Phase Transformation and Microstructure Characterization of Ceramic Porcelain with Different Ratio of Treated Fgd Sludge/Feldspar

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Abstract. The porcelain formulation containing percentages of treated FGD sludge waste from 5% up to 15% in replacement of feldspar were prepared. The porcelain mixture formulation were mixed by high energy planatery mill at speed 300 rpm for 1 hours. The powder were compacted by using hydraulic press and sintered at temperature 1200 °C for 3 hours. The sintered samples were characterized using X-ray fluorescene (XRF), X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and Thermogravimetry/ Differential scanning calorimetry (TGA/DCS). The primary effect concerning the addition of treated FGD sludge was the change of intensity composition (gypsum and anhydrate) in porcelain formulation. The XRD analysis has shown that the main component in sludge waste were gypsum and anhydrate.

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 (SO₃⁻₂) 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 sulphur 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 area around plant [2]. Therefore. A innovative strategy are needed to reduce the
negative impact of the sludge to the environment. Based on the elemental analysis, the sludge contain high amount of CaO, SiO₂, SO₃ which might be useful required in fabrication of ceramic based product.

2. Methodology

Different porcelain tile composition were formulated as shown Table 1 using mixture kaolin, silica, ball clay, feldspar and treated FGD sludge waste. 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 dried FGD sludge waste powders were further sintered in muffle furnace at 1100 °C for 3 hours with heating rate 5°C/min. The dried treated FGD sludge waste 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 size turn into powder form. Four ceramic porcelain formulation were formulated as shown Table 1 using mixture kaolin, silica, ball clay, feldspar and treated FGD sludge waste. The treated FGD sludge waste were added up to 5 wt% in gradual replacement of feldspar. The mixed composition were placed into tungsten jar and milled using planetary mill (Pulveridette 6 Classic Line Mono Mill, FRITSCH) again at speed 300 rpm for 1 hours. The ratio of tungsten ball to Powder used was 10:1 to provide a sufficient load to crush the mixture powder. 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 of powder particles 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 sinter at temperature of 1200 °C with soaking time and heating rate of 3 hours and 5 °C/min respectively. In this study, the samples will be characterized to determine their chemical and structural properties. The X-ray Fluorescence (XRF) was used to detect the elemental composition in dried samples. The Fourier Transform Infrared (FTIR) was used to qualitatively identify the functional group on samples using Perkin Elmer Spectrum 65 (model). X-ray diffraction (XRD) pattern of the samples were recorded by XRD-6000, Shimazu using Cu-Kα radiation. The measurement were made at temperature range 15-70 °C on 2θ with scan rate 1.0s/step. Thermal analysis of samples was also recorded by using TGA/DSC 2 HT METTLER TOLEDO.

3. Results and Discussion

3.1. Characteristic of FGD sludge

3.1.1. Chemical properties of sludges waste

The XRF results of FGD sludge waste are shown in Table 2. Composition of FGD sludge waste display calcium oxide (CaO) is the highest content with 22.00 wt% followed by sulphur trioxide (SO₃) with 12.20 wt% and silica (SiO₂) accounting for 1.51%.
### Table 2. Chemical analysis of used raw materials.

| Elemental oxides | CaO | SO\(_3\) | SiO\(_2\) | K\(_2\)O | Fe\(_2\)O\(_3\) | MgO | Al\(_2\)O\(_3\) | P\(_2\)O\(_5\) | NiO | ZnO |
|------------------|-----|----------|----------|--------|----------------|-----|----------------|---------------|-----|-----|
| FGD Sludge waste (wt%) | 22.0 | 12.2 | 1.51 | 0.625 | 0.452 | 0.409 | 0.354 | 0.328 | 0.0043 | 0.02 |

3.1.2. Phase analysis

The X-ray diffractometer of FGD sludge and treated FGD sludge is shown in Figure 1. As a result of XRD analysis both samples were found as anhydrite phase which are calcium sulfate (SiO\(_4\)Ca; ICSD card: 98-001-0224) were the major crystalline phase present. On the other hand, XRD analysis has shown that both samples also constituting gypsum (CaSO\(_4\).H\(_2\)O; ICSD card: 98-006-7711) which displayed as high crystallinity. The phase quantification by Rietveld method in figure 1 demonstrate that phase gypsum was contributed the highest percentages with composition 52.7% meanwhile anhydrite was contributed with composition 48.3%. However, it was found that when the FGD sludge was calcined, the peak intensity of anhydrite was increased with the highest percentage 97.1% while gypsum which calcium sulfate dihydrate was decreased with 2.9%. It is because, calcium oxide (CaO) and sulfur trioxide (SO\(_3\)) was higher compared other elements. In addition, the diffraction pattern of FGD sludge and treated FGD sludge were comprised the orthorhombic structure for anhydrite while gypsum with monoclinic structure. Crystal structure is important because it can affect the physical and chemistry of the samples.

![X-ray diffraction pattern of FGD sludge and treated FGD sludge waste.](image-url)
3.1.3. Functional group analysis

Figures 2 and 3 shows the functional group peaks of untreated and treated FGD sludge waste. FTIR confirmed the presence of CaSO$_4$ as the predominant component of untreated FGD sludge. All the characteristics band for treated FGD sludge were clearly present in FTIR spectrum for untreated FGD sludge. The band at 1093 cm$^{-1}$ and 666 cm$^{-1}$ for both samples were characteristic of C-O stretching and bending modes of sulfur, respectively [5,9]. Those peaks were indicated that some undissolved decomposition CaSO$_4$·2H$_2$O during sintering is still remain in treated FGD sludge [6]. The small bands around 3400 cm$^{-1}$ and 1681 cm$^{-1}$ were attributed the adsorbed water (OH) in the dihydrate structure for both samples. Johshi et al., (2015) suggested that normally stretching band vibration associated to water molecule in band around 3400 cm$^{-1}$ [10]. For treated FGD sludge, band that are typically associated with calcium sulfate hemihydrate at peak 980 cm$^{-1}$. Band typically associated with calcium carbonate were absent at peak 720 cm$^{-1}$ and 1453 cm$^{-1}$ or small [7].

![Figure 2. FTIR spectrum of FGD sludge.](image1)

![Figure 3. FTIR spectrum of treated FGD sludge.](image2)
3.1.4. **Thermal analysis**

![Figure 4. TGA/DSC curves of sludge.](image)

The thermogravimetric curve of TGA/DSC for sludge are shown in Figure 4. The weight loss started at around 37.74 °C occurred in number of stages up to 1200 °C and about 44% of the sludge weight was lost under air flow. The first at 13% decrease in the mass occurred in between 37.74 °C and 150 °C due to the removal of physical water. At 150 °C-174 °C range there is an endothermic event with mass loss which can be mainly related to the dehydroxylation of clay mineral [4]. Subsequently, mass loss at stage 174 °C-1110 °C ranges was observed. It can be related which may due to removal of water and composition of carbonates [8]. The weight loss observed above 1110 °C up to 1200 °C for the air flowing run may be due to decomposition/oxidation of organic compound containing sulphur and nitrogen [10].

4. **Conclusion**

The porcelain ceramic with different amount of FGD sludge substituted feldspar formulation was successfully produced. The primary effect concerning the addition of treated FGD sludge was the change of intensity composition (gypsum and anhydrate) in porcelain formulation. The XRD analysis has shown that the main component in sludge waste were gypsum and anhydrate. Disposal of sludge waste is proven to be able to be used as raw material substitution in porcelain formulation. Because of the less exploration of utilization FGD sludge waste in ceramic production, further study need to be done to verify the potential of FGD sludge as raw material in porcelain product.

**References**

[1] D Graves, J Smith, L Chen, A Kreinberg, B Wallace and R White 2017 *J. Environ. Manage* **201** p 357-365

[2] D Eliche-Quesada 2011 *Appl. Clay Sci.* **52** p 270-276

[3] G Brindley and M Nakahira 1959 *J. Am. Ceram.Soc.* **42** p 314–318

[4] B Pinheiro and J Holanda 2013 *Ceram. Int.* **39** p 57-63

[5] H Böke, S Akkurt, S Özdemir, E Göktürk and E Caner Saltik 2004 *Mater. Lett.* **58** p 723-726

[6] M Sun, J Hou, G Cheng, S Baig, L Tan and X Xu 2014 *Fuel* **125** p 66-72

[7] A Khalaf 2021 Rave.ohiolink.edu.

[8] S K Amin 2006 *Ceram.-Silik.* p 11-20
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