Effect of Carbon nanotubes addition on the foundry physical properties of Silica refractory nanocomposite: PART A

Y Tijjani\textsuperscript{1*}, F M Yasin\textsuperscript{2}, M H S Ismail\textsuperscript{3}, M A Azmah Hanim\textsuperscript{4}

\textsuperscript{1*} Department of Mechanical Engineering, Faculty of Engineering, Bayero University, Kano, Kano, Nigeria
\textsuperscript{1,2,3} Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia
\textsuperscript{4} Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia

*Corresponding author: ytijjani.mec@buk.edu.ng

Abstract. The foundry physical properties of carbon nanotube (CNT) reinforced silica refractory ceramic nanocomposites have been determined. The pristine CNTs (pCNTs) were acid treated and subsequently dispersed in distilled water to achieve a stable suspension of functionalized CNTs (fCNTs). The as-prepared suspension, natural crystalline powdered quartz (SiO\textsubscript{2}) and calcium oxide-clay; as binder and sintering aids (SA); stabilizer and mineralizer were mixed thoroughly by ultrasonication/ball milling, dried, cold compacted and densified by pressureless sintering consolidation technique via modified conventional powder processing. The comparable bulk density obtained for the sintered SiO\textsubscript{2}-x/fCNT-SA; x = 0, 0.01, 1 and 4 wt.% blends is an evidence of a complete densification and good homogenous dispersion of CNTs in the green matrices, thus better thermo-mechanical properties of the nanocomposites. Low linear/diametric expansion (1.37/1.57 ± 0.01%), high bulk density (1.735 ± 0.010 g/cm\textsuperscript{3}), moderate apparent porosity (41.28 ± 0.41%) and cold crushing strength (177 ± 9 kg/cm\textsuperscript{2}), and higher thermal shock cycles (7 ± 1 cycles) of 1 wt. % fCNT-silica nanocomposite brick as compared to those of monolithic conventional silica brick signified the possibility of potential application of CNT as an additive in conventional green silica refractory mixture for better foundry physical properties.

1. Introduction
Quartz or naturally occurring crystalline silica in the form of quartzite has been utilized as a source material for the production of silica brick; added with quicklime (CaO) as a binder, and mineralizer to speed up the polymorphic conversion of as-dried green silica brick from quartz to cristobalite and tridymite during the sintering process. Other materials employed as mineralizers are iron oxides, magnesium oxide, barium oxides, manganese dioxide, titanium dioxide, and carbonates, fluoride, and phosphates of metals like lithium, potassium, sodium; these usually reduce the refractoriness of silica, consequently, only a small amount should be added to the green silica blend [1-4].

In the production of silica refractory bricks, the most important, influential parameters are choice of raw materials and complex polymorphic transformation of silica phases during firing or on service. The choice of material is mostly dictated by the chemical composition; specifically for better properties, the combined amount of fluxes Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} should be less than 2 %, whereas alkalis content should be less than 0.35 %. Whereas, the amount of residual quartz determines the degree or completeness of silica transformation to its allotropic modifications [5]. Therefore, it could be suggested that the thermo-
mechanical properties of silica brick which can be described by a set of physical characteristics in relation to temperature, such as; density/porosity, coefficient of thermal expansion, cold crushing strength, thermal shock resistance, and thermal conductivity depend on the intrinsic raw material type/compositions and proportionally modifiable allotropic modifications of silica.

Owing to the unique arrangement of their carbon atoms, Carbon nanotubes possess a remarkable electrical, thermal, and mechanical properties [6, 7]. These properties offer the CNTs wide range of applications and studies in the field of nanomaterials that are unique and could not be achieved by either fiber or whisker reinforcement [8-18]. Apart from mechanical and physical effects, the carbon nanotube as a second phase reinforcement may benefit other functional properties viz. Thermal expansion coefficient [19-23], thermal shock resistance [24-29], etc.

Generally, silica/silica-based bricks have a poor thermal shock resistance which gave rise to an undue failure of the bricks especially when used for insulation. For instance, sudden exposure to atmospheric conditions from the high operating temperatures in a ceramic-lined crucible during metal pouring and in cupola furnace during temperature dropping [30]. To obviate this problem substantially, carbon nanotubes have been incorporated for the first time within the matrix of crystalline silica, so that they would facilitate the heat transfer within the matrix, hence reducing the high-temperature differential/gradient between the two parallel surfaces of the brick. Thus, decreasing the reversible thermal expansion and increasing the thermal shock resistance cycles of the bricks. Unfortunately, to date, there is no simple and unified standard test method for the determination and comparison of thermal shock resistance (TSR) of ceramic materials that would at the same time simulate the actual conditions in service, thermal cycles, and sample geometry (due to the delicacy and lack of feasibility and quantitative validation in assessing various ceramics). However, sample testing involving transient heating and cooling could be carried out but this is only reliable for comparative analysis of similar materials (in a particular simulated study and should not be generalized for other studies) [31, 32].

2. Experimental Procedure
This entails the functionalization of as-received pCNTs, morphological characterization of the pristine/functionalized CNTs, preparation and characterization of raw silica and clay, fabrication of CNT-silica bricks, and characterizations of the densified bricks.

2.1. Functionalization of CNTs
The pCNTs were obtained from the Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Sciences (Sichuan Sheng, China). They were grown by CVD, > 98 % purity, 10 – 20 nm diameter, and 10 – 30 μm length. Sulphuric acid 95-98% A.R/ACS, was purchased from the Ever Gainful Enterprise Sdn Bhd (Subang, Selangor, Malaysia).

To activate the surface of the pCNTs, 100 mg of the pristine was acid treated with 100 ml of 6M H2SO4. The mixture was then syndicated using a water bath sonicator (Bransonic ultrasonic cleaner, Mexico) for 6 hours at 60°C. After sonication, the residue was decanted and successively washed with distilled water in a centrifugator (Heraeus Biofuge Primo Centrifuge, USA) at 8000 RPM for 30 seconds. Finally, the as-washed residue was dried in an oven at 100°C for 24 hours.

2.2. Morphological characterization of pristine/functionalized CNTs (pCNTs/fCNTs)
SEM type S-3400, HITACHI, was used to evaluate the characteristic surface morphology of the pCNTs/fCNTs. Prior to the SEM analysis, to eliminate charging in the powdered samples; the samples while mounted on sample holders were sputtered and coated with gold for 3 minutes at 35 – 50 mA. The SEM micrographs for the pCNTs and fCNTs are as shown in Figure 1.

2.3. Preparation and characterization of raw quartzite and clay
This covers the purification and preparation of quartzite and clay (both obtained as-mined); washing, crushing, grinding, pulverizing, and sizing/grading of the powdered materials. Finally, the materials were characterized by Energy dispersive X-ray fluorescence spectrometer (ED-XRF) and X-ray diffraction (XRD; X’pert Pro Pananalytical PW 3040 MPD, Netherlands). Table 1 depicted the results of chemical and physical properties of powdered quartzite.
2.4. Fabrication of CNT-Silica bricks
The as-graded silica powder with particle size distribution; \(d_{0.1} = 2.259 \, \mu\text{m}, \ d_{0.5} = 20.166 \, \mu\text{m}, \ d_{0.9} = 71.208 \, \mu\text{m}\) (as characterized by Mastersizer, Malvern, UK), clay size < 75 µm and CaO powder (sintering aids), and stable suspension of fCNTs were used for the production of nanocomposite bricks. The formulations are as shown in Table 2. Typically, 5 g of the nanocomposite mixture was made (containing the highest percentage of the CNTs, 4 wt. %) using a wet method as follows: First, 0.2 g of CNTs were dispersed in 100 ml of distilled water and ultra-sonicated for 120 minutes to obtain a stable suspension of CNTs in distilled water. Second, 4.65 g quartzite, 0.05 g clay, and 0.1 g CaO were added to the CNT/distilled water suspension and ultra-sonicated for a further 120 minutes (Sonics Vibra cell VCX 130, using a power of 35–40 W, USA). Then, the nanocomposite mixture was dried in a hot plate at 150°C under sonication. The dried nanocomposite powder was milled in a mortar and subsequently mixed thoroughly using a mixer mill for about 120 minutes. Lastly, the mixed powder was tempered, cold compacted at a pressure of 100 MPa by hydraulic pressing machine, dried in an oven at 110°C overnight and finally, densified by a pressureless sintering process at 1450°C for 2 hours holding time and 5°C/minute heating rate in an argon environment. Pellets with dimension approximately Ø 21 mm x 8 mm height with Q-x/CNT-x; where x = 0.01, 1 and 4 wt.% (donated as QC-0.01, QC-1 and QC-4; silica with 0.01, 1 and 4 wt.% carbon nanotubes, Q stands for sintered quartzite plus sintering aids and C stands for CNTs) were produced. Also, plain pellets (silica without CNTs; QC-0) were prepared by the semi-dry method, compacted and consolidated in air under identical experimental conditions for comparison.

2.5. Determination of physical properties

2.5.1. FESEM/TEM
To ascertain the presence and structural integrity of the CNTs after the pressureless sintering, the morphologies of the sputter-coated CNT-silica brick samples were captured by Ultra High-Resolution Scanning Electron Microscope with Electron Diffraction X-ray Spectroscopy (FESEM/EDX, Nova NanoSEM 230). This was complimented with Transmission electron microscopy (TEM) image. For TEM, the sample was dispersed in acetone and then transferred onto holey carbon film, supported on a copper grid, for observation. Figure 2 depicts the FESEM and TEM micrographs. Also, to determine the proportion of residual quartz, the XRD analysis was carried out for the densified sintered samples.

2.5.2. Linear/Diametric expansion
These were measured as the percentage difference in length between as-dried and as-sintered samples as measured along the thickness (linear) or along the diametrical plane (diametric).

2.5.3. Bulk density and apparent porosity
These were obtained by Archimedes’ principle using distilled water as an immersion medium. The experiment was conducted in accordance with ASTM C 20 – 00.

2.5.4. Cold crushing strength (CCS)
The sintered test specimens of approximate dimension Ø21 mm x 8 mm height were subjected to compression test using an Instron model 3382 universal testing machine (UTM) and loading has been applied at the rate of 1 mm/min until fracture. The CCS was then evaluated with the aid of UTM simulation software.

2.5.5. Thermal shock resistance experiment
The resistance of the sample materials to the thermal shock has been investigated by determining the average number of cycles to destruction for at least seven samples. The test samples were heated to 1250°C at 2.5 – 5 °C/min heating rate and they were maintained at this maximum temperature for 30 minutes. After which samples were immediately transferred to cold water and left immersed for 10 minutes. Then, the samples were returned to the furnace and heated for further 10 minutes. This cycle was repeated until the entire samples were destroyed.
3. Results and discussions

3.1. Morphological properties of pCNTs/fCNTs.
In Figure 1, the morphology of pCNTs (a, b) and fCNTs (c, d) are compared based on the SEM micrographs. For both pCNTs and fCNTs, the characteristic graphitic bundled structure is observed and no trace of amorphous carbon is sighted. The sidewalls of the pCNTs as shown in a, and b are mostly smooth and defect free. This is because there is neither indication of prior chemical processes on the pristine such as chemical purification and/or oxidation by the manufacturers nor any preliminary chemical preparation was carried out on pCNTs, whereas the surfaces of the outer walls of the fCNTs are generally defected, as depicted in Figure 1 c, d. This may be due to the destructive effect of the oxidative agent on the outer layers of the walls, which gave birth to functional groups’ attachment [33] or defect resulting from mechanical ultrasonication of the nanotubes during the functionalization process [34]. Also, the transparency of the nanotubes has been reduced in case of fCNTs as compared to pCNTs after the introduction of the functional groups [35, 36]. It can be seen from the micrograph of fCNTs, the structure of the CNTs survives the aggressive action of a mineral acid as well as mechanical ultrasonication; acid functionalization. This may be due to the use of the mild aqueous acid solution, thereby avoiding nanotube structural damage by tubes scission resulted from treatment with concentrated acid [37]. The groove structure observed throughout the morphology of fCNTs as depicted in the Figure 1 c, and d, is the evidence of the functional groups’ attachment, which in turn would facilitate the homogeneous dispersion of the fCNTs in an organic solvent and finally the intended matrix in order to achieve a stable suspension and intimated filler-matrix interface, respectively [34].

![Figure 1. SEM micrographs of pCNTs (a) & (b), fCNTs (c) & (d)](image)

3.2. Characterization of raw quartzite and clay
The ED-XRF result of purified, ground and a graded sample of raw quartzite is as shown in Table 1. From the chemical analysis of the quartzite, the percentage of silica (SiO₂) 96.363 % is in accordance with the acceptable range of 96 – 97 % recommended for silica brick manufacture [2]. Also, the combined amount of Al₂O₃ and TiO₂ amount to 0.276 %, which is within the range of high-quality silica grade < 0.4 %. The cumulative alkali content 0.2 % is also as recommended < 0.35 % for acceptability of quartzite material to be used for refractory application [5].
The XRD analysis; based on the proportion of phase, density, name, and crystallite sizes of the raw quartzite is as shown in Table 1. The raw quartzite exists only in quartz polymorphic phase (as obtained from Rietveld analysis; 100% quartz Cristal lattice). Similar assertions were made by the previous researchers on silica refractory bricks by Almarahle [38], Alnawafleh [39], Brunk [40], Chesti [2], and Manivasakan, Rajendran [3]. The chemical and physical analyses of the purified clay demonstrated that it is predominately silica accounting for > 70 % SiO$_2$.

Various silica grain size distributions have been reported in the literature that resulted in high bulk density and products with improved physical and mechanical properties, for instance, 0.075 – 0.2 mm fine, 0.2 – 1.5 mm medium, and 1.5 – 3.0 mm coarse aggregates [2, 3, 38, 39, 41]. Nevertheless, the above-mentioned ranges and guidelines for grain size distributions as used in coarse ceramics for better densification are applicable to a limited extent in the silica brick manufacturing [5]. Hence, the present research adopted for the first time, very fine grain size distribution of the silica (in micro ranges) for compatibility between the matrix and the carbon nanotube fillers, and for the enhancement of physical properties of the bricks.

### Table 1. Chemical & physical properties of quartzite

| Oxides   | Percentage (%) | Characteristics    |
|----------|----------------|--------------------|
| SiO$_2$  | 96.363         | Mineral name Quartz |
| Fe$_2$O$_3$ | 0.57         | Bulk density (g/cm$^3$) 2.65 |
| SO$_3$   | 0.984          | Crystallite size (nm) 160.1 |
| K$_2$O   | Traces         | Percentage 100%     |
| CaO      | 0.18           |                    |
| Sm$_2$O$_3$ | 0.307       |                    |
| TiO$_2$  | 0.126          |                    |
| MgO      | Traces         |                    |
| Al$_2$O$_3$ | 0.15        |                    |

### 3.3. Effects of CNTs on the thermo-mechanical properties of silica brick

Some of the physical properties that represent the effects of thermal and mechanical loading on the silica bricks are tabulated in Table 2.

### Table 2. Physical properties of CNT-silica bricks

| Parameter                              | Q$^1$ (Silica brick without CNT) | QC-0.01 (Silica brick with 0.01 wt%CNT) | QC-1 (Silica brick with 1 wt%CNT) | QC-4 (Silica brick with 4 wt%CNT) | Recommended values for silica brick |
|----------------------------------------|----------------------------------|----------------------------------------|----------------------------------|----------------------------------|-----------------------------------|
| %/CNTs                                 | 0.00                             | 0.01                                   | 1                                | 4                                | -                                 |
| Diametric expansion (%)                | 1.60±0.01                        | 1.59±0.01                              | 1.57±0.01                        | 1.08±0.01                        | -                                 |
| Linear expansion (%)                   | 2.30±0.01                        | 2.30±0.01                              | 1.37±0.01                        | 0.57±0.01                        | -                                 |
3.3.1. Linear/diametric expansion

The influence of the varied percentage of CNTs on the linear and diametric expansion of densified CNT-silica samples is tabulated in Table 2. As the percentage of CNT increase from 0.01, 1, to 4 wt. %, both linear and diametrical expansions of the CNT-silica reduce as compared to those of the unreinforced sintered silica. Hence, the CNTs here may have acted as stabilizer taking care of the expansion in volume during the polymorphic conversion from quartz to tridymite and cristobalite. These linear growths on firing (for the plain silica) have been reported to have cumulatively account for 4 – 5 % [5, 40].

3.3.2. Bulk density/apparent porosity

The change that has been conferred on the bulk density and porosity obtained by Archimedes’ principal due to the variation in percentage CNTs is tabulated in Table 2. The bulk density slightly increases with the little addition of CNTs (0.01 wt. %) to plain silica brick while the apparent porosity decreases. As the percentage of the nanotubes increase to 1 and 4 %, the bulk density and apparent porosity reduces and increases, respectively. A similar trend has been reported when micro and nano TiO\(_2\) were incorporated in silica brick [3]. The slight reduction in densification with increased % CNTs may be attributed to agglomeration that could set in as the percentage of CNTs increase either due to the inhomogeneous dispersion of the CNTs or high CNTs loading. In the first case, a poor dispersion technique may lead to the formation of CNTs aggregates. These aggregates may not be infiltrated by crystalline SiO\(_2\) matrix during pressureless sintering. This may induce the development of porosity [42]. While in the second case, the quantity of CNTs particles may outweigh that of the quartzite particles which would lead to more interfaces and inevitably some CNTs may tangle, and interacting each other to form agglomerate by affinity through van der Walls forces. This would eventually lead to the formation of pores during the sintering process, thus lowering the densification of the brick [43]. Also, the low density could be due to degradation of the CNTs as a result of high sintering temperature and dwelling time [44]. Precisely, it could be thought that most of the survived nanotubes were successfully coated by CaO as can be seen in the QC-4 FESEM micrograph (Figure 2[c]). Whereas, the uncoated nanotubes may form the aggregates that lead to the development of pores (Figure 2[c]). Interestingly, as viewed from the Figure 2(c), the CaO-coated nanotubes are attempting to fill/bridge the voids. Also, TEM micrograph; Figure 2 (d) confirmed further the survival of coated-CNTs. The high porosity, for instance, about 61 % increment in porosity for 4 wt. %CNTs as compared to the unreinforced bricks could be exploited advantageously when the nanocomposite bricks are applied in the area of porous ceramics where thermal insulation is very paramount such as in the manufacture of lightweight silica brick. Burnout materials like sawdust, coke, etc., have been added to molding mixtures to produce silica insulating bricks [5]. The bulk densities of the CNT-silica bricks, 1.722 – 1.760 g/cm\(^3\) are close and fall within the recommended range of silica refractory bricks employed for general use and in dense glass industrial process 1.72 – 1.92 g/cm\(^3\) [41].

| Apparent porosity (%) | 32.62±0.02 | 30.37±0.40 | 41.28±0.41 | 52.45±0.44 | 22 – 26 [2] |
|-----------------------|------------|------------|------------|------------|------------|
| Bulk density (g/cm\(^3\)) | 2.65 | 1.738±0.000 | 1.760±0.010 | 1.735±0.010 | 1.722±0.002 | 1.72 – 1.92 |
| Cold crushing strength (kg/cm\(^2\)) | 400±23 | 650±17 | 177±9 | 86±5 | 250 – 400 [2] |
| Thermal shock resistance (cycles) | 4±1 | 2±1 | 7±1 | 5±1 | - |
| Residual quartz (%) | 7.8 | 14.1 | 1.1 | 11.3 | 1.5 maximum |

Where Q = sintered quartz + sintering aids (clay + CaO), C = CNT(s) = f\(\)CNT and Q\(^i\) = Un-sintered plain powdered silica

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3.3.3. Thermal shock resistance (TSR)/cold crushing strength (CCS)

The significance of %CNTs variation on thermal shock cycle to destruction and cold crushing strength of consolidated CNT-silica nanocomposites has been obtained experimentally and tabulated in Table 2. In the same pattern as bulk density, the cold crushing strength increases sharply to a maximum value of 650 kg/cm², with only 0.01 wt. % CNTs addition to unreinforced brick, then it drops drastically with increased %CNTs to a minimum value of 86 kg/cm² at 4 wt. %CNTs. This may be attributed to dropping in densification as agglomeration set in. An improved silica brick property has been reported to be the function of structural densification [2]. The average thermal shock resistance cycles, changes with the addition of %CNTs to a maximum of 7 cycles with 1 wt. % CNTs addition to unreinforced brick, 4 cycles for the plain brick, and a minimum of 2 cycles at 0.01 wt.% CNTs addition, accounting for a 75 % increment achieved in QC-1 as compared to the unreinforced brick (QC-0). This result is in line with the previous finding on the bulk density, apparent porosity, and cold crushing strength since thermal shock resistance is more dependent on toughness than the strength of the brick. Similar trend (irregular pattern with addition of second phase carbon natubes in the ceramic matrix) has been reported [24].

3.3.4. The microstructural characterization by XRD

As a feature of good conversion (for the sintered sample bricks), the residual quartz content should be limited to a maximum of 6 % and 1.5 % for coarse-crystalline and crypto-crystalline (fine crystalline) raw materials respectively [5, 40]. Based on this requirement, only sample QC-1 with 1.1 % residual quartz (Table 2) can be chosen as candidate brick formulation for better thermo-mechanical properties. Hence, the present finding can be used to justify the previous result of thermal shock cycle resistance and vice versa. It has been reported that the bricks with a high content of residual quartz are more susceptible to volume changes due to the residual quartz conversion into polymorphic cristobalite and tridymite in service (a term commonly referred to as irreversible after-expansion). The volume changes which accompanied these conversions would lead to a loosening of the structure and to a lower resistance against thermal shock [39]. Also, this further justifies the emergence and selection of QC-1 nanocomposite brick due to its lowest percentage of residual quartz content responsible for the highest cycle of thermal shock resistance to destruction. Unlike the irregular stochastic trend reported in Table 2 for the residual quartz content with the addition of carbon nanotubes in the current study, a more stable residual quartz trend (reduction of residual quartz content with increase nano TiO₂ content) has been reported when nano TiO₂ was added to silica ceramic matrix [3].

3.3.5. FESEM/TEM Observations

The FESEM micrographs of a) QC-0.01, b) QC-1 c) QC-4 and TEM micrograph of d) QC-4, after the pressureless sintering were depicted in Figure 2. The CNTs could not be sighted in a and b, whereas in c, dispersed and coated carbon nanotubes resembled materials have been sighted. This material has been confirmed (for QC-4) to be CNT by TEM micrograph; Figure 2(d).
Figure 2. FESEM micrographs of (a) QC-0.01 (b) QC-1 (c) QC-4 & TEM micrograph of (d) QC-4

4. Conclusion
It has been verified that the addition of 1 wt. % CNTs to conventional silica brick resulted in a decreased proportion of residual quartz, thus an increased in percentage tridymite, an improved in thermal shock resistance cycles, a low to high reduction in diametric and linear expansion respectively, and an acceptable cold crushing strength. Hence, we introduce 1 wt. % CNTs as additive, in silica refractory molding mixture for better foundry physical properties.

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