Reasons for crack propagation and strength loss in refractory castables based on changes in their chemical compositions and micromorphologies with heating: special focus on the large blocks

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ABSTRACT

Among the most significant problems in industrial refractory manufacture, especially of monolithic refractories, are the formation of cracks and loss of strength in green bodies or during heating of the refractory castables. These issues could be due to changes in their chemical compositions and micromorphologies with heating. This paper reviews the problems due to the addition of each raw material to a batch of refractory castables after curing and drying at 110°C as well as due to the firing of castables containing these materials. In the final section, suggestions are made for the production of large, heavy-weight blocks (e.g. electric arc furnace roofs) without the presence of calcium aluminate cement (noncement electric arc furnace roofs) to prevent cracking in large blocks.

1. Introduction

The mechanical strength and elastic modulus values of refractory samples (especially in monolithic refractories) throughout the curing, drying, and firing processes were strongly affected by the type as well as the amount of binders used. On the other hand, the total concrete or bulk elasticity depends on the elasticity modulus of both the aggregate (100–5000 μm) and matrix (<100 μm) and their relative mass values. All refractory components of a size less than 100 μm are known as matrices (i.e. fine alumina, reactive alumina, hydratable alumina, calcium aluminate cement, silica fume and colloidal suspensions, etc.). Therefore, when cement is used in a refractory castable’s matrix, the amount of cement as well as the content of Al₂O₃ in the cement will strongly affect the castable elasticity [1–10].

In all concretes and even refractory materials, moreover, the numerous defects in their structures (e.g. microcracks, pores, flaws, grain boundaries, and impurities), as well as the growth of these defects in the concrete structure usually lead to failure stresses and sometimes cause strength loss. Thus, when such refractory concretes are subjected to a mechanical load, thermal shock (sudden temperature change), corrosion, wear, abrasion, slag, or molten metal, these defects grow to reach critical levels and ultimately cause breakage in the body [7,11,12]. Monolithic refractories, on the other hand, are known as homogeneous isotropic materials containing randomly oriented micro-cracks which are uniformly distributed. According to the Hasselman theory, the number of cracks and their interaction in the microstructure, orientation, use of aggregates of different natures and fracture energy all play important roles in defining the influence of micro-cracks on the mechanical properties [7,13].

2. Cracks and/or strength loss in green bodies (during the curing and/or drying processes)

2.1. Binders

2.1.1. Hydraulic binder

Calcium aluminate cement and hydratable alumina are widely used in the formulation of monolithic refractories due to their promotion of initial hardening of the refractory components as well as to the green strength of the precast components (after demolding). Both these binders’ setting mechanisms are based on hydration reactions [3,6].

2.1.1.1. Calcium aluminate cement. Although the presence of calcium aluminate cement (CAC) in refractory castables results in desirable green strength, temperature variations strongly affect CAC-containing castables. At different temperatures, moreover, phases with particular characteristics, including density, strength, and crystal structure, that affect the concrete properties are created. These events are shown in Table 1 for a tabular alumina-based castable (with 20% CAC) throughout the curing, drying, and heating processes [7,14].

Drying helps transform CAH₁₀ (Ca₀Al₂O₃·10H₂O) with a hexagonal prismatic structure to C₂AH₈ (2Ca₀Al₂O₃·8H₂O) with a hexagonal plate structure, for example, and eventually turns it into C₂AH₆,
Table 1. Phases of high alumina castable production at different temperatures [14].

| Temperature, °C | Tabular alumina + 20% CAC-25 24 h cure/90% humidity |
|----------------|--------------------------------------------------------|
| 0–20           | AH₃ gel, CAH₁₅ CA (unhydrated)                         |
| 20–40          | AH₃, C₂AH₆, CAH₆ (X = 8–12) C₆AH₆                   |
| 40–60          | AH₃, C₂AH₆, CAH₆ (X = 8–12) C₆AH₆                   |
| 60–100         | AH₃, C₂AH₆, CAH₆ (X = 8–12) C₆AH₆                   |
| 100–350        | AH₃, C₂AH₆, CAH₆ (X = 8–12) C₆AH₆                   |
| 600–1300       | A, Ca, Ca₂, Ca₃                                      |
| 1400–1650      | Ca₄                                           |

(3CaO·Al₂O₃·6H₂O) spherical or cubic crystals. There are two primary problems that arise from this massive transition: (1) spalling highly likely to occur during the drying and heating period, and (2) this is accompanied by a loss of strength due to a reduction of the special surface as well as to the formation of voids around the large cubic crystals [14].

Thus, as stated above, one of the most important concerns for CAC-containing castables throughout the curing, drying, and heating stages is explosive spalling and strength loss as the heat rises. These kinds of castables are extremely sensitive to curing and heating conditions, which must be carefully controlled. These drawbacks can be reduced by reducing the cement content. For this reason, low cement castables (LCC) and ultra-low cement castables (ULCC) are used instead of regular cement castables (RCC), and, recently, more research has been conducted on non-cement castables (NCC). When it is necessary to use cement in a castable, the quality of the cement used must be considered as well, because this is another important factor in determining the strength of cement-containing castables on castables [3,4,15–17].

2.1.1.2. Hydratable alumina. Another hydraulic binder system which has attracted great attention for noncement castables is hydratable alumina (HA) with a large surface area (>150 m²/g). In contact with water or water vapor, this binder partially dissolves and rapidly generates a pseudo-boehmite or boehmite gel. This gel reduces the porosity of the structure and, after a short period of time and at above 20°C, converts it to crystalline bayerite (Al(OH)₃), which causes the particles to bond and increases the green mechanical strength. It should be noted that crystalline bayerite formation strongly depends on the hydration temperature, the time subjected to that temperature and the pH [3,4,18,19].

Although HA can be used as an optional binder in noncement castables, some drawbacks such as the need for longer mixing times until wet-out is achieved, as well as the risk of adding more water to the mix than recommended or risk due to the high specific surface area, can make it difficult to use. In addition, many researchers have reported that after HA comes into contact with water, a gel layer is formed on the surface of the HA particles, which results in a much less permeable structure, and the low permeability of the samples restricts the evaporation process and leads to a higher likelihood of explosive spalling during drying and initial heat-up [4,18–23].

Another problem with HA-containing castables is that the removal of free water shifts to higher temperatures during their gel-like phase. Hence, when this type of castable is compared with CAC-containing castables treated in a constant-temperature drying procedure, the sample containing HA loses its physically absorbed water over a longer period of time and does not easily permit the release of chemically bonded water at elevated temperatures. On an industrial scale, moreover, hydration of these castables continues not only during the curing process at room temperature but also during the drying and heat-up, and small amounts of water vapor may sometimes still remain in the castable at 650°C, a situation which requires more attention to prevent explosive spalling in precast blocks [14,18,19,24].

However, there are considerable differences between castables containing CAC and HA. Although CAC-containing castables offer better mechanical strength and thermal shock resistance, HA-containing castables provide lower apparent porosity, better volumetric stability, and improved high-temperature properties such as higher creep resistance. In addition, HA-containing castables do not need to be in humid environments to develop strength [1,14,18]. The use of a mixture of CAC and HA, does not seem to be a proper solution for improving the properties of the castable. A study by Braulio et al. [1] showed that when a mixture of these two binders is used, lower levels of mechanical strength are observed. The authors attributed the low strength of these castables to a high level of apparent porosity after 1 day of drying at 110°C (Figure 1).

2.1.2. Colloidal binder

The disadvantages of CaO in cement at high temperatures have led many researchers to consider replacing

![Figure 1](image-url)
this binder with various CaO-free binders. In addition to HA, CaO-free binders that are attracting greater attention include colloidal binders, such as colloidal silica (CS), colloidal alumina (CA), and colloidal spinel. Compared to CAC, a colloidal binder (sol), when used in a castable, causes it to dry easily and reduces the likelihood of cracking and explosive spalling because of its highly permeable structure. Use of this binder also reduces the processing time due to its low mixing time, high permeability and high drying rate [4,8,23,25].

However, the most significant thing about colloidal binders is the low green mechanical strength of the refractory castables containing them. The low mechanical strength of these castables may cause severe damage during demolding and transportation, thereby narrowing the range of applications of these binders. The mechanical strength of colloidal binder castables depends on the formation of a three-dimensional network of sol, which can be referred to as gelling and coagulation setting mechanisms. As shown in Figure 2 (which is for CS), the gelling process occurs when silanol groups are replaced by siloxane groups according to Equation (1). As regards the coagulation mechanism, an additive (usually comprising electrolytes) bridges the particles to form close-packed clumps. Both mechanisms are affected by the pH change, particle size and concentration of particles in sol (silica, alumina, spinel, etc.), the presence of electrolytes and organic liquids, and the temperature [4,15,23–26].

\[
-SiOH + HOSi- \rightarrow -SiOSi - + H_2O \quad (1)
\]

After sintering at higher temperatures (>1000°C), however, the conditions change and castables containing sol acquire greater mechanical strength than castables containing a hydraulic binder (Figure 3); the green strength has great importance in large blocks (e.g. electric arc furnace roofs). For this reason, many scientists are investigating ways of increasing the green strength of castables containing colloidal binders. One of the factors that can affect the strength of
castables containing colloidal binders is the amount of solid contents available in the sol or in the composition as well as the average particle size of the sol. It is recommended that a colloidal binder with an average particle size smaller than 14 nm and a high solid content should not be used in a castable, because these factors cause drying shrinking and may lead to internal stresses and crack formation [15,20,23–25].

One of the key factors for improving the green strength of castables containing a colloidal binder are setting agents, the most important of which are oxides (MgO and CaO), hydroxides (Mg(OH)$_2$ and Ca(OH)$_2$), and salts (MgCl$_2$, MgSO$_4$, CaCl$_2$ and CaSO$_4$). Among these setting agents, sintered MgO is one of the most commonly used alternatives. By forming of Mg(OH)$_2$ and removing hydrogen ions from Si-OH groups, MgO enhances siloxane bond formation and ultimately increases the gelation rate. But the problem arises that the impact of MgO on the castable setting occurs so rapidly that it reduces the proper working time and decreases the flowability, thereby actually creating more hassles [4,15,23,26].

Other methods proposed to improve the green strength of castables containing colloidal binders include the use of phosphates and sol freezing. But since it still remains a challenge to find a setting agent for increasing the green strength of castables containing colloidal binders, Peng and Myhre have recently suggested the use of microsilica-gel binders instead. According to their research, microsilica-gel improves the green strength of large pieces and facilitates easier handling of non-cement refractory castables [15,23,27–29].

### 2.1.3. Monoaluminium phosphate

As previously stated, phosphates can be used to increase the green strength of refractory castables. Among the numerous commercially available aluminium-based phosphate compounds, monoaluminum phosphate (MAP) is known to be the most common chemical binder in the refractory field. This is due to its desirable characteristics, including its solubility in water, high bonding strength and ability to react with basic and amphoteric raw materials at low temperatures. It should be noted, however, that the ambient temperature does not usually help to accelerate their hardening of high alumina refractories, so the addition of setting agents such as MgO and CaO should be taken into account. These additives lead to the formation of amorphous or crystalline phosphates and ultimately affect the hardening of the refractories. Although phosphate compounds are very popular due to their good adhesion and reduced risk of cracking under high heating rates after curing, little information is available on the setting mechanisms of these materials or their chemical reactions during installation and drying [5,15].

### 2.2. Magnesium oxide containing castables

Magnesium oxide or magnesia (MgO) is known as one of the most important raw materials used in the refractory industry. The presence of this oxide in refractory compositions is recommended due to its refractoriness, high corrosion resistance, and desirable spinel phase properties when reacted with alumina. When it comes into contact with water or water vapor, however, this raw material forms the following hydration products:

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \quad (2)
\]

\[
\text{Mg(OH)}_2 + \text{CO}_2 \rightarrow \text{MgO} + \text{H}_2\text{CO}_3 \quad (3)
\]

\[
\text{MgO} + \text{H}_2\text{CO}_3 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O(g)} \quad (4)
\]

The magnesium hydroxide or brucite (Mg(OH)$_2$) resulting from Equation (2) is formed when there is an abundance of water in the composition. The formation of brucite causes a significant increase in pH, which allows dissolution of CO$_2$ in water and formation of carbonic acid (H$_2$CO$_3$) (Equation (3)). According to Equation (4), this acid reacts with magnesia to form magnesium carbonate or magnesite (MgCO$_3$). In both cases (formation of brucite or magnesite), a significant increase in volumetric expansion (2.5-fold) is observed after completion of the reaction. The volumetric variations due to the formation of brucite affect the refractory structure and its properties and cause the formation of microcracks. Many researchers have investigated the hydration mechanism using a single of magnesia crystal for this purpose, while the magnesium grains used as refractory raw materials are polycrystalline and can generally be described as several single crystals bonded together. The boundaries between magnesium grains have a higher probability of reaction to water due to their higher free energy. In polycrystalline particles,
It should be noted in connection with mechanical strength that, as reported by some authors [34–37], castables containing finer magnesia (<45 μm) present better performance for all evaluated temperatures, than those containing coarser magnesia (<100 μm). Many refractory producers consider it as a major challenge to add fine magnesia particles to castables due to the major drawbacks related to the hydration of this component. As brucite formation is followed by an expressive volumetric expansion (which is linked to the difference in densities between magnesia (ρ = 3.58 g/cm³) and brucite (ρ = 2.34 g/cm³)) that usually results in crack generation as well as damage to the refractory structure during the curing or drying processes. Table 2 shows the formation of brucite at various temperatures in the presence of plain water and other hydrating solutions; a marked increase can be seen at temperatures ranging from 60 to 80°C.

Use of a magnesia anti-hydration technique (MAHT) could eliminate the drawbacks of magnesia and take advantage of the benefits of this suitable additive. Various methods can be considered for controlling magnesia hydration in refractory castables, the most important of which are as follows: (1) the magnesia source (i.e. particle size, specific surface area, purity, CaO/SiO₂ ratio, production route, magnesite calcination temperature, etc.); (2) the pH and temperature of the liquid medium; and (3) the interaction of magnesia with other castables’ raw materials (such as silica fume, CAC, or HA) as well as the use of various other additives [3,36].

2.2.1. Effect of the presence of silica fume on castables containing magnesium oxide
Among the best-described MAHT, microsilica (silica fume) is an especially good choice because it prevents cracking or strength loss by magnesia-containing castables after curing or drying. Additionally, this additive is the most popular due to its low cost and binder content control characteristics [3,36].

Silica fume is an amorphous submicron-sized form of SiO₂ that is added to castable formulations due to the ball-bearing effect associated with its spherical shape, which can improve the packing of particles as well as the flowability. Besides, when castables with these kinds of SiO₂ sources (amorphous and highly reactive) added are exposed to high alkaline environments (pH = 10–12), typical levels for MgO and CAC-

![Figure 4.](image)

Figure 4. Hydration mechanisms of (a) magnesia monocrystal and (b) polycrystalline magnesia [30].

Table 2. Weight percentage of the formed Mg(OH)₂ as a function of temperature for the hydration of a calcined magnesia source (5.0 m²/g) in water or hydrating solution (0.1 mol/L) for 30 min [34].

| Hydrating Agent | 30°C | 40°C | 50°C | 60°C | 70°C | 80°C |
|-----------------|------|------|------|------|------|------|
| Mg(CH₃COO)₂·4H₂O | 2.1  | 2.9  | 5.8  | 9.5  | 23.9 | 56.7 |
| CH₃COOH         | 2.6  | 3.2  | 5.3  | 9.6  | 17.6 | 44.5 |
| H₂O             | 2.1  | 2.7  | 5.5  | 7.5  | 12.9 | 16.1 |
containing castables), they partially dissolve to cause the formation of silicic acid. This acid has the ability to stick to the alkaline brucite layer (coating the magnesia particle surfaces) and to increase the magnesium–silicate–hydrated layer (MgHSiO₄), which is slightly soluble in water and in an alkaline environment. It also shows hydrophobic behavior that prevents magnesia hydration (Figure 5). Moreover, the combination of silicic acid with brucite leads to the formation of Mg₃Si₄O₁₀(OH)₂, a talc-like compound (Equation (5)). This compound is a gel phase that forms on the surface of magnesia particles and prevents the occurrence of excessive magnesia hydration. This is the reason that silica fume is well-known for its anti-hydration effect, but alumina additives exhibit inertness during the hydration process:

\[
\text{Mg(OH)}_2 + 4\text{H}_2\text{SiO}_4 \rightarrow \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 10\text{H}_2\text{O}
\]  

Equation (5)

It is also reported that a combination of silico-phosphates (rich in SiO₂ and presenting higher reactivity and solubility) can also be used as appropriate options for the rapid formation of M–S–H gel on the surface of magnesia particles, while also preventing the formation of brucite. This ultimately leads to the formation of castables with high flowability, high mechanical strength, and high elastic modulus values [3,31,32,36].

2.2.2. Effect of the presence of calcium aluminate cement on castables containing magnesium oxide

Saloma'o and Pandolfelli [3] have reported that the use of CAC in castables containing magnesia is not a suitable way to diminish the deleterious impacts of magnesia hydration. When CAC is used in magnesia-containing castables during the hydration of CAC, however, it greatly increases the castables’ pH (Equations (6) and (7)) due to release of OH⁻ in water. On the other hand, the presence of OH⁻ ions favors magnesia hydration (Equation (8)):

\[
\text{Ca(AlO}_2)_2 + 4\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{Al(OH)}_4^- \]  

Equation (6)

\[
\text{Al(OH)}_4^- \rightarrow \text{Al}^{3+} + 4\text{OH}^- \]  

Equation (7)

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{MgOH}^+ + \text{OH}^- \rightarrow \text{Mg(OH)}_2
\]  

Equation (8)

The authors state that the greater the amount of CAC in magnesia-containing castables, the further the pH of the suspension increases, which produces larger amounts of brucite. This greater production of brucite causes further apparent volumetric expansion, micro-cracks, and strength loss by the castables. In addition, the presence of larger amounts of CAC creates low refactoriness phases (such as 12CaO.7Al₂O₃), which should be considered in the design of the castable.

2.2.3. Effect of hydratable alumina addition on castables containing magnesium oxide

Using HA in addition to fine magnesia is an excellent alternative for the production of high-strength green castables. It is possible, moreover, to form structures with fine spinels after thermal treatment. These fine spinels lead to the formation of protective layers on the surfaces of refractory particles in this phase and protect them against corrosion when in contact with molten metal or slag. As seen in Figure 6, a different drying behavior is observed in magnesia castables, which are also HA. Comparison with a reference sample (magnesia-free sample) shows that no significant magnesia hydration occurs, moreover, due to the presence of HA in a castable (Figure 6-b). As shown in Figure 7, the high strength of castables containing HA has two explanations reasons: (1) adding HA does not cause changes in castables’ pH (while the CAC does change) and, in fact, the magnesia hydration does not increase; and (2) the combination of magnesia and HA leads to the formation of hydrotalcite (HDT), which belongs to a class of clay-like synthetic minerals (Mg₉Al₃(OH)₁₆(CO₃·4H₂O)). HDT is usually formed on the surface of magnesia particles where due to its low solubility in an alkaline medium and hydrogen bonding, it forms a protective coating on the surfaces of the magnesia particles which prevents hydration reactions while enhancing the bonding of the castables’ matrix particles and increasing their mechanical strength. Since these castables do not have a calcium binder in their chemical composition, compounds with low melting points are not produced and the castables’ refactoriness is increased [3,19,22]. A study by Ye and Troczynski [19] investigated the effects of HA on various types of magnesia, dead-burnt or fused magnesite and magnesium aluminate spinel aggregates. The authors finally concluded that, after drying at 110°C and firing at 816°C, the castables with HA as a binder and with dead-burnt or fused magnesite as the aggregate had higher strength than HA-bonded castables with magnesium aluminate spinel as the aggregate. This could be attributed to the hydration reaction between HA and dead-burnt or fused magnesite.

Figure 5. Sketch of silica’s antihydration mechanism for magnesia [36].
2.2.4. Effect of monoaluminum phosphate addition on castables containing magnesium oxide

The reaction of acid salts (liquid or solid) or phosphoric acid (H₃PO₄) solutions with basic or amphoteric oxides such as magnesia and alumina in refractories causes phosphate bonding. These products present desirable properties, such as high mechanical strength, good adhesion, and reduced risk of cracking under high heating rates. It should be noted that the concentration of phosphoric acid or phosphate compound, as well as the reactivity and solubility of the setting agents during the production process, must be controlled to achieve good bonding between particles. Phosphoric acid and/or monoaluminum phosphate (MAP) act as good binder sources for castables that facilitate connection between particles by the reaction of H₃PO₄ and Al(OH)₃ in the range of 25–90°C (Equation (9)) [5,38].

\[
3H₃PO₄ + Al(OH)₃ \rightarrow Al(H₂PO₄)₃ + 3H₂O \tag{9}
\]

2.2.5. Other efforts on castables containing magnesium oxide

In recent years, methods other than preventing the formation of brucite (causing microcracks) have been discussed, such as accelerating the formation of brucite and/or changing the morphology of brucite. The hydration agents that can be used include acetic acid, nitric acid, magnesium chloride, sodium acetate, ammonium chloride, magnesium acetate, and magnesium nitrate [33,34,39].

In an investigation, Souza et al. [34] used acetic acid (AA) as an agent favoring dead-burnt magnesia hydration to prevent the hydration form does not causing crack generation and damage to the refractory structure during the curing or drying processes. Acetic acid has the ability to react with magnesia to increase the speed of brucite formation and achieve greater homogeneity. It can be seen from Figure 8 that when acetic acid is not used, the elastic modulus decays as time passes. In fact, the formation of the brucite phase in the castables causes cracks, and these cause a decline in the elastic modulus. Adding 0.1 wt% AA, however, increases the elastic modulus.

2.3. Particle size distribution

Another important factor affecting the properties of castables (especially their strength) is particle size distribution (PSD), which has received inadequate attention in the literature. Generally, according to the Andreasen equation, higher strength is related to lower q-values (Equation (10)), where CPFT is cumulative percentage finer than, d is particle size, Dₘₚₙₙ is largest particle size (5000 µm), and q is the distribution modulus. Although the strength decreases with increases in the q-values, this strength loss is not solely due to the PSD, but also to the absence of flow when preparing castables [17,40].

\[
CPFT = \left(\frac{d}{D_{\text{max}}}\right)^q \times 100 \tag{10}
\]

The distribution of fine particle sizes is also important. The addition of particles in the ultrafine (sub-micron) and fine (a few microns) ranges helps to increase the castable packing, and the resulting compactness reduces the amount of cement and water required. Ultimately, the lower amount of water added to the castable helps to increase the strength of the sample after drying. At higher temperatures, this compactness...
also helps to improve sintering densification, which increases the resistance to corrosion. On the other hand, care should be taken not to use more micro-powders in castables, as this can also cause dilatancy that affects the green strength, and at higher temperatures (during sintering), it can cause larger pores and microcracks on the boundaries between the aggregates and matrix. It is clear that these microcracks are due to the separation of fine powders from the aggregates due to excess shrinkage \[17,41,42\].

Otroj and Daghighi \[40\] reported that small-diameter particles (<100 μm) with large specific surface areas (>1 m²/g) play an important role in bonding systems, in which adding nanoalumina particles results in the production of refractory castables with lower porosity and smaller pore sizes leading to higher strength. On the other hand, Zacherl et al. \[43\] discussed the positive impact of coarse grains (5–25 mm) on strong refractory skeletons. These authors have stated that castables with an optimum amount of larger aggregates will naturally shrink less than those with smaller aggregates causing less crack formation to occur. In fact, these large particles prevent the growth of cracks due to deflection of the cracks upon interaction with the large aggregates.

2.3.1. Porosity and voids
One of the most important results of particle packing in designing refractory mixes is the development of castables with low porosity. Higher compactness causes better workability and lower water requirements and consequently results in low shrinkage and high strength. Pores and cracks as well as grain boundaries provide open spaces for penetration that are directly exposed to service conditions such as molten metal and slag. The amount of molten material penetration and reaction with the working face of refractories depends strongly on the diameters of the open spaces. The larger the diameter of the open spaces (especially the pore diameter), the more easily they can be penetrated by molten metal or slag and suffer reduced wear resistance, thus promoting the corrosion process \[17,40,43,44\].

Silica fume is one of the most important additives that yield castables with the lowest level of porosity and the highest level of compactness. Practically, the ball-bearing effect of silica fume produces properly dispersed castables, and its small particles with their spherical morphology decreases the cement content of refractory castables. When the cement content of refractory castables is there reduced, the water demand in these castables is also very low. This ultimately improves the packing of the particles and flowability and reduces porosity (Figure 9). In addition, silica fume acts as a filler, that is, the addition of silica fume was also found to alter the pore size distribution in the direction of finer pores. Actually, one reason silica fume helps to produce good flowability in refractory castables is its creation of the volume to fill the voids between the coarser aggregates and to keep them apart. It must be considered, however, that the silica fume’s quality is also important for obtaining the desired properties \[6,17,36\].

Different binders also show different behaviors in terms of the final porosity of castables. In a related study, Ismael et al. \[4\] compared different binders (i.e., CAC, HA, CS) with refractory castables and observed that different binders provide different permeabilities (Figure 10). CAC and HA provide low-density products due to the hydration process and also reduce permeability. CS does not produce a hydrated phase, however, and after gelation, it creates an open, highly permeable structure. These authors added the same amount of water to all the formulas (including different kinds of binders). Although they expected to find the same value for apparent porosity, castables containing CS showed the highest (Figure 11). Due to the differences in the

**Figure 8.** Elastic modulus as a function of curing time for dead-burnt (DB)-containing castables with or without 0.1 or 0.2 wt% acetic acid (AA) \[34\].

**Figure 9.** Flow value and water addition for 1.5% cement tabular alumina-based refractory castables as a function of silica fume content \[17\].
Apparent porosity of castables based on different binder-containing compositions cured at 50°C [4].

Figure 10. Permeability measurements ($k_d$) as a function of curing time for different binder-containing compositions, cured at 50°C [4].

Figure 11. Apparent porosity of castables based on different binders, cured at 50°C [4].

Permeability of the castables, therefore, the water removal from castables containing CS will be faster in the drying and firing stages, but the low permeability of HA castables requires higher temperatures to expel the water vapor from the castable body, increasing the risk of explosion during drying or heating.

2.3.2. Water requirement
As previously stated, the smaller the amount of water required for castable production, the greater the green strength of the dried castables will be. As an example, a fireclay-based low-cement castable with 4–5 wt% water may develop a cold crushing strength (CCS) of 110 MPa. This value drops to 80 MPa with 6 wt% water and to around 50 MPa with 7 wt% water. The recommended amount of water addition to refractory castables should therefore be strictly followed. One of the key parameters that most strongly affects the water requirement of castables is the quality of the raw material (cement, aggregate, etc.) used. If low-quality porous aggregates are used in the castables, for example, more water will be needed to fill up the pores and the result will be castables with higher porosity, lower density, and lower strength. In addition, the amount of cement added to castables also affects their water requirement, such that the greater amount of cement added, the more water will be required for good workability of the castables. This can spoil the final properties of castable, such as their density and strength [14,17,41,43].

Water-reducing agents can be used to reduce the amount of water needed for refractory castable production. The common water-reducing agents used in high alumina castables are sodium citrate, gluconic acid, sodium or calcium lignosulphonate, and sodium gluconate as well as such superplasticizers as melamine formaldehyde sulfonate and naphthalene formaldehyde sulfonate. It should be noted, however, that although some of these water-reducing agents reduce the water requirement, they may also lead to a reduction in final strength [14].

2.4. Curing and drying behavior
Parameters that strongly affect the strength during curing and drying of monolithic refractory castables include the curing temperature and the drying rate [14,24,30,32,45]. A report by Saloma’o et al. [30] discussed the importance of curing temperature on the mechanical strength, total porosity and apparent volumetric expansion of castables containing magnesia. As shown in Figure 12, the mechanical strength reached its highest value with the lowest porosity in samples cured at 50°C and 80°C. After this point, volume expansion was observed, which resulted in a drop in mechanical strength and increase in porosity. When the curing temperature was 8°C, however, the mechanical strength showed an increasing trend through the seventh day of curing with no expansion observed.

The heating rate is another important parameter during the drying and firing of castable bodies. Choosing a high heating rate may lead to cracking or even explosions in refractory castables. The reason for these cracks or explosions can be attributed to the formation of destructive phases or, sometimes, to a too rapid heating rate, which increases the vapor pressure inside the castables. The addition of additives can improve the permeability of designed castables, however, and prevent cracking and explosions.

Polypropylene fibers (PP fibers) are among these additives. The degradation of PP fibers during thermal treatment at between 80 and 165°C usually results in channels or paths and induces an increase in the permeability level, thus favoring the release of water vapor. Adding 0.05–0.1 wt% of PP fibers to the castables and observing the heating rate applied can therefore reduce the likelihood of cracks and explosions in the castables. Table 3 presents the general characteristics of PP fibers, suggesting that the choice of the length and diameter of PP fibers depends on the type of refractory castables (vibrated, self-flowing, pumpable, etc.) and particle size distribution [14,32,34,45,46].

Thus, the addition of PP fibers leads to castable permeability, and the binder type chosen also has a great
influence on their permeability. Permeability is one of the most important properties for predicting the drying behavior and chemical impact of refractory castables. The permeability of refractory ceramics is usually expressed by constants derived from two main models: Darcy’s law and Forchheimer’s equation (Table 4). According to the above observations and in line with the permeability equations, colloidal binder-containing compositions indicate higher permeability levels and thus offer an easier route to water release than HA-containing compositions, because lower permeability levels indicate slower drying behavior. Thus, when we use these kinds of binders (especially HA) in castables that tend to have very thick cross-sections, such as monolithic electric arc furnace roofs (delta sections), extreme care needs to be taken in the drying process because these very thick castables are prone to cracks and explosions [4,14,15,24].

Table 3. General characteristics of the polypropylene fibers used in refractory castables [34,45,47,48].

| Length (mm) | Diameter (µm) | Density (g/cm³) | Melting point (ºC) |
|-------------|---------------|-----------------|-------------------|
| 1–10        | 8–30          | 0.91            | 80–165            |

Table 4. Commonly used equations for permeability evaluation of refractory ceramics [15].

| Model       | For noncompressible fluids | For compressible fluids |
|-------------|----------------------------|-------------------------|
| Darcy       | \( (P_1 - P_2/L) = (\mu/k_1) \nu \) | \( (P_1^L - P_2^L/2PL) = (\mu/k_1) \nu \) |
| Forchheimer | \( (P_1 - P_2/L) = (\mu/k_1) \nu^2 + (\rho/k_2) \nu \) | \( (P_1^L - P_2^L/2PL) = (\mu/k_1) \nu^2 + (\rho/k_2) \nu \)

Where \( P \) is the fluid pressure at the sample entrance (Pa); \( P_2 \) the fluid pressure at the sample exit (Pa); \( \nu \) the fluid velocity, given by the volumetric flow rate (Q) divided by the specimen cross-sectional area (A), orthogonal to the fluid flow (m/s); \( L \) the sample thickness (m); \( \mu \) the viscosity of the fluid (Pa·s); \( \rho \) the density of the fluid (kg/m³); \( k_1 \) the Darcian or viscous permeability constant (m²); \( k_2 \) the non-Darcian or inertial permeability constant (m); and \( P \) the fluid pressure at which \( \nu = \mu \) and \( \rho \) are measured or calculated (usually \( P = P_0 \) (Pa).

2.5. Effect of steel fiber addition to castables

Various metal fibers (steel fibers) have been developed to overcome the inherent problems of ceramics, such as their inherent brittleness, fairly low tensile strength, poor impact strength, and poor thermal shock resistance. The addition of randomly oriented steel fibers to monolithic refractories acts to hinder crack creation and prevent the spread of cracks which can lead to catastrophic failure of the refractory body. The network of the steel fibers holds the matrix together, moreover, and prevents spalling, while also improving such properties as toughness, tensile and bending strength, fatigue strength, impact strength, and thermal and mechanical shock resistance. It also reduces drying shrinkage. In fact, these steel fibers transform castables from very brittle materials to tough, tenacious composites [11,49,50].

As shown in Figure 13, the addition of steel fibers has the greatest impact at high temperatures (70% enhancement for products treated at 1400°C), while for dried samples, only a slight (5%) increase in CCS is observed. At high temperatures, hindering both sintering and crack spread actually increases the strength. But as was demonstrated in Figure 14, at 900°C, increased porosity has been presented as the reason why strength declines after 2 wt% of steel fibers [50].

3. Cracks and/or strength loss when firing castable bodies (during the heating stage)

3.1. Dehydration of calcium aluminate cement and/or magnesia

The disadvantages of the presence of CAC and the formation of hydrated phases during curing and drying were discussed in the previous sections. The worst impact of the presence of CAC on refractory castables occurs during the heating and firing of these refractory bodies, which
3.2. Formation of porosity during heating

As stated in section 3.1, the presence of CAC in castables increases their porosity at high temperatures. This strongly affects the corrosion resistance and final strength of refractory castables. Apart from the cement, moreover, other additives such as magnesia also increase porosity at high temperatures when added to castables [1,25,41,52–54].

In alumina-magnesia refractory castables, spinel formation ruled by the Kirkendall effect leads to an increase in the average pore size with gradual consumption of magnesia particles. This is highlighted when magnesia with a larger particle size (i.e. larger than 45 μm) is used. As the firing temperature is increased up to 1000°C, moreover, the porosity of refractory castables increases as a result of the Kirkendall effect. This is clearly illustrated by SEM images (Figure 16) [52,55–58].

However, there are a number of additives that can improve the porosity drawback of refractory castables containing CAC or magnesia at high temperatures, including, TiO$_2$, B$_2$O$_3$, Cr$_2$O$_3$, ZnO, ZrO$_2$, MgF$_2$, LiF, CaF$_2$, AlF$_3$, MgCl$_2$, and other inorganic salts. In fact, these additives accelerate the sintering process and also result in a higher degree of densification of refractory castables. This prevents microcrack propagation, while some of these additives even increase resistance to alkaline slag. As shown in Figure 17, the samples without TiO$_2$ contain a considerable number of pores (Figure 17(a)) thus adding this additive improves grain interlocking with smaller amounts of inter-granular porosity after sintering, while also increasing the average grain size. In fact, TiO$_2$ acts as a sintering aid in refractory systems; Nath and Tripathi have reported that when an Al$_2$O$_3$-Cr$_2$O$_3$ system has no TiO$_2$ content, the average grain size after sintering at 1650ºC is 4 μm (Figure 17(a)). With the addition of 1 wt % of TiO$_2$, however, the average grain size at the same sintering temperature increases to 5.5 μm (Figure 17(b)), and the further addition of TiO$_2$ in amounts of 2 wt % (Figure 17(c)) and 3 wt % (Figure 17(d)) leads to enormous average grain sizes of 31.9 μm and 69 μm, respectively. B$_2$O$_3$ is also known as a mineralizing and densifying additive, and when used in cement or phosphate-bonded formulations according to Equation (11) presents Al$_{18}$B$_4$...
due to the interaction of B$_2$O$_3$ with fine alumina at around 650–800°C. This phase favors increases in the refractory samples’ stiffness, mechanical strength, and erosion and thermal shock resistance [31,38,57,59–61].

$$9\text{Al}_2\text{O}_3(s) + 2\text{B}_2\text{O}_3(l) \rightarrow \text{Al}_{18}\text{B}_4\text{O}_{33(s)}$$  \hspace{1cm} (11)

### 3.3. Explosive spalling

In some refractory castables, depending on the binder type and formulation, small amounts of water vapor sometimes still evolve at temperatures up to 650°C. If the permeability is not sufficient to release generated

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**Figure 16.** Micrographs of samples containing MgO <45 µm after firing at different temperatures (1000, 1150, 1300, and 1500°C) for 5 h [52].

**Figure 17.** Scanning electron micrographs of samples sintered at 1650°C with different TiO$_2$ content: (a) no TiO$_2$, (b) 1 wt% TiO$_2$, (c) 2 wt% TiO$_2$, and (d) 3 wt% TiO$_2$ [61].
water vapor during drying or heating, of these types of castables, however the disparity between the amounts of vapor generated and released raises the pressure to a high level in the structure. If this vapor pressure level inside the castable exceeds the mechanical strength, it can cause explosive spalling [4,14,18,23,45].

In order to prevent these explosions and mechanical damage, it is necessary to create channels in the bodies of the refractory castables in order to facilitate the release of vapor pressure more easily, increase the drying rate, reduce internal pressure, and prevent the explosive spalling. There are several ways to create channels in refractory castables, the most important of which are the use of additives (i.e. polymeric fibers or metal powder such as Al) and changes in the particle size distribution (use of coarser aggregates in the castable (5–25 mm)) [4,14,31,43,46].

Polymeric fibers are among the most important and best-known means used in various refractory industries to reduce the internal pressure of refractory castables and inhibit explosive spalling. During melting and thermal decomposition (80–165°C), the PP fibers are removed from the body to create open spaces that allow water vapor and gases to be evacuated and reduce pore pressure. It should be noted that the addition of PP fibers has no effect on the permeability of the green bodies before they melt, as it does not provide a path to speedily water evacuation or water vapor release. The optimum amount of PP fibers recommended for refractory castables is 0.05–0.1 wt %. In addition to PP fibers, metal powders (particularly aluminum) with or without PP fibers can also be used to create permeability in dense castables. Aluminum powder reacts with water at ambient temperature in accordance to Equation (12) and produces hydrogen gas. When escaping from the green body, this gas creates small pores that enable steam to leave the castable during the drying process. It should be considered, however, that the use of aluminum powder has some inherent problems and may cause an explosive reaction in contact with air [4,14,31,43,46].

\[ 2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2\text{O} \uparrow \] (12)

3.4. Phase formation at high temperatures

3.4.1. Anorthite and gehlenite

Another drawback of the addition of CAC to castables is the presence of CaO in cement. The superfine silica and alumina particles react with this CaO at high temperatures (1000–1500°C), which leads to the formation of low melting phases, such as anorthite (CaO·Al₂O₃·2SiO₂) and gehlenite (2CaO·Al₂O₃·SiO₂). These phases cause reductions of the refactoriness and high temperature strength (hot strength). However, the use of Cr₂O₃ and super-ground calcined alumina instead of superfine silica particles forms a high-melting solid solution between Al₂O₃ and Cr₂O₃ and improves the hot strength. It should also be noted that the amount of CAC in a castable increases the likelihood that low-temperature phases, such as anorthite and gehlenite, will also increase at elevated temperatures [14,19,24,41].

3.4.2. Calcium dialuminate and calcium hexa-aluminate

Calcium dialuminate (CA₆) and calcium hexa-aluminate (CA₆) are formed by a reaction among CaO derived from the cement and alumina sources added to refractory castables at high temperatures. CA₆ generation is an expansive reaction detected at temperatures higher than 1100°C. When silica fume is added to refractory compositions, however, this SiO₂ can also react with CaO and Al₂O₃ to form glassy phases (low melting phases such as anorthite and gehlenite) as well as to reduce the amount of CA₆ generated. If a great amount of alumina is available, the CA₆ phase is completely consumed at higher temperatures, leading to the formation of CA₆, the generation of which causes a theoretical volumetric change (CA₆ = +13.6% and CA₆ = +3.01%). This volumetric expansion, especially during the formation of CA₆, may induce marked crack generation during the initial thermal treatment of high-alumina cement-bonded castables, leading to a reduction in mechanical properties [2,15,22].

Despite the physical properties of castables (porosity, pore size, cracks, grain boundaries, etc.) discussed above, formation of larger amounts of CA₆ and CA₆ might also lead to easy penetration of molten metal or slag and reduce the castable integrity. It has been reported that molten slag penetration, wear and corrosion of refractories at high temperatures are directly associated with the physical features and location of the CA₆ phase in the microstructure. Chemically, the presence of alumina in the matrix, the lack of calcium aluminates and the absence of a liquid phase (or liquid phase formation with high viscosity) ensures higher wear and corrosion resistance and prevents the generation of thick CA₆ and CA₆ layers, inhibiting expansion and further penetration. A possible alternative to inhibit CA₆ expansion in the matrix is replacement of CA₆ with HA as a binder [1,22,44].

CA₆ formation does not cause only detrimental effects; the presence of this phase also imparts benefits to refractory castables, properties. Its presence as a needle-like phase (or platelet-like phase in alumina-magnesia refractory castables), for example, can induce bridging among the castable particles, resulting in an interlocking effect, and can act as in situ whiskers, further toughening the material. Thus, these crystals enhance the overall thermo-mechanical behavior (thermal shock, creep resistance, hot mechanical strength, hot modulus of rupture, etc.) of the designed products [22,31,40,46,62].
3.4.3. Mullite
Despite all the benefits of mullite formation in castables, some authors \[13,15,24\] believe that a volume increase occurs during the formation of mullite at high temperatures that can promote cracking through the development of residual stresses.

3.4.4. Spinel
Reactions between alumina and fine magnesia at temperatures above 1000°C lead to the formation of \textit{in situ} spinel (MgAl$_2$O$_4$), and the temperature must be raised for the whole magnesia reaction in the batch. According to Wagner’s mechanism, due to the counterdiffusion of Mg$^{2+}$ and Al$^{3+}$ ions, the spinel phase is formed on both the magnesia and alumina sides (Figure 18), but this reaction leads to local shrinkage on the side of the magnesia particles, whereas it is followed by expansion at the alumina interface. As seen in the figure, the theoretical thickness ratio (R) of the spinel layers formed on the alumina and magnesia sides is 3:1, indicating a higher spinel formation rate at the Al$_2$O$_3$ interface \[2,31,51,52,55,62\].

In general, however, the most important parameter in this section is \textit{in situ} spinel formation expansive behavior. This behavior can be attributed to two causes: (1) density differences among the reactants and product (Al$_2$O$_3$ = 3.98 g/cm$^3$, MgO = 3.58 g/cm$^3$, MgAl$_2$O$_4$ = 3.60 g/cm$^3$) leading to a volumetric expansion close to 8%; and (2) generation of pores after magnesia diffusion (Kirkendall effect), which has greater relevance to volumetric expansion than the density differences. It should be considered that contact with MgO–MgO in the matrix does not add to the spinel expansion, as MgO shrinks after the reaction, whereas contact with MgO–Al$_2$O$_3$ and Al$_2$O$_3$–Al$_2$O$_3$ account for a considerable share of the castable volume change. Eventually, these expansive reactions, or even the thermal expansion mismatch among the castable phases, can lead either to interfacial separation between the aggregates and matrix or to microcracks, thus affecting the material’s performance \[2,31,52,55,62,63\].

![Figure 18. Spinel formation mechanism achieved through counterdiffusion of Al$^{3+}$ and Mg$^{2+}$ cations [31].](image)

Observing certain factors makes it possible to prevent significant overall expansion. One of these factors is the addition of colloidal alumina, since the use of colloidal alumina and nanoscaled magnesia particles, in addition to reducing the castables’ overall expansion, accelerates spinel formation and increases the sample’s stiffness. Other factors include the purity of the magnesia and alumina particles, fine particle content, particle size distribution, dispersion in the castable, number of contacts, reactions with other castable compounds, solid solubility of alumina at high temperatures, and diffusion of MgO vapor as well as higher Mg$^{2+}$ mobility in the oxygen lattice \[2,31,52,55\].

As already reported in section 2.2, various additives such as silica fume, CAC and MAP may be used in castables containing MgO. But what is the effect of these additives at high temperatures?

A further role of silica fume in castables of these type (castables containing MgO) is its ability to speed up high-temperature reactions. The liquid phase formation increases the ion diffusion and consequently promotes faster spinel formation. Silica fume can counterbalance expansion due to \textit{in situ} spinel formation, moreover, via a softening mechanism. It is important to be careful, however, in selecting the silica fume need to counterbalance the \textit{in situ} spinel expansion, for which we used a fine magnesia grain size (<45 μm). When a coarser MgO grain size (<100 μm) is used by contrast, the high silica fume contents seem to spoil the castables’ integrity, leading to massive overall expansion, large pores, and crack generation \[2,31,35\].

It should be noted that while a high fine fraction MgO/SiO$_2$ wt% ratio (>12 wt%) in the matrix causes massive expansion (>2%) and leads to cracks in the specimen, a low MgO/SiO$_2$ wt% ratio (<3 wt%) leads to massive shrinkage that can cause cracking. These events result in reduction of the castables’ hot properties at high temperatures. The most suitable MgO/SiO$_2$ wt% ratio would be between 4 and 8 (Figure 19), which reduces the likelihood of cracking, leading to better corrosion and creep resistance and hot modulus of rupture as well as to increased spalling resistance at high temperatures \[2,31,35\].

Although the addition of CAC to alumina-magnesia castables leads to an increase in their green strength, the elastic modulus values decrease considerably during the cooling stage because they are associated with an increase in the glassy phases (Figure 20). In addition to the formation of spinel at above 1000°C in these castables, the CA$_2$ phase may also be formed due to the presence of CaO, which leads to volumetric expansion and even to microcracks. Additionally, when silica fume was added to this castable composition, small amounts of other phases such as melilitte (2CaO.3MgO.5SiO$_2$) and anorthite (CaO.Al$_2$O$_3$.2SiO$_2$) were also detected. Increasing the temperature (to 1500°C) consumed these phases and appeared to cause liquid formation \[2,3,22\].
The presence of MAP in alumina-magnesia castables at high temperatures also causes drawbacks. One of these is the generation of low-melting compounds at high temperatures (such as Mg₃(PO₄)₂ ~ 1357°C and Mg(PO₃)₂ ~ 1165°C). Magnesia can break three-dimensional aluminum phosphate bonds, moreover, and reduce the mechanical strength of refractories [38].

3.5. Phase transformation

In the phase transformation and the coefficient of thermal expansion of refractory castables, a mismatch of some of the raw materials can sometimes cause microcracks to be developed by thermal shock load during heating or after firing of the castables. The raw materials that show this behavior most notably can be identified as titania (TiO₂) and even alumina (Al₂O₃). TiO₂ can be used to promote sintering of alumina or magnesium aluminate spinel. Since the density of the Al₂O₃ and TiO₂ (aluminum titanate) phases formed is lower than that of the raw material (Al₂O₃ = 3.98 g/cm³, TiO₂ = 4.23 g/cm³, Al₂TiO₅ = 3.68 g/cm³), the formation of these phases is accompanied by an increase in volume that can cause cracks in the castables [1,13,64,65].

Braulio et al. [1] reported that Al₂O₃ phase transformation (Equation (13)) also reduces mechanical strength in some cases. The authors observed this phenomenon when they used HA in refractory castables.

Boehmite → Gamma(γ) → Delta(δ) → Theta(θ) → Alpha(α)

(13)

3.6. Coefficient of thermal expansion

Differences between coefficients of thermal expansion (CTE) can lead to formation of micro-cracks in the matrix of a refractory castable and acts as crack branches when the castable comes under thermal stress. As an example, when coarse-grained magnesia (>45 μm) is used in magnesia-alumina castables, some of the coarse particles remain unreacted and cracks may occur during heat treatment due to a thermal expansion mismatch among magnesia, alumina, and spinel. As shown in Figure 21, all combinations displaying a CTE mismatch between magnesia and spinel exhibit cracks at the interfaces between magnesia grains and the spinel matrix [31,35].

Additionally, Jingjie et al. [59] noticed the effect of Cr₂O₃ on the CTE of magnesia-spinel refractory castables. As shown in Figure 22, the addition of Cr₂O₃ up to 2 wt% can reduce the CTE. The cause of this CTE reduction is the formation of microcracks resulting from the different thermal expansion behaviors of multiple phases to accommodate increases in the volume of the specimens at high temperatures. It should be noted that excessive addition of Cr₂O₃ (more than 2 wt%) increases the CTE again.

4. Final remarks and challenges for the future

Among the major challenges in the area of monolithic castables, highlights might include either the formation of cracks after the castables are molded or their lack of sufficient strength inside the mold or during removal from the mold. These challenges become threats when large monolithic pieces are to be made. When casting monolithic electric arc furnace roofs (delta sections) or monolithic steel ladle linings without using calcium aluminate cement, for examples, serious challenges (i.e. crack propagation and strength loss) arise.

Since we omit cements, and also due to the large size of the blocks, ignoring a certain number of parameters could cause catastrophes. Such crucial factors include selection of an appropriate binder (application of hydratable alumina, microsilica-gel or colloidal suspension, etc.), suitable steel fibers, polypropylene fibers, drying methods, and heating rates.
Another important parameter is use of the optimum amount of light-weight aggregates (e.g. bubble alumina) and dense aggregates larger than 5 mm (5–25 mm) as part of the body skeleton in large blocks. Light-weight aggregates not only improve thermal shock resistance, but they also reduce the weight of large blocks. Dense aggregates larger than 5 mm not only produce stronger skeletons, moreover, but they also increase thermal spalling, wear, and abrasion resistance. In addition, as coarse aggregates are well-dispersed in precast blocks, crack propagation is hindered due to deflection or branching after interaction with the large aggregates, which greatly enhances thermal shock resistance.

As discussed above, large monolithic cast pieces of noncalcium aluminate cement with high green strength can be produced in two different ways, as follows:

(i) Using optimum amounts of either hydratable alumina or colloidal alumina nanoparticles for monolithic electric arc furnace roofs in which main raw materials are Al₂O₃ and MgO. Due to the presence of calcium aluminate cement, silica fume, and silica sol in castables of Al₂O₃-MgO face challenges of their own (at low or high temperatures). Certain binders, such as hydratable alumina, colloidal alumina or a combination of

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**Figure 21.** Forsterite, monticellite, and spinel reaction layers indicated by L in figure at the edge of remnant MgO grains for high silica fume-containing castables (0.5 and 1 wt%) and cracks at the MgO–spinel interface after firing at 1500°C for 5 h [35].

**Figure 22.** Effect of Cr₂O₃ addition on the coefficient of thermal expansion [59].
these, can therefore be used in these castables to prevent cracking. Thanks to their nanometric particles, these binders decrease the spinelization temperature. Another benefit of these binders is green strengthening to produce large pieces without calcium aluminosilicate and with no structural cracks.

(ii) Recently, microsilica-gel has been recommended instead of colloidal binders in noncement pieces. A combination of microsilica-gel and any of two binders, such as hydratable alumina or phosphate, can therefore be employed to produce large blocks without calcium aluminosilicate cement. These also have the high green strength to prevent cracking in $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ systems. Use of such binders creates a purely mullite phase at high temperatures after phase transformation, since there are only $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ oxides in the final batch. As a consequence, the high thermal properties of large manufactured pieces do not undergo any decay.

Disclosure statement

No potential conflict of interest was reported by the author.

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