Relationship between drying rates and mechanical properties in refractory concretes

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ABSTRACT

The effect of drying rates on compressive strength was investigated in two aluminosilicate refractory concretes with different water content, which were cured at room temperature and dried at 3 heating rates (30, 40 and 50°C/h) up to 260ºC with different holding times. The results show that the lightweight refractory concrete developed better mechanical resistance with 48% of water content and heating rate of 40ºC/h, while for dense refractory concrete the best conditions were 12% of water content with heating rates of 30ºC/h, both during 2 hours of holding time.

KEYWORDS

Refractory concrete, drying-curing process, mechanical strength.

RESUMEN

Se investigó el efecto de las velocidades de secado sobre la resistencia a la compresión en dos concretos refractarios silicoaluminosos con diferente contenido de agua, los cuales se curaron a temperatura ambiente y se secaron a 3 velocidades de calentamiento (30, 40 y 50°C/h) hasta 260°C con diferentes tiempos de permanencia. Los resultados muestran que el concreto refractario aislante desarrolló mejor resistencia con 48% de agua y velocidad de calentamiento de 40ºC/h, mientras que para el concreto refractario denso las mejores condiciones fueron 12% de agua y velocidad de calentamiento de 30ºC/h, ambos durante 2 horas de permanencia.

PALABRAS CLAVE

Concretos refractarios, procesos de curado-secado, resistencia mecánica.

INTRODUCTION

In last decades there have been great scientific/technological advances and an industrial revolution in all areas, so the need for obtaining appropriate materials that meet the process requirements of several applications have been identified. One of the materials with great importance are the refractories, and in turn the improvement of their properties. Refractory materials are usually applied to facilitate the production of other materials such as metals, ceramics, etc., because they are used as lining for ovens and high temperature reactors .[1] During their service life refractories are subjected to high temperatures that can reach up to 1900˚C. In addition, they must withstand other effects such as abrasion, erosion, and acid action, among others.

Nowadays, thanks to the incessant technological development, coupled with the desire of producers to both increase productivity and to achieve greater life of the refractory concretes,[2-9] a variety of grades can be found for several applications. The steel industry, nonferrous metal, ceramics, pottery, and petrochemicals cannot function today without the use of aluminosilicate refractory concretes.[2] Among others, the reduction in installation costs and the reduction of joints, give to refractory concrete (monolithic refractory) significant advantages in terms of service against the shaped refractory. These factors are the main causes of increased use. The largest user of these materials is the steel industry, with a consumption of 60% of world refractories production.

Some desirable properties in refractory concretes used at high mechanical and chemical resistances, and the curing-drying process play an important role in the production of products with such properties. In conventional castable refractories, water content is a factor that affects the mechanical strength of concrete bonded with calcium aluminate cements. [10-21] The smaller amount of water is expected to be added in the mixture. However, the decrease in water content affects their resistance due to their insufficiency to achieve the cement hydration, and flowability, too low hydration to obtain a well-compacted concrete.

Research regarding the curing drying of refractory concrete indicates [22] that this is a complicated process that must be carefully controlled because the final properties depend on it. The micro porous structure and capillaries avoid the release of steam and this results in an increased pressure within the material. A too fast drying rate can induce a high pressure which could generate some material degradation or explosion. On the other hand, if appropriate curing and drying processes allow to develop a strong hydraulic bonding which is a crucial factor for obtaining good mechanical properties.

This ceramic system involves the reactions of calcium aluminates with water added to the mixture to form calcium aluminates hydrates ($CaO.Al_2O_3.10H_2O$, $2CaO.Al_2O_3.8H_2O$, and $2CaO. Al_2O_3.xH_2O$) and hydrated alumina ($Al_2O_3.3H_2O$ and $Al_2O_3.H_2O$). The most common reactions during the hydration of calcium aluminate cements are presented in table I. During the drying process, water elimination, occurs in several steps. At low temperature, the dry out is mainly due to the free water vaporization which markedly increases when temperature is close to 100°C. After that, the release of water occurs because of the conversion of high hydrates ($CaO.Al_2O_3.10H_2O$) to low hydrates ($2CaO.Al_2O_3.8H_2O$, $3CaO.Al_2O_3.6H_2O$). The conversion rate is a function of the water percentage added to cement/concrete, the pH of the water, cement particle size, the surface area of the matrix, chemical and mineralogical composition of cement, the reaction CaO/Al_2O_3, the temperature of the environment and the dry mixture, in addition the rate of heating during drying and curing. [22-25]

At low temperature, the strength of concrete depends largely on the quality of hydraulic bonds formed during the curing process. At high temperature, it depends on the matrix porosity created during drying. According to this, it is assumed that the concrete with high cement content requires high amounts of water, which is translated to more porosity created by the mechanical water and converting phase in the matrix. In addition, the refractory concrete experiences dimensional changes, mainly shrinkage during the stage of dehydration and phase transformations. [26]

By the present study aims to evaluate drying and curing processes in two types of commercial refractory concrete, seeking the most adequate drying conditions to provide good mechanical properties.

Table I. Hydration and drying reactions of aluminosilicate refractory concrete.

Reaction	Description (Temperature ºC)
Hydration reaction	
$CaO.Al_2O_3 + 10H_2O \rightarrow CaO.Al_2O_3.10H_2O$	< 20°C
$2[CaO.Al_2O_3] + 11H_2O \rightarrow 2CaO.Al_2O_3.8H_2O + Al_2O_3.3H_2O$	25 - 30°C
$3[CaO.Al_2O_3] + 9H_2O \rightarrow 3CaO.Al_2O_3.6H_2O + Al_2O_3.3H_2O$	25 - 30°C
Drying and curing reaction	
$6[CaO.Al_2O_3.10H_2O] \rightarrow 2[3CaO.Al_2O_3.6H_2O] + 4[Al_2O_3.3H_2O] + 36H_2O$	≈110°C
$3[2CaO. Al_2O_3.8H_2O] \rightarrow 2[3CaO.Al_2O_3.6H_2O] + Al_2O_3.3H_2O + 9H_2O$	≈110°C
$6[CaO.Al_2O_3.10H_2O] \rightarrow 2[3CaO.Al_2O_3.6H_2O] + 4[Al_2O_3.H_2O] + 46H_2O$	150 - 350°C
$3[2CaO. Al_2O_3.8H_2O] \rightarrow 2[3CaO.Al_2O_3.6H_2O] + Al_2O_3.H_2O + 11H_2O$	150 - 350°C

MATERIALS AND METHODS

Materials

Two types of commercial refractory concretes were investigated, and the chemical and mineralogical composition is presented in table II. The lightweight refractory concretes can be used at temperatures around 1100ºC and in the case of dense refractory concretes its service temperature is above 1400ºC, according to CaO-SiO_2-Al_2O_3 phase diagram (figure 1).

Table II. Chemical and mineralogical composition (wt.%) for refractory concretes.

Starting material		
	wt.%	
Compound	Lightweight refractory concrete	Dense refractory concrete
Al_2O_3	43	60
SiO_2	36	32.5
CaO	12.5	5
Fe_2O_3	4.5	1.5
Others	<4.0	<1.0
XRD analysis (Cristalline phase intensity)		
Quartz (SiO2)	xxxx	xxxx
Cristobalite	xx	xx
Corundum	xx	xxxx
Kyanite(Al_2SiO_5)	x	x
$Ca_3Al_2O_6$	xx	x

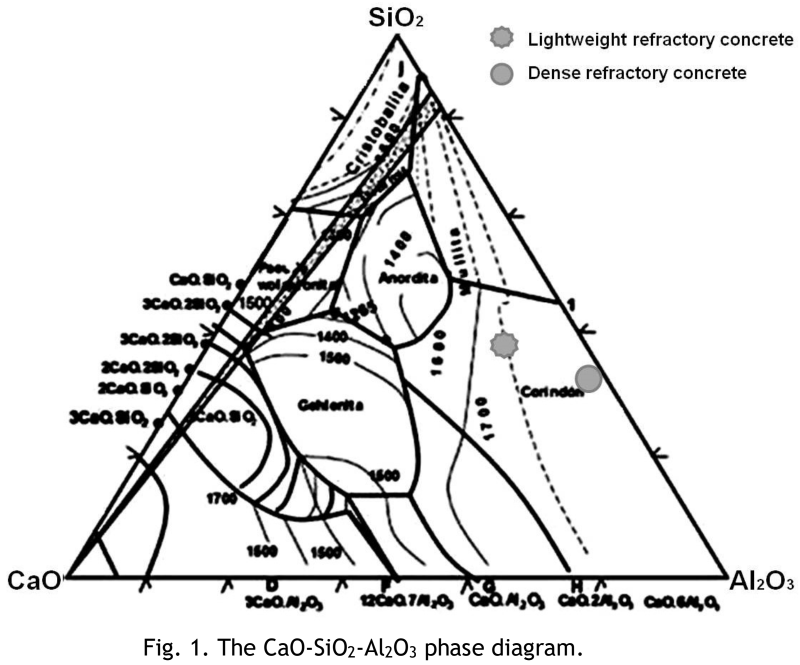

Fig. 1. The CaO-SiO_2-Al_2O_3 phase diagram.

The particle size distribution of both refractory concretes was obtained. The distribution in the lightweight refractory concrete is narrower than in denser ones, which have a wider distribution (figure 2). A wide particle size distribution with a high content of fine particles allows the obtaining materials with a high packing and to the need of small water addition to obtain a sufficient flowability necessary for casting. Narrow particle size distribution needs the addition of more water, which results in a poor packing with a high porosity.

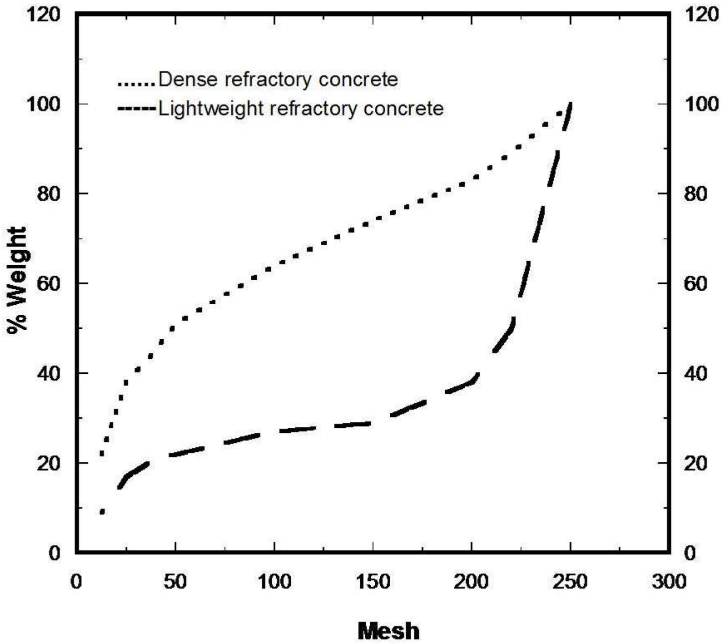

Fig. 2. Particle size distribution of lightweight and dense refractory materials.

The experimental parameters conducted are shown in table III, where the variables are heating rates, holding time, and percentage of water.

Table III. Experimental Parameters.

Specimen	Moisture (% H_2O)		Drying and curing rate (°C/h)	Holding time, (Isotherms,h)
	Dense refractory	Lightweight refractory		
A	12	48	30	1
B	12	48	40	1
C	12	48	50	1
X	14	53	30	1
Y	14	53	40	1
Z	14	53	50	1
A′	12	48	30	2
B′	12	48	40	2
C′	12	48	50	2
X′	14	53	30	2
Y′	14	53	40	2
Z′	14	53	50	2

Preparation and Characterization of the Specimen

5 x 5 x 5cm specimens were prepared for each refractory concrete, according to ASTM C-862. [27] The concretes were mixed with different percentages of water for 3 minutes, then the mixture was poured into cubic molds greased to facilitate to be demolded. Finally, the molds were covered with a plastic film to prevent the moisture loss and cured at room temperature during 24 h. Then, the specimens were weighed and dried in an oven under a controlled heating program until a temperature of 260°C was reached, according to experimental parameters presented in table III, with weight loss during treatment. The drying process was carried out using heating curves designed specifically for this study (see figure 3).

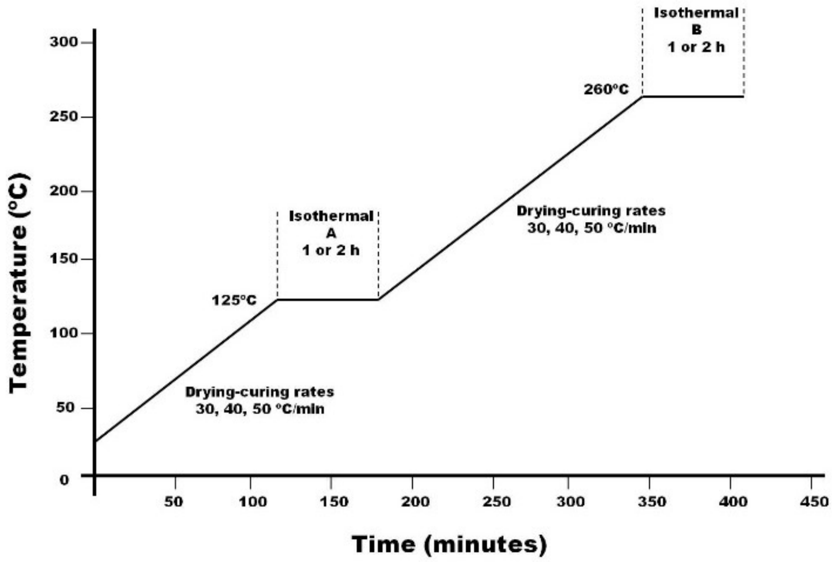

Fig. 3. Heating curve for the drying and curing processes.

The phase analysis was carried out on a Siemens D5000 diffractometer using Cu-α radiation in the range of 5-90 °, step scan 0.02 and step time 1.0 s. Measures parameters to evaluate lightweight refractory concrete by thermal analysis DTA/TGA are 100 ml/min airflow, a heating rate of 10 °C/min from room temperature to 850 °C in an air atmosphere carried in thermogravimetric analysis equipment DTA/TGA SDT 2960 V3.0F. Determination of porosity in the refractory specimens was conducted following the procedure of boiling water method (ASTM C-020). [28] The compressive strength was evaluated using 10 specimens for each formulation listed in table III and the average value was obtained. For mechanical properties, the specimens were tested in a hydraulic compression machine CONTROLS. Model: Q0701 / A, at a speed of 1 mm /s (ASTM C-133). [29]

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The results obtained by XRD showed that in lightweight refractory concrete the crystalline phases identified were quartz, cristobalite, corundum, $Ca_3Al_2O_6$, calcium aluminate C_2AH_8 ($Ca_2Al_2O_5.8H_2O$). The difference between the green and dry-cured state is mainly the hydrated calcium aluminate, due to the increased concentration of water to accomplish a complete chemical reaction (see figure 4).

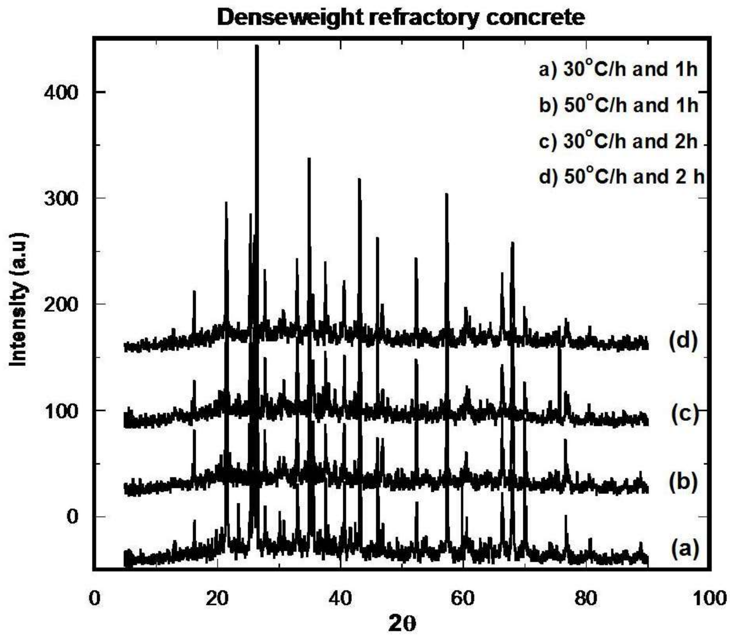

Fig. 4. XRD pattern for lightweight refractory concrete.

Figure 5 shows the XRD patterns of the dense refractory concretes which shows that the phases presented were: quartz, cristobalite, corundum, $Ca_3Al_2O_6$, calcium aluminate C_2AH_8 ($Ca_2Al_2O_5.8H_2O$), kyanite, aluminum oxide. [29]

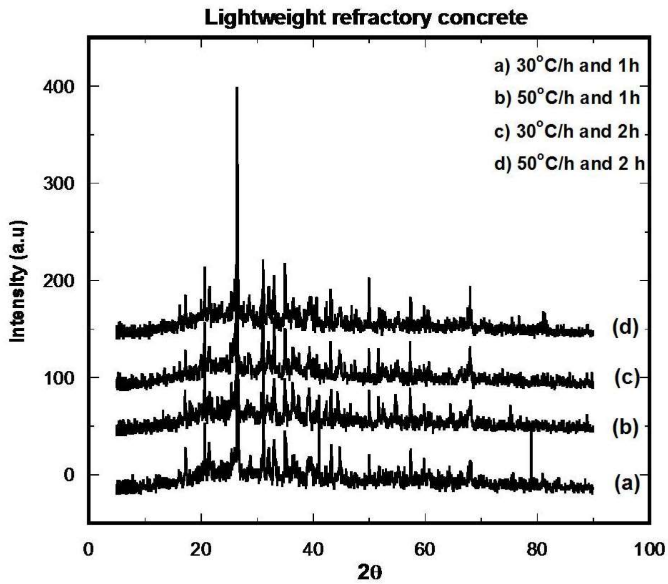

Fig. 5. XRD pattern for dense refractory concrete.

Thermal Analysis (DTA/TGA)

Thermal analysis was performed by DTA/TGA on lightweight refractory concrete since it contains the greatest amount of added water, and it is more sensible to changes during the drying process. This analysis indicates that phase transformations occur at approximately 40 °C, 90 °C, 260 °C and 290 °C. All these transformations are related to metastable compounds, the conversion of high hydrates to low hydrates. The C_3AH_6 formation takes place at temperatures above 30°C, this change relates with the changes shown in the thermogram at about 40°C. Other phase transformations are carried out at about 90°C and relate to the stabilization of calcium hydrate. At temperatures between 150-310°C several transformations and the formation of C_3AH_6 ($3CaO.Al_2O_3.6H_2O$), AH_3 ($Al_2O_3.3H_2O$) and boehmite AH ($Al_2O_3.H_2O$) occur. These phases are positive for the development of mechanical strength in the refractory concrete. C_3AH_6 hydrates ($3CaO.Al_2O_3.6H_2O$) and AH_3 ($Al_2O_3.3H_2O$) decompose completely at 350°C, these changes are associated with changes that occur in the thermograms (see figures 6 and 7).

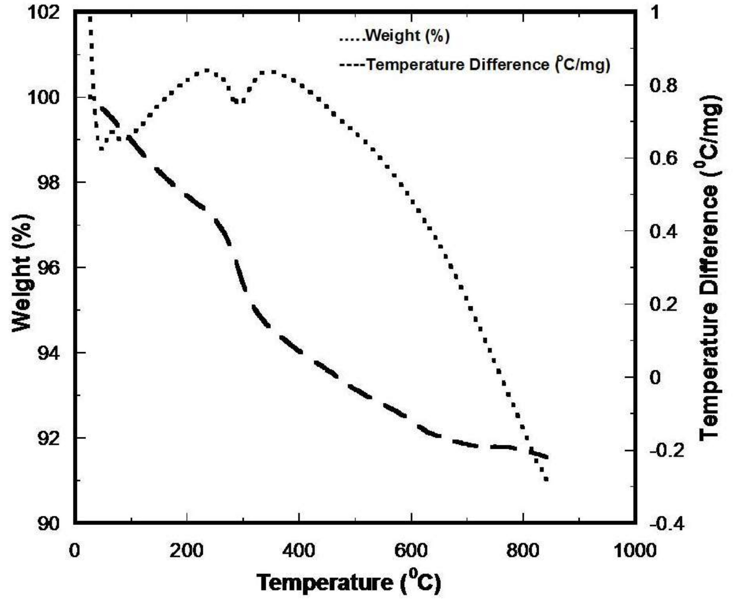

Fig. 6. Thermogram of lightweight refractory concrete after drying. Its variables are 48% moisture, holding time of 2 h and a heating rate of 30°C /h.

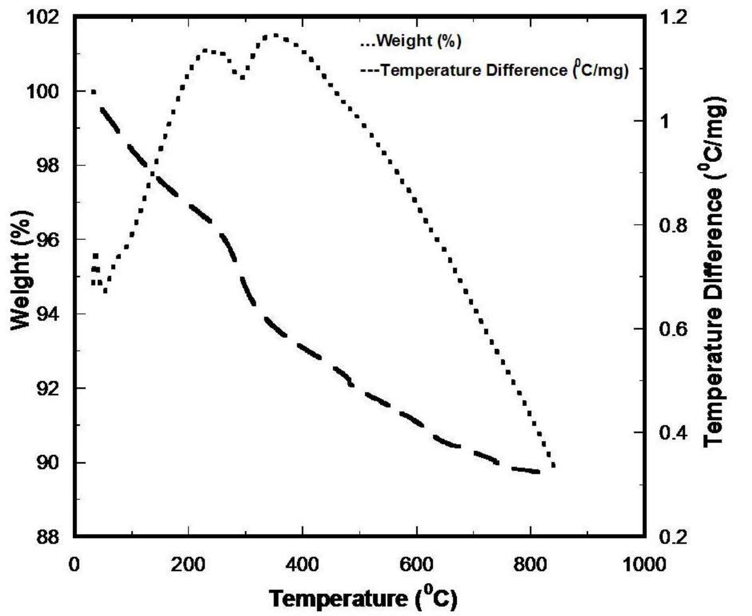

Fig. 7. Thermogram of lightweight refractory concrete after drying. Its variables are 48% moisture, holding time of 2 hours and a heating rate of 50 °C /h.

Porosity Analysis

In figures 8 and 9, porosity results in the lightweight and dense refractory concretes, are shown respectively. In both refractory concretes, the porosity is greatly affected by the amount of water added. In the lightweight refractory concrete in a drying process with an isotherm of 1 h, a characteristically behavior is shown where at higher drying rates, the trend is towards less loss of moisture. In other words, there is a decrease of porosity, thus it is assumed that some trapped moisture may still exist in the material. However, if the holding time in the isotherms is greater (2 h) and the drying rates increase, loss of moisture (porosity) tends to increase; this can be attributed to increased elimination of water through open porosity contained in the material.

In the dense refractory concrete with isotherms of 1 h the porosity tends to increase at higher drying rates; this means that there is a tendency to eject higher water content. On the other hand, with isotherms of 2 h an increase of the drying rate corresponds with a tendency towards a reduction in levels of porosity.

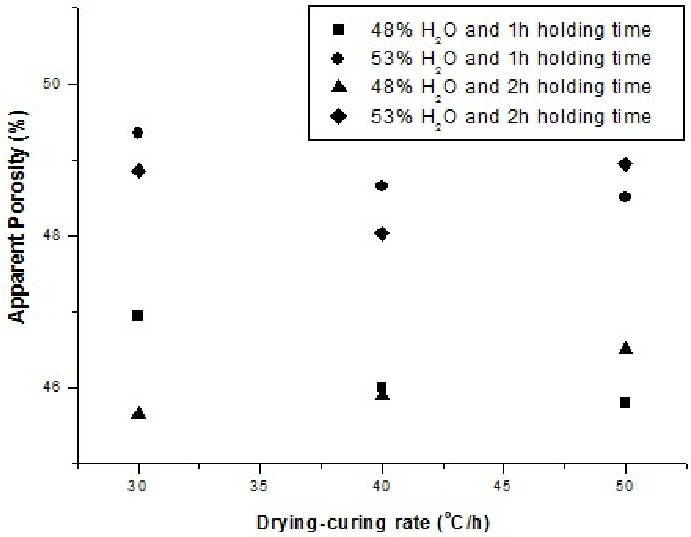

Fig. 8. Porosity vs drying-curing rates in lightweight refractory concretes.

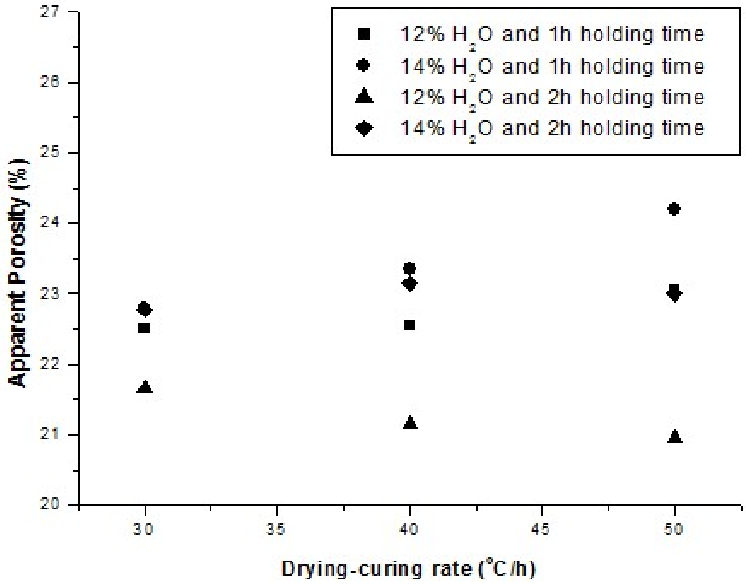

Fig. 9. Porosity vs drying-curing rates in dense refractory concretes.

Mechanical Properties

Figure 10 shows the results of the compressive strength of lightweight refractory concrete, where it notes that the mechanical strength decreases drastically when increases the percentage of moisture and decreases when increasing the drying rates. However, there is an increase in mechanical strength when the holding time (isotherms) is longer, this is because there is more time for the drying process. The optimal parameters, which reached a higher compressive strength in lightweight refractory concrete (2.793 MPa) proved to be a 48% moisture, drying rates of 40 ° C/h with an isotherm of 2 h.

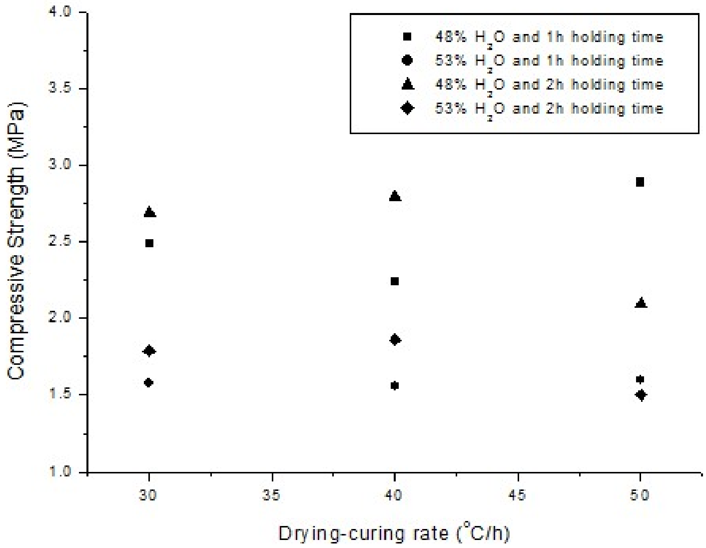

Fig. 10. Compressive strength vs drying-curing rates of lightweight refractory concrete.

The results of the compressive strength of dense refractory concrete are presented in figure 11, where again the same behavior that was observed in the lightweight refractory concrete was presented here, where there is a drastic decrease in compressive resistance with the increase of moisture. In turn, it is observed that the mechanical strength increases when the concrete remains in longer holding time. Moisture of 12% with a drying rate of 30ºC/h and an isotherm of 2 h were the optimal parameters where the highest compressive resistance was achieved for dense refractory concrete (15.91 MPa).

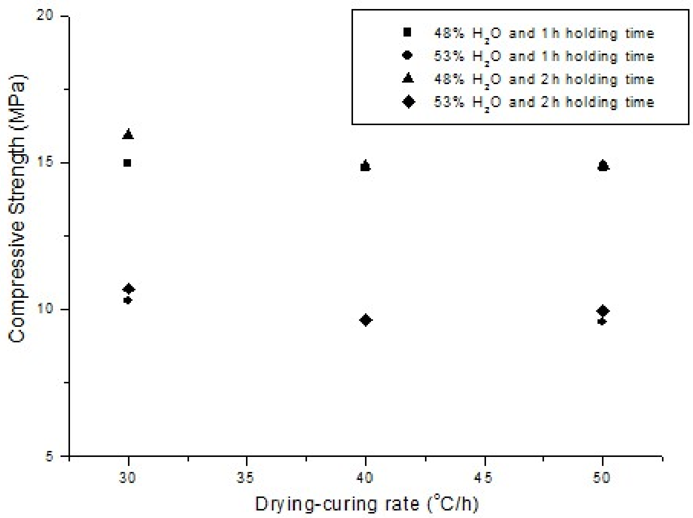

Fig. 11. Compressive strength vs drying-curing rates of dense refractory concrete.

CONCLUSIONS

Lightweight refractory concretes have high porosity due to the high concentration of water used in their preparation. Thus, increasing the drying rate results in a less loss of moisture. However, if the holding time is greater, the loss of moisture increases because it allows the elimination of water through the open porosity in the material.

Dense refractory concretes have low porosity in comparison to the lightweight refractory concretes. In this case, there was not a clear influence of drying rates on porosity content because the type of porosity registered was closed.

The mechanical strength decreases with the increasing moisture and drying rates for both types of concretes studied. Optimal parameters, which reached a higher compressive resistance in lightweight refractory concrete (2.79 MPa) proved to be a 48% moisture, drying rates of 40°C/h with an isotherm of 2 h. Moisture of 12% with a drying rate of 30ºC/h with an isotherm of 2 h were the optimal parameters where the highest compressive resistance for dense refractory concrete was achieved (15.91 MPa).

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