Study the Structure Characterization of Porcelain Formulation at Different Sludge Content

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Abstract. Porcelain formulation in the form of pellets have been studied by substituted fluxing materials with treated FGD sludge at different percentages. In this work, treated FGD sludge was added in percentages from 5% up to 15% uniaxially pressed at 11 MPa, dried and then sintered at temperature 1200 °C for 3 hours. Weight loss, volume shrinkage/expand, bulk density, densification, porosity and flexural strength were investigated on sintered samples. This demonstrated that the treated FGD sludge addition in porcelain formulation has influenced on the sintered samples. It was concluded that the treated FGD sludge waste could be used as a suitable raw material source for production of porous porcelain ceramic due to their organic and inorganic content.

1. Introduction
Flue gas desulfurization (FGD) is well established air treatment technology for removal SO₂ prior to discharge. The most common FGD processes are by passing the flue gas through a crushed limestone water or lime slurry. During the flue gas and limestone slurry interaction under natural atmospheric condition, SO₂ dissolve in the water as sulphite (SO₃²⁻) and is subsequently precipitated by Ca²⁺ to form calcium sulfite (CaSO₃). When excess air is forced into the system during SO₂ scrubbing the resultant calcium sulfite (CaSO₃) react with oxygen in the presence of water to form calcium sulfate (CaSO₄). The production of sludge of calcium sulfite (CaSO₃) and calcium sulfate (CaSO₄) is the major disadvantages of wet nonregenerable processes in FGD. This sludge is usually stored in ponds or used as landfill. The disposal of flue gas desulfurization waste may emit sulphurous gases into atmosphere even when chemically stabilized [1]. In NEGM, approximately 30 MT (million tons) of sludge from FGD are produced every month. The disposal of such a huge quantity of the sludge is a problem in areas around plant [2]. Therefore, a innovative strategy are needed to reduce the negative impact of the sludge to the environmental. Nowdays, the porous ceramic is consider high potential to develope and investigate due to porous ceramic had been use in various field application such as water purifying, catalyst support and bioceramic. Based on the elemental analysis, the sludge contains high
amount of alkali and alkaline oxides which might be useful to replacement of feldspar in the fabrication of ceramic porous product.

2. Methodology
Different porcelain composition were formulated as shown Table 1 using mixture of kaolin, silica, ball clay, feldspar and treated FGD sludge waste. The treated FGD sludge waste was added up to 5 wt% in gradual replacement of feldspar. A standard composition (kaolin 25 wt%, silica 30 wt%, ball clay 25 wt% and feldspar 20 wt%) referred to as 0 wt% treated FGD sludge waste formulation was used as reference. The FGD sludge waste was collected from Nippon Electric Glass Malaysia (NEGM) company. The dried FGD sludge waste powders were calcined in muffle furnace at 1100 °C for 3 hours with heating rate 5°C/min. The dried treated FGD sludge wastes were crunched by hammered manually to earn smaller size of hard solid. After that, the smaller size of hard sludge waste were milled using planetary mill (Pulveridette 6 Classic Line Mono Mill, FRITSCH) at speed 300 rpm for 3 hours to gain finer particle size. The powder of mixtures of samples with different composition were placed into tungsten jar by using planetary mill (Pulveridette 6 Classic Line Mono Mill, FRITSCH) again with speed 300 rpm at 1 hours. The ratio of tungsten ball to powder used was 10 : 1 to provide to ensure homogeneity of mixtures and provide a sufficient load to reduce the particle size of the mixture powders. Then, the finer mixture of powder were obtained from milling process was then sieved to achieved more homogeneous powder for characterization step.

The mixture of powder form were sieved using 45 μm in order to obtain a uniform size powder for the purpose of powder compaction. The mixture powders were then pressed into 12 mm diameter pellets via uniaxial hydraulic press at 11 MPa and sintered at temperature of 1200 °C with soaking time 3 hours and heating rate 5 °C/min respectively. Meanwhile for rectangular die at 10.00 cm was done at 58 MPa and sintered at 1200 °C with soaking time 3 hours and heating rate 5 °C/min respectively. The percentage of porosity and densification of samples were obtained by dividing bulk density (obtained from Archimedes principle) with theoretical density of sintered samples. Meanwhile, percentage of weight loss and diameter shrinkage of samples were calculated based on the particular data measured before and after sintering process. The flexural strength was determined by three point bending test at a loading rate of 1.0 mm/min according to the ASTM C674-88 standard model INSTRON 3367 (Maks :30kN).

Table 1 : Porcelain formulations (wt%).

| Raw materials    | 0 wt% FGD | 5 wt% FGD | 10 wt% FGD | 15 wt% FGD |
|------------------|-----------|-----------|------------|------------|
| Kaolin           | 25        | 25        | 25         | 25         |
| Silica           | 30        | 30        | 30         | 30         |
| Ball Clay        | 25        | 25        | 25         | 25         |
| Feldspar         | 20        | 15        | 10         | 5          |
| Treated FGD sludge| 0         | 5         | 10         | 15         |

3. Result and Discussion

3.1. Characterization treated FGD sludge

3.1.1. Dimensional changes

Figures 1-6 showed the physical properties of different percentages amount of treated FGD sludge waste addition in pellets of porcelain formulation. It was found that, the presence of treated FGD sludge addition in porcelain formulation were affected the result of samples. From the Figure 1, the weight loss of samples during sintering process were in (6.45% - 30.65%). From Figure 1, it showed continuously increasing the weight loss with increase amount of percentages treated FGD sludge waste. Meanwhile, without presence treated FGD sludge showed the lowest percentages of weight loss. It can
be related due to the decomposition of sulfur dioxide (SO₂) which present in porcelain formulation during sintering process. The more treated FGD sludge was added, the more weight loss will inevitably increase due to the high content of sulfur dioxide (SO₂) [3].

Furthermore, Figure 2 also displayed the percentages of densification of samples were decreased when amount percentages of treated FGD sludge were increased. Moreover, the amount bulk density were also decreased with the increasing amount of percentage treated FGD sludge. Thus, the addition treated FGD sludge in samples of porcelain formulation were affected the higher percentages porosity in Figure 5 of samples and reduced percentages of densification [7]. According to Ishak et al. [8] which stated that, decreasing the densification has also resulted the decreasing in bulk density of samples which some powder were might burnt off during sintering process.

![Figure 1. Percentages of weight loss in porcelain formulation with addition of treated FGD sludge.](image1)

![Figure 2. Percentages of densification in porcelain formulation with addition of treated FGD sludge.](image2)
Figure 3. Percentages of bulk density in porcelain formulation with addition of treated FGD sludge.

As for shrinkage/expand properties, the percentage of volume shrinkage of sintered samples were decreased with the higher contain of treated FGD sludge added in samples as shown in Figure 4. The samples were shrank at 18.44% to 13.98% at value 0 wt% to 5 wt% of treated FGD sludge. Moreover, the samples were found expanded -1.81 to -43.40% for samples that contain 10 wt% and 15 wt% of treated FGD sludge. The presence of amount feldspar in porcelain formulation, it promotes liquid phase sintering which yield value of shrinkage much higher compared than others samples. In addition, as the explained by Galusek et al. [4] during the intermediate phase of sintering, the microstructure of the sample were undergoing rapid inter-particle neck growth and coalesce. It diffused into empty space creating grain boundaries interface [4,5]. As a result, the movement of atoms get into empty space will cause the samples to be shrank [4]. However, upon adding increasing amount of treated sludge in the porcelain formulation, the samples expand up to certain level of addition. It may due to the increasing amount of treated sludge and decreasing feldspar in porcelain formulation resulted in high amount of gas release during the sintering process and consequently cause expansion of samples [10,11]. This is a reason why volume shrinkage decrease at about 5 wt% and expand at about 10 wt% to 15 wt% of treated FGD sludge addition.

Figure 4. Percentages of volume shrinkage in porcelain formulation with addition of treated FGD sludges.
The Figure 5 shows the percentage of porosity as function of treated FGD sludge added in the porcelain formulation. As shown in the figure 5 the porosity content tend to increase with increasing treated FGD sludge addition. This indicates that the replacement of feldspar in porcelain formulation decreases the vitrification which reflect on higher porosity mainly at 15 wt% of treated FGD sludge. Previous study has demonstrated that the presence of fluxes in ceramic raw materials with a relatively high amount of alkaline oxides, would react with silica and alumina promotes liquid phase formation that facilitates the densification. The liquid phase surrounds the solid particles and by surface tension enables the particles to approach each other and so close the porosity, which improves the structural compaction of the ceramics [11, 12]. However, the samples has increased the porosity with increasing treated FGD sludge. [6]. It may due the higher heating temperature which make the waste gases liberating them from decomposition of organic treated FGD sludge and increasing the porosity of samples. Potential source of gas evolution in samples could be the clay itself absorbed as well as chemically held water, sulfur dioxide and entrapped air [13].

![Figure 5](image)

**Figure 5.** Percentages of porosity in porcelain formulation with addition of treated FGD sludge waste.

### 3.1.2. Mechanical Properties

The flexural strength of pellets of porcelain formulation with addition treated FGD sludge is shown in Figure 6. The mechanical behaviour is quite correlated with studied properties. The samples of porcelain formulation displayed flexural strength value within 6.22 MPa-45.81 MPa ranges. The flexural strength of samples were decreased with increasing percentages of treated FGD sludge in porcelain formulation. As shown in Figure 6, sample with 15 wt% FGD has the lowest percentages of flexural strength among the studied samples. Significant difference in flexural strength are due the contain increasing treated sludge and decreasing feldspar in samples as well as higher porosity. The higher of porosity resulted the reducing of crunching strength of samples. This can be explained by the fact that during sintering process, treated FGD sludge powder that contain calcium sulfite and released sulfur dioxide (SO$_2$) gaseous [9]. In temperature of 1200 $^\circ$C, the organic matter was totally destroyed and responsible for the higher porosity in sample subsequently produced some holes and channel inside samples which was attributed at lowest flexural strength [14].
4. Conclusions
The following conclusion may be drawn the experimental results as the discussion. The different amount percentages of treated FGD sludge were mixed with porcelain formulation at percentages reaching 15%, dry ground, molded presses uniaxially at 11 MPa and 58 MPa respectively. Sintering process was performed for soaking time at 3 hours. The result showed that the high amount of treated FGD sludge has increased the porosity and reduced the densification as well as lower flexural strength of sintered samples. This demonstrated that the treated FGD sludge addition in porcelain formulation has influenced on the sintered samples. It was concluded that the treated FGD sludge waste could be used as a suitable raw material source for production of porous porcelain ceramic due to their organic and inorganic content.

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