Physical and Mechanical Properties of Non-Stoichiometric Cordierite with Treated FGD Sludge Addition Sintered at 1250°C

Fatin Fatini Othman¹, Banjuraizah Johar¹*, Shing Fhan Khor², Nik Akmar Rejab³ and Suffi Irni Alias¹

¹Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
²Faculty of Electrical Engineering, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.
³School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (USM), Penang, Malaysia.

E-mail: banjuraizah@unimap.edu.my

Abstract. The effects of addition treated FGD sludge in non-stoichiometric cordierite, by benefiting from its high mechanical strength and good thermal performance, can hold promise for more practical applications of non-stoichiometric cordierite. Treated FGD sludge waste from borosilicate glass industrial were used as a flux to reduce the sintering temperature of cordierite. Cordierite ceramics were prepared using silica (SiO₂), alumina (Al₂O₃), talc, kaolin, magnesia (MgO) and treated FGD sludge via solid-state reaction method. The cordierite were prepared by adjusting the ratio of FGD sludge and magnesia in the cordierite composition, respectively. 4 composition of cordierite with 0%, 1.5%, 3.0% and 4.5% of FGD sludge were prepared to obtain the formation of α-cordierite that can be determine by X-ray diffraction (XRD) analysis. Porosity, density, shrinkage and flexural strength for each of cordierite composition were determined to obtain the best composition of treated FGD sludge required for sintering aids of cordierite. Only FGD 3.0% able to synthesis pure α-cordierite while FGD 1.5 % shows an improvement in both porosity and density. The increasing amount of treated FGD sludge lead to decreasing in mechanical strength of cordierite ceramic due to porous formation.

1. Introduction
Cordierite-based ceramics has gained great interest, mainly owing to its good mechanical behavior as well as to its attractive thermal and dielectric properties [1] that suitable to use in numerous applications such as refractory products, electro-ceramics, tablewares and as a kiln furniture [2]. The properties of cordierite greatly depend on the densification of samples which is related to the amount of porosity present [3]. Dielectric and thermal properties not only depend on crystalline phases of glass-ceramics but also their total porosity as well as pore size and shape [4]. Porosity of ceramic played such a crucial rules which determine the hardness and strength of a ceramic. To reduce the formation of porous cordierite, the addition of sintering aids or nucleating agent are essential to avoid a grain growth [5] due to high sintering temperature as it can consolidate the cordierite ceramic at low sintering...
temperature. Thus, the sintering aids is essential additives in cordierite synthesis. Magnesium oxide or zirconia are the other example of sintering aids can be used in synthesis cordierite [6].

Flue Gas Desulfurization (FGD) is a process of waste incineration to eliminate sulfur dioxide (SO₂) and carbon dioxide (CO₂) [4,5]. FGD waste is primarily composed with CaO, SO₂ and other flue gas that can be found at waste incineration. When excess air is forced into system during SO₂ scrubbing, the resultant calcium sulfite (CaSO₃) reacts with oxygen in presence of water to form calcium sulfate dehydrate (CaSO₄•2H₂O) [7]. Based on the elemental analysis, the preliminary study had demonstrated that the FGD sludge rich with oxides that are generally required in fabrication of ceramic-based product [8].

Nowadays, in order to overcome the environmental pollution that causes by the waste and to reduce a massive production of wastes, synthesizing and understanding the structural and physical basis of FGD sludge waste are necessary [7-10]. This project was carried out to synthesize α-cordierite and used treated FGD sludge as a dopant to enhance the crystallization and sinter ability of ceramic body.

There are three types of cordierite that had been classified such as α-cordierite, β-cordierite and μ-cordierite. High purity of α-cordierite came in favor as it has unique properties such as very low coefficient of thermal expansion, dielectric constant and density [11]. Boron has been an essential ingredient in ceramic glazes and porcelain (vitreous) enamels for centuries [12]. It can initiate glass formation and reduce glass viscosity, helping to form a smooth surface and reduce thermal expansion [11-13]. By reusing the valuable chemical content from the sludge wastes, thereby it provides an alternative solution to mitigate pollution problems and reduce cost investment on waste management. Hence, the objective of the present work is to investigate the effect of treated sludge at different ratios to the non-stoichiometric cordierite at 1250°C sintering temperature.

2. Materials and Method

2.1. Materials

The raw material used for this research are silica (SiO₂), magnesia (MgO), alumina (Al₂O₃), talc (3MgO•4SiO₂•H₂O) and kaolin (Al₂O₃•2SiO₂•2H₂O). Non-stoichiometric cordierite composition of 2.8 MgO, 1.5 Al₂O₃, 5 SiO₂ was used with addition of treated FGD sludge at different weight percentage via solid-state method and subjected to 1250°C of sintering temperature.

Treated sludge obtained after FGD sludge was subjected to high calcination temperature (1100°C) for 3 hours to emit all gaseous. Then, the treated sludge crushed into a fine particle (300 mesh) before mixed it with the other raw material based on the ratio approved.

2.2. Method

Four cordierite compositions with different amount of sludge content (0%, 1.5%, 3.0% and 4.5%) were prepared for this research as shown in Table 1. Each composition were weighted and milled using planetary mill and tungsten carbide as grinding media for 1 hour at 300 RPMs. The powder mixture were then pressed into a cylindrical shape die with 12 mm diameter under 11 MPa pressure to obtain a pellet structure while for the flexural test, the mixture powder were pressed into a 10 cm x 1 cm rectangular die under 58 MPa pressure to obtain a rectangular shape of samples. Finally all green sample were sintered at 1250°C temperature for 3 hours with heating rate of 5°C/min. All of the sample were labelled by their weight percentage of treated FGD sludge used, such as FGD 0%, FGD 1.5%, FGD 3.0% and FGD 4.5%.
Table 1. The composition of each sample studied in this research.

| Raw Material           | Weight percentage (%) |
|------------------------|------------------------|
|                        | FGD 0  | FGD 1.5 | FGD 3.0 | FGD 4.5 |
| Silica, SiO₂            | 0.13   | 0.13    | 0.13    | 0.13    |
| Talc, 3MgO•4SiO₂•H₂O    | 29.49  | 29.49   | 29.49   | 28.49   |
| Magnesia, MgO           | 4.50   | 3.00    | 1.50    | 0       |
| Kaolin, Al₂O₃•2SiO₂•2H₂O| 61.82  | 61.82   | 61.82   | 61.82   |
| Alumina, Al₂O₃         | 4.05   | 4.05    | 4.05    | 4.05    |
| FGD Sludge, CaSO₄      | 0      | 1.50    | 3.00    | 4.50    |

3. Results and Discussion

3.1. Properties of FGD sludge after subjected to 1100°C sintering temperature

The main composition of FGD sludge used in this research were gypsum (CaSO₄•2H₂O) and anhydrite (CaSO₄). XRD result for FGD sludge and treated FGD sludge after subjected to the calcination process (Figure 1) shows that only anhydrite phase remains in the FGD sludge as evaporation of H₂O, which took place at high calcination temperature. The improper storage of treated FGD sludge after calcination causes the CaSO₄ in anhydrite to absorb moisture and change its chemical composition to CaSO₄•2H₂O, also known as gypsum. Thus, the presence of a small amount of gypsum in treated FGD sludge is reasonable in this case. The main purpose of calcining FGD sludge is to decompose sulfur from FGD sludge, but it didn’t occur completely as sulfur can still be found in the treated FGD sludge powder.

![Figure 1. The XRD result for both FGD sludge and treated FGD sludge after subjected to 1100°C sintering temperature.](image)

3.2. Microstructure, physical and mechanical properties of non-stoichiometric cordierite with addition of treated FGD sludge.

3.2.1. Microstructure properties of sample

The XRD pattern for the sample using a non-stoichiometric cordierite formulation can be observed in Figure 2. In XRD analysis, the three types of cordierite (α, β, and μ-cordierite) formation was observed and discussed. Based on the XRD pattern in Figure 2, all samples indicate a present of α-cordierite but...
different in the amount. Some unidentified peak also can be found in XRD pattern for all of the samples as those peaks didn’t represent a cordierite phase. Based on the XRD analysis, β-cordierite not found in each sample. The ICSD data used for α-cordierite was 98-004-1938, β-cordierite was 98-010-9834 and finally for μ-cordierite was 98-001-3453.

![Figure 2. XRD pattern for all 4 different type of treated FGD sludge used in cordierite composition.](image)

All samples recorded a displacement in XRD pattern, which may be caused by uneven surface of the sintered pellet due to poor sample preparation. Table 2 shows the displacement value for each sample had recorded. Before determining the phase of each peak, all samples have been undergone a treatment process to adjust their displacement.

| Sample    | Displacement, 2Theta (2θ) |
|-----------|---------------------------|
| FGD 0%    | 0.230                     |
| FGD 1.5%  | 0.508                     |
| FGD 3.0%  | 0.406                     |
| FGD 4.5%  | 0.406                     |

Among all of the samples, only FGD 3.0 % were successfully synthesis pure α-cordierite as the XRD pattern for FGD 3.0 % were exactly the same as the XRD pattern from ICSD database, as shown in Figure 3. As seen from figure 3, it is safe to conclude that the presence of treated FGD sludge promotes the synthesis α-cordierite via non-stoichiometric cordierite formulation. However, it began to decrease at the addition of 4.5% of treated FGD sludge as the XRD pattern of FGD 4.5 % sample didn’t show similarities with α-cordierite compared to FGD 3.0 % sample.
3.2.2. Physical properties of sample

Figure 4 shows the density and porosity value of investigated samples at different quantities of treated FGD sludge. The figure clearly shows that only FGD 1.5% recorded the improvement in both porosity (17.04%) and density (82.96 kg/m³) compared to the sample without any addition of treated FGD sludge, i.e., FGD 0% (20.31% and 79.69 kg/m³). The increase in the amount of treated FGD sludge used in the sample resulted in increased porosity and decreased densification. Porosity in cordierite is increased due to the grain growth and the decomposition process of sulfur dioxide, SO₂ from the treated FGD sludge occurs during the sintering process of the cordierite body. This can be explained by the XRD result of treated FGD sludge above, where it composed with rich-sulfur content, CaSO₄ and CaSO₄•2H₂O. This might be due to gaseous decomposition still occur during the sintering process. Eq. (1) shows the decomposition of sulfur dioxide at high sintering temperature. Several researchers [13, 14] have reported the magnesium, Mg can causes a grain growth phenomenon. Therefore, the reduction of Mg content in FGD 1.5 % reduces the phenomenon of grain growth, thereby imporving the performance of FGD 1.5%. In conclusion, the optimum amount of treated FGD sludge required to synthesis cordierite is FGD 1.5 % only.

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CaSO_4 = CaO + SO_2 + \frac{1}{2} O_2
\]  

(1)

All samples in this research shown a decreasing in volume due to the shrinkage process. The highest rate of volume’s change (Δ Vol.) after subjected to the sintering process shows the great ability of cordierite to shrink and obtain a dense microstructure. As shown in Figure. 5, FGD 0% has the highest shrinkage rate, followed by FGD 1.5%, FGD 3.0% and FGD 4.5%. The shrinkage variation on the sample pellets indicates that treated FGD sludge in the cordierite composition could affect the shrinkage ability to obtain a dense body as it develops a large volume of air void.
3.2.3. Mechanical properties of sample.
Flexural test can give a crucial hint about the mechanical properties of the sample. Figure 6 shows that the flexural strength of the samples decreases with the increasing amount of treated FGD sludge. This is because sulfur dioxide decomposes during the sintering process, and the porosity of the sample increases with the addition of treated sludge. Lian et al. [15] stated that the strength of porous media was significantly affected by the porosity of its internal structure. The presence of a large volume of air voids in porous media can cause the internal material too weak in their bonding [16] and thus, weakening the ability of media to withstand the pressure subjected on it.
Figure 6. Flexural stress of cordierite at maximum flexural load (MPa).

4. Conclusion
This research study was mainly focusing on the characteristic and mechanical properties of the sample after substitution of MgO with treated FGD sludge. The parameter for this study is the effect of treated FGD sludge on the non-stoichiometric cordierite. From the early testing result, it’s showed that additional treated FGD sludge help to decreasing the sintering temperature of cordierite from 1300 °C to 1250 °C but not for their strength. It is proven as the sample FGD 3.0% able to synthesis pure α-cordierite compared to FGD 0%. FGD 1.5% also recorded an improvement in density and porosity but not in their strength. The increasing amount of treated FGD sludge could impact the strength of the sample as the formation of porous media took place in the sample. To obtain the best strength’s result of the sample, FGD sludge need to be treated at 1300 °C and above to ensure zero sulfur dioxide could emitted during the sintering of cordierite at 1250 °C. To cope with the sludge waste disposal’s problem, FGD sludge can be reuse back as one of the main key factors to synthesis a porous cordierite.

References
[1] S. Martinović, M. Vlahović, M. Dojčinović, M. Pavlović and T. Volkov Husović 2018 Mater. Lett. 220 p 136–139
[2] A. Chowdhury, S. Maitra, H. S. Das, A. Sen, G. K. Samanta and P. Datta 2007 InterCeram Int. Ceram. Rev. 56(2) p 98–102
[3] H. Li, C. Li and L. Wu 2020 J. Alloys Compd. 826 p 154121
[4] K. Tabit, M. Waqif and L. Saâdi 2020 Mater. Chem. Phys. 254
[5] M. Rundans, I. Sperberga, G. Sedmale and G. Stinkulis 2013 IOP Conf. Ser. Mater. Sci. Eng. 47(1)
[6] J. Sheikh-Ahmad and J. P. Davim 2011 Mach. Technol. Compos. Mater. Princ. Pract. p 116–153
[7] G. Qimin, I. Noriaki and K. Kato 1996 Kagaku Kogaku Ronbunshu 22(6) p 1406–1407
[8] X. Ma, T. Kaneko, G. Xu and K. Kato 2001 Fuel 80(5) p 673–680
[9] H. Zhang, S. Yu, L. Shao and P. He 2019 J. Environ. Sci. 75 p 370–377
[10] X. C. Qiao, C. S. Poon and C. Cheeseman 2006 Waste Manag. 26(2) p 141–149
[11] L. Jia, Y. Tan, C. Wang and E. J. Anthony 2007 Energy and Fuels 21(6) p 3160–3164
[12] D. Shun, D.-H. Bae, I.-K. Jang, K.-H. Park and S. K. Park 2012 Adv. Mater. Phys. Chem. 02(04) p 189–192
M. A. Fakhari, A. Rahimi, M. S. Hatamipour and A. Fozooni 2017 *Can. J. Chem. Eng.* 95(6) p 1150–1155

J. Banjuraizah, H. Mohamad and Z. A. Ahmad 2009 *J. Alloys Compd.* 482(1–2) p 429–436

C. Lian, Y. Zhuge and S. Beecham 2011 *Constr. Build. Mater.* 25(11) p 4294–4298

L. Li and M. Aubertin 2003 *Can. J. Civ. Eng.* 30(4) p 644–658

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