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# Reuse of Marble Sludge Slime in Ceramic Industry

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## ABSTRACT

Ceramic industry is capable of incorporating and reusing different types of industrial waste materials. Recently, the reuse of ornamental stone cutting sludge slime in this industry is becoming a common practice. This work investigates the changes in the physical and mechanical properties of the produced ceramic tiles from raw materials containing marble sludge slime produced in the ornamental stone processing industry in Jordan. The results show that partial replacement of kaolin, feldspar and $CaCO_3$ by the sludge slime caused a deformation out of the plane (binding) of the produced tiles. However, the replacement of all the pentonite by sludge slime did not affect the mechanical strength of the produced tiles and significantly decreased the shrinkage values of the tiles from 1.66% to 0.5 %. The results presented in this paper show that all of the produced sludge slime can be consumed successfully in ceramic production, which would decrease the expensive management of the residues with landfill and preserve an equivalent amount of natural mineral resources (pentonite); thus increasing the environmental sustainability.

**KEYWORDS:** Marble, Sludge slime, Ceramic, Pentonite, Shrinkage, Clay.

## INTRODUCTION

Low costs of both land and construction materials have increased the investment in the construction sector of Jordan. The presence of high quality construction materials which are quarried and produced locally makes them available at competitive and stable prices. Among construction material industries in Jordan are the ornamental stone industry, mainly marble and granite that are of high importance and widespread. Rocks of different colors are quarried at depths of (20-60 m) from various sites and processed in more than 2000 registered factories in Jordan to produce marble. The cutting and polishing of parent rocks are responsible for generating large amounts of sludge slime. The high daily -produced amounts of sludge slime and the difficulty in reducing their volume by suitable treatment methods cause high transportation costs for disposal. Moreover, the sludge slime mud is usually disposed into sanitary land fills, without any treatment, causing not only economical but also serious environmental problems. Recently, alternative methods have been developed to reuse several types of industrial waste materials, including there incorporation in clay-based ceramic products (Tay, 1987; Churchill, 1994; Perez et al., 1996; Stefanov, 1986; Komissarov et al., 1994; Pereira et al., 2000; Pavlova, 1996). The ceramic industry, especially the sector devoted to the fabrication of building products, is very capable of incorporating and reusing different types of industrial waste materials (Anderson and Jackson, 1983; Alleman, 1989;Bazadjiev et al., 1991; Dominguez and Ulmann, 1996; Dondi et al., 1997; Silva and Zwonok, 1998; Caligaris et al., 2000;

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Crespo and Rinco´n, 2001; Pisciella et al., 2001; Pereira et al., 2004;Monteiro et al., 2004; Oliveira et al., 2001; Knight, 1999; Knirsch et al., 1998; Ferreira et al., 1999).

**Table 1: Chemical composition of raw materials, as determined by XRF**

| Raw material, w% | CaO | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | LoI |
|---|---|---|---|---|---|---|---|---|---|
| Kaolin | 0.5 | 57 | 21 | 5 | 0.15 | 0.1 | 0.7 | 0.25 | 14 |
| Feldspar | 8.09 | 57.71 | 17.08 | 6.41 | 0.86 | 0.1 | 3.8 | 3.74 | 19.21 |
| $CaCO_3$ | 55 | 0.012 | 0.003 | 0.0012 | 0.002 | 0 | 0.0002 | 0 | 43 |
| Pentonite | 8.09 | 50.21 | 11.11 | 6.86 | 3.45 | 0.1 | 2.81 | 1.34 | 5.14 |
| Sludge slime, slime | 53.45 | 2.43 | 0.39 | 0.13 | 1.92 | 0.11 | 0.02 | 0.05 | 44.57 |
| Clay | 1.55 | 50.21 | 16.84 | 4.36 | 0.23 | 0.08 | 1.05 | 0.74 | |

**Table 2: Replacement of raw materials by different proportions of sludge slime**

| Composition<br>Raw materials w,% | S1 (Blank) | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 |
|---|---|---|---|---|---|---|---|---|---|
| Kaolin,% | 68 | 50 | 40 | 30 | 68 | 68 | 68 | 68 | 68 |
| Feldspar,% | 15 | 15 | 15 | 15 | 7.5 | 0 | 15 | 15 | 15 |
| $CaCO_3$,% | 12 | 12 | 12 | 12 | 12 | 12 | 8 | 0 | 12 |
| Pentonite,% | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 0 |
| Sludge slime, slime% | 0 | 18 | 28 | 38 | 7.5 | 15 | 4 | 12 | 5 |

**Table 3: Chemical composition of raw material mixtures, as determined by raw mix design software**

| Mix Composition | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ |
|---|---|---|---|---|---|---|---|---|
| S1 | 47.42 | 16.84 | 4.36 | 1.55 | 0.23 | 0.08 | 1.05 | 0.73 |
| S2 | 47.54 | 16.86 | 4.37 | 4.23 | 0.33 | 0.09 | 1.05 | 0.73 |
| S3 | 32.14 | 11.07 | 3.0 | 16.38 | 0.73 | 0.11 | 0.86 | 0.68 |
| S4 | 26.68 | 9.01 | 2.51 | 21.67 | 0.90 | 0.12 | 0.79 | 0.66 |
| S5 | 43.27 | 15.59 | 3.89 | 4.96 | 0.31 | 0.09 | 0.76 | 0.45 |
| S6 | 39.12 | 14.34 | 3.42 | 8.36 | 0.39 | 0.10 | 0.48 | 0.18 |
| S7 | 47.51 | 16.86 | 4.37 | 3.69 | 0.31 | 0.09 | 1.05 | 0.73 |
| S8 | 47.71 | 16.89 | 4.38 | 7.97 | 0.46 | 0.11 | 1.05 | 0.74 |
| S9 | 47.42 | 16.84 | 4.36 | 8.15 | 0.23 | 0.08 | 1.05 | 0.73 |

**Table 4: Physical properties of the tested samples**

| Parameter | S1, Blank | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 |
|---|---|---|---|---|---|---|---|---|---|
| F.M.R., $kg/cm^2$ | 188.3 | 133.4 | 82.2 | 44.8 | 197.2 | 251.3 | 222 | 225.8 | 177.7 |
| Shrinkage, % | 1.66 | 1.37 | 1.53 | 1.5 | 2.07 | 2.66 | 1.62 | 1.95 | 0.5 |
| | 1.58 | 0.96 | 0.92 | 1 | 1.88 | 2.26 | 1.8 | 1.76 | 0.4 |
| L.O.I., % | 11.9 | 17.4 | 20.7 | 24.5 | 15.6 | 20.2 | 13 | 13.3 | 15.5 |
| W.A., % | 11.6 | 15.4 | | | 12.1 | | | 12.1 | 16.8 |

F.M.R. - Firing Mechanical Resistance.
L.O.I. – Loss On Ignition.
W.A. – Water Absorption.

The most used raw materials in the traditional ceramic industries can be basically divided into three categories: plastic components (clays), fluxing components (feldspar) and inert components (quartz and sand). Clay materials used in the ceramic industry show an extensive range of compositions, which allows the incorporation of a wide variety of industrial waste materials. Some wastes are very analogous in composition to the raw materials used, moreover they often contain materials that can also be helpful in improving the fabrication of ceramic products. Marble is formed predominantly of calcite ($CaCO_3$), feldspar and quartz. Recent studies demonstrated the possibility of incorporating marble and granite sludge slime as additives into clay-based ceramic products (Boccaccini et al., 2000; Ferreira et al., 2002; Torres et al., 2004; Hernadez-Crespo and Rinco´n, 2001).

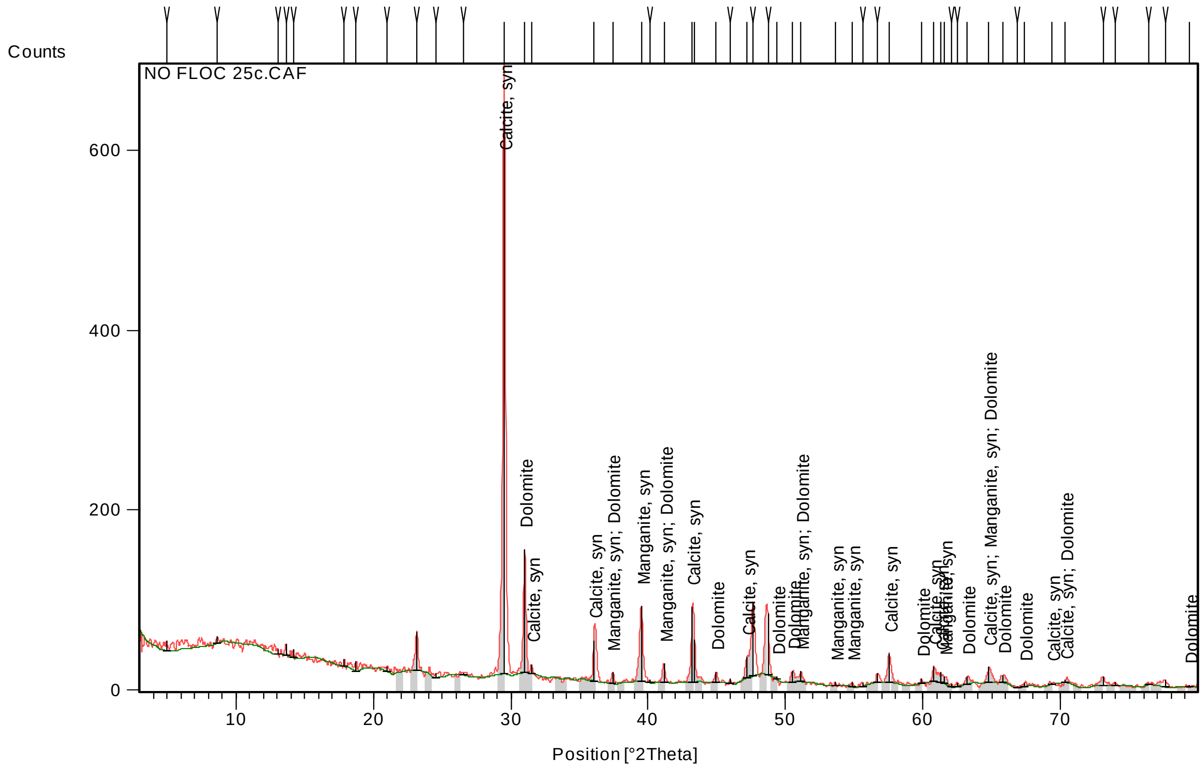


**Figure 1: X-ray Diffraction Patterns of Marble Sludge Slime**

The present work aims at studying the possibility of recycling the sludge slime generated in natural marble cutting industry to substitute one single material of the raw materials used in ceramic industry. The objective can be achieved by partially replacing each raw material used in ceramic manufacturing in the International Ceramic Industries Co.(ICIC) –Jordan, by the sludge slime generated in the International Company for Marble and Granite (ICMG) – Jordan. The influence of sludge slime reuse on the main physical and mechanical properties of the produced ceramic tiles will be investigated.

## MATERIAL AND METHODS

### Experimental procedure

The main raw materials used in ceramic manufacturing in the (ICIC) are: kaolen, feldspar, pentonite and $CaCO_3$. In this work, each raw material in the standard mixture (blank) used has been partially replaced by marble sludge slime. The sludge slime was collected directly from the ornamental stone cutting industry (ICMG) and analyzed for its chemical composition. Both sludge slime and raw materials were analyzed using (X-ray fluorescence, EDX-700, Shimadzu). The mineral constituents of the dried and sintered sludge slime were determined using x-ray diffraction system (Philips-X` pert MpD). The fine powder samples were randomly mounted on special slides and then scanned between 2◦ and 65◦, using Ni-filtered Co K-α- radiation, 40 kV/40mA, divergent and scattering slits of 0.02◦ mm, a receiving slit of 0.15 mm, with stepping of 0.01◦ and scanning speed of 3◦/min. The particle size distribution of the as-received sludge slime was measured using the laser particle size analyzer (Analysette 22 Compac/ FRISCH).

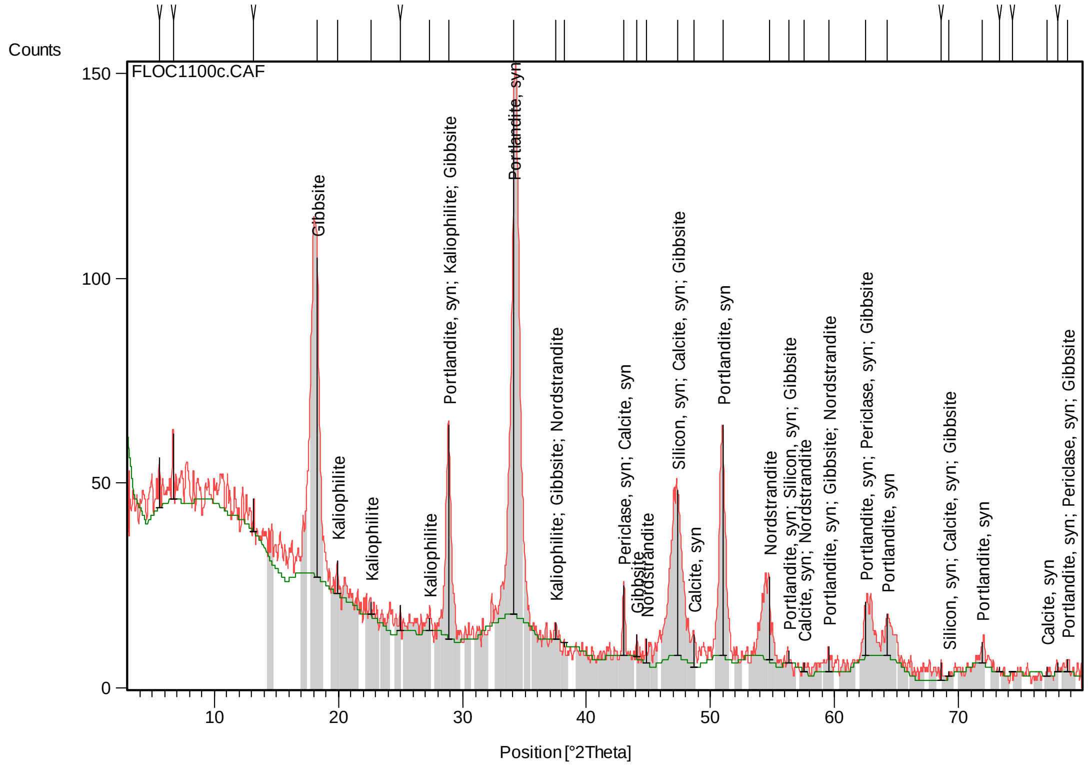


**Figure 2: X-ray Diffraction Patterns of Sintered Marble Sludge Slime**

Nine mixtures (S1,S2, …,S9) of raw materials, the mass of each is 2 kg, containing different wt.% of marble sludge slime were prepared. The chemical compositions of the prepared mixtures have been determined by raw mix design software. Ceramic tiles were produced from the above mixtures by a traditional method used in the (ICIC). The method involved mixing of the dry components followed by the addition of controlled amounts of water-65% and homogenization in a ball mill ( SCI, Italy) for 2 to 3 hours until reaching the required fineness. The required fineness was achieved when the dry mass retained on sieve 63 reached (5.5 - 6.5) grams after sieving 100 ml (1570 g) of the mixture. The mixture was dried in an oven (Welko) at a temperature of 150 ◦C for 3 hours, then the dry mixture was processed in a crusher and sieved to obtain a powder of uniform particle size distribution. The produced powder was moisturized up to 6% using spray gun (Binks Bullows). The moisture content was controlled using the gravimetric method. Slabs with dimensions of (199.8mm×79.9mm×7 mm) and a mass of 235 g were formed and subjected to a uniaxial pressure of 30 MPa using a plunger (Welko S.P.A.). The compacted samples were dried at a temperature of 150°C for 1-hour after which the weight of the slab was measured again to determine the loss of weight after drying. Subsequently, the samples were sintered at temperatures from 450 up to 1070 °C, then cooled to 630°C within 40 minutes. The heating rate and the sintering time used in this work were so chosen to simulate the actual sintering process used in the (ICIC).

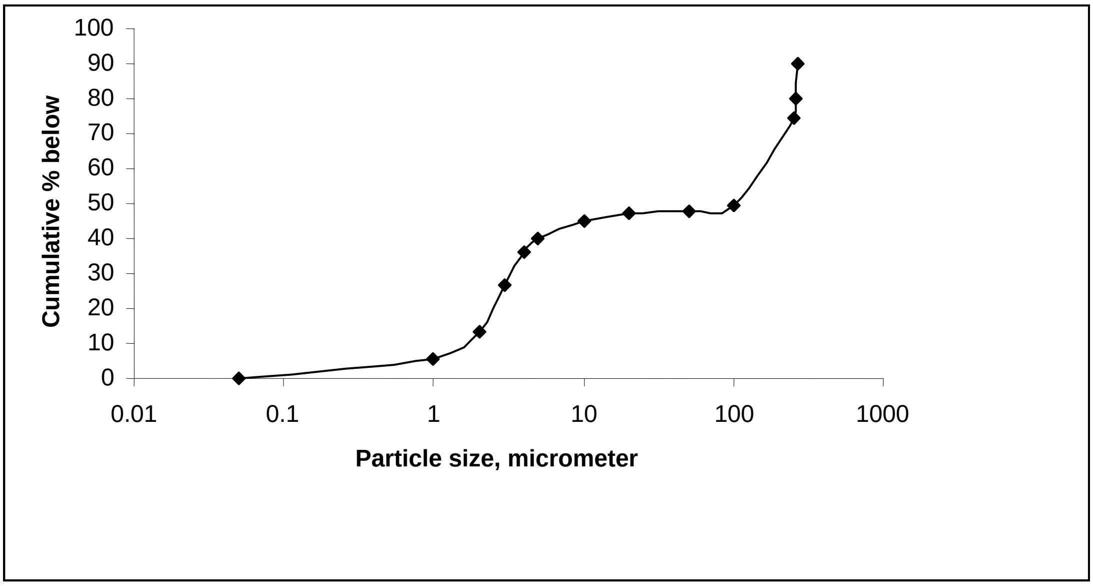


**Figure 3: Particle Size Distribution of Sludge**

The physical properties of the produced slabs, Firing Mechanical Resistance (FMR), Loss On Ignition (LOI), Water Absorption (WA) and shrinkage have been determined. The FMR of the sintered specimens was measured with a universal testing machine (Welko, Italy) in three-point bending tests at a constant cross-head speed of 0.5 mm/min. Water absorption value was calculated as the increase ratio in slab weight after submerging the sintered sample in boiled water for 2 hours. The Loss On Ignition (LOI) was calculated as the loss of slab weight after ignition compared to the weight of the compacted slab before ignition. The weight was measured using an analytical balance (Precisa 400 M), the reduction in both length and width of the compacted slab after ignition represented the shrinkage values.

## RESULTS AND DISCUSSION

In terms of chemical composition, the major differences between sludge slime and clay are the higher alkaline earth oxide content (particularly CaO) and the high LOI value of the sludge slime (Table 1), because these might make some changes in the clay mixture behavior after sludge slime addition. The clay materials present a typical composition and are constituted mainly by silica, alumina and minor contents of Mg, Ca, Na and K oxides. Iron oxide content (4.36 wt.%) is responsible for a darker coloring of the sintered samples. The chemical composition of sludge slime shows high (CaO) and low argillaceous ($SiO_2$, $Al_2O_3$ and $Fe_2O_3$) material contents compared to clay composition. The mineralogical analyses show that the dried marble sludge slime is formed basically of $CaCO_3$,MnOOH and $CaMg(CO_3)_2$ (calcite, manganite and dolomite (Figure 1), while the sintered sludge slime is formed of $Ca(OH)_2$, MgO, Si, $KAlSiO_4$, $CaCO_3$ and $Al(OH)_3$ (portlandite, periclase, silicon, kaliophilite, calcite, gibbsite and nordstrandite) (Figure 2).

In Table 2, S1 represents the mixture of the blank sample, which has no sludge slime added. In mixtures S2, S3 and S4, kaolin was replaced by sludge slime of 18, 28 and 38 wt.%, respectively. In mixtures S5 and S6, feldspar was replaced by sludge slime of 50 and 100 wt.%, respectively, while calcium carbonate ($CaCO_3$) was replaced by the sludge slime with 34 and 100 wt.%, in mixtures S7 and S8, respectively. In S9, all of the pentonite was replaced by the sludge slime. The chemical composition of the prepared mixtures, as determined by raw mix design software, is shown in Table 3.

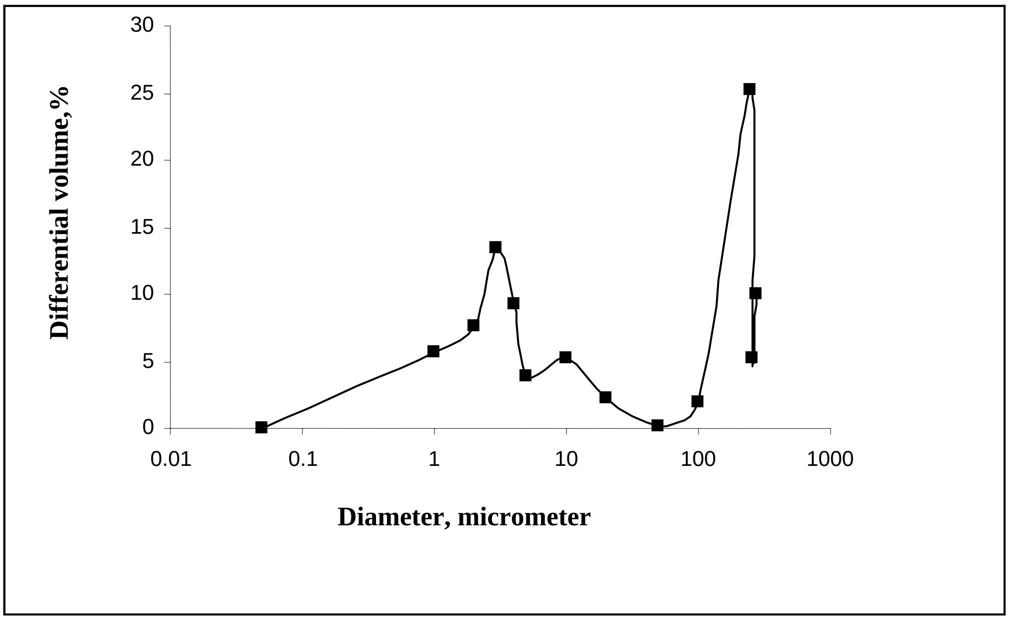


**Figure 4: Differential Particle Size Distribution of the Sludge**

The values shown in Table 4 present the average of five bodies for each value. The Loss On Ignition (LOI) is higher in mixes that have sludge slime content, due to loss of adsorbed water and volatile materials at temperatures up to 700ºC, followed by a weight loss that can be attributed to the carbonates decomposition ($CaCO_3 = CaO+CO_2$) (Acchar et al., 2006). In terms of oxides, the sludge slime material consists basically of CaO, MgO and $SiO_2$, with minor contents of $Al_2O_3$, $Fe_2O_3$, $K_2O$ and $Na_2O$. The Loss On Ignition (LOI) is slightly higher than what would be expected if all CaO present resulted from the decomposition of calcite, suggesting that dolomite might also be presented. The non-plastic character of the sludge slime improved (reduced) drying shrinkage (Table 4), because the sludge slime causes an expressive shrinkage due to the formation of liquid phase at high temperatures, followed by a strong expansion that can be attributed to the formation of a new crystalline phase composed of calcium oxide and alumino-silicates (e.g., anorthite $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$). Similar behavior was also reported in the literature for clay materials with high calcium oxide content (Hatzl and Gehiken, 2001).

Replacing kaolin ( plastic material) by the sludge slime (non-plastic material) mixes S2, S3 and S4 caused an increase in (CaO) and a decrease in argillaceous ($SiO_2$, $Al_2O_3$ and $Fe_2O_3$) content due to high ratios of sludge slime in the mix (Table 3). The results presented in Table 4 show that for mixes S2, S3 and S4 a decrease in both (FMR) and shrinkage values and an increase in the (LOI) and absorption values are noticed compared to the values for the blank mix S1. The proportioning of calcareous (CaO) and argillaceous ($SiO_2$, $Al_2O_3$ and $Fe_2O_3$) content is responsible for producing the adhesive and cohesive (cementing) materials that significantly affect the properties of the sintered bodies. However, in mixes S5 and S6, the optimum proportioning between calcareous and argillaceous content increased the (FMR), while shrinkage, (LOI) and (WA) values have been adversely affected. Replacing the sludge slime by $CaCO_3$ in mixes S7 and S8 showed an improvement in (FMR) values, where the other parameters have been slightly affected due to the high $CaCO_3$ content in the sludge slime. However, replacing all the pentonite by the sludge slime S9 slightly decreased the (FMR) value and significantly improved the shrinkage of the sintered bodies.

Absorption values obtained in this work (Table 4) for clay with marble sludge slime are slightly increased compared to blank samples, due to the increase of CaO content. However, it did not affect the quality of the sintered bodies. It should be noticed that replacing each single raw material except the pentonite by the sludge slime caused a deformation out of the plane (bending) of the sintered bodies.

Figures 3 and 4 show the particle size distribution and the differential size distribution of the marble sludge slime, respectively. The major feature to be noted is the large particle sizes in the sludge slime; the average particle size $D_{50}$ is about 45 μm, while the $D_{10}$ and $D_{90}$ are about 1.66 and 272 μm, respectively. There is one coarse population centered at about 250 μm. The largest measured particle size is about 275 μm. This particle size distribution shows that the fineness of the sludge slime is suitable for being directly incorporated into ceramic industry.

## CONCLUSIONS

The obtained results in this work support the possibility of replacing pentonite used as raw material in ceramic industry by marble sludge slime. Replacing pentonite by sludge slime significantly reduced the shrinkage values of the produced tiles, where the other physical properties of the tiles have not been significantly affected. Since the ceramic industries processes consume huge amounts of raw materials, the results presented in this work show that all of the produced sludge slime can be consumed, which will avoid expensive management of the residues with landfill, and preserve an equivalent amount of natural mineral resources (pentonite).

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