Measurement of Mechanical Properties of Re-Cycled Waste Refractory Brick

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Abstract:

Misrata Iron and Steel Complex waste brick used in this study was subjected to cleaning and crushing to granules of 30 mm size. The resultant granules were hammer milled to powder particles of an average size of 1 mm and then sieved to give coarse + 0.355 mm waste powder. A high energy ball mill was used to convert this waste powder to nano-crystalline powder with a crystallite size in the range from 45 to 51 mm.

The present work involved the preparation of three powder batches with each batch composed of nano–crystalline powder, +0.355 mm waste brick powder, and Sebha Kaolin clay powder of 75 microns particle size. These batches were pressed, dried at a temperature of 110°C, and finally sintered at 1000, 1300, and 1500°C.

X – Ray Diffraction (XRD) analysis was used to characterize the refractory waste bricks, waste coarse powder, kaolin clay, and waste nano–powder. The research also involved the measurement of mechanical properties of waste bricks and sintered final products.

The obtained results revealed the presence of a molten glassy phase at the sintering temperature of 1500 °C. This had a weakening effect on the mechanical properties and hence limited the maximum working temperature of the produced bricks to 1300°C.

The optimum amount of nano-powder component in the powder batches was found to be 30 % as it led to the achievement of the best crushing and flexure strength values for the bricks sintered at 1300°C.

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]. 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 [2,3]. 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 [**4**] while in Misrata Iron and Steel Complex it is about 5000 tons of spent refractory linings constitute a major percentage of the industrial waste generated by metal manufacturing plants. 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 [5].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**].

This research study focused on investigating the processing and mechanical 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 X-Ray Diffraction (XRD) technique.

2. Experimental Work:

2.1 Specimens 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 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).

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.

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.

2.2 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 Kcan 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 :

2.3.1 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 (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 %.

2.3.2. 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.

2.3.3 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).

2.3.4 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 verniercallipers.

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

2.4Measurement of Mechanical Properties:

2.4.1 Cold Crushing Strength :

Cold crushing strength was measured for the starting waste brick pieces (50 × 50 × 50 mm) and 3 batches of final sintered shaped products at the sintering temperatures of 1000, 1300, and 1500 °C. The measurement was carried out at room temperature by placing the specimen on a flat surface followed by the application of a uniform load to it through a bearing block. The test was performed in accordance with the standard ASTM C133-97 (Re-approved in 2003) using a hydraulic compression testing machine and a University tensile test machine. The load at which crack appears on the refractory specimen represents the cold crushing strength of the specimen which is then measured directly by software built in the machine.

2.4.2 Bending Test:

The flexure strength was measured for all sintered samples using a Tecno Tester (Model; E.DE Nicola, Italy) at a rate of 1Newton/second. The total number of samples tested was **27,** where 3 samples were taken from each batch which in turn had 3 differently composed powders shaped and sintered at the three temperatures 1000, 1300, and 1500 °C. Samples dimensions were fed into the machine built-in software to calculate the flexure strength directly from instrument shown in **Figure 2** below.

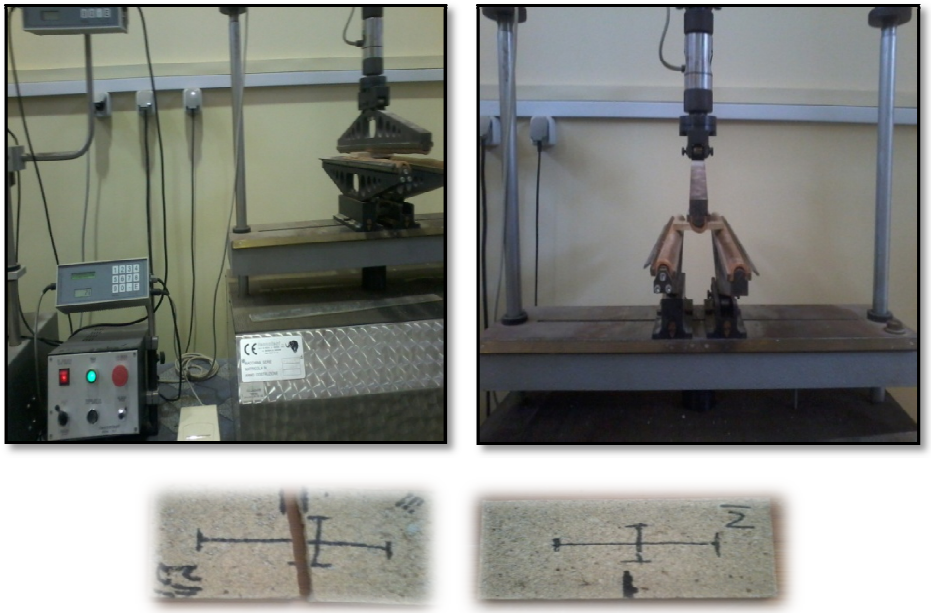

Figure 2: Bending Tecno Tester and test samples.

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** shown below;

Table 1: Phase Composition of waste bricks samples

Brick sample Number	Compound Name	Chemical Formula	SemiQuant [%]
1	Quartz	SiO_2	44.12
	Bischofite	$MgCl_2.6H_2O$	36.27
	Mullite	$Al_6Si_2O_{13}$	19.61
2	Compound Name	Chemical Formula	SemiQuant [%]
	Quartz	SiO_2	43.49
	Bischofite	$MgCl_2.6H_2O$	32.29
	Mullite	$Al_6Si_2O_{13}$	24.22

Brick sample Number	Compound Name	Chemical Formula	SemiQuant [%]
3	Compound Name	Chemical Formula	SemiQuant [%]
	Quartz	SiO_2	46.39
	Bischofite	$MgCl_2.6H_2O$	22.68
	Mullite	$Al_6Si_2O_{13}$	30.93
4	Compound Name	Chemical Formula	SemiQuant [%]
	Quartz	SiO_2	43.00
	Bischofite	$MgCl_2.6H_2O$	33.78
	Mullite	$Al_6Si_2O_{13}$	23.22
5	Compound Name	Chemical Formula	SemiQuant [%]
	Quartz	SiO_2	46.36
	Bischofite	$MgCl_2.6H_2O$	21.85
	Mullite	$Al_6Si_2O_{13}$	31.79
6	Compound Name	Chemical Formula	SemiQuant [%]
	Quartz	SiO_2	42.55
	Bischofite	$MgCl_2.6H_2O$	36.17
	Mullite	$Al_6Si_2O_{13}$	21.28

The above 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 strength at high temperatures. Mullite also shows a uniform thermal expansion, and its formation in a body makes for good thermal shock resistance.

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.**

Table 2: Phase composition of the homogenized powder sample

Specimen No:-	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

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.

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

Compound Name	Chemical Formula	SemiQuant [%]
Kaolinite	$Al2[Si2O5(OH)_4]$	86.96
Quartz	SiO_2	13.04

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**.

Table 4: 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 the *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 nanomaterials. An illustration of the computer software used for the calculations is shown in **Figure 3.**

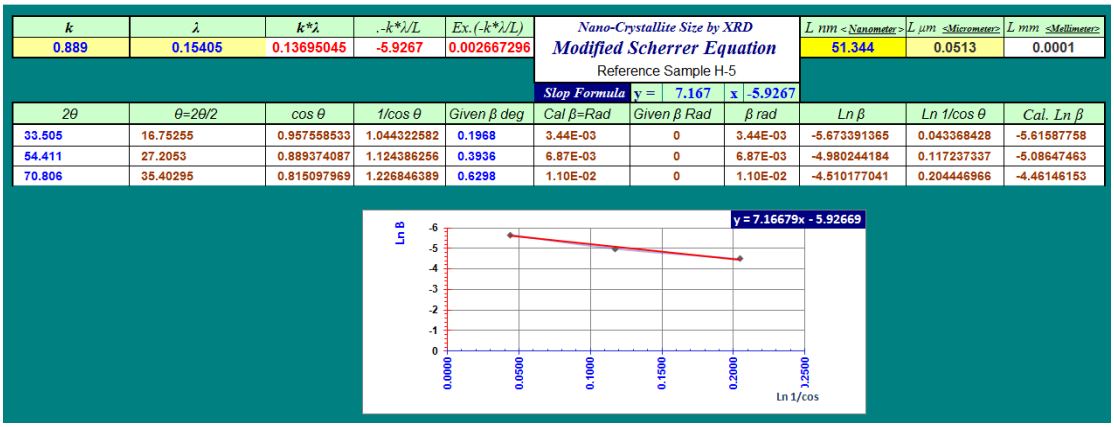

Figure 3: An illustration of the computer calculation of the crystallite size for the powder milled for 5 hours

Phase composition for the above-mentioned three nano powder samples are shown below in **tables 5**, **6**, and **7**, and **Figure 4** shows the XRD pattern for the powder milled for 10 hours.

Table 5: Phase composition of sample milled for 5 hours

Specimen No	Compound Name	Chemical Formula	SemiQuant [%]
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 6: Phase composition of sample milled for 10 hours

Specimen No	Compound Name	Chemical Formula	SemiQuant [%]
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 7: Phase composition of sample milled for 15 hours

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

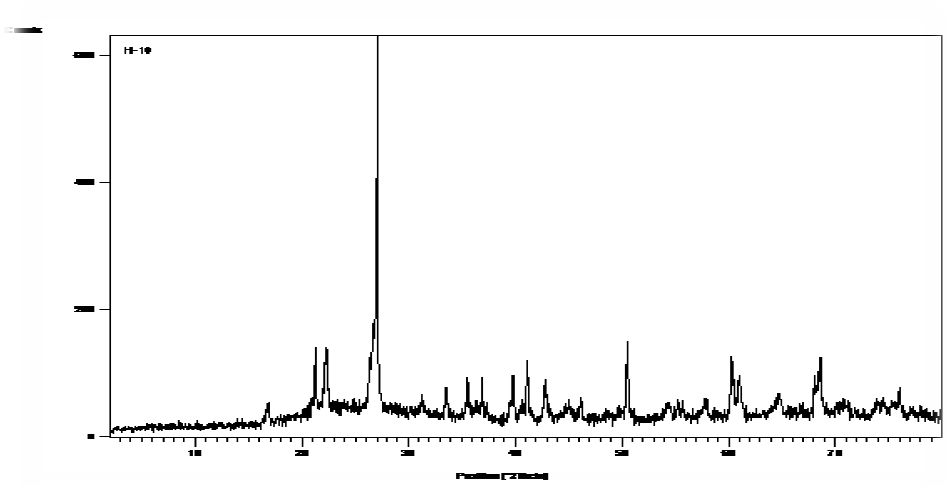

Figure 4: XRD pattern for the powder milled for 10 hours.

Based on XRD investigative work of all powder samples mentioned above, it was found that the 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.

3.3Cold Crushing Strength:

3.3.1 Waste Refractory Brick Samples:

The six waste brick samples were subjected to cold crushing strength measurement in which the cross-sectional area was 5 ×5 = 25 cm^2, as is shown in **table 8**.

Table 8 : Cold crushing strength of waste brick samples

Sample Number	Max. load (N)	Cold crushing strength (N/mm^2)
1	97.1	38.82
2	87.9	35.18
3	86.3	34.51
4	143.9	57.56
5	204.5	81.81
6	154.8	61.92

3.3.2 Sintered Final Shaped Products:

Cold crushing strength of sintered specimens was measured and the obtained values are given in **table 9** and shown graphically in **Figure 5**.

As can be seen from the presented values, all specimen batches have the same trend of rising crushing strength when firing temperature being increased from 1000 to 1300°C. It can also be noted that the second and third specimen batches suffered a drop in strength as firing temperature was increased from 1300 to 1500°C. However, the most encouraging result is shown by all the specimen batches fired at 1300°C, for which the crushing strength going up with increasing nano–powder fraction content. This clearly shows the potential benefit of using nano–sized powder particles as an important component of powder batches to enhance the cold crushing strength of refractory bricks.

Table 9 : Cold crushing strength of final shaped sintered products

Specimen batch	Strength (N/mm^2)	Sintering temperature (°C)
45 : N1 : 45	19.83	1000
	28.77	1300
	36.36	1500
40 : N2 : 40	17.88	1000
	57.48	1300
	47.18	1500
35 : N3 : 35	16.07	1000
	124.08	1300
	116.32	1500

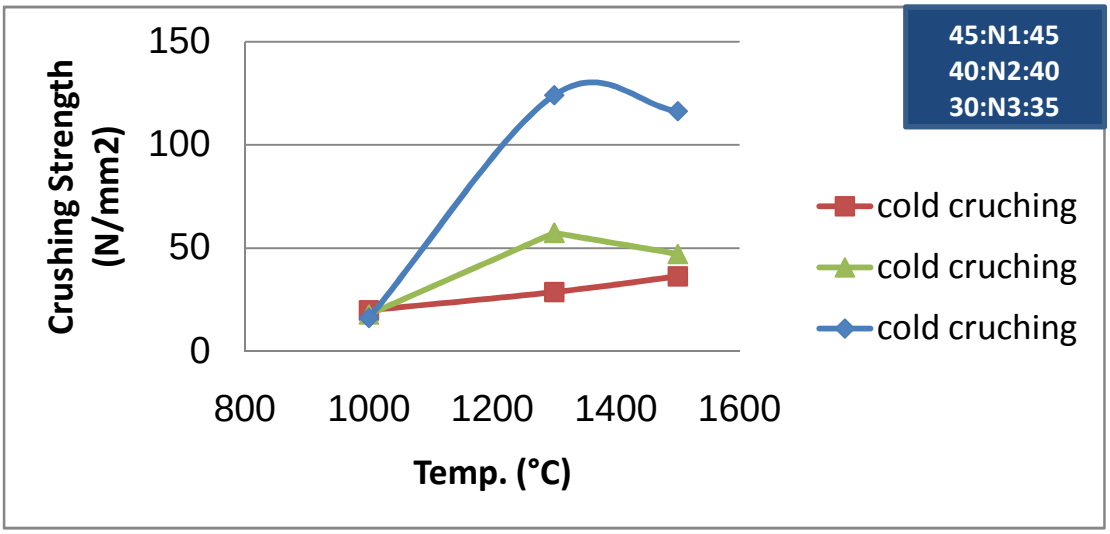

Figure 5 : Cold crushing strength as a function of firing temperature

3.4 Bending Measurements of Sintered Final Products:

The obtained values are as shown in **table 10** and presented graphically in **Figure 6**. All specimen batches show an increase in flexure strength as the firing temperature used increased from 1000 to 1500°C, with the batch 45:N1:45 showing the highest bending strength. Once again it can be observed that as the nano–powder fraction increased, this

led to an improvement in flexure strength for the specimen batches fired at 1300°C. This further shows the possible advantageous influence of having nano–sized powder particles component in the powder mix used for the production of refractory bricks.

Table 10 : Bending strength values for sintered final shaped products

Specimen Batch	Flexure Strength (N/mm^2)	Sintering Temperature (°C)
45 : N1 : 45	2.80	1000
	20.59	1300
	38.46	1500
40 : N3 : 40	2.84	1000
	22.19	1300
	25.53	1500
35 : N3 : 35	4.06	1000
	27.96	1300
	32.87	1500

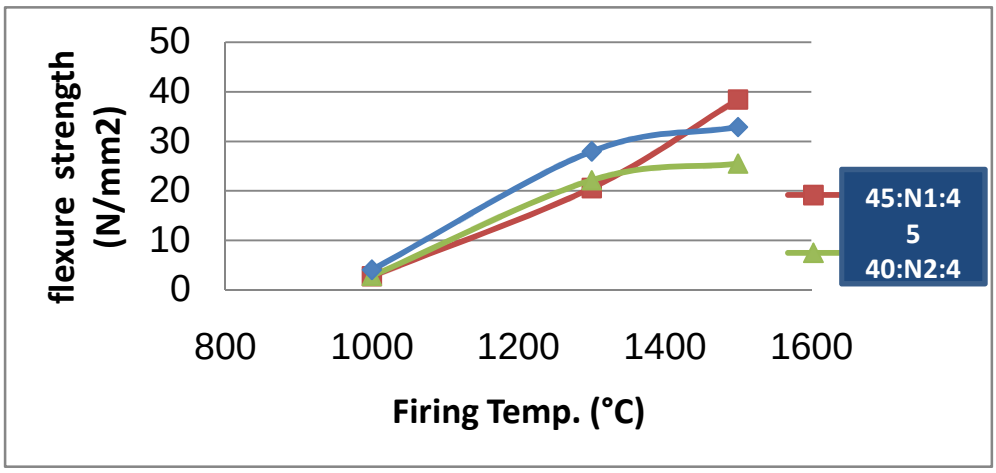

Figure 6: Bending strength versus Firing temperature

4. Conclusions:

- Recycled bricks produced via the method reported in this present investigation may help to decrease the amount of waste bricks found at the Misrata Iron and Steel Complex.

- The optimum milling time for the production of nano-sized powder using a high energy ball mill was 10 hours.
- Sintering at 1500 °C led to the melting of a glassy phase which reduced the mechanical strength of the produced bricks. Hence, the safe working temperature for the bricks must not exceed 1300 °C.
- Based on the obtained results in this study, it may be concluded that the optimum amount of nano-sized powder is 30 % as this gave the best figures for cold crushing and flexure strength measured for the specimens sintered at 1300 °C.

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