rate for different volume fractions [3]

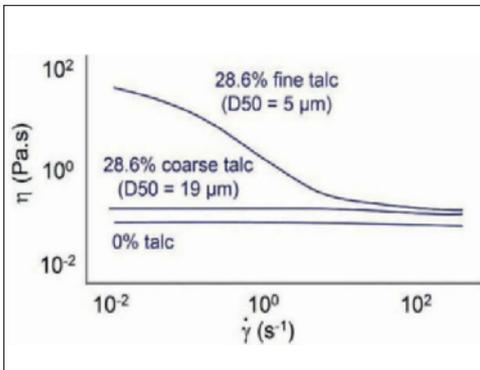


Fig. 3 Impact of particle size on the flow behaviour of a talc/epoxy system [3]

Newtonian behaviour. With increasing volume of the solids fraction the shear-thinning behaviour becomes more evident. At solids contents of greater than 50% of the maximum solids content, collisions between particles increase and the free movement of particles is significantly blocked. Viscosity therefore increases with shear rate; the system is shear-thickening (dilatant) at high shear rates.

At constant mass of the solids in the suspension, the viscosity increases with the reduction of the particle size (Fig. 3).

Because of the higher number of smaller particles, more particles interact and lead to more resistance to flow. High solids loads of ultra-fine particles therefore lead to high viscosity levels in suspensions.

Not only the particle size but also the particle size distribution (PSD) of the solids phase is important for the viscosity of the suspension. The packing density of a material with a broad particle size distribution (bi- and multimodal) is higher than for the same material with a narrower PSD (monomodal). The effects on viscosity can be explained with reference to the Krieger-Dougherty equation. For a monomodal material, the maximum volume fraction is around 62%. With a bi- and multi-

modal solids fraction, smaller particles can fill the gaps between larger ones, and the maximum solids content is higher – around 74% [3].

Optimising the particle size distribution of the solids phase in a suspension leads to reduced viscosity of the system at constant volume fraction (Fig. 4). In reverse at constant viscosity the solids content of the suspension can be increased. As solids content increases the amount of water is consequently reduced (Fig. 5).

• **Zeta potential and deflocculation**

In addition to the described impact of solids content, particle size and particle size distribution on the rheology of suspensions, the electrical charge present at the particle surface of the solids particles is an important factor influencing the level of interaction between the particles in a suspension.

All inorganic particles assume a charge when dispersed in water.

Suspensions of similarly charged particles dispersed in water are stabilised through an effect described by the *Helmholtz* double layer model (Fig.6). The first layer is the charged surface of the particle. It creates an electrostatic field which affects the ions in the water. In response, the ions create a diffuse layer of equal and opposite charge, effectively rendering the surface charge neutral. The diffuse layer creates a potential surrounding the particle, the so-called zeta-potential that differs from the bulk electrolyte.

The size of the double layer will depend on the amount of charge upon the particle surface. A high charge, whether positive or negative, will result in a thick double layer that stops particles getting close to each other. This is typical for a stable, well deflocculated suspension having a low viscosity. Conversely, a low surface charge requires less counter ions and so thinner double layers are formed. Accordingly, particles then tend to flocculate more easily leading to high viscosity suspensions.

The unwanted agglomeration of particles in particular in suspensions with high solids content, is counteracted by the addition of deflocculating agents. The electrostatic forces are influenced in a way that the distance between the solids particles is enlarged and thus flocculation prevented. Since the strength of the attractive forces depends on the pH-value of the water and the dispersed solids, different addition levels and combinations of de-

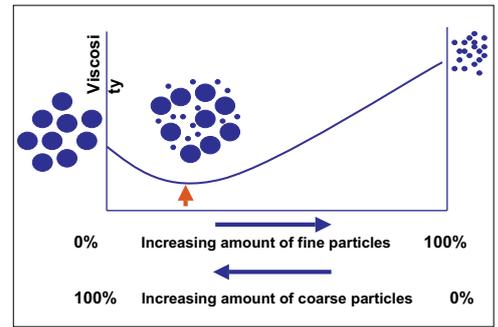


Fig. 4 Viscosity as a function of bi-modality [3]

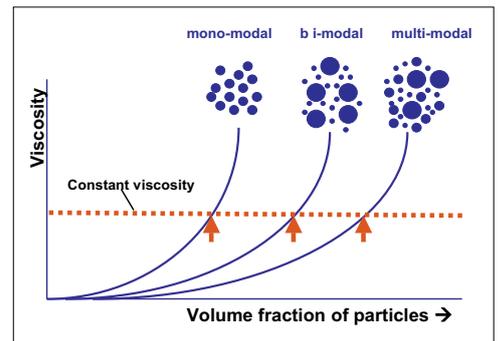


Fig. 5 Increased solids content (reduced water content) at constant viscosity as a function of bi- and multimodality

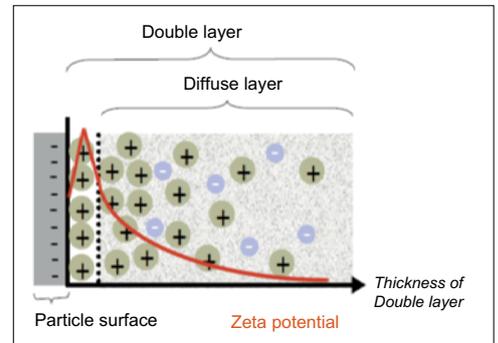


Fig. 6 Double layer and zeta potential [3]

flocculants are necessary to achieve the optimum for each system.

Deflocculation in aqueous suspensions involves three mechanisms that can be individual or in combination depending on the deflocculant [1, 5]:

- Electrostatic deflocculation (cation exchange), influencing the thickness of the electric double layer of the raw material particles
- Steric repulsion by polymer chains attached to the surface of the particles. The adsorbed chains act as a spacer to keep the suspended particles separated at a sufficient distance to prevent the attraction.

- Complexion of interfering cations (Ca^{2+} ; Mg^{2+}).

3 Castable composition

Properties of a castable, such as porosity, mechanical strength and corrosion resistance, are strongly dependent on the water content required to achieve good workability of the castable. Therefore the objective is to reduce the water demand of high performance castables to the lowest possible level.

The viscosity of the matrix controls the flow behaviour and hence the workability of the refractory castable. A matrix with lowest possible viscosity at high solids content is therefore important.

In practice when reporting about matrix fines it is customary to just refer to the $<45 \mu\text{m}$ or $<63 \mu\text{m}$ fraction rather than looking closely at the distribution within this fraction.

The matrix of modern low cement (LC) and ultra-low cement (ULC) castables can be considered as a suspension with relatively high solids content.

For high alumina and spinel castables the matrix is composed of:

Tab. 1 Properties of matrix fine products

Material/Properties	BET [m^2/g]	D_{50} [μm]
Clay	–	2–4
Silica Fume	15–30	0,15
Tabular T60/64 $<45 \mu\text{m}$		5–16
Spinel AR 78 $<20 \mu\text{m}$		2,0
CAC 70		6–13
Calcined alumina $<45 \mu\text{m}$ general purpose	0,7–1,5	3–5
Reactive alumina, submicron	7–9	0,5
Reactive alumina, bimodal	2,6–2,9	2,1–2,9

- calcium aluminate cement (CAC)
- calcined and reactive aluminas
- silica fume
- aggregate fines (tabular alumina or spinel)
- deflocculating agents.

Typical properties of the matrix products are listed in Tab. 1. The CAC 70 and the aggregate fines $<45 \mu\text{m}$ have a comparably high d_{50} value and a broad particle size distribution. They can be considered as the “coarse” part of the matrix, whereas silica fume and special reactive aluminas are at the “fine” end with d_{50} values of $<1 \mu\text{m}$.

4 Silica fume or reactive alumina?

The question is not whether to use either silica fume or reactive alumina? The final application conditions such as temperature and stresses in the lining will define whether a silica fume containing or a pure alumina based matrix is preferable.

In literature it is often stated that silica fume is mandatory in low cement castable matrices to achieve good flowability values. In addition to the high fineness, this is often due to the spherical shape of the fumed silica indicating a lower resistance against shear. This statement was valid at the beginning of the development of low cement formulations in the 1980s. At that time no other economically acceptable ultra-fine material existed to fill the particle gap $<1 \mu\text{m}$ as described by Clavaud, *et al.* [6]

With the development of ultra-fine reactive aluminas and later bi- and multi-modal aluminas this statement is no longer valid.

Various investigations [7–9] have proved that a good refractory castable flowability can also be achieved with pure alumina based matrices. Formulations based on bi- and multimodal reactive aluminas such as CL 370, CTC 50 or E-SY 1000/2000 have produced excellent flow values at water levels of even below 4,5 % (Tab. 2).

A review of matrix aluminas for refractory formulations is given by Kockegey-Lorenz, *et al.* [10].

4.1 Particle size and particle size distribution

Silica fume and reactive alumina behave differently in a suspension. It is important to understand the differences between these two matrix components when replacing one with the other.

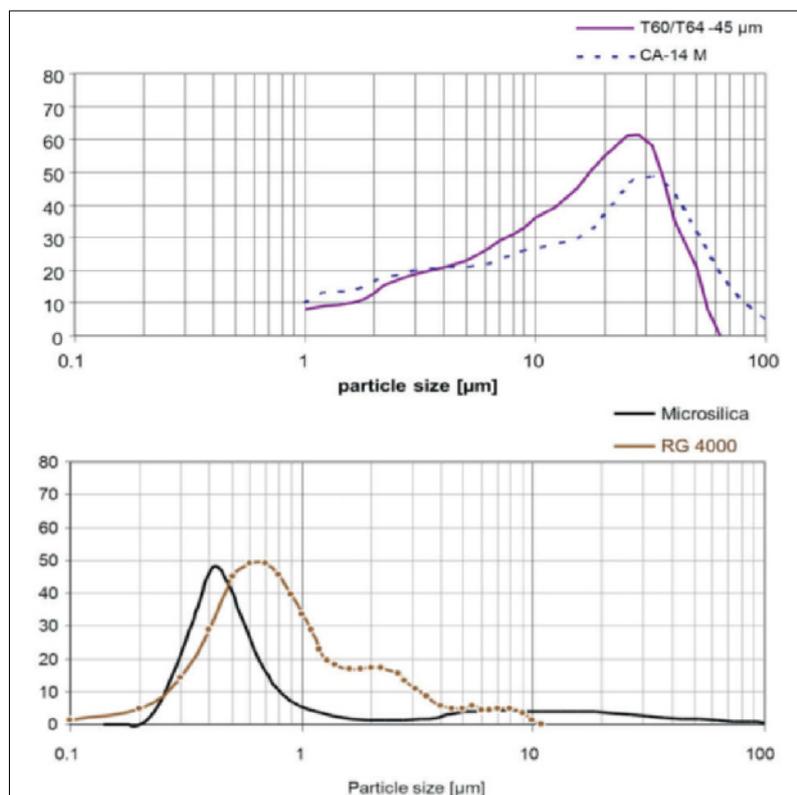


Fig. 7 Particle size distribution of calcium aluminate cement CA-14 M and tabular T60/T64 $<45 \mu\text{m}$. Particle size distribution of reactive alumina RG 4000 and microsilica 971 U

Tab. 2 Flow values of vibrating and self-flowing castables with bi- and multimodal matrix aluminas

		Components [%]			
		VIB 1	VIB 2	SFL 1	SFL 2
T60/T64	3–6 mm	20	25	25	30
	1–3 mm	20	20	15	10
	0,5–1 mm	10	10	11	10
	0–0,5 mm		20		
	0,2–0,6 mm	10		6	10
	0–0,2 mm	15		12	5
	<45 µm			9	
	<20 µm	7			20
Cement CA-270		5	5	5	5
ADS3 / AD1		1	1	1	1
Matrix alumina	CTC 30	13			10
	E-SY 1000		20		
	CTC 50			17	
H ₂ O		4,0	4,2	4,4	4,1
Vib flow after 10 min [mm]		209	195		
Self-flow after 10 min [mm]				253	245

Although silica fume and reactive alumina are both considered as ultra-fine particles, their specific weight differs significantly. All models for the design of an optimised PSD, either for aggregates or for the matrix are based on volume and not weight percentages. Therefore it is essential to recalculate the amount of a component when, for example, replacing silica fume by a reactive alumina. With a density ratio of reactive alumina to silica fume of 3,9 g/cm³ to 2,3 g/cm³ at 1,74 the mass per-

centage of reactive alumina in a formulation has to be increased by this factor. For example: 3 mass-% silica fume has to be replaced by about 5 mass-% reactive alumina of comparable fineness to achieve the same volume fraction.

The d_{50} of microsilica is slightly lower when compared to the d_{50} of a reactive alumina. Also the particle size distribution is narrower pointing to a more monomodal system (Fig. 7).

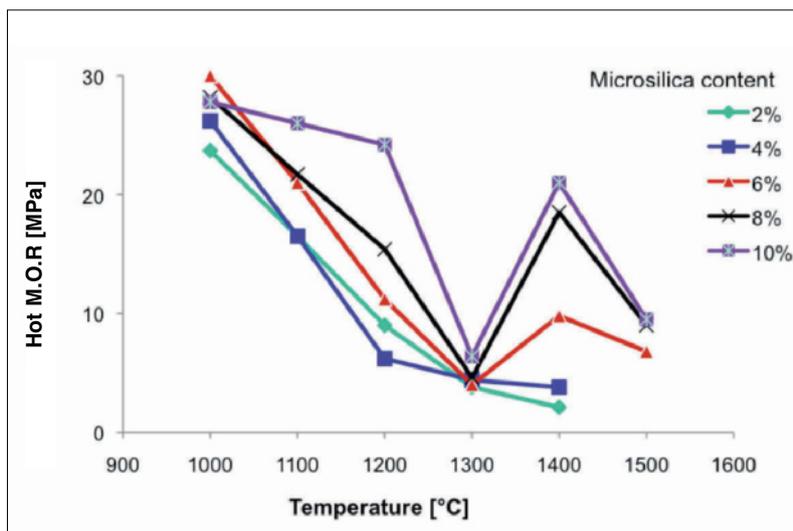


Fig. 9 HMOR of a tabular alumina castable with 1,5 % cement as a function of temperature for different microsilica contents [14]

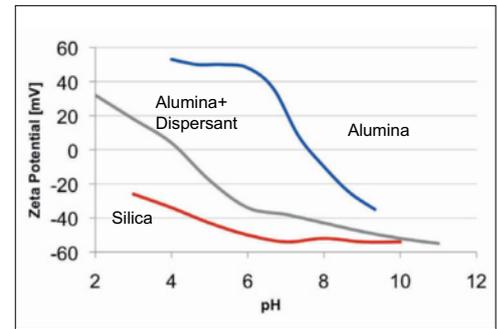


Fig. 8 Zeta potential measurements for silica and alumina [13]

Reactive alumina such as RG 4000 has a broader particle size distribution which increases the packing density of the particles in the solids fraction of the matrix. The available product range of reactive aluminas allows the combination of several monomodal grades to optimise the combination of different grain sizes up to the coarse matrix components such as the cement or the aggregate fines. High solids contents at low viscosity levels are achievable with these specially designed aluminas. This leads to a low water demand of the refractory castable. Silica fume containing castables require the addition of a coarser alumina so that the system does not get overloaded with ultra-fine particles. Aggregates such as tabular alumina <20 µm are the premium choice for low water demand. Calcined aluminas with a comparable d_{50} value also work but increase the water demand because of their remaining agglomerates [10]. The addition of alumina to silica fume containing matrices is also important as a partner for the potential mullite formation during use at high temperatures. Without sufficient alumina no mullite can be formed. As a general rule three times more alumina than silica fume is required for mullite formation in the matrix. A high amount of silica fume is a potential drawback because the matrix system can easily get overloaded with small particles. The viscosity of the suspension increases with the same solids content, as shown in Fig. 3. In practice this effect can be observed in attempts to further increase the flowability of LC-castables with a matrix containing ultra-fine, bi- or multimodal alumina. The general feedback is that by increasing the additions of silica fume the castable gets stickier and loses its flowability. This sticky behaviour can be translated as higher viscosity of the matrix or the need for a higher water addition to achieve the same viscosity levels as before.

Tab. 3 Formulations of spinel-containing and spinel-forming castables for steel ladle application

	SP	SF	SP-SF	SP-SF-NC
	Spinel	Spinel Forming	Spinel + Spinel Forming	Spinel + Spinel Forming
Mix	LCC	ULCC	ULCC	NCC
Components [%]				
T60/T64	50	75	50	55
Alumina	20	16,5	25	30
Spinel AR78	25		20	10
Cement CA-14 M	5	3	2,5	–
Alphabond 300	–		–	3
Magnesite 90MY	–	5	1,95	2,5
Microsilica 971U		0,5	0,5	0,5
MgO content total	5,5	5	6,3	4,5
H ₂ O	5,0	5,5	5,0	5,3

4.2 Zeta potential and deflocculation

Deflocculation is most stable at the points with the highest potential at a given pH value. As described by *Myhre* [11], microsilica has a negative surface charge of around 20–30 mV in aqueous systems, the zero point of charge of microsilica being around a pH of 2–3. Alumina, however, has its zero point of charge at a pH-value of 9 [12].

In cement based castable systems the pH of the matrix is slightly basic with pH-values >7. At this pH-level microsilica has a high zeta potential and requires low amounts of deflocculating agents to achieve high repulsion forces, whereas alumina requires more sophisticated deflocculating agents to achieve stabilisation in the suspension (Fig. 8). The use of traditional deflocculants for a pure alumina bond is therefore generally possible, but requires higher amounts than for silica fume to achieve a stable suspension. The use of more

sophisticated deflocculating agents such as dispersing aluminas leads to low viscosity of the matrix at low water levels. With fineness <1 µm, both silica fume and reactive alumina have particles that can be considered as colloids. Unlike other fine dispersed particles, colloidal particles do not segregate in water and their behaviour in a suspension is determined mainly by the very large surface/volume ratio. The specific surface area (BET) of silica fume is significantly higher than that of reactive alumina (Tab. 1) indicating a high amount of colloidal particles. Although the high surface area of silica fume is beneficial for the strength development at lower temperatures, it is at the same time a disadvantage when considering its sensitivity against impurities that might cause flocculation of the suspension. It is common knowledge that impurities in the matrix have an influence on the deflocculation system. This includes, amongst others, Ca²⁺-ions released by the cement. The cement hydration and the interaction between the deflocculant and the ultra-fine matrix components, will, over time, influence the viscosity of the matrix. Finally the viscosity reaches levels where no further flow can be noted. The reactions occurring are complex and investigations are still on-going to better understand the interactions in colloidal suspension. Practical experience has proven that with the use of dispersing alumina, either ADS/ADW for pure alumina based systems, or M-ADS/M-ADW for silica fume-containing matrices, good flow behaviour, in combination with an adjustable working time, can be achieved.

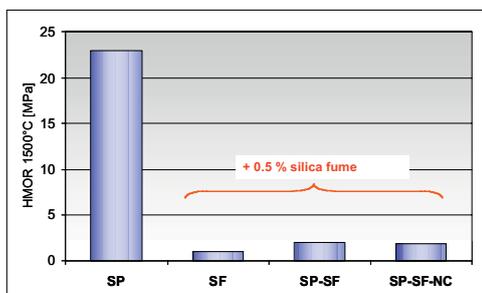


Fig. 10 Hot modulus of rupture (HMOR) at 1500 °C of spinel-containing and spinel-forming castables and mixtures thereof [19]

4.3 Impact of ultra-fine particles on high temperature behaviour

The hot strength of castables is mainly achieved by the reaction of fine alumina with cement, forming CA₆, or the formation of mullite from silica fume and matrix alumina. The presence, and the amount of liquid phase in the system is also essential for the thermo-mechanical stability at a given temperature.

Alumina based castables with microsilica in the matrix are represented by the phase diagram CaO-Al₂O₃-SiO₂. It is explained by *Myhre* that mullite formation starts from a temporary melt. As shown in Fig. 9, this melt formation significantly reduces the hot modulus of rupture (HMOR) of ULC castables at 1300 °C. With a rise in temperature and increasing mullite formation, the HMOR increases again. In an optimised matrix composition with high microsilica content and low CaO levels (ULC), the majority of the melt is consumed by the mullite reaction, and no longer negatively influences the hot strength of the material. However, at temperatures above 1500 °C even for low lime contents the formation of mullite could not be confirmed and the increased melt formation led to a decrease of HMOR [14].

The effect of silica addition to high alumina castables was also discussed by *Kriechbaum, et al.* [15]

For cement-bonded silica-free mixes the development of the hot strength is mainly associated with the formation of calcium aluminates. At temperatures >1000 °C CA₂ is formed by the reaction of CA with alumina. The reaction continues above 1300 °C towards thermodynamic equilibrium, with CA₆ formed from CA₂ and Al₂O₃ [16]. The final content of CA₆ depends on the amount of alumina that is available as a partner for the reaction. In the case of a CAC 70 it requires 2,5 times more alumina than cement in the matrix to achieve a full conversion to CA₆. For high purity mixes, the CA₆ is formed by a solid state reaction creating a strong bridging effect between the particles [17]. This also includes spinel containing castables typically used for steel ladle applications.

The formation of liquid phase in these castables can be estimated using the phase diagram CaO-MgO-Al₂O₃-SiO₂. As described by *Buhr* the presence of silica in the matrix has a significant impact on the formation of liquid phase for spinel containing castables. The temperature where melting starts de-

creases from $>1820\text{ }^{\circ}\text{C}$ for SiO_2 -free formulations to $<1400\text{ }^{\circ}\text{C}$ for SiO_2 -containing ones [18]. In laboratory trials comparing four typical magnesia-alumina castables for steel ladles, this finding was confirmed [19]. The compositions of the test castables are shown in Tab. 3.

All other formulations, except the castable based on pre-reacted spinel, contained 0,5 % microsilica to counteract unwanted magnesia hydration and excessive expansion caused by the spinel formation. The measurements of HMOR at $1500\text{ }^{\circ}\text{C}$ confirmed the negative influence of silica fume. The spinel containing mix reached a HMOR of 23 MPa whereas none of the silica containing mixes showed a significant hot strength (Fig. 10). According to Braulio, *et al.* [17] the liquid phase reaction causes the formation of only small CA_6 crystals in the matrix, embedded in a glassy phase. The thermo-mechanical properties of these type of castables are therefore significantly reduced.

5 Summary and outlook

One of the objectives for the development of high performance castables is good flowability and reliable workability at low water demand. This ensures easy filling of the mixes through small gaps, good distribution behind large formers and complicated shapes and the ability to pump the castable over longer distances. Installations using the defined water content guarantee that physical and chemical properties which were targeted during the development stage, are achieved.

Various factors have to be considered to achieve a matrix with low viscosity at a high solids content.

- A broad particle-size distribution of the matrix fines helps to achieve optimised packing and therefore a high solids content with respect to the low water demand of the suspension. An extensive range of specialty aluminas enables well-controlled PSDs, so that the particle-size distribution of the matrix fines can be steered accurately.
- Additives are required to counterbalance agglomeration of the particles in a suspension. With the use of efficient deflocculating agents like dispersing aluminas ADS/ADW

or M-ADS/M-ADW it is possible to achieve a stable deflocculation with high particle load and at the same time control the hydration of the cement.

LC- and ULC-castables with good flowability can be achieved either with silica fume or with pure alumina in the matrix. However, the physical properties of castables containing a pure alumina matrix or microsilica are different. At lower temperatures good thermo-mechanical strength can be achieved with silica-containing castables. The formulation of these castables requires a good understanding of the interaction of the matrix components (cement, silica, and alumina) to create the desired mullite formation. Variations or inaccuracies in the matrix composition will lead to increased melt formation resulting in poor thermo-mechanical behaviour. At higher temperatures LC- and ULC-castables with a pure alumina matrix exceed the HMOR-values that can be achieved with silica containing mixes. For temperatures $>1500\text{ }^{\circ}\text{C}$ high thermo-mechanical strength of castables can only be achieved with pure alumina matrix systems. Even small amounts of silica in the range of 0,5 % have detrimental effects on the HMOR-values. This is especially in the case of high demanding applications where high hot strength, and erosion resistance are required. In these applications an alumina-based matrix is the only option.

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