UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN

FACULTAD DE INGENIERÍA MECÁNICA Y ELÉCTRICA

DIVISIÓN DE ESTUDIOS DE POSGRADO

"STUDY OF CORROSION MECHANISMS IN REFRACTORY CASTABLES UNDER THE INFLUENCE OF LIQUID OXIDES"

LUIS TADEO IBARRA PLATA

TESIS

EN OPCIÓN AL GRADO DE MAESTRO EN CIENCIAS DE LA
INGENIERÍA MECÁNICA CON ESPECIALIDAD EN
MATERIALES

CD. UNIVERSITARIA AGOSTO 2020

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Universidad Autónoma de Nuevo León
Facultad de Ingeniería Mecánica y Eléctrica
Subdirección de Estudios de Posgrado

Los miembros del Comité de Tesis recomendamos que la Tesis "Study of Corrosion Mechanisms in Refractory Castables under the Infuence of Liquid Oxides", realizada por el alumno Luis Tadeo Ibarra Plata, con número de matrícula 1421708, sea aceptada para su defensa como requisito para obtener el grado de Maestría en Ciencias de la Ingeniería Mecánica con Especialidad en Materiales.

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ABSTRACT

Corrosion in refractories in a commercial furnace is a very complex phenomenon, which involves chemical and physical wear. In this work three refractory castables (A, B, and D) are being characterized and studied to compare their properties and determine their corrosion mechanisms in the presence of slag obtained from a steel furnace. The chemical composition of the slag consists of CaO, SiO_2, alumina and Fe_2O_3. Using a heating microscope it was determined that the slag starts to melt around 1300 C. The chemical composition of the castables consist mainly of alumina (86%, 91% and 92% respectively) with a variation in material A which contains 5.8% MgO. Prismatic bars were made and sintered at 1400 C to run the hot modulus of rupture at 1000 ºC. A non-destructive technique was used to investigate the Young's modulus of the specimens before and after sintering.

The corrosion tests were performed at 1400 C in cubic crucibles (8x8 cm) with 50 g of slag.

Until now, the investigated castable samples exhibit positive values of Young's Modulus and Hot Modulus of Rupture (HMOR). The corrosion tests showed a high impact on the castables integrity, which can be seen in the multiple cracks formed after the test. This can be explained by the presence of SO_3 in the slag composition.

CHAPTER 1

INTRODUCTION

Refractory materials are an important class of ceramics that are utilized in large quantities and are important components of the equipment used in the production, refining, and handling of metals and glasses, for constructing heat-treating furnaces, and for other high-temperatures processing equipment.[1,2] Charles A. Schacht[3] defines refractories as materials which are supposed to be resistant to high temperatures and are exposed to different degrees of mechanical stress and strain, thermal stress and strain, corrosion from solids, liquids and gases, gas diffusion, and mechanical abrasion at various temperatures.

Corrosion resistance is one of the most important features of refractory castables, since they are commonly exposed to molten liquid oxides. It is caused by mechanisms such as dissolution in contact with liquid, penetration of the vapor or liquid in the pores, etc. [3]

The corrosion process can be defined according to literature as an interaction (which involves phenomena of dissolution and precipitation of new crystalline compounds) between a solid phase and a fluid phase that has a negative effect to either of the phases. [11, 12] This process also leads to the degradation of the material surfaces or grain boundaries, as a consequence of chemical attack by a corroding fluid, and to a decrease in the strength of the structure.

Corrosion by liquid oxides is one of the most severe modes of degradations that limit the lifetime of the refractory linings. In lining materials in contact with slag during ladle refining of steel is usually described in three major categories: dissolution, penetration and erosion. In literature it is mentioned that microstructures of corroded refractories have the following features to be considered before interpreting them:

- They are multi-component and heterogeneous ceramics.
- The microscopic observations were carried out at room temperature, there are certain vitreous phases existing at very high temperatures, and they evolve once the material starts to cool. [11]

CHAPTER 2

THEORETICAL FUNDAMENTALS

2.1 Refractory materials

Refractories are defined by Charles A. Schacht[3] as materials which are supposed to be resistant to high temperatures and are exposed to different degrees of mechanical stress and strain, thermal stress and strain, corrosion from solids, liquids and gases, gas diffusion, and mechanical abrasion at various temperatures. Accordingly, the most important properties of these materials include the capacity to withstand high temperatures without melting or decomposing, and the capacity to remain unreactive and inert when exposed to severe environments. Additionally, the ability to provide thermal insulation is often an important consideration. [2] Nevertheless, sometimes it can be better to have a high thermal conductivity.

2.1.1 Thermo-mechanical Properties

a. Refractoriness

Refractory materials have a quite inhomogeneous structure consisting of pores, aggregates and matrix. Therefore, it is not possible to talk about a fixed melting point. Refractory materials are characterized usually by a range of softening temperatures using pyrometric cones. [3]

b. Refractoriness under load (RUL)

Besides the pyrometric cones, the deformation behavior at high temperatures can bet tested with the Refractoriness under load (RUL). Under load pressure a plastic flow from the crystalline phase can occur, which can be neglected in the usual pressures. The higher the proportion of the melt phase and the lower the viscosity, the more the softening is pronounced. Besides, the structure of the crystalline phase has an important influence. *Needle-like* crystals give the specimen a greater resistance than round ones do. [3]

In order to perform the *RUL* (under the DIN 51064 standard), a cylindrical specimen must be constructed with a diameter of 50 mm and a height of 50 mm under a load pressure of 0,2 N/mm^2. Then the sample has to be heated and its height continuously measured. [3] Since the expansion of the apparatus used during the *RUL* test is a problem, other tests can be performed to determine the resistance of refractory materials at higher temperatures such as Creep in compression (CIC). For the CIC test the same RUL specimens can be used. According to the percent of compression from the highest registered value of expansion during the RUL test (0,5, 1, 2 and 5 %) four temperatures are defined. Then two sensors are placed above and under the specimens to determine the real change of their height. In the CIC test the compression of the sample after it reaches its highest value of expansion is measured. This is done, by maintaining this temperature constant under a load pressure of 0,2 N/mm^2 for several hours.

c. Modulus of rupture

Modulus of rupture can be measured at high and low temperatures. Since refractories are used at elevated temperatures, the hot modulus has been prescribed and required by users as the most important test criterion for selection and use of refractories. The cold modulus of rupture of a refractory material indicates the flexural strength and its suitability for use in construction since the test is ran at room temperature.

d. Thermal Expansion [3]

Most refractories expand during the heating up, leading to the damaging of refractory products, resulting in the cracking of the lining. Hence, thermal expansion measurements are really important in the design of refractory materials. They should always be designed in such a way that the maximum temperature attainable in the system is lower than the softening of melting temperature of the refractory ingredients. Thermal expansion is defined as a permanent linear change and is measured by the changes in the longest linear dimensions.

e. Thermal Shock [3-5]

Thermal shock resistance is the measure of the refractory when it is exposed to alternate heating and cooling. Since refractory systems expand while being heated and contract during cooling, mechanical stresses are generated due to the thermal expansion of the material and if they are higher than its resistance, cracks may appear. Nevertheless, refractories having structures with built-in microcracks of defects show better thermal shock resistance than with rigid systems.

According to the standard DIN 51068 the thermal shock resistance can be determined. A sample is heated in a furnace to 950 °C and immediately cooled with cold (room temperature) water or air. This procedure has to be repeated until first cracks are observed. If after 30 repetitions of the procedure a destruction of the material does not occur the test must be aborted.

f. Thermal conductivity [4]

The thermal conductivity λ (with SI units *J/mKs* or *W/mK*) is a coefficient that depends on the material and can be calculated with the next equation:

$$Q = \lambda A \Delta T t / d$$

Where Q is the heat quantity which flows in a certain time t under the influence of a temperature gradient ΔT through a wall surface A with a thickness d.

Thermal conductivity also depends on the chemical composition of the refractory material, its structure, porosity and the sintering temperature.

2.1.2 Mechanical Properties

a. Density and porosity [3]

Many physical properties of the refractories are related to density and porosity such as mechanical resistance and thermal properties. Porosity is the percent of volume that consists of cavities. The density ρ and the raw density ρ_R can be used to determine the total porosity P_T using the next equation:

$$P_T = 1 - \frac{\rho}{\rho_R}$$

Density ρ differentiates from raw density ρ_R because the first one does not include pores of the specimens. It can be measured with a pycnometer milling the material until a fine powder is obtained.

2.1.3 Chemical properties

The chemical properties of a refractory are mainly determined by their chemical composition including the bonding system of the material. These properties play a vital role during the formulation of a refractory. Their composition must be appropriate according to the process in which they are going to be used. For example, refractories used in iron making processes are made of alumina and silica since the liquid slag is slightly acidic, on the other hand for steel making processes basic magnesia refractories are chosen. [3]

Refractory materials can be classified according to their chemical composition. This will be discussed in further chapters.

2.2 Classification

2.2.1 Classification according to chemical behavior

Based on their chemical behavior refractories are divided in three groups: acid, basic and neutral.

Table 1 Composition of refractories (weight percents) [2]

Refractory	SiO_2	Al_2O_3	MgO	Fe_2O_3	Cr_2O_3
Acidic					
Silica	95-97				
Mullite	28	72			
High-alumina firebrick	10-45	50-80			
Basic					
Magnesite			83-93	2-7	
Olivine	43		57		
Neutral					
Chromite	3-13	12-30	10-20	12-25	30-50
Chromite-magnesite	2-8	20-24	30-39	9-12	30-50

a. Acid Refractories

An acidic material contains an excess of silica content (SiO_2) over basic materials (which usually contain CaO) considering neutral a CaO/SiO_2 ratio of 1,0. Therefore, it can be said that an acidic material contributes silica in a corrosion reaction, and a basic material contributes CaO or MgO in a corrosion reaction. [3] As can be seen on Table 1, common acidic refractories include silica, alumina and fireclay. Alumina concentrations higher than 45% constitute the high-alumina refractories. [2]

b. Basic Refractories

These refractories, as mentioned before, are made primarily of MgO or CaO. Pure MgO has a high melting point, good refractory properties and good resistance to attack by the basic environments found in steel making processes. [1] Commonly, basic refractories are more expensive than acid refractories.

c. Neutral Refractories

Refractories which are considered neutral are typically used to separate acid and basic refractories, preventing them from attacking one another. [2]

2.2.2 Classification according to manufacturing method

According to the method of manufacture, refractories are divided into two categories: shaped and unshaped refractories.

a. Shaped refractories

Bricks or similar shapes (like cast shapes) are included. The main goal of the brick making process is to attain the highest possible density. [1]

b. Unshaped refractories

They are also called *monolithic refractories* and there are different kinds of them: plastics, ramming mixes, mortars, coatings, and castables and gunning mixes. The physical characteristics of plastics and ramming mixes are their ease of ramming to consolidate to proper density. For mortars and coatings, they should have appropriate consistency to be used according to the specific applications. For castables, which were studied for this thesis, the most important characteristics are particle size distribution, setting and strength development and the bonding system. [1]

2.3 Unshaped Refractories

Refractory castables are a large group of materials that have evolved and grown significantly in the past thirty years. They consist of some very complex and technical formulations, finding use in a variety of very demanding and severe industrial applications.

Monolithic refractories consist of a mixture of refractory raw materials and binders and their shaping and heat treatment take place during installation. [3,4]

2.3.1 Classification

According to literature [3,4] they can be classified taking into account different criteria:

According to its use:

- For monolithic constructions and reparations,
- for laying and grouting and
- for paints and surface protection.

According to their installation method:

- Refractory concretes
    - Conventional refractory concretes
    - Liquefied refractory concretes
    - Chemically bonded refractory concretes

- Gunned refractories
- Moldable refractories
    - Plastic masses
    - Ramming masses
- Refractory mortars

According to the bonding system:

- Ceramic
- Hydraulic
- Organic-chemical
- Inorganic-chemical
- Inorganic-organic-chemical

Alumina and alumina-silicate refractory castables may further be classified in many ways.

According to their cement content:

- Medium cement castables (MCC) with > 2,5 %w CaO
- Low cement castables (LCC) with > 1 and < 2,5 %w CaO
- Ultra low cement castables (ULCC) with > 0,2 and < 1,0 %w CaO
- No cement castables (NCC) with < 0,2 %w CaO

Chemistry and/or mineralogy

- Alumina content/refractoriness
- Mineral base

Density/thermal insulating value

- Dense (>1920 kg/m^3)
- Medium weight (1600-1920 kg/m^3)
- Light weight/insulating (<1600 kg/m^3)

Flow/placement characteristics

- Vibrating
- Casting
- Free-flow
- Shotcrete

2.3.2 Components

As said before, refractory castables or concretes are combinations of refractory aggregates (40-80%), modifiers (5-30%), bonding agents (2-50%) and admixtures (<1%). [2]

Refractory aggregates. They constitute the basic skeleton of the castable and account for the largest amount of the formulation. Their size can range from 20 mm to 300 µm according to the desired particle size distribution. [2].

Modifiers. In order to achieve other desired properties and attributes such as expansion control, bond enhancement, etc., modifiers are added to the castable composition. [2]

Table Common Refractory Fillers and Modifiers [2]

Filler/Modifier	Chemical formula	Function
Fine milled aggregates	Various	Chemistry/mineralogy adjustment, bond modification/development
Alumina		
Calcined	α-Al_2O_3	Chemistry adjustment, bond modification/development

Reactive	α-Al_2O_3	Flow/rheology control, bond modification/development
Silica		
Quartz	SiO_2	Shrinkage control (aprox. 800 °C)
Fume	SiO_2	Flow/rheology characteristics, bond modification/development
Kyanite	$3Al_2O_3*3SiO_2$	Shrinkage control (1325°-1410°C), chemistry/mineralogy adjustment
Clay	Hydrated alumino-silicate	Filler, flow/rheology control
Zircon	$ZrSiO_4$	Reduce metal, slag, alkali attack
Graphite/Carbon	C	Reduce metal, slag attack
Fly ash	Varies	Low-temperature filler

Bonding agents [2-5]. There are various types of bonding agents which can be divided into the following categories: ceramic, hydraulic, organic and chemical bonding agents.

In hydraulic binders, the most common reactions during the hydration of calcium aluminate cements are the formation of CAH_{10} which occur at room temperatures lower than 20 °C.

$$CaO \cdot Al_2O_3 + 10H_2O \rightarrow CaO \cdot Al_2O_3 \cdot 10H_2O$$

At higher temperatures the hydrate phases are not thermodynamically stable, because the conversion to C_2AH_8 may occur. [5]

$$2[CaO \cdot Al_2O_3] + 11H_2O \rightarrow 2CaO \cdot Al_2O_3 \cdot 8H_2O + Al_2O_3 \cdot 3H_2O$$

In alumino-silicate castables systems, calcium aluminate cements are still the principal bonding agents. Nevertheless when CaO is present in the refractory composition it reduces refractory properties of materials consisting of Al_2O_3-SiO_2 and Al_2O_3-MgO systems. In some studies made by M. R. Ismael et. al. [5] colloidal silica is used as bonding agent and it has been reported that it improves mechanical resistance compared with materials containing calcium aluminate cements. They also present an important increase in mechanical resistance at elevated temperatures (750-1500°C) due to possible formation of mullite.

During curing and drying is in the matrix where the highest amount of porosity is produced, due to the decomposition of the hydrates and liberation of water.

To prevent explosion sometimes organic fibers are added to allow the exit of water at higher velocity. [2]

2.4 Alumina-silicate based refractories

In alumina and alumina-silicate based refractory castables, microsilica has become a common ingredient. That is because microsilica is known for its positive effect on the flowability of the material, the decreasing of its porosity and the formation of mullite at very high temperatures. In addition, microsilica has the ability to react and form strong bonds at both relatively low and high temperatures. Nevertheless, it has been shown that at temperatures above 1000 °C the silica containing castables softens and loose strength probably caused by transfer of lime from the cement of the castable. It can be solved by maintaining the microsilica addition above a certain limit (it has been shown in literature that the adequate microsilica content is lower that 3% in LCC [6-7]) and lower the cement content. By doing so, a mullite forming reaction may occur which can be proved when the strength increases at temperatures above 1300 °C. [8] Usually, microsilica particles have an average size of 0.15 microns and are an amorphous form of silica which may contain smaller quantities of impurities like C, Na or K formed along the production route. [6]

The silica-alumina refractories are materials which are broadly used because of in-situ formation of mullite. These refractories can be used in many applications such as: coating of laboratory furnaces, refractory supports, thermal insulating, industrial ceramics and pottery, etc. [9-10] In the work made by K. Ghanbari Ahari et. al. [10] it was reported that alumina did not form a hydrated compound with silica under the conditions the experiments were performed. Mixing fumed silica with hydratable alumina or reactive magnesia may lead during firing to formation of compounds with high melting point, such as mullite or forsterite, in the bond phase of monolithic refractories.

2.5 Structure and properties of mullite

The importance of mullite can be explained by its high thermal stability and the favorable properties like low thermal expansion and conductivity, high creep resistance, high corrosion stability and strength and fracture toughness. As well as the fact that the starting materials are available in big quantities on earth. [13-14]

The average structure of mullite can be derived from the closely related but structurally more simple sillimanite. Mullite can be derived from sillimanite by a coupled substitution.

2.6 Low cement castables

Refractory castables bonded with CAC need careful drying procedures to prevent spalling, especially when curing at temperatures below 20 °C. When the refractory starts to harden, the CAC dissolves in water and releases calcium, aluminum and hydroxyl ions. The structure is hardened when these ions form calcium aluminate hydrates. [15] Complete hydration of cement phases not only increases the mechanical strength of castables but also decreases the content of free water retained within the castable. On the other hand, under partial hydration, the cement that has not reacted does not play an important role in the development of green mechanical strength and leaves free water available to promote steam pressurization. That is why curing time is an important aspect in the processing of refractory castables based on calcium aluminate cements. [16]

Since the high lime content of high cement castables leads to the formation of low melting phases such as anorthite and gehlenite at elevated temperatures, they may cause volumetric expansion [17] and they are usually porous and open textured. Due to the large amounts of water required many researchers have found themselves in the necessity to develop low cement castables with better properties.[18] Because lower cement contents means longer working time, less water demand and better mechanical strength. [19] Despite magnesia-alumina castables are not the main topic of this research work it is important to mention that when silica is added to this type of materials, it reacts with alumina and magnesia to produce glassy phases that reduce volumetric expansion. These chemical interactions play an important role in the castable's elastic modulus behavior. [17]

2.7 Corrosion

1.7.1 Definition

Corrosion resistance is one of the most important features of refractory castables, since they are commonly exposed to molten liquid oxides. It is caused by mechanisms such as dissolution in contact with liquid, penetration of the vapor or liquid in the pores, etc. [3]

The corrosion process can be defined according to literature as an interaction (which involves phenomena of dissolution and precipitation of new crystalline compounds) between a solid phase and a fluid phase that has a negative effect to either of the phases. [11-12] This process also leads to the degradation of the material surfaces or grain boundaries, as a consequence of chemical attack by a corroding fluid, and to a decrease in the strength of the structure. [1, 20]

Corrosion by liquid oxides is one of the most severe modes of degradations which limit the lifetime of the refractory linings. In lining materials in contact with slag during ladle refining of steel is usually described in three major categories: dissolution, penetration and erosion. [11-12, 21-22] In literature is mentioned that microstructures of corroded refractories have the following features to be considered before interpreting them:

- They are multi-component and heterogeneous ceramics.
- The microscopic observations are carried at room temperature and there are certain vitreous phases existing at very high temperatures and they evolve once the material starts to cool. [11]

CHAPTER 3

BACKGROUND

3.1 Corrosion

J. Porier et. al. [11] did a research work comparing two high alumina refractory materials based on andalusite and bauxite. The post-mortem analysis of the crucibles permitted the identification of four zones: the slag zone, the precipitation zone, the penetration zone and the unaffected refractory zone.

The slag zone. A glassy slag layer was observed at the bottom of the crucible. Its composition changed with a decrease in CaO and an enrichment in SiO_2.

The precipitation zone. It is formed by a succession of monomineral layers (corundum, calcium hexaaluminate and calcium dialuminate) of crystals surrounded by glass.

The penetration zone. It was found that the slag invaded the matrix by capillary penetration and mixes with the intergranular liquid by diffusion.

The refractory zone. This zone is composed of unaffected bauxite or andalusite refractories.

Shaowei Zhang et al. [21] said that in general, the dissolution of Al_2O_3 into lime-alumina-silica slags can be homogeneous or heterogeneous. Homogeinity means that between Al_2O_3 and molten slag as ions from the Al_2O_3 dissolve directly into the melt; on the other hand, heterogeneity occurs when one or more solid reaction products form at the Al_2O_3/slag interface separating the oxide from the slag.

Charles A. Schacht [3] in his work explains the case of two high alumina refractory bricks (70% and 90% alumina) interacting with a silica-alumina-lime slag. Using a phase diagram he was able to predict, for example, that the slag and the refractory composition produce liquid phases whenever they are in contact and they reach the temperature of 1265 °C. He also proposed a corrosion process for a 70% alumina brick: a) the slag coated the surface of the hot refractory, and corrosion began as the surface temperature exceeded about 1265-1380°C. The reaction can be expressed in words as “Calcium (iron) alumino-silicate slag reacts with 70% alumina refractory forming a gehlenite-anorthite glass with solution of mullite and bauxite in the slag.” b) Slag penetrated the refractory, filling the pores with liquid and dissolving the bond phase (mullite) until the local CaO content of the slag dropped below about 20%. Behind this area, mullite reappeared and exhibited crystal growth to a progressively lower extent until the freeze plane for slag in the brick was attained.

Shaowei Zhang, et. al. [21] studied the dissolution of commercial white fused and tabular Al_2O_3 grains into a model silicate slag. They found that unsaturated slags, with respect to Al_2O_3 dissolved both types of alumina at 1450ºC and 1600ºC. Some layers, such as CA_6 and hercynitic spinel were found at the Al_2O_3/slag interfaces. Compared with the CA_6 layers the spinel layers were not continuous, and they had no significant effect on the dissolution process, although their formation at temperature might have increased the slag viscosity in the boundary layer and helped decrease slag penetration.

Salah A. Abo-El-Enein et. al. [23] performed a research work in which bauxite-based and kaolin-based refractory castables were carefully prepared with a binder mixture of 80% alumina and MA-spinel either preformed or in situ. The microstructure and refractory properties were determined with XRD analysis, permanent linear changes, SEM, EDS and the RUL test. From this investigation and according to the XRD patterns it was concluded that a corundum phase and a mullite phase is formed in all of the bauxite-based castable samples. The studied specimens showed positive PLC and good volume stability. In general, the investigated castable samples showed a somewhat decrease in penetration by the molten slag and a light increase in corrosion as the spinel content increases.

Houng-Yi Yang and C. F. Chan [24] reported that Cr_2O_3-containing high-alumina refractories have better slag resistance than those with no content of Cr_2O_3 due to the formation of a dense Cr-spinel layer at the slag/refractory interface at the temperature of the slag test. It was also reported a formation of a Cr_2O_3-Al_2O_3 solid solution, which reinforced the bonding matrix.

3.2 Hypothesis

According to the CaO-SiO_2-Al_2O_3 phase diagram, it appears that at 1400 °C the refractory castable will react with the slag and there will be the presence of corrosive liquids.

3.3 General Objective

Determine the corrosion mechanisms in presence of slag obtained from a steel furnace.

2.3.1 Specific objectives

- Obtain the samples of different refractory castables.
- Perform the penetration and attack test with the slag (according with DIN or ASTM).
- Characterize the samples by XRD and SEM.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Materials

Three commercial refractory castables (A, B, D) were selected with the purpose of studying their properties and to determine their corrosion mechanisms under the influence of slag from a foundry.

The chemical compositions of each castable and slag were determined using the X-Ray Fluorescence technique, the results obtained can be seen on Tables 4.1.1 to 4.1.4.

Table 4.1.1 Chemical composition of castable A

Component	Percentage
SiO2	5,07
Al2O3	86,96
Fe2O3	0,15
CaO	1,39
MgO	5,85
Na2O	0,41
ZrO2	0,17
Summe	100,00

Table 4.1.2 Chemical composition of castable B

Component	Percentage
SiO2	6,42
Al2O3	91,31
Fe2O3	0,11
CaO	1,39
Na2O	0,59
ZrO2	0,19
Summe	100,00

Table 4.1.3 Chemical composition of castable D

Component	Percentage
SiO2	5,76
Al2O3	91,86
Fe2O3	0,11
CaO	1,50
Na2O	0,56
ZrO2	0,21
Total	**100,00**

Table 4.1.4 Chemical composition of slag

Component	Percentage
SiO2	9,08
Al2O3	2,52
Fe2O3	7,93
TiO2	1,00
CaO	58,76
MgO	4,28
K2O	0,14
Na2O	0,06
MnO	0,20
P2O5	0,08
ZrO2	0,01

SO3	14,48
F	1,41
Cl	0,03
SrO	0,02
Summe	100,00

The mineralogical composition was determined by X-ray diffraction and the melting point of the slag was obtained by heating microscope, which consist in a non-contact technique that based upon an advanced image analysis of a specimen subjected to a thermal treatment.

4.2 Production of samples

Using the ball-in-hand test (ASTM-C860) it was determined that the required amount of water the castables needed was 4.5 wt%. The specimens were fabricated according to the following procedure (ASTM-C862):

- The material is weighed including the correct amount of water.
- The mixer was turned on with a paddle attachment for 30 seconds to homogenize the mixture.
- After that time 80% of the water is added to the mixture and then it gets mixed for 5 minutes at medium velocity.
- The remaining water is added, and everything gets fold in for 2 minutes.
- The mixture was casted in the molds with a vibration time of 2 minutes
- The molds were left to cure for 24 hours and then to dry for 1 hour at 110ºC.
- Some of the specimens were sintered at 1400ºC with a dwell time of 4 hours.

4.3 Characterization of specimens after drying and sintering.

All the samples were measured to obtain their weight, length, width and height before and after sintering and with those data the linear change was calculated.

Before and after sintering, the Young's Modulus was obtained at low and high temperatures with a non-destructive technique called Resonant Frequency Damping Analysis (RFDA). The knowledge of the elastic properties of refractory products at application temperature represents fundamental information to design a performing material. This method exhibits the advantage of enabling measurements at high temperature and under different atmospheres. The sample is excited by a light mechanical impulse and oscillates with one or several resonant frequencies. The resulting signal is recorded to calculate the elastic values of the samples based on the damping behavior. (ASTM-C1198) [25-30]

After that procedure, the Modulus of Rupture at high temperatures was tested at a temperature of 1000ºC (ASTM-C583)

For the corrosion test, small cubic bricks (8x8x8cm) were produced for each material and a hole with a diameter of 40 mm was drilled in the center. Afterwards, it was filled with 50 g of slag; this test was held at a temperature of 1400ºC with a dwell time of 4 hours (ASTM-C833) [31]

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 XRD Results

In all samples Corundum, Calcium oxide and Beta Alumina were found. In the castable A, which contains MgO the spinel phase is present and the calcium oxide from the binder which indicate the presence of calcium aluminate cement as binder (see figures 5.1.1 – 5.1.3).[32-33]

No phases containing silica were found with this technique. The following hypothesis can be made: the SiO_2 does not react with the Al_2O_3, and stays in the sample as tridymite or cristobalite, it could be possible that the amount is so small, that the hkl reflections on the diffractogramm cannot be seen.

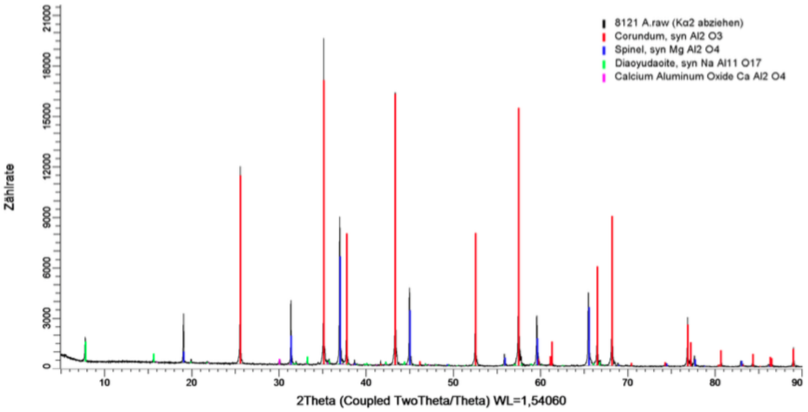


Figure 5.1.1 XRD diagram of castable A

Corundum and calcium dialuminate (CA_2) are present in castable B as main phases. It is important to mention that the CA_2 is one of phases that constituent the aluminous cements which play an important role in the hydration process of concretes. (Figure 5.1.2)

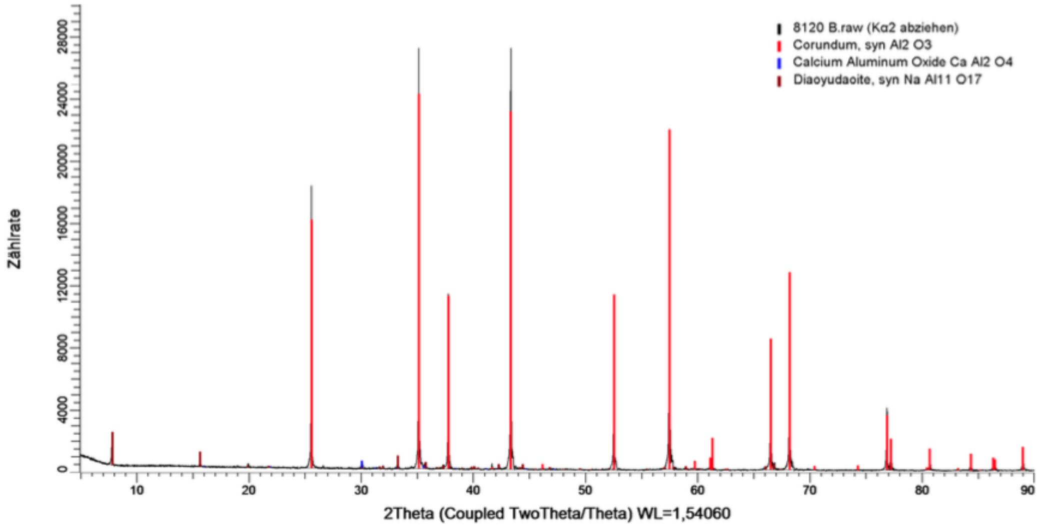


Figure 5.1.2 XRD Diagram of Castable B

In the case of castable D the mineralogical composition is seems that the other samples, corundum and calcium aluminate phases are present, see Figure 5.1.3

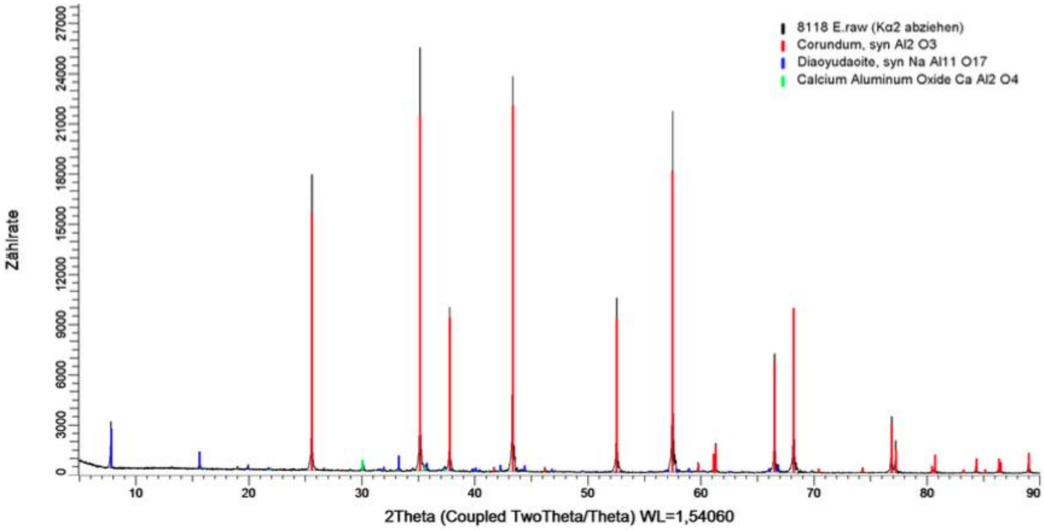


Figure 5.1.3 XRD Diagram of Castable D

5.2 Heating microscope (Slag melting point)

With the aim to know the adequate temperature for the corrosion test, the melting point to the slag was determined by heating microscope and Figure 5.2.1 shows that the slag melts between 1300 ºC and 1350 ºC. According to this result, the corrosion test temperature was set at 1400 ºC.

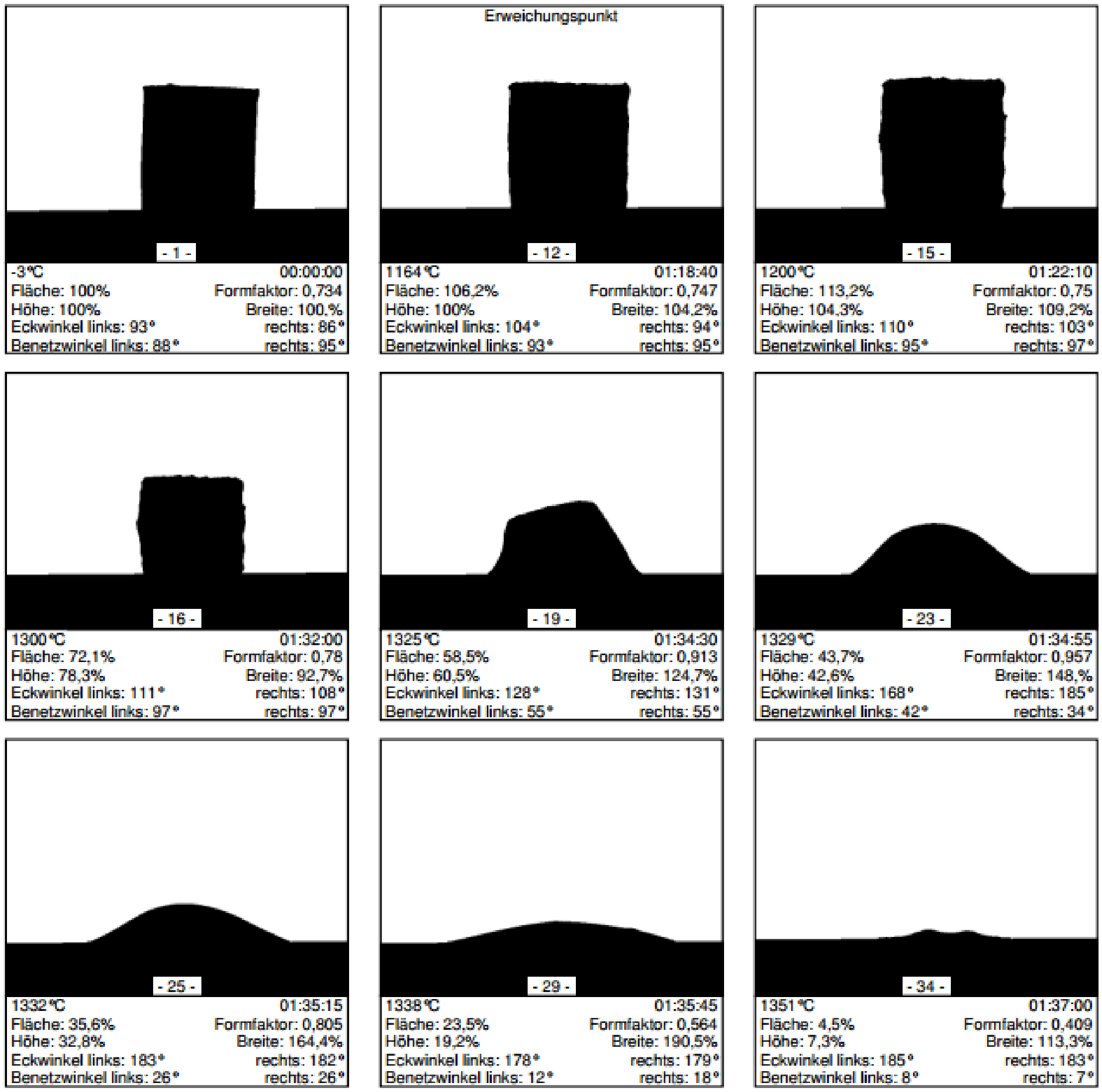


Figure 5.2.1 Heating microscope results of for slag.

5.3 RFDA Results

The results obtained in Young’s modulus and hot modulus of rupture are shown in Table 5.3.1, the value more higher was obtained for the sample B. The knowledge of the elastic properties of refractory products at application temperature represents fundamental information to design a performing material.

Table 5.3.1 RFDA and HMOR Results

	110 ºC	Sintered at 1400 ºC	1000 ºC
Material	Young’s Modulus (GPa)	Young’s Modulus (GPa)	HMOR (MPa)
A	62.075	135.88	15.452
B	54.086	134.484	17.366
D	51.59	102.05	13.782

5.4 Corrosion test

Two main areas of dissolution can be differentiated in the refractory castables. One where every component of the refractory —matrix and aggregates— were completely dissolved and another one, in which the slag only was infiltrated in the matrix. At the bottom of the refractory, it can be observed that the phenomenon called flux line erosion occurred during the test (see figures 5.4.1 and 5.4.2).

The high level of spalling observed in the castables may have occurred due to the difference of thermal expansion coefficient between the components formed in the slag and the original material.

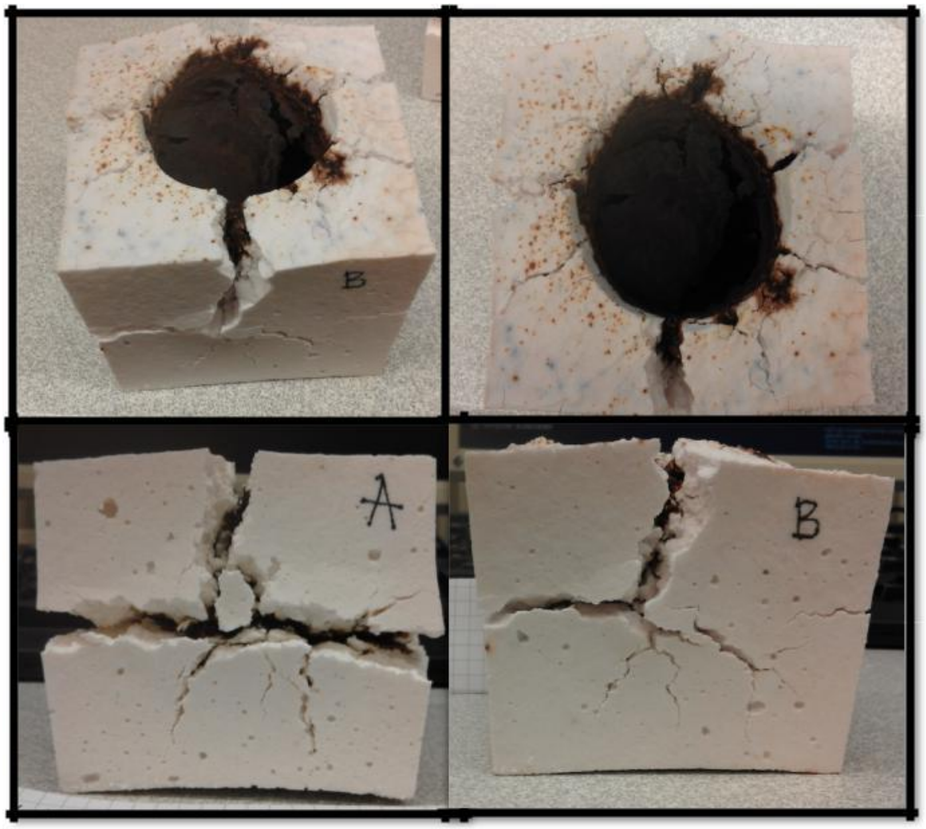
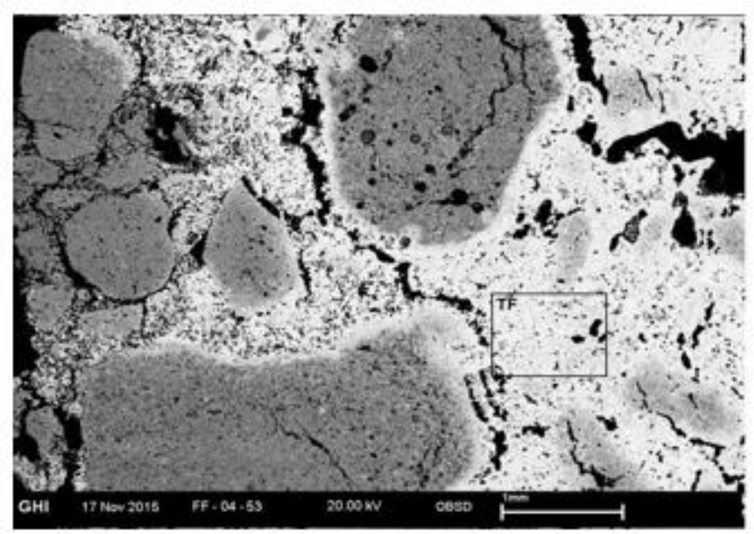


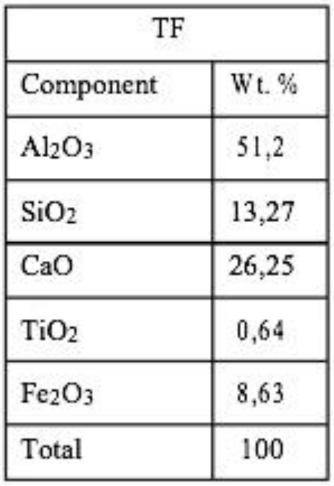
Figure 5.4.1 Specimens after test.

Figure 5.4.2 Corroded specimen.

It was possible to identify a complete dissolution of the refractory matrix and some micro-cracks in the aggregates. It can also be observed a superficial dissolution of the aggregates that may have been stopped by the formation of calcium hexaluminate, since in the literature it has been mentioned that the formation of CA_6 layers can stop the slag from infiltrating the material (Figure 5.4.3). [21, 33]

The aggregates of this material showed an initial dissolution done by the slag with a size of around 0.1 mm, and the chemical composition indicate the penetration of molten slag for the presence of high content of iron oxide coming of this.

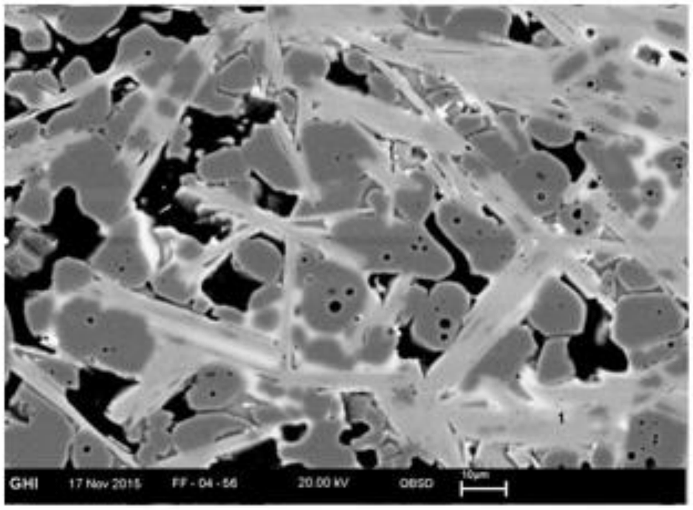


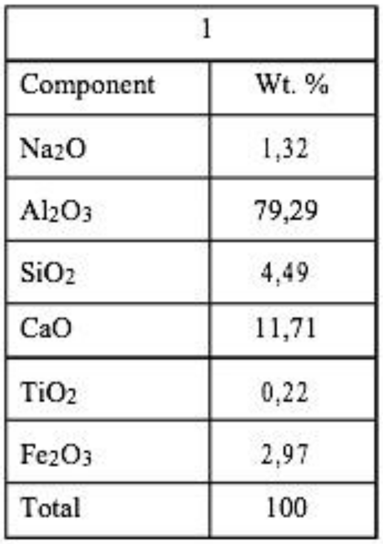


TF	
Component	Wt. %
Al_2O_3	51,2
SiO_2	13,27
CaO	26,25
TiO_2	0,64
Fe_2O_3	8,63
Total	100

Figure 5.4.3 SEM image of castable A and composition of matrix after test

In an amplification of the interface between the aggregates and the dissolved matrix in castable A, and taking into account that the slag melts at approximately 1350ºC it can be determined that the solution was liquid at the test temperature (1450 ºC) and during cooling CA_6 crystals were formed (see figure 5.4.4)

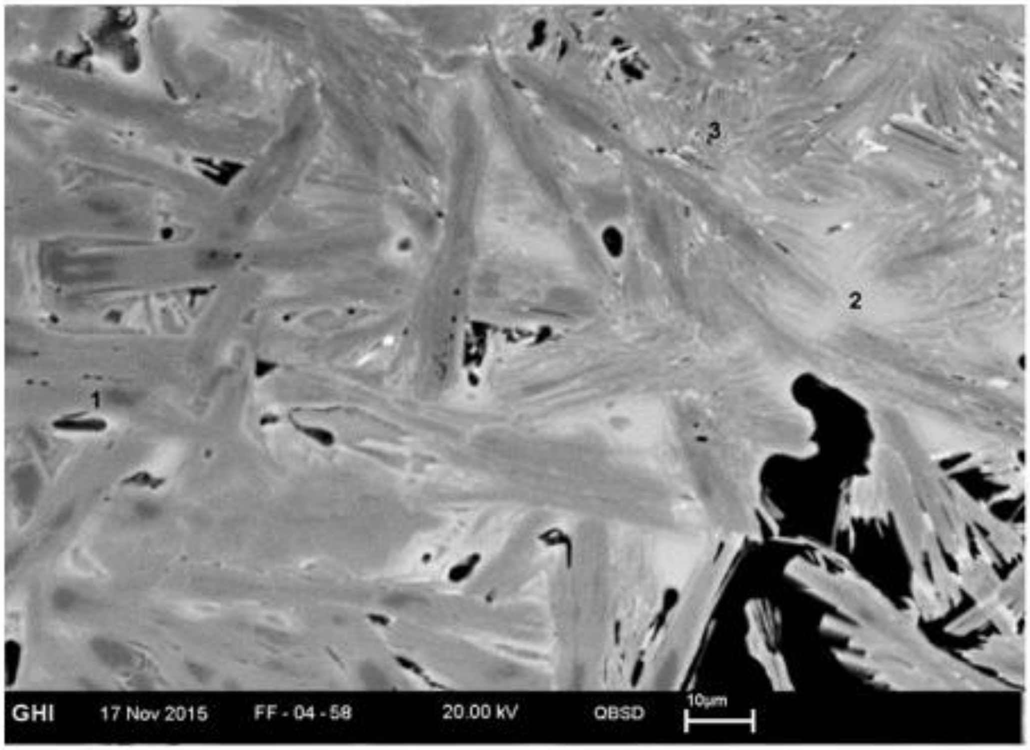


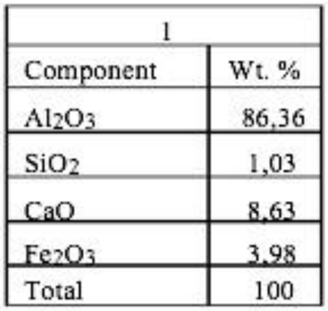


1	
Component	Wt. %
Na_2O	1,32
Al_2O_3	79,29
SiO_2	4,49
CaO	11,71
TiO_2	0,22
Fe_2O_3	2,97
Total	100

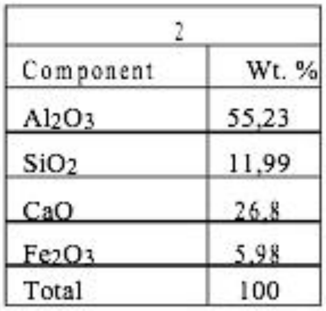
Figure 5.4.4 SEM image of interface between aggregates and dissolved matrix of castable A.

With this figure (5.4.5), it can be confirmed that the solution was liquid at 1450 ºC and the formation of a glassy phase during cooling. By determining the composition of the crystals in point 3 it was proved that they consisted of a glassy phase and CA_6 with an impurity of iron oxide.

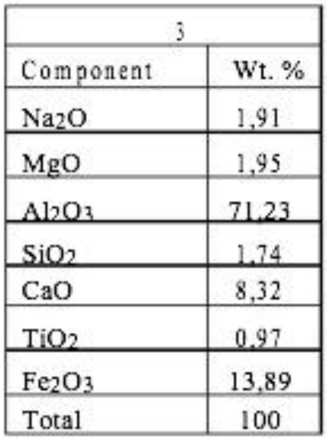




1	
Component	Wt. %
Al_2O_3	86,36
SiO_2	1,03
CaO	8,63
Fe_2O_3	3,98
Total	100



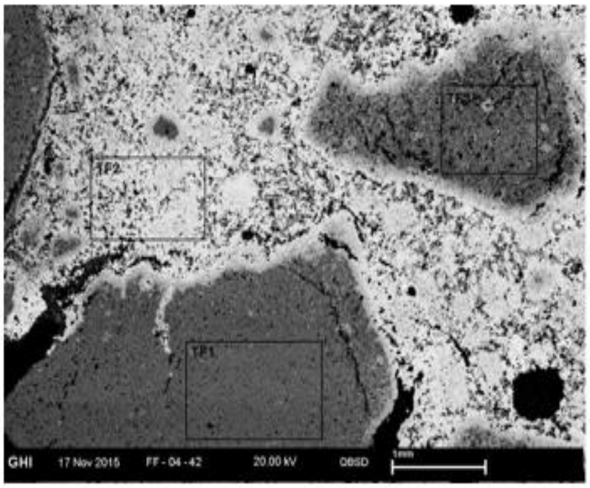
2	
Component	Wt. %
Al_2O_3	55,23
SiO_2	11,99
CaO	26,8
Fe_2O_3	5,98
Total	100



3	
Component	Wt. %
Na_2O	1,91
MgO	1,95
Al_2O_3	71,23
SiO_2	1,74
CaO	8,32
TiO_2	0,97
Fe_2O_3	13,89
Total	100

Figure 5.4.5 SEM image of interface between aggregates and dissolved matrix of castable A.

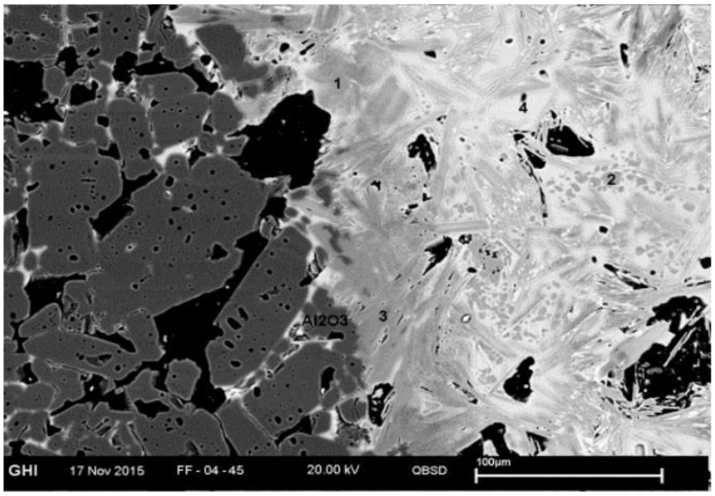
In castables B and D it was observed the same behavior as in castable A, regarding the formation of a glassy phase and calcium hexaluminate. The SEM images also show the precipitation of a phase that could be ghelenite. (Figures 5.4.6 and 5.4.7)



TF2	
Component	Wt. %
Na_2O	1,32
Al_2O_3	62,44
SiO_2	7,94
CaO	17,4
TiO_2	0,31
Fe_2O_3	10,58
Total	100

TF3	
Component	Wt. %
Na_2O	1,2
Al_2O_3	89,59
SiO_2	2,73
CaO	5,18
Fe_2O_3	1,29
Total	100

Figure 5.4.6 SEM image of castable B.



1	
Component	Wt. %
Al_2O_3	80,08
CaO	8,29
Fe_2O_3	11,63
Total	100

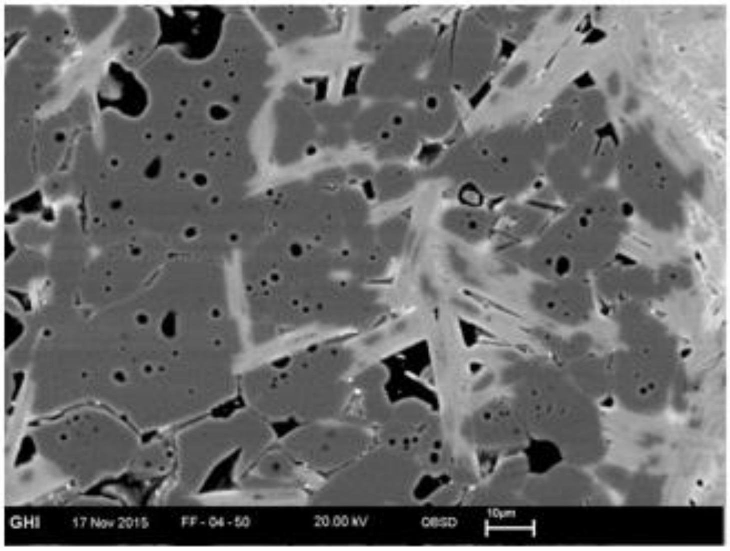
2	
Component	Wt. %
Al_2O_3	46,34
SiO_2	16,61
CaO	34,08
Fe_2O_3	2,98
Total	100

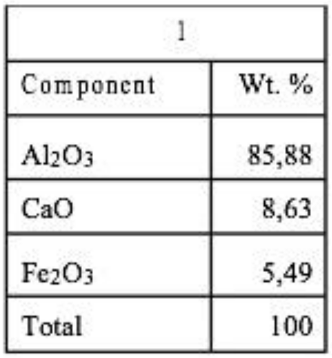
3	
Component	Wt. %
Al_2O_3	85,83
CaO	8,54
Fe_2O_3	5,63
Total	100

4	
Component	Wt. %
Al_2O_3	34,62
SiO_2	21,73
CaO	40,57
Fe_2O_3	3,08
Total	100

Figure 5.4.7 SEM image of interface between dissolved matrix and aggregates of castable B.

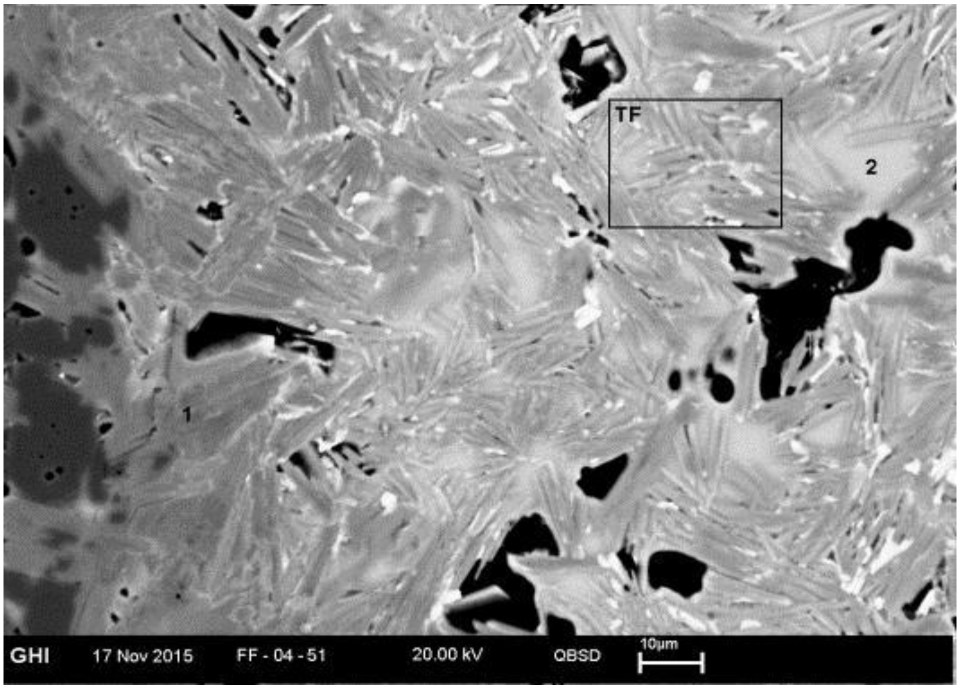
In castable D, according to the SEM images it was observed a phase rich in alumina, silica, iron and calcia, which was formed during the cooling of the material after the corrosion test (see figures 5.4.8 and 5.4.9)





1	
Component	Wt. %
Al_2O_3	85,88
CaO	8,63
Fe_2O_3	5,49
Total	100

Figure 5.4.8 SEM image of castable D



TF	
Component	Wt. %
Al_2O_3	62,46
SiO_2	6,99
CaO	15,9
Fe_2O_3	14,65
Total	100

1	
Component	Wt. %
Al_2O_3	87,11
CaO	8,51
Fe_2O_3	4,37
Total	100

2	
Component	Wt. %
Al_2O_3	34,7
SiO_2	21,54
CaO	39,73
Fe_2O_3	4,03
Total	100

Figure 5.4.9 SEM image of castable D.

5.5 Mechanism of corrosion-erosion wear

1. As mentioned in literature [11] four main regions were found in the refractory: the slag zone, the precipitation zone, the penetration zone and the refractory zone. The slag infiltrates the castables through the pores and cracks formed right after sintering dissolving the matrix producing a liquid solution, which can be defined as homogenoeus, rich in silica, calcia and alumina.

2. During cooling, due to the difference of thermal expansion coefficient between the slag-matrix solution and the undamaged refractory, several cracks and spalling are formed causing the destruction of the crucibles.

3. During cooling, as said in literature [11] the precipitation zone is formed by a succession of monomineral layers (calcium hexaaluminate) of crystals surrounded by glass. CA_6 precipitates from the slag-matrix solution preventing further penetration of the slag according to literature.

CHAPTER 6

CONCLUSIONS

Even when all materials showed low values of Young's moduli and HMOR, Materials A and B showed better mechanical properties at high temperatures than material D. In the case of castable A it could be due to the presence of preformed spinel in the mixture.

The post-mortem analysis of the specimens that were submitted to the corrosion test showed that their behavior was very similar in the three cases. All of them were completely destroyed with a high amount of spalling which could be caused by the difference of thermal expansion coefficient between the slag and the refractories.

It is suggested that the slag penetrated the castable through the pores and cracks formed during cooling right after sintering, dissolving the matrix and infiltrated to the aggregates with micro-cracks. The SEM analysis in all three cases showed the formation of calcium hexaluminate and a glassy phase rich in alumina, silica and calcia. Which lead us to infer that there was a liquid solution at 1400ºC.

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