Characterisation Of FGD Sludge From One of Glass Industrial in Malaysia and Their Potential as Ceramic Mould

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Abstract. Flue Gas Desulfurization (FGD) is a waste incineration process used to eliminate sulfur dioxide (SO₂) from flue gas power plants. Limestone/gypsum was injected into the plant to trap sulfur dioxide and change their chemical composition from calcium carbonate to calcium sulfate dehydrate, known as FGD sludge wet scrubber. Nowadays, it is necessary to overcome the environmental pollution caused by the massive production of FGD sludge waste through recycling. In this research, FGD sludge was characterised to reveal its chemical composition, crystalline phase, and FTIR spectra characteristics. FGD sludge recorded a moderate alkaline with a pH of 8.24. Based on the XRD result, FGD sludge was mainly composed of gypsum (CaSO₄•2H₂O) and anhydrite (CaSO₄). XRF analysis also shows that FGD sludge was mainly composed of calcium oxide, sulfur trioxide, silica, and potassium oxide.

1. Introduction

FGD sludge is a synthetic by-product generated from the FGD process in power plants. It is a commonly-used method for eliminating SO₂ in wet scrubbing by spraying a polluted gas stream with limestone to lessen the emission of pollutants, thereby generating waste called FGD sludge waste powder [1]. FGD waste is primarily composed of SO₂ and other flue gas found at waste incineration. When excess air is forced into a system during SO₂ scrubbing, the resultant calcium sulfite (CaSO₃) reacts with oxygen in the presence of water to form calcium sulfate (CaSO₄) [2,3]. It has several beneficial applications in cement production, agriculture, and construction of structural fills [4]. Ironically, these wastes can be used as a substitute material in the production of Plaster of Paris and ceramic. According to a previous study, oxide-rich sludge is generally required to fabricate ceramic-based products [4].

The sludge contains fluxing elements and boron, which are beneficial as sintering aids and nucleating to produce glass, glass-ceramic, and polycrystalline ceramic [6]. Besides, these wastes can also be used as substitute materials in ceramic mould production because it contains gypsum, a primary raw material for ceramic mould and plaster ceiling materials [7]. With this, characterisation of FGD sludge waste is important to determine their potential ability in the production of ceramic.
At present, almost all the flue gas desulfurisation sludge produced is disposed of in holding ponds or landfills due to its sulfur content. Such implementation may lead to heavy metal leaching from rainwater and pollute the groundwater and river [7]. Stabilisation or fixation and placement in landfills is also one of the most common disposal methods. This kind of treatment requires lots of expenses. Therefore, to reduce the operational cost of disposal, this sludge can be reused as one of the main components in ceramic production. In this way, the operating cost of sludge waste disposal can be significantly reduced, and the company that produces these wastes can also benefit from it.

2. Materials and method

This study used waste products from the flue gas desulfurisation process at the Japanese Electric Glass Factory. Those waste products are also known as FGD sludge wet scrubber that initially come in powder form.

The characteristic of FGD sludge and its effect on the environment is the main type of testing to be conducted. pH (BS1377-3:1990 standard), XRF analysis, XRD analysis, FTIR could determine its chemical properties while for physical properties of FGD sludge, analysis such as LOI, weight loss, rate of absorption, and plastic limit (ASTM D4318 Standard from Atterberg Limit) were conducted. The effect of FGD sludge on plant growth and the aquatic environment was also investigated. A fine-grain particle of FGD sludge was obtained from sieving proceed with 500 mesh opening.

3. Results and discussion

3.1 Characteristic of FGD sludge

FGD sludge from Nippon Electric Glass Sdn. Bhd. was obtained and analysed. In this study, by analysing its chemical and physical properties to evaluate its potential as plaster of Paris.

3.1.1 Chemical properties of FGD sludge

FGD sludge recorded a moderately alkaline with a pH reading is 8.24. This is primarily attributable to the limestone (calcium carbonate) used in most FGD technologies by acting as an alkali sorbent to capture acidic compounds such as sulfur, resulting in the formation of solid alkali particles [7]. The mixture of sludge and distilled water released some heat from a reaction, and the recorded temperature is 28.2°C, slightly above the room temperature. Table 1 shows the numerical chemical composition of FGD sludge. The main components detected on FGD sludge were calcium oxide (CaO), sulfur trioxide (SO₃), and silica (SiO₂), corresponding to 22.04%, 12.2%, and 1.51%, respectively. The others component, such as chlorine (Cl), zinc oxide (ZnO), nickel oxide (NiO), bromine (Br) also present in it.

| Component (%) | CaO  | SO₃  | SiO₂ | K₂O  | Fe₂O₃ | MgO  | Al₂O₃ | Others |
|---------------|------|------|------|------|-------|------|-------|--------|
| FGD Sludge    | 22.04| 12.20| 1.51 | 0.63 | 0.45  | 0.41 | 0.35  | 62.41  |

Figure 1 shows the XRD pattern of FGD sludge. The crystalline phase detected in FGD sludge was gypsum (98-001-1992) and anhydrite (98-000-5306). The characteristic peaks of gypsum were located at 7.628Å, 4.28884Å, 3.80322Å, 3.06858Å, 2.68595Å, and 2.22011Å, while the characteristic peaks for anhydrite were located at 3.50221Å, 2.68595Å, 2.33041Å, 2.08666Å, and 1.64865Å. Based on Scherrer method, the crystallite size for gypsum and anhydrite is 746μm and 338μm, respectively. For each of the mentioned crystalline phases, all of these data were obtained from the ICSD reference pattern and Rietveld refinement method. In conclusion, FGD sludge composed 57.6% of gypsum and 42.4% of anhydrite.
Fourier transform infrared (FTIR) is one of the most useful analytical techniques used to determine the material’s molecular composition and structure based on the sample’s absorbance of infrared radiations (IR) at various wavelengths [8]. Figure 2 shows the FTIR spectra of FGD sludge. Based on the figure, many peaks were detected, indicating FGD sludge was a complex structure material. Two peaks in the range between 2700 and 3600 cm\(^{-1}\) (2786.64 and 3355.63 cm\(^{-1}\)) indicate a single bond to hydrogen area. For 3355.63 cm\(^{-1}\) was a hydrogen bond, and it has a broad absorption band that occurred in the range of 3650 to 3250 cm\(^{-1}\). At 2786.64 cm\(^{-1}\) shows a peak for aldehyde because Rachmawati stated that aldehyde peak could be found between 2700 and 2800 cm\(^{-1}\) [9]. Also, a peak at 1731.56 cm\(^{-1}\) indicates the presence of anhydrite, which is parallel to the XRD result. James stated that the peak in the range of 1775-1740 cm\(^{-1}\) and 1830-1800 cm\(^{-1}\) shows the presence of anhydrite [10].
3.1.2 Physical properties of FGD sludge

Thenmuhil et al. (2014) reported that the loss on ignition (LOI) value of Plaster of Paris is 45.6% [11]. In the present study, FGD sludge recorded a value of LOI at 41.2701% after subjected to 1100°C. Such close value indicates that the organic matter in FGD sludge and Plaster of Paris are nearly the same. Figure 3 shows the daily weight change after FGD sludge was left opened at room temperature, while table 2 shows the weight loss rate value of the sludge after being left opened at room temperature. The rate of weight loss of FGD sludge was calculated using equation (1). The weight of FGD sludge decreases as it was left open was due to the loss of moisture/water. The maximum weight loss rate for FGD sludge was 5% (reach an equilibrium state). The evaporation process and the fact that liquid water flows from the inner to the outer surface due to convective heat transfer [11] explains the phenomenon of FGD sludge’s weight loss.

$$\text{Rate (\%)} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$  

(1)

![Figure 3. Changes of FGD sludge’s weight per day(s).](image)

| Day(s) | 1st day | 2nd day | 3rd day | 4th day | 5th day |
|--------|---------|---------|---------|---------|---------|
| FGD sludge (%) | 1 | 3 | 5 | 5.5 | 5.5 | 5.5 |
| 2 | 3 | 5 | 5.5 | 5.5 | 5.5 |
| 3 | 2.5 | 4.5 | 4.5 | 4.5 | 4.5 |
| Average | | | | | 5.0 |

A slight amount of distilled water was added to a fine-grain FGD sludge and was rolled over to be shaped into a thread following ASTM D4318. The FGD sludge has a measured plastic limit of 38.69%, while FGD scrubber material recorded by Pease has a measured plastic limit of 28% [12]. Based on these values, FGD sludge requires 38.69 wt% of water to gain its plasticity formation and change its properties from solid to semi-solid. Fig 4 shows the FGD sludge’s condition after being rolled into a thread. Since FGD sludge could easily remove its moisture, the steps taken to shape FGD sludge into a thread was done carefully to obtain an accurate result of their plastic limit.
3.2 Effect of FGD sludge on the environment

Landfill disposal is the most common way of disposal of industrial waste. This method is also common for FGD sludge disposal. The increasing amount of unattended sludge disposal in landfills could lead to major land pollution, which consequently may affect the groundwater sources beneath it. Hence, the effect of FGD sludge on plant growth was investigated by preparing sludge with 5 compositions (0%, 25%, 50%, 75%, and 100%) and mixed with the same type of soil. Next, mung beans (*Vigna radiata*) were planted on those mixtures. Based on the result in figure 5, all of the mung beans planted in soil containing FGD sludge did not show any sign of growing after 10 days of planting, but it grows well in soil without FGD sludge. On the first day after planting, a tiny sprout can be seen in the 0% of sludge. The mung bean’s plant can grow up until 10-20 cm long in 0% sludge after 10 days. From this observation, it is safe to say that FGD sludge may negatively affect plant growth.

The underlying cause of this situation is that FGD sludge causes the pH of the soil to be alkaline. According to Ryczkowski (2018), plants that grow in alkaline soil may exhibit nutrient deficiencies. In average, mung beans perform better at pH 6.2 [13]. Therefore, a higher pH condition may negatively affect mung beans growth. In addition, a large amount of gypsum in FGD sludge may eliminate essential plant nutrients in soil such as aluminium, iron and manganese [14]. Elimination of these essential plant nutrients may subsequently affect the growth of plant negatively. Clark *et al.* (2001) also mention that FGD sludge contains excessive amounts of soluble salts such as Mg, Na, Cl and Al that ma be hazardous to plants and negatively affecting the plant growth [15].

The effect of FGD sludge on the aquatic environment was also analysed. FGD sludge dissolved in an aquarium filled with filtered water in 24 hours. After 24 hours, two Siamese fighting fishes (*Betta splendens*) were left in two separate aquarium containing dissolved FGD sludge. The other two fishes were left in two separate aquarium filled with normal filtered water. The behaviour demonstrated by the fishes were analysed. Based on the result, the fishes left in an aquarium filled with dissolve FGD sludge...
exhibited stress signs such as clamped fins (see Fig 6), poor appetite and lethargy. Also, a ‘stress stripes’ was observed in one of the Betta fishes left in an aquarium filled with FGD sludge. Since Betta fish can tolerate alkaline water at pH in average 8.2 [16], the alkalinity property of FGD sludge was not the contributable factor to the sudden changes of Betta fishes behaviour. Instead, it was believed to be caused by the sulfur dioxide in the dissolved FGD sludge’s water. There was no study to support this hypothesis. However, a study conducted by Gibson demonstrated that pig consuming barley with high sulfur dioxide content has cardiac hypertrophy syndrome [17]. Therefore, the stress behaviour demonstrated by the fish was hypothetically due to the presence of sulfur dioxide.

Figure 6. The condition of Betta fish in FGD sludge’s solution.

4. Conclusion
This study investigates the characteristic of FGD sludge and assessing its potential to be used in the production of Plaster of Paris. The underlying reason for assessing its recycling potential is because the current disposal method for FGD sludge poses a high risk of environmental pollution. The main components of FGD sludge and its properties were analysed to assess its potential to be used in Plaster of Paris production. The main components of FGD sludge detected were gypsum and anhydrite. Disposal of component like gypsum is proven to be used as substitution material in Plaster of Paris production as the raw material used to produce Plaster of Paris is gypsum. Therefore, utilisation of gypsum in FGD sludge might result in less exploration for natural gypsum and less disposal of harmful FGD sludge in the landfill. Further study on the production of Plaster on Paris with FGD sludge needs to be done to verify this potential.

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