
Castables with $\text{MgO-SiO}_2\text{-Al}_2\text{O}_3$ as bond phase

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The fine art of



CASTABLES WITH MgO-SiO₂-Al₂O₃ AS BOND PHASE

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ABSTRACT:

Cement-free castables based on the hydration products of magnesia and microsilica were made with additions of alumina and selected aggregates so that the compositions were within the alkemade triangle periclase-spinel-forsterite. The bond-phase was composed in a manner so that it would after firing consist mainly of forsterite and spinel to which aggregates of either periclase, spinel or olivine was added. Using the right deflocculant, this castable was self-flowing at low water additions. Cold properties like flow and cold strength is presented together with hot-M.O.R. data obtained on prefired samples.

INTRODUCTION:

Refractory castables containing spinel has the recent years become common, and a part of many refractory producers portfolio. These castables have normally a cement bond and contain either pre-formed spinel, or magnesia and alumina that is supposed to form spinel upon firing. The latter alternative is cheaper, but here one have to consider the significant volume expansion that accompanies the formation of spinel from the oxides. If this is unaccounted for, a disruptive expansion causing cracking may be seen when the product is fired.

In most cases, refractory castables contain microsilica. This is to reduce the water for casting and hence the porosity of the fired product. For corundum-spinel castables, it has been shown¹ that even tiny amounts of silica drastically reduces the hot strength of the refractory, even though according to the phase diagram, a mullite bonded corundum-spinel castable should be viable. A thorough examination of the phase diagram shows however that there are so many sub-solidus reactions occurring during heat up that strong refractories based on corundum, spinel and mullite is most unlikely, at least on a short term². The equilibria in question shifts over relatively narrow temperature ranges (1400-1500°C) so in practice, such a refractory would probably

not be a strong body at steel-making temperatures. Nevertheless, even for spinel castables, microsilica is sometimes being used, although usually in small amounts (1-2%?). It seems as if the microsilica is added to give softening to compensate for the disruptive expansion of the spinel formation. Since microsilica for these reasons normally is not used in significant amounts, relatively much water has to be added for casting. Even with submicron alumina as superfines, water additions are higher than if microsilica was utilized to a full extent. Experiments on particle packing has shown that there seems to exist a minimum water addition for superfine alumina corresponding to 15-16% porosity while less than 10% porosity may be obtained with microsilica³.

Based on these observations, it was found that castables within the compatibility triangle periclase-spinel-forsterite would have a better chance of gaining good hot strength than those within the triangle corundum-spinel-mullite. To minimize the content of impurities, it was decided to make castables with a bond system based on the coagulation products between MgO-SiO_2 and H_2O . This bond system has been described elsewhere^{2,4,5} and has to the Authors knowledge also been used by some refractory producers. Its main disadvantages seems to be control of set time and a tendency of explosive spalling. Thus the scope for the present investigation was to make castables within the compatibility triangle periclase-spinel-forsterite using the MgO-SiO_2 bond. The castable should also preferentially be self flowing at low water additions.

CASTABLE COMPOSITION:

As mentioned above, the castables should be based on the hydration product of MgO-SiO_2 with a net composition such that it would be placed within the alkemade triangle periclase-forsterite-spinel. Among raw materials for such castables are spinel and olivine, the latter a cheap natural source that transform mainly into forsterite upon firing. Fine alumina was added to compensate for an expected shrinkage caused by the formation of forsterite from magnesite and microsilica. This should give spinel that should compensate for some of the shrinkage. The bond phase was common for all castable compositions being based on milled magnesite, microsilica and calcined alumina. This should after firing give a phase assemblage of approximately equal amounts of periclase and forsterite with some spinel. This is of course provided equilibrium is established. To this bond phase, either olivine, magnesite or spinel was added to make up essentially forsterite, periclase or spinel castables all with some of all three components. Figure 1 shows the phase diagram magnesia-alumina-silica with the approximate composition of the bond phase and the three castables indicated. The bond phase is the composition in the center of the four.

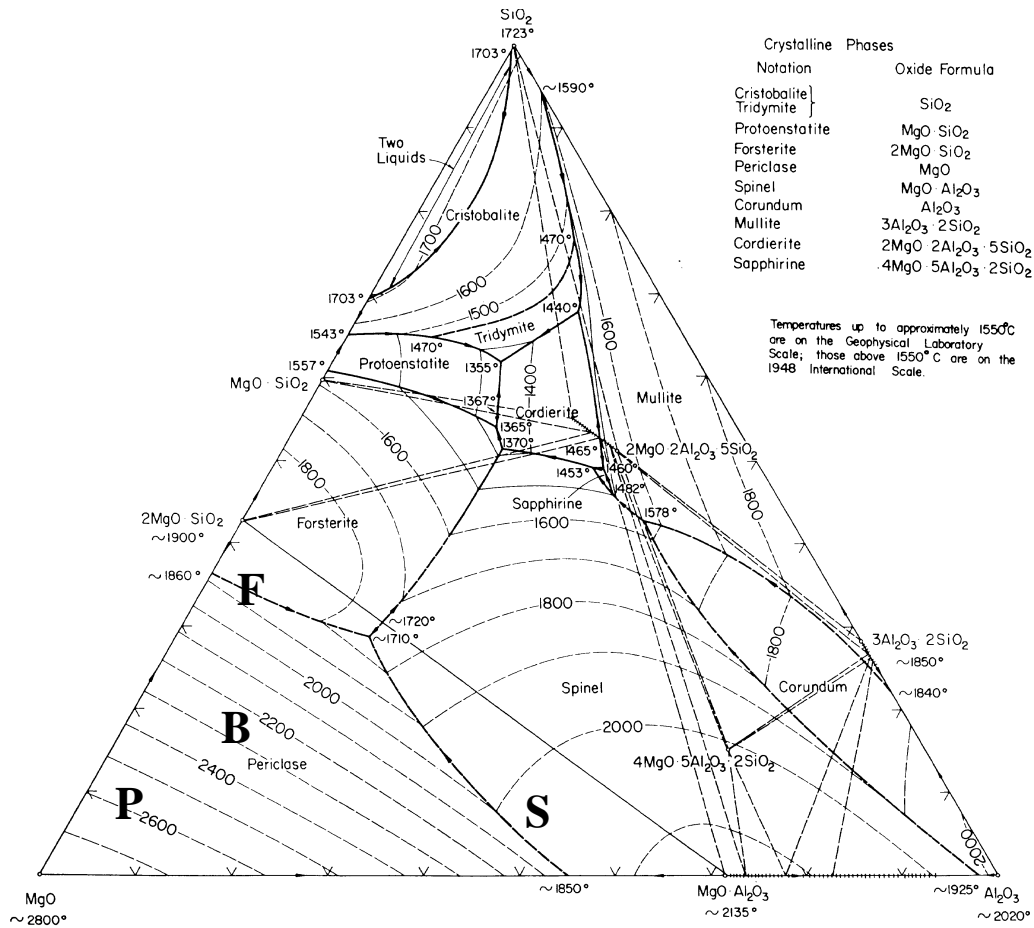


Figure 1: The system MgO-Al₂O₃-SiO₂ after Muan and Osborn.⁶ **F** indicates the forsterite castable, **P** the periclase and **S**, the spinel castable. **B** is the common bond phase.

The castables were composed to match a particle size distribution with a q-value of 0.25 according to the model given by Andreassen⁷. A such particle size distribution has been found to give castables with semi self flowing properties at very low water additions (around 13 vol%) provided use of the right superfines and a deflocculated system. It is important to use microsilica that is easily dispersed to get optimum flow. It was found difficult to get proper dispersion since the traditional deflocculants used in refractory castables did not give good flow at the low water addition that was aimed for (13 vol%). It was finally found that 0.25% Vanisperse CB, a deflocculant originally designed for carbon black (hence CB) gave the best flow. This deflocculant is a by-product from vanilla-production (Borregaard, Norway) and is also the only to us known additive that is able to retard set of the MgO-SiO₂ bonded castables. Choosing the right milled grade MgO is also important to get the right flow. It seems important to mill a dead burned quality to keep the reactivity down. A proper particle size distribution is of course also important.

Table 1 shows the castable composition of the present investigation. The magnesite was a deadburned magnesite from Billiton (Nedmag99), microsilica was from Elkem Refractories, spinel from ALCOA, calcined alumina from British ALCAN, Olivine from A/S Olivin and Vanisperse CB from Borregaard (latter two are Norwegian companies).

Table 1: Castable composition

Castable components:	Spinel	Forsterite	Magnesite
Weight %:			
Magnesite: -100 micron	35	35	35
Microsilica 983U	8	8	8
Calcined alumina: BACO MA95D2	5	5	5
Spinel AR78: 1-3mm	28		
Spinel AR78: 0.5-1mm	12		
Spinel AR78: 0-0.5mm	12		
Olivine 1-5mm		20	
Olivine AFS20		20	
Olivine AFS30		12	
Magnesite: 1-4mm			28
Magnesite: 0.5-1mm			19
Magnesite: <0.5mm			5
Vanisperse CB (deflocculant)	0.25	0.25	0.25
Water (13 vol%)	4.57	4.65	4.5

PROCEDURE:

Castable mixing:

After the ingredients were dry-mixed in a Hobart mixer for 4 minutes, 13 volume percent water was added and the castable wet mixed an additional 4 minutes.

Flow measurements:

Flow measurements were performed using the flow cone described in ASTM C230. The testing was performed on a vibration table set at a double amplitude of 0.75mm. Initially, after filling the castable into the cone, the cone was removed and the castable allowed to spread by the action of gravity alone. When the spreading stopped (normally within 2 minutes), the percentage increase in the diameter of the spread cone was taken as the free flow value. The spread castable was then subjected to 15 seconds vibration,

and the resultant spreading taken as the vibra flow value. I.e. both tests were performed on the same castable sample.

Cold strength:

Strength was measured on samples of 40x40x160mm (ASTM C348) cured for 24 hours before drying at 110°C. Samples were then fired at 600 and 1000°C for 12 hours. Subsequently, strength was tested on the dried sample (110°C) and on the fired samples. The cold strength testing was performed according to ASTM C348 (flexural strength) and ASTM C109 (compressive strength).

Hot M.O.R.:

Hot M.O.R. testing was performed on samples of 25x25x150mm in accordance with PRE/R18. The samples were pre fired for 24 hours at test temperature and allowed to cool before being loaded into the test machine. The heating rate was 300°C/h for both the pre firing and the testing, and the samples were allowed to equilibrate at test temperature for at least 30 minutes prior to testing.

Permanent Linear Change:

Permanent linear change (PLC) was measured on 40x40x160 mm prisms. As the reference state, wet prisms directly after demoulding was chosen as opposed to the 110°C dried prisms generally used. This was done because it has been realized that a significant amount of the PLC occurs during the drying of a castable. Experiments on various types of castables have shown that the PLC during drying amounts to -0.2 to -0.5%, a significant shrinkage normally not accounted for.

RESULTS AND DISCUSSION:

Flow:

Table 2 shows the flow values for the three castable compositions obtained by the use of 13 volume% (4.5-4.6wt%) water. Generally, a free flow value of above 40-50 is enough for pumping, while higher values are necessary to make the castable self flowing. With some vibration however, a castable with a free flow of 50 is easily installed for almost any application. We see that both the forsterite composition and the magnesite composition give good free flow while the spinel composition is adequate, but somewhat lower. All vibra flow values are excellent.

Table 2: Flow of the magnesite bonded castables.

Castable:	Spinel	Forsterite	Magnesite
Free flow [%]	60	80	80

Cold strength:

The cold crushing strength (compressive strength) after drying and firing at 600 and 1000°C is shown in Figure 2. It is seen that the MgO-SiO₂-Al₂O₃ bond is capable of giving strengths well above 100 MPa, a strength that is maintained up to 600°C. A severe drop in strength at 1000°C has earlier been seen for castables with the MgO-SiO₂ bond⁵, here with fine alumina in the bond phase, this drop seems to be somewhat less severe. The actual reason for this lowering in CCS around 1000°C has not been understood, but crystallization of MgO-SiO₂ species may play a role.

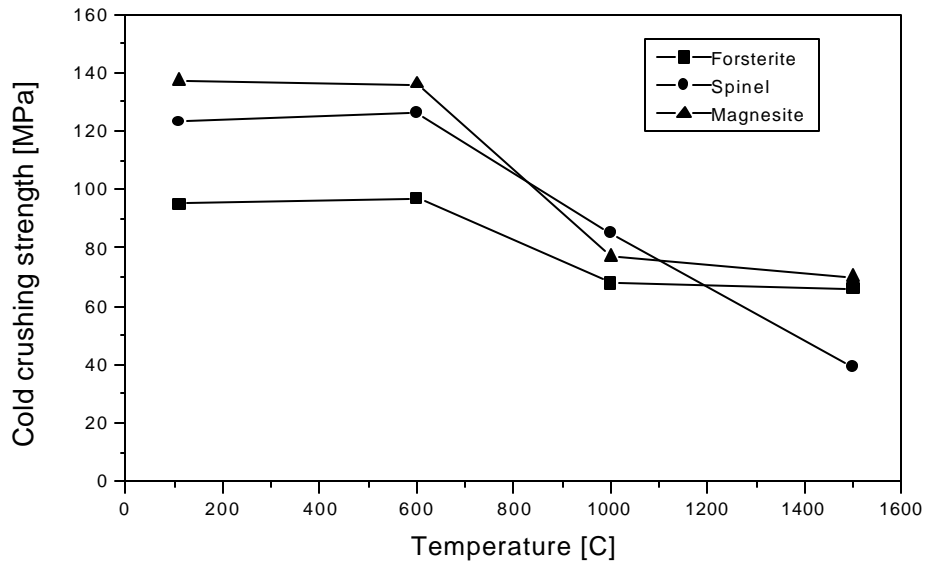


Figure 2: Cold crushing strength of the MgO-SiO₂-Al₂O₃ based castables as a function of firing temperature.

The cold M.O.R of the castables is shown in Figure 3. The drop in crushing strength around 1000°C is not present here, except for the magnesia castable. The results of the magnesia castables are in good correlation with earlier results, although the values here are somewhat lower. The present bond system is however slightly modified containing alumina.

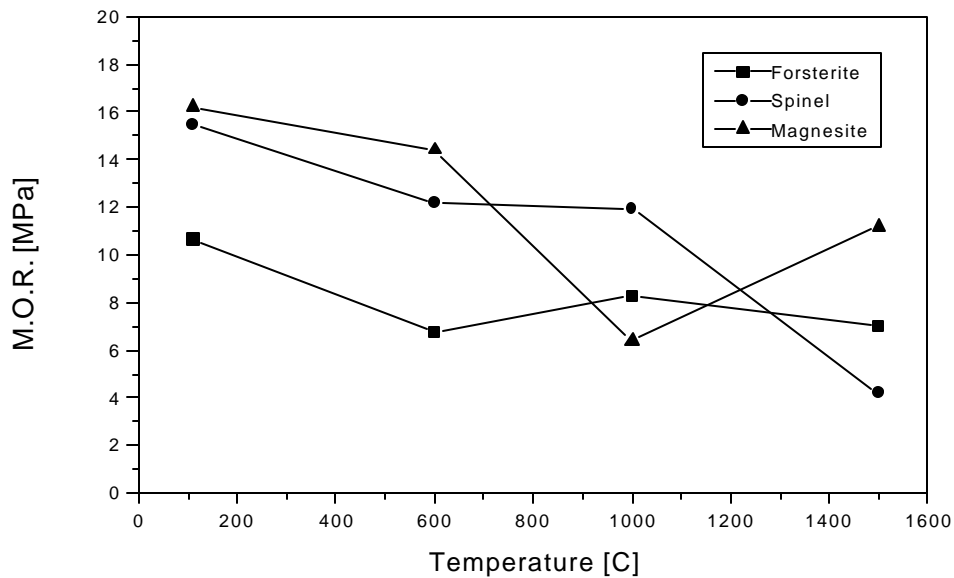


Figure 3: Cold Modulus of Rupture of the $\text{MgO-SiO}_2\text{-Al}_2\text{O}_3$ based castables as a function of firing temperature.

Hot strength:

In real life, it is the hot M.O.R. that matters, not the cold. Generally the hot M.O.R. values are similar, or slightly above the cold equivalents at temperatures up to approximately 1000°C . It is therefore generally accepted to use cold M.O.R. values as an approximation up to 1000°C instead of the often more elaborate hot-testing. Figure 4 shows the hot M.O.R. values of the castables at 1200 , 1300 , 1400 and 1500°C . All samples had 24 hours pre-firing at test temperature and the values are the mean of 2 parallels, the single results were normally within plus/minus 1 MPa of the mean. The increase in strength when the temperature is increased from 1200 to 1300°C for the magnesite castable, coincides with the increase for the forsterite castable, while the spinel castable decrease in strength. As all three castables have a common bond phase, i.e. the fraction below 100 micron, it is somewhat surprising to find these quite significant differences already at 1300°C . Obviously there is something about the spinel that is incompatible with the MgO-SiO_2 bond. It has earlier been demonstrated¹ that even a 0.2% silica addition to alumina-spinel castables could drastically reduce hot strength at 1500°C . That was however for alumina-rich castables and should therefore not necessarily apply to the magnesite rich compositions of the present investigation. At 1300°C the forsterite and the magnesite castable have similar strengths with the spinel castable being somewhat lower. At 1400°C however, the picture is changed, with the magnesite at a low level together with the spinel castable and the forsterite castable

maintaining its strength. At 1500°C the spinel castable and the magnesite castable have become so soft that the strength is barely measured, around 2-3MPa, while the forsterite castable still maintains its strength. As a matter of fact, the lowering in strength at 1500°C for the forsterite castable is so small that it could well be caused by common variation of the hot M.O.R. testing results. At 1500°C the spinel and magnesite samples showed soft, plastic fracture, the forsterite sample had brittle and transgranular fracture.

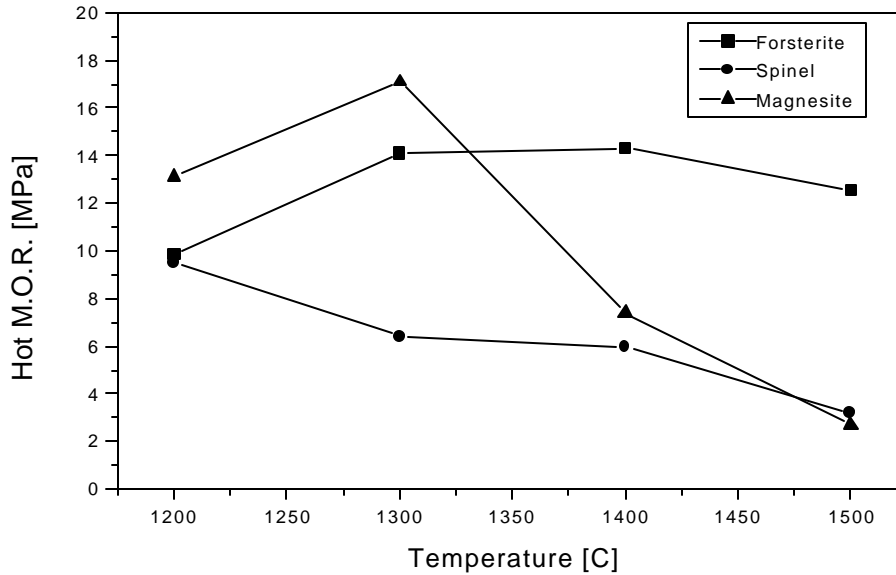


Figure 4: Hot Modulus of Rupture of prefired (24h) samples as a function of temperature.

The low strength combined with visual observation of the samples indicate that there is some sort of incompatibility between the bond phase and the spinel aggregate. So seems also to be the case with the magnesite composition. With olivine however, the castable is significantly strengthened. The reason may be connected to the transformation of olivine to forsterite upon firing. A simultaneous formation of forsterite both from olivine and in the bond phase assures a good bond between the aggregates and the bond phase. Furthermore as olivine is somewhat deficient in magnesia to give forsterite, reaction between the aggregates and the magnesia of the bond phase is likely to result in better bonding. With spinel or periclase, a reaction between the bond phase and aggregates is unlikely, resulting in lower strength because of poor bonding.

Permanent Linear Change:

Figure 5 shows the permanent linear change of the three castables as a function of temperature. Here, the reference state is “prisms as demoulded”, i.e. still “wet”, hence

the negative values at 110°C. The shrinkage during drying is between 0.2 and 0.3%, a value not uncommon for castables. Between 110 and 1000°C the dimensions are close to constant, while at 1500°C, differences are appearing. The forsterite castable shows a significant expansion, this may be connected to mineralogical changes of the olivine with formation of forsterite and iron containing species. The spinel castable also shows an expansion, the origin may be formation of spinel. The periclase castable however shrinks significantly. This excessive shrinkage may be caused by sintering aided by liquid formation, an assumption strengthened by the observed softness at 1500°C hot M.O.R. testing. The spinel sample is also soft at 1500°C. Excessive shrinkage seems however not to occur.

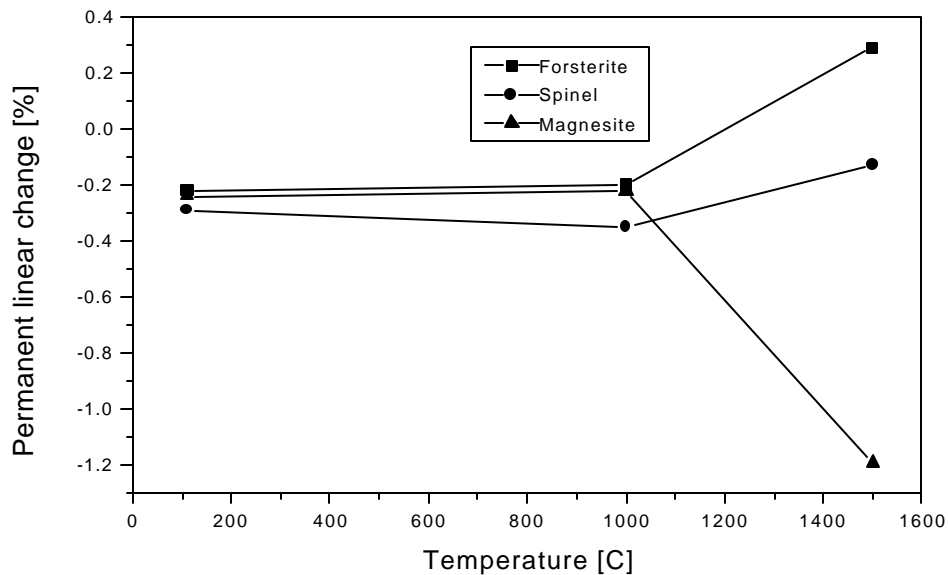


Figure 5: Permanent Linear Change of the MgO-SiO₂-Al₂O₃ based castables as a function of firing temperature.

CONCLUSION:

It is possible to make self flowing castables based on the MgO-SiO₂ bond with water additions as low as 13 volume%. This is comparable to what has been found in alumina based ultralow and low cement systems. Good flow is however dependent on the choice of both right quality of milled magnesia and the proper deflocculant at the right amount. With the present bond system containing some alumina, castable compositions with olivine, spinel and magnesia were prepared. These castable had good strength up to 1000°C where a drop in compressive strength was observed. The hot M.O.R.

results showed that the olivine based castable had superior strength at 1400 and 1500°C, possibly caused by enhanced bonding between bond phase and aggregates due to mineralogical transformations.

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