
The Use of Microsilica in Refractory Castables

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Abstract:

The technology of preparing refractory castables is presented focusing on the use of microsilica. Predictive flow control by the use of particle size distribution and set time control at high temperatures are the main aspects of the refractory castable technology that is presented in this paper.

Introduction:

The word microsilica has become generic for condensed silica fumes produced as by-products of silicon and ferro-silicon production. Microsilica, also known as fumed silica, volatilized silica etc. normally originates from the loss of SiO(g) which is an intermediate species in the production of silicon or ferrosilicon. It is difficult to state exactly when the term “microsilica” first appears, but in the early 1980’s Elkem registered Elkem Microsilica as a trade name for their fumed silica. It is probable that this is the origin of the generic use of microsilica.

The fumes:

Silicon and ferrosilicon is produced in large electrical smelting furnaces by the reduction of quartz (SiO₂) with carbon. The raw materials are added from the top of furnace and form a stack. The actual reduction to metal occurs in the bottom of the stack. Quartz and the other raw materials are added as fairly large lumps which heats up on their voyage down the stack. The carbon may be added as a range of sources like coal, coke or charcoal; which one that is used is normally the result of economic and other considerations. Additional to the carbon, normally wood-chips are added to improve the texture of the stack.

In the bottom of the furnace, where the temperature exceeds 2000°C the reduction takes place through a series of intermediate reactions. One of these reactions produce the fairly volatile species silicon monoxide (SiO) that at temperatures above approximately 1800°C has a vapor-pressure exceeding 1 atmosphere. This gas which at that time is under pressure ejects upwards in the stack, most gets trapped as it condenses, but some escapes and gets oxidized when it comes in contact with the air above the stack. This is the origin of microsilica. Of course, as a lot of energy is used in the partial reduction of quartz to silicon monoxide, this represents a loss for the metal producer. Therefore most metal producers aims for a minimum

¹ Most of the following has been presented in earlier publications, but has been modified and adapted to the format and scope of the present paper. For a full listing and copies of papers by the staff at Elkem Materials, please contact one of the Authors at the address given.

silica loss. Nevertheless, some silicon monoxide will escape the stack and give microsilica. Typically 10-15% of the quarts ends up as microsilica under good furnace operation.

It is not only silicon monoxide that leaves the furnace. Also a number of impurities are volatilized. The source of which are the raw materials. Typical volatile impurities are oxides of alkalis. One of the more significant impurities is carbon of various sources. The carbon of the microsilica is present as several forms: coke residues, silicon carbide, some tar related organics and finally as carbon black.

Above the top of the furnace, which essentially is an open construction, a hood is placed and with the aid of huge fans, the volatiles are sucked off and forced through a filter. Because of the suction and because the furnace is top-charged, also larger particles like wood-chips, coke residue and quarts dust are collected together with the fumes.

Because of the above mentioned introduction of foreign matter, microsilica has to be beneficiated to give a high quality product. In Figure 1 microsilica production is schematically shown: The raw materials are fed into the top of the furnace (A). The volatiles are sucked off by a fan (D). To get rid of the coarse particles, the microsilica is treated in a pre-collector (C). The gas is then blown into a baghouse filter and collected as “raw” microsilica. Further treatment may be given to achieve desired properties of the product. It should be mentioned that other filtering equipment than baghouse filters have been and are being used.

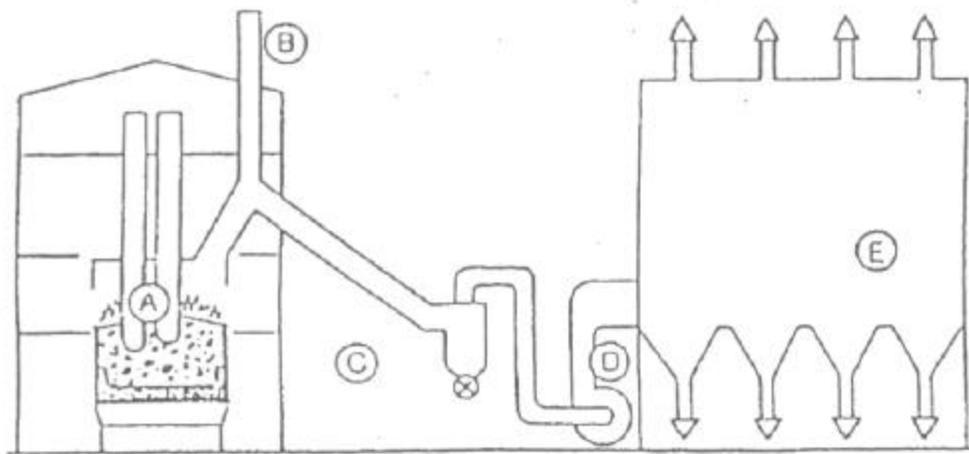


Figure 1: Simplified flowsheet of the production of microsilica. (A) Furnace, (B) Chimney, (C) Pre-collection, (D) Fan, (E) Baghouse filter.

What is microsilica?

If we grab a handful of microsilica, the appearance is a fine powder with variable color from almost black to slightly off-white. There is a strong correlation between the color and the carbon content. This correlation is not straight forward though, since the carbon may be present as coke residue or as silicon carbide additional to carbon black which is the impurity

influencing color. A closer examination of the microsilica by electron microscopy reveals sub-micron spheres with a mean particle size of approximately 0.15 micron. The surface area, as determined by nitrogen adsorption (BET), typically gives values around 20 m²/g which is equivalent to a spherical diameter of 0.14 micron, i.e. close to the results obtained by electron microscopy.



Figure 2: Micrograph of a microsilica cluster showing spherical appearance of the individual particles.

Chemically, microsilica consists of amorphous SiO₂ with variable purity. Without going into detail, it may be stated that there is a close relation between the furnace operation and the quality of the microsilica. Hence traditionally, the purity of the microsilica tends to be rather variable, reflecting the furnace operation at the time it was collected. As the metal normally is the main product and microsilica the by-product, a variation in the performance of the microsilica should thus be expected. This is true for all grades of microsilica except for Elkem Microsilica grade 971U, 971D and 983U since these are produced as main products with the silicon metal as the by-product.

A typical analysis of a high quality refractory grade microsilica is given in Table 1.

Table 1: Typical analysis[%] of a high quality refractory grade microsilica.

| Component | SiO ₂ | Al ₂ O ₃ | CaO | Fe ₂ O ₃ | MgO | Na ₂ O | K ₂ O | C | pH |
|-------------|------------------|--------------------------------|-----|--------------------------------|-----|-------------------|------------------|-----|-----|
| Microsilica | 97.5 | 0.4 | 0.2 | 0.1 | 0.1 | 0.1 | 0.3 | 0.5 | 6.0 |

The crystallinity of microsilica is variable according to source and beneficiation, but values below 0.3 % by weight¹ have been reported. Unpublished work on recent microsilica production (Elkem Microsilica 983U) did however not show any traces of crystallinity. Microsilica consist of spheres with an average diameter of about 0.15 micron. These spheres are the building units of primary aggregates that are a few spheres bonded together by material bridges.² When the particle size distribution is analyzed in a laser diffraction equipment, even well dispersed samples will show a d₅₀ of around 0.5 micron. Figure 3 shows a typical particle size distribution of a well dispersed microsilica as measured by laser diffraction (Microtrack).

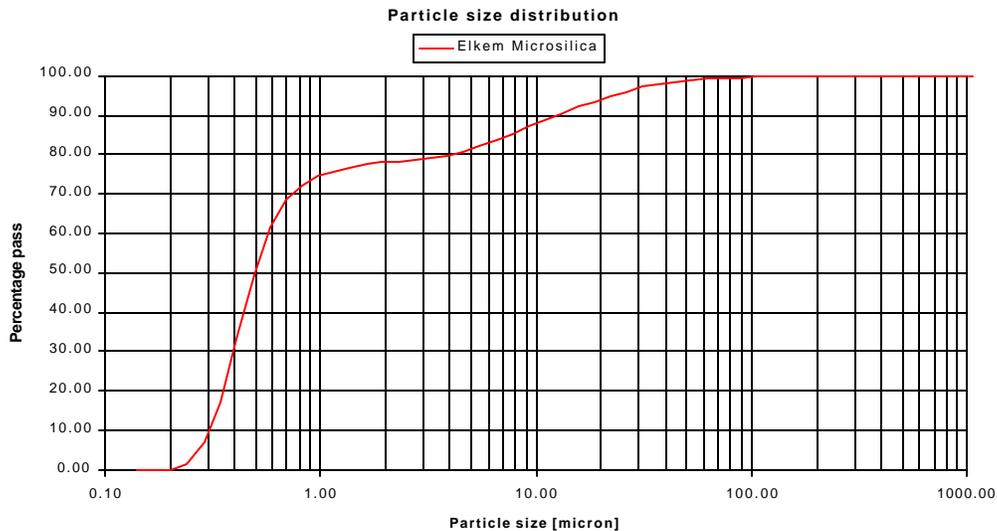


Figure 3: Typical particle size distribution of a well dispersed microsilica as measured by laser diffraction.

The distribution around 0.5 micron may be explained by the primary aggregates. Imagine three 0.15 micron spheres that are linearly attached to each other. This will make up a rod like structure of approximately 0.45 micron length. If this rod-like structure is dispersed in a liquid it spins around and may thus be registered as a sphere of diameter 0.45 micron. Generally, the primary aggregates are of a three-dimensional nature consisting of a higher number of primary spheres. Under any circumstances, the measured particle size distribution of microsilica must not uncritically be applied. Numerous results from the laboratory have shown that in castables the effect of microsilica is equivalent to a powder with d₅₀ around 0.15 micron and with a wide particle size distribution.

The past:

Although not readily available in the past, microsilica has been used in refractories for almost 50 years. In the USA, it seems like the Permanente company (later Kaiser) was using microsilica to form forsterite bonding in magnesite and chrome-magnesite bricks. Also the production of forsterite bricks is mentioned in their patent from 1948.³

In Norway, Elkem started investigating possible applications for microsilica in the late 40's, and was granted a patent⁴ in 1952 covering the formation of ceramic compounds of cristobalite, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$).

In the years to follow, studies were undertaken at Elkem and The Norwegian Institute of Technology, investigating the use of microsilica in a range of meta-silicate systems for possible applications in ceramics and refractories.

Reaction-sintering of the silicates enstatite ($\text{MgO} \cdot \text{SiO}_2$), pyroksene ($\text{Mg}(\text{Ca},\text{Fe})\text{SiO}_2$), diopside ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$) and wollastonite ($\text{CaO} \cdot \text{SiO}_2$) was investigated, using microsilica in combinations with olivine, soft-burned dolomite and limestone. These investigations seem to have been rather preliminary. However, of special interest should be mentioned the "surprisingly strength and hardness" obtained by firing olivine and microsilica at 850-900°C, with no new phases (i.e. no enstatite) being formed. Likewise, firing of limestone and microsilica at temperatures in excess of 1000°C resulted in a strong, lightweight body of wollastonite.

Attempts were also made to synthesize cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) from olivine, corundum and microsilica. Again a rather strong ceramic body was formed, but no cordierite detected. Ceramic compositions in the system enstatite-cordierite were also investigated by combining olivine with microsilica and ball clay. A lowering of the sintering temperature combined with improved plasticity was obtained.

Even though these old trials might be considered a curiosity, some of the ideas are still valid. Also, one should bear in mind that the microsilica used in these experiments had a rather high impurity level (SiO_2 approx. 92%). In the early 1980's, Elkem once again investigated the use of microsilica in ceramic bodies and glazes. The conclusions above were confirmed.

Although the practical introduction of refractory concretes was taking place as early as in the 1920's,⁵ microsilica was not introduced in these products until the late 1950's. It seems like Harbison-Walker⁶ was pioneering these products, although with seemingly limited commercial success. The variability in both the qualities of microsilica and the calcium-aluminate cement at the time may explain this.

Harbison-Walker also received a patent⁷ in 1964 on the additions of microsilica to silica bricks. According to the patent, bricks with improved abrasion and thermal shock resistance were obtained.

Production of a silica brick completely based on microsilica was patented by Elkem in 1973.⁸ The patent describes a method of obtaining tridymite bricks by mixing microsilica with small amounts of lime and an ammonium salt.

It was the well-known patents of Prost⁹ and Lafarge¹⁰ that presented the guidelines for the development of modern low-cement castables. It is reasonable to believe that a major part of the castables containing microsilica being produced today are based on these patents.

Bond systems - castables:

A "standard" bond system in low-cement castables is consisting of calcium - aluminate cement, microsilica, a finely milled calcined alumina and a dispersant. A large variety of modifications/extensions of this basic system is possible.

As microsilica normally are the finest particles in the system, having a specific surface area of approx. 20m²/gram, surface properties and impurities are important in determining the casting and setting properties of a castable. The microsilica may contribute more than 50% of the total particles surface area in certain mixes.

Microsilica normally has a negative surface charge of approximately -20 to -30 mV in aqueous systems, the zero point of charge being around pH 2-3. Cement and alumina may show a slightly positive charge depending on pH. Hence, a slurry mix of these components will not be stable, but prone to coagulation. Additional, and more important in this context is that even tiny amounts of Ca²⁺ ions in a silica slurry causes coagulation. The cement is here the obvious source of calcium. The coagulation is caused by the calcium being absorbed on the silica surface. The coagulation products are voluminous and rather stiff and the result is a castable that at the best could be a fairly hardly placed vibratable or commonly more like a ramming mix unless significantly more water is added. Thus to prevent this coagulation, the calcium ions has to be prevented from absorbing on the silica surface. This may either be done by having a pH below 5, but as this may affect setting, addition of a proper amount of a polyelectrolyte or a surface active agent is the common stratagem. The surface active agent, normally termed deflocculant (in Portland cement based systems termed plasticiser or superplasticiser), is believed to absorb to surfaces thus hindering the absorption of calcium but also creates an equal, normally negative charge of the particles of the bond system. As the particles then will repel each other, casting can take place at reduced water additions. Deflocculants commonly used are phosphates, e.g. sodium hexametaphosphate (Calgon) at approximately 0.2 wt% addition level, and polyacrylates (Darvan 811D, 0.05 wt%).

The deflocculating mechanism may vary. Results indicate that the phosphates adheres to the microsilica surface, more or less "cleaning" the surface from other impurities, whereas some high molecular weight organic molecules might "curl up" between the particles, keeping them apart. When applying phosphates in a castable, one may observe a black surface film on the castable being formed during vibration. This seems to be carbon-containing impurities from a.o. the microsilica surface. This effect may not be observed with other deflocculants.

The effect of microsilica in a fresh castable is at least dual. Once properly dispersed, one important property is to reduce the cement content of refractory castables due to the small particle size of microsilica. According to the patents by Prost and Lafarge, the cement content of refractory castables may be reduced to approximately 1% by the use of carefully graded particles all the way down to sub-micron sizes. The use of superfine particles is based on the

assumption that in a castable with a classical grain size distribution, the density is limited by intergranular voids that are filled with excess water during installation. These voids may be filled by successively finer particles, thus replacing the water. The use of these principles has led to refractory castables with very low water demand, and consequently high compactness. Use of microsilica may reduce the open porosity from about 20-30% to 8-16% after firing at 1000°C, and the drop in mechanical strength that is experienced in conventional castables at intermediate temperatures alters to a steady increase. The beneficial effects of microsilica in castables are well established both in theory and practice. Dense packing is achieved, and the cement content may be drastically reduced. Cement contents resulting in lime contents of 2.5-0.2% is now readily available. Lime contents from cement of 2.5-1% is now classified as low-cement castables while lime contents of 1-0.2% is classified as ultralow-cement castables.

Acting as a filler is not the only effect of microsilica in refractory castables. It has been shown in studies of cement pastes with microsilica that a certain fraction of the microsilica reacts with the cement and water to form so-called CASH phases in addition to the CAH and AH phases normally found in hydrated cement. The CASH phases are of zeolitic nature and the amount of these hydration products are dependent on the quality (purity) of the microsilica.¹¹ The addition of microsilica was also found to alter the pore-size distribution towards finer pores, an effect that is probably more of physical than chemical nature. During heating, the CASH phases convert to CAS_2 and (probably) to cristobalite or quartz. Excess microsilica also crystallizes.

It should be stressed that successful use of both low, and in particular, ultralow-cement castables is dependent on proper use and installation. Due to their high content of fines, these castables are usually thixotropic, and requires vibration for placement. The recommended water addition should be strictly followed as the quality of the final refractory is very dependent on proper installation. The water should be potable. One common problem found on site is the lack of suitable mixers. This results often in too much water added, a practice that is detrimental to the final properties of the castable. As an example,¹² a fireclay based low-cement castable with 4-5% water may develop a cold crushing strength of 110 MPa. This value may drop to 80 MPa with 6% water, and around 50 MPa with 7% water. In addition, the set-time may be negatively influenced and the final product will become more porous.

Particle Packing:

The use of particle size distribution (PSD) as tool in the construction of refractory castables has in the recent few years become more common. Particle size distributions as such have been employed for a number of years though, but on a rather limited scale i. e. for the coarser end of the distribution. New methods of particle size measurements have made it possible to analyze the sub-sieve fractions to a fuller extent, and it has been found that these are at least, if not more, important as the coarse end of the distribution.¹³

Often, the aim of refractory producers is to get as dense refractory structures as possible. In the case of castables, as flow is required, there has normally been a compromise between density and ease of placement. Since the added water transforms to porosity upon heating, minimizing the water addition has been one of the major tasks in the development of castable technology. Theoretically, one would expect that if the individual particles of the castable

packed perfectly, i. e. to 100% density, then the water addition should be at the minimum. A combination of 100% packing density together with flowability is however ruled out primarily because flow is the effect of particles being able to move relative to each other. 100% packing density gives no room for movement and is thus contradictory to flow.

Packing principles:

Even though 100% packing density is not obtainable, control of the particle size distribution of a castable is of vital importance. Mainly for two reasons:

- i) The particle size distribution may decide whether the castable is of a vibratable or a self flowing type.¹⁴ It is possible to design a castable to be either by using PSD analyses.
- ii) Although 100% packing density is contradictory to flow, a solids structure with optimum packing theoretically requires less water for placement than castables with imperfect packing.

To prepare a powder mix that has optimum packing, one must first of all know what the PSD should look like, and secondly what is the PSD of your mix? The first criterion is given by a packing model. Since castables consist of mixtures of powders with continuous distributions, one must look for models dealing with such. Although a number of packing models have been presented over the last century, there are only a few that have been used to any extent in the preparation of refractory castables. The models of Furnas and Anderegg^{15,16} and Andreassen¹⁷ may stand as the classical examples. The model of Furnas and Anderegg is however difficult and cumbersome to use. The model of Andreassen is much simpler but has, to some extent undeservedly, been criticized because of its semi-empirical nature. One interesting aspect of the Andreassen model is that it is not requiring any shape factor. It only requires the different particles to be of similar shape. The main objections that has been raised against the Andreassen equation has been that the model supposes infinitely small particles. To overcome this problem, Dinger and Funk, by combining the Andreassen and the Furnas distribution, made a modified Andreassen distribution in which a minimum particle size was incorporated.¹⁸ The resultant model is much easier to use than the one given by Furnas, and is frequently called the "modified Andreassen" or the "Dinger and Funk" equation. The shape of the models, when plotted in a logarithmic diagram is a straight line for the Andreassen distribution and lines with downwards curvature for the modified Andreassen and the Furnas distribution. As a matter of fact, for a given set of parameters, the modified Andreassen and the Furnas distribution give identical distributions. Below is given the models as proposed by Andreassen and Dinger and Funk (modified Andreassen):

Andreassen:

$$CPFT = (d/D)^q \cdot 100$$

Modified Andreassen:

$$CPFT = [(d^q - d_m^q) / (D^q - d_m^q)] \cdot 100$$

CPFT: Cumulative Percent Finer Than
d: Particle size

d_m : Minimum particle size of the distribution

D: maximum particle size

q: distribution coefficient (q-value)

One important aspect when dealing with particle size distributions is that they are always based on volumes. So for mixtures of powders with different densities, the amounts always has to be transformed to volumes in order to give volume percents. The parameters of the Andreassen and the modified Andreassen equation are the same i.e. the q-value is identical for both. One important result presented by Dinger and Funk was the influence of the q-value on packing. By computer simulations they found that if the q-value was 0.37 or lower, then 100% packing density was possible for infinite distributions, while for q-values above 0.37, there is always porosity¹⁹. So, to get dense packing, the q-value should not exceed 0.37. As a curiosity it may be mentioned that Andreassen, in his original paper from 1930 indicated the q-value to have an optimum value somewhere between 1/3 and 1/2.

The Furnas distribution has been much used in refractories. A common experience when using this distribution on castables has been that flow is improved by adding more of the finest fraction. By adding more of the superfines, the downward curvature of the distribution is straightened. Or put slightly different, adding more superfines changes the distribution from a Furnas type towards an Andreassen type. Thus in spite of the imperfections of the Andreassen distribution, it has been found that it works better for refractory castables than those of the Furnas type²⁰ on systems with microsilica.

Results from systems based on the Andreassen equation have indicated that in order to get good flow for castables, the q-value should not exceed approximately 0.3. Model systems based on fused alumina have shown¹³ that by manipulating the q-value in the range 0.2 to 0.3, one may influence the flow pattern of the castables. If relatively high q-values are used (i.e. close to 0.3) then the castables are vibratables, for lower q-values (<0.25) self flow is dominant. Thus, by manipulating the PSD it is possible to design either type of castable. The effect of reducing the q-value is an increase in fines content. Flow of castables seem to be very influenced by particle interactions, particularly between coarser particles, so that an increase in the fines content effects a separation of the coarser particles. A separation of the particles by a viscous liquid containing water together with fines and superfines seems to be essential for creating flow in such systems.²¹

To manipulate the PSD one must make a representation of the composite PSD of the experimental mixture. Below is given one example of how this may be done.

Preliminary requirements:

- 1) A particle size distribution is generally speaking a listing of the cumulative volume percent of the particles against the size of the particles. For each component of the mixture, a particle size distribution is required. It is important that the PSD is as complete as possible from the finest to the coarsest sizes. Particular effort should be made to include values in the fines and superfines region since it has been found that PSD of particles below 50 micron may play a decisive role. Normally, individual PSDs are obtained by the use of analytical techniques like laser diffraction or settling. When measuring PSD of fine

powders there are a few precautions to consider though. The powder must be properly dispersed, and premature settling must be prevented if suspensions are used. For milled fractions of relatively heavy material like corundum it may be necessary to wet-sieve and then analyze the finest fraction in the particle size analyzer. Afterwards the sieved and the analyzed data may be combined to make the PSD of the milled corundum.

- 2) Grain density of the fraction. For finely milled material this is normally close to the specific gravity. For materials with closed porosity, the grain density has to be determined.

When the PSD and the density of the different components are available, the first step is to calculate the volume of each component (V_i) by the use of the amount N_i and the density ρ_i . Because the amount is converted to absolute volume, it may be entered either as percent or as weight. The weight unit should of course comply with the unit used in the density.

$$V_i = N_i / \rho_i$$

The volume fraction X_i may then be calculated:

$$X_i = V_i / \sum_{i=1}^n V_i$$

Then for each component, multiply the CPFT for each size with the corresponding volume fraction. This gives the contribution from each size class of component “i” to the PSD of the entire mix.

$$CPFT^{mix,i} = X_i \cdot CPFT_i$$

Then add the CPFT for each size class for all components to give the composite CPFT for the given size class:

$$CPFT^{mix} = \sum_{i=1}^n CPFT^{mix,i}$$

By now, each size class should have a corresponding composite CPFT, $CPFT^{mix}$, that contains elements from all components. If the calculations are done correctly, then the listing should start at 100 for the largest sizes, and end at 0. A plot of the composite CPFT against

the size classes should also give a curve without any dips. If dips occur, then it is likely that either the calculation is wrong or that one or several of the individual PSD contain errors causing dips.

In Figure 4, such a composite PSD is given together with the PSDs of the individual components. The composite PSD is here designed to match an Andreassen distribution with a q -value of 0.26 and $D=4000$ micron. The Andreassen distribution is indicated as the straight line touching the composite PSD.

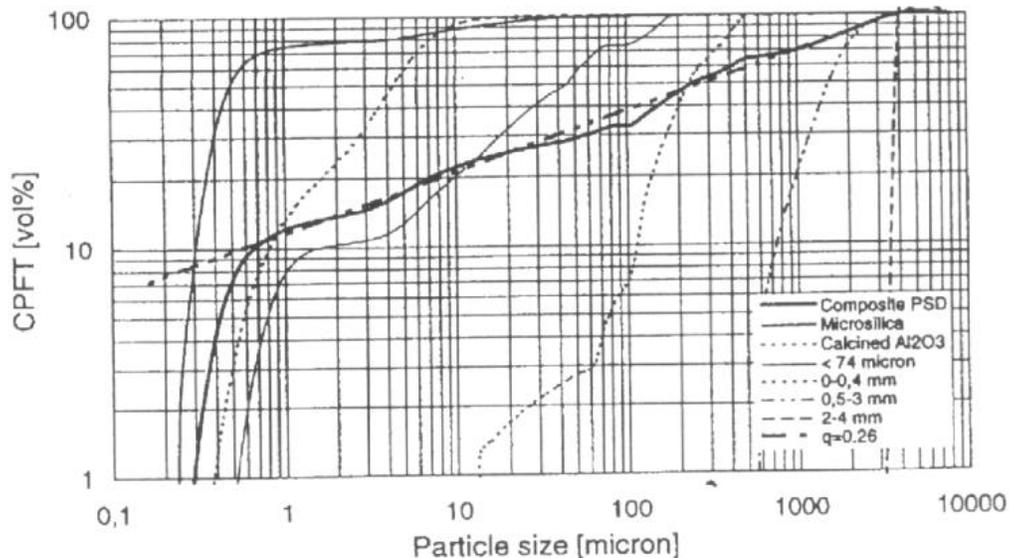


Figure 4: PSD; the individual PSDs that have been used in the construction of a composite PSD to match an Andreassen distribution with a q -value of 0.26 and $D=4000$ micron.

The calculations are not advanced, but numerous. It is therefore an ideal task for spread-sheet calculations. Composite particle size distributions makes it simpler to use overlapping and open fractions in the manufacture of refractory castables. This way the number of components in a refractory mix may be reduced. E.g. it is possible to manufacture a refractory castable consisting of 45 components. Other areas of use is in research and development, either to make castables according to some predetermined PSD or to check and/or repeat some particularly successful castable with other raw materials. If a milled fraction for some reason has changed characteristics, it is relatively simple to adjust the recipe so that the PSD is maintained. This way a significant amount of labor may be saved.

About the choice of model:

The use of the Andreassen distribution is based on results from the laboratory using particle size distributions as shown in Figure 4. What regards the individual particle size distributions of the components these are probably close to correct, except for that of the microsilica. For reasons mentioned under “What is microsilica” it may be doubtful if the PSD that is obtained by laser diffraction is relevant in this context. However as it is difficult to establish an “effective

PSD” by analytical methods, it has been chosen to use the PSD as given by laser diffraction. As long as microsilica is the finest fraction that is used it does not influence too much on the composite PSD. The shape of the PSD of microsilica is reflected in the composite PSD and suggests that the Andreassen equation may be applicable if the deviation at the very low size classes is ignored. It may well be so that the modified Andreassen equation (Dinger and Funk) is the correct distribution to aim for, if one establishes a sufficiently small d_n . However as the two distributions are close to equal for the bulk of the distribution and because the deviation probably is within the “unmeasurable” range below 1 micron, practical considerations makes the Andreassen equation the preferred choice.

About superfine powders:

It has been shown that if the Andreassen distribution is applied, then it is possible to get 100% packing density for an infinite distribution if the q -value is 0.37 or lower. Addition of coarse material is an old and much applied way of increasing the bulk density of concretes, but it has limitations:

i) Addition of coarser material may lower strength because cracks tend to be of the same size as the grains. Larger cracks lowers strength. It may have positive effects like improved thermo-shock resistance though.

ii) Even though the fraction of pores may be lowered by adding coarse material, it does not decrease the porosity in the bond phase. Often the contrary is experienced although not recognized. Because of particle-particle interactions, coarse castables tend to have lower flow, and it is thus tempting to add more water. Simplified, the added water fills up voids in the particle structure, and excess water separate particles by spreading onto the surfaces. The amount of water added should therefore be proportional to the surface area of the castable, not the weight, if the voids are considered constant. It is the combination of packing, surface and water addition that makes the porosity in the final refractory structure. Adding coarse material does not add significantly to surface, and if done properly, neither to voids. Thus a coarse castable should contain less water in percent than a fine to maintain the pore size distribution.

Even though addition of coarser material improves packing density the maximum size is normally restricted to a few mm. In practice, to increase packing density, one has to expand the particle size distribution towards finer and finer particles. This was what was going on in the development of low and ultralow-cement castables in the 1960's and early 1970's.^{9,10} Although the effect of finer particles on packing was no new knowledge (e.g. Andreassen and Furnas in the 1930's), superfine particles had not been used earlier primarily because of two reasons: Firstly, superfine powders (i.e. sub-micron powders) were not readily available at the time, and secondly the powders available were difficult to use because of problems connected to dispersion and variability. There is a close link between the advent of the low-moisture castables and the use of effective dispersants. It must be stressed that packing principles are only applicable on dispersed systems and agglomeration is a phenomenon that becomes very apparent in certain mixtures of fine powders.

From a packing point of view, the use of extremely small particles could make it possible to make a very dense packing. There is however at least one obstacle that makes it unlikely that the use of extremely small particles ($\ll 0.1\mu\text{m}$) would succeed:

A very dense packing results in extremely small inter-particle distances. When particles get closer than a predetermined limit, they inevitably interact. The increased friction between the particles, hinders flow.

We know that the packing may be improved by addition of very fine material. However as the surface area of a mix mainly is located in the fines, the surface area of the mix will increase. Since any water addition is distributed on that surface, this will have a strong effect on the inter-particle distances. If, as an example fine particles with a surface area of $20\text{ m}^2/\text{g}$ is replaced with the same amount (weight) of particles with a surface area of $200\text{ m}^2/\text{g}$, the average inter-particle distance will be reduced to approximately 10% of the original one. Since the distance between particles influences flow, it is likely that problems would occur. Alternatively, to maintain the inter-particle distances, more water could be added. Here, approximately ten times more water would maintain the original inter-particle distance. Increasing water addition is however not wanted because of the transformation to porosity upon firing. Thus a compromise has to be made in which the packing is optimized while keeping the surface area (inter-particle distance) at a tolerable level. At what distance particle-particle interaction starts to become problematic is difficult to predict, but distances of 50-70nm has been mentioned in literature.²² For very well defined systems, distances from approximately 50 down to around 20nm have been calculated by this author, with microsilica as the principal surface carrying component.

Flow and flow decay:

A castable having the proper flow should set at the right time after installation in order to be successful. The set time is one of the most important aspects of a castable, and also perhaps the one that is most difficult to control. Set time seems to be influenced not only by the individual characteristics of the raw materials, but to a large extent by synergistic effects from interactions between individual components. This makes it almost impossible to predict the behavior without testing. Although the set time traditionally has been unpredictable, the quality of cement and other reactive components has over the years improved so that acceptable set times are usually obtained with minor corrections only. Corrections in set time is normally done by the use of accelerators or retarders or combinations. An adjustment of the amount of deflocculant may also influence set time significantly. It may, without exaggeration, be said that it is the control of set time that is the element of "art" in the "handicraft" of castable production. Typical retarders include citric acid additions up to approximately 0.1wt% while sodium carbonate has been used as accelerator. The testing of set time may be performed in the laboratory. One test may be the testing of flow versus time. This is normally referred to as "flow decay" testing. The time a castable maintains its initial flow, or when it reaches a predetermined, lower flow, may be taken as the "open time" or "work time" for that castable. As the set time is highly influenced by the temperature, the testing should be performed on material at conditions similar to those found "on site".

Examples:

Flow:

In this section an examples are given concerning flow and flow decay. This is intended to be a guideline only, since the properties, particularly flow and water demand, are strongly influenced by variability in the raw materials as will be demonstrated in the following examples. Generally, the major "problematic" variability is connected to water soluble components, in practice the cement, and any superfine material that is added. It is therefore important to use proper additive package, i.e. deflocculants/retarders/accelerators, to gain the right results when testing a mix. A successful use of PSD analyses is dependent on a deflocculated system, and a wise step in castable development is to start without soluble ingredients, i.e. cement. Instead of cement one may add a similar volume (constant PSD!) similarly ground inert material. Deflocculants has to be used though to ensure proper dispersion of the superfines. After the PSD has been established this way, cement is added, and if the castable does not behave similar to the cement-free, then probably the cement is the cause of the problem. Frequently, premature setting is seen. Although not recognized, it manifests as a higher water demand. For such mixtures, the addition of retarder brings down the water demand. In Table 2 and 3 are compositions based on white fused alumina with a constant particle size distribution given. The PSD follows an Andreassen distribution with a q-value of 0.25.

Table 2: No/ultralow-cement castables. q-value = 0.25.

| Microsilica/reactive alumina (vol%) | 100/0 | 75/25 | 50/50 | 25/75 | 0/100 |
|-------------------------------------|-------|-------|-------|-------|-------|
| Weight %: | | | | | |
| Alphabond 200 (hydraulic alumina) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Cement (CA-26) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| White fused alumina: | | | | | |
| -74 micron | 20 | 19.5 | 19.5 | 19 | 19 |
| 0-0.4mm | 22 | 21.5 | 21 | 21 | 20.5 |
| 0.5-3mm | 32 | 31.5 | 31 | 30.5 | 30 |
| 2-4mm | 10 | 10 | 9.5 | 9.5 | 9.5 |
| Microsilica (983U) | 8 | 6 | 4 | 2 | 0 |
| CT3000SG (superground alumina) | 0 | 3.5 | 7 | 10.5 | 13.5 |
| HVA SG (calcined alumina) | 7 | 7 | 7 | 6.5 | 6.5 |
| Citric acid (retarder) | | | | | 0.03 |
| Darvan 811D (deflocculant) | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Water (13 vol%) | 4.10 | 4.02 | 3.97 | 3.92 | 3.85 |

Table 3: Low-cement castables with 6% cement. q-value = 0.25.

| Microsilica/reactive alumina (vol%) | 100/0 | 75/25 | 50/50 | 25/75 | 0/100 |
|-------------------------------------|-------|-------|-------|-------|-------|
| Weight %: | | | | | |
| Cement (CA-14C) | 6 | 6 | 6 | 6 | 6 |
| White fused alumina: | | | | | |
| -74 micron | 15 | 14.5 | 14.5 | 14 | 14 |
| 0-0.4mm | 22 | 21.5 | 21 | 21 | 20.5 |
| 0.5-3mm | 32 | 31.5 | 31 | 30.5 | 30 |
| 2-4mm | 10 | 10 | 9.5 | 9.5 | 9.5 |
| Microsilica (983U) | 8 | 6 | 4 | 2 | 0 |
| CT3000SG (superground alumina) | 0 | 3.5 | 7 | 10.5 | 13.5 |
| HVA SG (calcined alumina) | 7 | 7 | 7 | 6.5 | 6.5 |
| Citric acid (retarder) | | 0.03 | 0.03 | 0.05 | 0.05 |
| Darvan 811D (deflocculant) | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Water (13 vol%) | 4.15 | 4.10 | 4.05 | 3.96 | 3.93 |

The castables have all the same PSD, but the superfines fraction is modified from pure microsilica through mixtures to pure reactive alumina (CT3000SG from ALCOA). The reactive alumina was chosen because of similar PSD as microsilica when measured by laser diffraction. When microsilica is substituted by reactive alumina on a volume basis, then 2wt% microsilica has to be replaced by 3.5wt% reactive alumina. The reason is the big difference in specific gravity of alumina and microsilica (approx. 3.9 and 2.2 resp.). This influences all ingredients in the mixture as seen in the tables. However, the hydraulic components are kept constant. It is well documented that the use of microsilica has a retarding effect on the set of refractory castables. Likewise was it experienced that the reactive alumina was an effective accelerator. This was to such a degree that even for the no/ultralow-cement mixture one had to use retarder to prevent flash-setting during mixing. Another effect caused by differences in density is that by substituting microsilica with reactive alumina, the amount of water to make a given volume percent water addition is lowered. The reason is that when the theoretical density is increased by the substitution of microsilica with alumina, then the fraction occupied by a given weight of water will increase. To have a constant volume fraction water, the amount must thus be reduced.

The flow was measured on 3 kg samples immediately after 4 minutes wet-mixing. The flow-value represents the percentage increase in the diameter of a flow-cone as described in ASTM C230: The fresh castable was filled into the cone placed on a vibration table, the cone was removed and the castable allowed to spread by gravity alone until spreading ceased. Normally the spreading was finished after less than one minute. After measuring the flow, the spread castables was subjected to 15 sec. of vibration at an amplitude of 0.75mm. The flow without vibration is termed free-flow and that after vibration, vibra-flow. A free-flow value above approximately 50% is normally regarded pumpable (unless the castable is dilatant). Castables with vibra-flow values above approximately 60 are placeable by vibration. In table 4 are given the resultant flow values of the mixes presented in Table 2 and 3.

Table 4: The dependence of flow on superfines composition. 13 vol% water.

| MS/CT3000SG (vol%): | 100/0 | 75/25 | 50/50 | 25/75 | 0/100 |
|----------------------------|-------|-------|-------|-------|-------|
| No/ultralow-cement: | | | | | |
| free-flow value [%] | 63 | 48 | 22 | 7 | 6 |
| vibra-flow value [%] | 136 | 132 | 98 | 72 | 68 |
| 6% cement: | | | | | |
| free-flow value [%] | 64 | 48 | 12 | 4 | 0 |
| vibra-flow value [%] | 136 | 115 | 92 | 72 | 52 |

There are two striking results presented in Table 4. Firstly, the very good match in flow values of the two castables and secondly, the dependence of the flow on the superfines. Estimating the precision of the flow measurements to be approximately ± 5 , most of the corresponding results (same superfines) are close to the expected variation. This is so because of the use of the same raw-materials together with the same water addition in terms of volume. The effect of the reactive alumina has been presented elsewhere²³ and the additional results presented here (the LCC, Table 3) verifies that particularly the free-flow is reduced by the introduction of reactive alumina. Another example of a castable based on PSD is given in the Table 5. This is similarly to the preceding examples also based on a q-value of approximately 0.25:

Table 5: SiC based castable. q=0.25.

| | |
|-----------------------------------|------|
| Weight %: | |
| Alphabond 200 (hydraulic alumina) | 0.5 |
| Cement (CA-14) | 0.5 |
| Silicon carbide: | |
| -75 micron | 5 |
| -1mm | 30 |
| 8/14 mesh | 30 |
| Fused alumina, -75micron | 17 |
| Microsilica (983U) | 8 |
| Baco MA95R (calcined alumina) | 9 |
| Darvan 811D (deflocculant) | 0.05 |
| Water (12.9 vol%) | 4.60 |

The resultant free-flow and vibra-flow were 69 and 132 respectively. I.e. close to the expected values from Table 4. Here only 12.9 vol% water was used as opposed to 13 vol% in the other mixes. In terms of weight, the deviation is close to negligible however; 0.02 wt%.

Flow decay:

The first sequence in the setting of a castable is loss of flow, i.e. it becomes impossible to place. Control of the set time has always been one of the most wanted but also perhaps the

most difficult aspect of refractory castable technology. One way of monitoring the evolution of this first stage of setting is by measuring the flow of a castable as a function of time, commonly called flow decay measurements.

For the flow decay measurements, sufficient material was mixed to perform a number of flow tests. This amount was stored in a container either covered with a moist blanket or with a tight lid to avoid evaporation. At a predetermined time, a sample was taken and flow was tested according to the procedure described under Examples, Flow above. Flow decay was tested on the compositions in Table 2 and 3 with different additions of retarder (citric acid) and at 5, 20 (ambient) and 35°C, with emphasis on 35°C. For the testing at 5 and 35°C, the homogenized dry mix was tempered overnight in a refrigerator or heating cabinet prior to mixing with tempered water. After wet mixing, the castable was stored in the temperature controlled enclosure and samples were withdrawn from this at test time.

Flow decay and particle size distribution:

Figure 5 shows the free-flow of ultralow-cement castables with different particle size distributions as a function of time. The temperature was 20°C. The raw materials are the same as for the ULCC presented in Table 2, but the composition was changed to accommodate for the different particle size distributions represented here by their distribution coefficients (q-values). 13 volume% water was used. We see that the free flow is significantly influenced by the q-value, lower q-value gives higher free flow. These results are in accordance with earlier data stating that high free flow is attained by the use of particle size distributions with low q-value. A low q-value implies a high level of microsilica, here q-values of 0.28, 0.25 and 0.22 represents microsilica contents of 4.5, 8 and 10% respectively. A full listing of the castable composition is given in reference.²⁴ Additional to the fact that low q-values improve free flow, also the time it takes until the free flow start to decline is proportional to the microsilica content. It has been known, since the appearance of the low-cement castables, that microsilica could have a retarding action on set. One have sought to explain this behavior by the microsilica covering the cement surface and thereby hinder the dissolution of the cement. Without judging the contents of such theories, one may simply state that more microsilica in a castable mixture seems to have a retarding effect. Here the effect is that a castable with a q-value of 0.25 (8% microsilica) makes it possible to maintain free flow for around 3 hours whereas a q-value of 0.28 (4.5% microsilica) leaves little time until the flow decay commences.

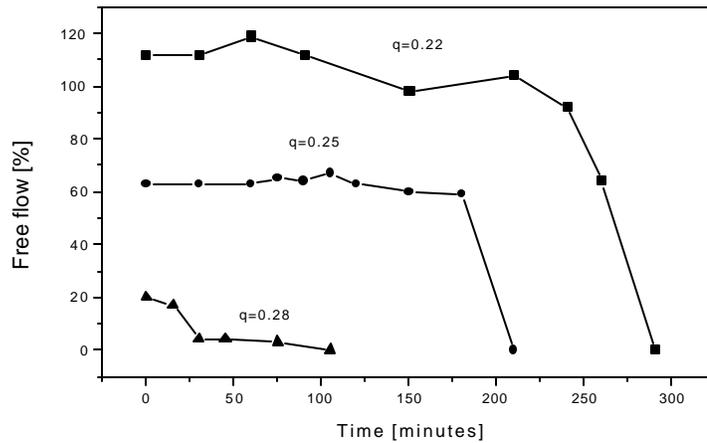


Figure 5: Free flow as a function of time and particle size distribution at 20°C. Ultralow cement castable compositions with 13 vol% water. The q-value refers to the model described by Andreassen. Increased q-value decreases microsilica content. No retarder is used.

Flow decay and microsilica/reactive alumina ratio:

Flow decay was measured for the castable compositions of Table 2 and 3. Figure 6, shows the free flow as a function of time for the compositions with q=0.25, 0.5% cement (Table 2). We see that the free flow is strongly affected by introduction of reactive alumina. Particularly the work time (time to flow loss) is more or less eliminated already at 25vol% reactive alumina. Addition of citric acid (0.03%) to the 100vol% reactive alumina composition seemingly increases work time although the effect is somewhat questionable due to an overall very low free flow value for this composition. If the work time is improved by the addition of citric acid, then this may be taken as an indication of the reactive alumina being a powerful accelerator in this bond system.

Figure 7 shows the same castables as Figure 6, this time the vibra flow values. Much of what has been said about the results in Figure 6 above could be repeated with the indications of the reactive alumina acting as an accelerator being somewhat more pronounced. Of course, the data may be interpreted the other way, with microsilica retarding the system.

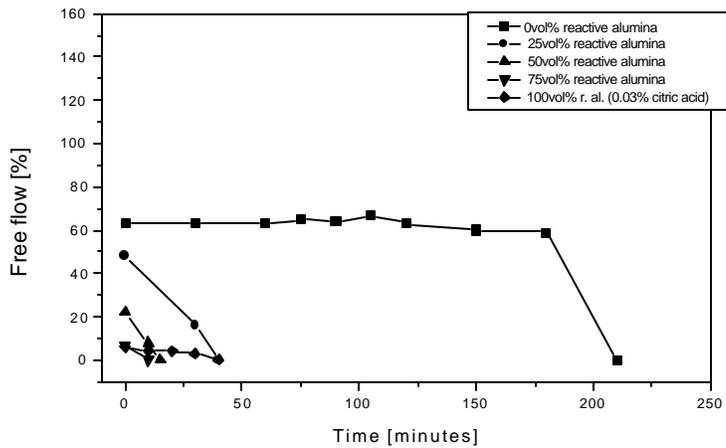


Figure 6: Free flow as a function of time and superfines composition. $q=0.25$, 0.5% cement. Fused alumina based castables with 13vol% water. Castables without retarder unless indicated.

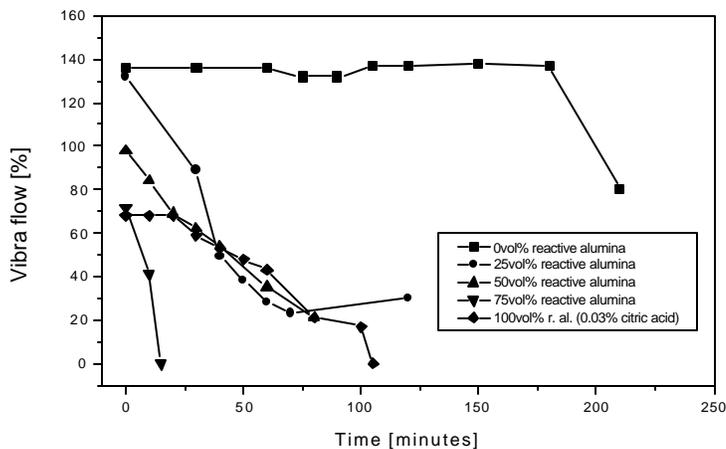


Figure 7: Vibra flow as a function of time and superfines composition. $q=0.25$, 0.5% cement. Fused alumina based castables with 13vol% water. Castables without retarder unless indicated.

With 6% cement, the pattern is similar, but this time most of the compositions had to be retarded with some citric acid. Citric acid (retarder) had to be added when reactive alumina was used in the 6% cement compositions. Without the retarder, the castables would not transform into the “wet” stage during mixing at this low water content. Figure 8 shows the free flow of castables with a q -value of 0.25 and 6% cement (Table 3). This is essentially the same castable as those presented in Figure 6 and 7, but this time with 6% cement. The increased cement content necessitates use of retarder, and even then, the work time is much shorter than

the castables presented in Figure 6. Nevertheless, the same conclusions may be drawn with respect to acceleration by the reactive alumina etc.

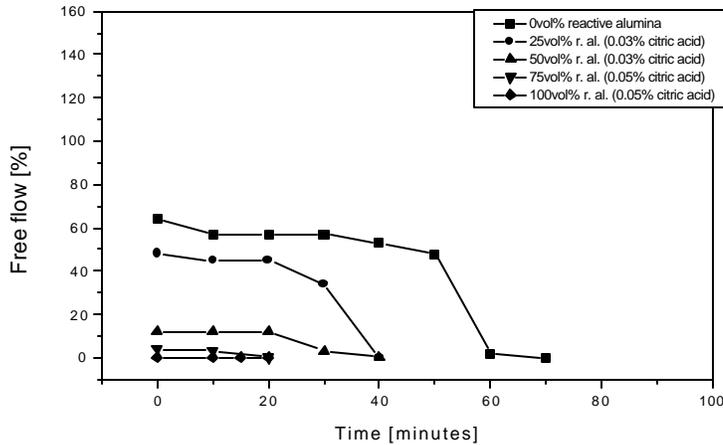


Figure 8: Free flow as a function of time and superfines composition. $q=0.25$, 6% cement. Fused alumina based castables with 13vol% water.

Flow decay and temperature:

For the rest of the flow decay investigation, we will confine to the castable compositions with 100% microsilica in the superfines, i.e. with a q -value of 0.25 and 8wt% microsilica. Water for casting will remain at 13 volume%.

Temperature is known to have a strong influence on set time of refractory castables. Figure 9 shows the free flow as a function of time for the ultralow cement castable of Table 2 at 5, 20 and 35°C. We see that the flow decay is strongly activated by temperature, free flow is maintained for more than 5 hours at 5°C, while at 35°C all free flow is lost within approximately 40 minutes. The initial free flow is higher at 5°C than at 20 and 35°C, but due to few results it is not possible to state whether this is a general trend. At 5 and 35°C problems connected to placement could be expected. At 5°C the problem is delayed set, at 35°C, placement of the castable could be problematic because of the rapid flow loss.

Figure 10 shows the vibra flow for the same castable at the same temperatures. Essentially the same conclusion may be drawn, however the superior flow at 5°C seems not that pronounced. The rapid flow loss at 35°C will definitely cause installation problems if used under such conditions.

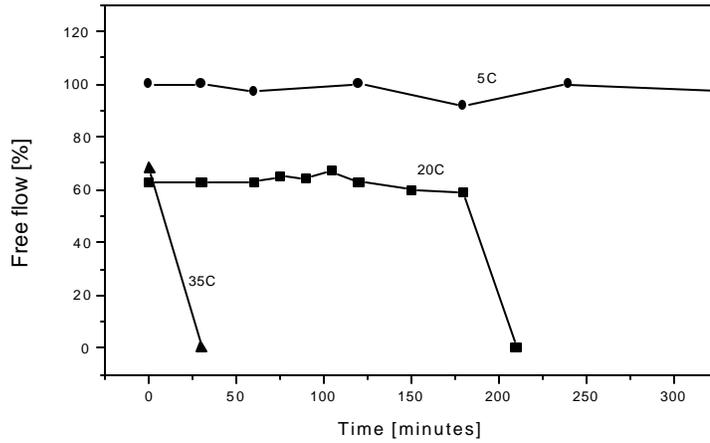


Figure 9: Free flow as a function of time at 5, 20 and 35°C. Ultralow cement castable composition with 13 vol% water (4.10 wt%).

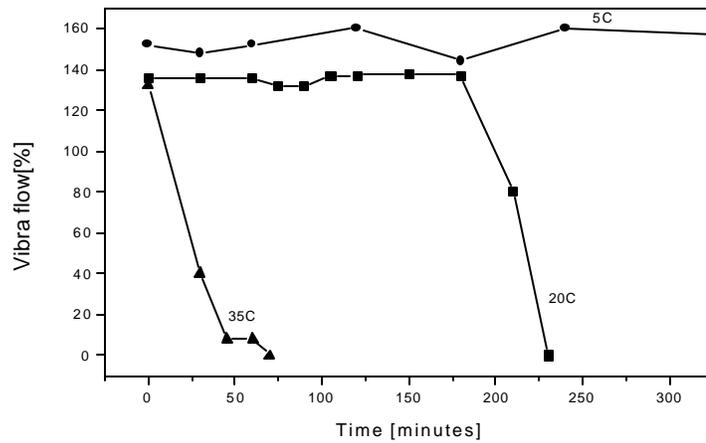


Figure 10: Vibra flow as a function of time at 5, 20 and 35°C. Ultralow cement castable composition with 13 vol% water (4.10 wt%).

Somewhat surprisingly, there does not seem to be big differences in the flow decay behavior at 35°C if 6% cement is used in the castable mixture (LCC of Table 3). This is seen in Figure 11 showing the vibra flow as a function of time at 5, 20 and 35°C for the low cement castable. At 20°C however, the set is significant quicker, a full flow loss is experienced after slightly more than one hour.

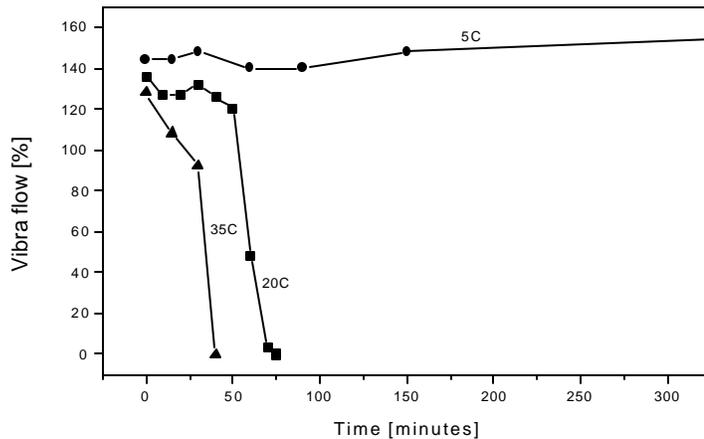


Figure 11: Vibra flow as a function of time at 5, 20 and 35°C. Low cement castable composition with 13 vol% water (4.15 wt%).

As demonstrated, rapid flow decay is a problem that is often encountered in hot environments. This necessitates use of special actions in order to compensate for this highly unwanted temperature effect. Typical are the castables of Fig 9 to 11 at 35°C. We see here that the flow starts to decay instantaneous and that it is unlikely that these castables could be successfully placed. To compensate for the flow loss, one could add more water, but as this transforms into porosity upon firing, water addition should be kept at a minimum. A common procedure is to use ice-cold water. The effect of this is variable though since the water typically amounts to only 4-5wt%. Hence a lowering in temperature of the mix of roughly 7-8°C could be expected by the use of 5wt% water (water 0°C as compared to 35°C, a dry mix with a heat capacity of 1 kJ/kg K at 35°C). This could be enough to make the castable placeable, but as it heats up during mixing, the effect is variable. It does also imply the availability of ice.

Another stratagem is to add chemical retarders. This is often feasible if one knows what conditions the material is intended to be used under. Addition of retarder at site may also be done in accordance to the ambient temperature. One of the commonest chemical retarders is citric acid, or salts (sodium) of citric acid.

The effect of citric acid on flow at 35° C:

Since the present castables had a too rapid flow decay at 35°C, it was decided to investigate the effect of citric acid addition. Experience has shown that castables are very sensitive to the amount of citric acid addition so by experience the addition level should preferentially stay below 0.1wt%. For the ultralow cement castable addition levels were 0 to 0.06wt% at increments of 0.02. For the low cement castable 0 to 0.09wt% were added at increments of 0.03. With the exception of the citric acid addition, the experimental procedure was as described earlier for samples tested at 35°C. All compositions were demouldable within 24 hours.

Figure 12 shows the effect of citric acid addition on free flow of the ultra low cement castable. It is seen that by adding 0.02 wt% citric acid, the free flow is maintained for a time sufficient for placement. Higher addition levels prolong the time till flow decay commences.

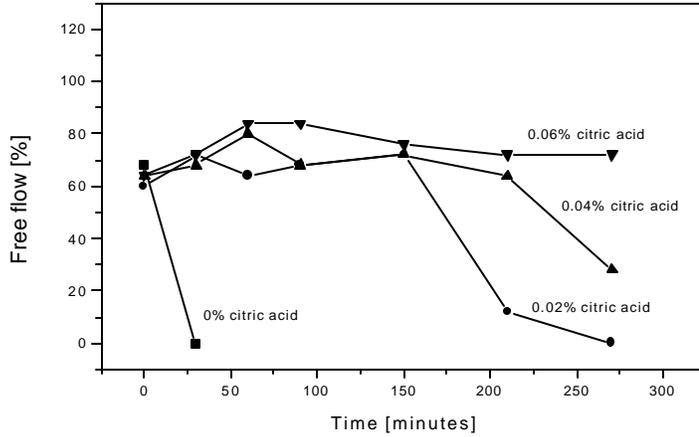


Figure 12: Vibra flow at 35°C as a function of time and citric acid addition. Ultralow cement castable composition with 13 vol% water (4.10 wt%).

Figure 13 shows the effect of citric acid addition on vibra flow for the ultralow cement castable (same as in Fig. 12 but vibra flow).

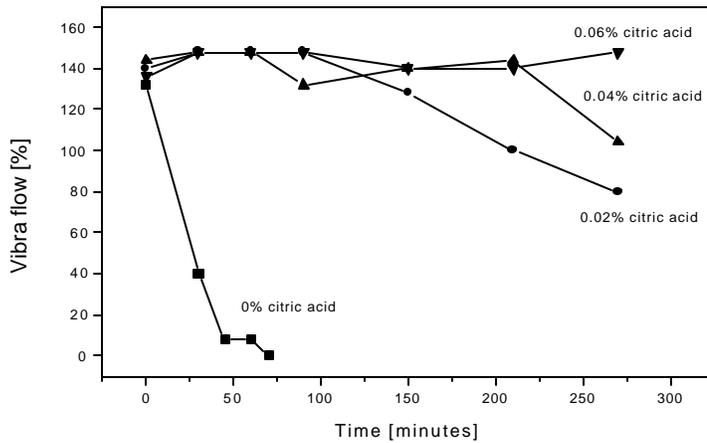


Figure 13: Vibra flow at 35°C as a function of time and citric acid addition. Ultralow cement castable composition with 13 vol% water (4.10 wt%).

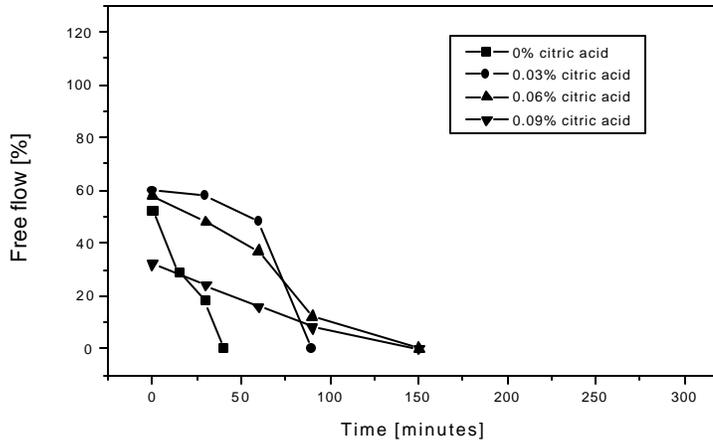


Figure 14: Free flow at 35°C as a function of time and citric acid addition. Low cement castable composition with 13 vol% water (4.15 wt%).

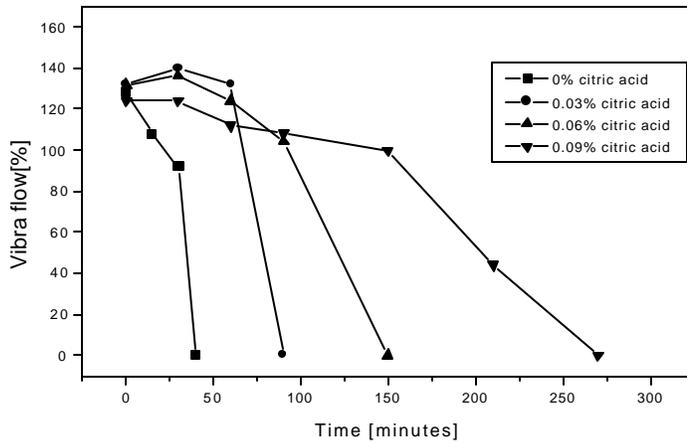


Figure 15: Vibra flow at 35°C as a function of time and citric acid addition. Low cement castable composition with 13 vol% water (4.15 wt%).

With 6% cement, the picture is somewhat altered. The time till flow decay is reduced, and larger dosages of citric acid is required to get sufficient retardation. Figure 14 and 15 shows the flow decay of the low cement composition as a function of time and citric acid addition. In Figure 14, the free flow is shown. We see here that it becomes difficult to maintain free flow for substantial time even with addition of citric acid. As a matter of fact, if too much citric acid

is used, here 0.09%, flow is lost. This has been seen as a general trend for other mixes, if the citric acid addition exceeds approximately 0.1% the castable becomes sticky. Stickiness hinders the free flow as shown in Figure 14 (0.09% citric acid). Also the vibra flow may suffer if the addition level gets too high. The vibra flow is however more forgiving so that higher dosages is necessary to lower the flow significantly. A slight lowering of the vibra flow is however seen for the 0.09% addition level of Figure 15. The retardation seems to be fairly proportional to the addition level, showing that also at 35°C it is possible to adjust this castable by with citric acid.

Strength

The compositions presented in Table 2 and 3 were cast and cured for 24 hours before demoulding. After drying at 110°C for 24 hours, prisms were fired for 12 hours at 600 and 1000°C before testing. Figure 16 and 17 shows the resultant cold crushing strength for the ultra low cement castable and the low cement castable. It is seen that the substitution of microsilica with reactive alumina lowers the CCS for the ultralow cement castables while for the low cement castables, some substitution seems to improve the CCS. A full substitution however lowers strength. Generally, the low cement castables exhibit a very high CCS with several results above 225MPa which was the maximum load of the testing equipment.

Notes on hot-strength

The hot-strength of the castables is another important property that will not be dealt with in detail here, but results have clearly shown that very good hot strength have been obtained with the 100% microsilica, ultralow cement castable. Substitution of microsilica with reactive alumina lowers hot strength except for the 100% alumina castables where very good hot strengths have been observed, particularly for the low cement composition. The use of only reactive alumina should however be restricted to pure alumina aggregates since even traces of silica may be detrimental to their hot-strength. Another important aspect to consider is the high price of reactive alumina as compared to microsilica. This difference gets even larger by the fact that in order to have a constant particle size distribution approximately 1.8 times more reactive alumina than microsilica has to be added. The latter is of course caused by the differences in density (3.9 and 2.2 for alumina and microsilica resp.).

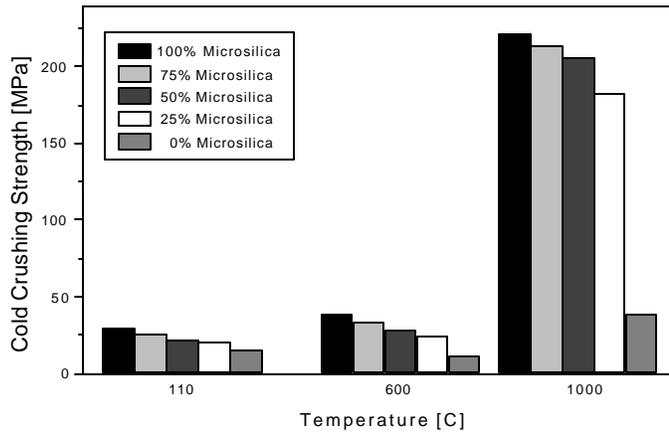


Figure 16: Cold crushing strength after drying and 12h firing as a function of superfines composition. Ultralow cement castables with 0.5% cement.

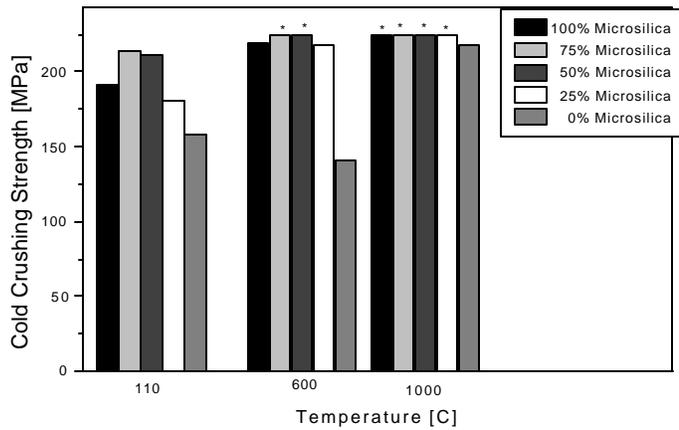


Figure 17: Cold crushing strength after drying and firing as a function of superfines composition. Low cement castables with 6% cement. An asterisk indicates a strength higher than 225 MPa which was the maximum load of the test equipment.

Conclusion:

This presentation that has been focusing on various aspects and effects of the use of microsilica in refractory castables has shown that castables with predictive and attractive properties may be prepared by the aid of particle size analyses. The use of microsilica not only improves flow, particularly self flow, but also improves the set time control as demonstrated under Flow Decay.

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