Study of the Thermal Durability of Refractory Mortar Prepared from Local Clay Mixed with Different Percentage of Silica

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Abstract
Refractory mortar was prepared from the mixing of locally fire clay with different percentage of silica powder (30,40,50,60)wt% by using Pyrometric Cone Equivalent PCE . According to the U.S. Standard ASTM C24, the samples were prepared by using Hand – molding method and dried at temperature 110ºC and finally firing at different temperature (1000,1100,1200,1300)ºC according to burning program to study the effect of temperatures for these specimens on the thermal durability .It was shown that the increasing in the percentage of silica content increased the durability of heat specimens, and the best degree of burn was 1300°C.

Keyword: (Refractory, Mortar, Clay, Silica, Refractoriness)

دراسة قوة التحمل الحراري للاسمنت الناري المحضر من الاطيان المحلية والمخلوط مع نسب مئوية مختلفة من السليكا

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الخلاصة:
الاسمنت الناري الذي تم تحضيره من خلال استخدام اطيان حرارية متوفرة محليا وتم خلطه مع نسب مؤية مختلفة من السليكا % (30,40,50,60) من خلال استخدام طريقة التحمل الحراري للحراريات وحسب المواصفة الامريكية (ASTM C 24) وقد استخدمت طريقة القولبة اليدوية لتحضير النماذج وبعدها تم تجفيفها في درجة حرارة (110°م) واخيرا حرقت بدرجات حرارة مختلفة (1000,1100,1200,1300°م) وحسب برنامج حرق معين لحساب قابلية تحملها الحراري في هذه الدرجات وقد اظهرت النتائج ان زيادة نسبة السليكا في الاسمنت الناري تزيد من قابليتها لتحمل درجات الحرارة، وان افضل درجة حرارة حرق كانت 1300°م.

Introduction

Ceramic Materials

Ceramic materials are often the most important technologies at the heart of practical devices [1]. Ceramics are compounds between metallic and nonmetallic element; they are most frequently oxides, nitrides, and carbides. The wide range of materials that fall within this classification includes ceramics that are composed of clay minerals, cement, and glass [2]. Most ceramics materials fall into an application-classification scheme, figure 1- presents this classification [3].

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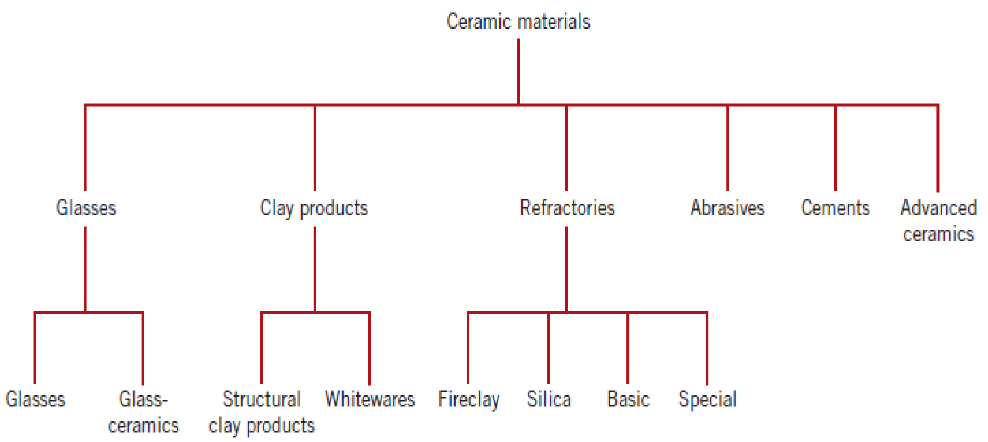

Figure 1- Ceramic classification[3]

Ceramics are typically insulative to passage of electricity and heat and are more resistant to high temperatures and harsh environments than metals and polymers. With regard to mechanical behavior, ceramics are hard but brittle [2].

Theoretical Part

Refractories, a nonmetallic material, are hard to melt at high temperature with enough mechanical strength and heat resistance to withstand rapid temperature changes, including repeated heating and cooling. They have also good corrosion and erosion resistance to molten metal, glass, slag, and hot gases etc. Because of good thermal stability of refractories they are used in kilns, furnaces, boilers, incinerator and other applications in industries like iron and steel, nonferrous metals, cement, glass, ceramics, chemicals etc.[4]

Refractory binding material is a synthetic polymeric composite used in fastening refractory bricks together and to the walls of process kiln or furnaces.[5]

Cements

In the most general sense of the word, a cement is a binder, a substance that sets and hardens independently, and can bind other materials together. Several familiar ceramic materials are classified as inorganic **cements:** cement, plaster of paris, and lime, which, as a group, are produced in extremely large quantities. The characteristic feature of these materials is that when mixed with water, they form a paste that subsequently sets and hardens.[2]

Fireclay Refractories

The primary ingredients for the fireclay refractories are high-purity fireclays, alumina and silica mixtures usually containing between 25 and 45 wt% alumina. According to Figure.(2) the SiO_2–Al_2O_3 phase diagram, It embraces the melting behavior of clay and of clay – silica mixes and indicates the reactions taking place during firing.

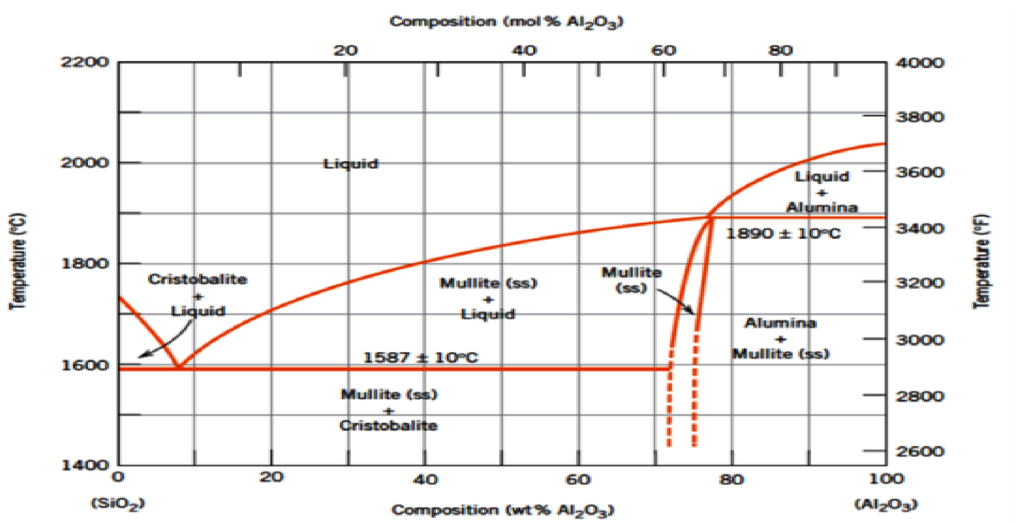

Figure 2- SiO_2–Al_2O_3 phase diagram[2]

Over this composition range the highest temperature possible without the formation of a liquid phase is 1587°C. Below this temperature the equilibrium phases present are mullite and silica (cristobalite).[2]

Refractory mortars are used in laying refractory bricks and shapes and serve the following purposes: to bond the brick-work into a solid unit so that it will be more resistant to shocks and stresses, to provide a cushion between the slightly irregular surfaces of the bricks so that one course of brick work will have a firm bearing on the course below it, and also to make a wall gastight or to prevent penetration of slag into the joints. The best mortars are combinations of a plastic clay and a volume-constant grog, as the use of raw fireclay alone as a mortar is confined to low-temperature application. Mortars are sometimes thinned with water and used as coatings for the face of the refractory walls in order to seal the joints further or to protect the wall from destructive elements in the furnace. Plastic refractory are composed of a coarse aggregate of crushed firebrick or grog bonded with plastic fireclay and are used for three general purposes. The first is for making molded refractory shapes to be used in the furnace in the green state; the second is to form a molded monolithic wall or furnace structure; and the third is to repair and patch worn brick work.[7]

Mullite. A mixture of alumina and silica, mullite is valuable because of its low thermal expansion and resistance to spalling and deformation under load. The specific composition of a given specimen depends on the method of synthesis. Mullite was used originally as a spark plug insulator. In recent years it has found extensive use in kiln furniture applications, and as liner material in tube-type furnaces.

The properties of mullite are given in Table1. The data are taken from different sources, which are identified in the table. Differences are presumed to be a result of somewhat different final compositions due to different source materials and different manufacturing procedures.[6]

Table 1-The Properties of Mullite[6]

Property	Units	Kyocera dense, K635	Coors	Materials Engineering
Density	g/cm^3	2.6	2.82	3.0–3.3
Water absorption	%	None	None	None
Coef. linear thermal expansion	$10^{-6}/K$			
25–200°C		4.6*	3.7	4.9–5.4§
25–800°C		4.8‡	4.8	
25–1000°C			5.0	
Maximum service temperature	°C	1110	1700 (no load)	1650–1700
Thermal conductivity	W/(m · K)			
20°C				
400°C		2.1†	4.1	2.39–2.51†
800°C				
Tensile strength	10^3 lb/in^2			
25°C				
1000°C				
Compressive strength	MPa (10^3 lb/in^2)			
25°C				
1000°C		(98)	551	(100–150)
Flexural strength	MPa (10^3 lb/in^2)			
25°C		(20)	186	
1000°C			151	
Modulus of elasticity	GPa		155	

*40–400°C.
†Values were converted to SI from English.
‡40–800°C.
§68–212°F.

Refractoriness

This is the ability of a refractory to withstand high temperature with no load applied. It's a degree in aluminosilicate refractories depends on the content of alumina. Refractoriness is measured by a standard technique and practically reported in Pyrometric Cone Equivalents, PCEs. The test measures the softening point of a refractory material by comparing the behavior of its test cone Figure.(3) with reference cones of standard composition designated by PCE values between 12 and 42 in the Orton series.[7]

Determination of refractoriness (PCE)

The refractoriness or softening point was determined using the method of pyrometric cone equivalence (PCE). A1600°C Electric Kiln was used for the test. The pyrometric test cones were prepared from the same moulding mass used for the cement. The test cones were mounted on a refractory plaque along with some standard cones whose softening points are slightly above or below that expected of the test cones. The triangular base was cemented to the plaque such that the edge of the test cone perpendicular to the base is vertical; and the face of the cone about which bending takes place is inclined at 82° to the horizontal. The plaque was then inserted into the electric kiln. The temperature was raised to 1200°C at the rate of 10°C per minute. The refractoriness for each test cone is the number of the standard pyrometric cone that has bent over to a similar extent as the test cone. The temperature corresponding to the cone number was read off from the ASTM.[7]

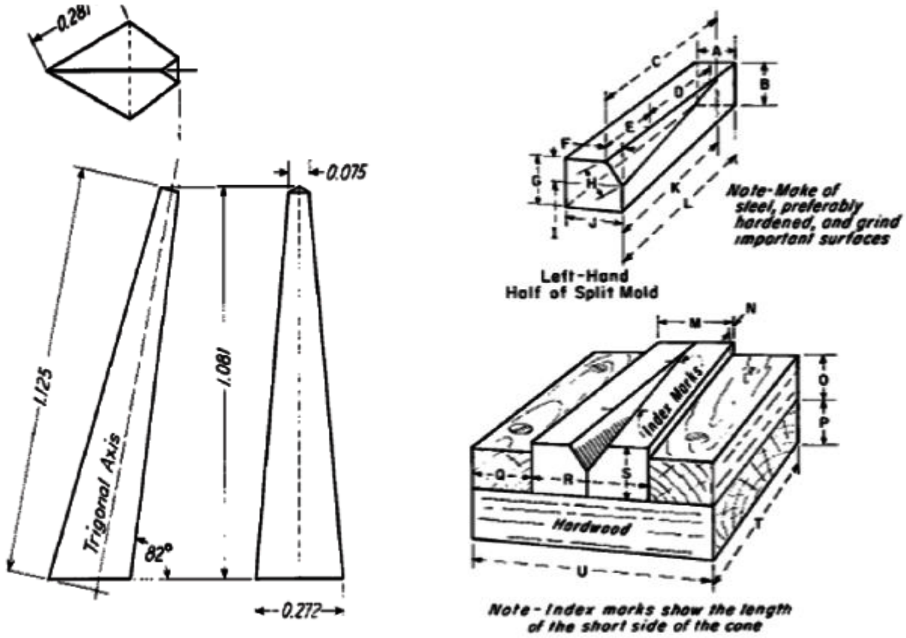

Figure 3- PCE wood Molding[7]

Experimental work

The present research has been based of Binding Materials for cement Kilns with different percentage of Silica, By using ASTM (C24) to prepare the samples with different percentage of Silica to fined the soften point of the samples with different degree of heat in the experimental work we used hand molding method to prepare the sample in shape like Zakr triangle as shown in the ASTM (C24)[8].

I've been bringing raw materials, which is a fire clays and silica sand from a company Geological Survey of the Ministry facility of Industry and Minerals, it has been crushing and grinding of raw materials through the use of electric grinder and grinding material size (212µm) to prepare the sample in form of a triangle is called a triangle Zakr as shown in ASTM C24 and was drying samples in an oven temperature of 115°C for two hours and then was burned in an oven temperature up to 1600°C and where burned samples at different temperatures to see safe temperature that works on it.

Refractoriness Test

Test cones were prepared by mixing each clay sample aggregate with sufficient quantity of water to make the clay become plastic and molded by hand into a cone shape and the composition of this mixture listed in Table (2). The samples were dried and fired to a temperature of 900°C in a furnace. Pyrometric cones designed to burned at 1000°C, 1100°C, 1200°C were placed round the samples and the temperature rose to above 1000°C at 10°C per minute. The pyrometric cone equivalent (P.C.E) of the samples was recorded to be the number of standard pyrometric cone corresponding to the time of softening to the test cone[7].

Figure 4(a)- Choosing samples of refractoriness test before firing

Figure 4(b)- Choosing samples of refractoriness test after firing

Result and Discussion

Practical experiment proved that by increasing Silica proportion in the Refractories binding increasing the durability of the degree of heat that can work on it . Figure.(4-a) Shows that four samples put in plaque, the samples before burning but in the Figure(4-b) the samples burn in four degree of heat first in 1000°C, all the samples are good except sample No.(2), so this sample work in this degree and in the 1100°C samples No.(3) failed so this sample work in this degree and as same as for the two other samples like No.(1) work in 1200°C and No.(4) work at 1300°C, because when burning the samples on 1000,1100,1200,1300C° New phases will happening:

1- In the range between 950-1100°C amorphous Silica interact with γ-Al_2O_3 to develop first Mulitte (Cryptocrystalline) with Silica.

$$\gamma\text{-}Al_2O_3+2SiO_2 \xrightarrow{950\text{-}1100°C} 3Al_2O_3.2SiO_3$$

In fact the reaction in prefix step obtain in two stage : In first stage and in 950°C formed γ-Al_2O_3 and return crystallize to Mullite in 980°C and in 100-1150°C change amorphous Silica to Cristobilite [9].

$$3Al_2O_3.2SiO_2+4SiO_2 \xrightarrow{1150°C} 3Al_2O_3.2SiO_3+4SiO_2$$

With formation glassy phase and pores.

2- In 1200°C finish development of Mullite and apparition needle shapes[10].

The XRD Figure 5 of the samples that burn in 1350°C proved that Mullite development:

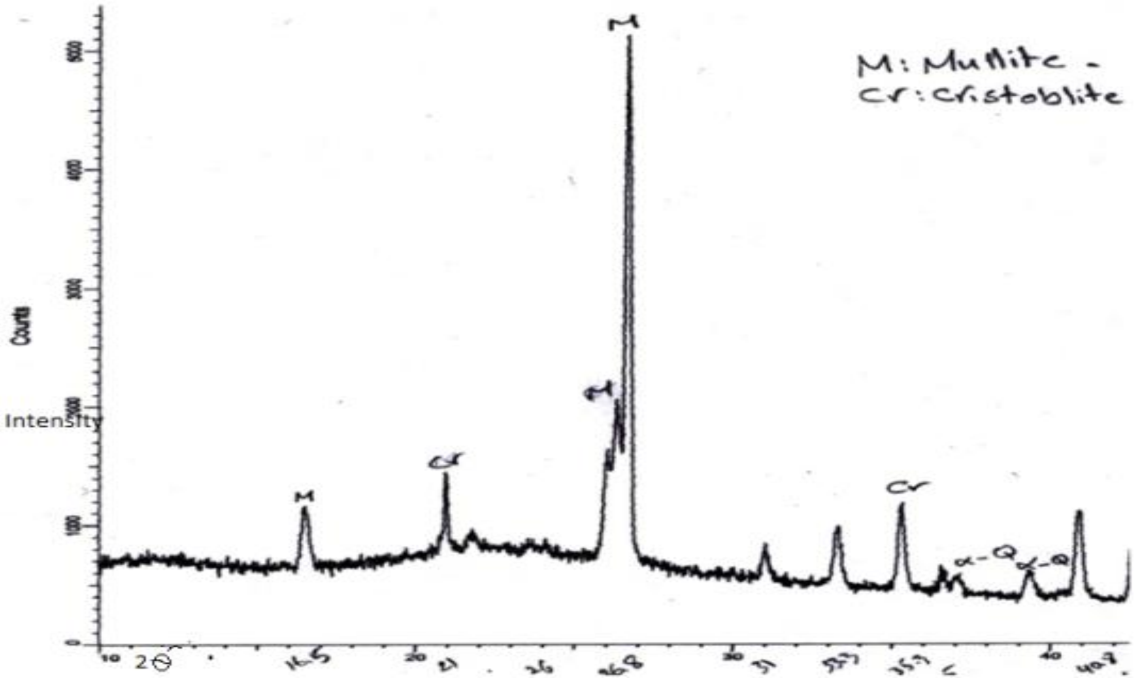

Figure 5- XRD of Burning Samples in 1350°C

Table 2-Shown the Composition of Cement Klin Refractory

No. of Sample	Fire clay g	Binder Kaolin g	Silica Sand g	Silica SiO2 wt%	Proper Degree of Work ℃
1/A	30	15	5	30 – 40	1000
2/A	25	15	10	40 – 50	1100
3/A	15	15	20	50 – 60	1200
4/A	5	15	30	60 – 70	1300

Conclusions

The good stand of samples in high firing degree return to the increase percentage of Silica in the content of SiO_2-AL_2O_3 and the second reason return to the high degree of firing Mullite phase that is formed as a result of the reaction between silica and alumina and it has a high resistance to melting and minimum thermal expansion.

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