

SPINEL FORMING CASTABLES: PHYSICAL AND CHEMICAL MECHANISMS DURING DRYING

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ABSTRACT

Spinel and spinel-forming castables are more and more used or tested in ladle applications for the steel industry. Recent publications have shown that a finely dispersed spinel assures a very good slag resistance. This type of fine dispersion can be achieved with the spinel-forming technology. This technology, however, induces a more difficult control of placing properties as well as cracking during drying due to the use of MgO, which is very reactive with water.

Recent publications [1,5,6] have shown how good workability can be achieved for spinel and spinel-forming castables. Parameters such as silica fume, admixtures, quality and fineness of magnesia and their influence on flow decay and workability have been investigated and presented. Chemical and physical interactions between the individual castable components have been studied and discussed as well.

This paper presents results on the drying behavior of spinel forming castables. Different magnesias, admixture systems and the impact of silica fume have been studied. Upon drying MgO reacts to form brucite - a reaction with a volume expansion leading to cracks in the castable. This mechanism has been simulated in an autoclave test and monitored on castables subjected to a constant heating profile.

Results comparing the two tests are shown and discussed. Recommendations relative to raw material selection and formulation logic are presented in order to minimize cracking during drying.

1. INTRODUCTION

Castables used in steel ladles often contain Al₂O₃-MgO spinel in order to increase the chemical and physical resistance to liquid steel and slag. Two technologies can be distinguished to achieve these types of castables -the spinel addition through preformed Al-Mg spinel and the spinel formation through MgO addition [1].

In the spinel forming type of castable MgO reacts during heat-up with Al₂O₃ to form a finely dispersed spinel and the castable exhibits excellent performance with respect to slag corrosion resistance [2,3,4]. These castables are mostly based on calcium aluminate cement (CAC) with 70% alumina and contain fine reactive alumina and MgO. Due to the reactive nature of MgO a special attention has to be paid to master workability [5]. As for LCC technology two logics can be found - mastering placing

with a combination of several additives or the use of silica fume which allows, together with admixtures an enhanced flow as compared to the no-silica fume solution [6].

The second undesired phenomena encountered when MgO is included in a castable is its reactivity during heat-up of the castable. That phenomena, called slaking, can lead to cracking or even destruction of the material.

2. HEAT-UP AND DRY-OUT

During heat-up of the castables water vapor moves within the material and will eventually be driven out. Water exists either as physically or chemically bound water or excess free water needed to achieve suitable placing properties.

The removal of the water will create stresses within the pore system of a castable what as for very porous material can lead to cracking [7]. If high pressures due to high temperatures or fast heating are created even explosive spalling can be observed [8]. Additionally, the loss of chemically bound water, will de-integrate the hydrated phases which leads to an additional strength loss. For ordinary concrete the material will be destroyed or exhibit low strengths around 1000°C. In conventional refractory concrete a strength gain due to sintering of the anhydrous phases will follow the original loss and keep the material intact [9].

In Low Cement Castables (LCC) the intermediate strength loss does not even appear since very little water is used for placing and the chemically bound water is liberated over a wider temperature range allowing a more gentle dry-out [9,10], provided an adapted heat-up profile is used because a rapid heat-up can cause explosive spalling as mentioned earlier.

Water can, on the other hand, also react with constituents of the concrete. This is always encountered when autoclaving of concrete is applied. For a drying process, conditions similar to autoclaving will exist in the interior of the concrete for a certain time depending on the dry-out regime. For spinel forming castables it is the MgO which bears a high potential for this mechanism. MgO reacts with water to form brucite [Mg(OH)₂].

Kitamura [11] has studied this phenomena and explains the slaking phenomena by formation of brucite Mg(OH)₂ on the grain boundaries within a polycrystalline MgO particle. His

so-called dusting phenomena, is schematically shown in Figure 1.

In order to minimize this effect the following suggestions can be found in the literature:

- Quality of MgO: Few grain boundaries and impurities such as CaO, SiO₂, B₂O₃ seem to diminish the tendency to slaking [3, 12].
- Surface coating: A surface layer acting as a diffusion barrier is proposed as a method to reduce the negative effects of slaking.
- Additives: Silica fume or silica flour [5, 11] as well as aluminum lactate [12] have been proposed as additives reducing the slaking tendency of such castables.

It should not be neglected that the addition of impurities in form from SiO₂ or CaO can reduce the hot strength behavior.

Based upon the results previously published [13], two magnesia types were selected for further investigation along with two formulation logics. A seawater magnesia product (DBM2) was compared with the reactive lightly calcined magnesia with a high surface area (CCM). The objective was to assess the impact of the formulation type, along with magnesia type, upon the placing characteristics and the resistance to destructive cracking during dry-out. These two magnesia types had very fine particle size distributions with 100% passing 45 microns.

The two formulation logics chosen were an LCC castable without fume silica and an ULCC castable with a small fume silica addition. These model formulations are shown in Table 1. As for each formulation type and magnesia, the additive system was optimized to yield satisfactory placing properties.

In the case of the reactive calcined magnesia a more complicated additive package was needed to compensate for the inherent greater reactivity of this high surface area magnesia. The additive systems used are detailed in Table 2.

Additive System 1 was used for the high purity dead burnt magnesia (DBM 2) and additive System 2 for the reactive calcined magnesia. As shown in Table 2 the dispersing additive basis was kept constant for each magnesia type. Changes were made to the retarding system. The placing properties were determined by targeting an initial vibration flow value of 200 +/- 20 mm and the required water demand measured along with the castable working time. Subsequently test pieces

were prepared for physical property and autoclave testing.

For some autoclave tests samples were prepared representing the binder phase (<80mm) of the castables shown in Table 1.

3. TESTING

A method to evaluate the slaking resistance of the MgO was developed based on previously reported tests [2]. A series of sealed steel 'bombs' with removable lids were produced into which cylindrical test pieces (30 cm³) were introduced. Inside each container a quantity of distilled water was also placed. These bombs were then sealed and placed in a dryer at varying temperatures (max 170°C) for varying periods up to 72 hours. The water pressure generated inside these bombs was proportional to the temperature and calculated pressures of 3, 5 and 8 bars were used.

After testing the samples were withdrawn and several types of evaluation performed. The presence of brucite [Mg(OH)₂] was established by X-ray diffraction and integration of peak heights yielded a ratio of brucite peak height to alumina for each test.

This showed clearly the increasing amount of brucite as a function of exposure time. It was also evident that very small quantities (0.5%) of magnesia were sufficient to provoke destruction of the castable. Polished sections showed clearly the cracks radiating from individual magnesia grains, which had reacted on the surface to form brucite.

However this method was not able to differentiate between samples which had cracked and those that were still sound. Samples were also evaluated by ultra-sonic before and after the test. This showed clearly the change in structure linked to the formation of cracks. Typically ultrasonic velocity decreased from around 3800 m/s to 2300 m/s when cracking occurred. It appeared as if there was a certain threshold value for magnesia above which hydration and brucite formation would always be seen.

The third and simplest form of assessment was a visual inspection for cracks and this was the method retained. The previous method of assessment has shown that the destruction of the castable occurred abruptly and therefore the most useful assessment criteria were simply sound or unsound after test. A series of five gradings as shown in Table 3, from no change to complete destruction, were used to assess each sample.

The castables themselves were evaluated by measuring the following physical properties:

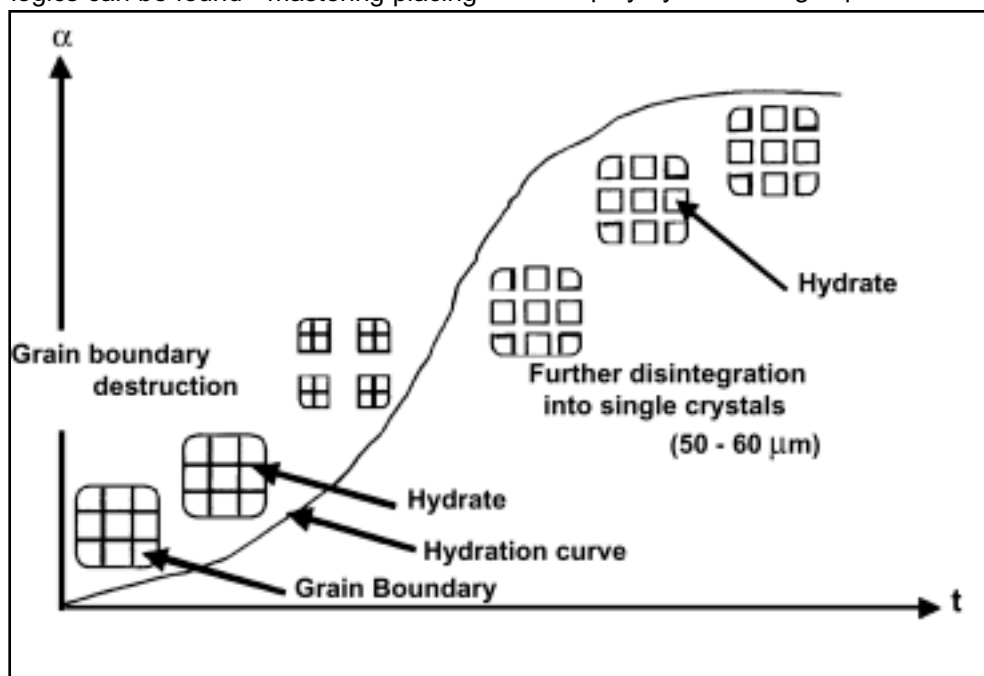


Figure 1. Hydration model of MgO-Polycrystals according to Kitamura

Table 1 Model castable compositions

COMPOSITION	LCC	ULCC
Tabular Alumina		
1/4-8 mesh	20	20
8-14 mesh	25	25
14-28 mesh	10	10
<48 mesh	12	12
<100 mesh	10	10
<325 mesh	4	5
Alumina P152SB	8	8
Fume Silica :971 U	-	2
Magnesia 100% <45	5	5
Cement : Secar 71	6	3

Table 2. Additive systems

% ADDITION TO DRY CASTABLE MASS	ADDITIVE SYSTEM 1	ADDITIVE SYSTEM 2
Darvan 7S	0.05	0.25
Citric Acid	0.003	0.03
Sodium Citrate	-	0.01
Sodium Carbonate	0.002	0.01

Table 3. Resistance ratings in autoclave test

STATE OF SAMPLE	RATING
No changes visible	5
Some cracks	4
Cracks become grooves	3
Sample in several pieces	2
Total destruction	1

- Water demand
- Initial flow and flow decay
- Working time
- Cold crushing strengths at 24 hours; after 110, 400, 800,1100 and 1500°C
- Permanent linear change after 800, 1100 and 1500°C

4. RESULTS

Autoclave tests

For all test conditions what exposure time and different temperatures are concerned the high surface area MgO (CCM) did not cause any destruction of the test samples in the autoclave. All samples regardless of type of formulation used stayed intact. As mentioned in an earlier report it is suspected that this type of MgO is protected by a surface coating. Additionally a high fineness allowing a homogeneous distribution of the material within the matrix of the castable will certainly reduce stresses induced through dimensional changes of the particles.

The resistance of the DBM2 magnesia is shown in Figure 2 for different temperatures and times of exposure. In general DBM2 is more sensitive to slaking. At lower temperatures of 132°C and a five hours testing samples stay intact where an increase to 170°C or a prolongation to 24 hours testing will lead to a destruction of the sample. A slight improvement can be seen for the ULCC formulation where silica fume is added to the formulation. It has been reported that silica fume not only improves placing but also can reduce the slaking tendency.

The flow decay curves are given for the two magnesias in the two castables in Figure 3. Additionally the water demand is indicated in the diagram.

The ULCC castable with silica fume addition shows an excellent flow behavior with very little flow decay when used with the DBM2 magnesia. The same magnesia gives a very good performance in the LCC castable without silica

fume. The water demand is slightly higher. This shows again for the spinel forming type castable the beneficial influence of silica fume on flow behavior.

The more important parameter is however the type of magnesia. CCM exhibits, despite a much higher water addition, a very poor flow behavior with working times lower than for the DBM2 magnesia. It should also be kept in mind that a more complicated, 4 component admixture combinations had to be used to control placing properties of this reactive, calcined MgO.

Flexural and compressive strengths after heating showed the same trends. In Figure 4 the cold crushing strengths are shown.

The CCM shows the highest early strengths. The strength minimum occurs rather around 1100°C as compared to DBM2 at 400-800°C. The ULCC castable with silica fume shows very high strengths after 1500°C. Due to melting of gehlenite, an effect can be observed with all silica fume containing castables.

The higher reactivity of the CCM magnesia leads also to an earlier spinel formation as seen with the X-ray diagrams. This is supported by the PLC values especially at 1100°C as shown in Figure 5. At 1500°C the PLC values of the ULCC castables are more influenced by the presence of silica fume but DBM2 seems to have caught up with CCM what the spinel formation is concerned.

In none of the fired castables - contrary to autoclaved samples - could brucite be detected.

5. CONCLUSIONS

The choice of magnesia will very strongly influence the mix design and subsequent performance of a spinel forming castable.

A finely dispersed calcined MgO with a high surface area is very reactive which induces problems with placing

even when used with sophisticated admixtures.

On the other hand, it allows for good early strength and a fast spinel formation, which seems to occur at lower temperatures.

The tested reactive MgO showed also an excellent resistance to slaking. This could be due to a surface treatment and/or very finely distributed particles.

Dead burned MgO is less reactive and can very easily achieve excellent placing characteristics combined with a low water demand.

Spinel formation occurs at slightly higher temperatures.

The tested MgO showed a higher sensitivity to slaking. The employed castable, however, did not show a distinct damage due to slaking.

Silica fume definitively helps improve placing properties and can reduce the effects of slaking. It limits, however, the maximum usage temperature due to the low melting phases.

Further studies are planned with respect to modeling moisture transfer upon heating and its possible impact on slaking.

6. REFERENCES

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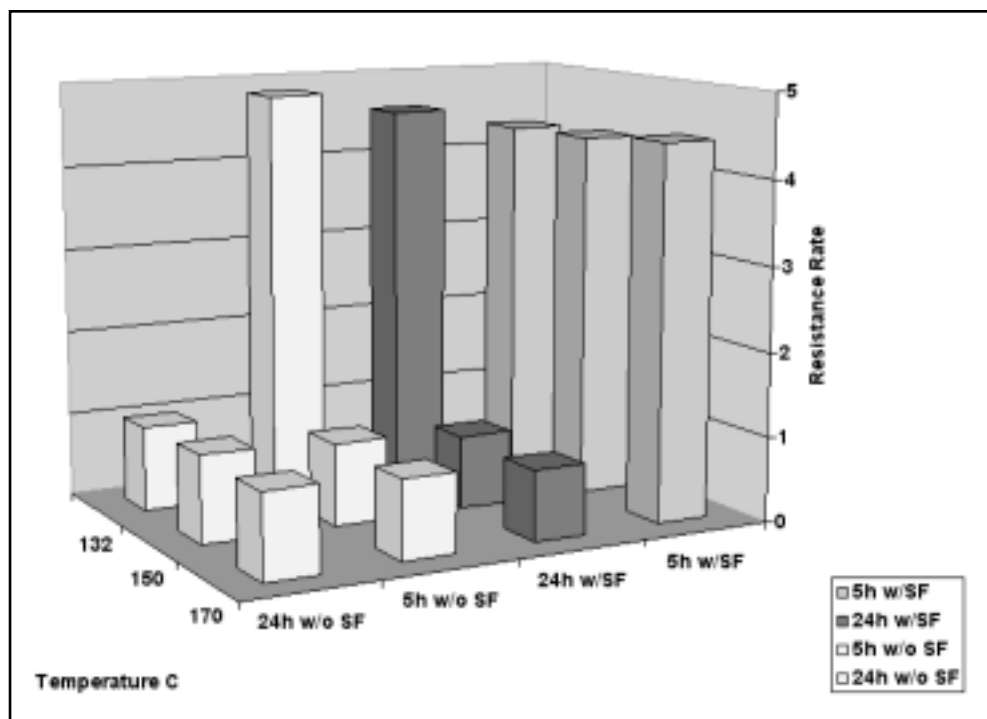


Figure 2. Performance of formulations with DBM2 in the autoclave test

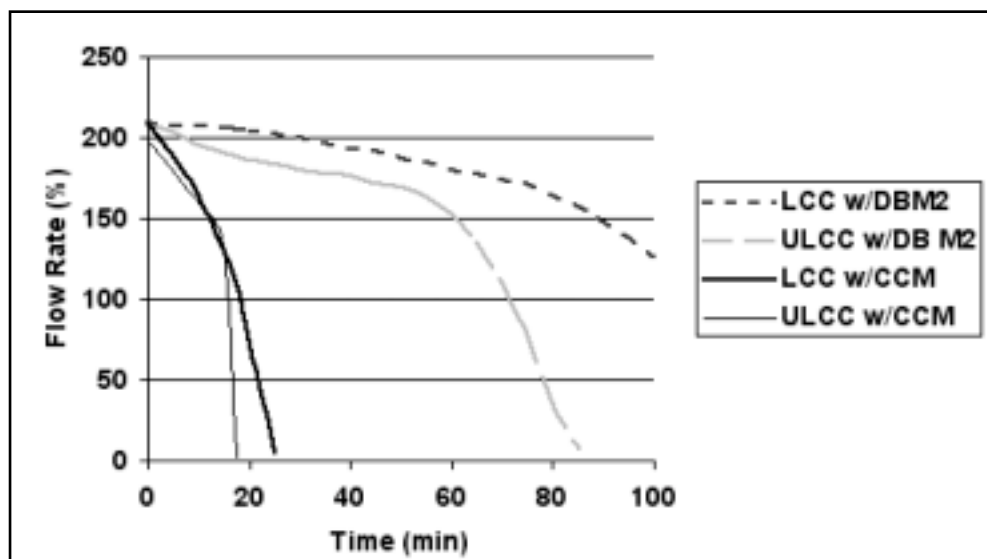


Figure 3. Flow decay curves of the different castables investigated

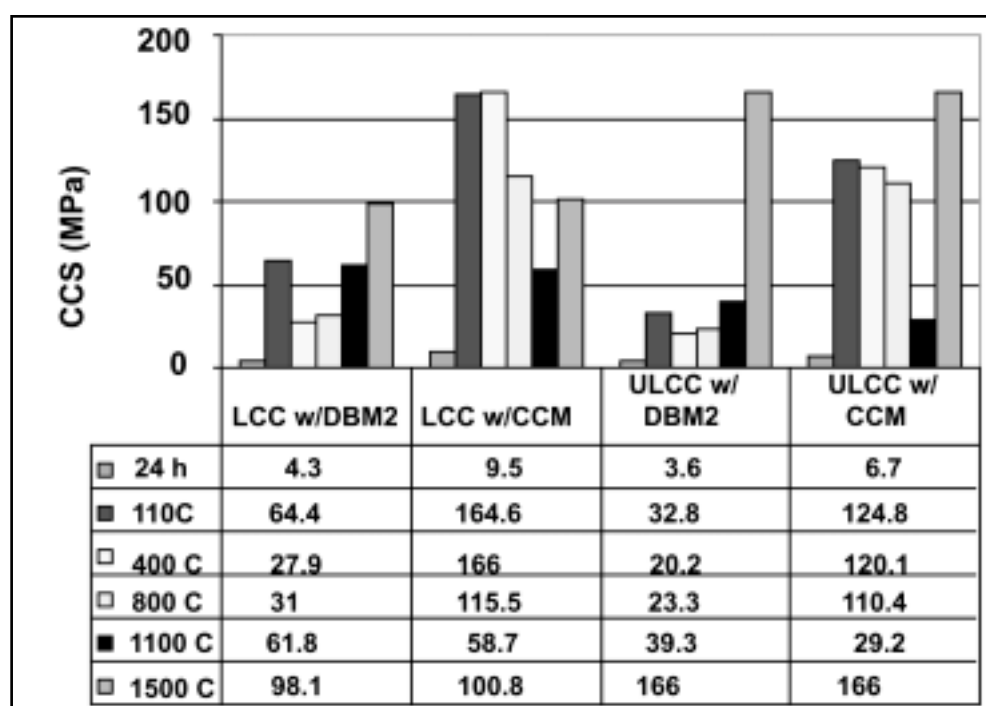


Figure 4. Cold crushing strengths in MPa for the castables after different temperatures

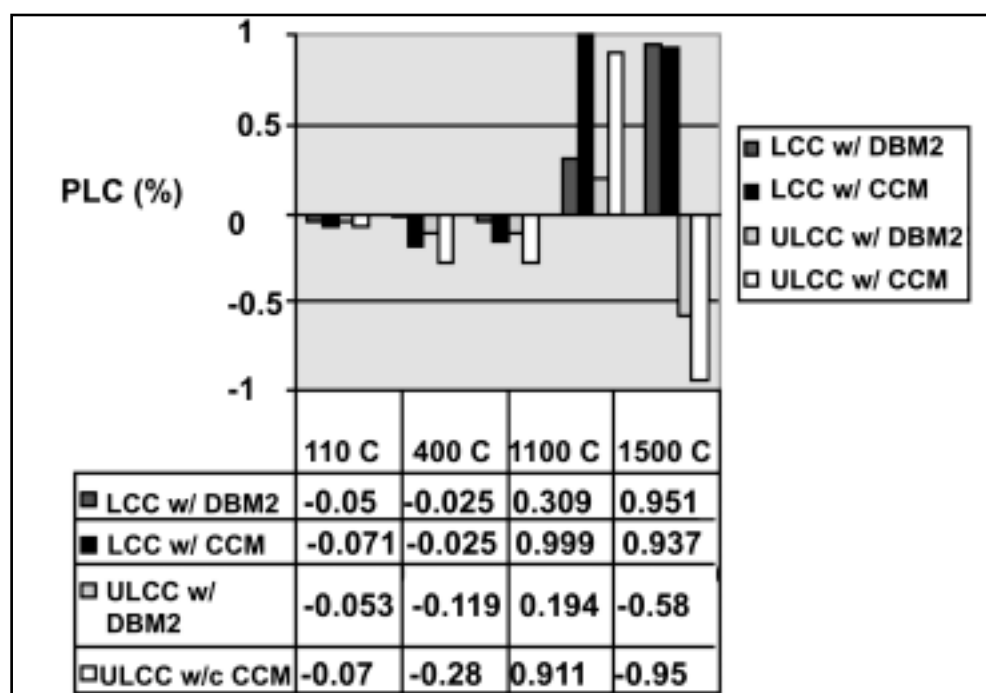


Figure 5. Permanent linear change after heating to different temperatures