Influence of Nano – Sized Powder Content On Physical Properties of Waste Acid Refractory Brick

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ABSTRACT

The present research work involved cleaning contaminated acid resistance refractory brick waste, i.e. that which was in direct contact with the furnace contents. The waste acid resistance brick was obtained from the sixth furnace of Misrata Iron and Steel Complex. The waste brick was crushed to 30 mm size granules, and further ground by hammer milling to 1 mm. The 1 mm sized powder was sieved to give over-sized (+0.355 mm) waste powder. 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 51 nm. Three powder batches were prepared. Each powder batch was made up of three components; brick waste Nano-powder, coarse over-sized (+0.355 mm) waste brick powder, and 75 micron-sized local Sebha Kaolin clay. All powder batches had equal fractions of coarse waste powder and kaolin clay. These powder batches were pressed, in a semidry state, at a pressure of **100 Pa**. The 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, Sebha kaolin clay, and waste Nano-powder using the technique of X-ray diffraction analysis (XRD) was carried out. The work also involved the measurement of physical properties; bulk density, porosity, and volume shrinkage of waste bricks and sintered final products.

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Melting of a glassy phase was observed at the firing temperature of 1500 °C. The presence of this phase had a negative effect on the physical 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 the most enhancing effect on the physical properties of bulk density, volume shrinkage, and porosity 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 of a good binding material.

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 (Walker 1986). 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 (Hasselman, 1970 pp. 1003 – 1037 and ASTM Handbook Committee, 1998).

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. While in Misrata Iron and Steel Complex it is about 5000 tons of spent refractory linings which constitute a major percentage of the industrial waste generated by metal manufacturing plants (Bennett, 2002, pp. 3-15).

The physical properties of the refractory are expected to be improved by the Nano-crystalline structure having grain size less than about 100 nm. This structure can be obtained through a deformation processing technique such as high-energy ball milling (Bhatia, 2012).

The present research work focused on investigating the processing, and the physical properties of the powder of acid refractory brick waste after being ground and milled to the Nano-crystalline size. Characterization of starting refractory waste powder, kaolin clay and ground powders as well as sintered shaped products was carried out via the XRD technique. The work also involved measuring bulk density, shrinkage, absorption of water, porosity and specific gravity.

The main objectives of the present study, in general, included;

- Investigating the influence of decreasing particle size of refractory waste powder to the Nano-size range on the physical properties of the final shaped products,
- Determination of the optimum processing conditions and shaping parameters of the final product. These parameters would include; among others, processing temperature and time, and crystallite size of waste refractory powder.

2. EXPERIMENTAL WORK

2.1 Selection of Refractory Brick Waste Samples

Six samples of acid resistance refractory brick waste were collected from Misrata Iron and Steel Complex. The selected brick ($240 \times 115 \times 100$ 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.

2.2. Cleaning and Hammer Milling of 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 are then crushed manually with a hammer to about 30mm in diameter pieces. These pieces were then milled to a powder of overall particle size of about 1 mm using a crushing hammer mill (Hammer Muehle HW1-2008, Germany).

2.3 Sizing (Sieving) and Homogenization

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 rest of the various sizes were rejected. The separated over-size powder was used later for the production of Nano-powder.

2.4 Production Of Nano - Powder

Milling of the over-sized (+0.355 mm) refractory waste powder was performed using a high energy centrifugal ball mill [Model S100, Retsch GmbH]. **Figure 1** shows a picture of this mill.



Figure 1: The centrifugal ball mill used in the present work.

Dry milling was carried out in a 250ml 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. X-Ray Diffraction (XRD) technique was used to confirm the attainment of Nano-sized powder particles.

2.5 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-K α radiation (wavelength, $\lambda = 0.15405$ nm) at a scanning speed of 0.10 per second in 20. 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 $\lambda Cu k\alpha_1 = 0.15405$ nm, the peak at $2\theta = 170^\circ$ must be more than ten times wide with respect to the peak at $2\theta = 10^\circ$, which is never observed. A *Modified Scherrer* equation was put forward by A. *Monshi et al* (Monshi, A., et al 2012, pp. 154 – 160), 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 $\ln \beta$ against $\ln (1/\cos\theta)$ 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.

2.6 Sintering Trials

2.6.1 Materials

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 $(75\mu\text{m})$ 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 %.

2.6.2. Mixing

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 manually by 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.

2.6.3 Compaction

This process 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).

2.6.4 Drying

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.

2.6.5 Sintering

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 calipers. This work was carried out at the laboratories of the Industrial Research Centre, Tripoli.

2.7 Bulk Density, Porosity, and Shrinkage Measurement

Cubic sample pieces of dimensions (50×50×50 mm) were cut from the starting six waste brick samples. The test specimens were dried to a constant weight by heating at 110 °C in a drying oven and the dry weight, D, was determined in grams to the nearest 0.1 g. The test specimens were placed in water and boiled for 2 hours. After the boiling period, the test specimens were cooled to room temperature while still completely covered with water for 12 hours. Suspended weight, S, and saturated weight with water, W, were then both determined.

Shrinkage, bulk density and apparent porosity were calculated using the formulae:

$$Volume \ s \ rinkage \\ = \frac{volume \ of \ green \ sample - volume \ of \ fired \ sample}{volume \ of \ green \ sample}$$

$$Bulk \ density = \frac{dry \ weig \ t}{bulk \ volume}$$

$$Apparent \ porosity = \frac{soaked \ weig \ t - dry \ weig \ t}{soaked \ weig \ t - suspended \ weig \ t}$$

3. RESULTS AND DISCUSSION

3.1 Powder Phase Composition

3.1.1 Refractory Waste Brick Powder

The phase composition of the six waste acid resistance refractory bricks as determined by XRD analysis is given in table (1), **the** table shows that the six waste bricks contain silica quartz, bischofite or hydrous magnesium chloride, and mullite. The latter has the formula $3Al_2O_3.2SiO_2$, i.e. it contains 72% Al_2O_3 , and its refractoriness is 1810-1850 °C. It occurs rarely in nature, but is found in many fired ceramic bodies. It forms long, needle-like crystals interlocking of which gives good mechanical. Mullite also shows a uniform thermal expansion, and its formation in a body makes for good thermal shock resistance.

Table 1: Phase Composition of waste bricks samples

Brick sample Number	Compound Name	Chemical Formula	SemiQuant [%]
	Quartz	SiO ₂	44.12
1	Bischofite	MgCl ₂ .6H ₂ O	36.27
	Mullite	Al ₆ Si ₂ O ₁₃	19.61
2	Compound Name	Chemical Formula	SemiQuant [%]
	Quartz	SiO ₂	43.49
	Bischofite	MgCl ₂ .6H ₂ O	32.29
	Mullite	$Al_6Si_2O_{13}$	24.22

	Compound Name	Chemical Formula	SemiQuant [%]
2	Quartz	SiO ₂	46.39
3	Bischofite	MgCl ₂ .6H ₂ O	22.68
	Mullite	Al ₆ Si ₂ O ₁₃	30.93
	Compound Name	Chemical Formula	SemiQuant [%]
4	Quartz	SiO ₂	43.00
7	Bischofite	MgCl ₂ .6H ₂ O	33.78
	Mullite	$Al_6Si_2O_{13}$	23.22
	Compound Name	Chemical Formula	SemiQuant [%]
5	Quartz	SiO ₂	46.36
	Bischofite	MgCl ₂ .6H ₂ O	21.85
	Mullite	$Al_6Si_2O_{13}$	31.79
	Compound Name	Chemical Formula	SemiQuant [%]
6	Quartz	SiO ₂	42.55
	Bischofite	MgCl ₂ .6H ₂ O	36.17
	Mullite	Al ₆ Si ₂ O ₁₃	21.28

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 (2).

Specimen	Compound	Chemical Formula	SemiQuant [%]
No:-	Name		
Sample of	Quartz	SiO ₂	39.83
six mixed	Bischofite	MgCl ₂ .6H ₂ O	29.20
samples	Mullite	$Al_6Si_2O_{13}$	30.97

Table 2: Phase composition of the homogenized powder sample

3.1.2 Sebha Kaolin Clay Powder

Phase composition of Sebha kaolin clay is as shown in table 3. The analysis shows the presence of some free silica.

Compound Name	Chemical Formula	SemiQuant [%]
Kaolinite	$Al_2[Si_2O_5(OH)_4]$	86.96
Quartz	SiO ₂	13.04

Table 3: Phase and oxides composition of Sebha kaolin clay.

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 4.

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

Table 4: Crystallite size of homogeneous powder

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 the modified Scherrer equation.

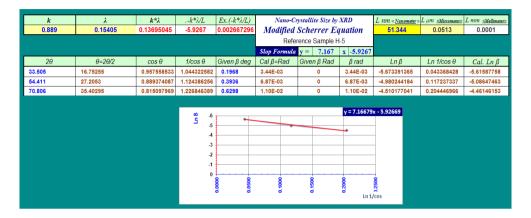


Figure 4.13 Computerized calculations of nano powder crystalline size

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 nanomaterials. An illustration of the computer software used for the calculations is shown in Figure 2.

Phase composition for the above-mentioned three nano powder samples are shown below in tables 5, 6, and 7, and Figure 3 shows the XRD pattern for the powder milled for 10 hours.

Figure 2: An illustration of the computer calculation of the crystallite size for the powder milled for 5 hours

Specimen No	Compound Name	Chemical Formula	SemiQuant [%]
5 hours of	Quartz	SiO_2	40.91
milling time	Bischofite	MgCl ₂ .6H ₂ O	30.00
	Mullite	Al ₆ Si ₂ O ₁₃	29.09

Table 5: Phase composition of sample milled for 5 hours

Table 6: Phase composition of sample milled for 10 hours

Specimen No	Compound Name	Chemical Formula	SemiQuant [%]
10 hours of	Quartz	SiO ₂	41.67
milling time	Bischofite	MgCl ₂ .6H ₂ O	27.78
	Mullite	Al ₆ Si ₂ O ₁₃	30.55

Table 7: Phase composition of sample milled for 15 hours

Specimen No	Compound Name	Chemical Formula	SemiQuant [%]
15 hours of	Quartz	SiO ₂	44.12
milling time	Bischofite	MgCl ₂ .6H ₂ O	34.31
	Mullite	$Al_6Si_2O_{13}$	21.57

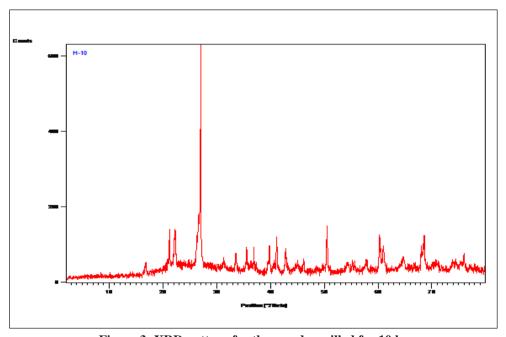


Figure 3: XRD pattern for the powder milled for 10 hours.

Based on XRD investigative work of all powder samples mentioned above, it was found that the Nano powder 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 Physical Properties Measurement

3.3.1 Acid Resistance Waste Refractory Brick

The physical properties measured included porosity, water absorption, apparent specific gravity, and bulk density.

The obtained values are for the six waste brick samples in an ascending order, labeled 1 to 6. The values are given in table 8 and presented graphically in Figures 4 and 5.

Table 8: Measured physical properties of waste brick

Brick number	Porosity (%)	Water absorption (%)	Apparent specific gravity (g/cm³)	Bulk density (g/cm³)
1	11.53	5.42	2.40	2.13
2	11.89	5.93	2.28	2.01
3	8.27	3.94	2.28	2.10
4	9.78	4.68	2.31	2.09
5	10.07	4.89	2.29	2.06
6	9.29	4.47	2.28	2.08

As can be seen from the table shown above, the six bricks seem to have almost the same values of bulk density and apparent specific gravity. However, there is a slight variation in values for the porosity and water absorption.

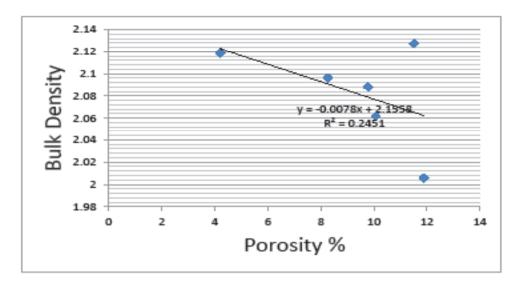


Figure 4: Variation of Bulk Density as a function of Porosity (%).

The plotted values of bulk density versus porosity show a certain degree of scatter. However, the general trend seems to show a decrease in bulk density with rising porosity as the graph above shows.

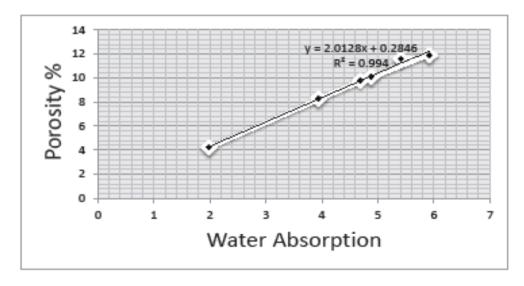


Figure 5: Porosity (%) against water absorption.

Figure 5 shows a good straight line relationship for the variation of porosity with water absorption, i.e. as would be expected, the water absorption increasing with the percentage of pores present in the brick samples.

3.3.2 Sintered Shaped Final Products

Bulk density of the sintered specimens made from three batches was measured at the three sintering temperatures. The batches contain decreasing equal proportions of the coarse homogenized waste powder and the Sebha Kaolin clay, while the third component is an increasing amount (10, 20, and 30) waste nano-powder.

The tabulated bulk density values (table 9) represent the average of three readings.

Figure 6 is a plot of bulk density against sintering temperature and it shows that for all batch compositions the bulk density increasing as the temperature of sintering increased from 1000 to 1300 °C. Further, the batch **45:10:45** had a continued increase in bulk density as the sintering temperature was increased to 1500 °C. However, there was a clear drop in bulk density at 1500 °C for the other two batches with the largest drop shown by the batch **35:30:35**. Increasing the nano powder fraction from 10 to 30 % appears to have a negative effect on bulk density at the sintering temperature of 1500 °C, and so the amount of nano powder in the batch should not go beyond 10 % for the bulk density values to remain high.

It must also be mentioned that the sintered specimens suffered from melting of the glassy phase at the temperature of 1500 °C. This would obviously lead to a decrease in bulk density and a reduction in mechanical strength at high temperatures.

Although, it can be noted that at 1300 °C the bulk density actually increases with increasing amount of nanopowder component.

Powder Batch	(Sintering Temperature (°C	(Bulk density (g/cm ³
	1000	1.83
45:10:45	1300	1.97
	1500	2.032
	1000	1.74
40 : 20 : 40	1300	2.032
	1500	1.99
	1000	1.73
35:30:35	1300	2.065
	1500	1.91

Table 9: Bulk density of sintered products.

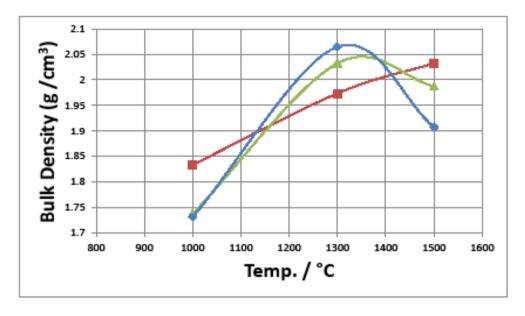


Figure 6: Bulk Density vs. Sintering Temperature for Final Products.

Volume shrinkage of sintered shaped products was measured at the three sintering temperatures and the values obtained are given in table 10 and shown graphically in Figure 7.

Table 10: Variation of volume shrinkage (%) with sintering temperature

Specimen Batch	(%) Volume Shrinkage	(Sintering Temperature (°C
45 . 10 . 45	9.08	1000
45:10:45	20.65	1300
	18.43	1500
	1.98	1000
40 : 20 : 40	23.31	1300
	9.12	1500
	5.77	1000
35:30:35	22.83	1300
	7.06	1500

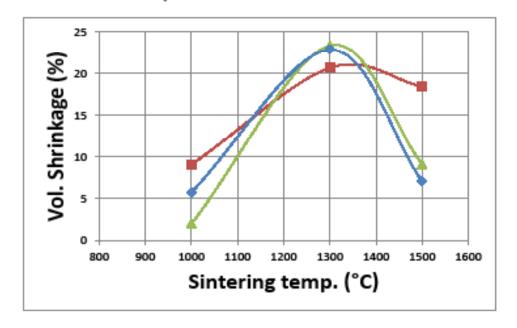


Figure 7: Volume shrinkage as a function of sintering temperature.

As can be seen from Figure 7, volume shrinkage increases for all specimen batches as the sintering temperature is raised from 1000 to 1300 °C. However, a sharp drop of shrinkage is observed when the temperature rose to 1500 °C. This may be due to the melting of increased amounts of the glassy phase which occurs at this temperature. It may also be noticed that the volume shrinkage increased as the fraction of Nano powder went up from 10 to 20. This indicates that increasing the amount of ultrafine Nano powder will lead to even higher values of volume shrinkage.

Porosity values for the sintered specimens are presented in table 11 and shown graphically in Figure 8.

All sintered specimens batches show the same trend with percentage porosity decreasing as the firing temperature increased from 1000 to 1500 °C. It should be noted that the large drop in porosity values clearly observed at the temperature of 1500 °C would be due to the formation and melting of the glassy phase. It can also be observed that increasing the fraction of Nano powder from 10 to 30 appeared to have an effect on porosity reduction, it went down from about 19.67 to 15.13 % when firing temperature was raised from 1000 to 1300 °C.

Specimen Batch	Porosity (%)	Sintering Temperature (°C)
	29.68	1000
45:10:45	19.67	1300
	5.25	1500
	32	1000
40:20:40	19.92	1300
	4.99	1500
	29.94	1000
35:30:35	15.13	1300
	9.12	1500

Table 11: Porosity measurements for the sintered final products.

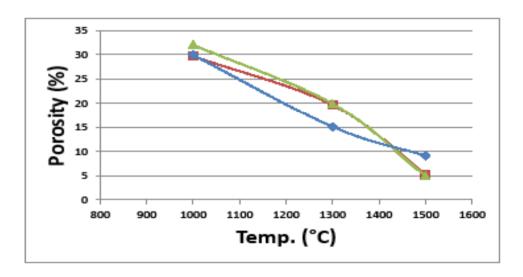


Figure 8: Porosity (%) versus sintering temperature

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 course 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 the physical 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 the physical properties of bulk density, volume shrinkage, and porosity. The fired specimens maintained their shapes without undergoing any deformation, and had no cracks and no colour change up to 1300 °C. This would mean that the most suitable refractory brick powder batch is 30: 35: 35 with the local Sebha kaolin clay playing the role of a good binding material.

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