Influence of Nano-Sized Powder Content on Thermal Properties of Waste Refractory Brick

Dr. Nabile Hassine and Hana Jamhour
Dept. of Materials and Metallurgical Engineering, Faculty of Engineering
Tripoli University

Abstract:

The present research work involved cleaning contaminated acid resistance refractory brick waste. The waste brick was crushed to 30 mm size granules, and further ground by hammer milling to 1mm. The over-sized powder (+0.355 mm) was subjected to high energy ball milling to produce nano-powder with particles sizes ranging from 45 to 51nm. Each powder batch was made up of three components; brick waste nano-powder, coarse over-sized waste brick powder, and 75 micron-sized local Sebha Kaolin clay. The pressed powder batches were then dried at a

temperature of 110 °C before being fired at 1000, 1300, and 1500 °C to produce shaped final products.

Characterization of starting refractory waste bricks, waste coarse powder, and waste nano-powder using the technique of X –Ray Diffraction (XRD) was carried out. The work also involved the measurement of thermal properties of sintered final products. Melting of a glassy phase was observed at the firing temperature of 1500 °C. The presence of this phase had a negative effect on thermal properties. Hence, based on the obtained results of the present research work, this limited the recommended maximum working temperature of the produced bricks to 1300 °C. The inclusion of 30 % of nano-sized powder particles as a component in the refractory powder batches had a positive effect on thermal conductivity of the final shaped products fired at 1300 °C. This would mean that the most suitable refractory brick powder batch is ***35 : 30 : 35*** *with the local Sebha kaolin clay playing the role as a good binding material.*

KEYWORDS: *Refractory brick, Nano-powder, High energy ball milling, Thermal properties.*

1. Introduction:

There are several steel industries that use refractory materials for their furnace linings. These ceramic liners undergo rapid temperature changes during each liquid metal pouring cycle, which introduces stress gradients leading ultimately to the nucleation and growth of cracks by a phenomenon that is generally known as thermal shock [1, 2]. Thermal shock leads to loss of stiffness, mechanical strength and overall material

degradation. The damage caused results in furnace shutdown for the replacement of brick and the result is significant economic losses in lost production time and the brick replacement. It also represents the most significant cost in the maintenance of steel production plants. Other factors contributing to damage of liners include erosion of refractory bricks because of high temperatures and wear of refractories due to chemical attack of slag [3,4].

The concept of waste minimization and recycling has gained importance in modern research with emphasis shifting towards natural resources saving and environmental protection. Approximately three million tons of spent refractory materials are generated annually in the United States of America by the ferrous, nonferrous, and glass industries [5] while in Misurata Iron and Steel Complex it is about 5000 tons [6] of spent refractory linings constitute a major percentage of the industrial waste generated by metal manufacturing plants [5]. The physical and mechanical properties of the refractory are bulk density, apparent porosity, crushing strength, refractoriness under load, thermal expansion, thermal conductivity, thermal shock resistance and modulus of deformation. These properties are expected to be improved by the nano-crystalline structure having either particle size or grain size less than about 100 nm. This structure can be obtained through a deformation processing technique such as high-energy ball milling [6].

The present research work focused on investigating the processing and thermal properties of the powder of an acid refractory brick waste after being ground and milled to the nano-crystalline size. The waste brick was obtained from the sixth furnace of Misrata Iron and Steel Complex.

Characterization of starting refractory waste powder, kaolin clay and ground powders as well as sintered shaped products was carried out via the XRD technique.

2. Experimental Work:

2.1 Powder Samples Preparation:

Six samples of acid resistance refractory brick waste were collected from Misrata Iron and Steel Complex. The selected brick (240 × 115 ×100 mm) was used in the lining of the sixth furnace which operates at a temperature of 1000 °C.

Local Sebha kaolin clay powder was collected and prepared for use as a binder in the making of experimental refractory brick samples.

The surfaces of waste brick samples were cleaned by a water saw jet, pressed using a compression machine so as the cleaned samples can be broken up into small pieces. These pieces were then crushed manually with a hammer to about 30 mm in diameter pieces. These pieces were then milled to a powder of overall particle size of about 1 mm using a hammer mill (Hammer Muehle HW1-2008, Germany). The hammer milled powder samples were passed through the different sieves **(0.355, 0.18, 0.125, 0.09, 0.045mm)** for about 25 minutes which produced various sizes of powder. The oversized particles (+**0.355 mm**) from all the six waste bricks were separated and used to produce a homogeneous sample using a homogenizing machine. The separated over-sized homogeneous powder was used later for the production of nano-powder.

Milling of the over-sized (+ 0.355 mm) refractory waste powder was performed usnig a high energy centrifugal ball mill [Model S100, Retsch GmbH]. Dry milling was carried out in a 250 ml steel jar using 4, 10, 12, and 13 mm diameter stainless steel balls. After every milling run, the steel jar would be cleaned with ethanol and silica sand to minimize iron contamination of the milled powders. The time of milling, in hours, was varied from 5 to 15, in steps of 5. The reversing operation setting is 35 seconds running time, rundown and stop for 1 second followed by a change in direction of rotation, 35 seconds running time, etc. This is repeated until the total running time has expired. The speed of the mill was set to 300 rpm. Higher speeds were practically not suitable due to increased agitation of the machine. The ratio of the weight of the steel balls to the refractory waste powder was chosen to be 10:1. As the quantity of the material to be milled should not exceed approximately 1/3 of the grinding jar volume; the jar was loaded with a fixed amount, for all runs, of 50 grams of the waste acid resistance refractory brick powder. The weight of steel balls was about 500 grams. XRD technique was used to confirm the attainment of nano–sized powder particles.

2.2. X – Ray Diffraction Analysis:

X-ray diffraction (XRD) was used to estimate the crystallite size of the milled powder particles. The XRD patterns were taken using a computerized X-ray Diffractometer (Model: PW 1800 of M/s Philips NV, Holland) at the Petroleum Research Centre, Tripoli. All X-ray diffractograms were taken by Cu-Kα radiation (wavelength, λ= 0.15405nm) at a scanning speed of 0.10 per second in 2θ. A tube voltage of 40 kV, a tube current of 30 mA, and a time constant of 10 seconds

were used. The fine powder were run at 0.0200 °θ step and scan step time of 0.5000.

Scherrer equation, $L = K\lambda / \beta \cos\theta$, was developed in 1918, to calculate the crystallite size (L) by XRD radiation of wavelength λ (nm) from measuring full width at half maximum of peaks (β) in radian located at any 2θ in the pattern. Shape factor of K can be 0.62 – 2.08 and is usually taken as about 0.89. But, if all of the peaks of a pattern are going to give a similar value of L, then $\beta \cos \theta$ must be identical. This means that for a typical 5 nm crystallite size and λ *Cu* $k\alpha_1$ = 0.15405 nm, the peak at 2θ = 170° must be more than ten times wide with respect to the peak at 2θ = 10°, which is never observed. A ***Modified Scherrer*** equation was put forward by *A. Monshi et al* [7] to provide a new approach to the kind of using Sherrer equation, so that a least squares technique can be applied to minimize the sources of errors. *Modified Scherrer* equation plots ln β against ln(1/cosθ) and obtains the intercept of a least squares line regression from which a single value of L is obtained through all of the available peaks. This novel technique is applied for calculating the average crystallite size of the milled waste refractory brick powder used in the present research work.

2.3 Sintering Trials:

Sintering is carried out on a powder mix made up of the following components:

- Acid resistance brick waste homogenization powder (+0.355 mm) used as a coarse powder component,
- Sebha kaolin clay (75µm) used as a medium particle and as a source of bonding material, and

- Nano-sized refractory waste powder with the varied weight fractions designated as N1 = 10, N2 = 20, and N3 = 30 wt %.

Three powder batches were prepared, with each batch weighing 100 grams. Mixing of the above-mentioned powder components was performed in a closed plastic container with the addition of 15 ml of distilled water. The mixing was carried out by manually shaking the closed plastic container and with the use of polyethylene balls as a mixing medium to improve blending. Polyethylene balls are suitable for mixing and blending since they are light weight and approximately soft. Hence they will not lead to crushing of the powder particles and also, any remained polyethylene in the powder mixture will be evaporated easily upon heating. The composition of the above-mentioned three powder batches is as given below;

1. **45 : N1 : 45**
2. **40 : N2 : 40**
3. **35 : N3 : 35**

The equal first and third numbers represent the fractions of the over-sized (+0.355 mm) coarse waste refractory powder and the kaolin clay powder respectivly. As mentioned above, the designations N1, N2, and N3 represent the weight fractions of the nano - sized refractory waste powder.

Compaction was carried out by pressing 100 gram of powder at a pressure of 100 bar and with a holding time of 30 minutes in a die using a hydraulic pressing machine (Model; Sassuolo, Ceramic Instruments, Italy).

The prepared shaped green bodies were dried at a temperature of 110°C for 24 hours in a drying oven (Model; Memmert, Germany). After drying, samples dimensions were measured using a vernier callipers.

The shaped green samples were initially heated from room temperature to 600°C and were held at this temperature for 45 minutes. The temperature was then increased over a time period of 90 minutes to the firing temperatures of 1000, 1300, and 1500°C and using the same soaking time for all the three temperatures of 60 minutes. The samples were then left to cool in the furnace until the following day. This heating schedule was accomplished using a Nabertherm sintering furnace. Dimensions of sintered samples were then measured using a vernier callipers. This work was carried out at the laboratories of the Industrial Research Centre, Tripoli.

2.4 Thermal Conductivity Measurement:

This was measured for all sintered samples using a Lee's Disc apparatus (Model; Griffin and Georgette TD), at the Physics Department Laboratories, Tripoli University. The test sample was in the shape of a disc of a radius 2.14 mm, [8].

2.5 Thermal Shock Resistance:

Information on the thermal shock behavior of refractories can be obtained by the use of water quenched test. This was carried out on the, disc shaped, sintered specimens which had a nano-waste powder content of 10 wt % (N1). The sintering temperature for this particular specimen was 1300 °C.

The sample was heated in a furnace at a heating rate of 10 °C/min. to a specified temperature of 1000 °C. The sample was soaked at this temperature for 1 hour to reach thermal equilibrium within the sample. It was then quenched in a water bath maintained at room temperature. Heating and quenching were repeated several times.

2.6 Thermal Expansion Coefficient Measurement:

This was carried out on the specimens sintered at 1300 °C using the Orton dilatometer [Model DIL 2016 STD, Orton Ceramic Foundation, Westerville, USA]. The Orton dilatometer is designed to automatically measure the linear change of a sample under controlled heating or cooling conditions as a function of time and temperature. The dilatometer has a structure that supports and houses a furnace, sample holder assembly, measuring head assembly, and the special Orton controller/computer to control the dilatometer operation.

The furnace heats the sample, the LVDT (an analog device that continuously measures the amount of a linear change) at the end of the probe rod monitors the sample expansion/shrinkage, and the thermocouple monitors the furnace and sample temperature. The LVDT and sample temperature signals are saved in the Orton controller/computer, and are sent to the Orton software on the personal computer system supplied by the user. The Orton software applies corrections for sample holder/probe rod movement, and the results are calculated as percent linear change (PLC) and displayed as a function of temperature. The coefficient of thermal expansion, α, could be calculated using the formula;

$$CTE_{(T1\ to\ T2)} = \frac{PLC_{at\ T2} - PLC_{at\ T1}}{T2 - T1}$$

Where

CTE = Coefficient of Thermal Expansion,

PLC = Percent Linear Change.

T1 and T2 are temperatures where T2 is higher than T1 which is usually taken as room temperature.

This work was performed at the Ceramics laboratory, Department of Materials and Metallurgical Engineering, University of Tripoli, Libya.

3. Results and Discussion :

3.1 Powder Phase Composition:

All six brick samples were thoroughly mixed in a homogenizing machine to produce one homogeneous powder sample which was milled in a high energy ball mill to produce nano–powder. This homogeneous powder sample was subjected to XRD to determine its phase composition as is shown in **table 1** and the XRD pattern in **Figure 1.**

Table 1. Phase composition of the homogenized powder sample

Specimen Number	Compound Name	Chemical Formula	SemiQuant [%]
Sample of six mixed samples	Quartz	SiO_2	39.83
	Bischofite	$MgCl_2.6H_2O$	29.20
	Mullite	$Al_6Si_2O_{13}$	30.97

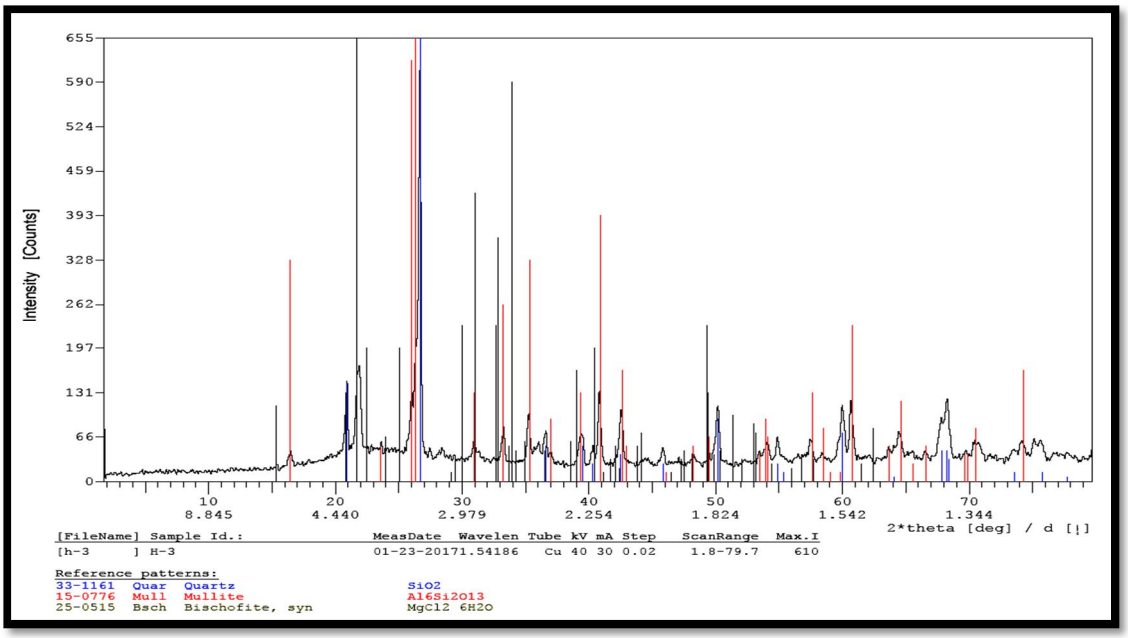

Figure 1: XRD pattern of the homogenized powder sample

3.2 Nano–Homogenized Waste Brick Powder:

The homogeneous powder sample was subjected to high energy ball milling to convert it to nano–sized powder and the results obtained are as given in **table 2**.

Table 2 Average crystallite size of homogeneous powder

Milling time (hours)	Crystallite size (nm)
5	51
10	47
15	45

The conversion of the coarse homogeneous powder to the nanometer size was found to be possible using a high energy ball milling technique using variously sized steel balls as a grinding medium. This sort of grinding medium appears to reduce the problem of the powder caking onto the sides of the mill and not receiving any further size reduction. In other words, the use of differently sized steel balls as the grinding medium seems to facilitate the subjection of powder particles to continuous impact and size reduction leading eventually to the required nano-sized particles. In the present research work, the crystallite size was successfully reduced to the size range of 51 to 45 nm over an increasing milling time from 5 to 15 hours.

The crystallite size was calculated using a *modified Scherrer* equation. The obtained sizes are all less than 100 nm and hence the powder can be considered as nano-sized and should have the potential advantages and properties improvement exhibited by nano-materials. An illustration of the computer Excel calculation of the crystallite size for the powder milled for 10 hours is shown in **Figure 2**.

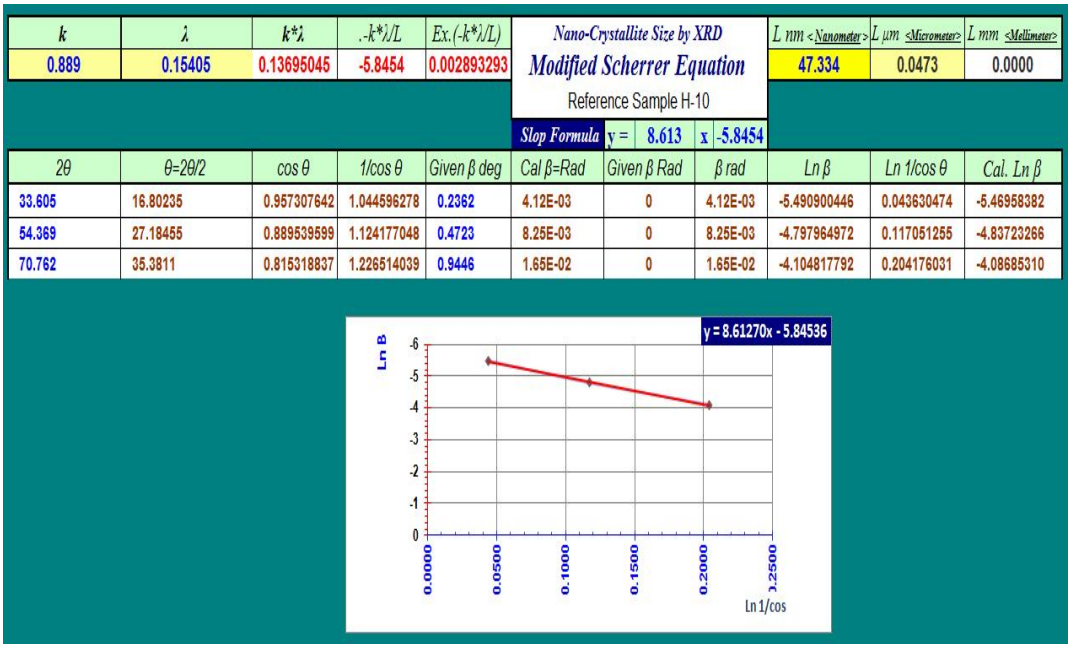

Figure 2: Computer calculation of crystallite size of nano – sized powder

Phase composition for the above mentioned three nano–powder samples are shown below in **tables 3**, **4**, and **5**.

Table 3 Phase composition of sample milled for 5 hours

Specimen No	Compound Name	Chemical Formula	Semi Quant [%]
5 hours of milling time	Quartz	SiO_2	40.91
	Bischofite	$MgCl_2.6H_2O$	30.00
	Mullite	$Al_6Si_2O_{13}$	29.09

Table 4 Phase composition of sample milled for 10 hours

Specimen No	Compound Name	Chemical Formula	Semi Quant [%]
10 hours of milling time	Quartz	SiO_2	41.67
	Bischofite	$MgCl_2.6H_2O$	27.78
	Mullite	$Al_6Si_2O_{13}$	30.55

Table 5 Phase composition of sample milled for 15 hours

Specimen No	Compound Name	Chemical Formula	Semi Quant [%]
15 hours of milling time	Quartz	SiO_2	44.12
	Bischofite	$MgCl_2.6H_2O$	34.31
	Mullite	$Al_6Si_2O_{13}$	21.57

Based on the above XRD investigative work of all powder samples mentioned above, it was found that the nanopowder milled for 10 hours was closely matching in composition the coarse over-sized (+0.355 mm) homogeneous powder. In addition, this nano–powder had the least degree of agglomeration and hence was the most suitable for preparing the three powder batches used for the sintering trials.

3.3 Thermal Conductivity of Sintered Final Products:

Thermal conductivity values obtained for the sintered final products are shown in **table 6** and plotted against firing temperature in **Figure 3**.

It can be seen that all the specimen batches fired at 1300°C show increased thermal conductivity, which then drops to very low values as firing temperature is increased to 1500°C. This may possibly be explained by the fact that a glassy phase has formed and melted at this temperature. Glass is a poor conductor of heat and hence its formation would lead to a noticeable reduction in thermal conductivity as exhibited by the obtained data.

It can be noted that for the specimens sintered at 1300°C, there is a sharp rise in thermal conductivity as the nano–powder fraction content increased from 10 to 30. High thermal conductivity would be advantageous for the use of refractory bricks leading to enhanced thermal

shock resistance and better resistance to thermal stresses. This further illustrates the potential benefits of using nano–powders as one of the essential powder batches constituents in the making of refractory bricks with highly improved thermal properties.

Table 6 Thermal conductivity measurements for sintered final products

Specimen Batches	Thermal Conductivity (J/sec.m.°C)	Firing temperature (°C)
45: N1 : 45	0.000801	1000
	0.00107	1300
	0.00069	1500
40 : N2 : 40	0.0019	1000
	2.62	1300
	0.037018	1500
35 : N3 : 35	0.0011	1000
	2.42	1300
	0.00069	1500

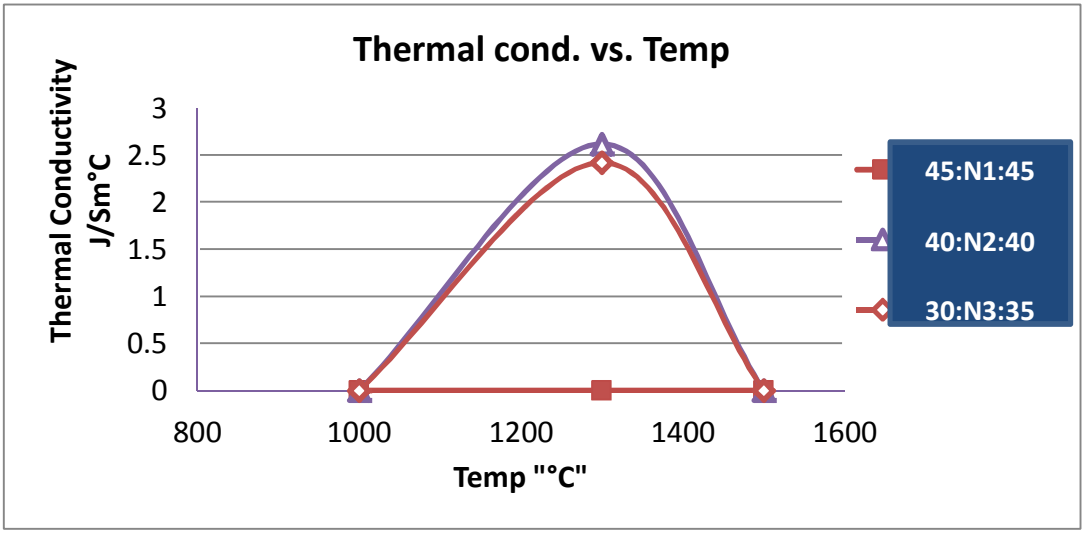

Figure 3: Thermal conductivity versus Firing Temperature

3.4 Thermal Expansion Coefficient Measurement:

It is common practice to describe the thermal expansion characteristics of a material by referring to its coefficient of thermal expansion value which is the amount of thermal expansion per degree. This was measured for the final products sintered at 1300°C and the values obtained are given in **table 7** as a function of batch composition. The obtained values are within the expected range for alumina–silica refractories, there appears to be no difference in thermal expansion coefficient values as the waste nano–powder content increased from 10 to 30 wt%.

Table 7 Coefficient of Thermal Expansion as a function of batch composition

Specimen Batch	Thermal Expansion Coefficient ($°C^{-1}$)
45 : N1 : 45	5.3×10^{-6}
40 : N2 : 40	5.4×10^{-6}
35 : N3 : 35	5.4×10^{-6}

4. CONCLUSIONS

The following conclusions may be drawn;

- Waste refractory brick piles at the Misrata Iron and Steel Complex may be reduced through the production of recycled thermal bricks which can find use for lining high temperature furnaces working at temperatures up to 1300°C. This will contribute towards having a better and cleaner environment by minimizing waste pollution.
- Nano-sized powder may be obtained by subjecting coarse waste brick powder to high energy centrifugal ball milling for 5 to 15 hours, with

the 10 hour time period being considered the optimum milling time. In addition, the powder milled for 10 hours had a composition closely matching that of the coarse over – sized (+0.355) homogenous powder.

- Melting and formation of a glassy phase were observed in the powder batches fired at a temperature of 1500°C. Additional work involving firing of shaped pure nano-powder specimens clearly showed, by visual inspection and the specimens shape loss, the occurrence of melting at the sintering temperature of 1500 °C.
- The presence of this phase had a negative effect on thermal properties. Hence, based on the obtained results of the present research work, this limited the recommended maximum working temperature of the produced bricks to 1300 °C.
- The inclusion of 30 wt % (N3) of nano-sized powder particles as a component in the refractory powder batches had the most enhancing effect on the thermal conductivity of the final shaped products fired at 1300 °C. The fired specimens maintained their shapes without undergoing any deformation, and had no cracks and no colour change, compared to the colour of the original specimens, up to 1300°C. This would mean that the most suitable refractory brick powder batch is **35 : N3 : 35** with the local Sebha kaolin clay playing the role of a good binding material.

5. ***References:***

[1] Sugita, K., "Historical Overview of Refractory Technology in the Steel Industry", Nippon Steel Technical Report No. 98, 2008.

[2] Kornmann, M., "Clay Bricks and Roof Tiles, Manufacturing and Properties", Paris: Lasim, ISBN 2 – 9517765 – 6 – X, 2007.

[3] Aderibigbe, D., " Performance Evaluation of Refractory Bricks Produced from Locally Sourced Clay Materials", J. of Applied Science and Environmental Management, pp. 151 – 157, Vol. 18, 2014.

[4] Bennett, J., and Kong, K.S., Ceramic Transactions, pp. 3-15, Vol. 132, 2002.

[5] ASTM Handbook Committee, "Powder Metal Technologies and Applications", Volume 7, 1998.

[6] Bhatia, B.A, https://pdhonline.com/courses/m158content,pdf,(2012).

[7] Monshi, A., et al., World Journal of Nano Science and Engineering, pp. 154 – 160, Vol. 2, 2012.

[8] ASTM C 202 – 93: Standard Test for Thermal Conductivity of Refractories, ASTM International, 2013.