

## Fly ash-based frit as a sintering aid for ceramic body

Vu Thi Ngoc Minh<sup>1\*</sup>, Cao Tho Tung<sup>1</sup>, Vu Hoang Tung<sup>1</sup>, Nguyen Duong Dinh<sup>1</sup>, Pham Hung Vuong<sup>2</sup>

<sup>1</sup>School of Chemical Engineering, Hanoi University of Science and Technology

<sup>2</sup>Advanced Institute for Science and Technology, Hanoi University of Science and Technology

### KEYWORDS

Fly ash  
Frit  
Ceramic body  
Sintering

### ABSTRACT

Coal fly ash is characterized by high silica and alumina contents, making it suitable as a raw material for aluminosilicate ceramics. However, direct use of fly ash reveals obstacles such as high porosity, black core, cracking, and swelling. This work synthesized frit by melting a mixture of fly ash, quartz, limestone, and soda. TG-DSC analysis showed that the glass transition point of the frit occurs at approximately 600 degrees Celsius. Ceramic bodies from raw mixes containing various frit amounts were prepared and characterized. The results showed that with 4% being frit, the firing temperature could be reduced by 30 degrees Celsius, along with decreased water absorption and increased flexural strength. Besides, no swelling, cracks, or black cores occur. These observations indicate that fly ash-based frit is viable as a sintering aid in ceramic production.

### 1. Introduction

Fly ash is the solid residue from coal combustion, characterized by high SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents. Most of the generated fly ash is used in construction worldwide, mainly as a pozzolan additive for concrete and cement, mine backfill, and reclamation of low-lying areas [1, 2]. However, for safety reasons, fly ash containing high levels of CaO and unburnt carbon is not suitable as a pozzolanic additive for building materials [3]. As a result, a large amount of fly ash remains in storage sites, causing environmental concerns such as wind-blown dust [4] and heavy metal release into surface water and groundwater [5, 6].

Ongoing attempts focus on utilizing fly ash as a raw material in other applications with a higher added value, such as toxic flue gas absorbents [7, 8], industrial wastewater treatment [9-11], and raw material for bricks [12, 13], tiles [14, 15], refractory materials [16, 17], glass [18, 19], and glass ceramics [20, 21]. However, when using fly ash as a raw material for bricks and tiles, there are apparent defects that should be addressed, including black cores, swelling, cracking, and low bulk density [22, 23].

Studies on waste co-treatment in brick and tile production show that waste glass can reduce the sintering temperature while improving the product's physical properties [24, 25]. This approach motivates the present study to synthesize glass from fly ash by the frit manufacturing technique and use it as a flux for ceramic tile.

### 2. Methodology

This work used fly ash, quartz, limestone, soda ash, clay, kaolin, and feldspar as raw materials for frit and ceramic bodies. Their chemical compositions are shown in Table 1. The frit was synthesized from fly ash (46.9 wt.%), limestone (22.8 wt.%), quartz (14.9 wt.%), and soda (15.5 wt.%). In each batch, 100 g of the powdered raw mix was fed into high alumina crucibles and melted at 1450 °C. After 30 minutes of holding at this temperature, the molten product was poured into a water bath to form frit. The glass transition temperature of the frit was determined by TG-DSC thermal analysis with a heating rate of 10 °C/min in the air on a Setaram Labsys Evo instrument.

**Table 1.** Raw materials chemical composition.

Material	Chemical composition (wt. %)								
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	LOI
Fly ash*	52.16	23.65	5.97	1.94	1.09	3.30	0.19	0.91	9.46
Quartz	98.4	0.71	0.14	0.03	0.00	0.15	0.00	0.00	0.36
Limestone	0.11	0.31	0.01	52.53	0.43	0.00	0.00	0.00	41.27
Soda	0.05	0.05	0.00	0.08	0.00	0.00	56.55	0.00	36.3
Clay	60.5	20.07	6.04	0.21	0.85	2.63	0.33	0.9	6.73
Raw kaolin	58.06	24.6	3.72	0.28	0.35	1.77	0.24	0.89	8.5
Feldspar	74.68	14.36	0.17	0.35	0.4	6.12	2.38	0.03	1.14

\*The fly ash is collected from Mong Duong I power plant, Vietnam.

The raw mixes of ceramic bodies comprise clay (45%), kaolin (44%), feldspar (11 – 1%), and frit (0 – 10%), as presented in Table 2. They are labeled as F0, F2, F4, F6, F8, and F10, with the digits representing the weight percent of frit. Sample F0 sintered at 1170 °C is taken as the reference. The raw mix was ground in a ball mill until passing the openings of a 0.063 mm sieve and then dried to a constant weight. The dried samples were cooled to room temperature, pounded until passing the openings of a 1.0 mm sieve, mixed with 5% water, and incubated in sealed plastic bags for 24 hours to distribute their moisture content evenly before forming into 101,2 × 20,5 × 11 mm bars. They were dried at 110 °C for at least 4 hours before firing in an electric furnace at 1170, 1150, and 1140 °C. The heating rate of the furnace was 10 °C/min. The samples were held at the sintering temperature for five minutes before being cooled naturally. The crystalline phases of the obtained ceramic bodies were characterized on a Bruker D2 Phaser X-ray diffractometer.

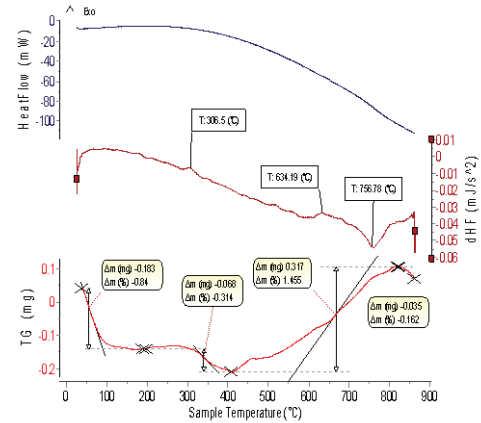
**Table 2.** Ratio (wt.%) of materials in the ceramic raw mixes.

Sample label	Clay	Kaolin	Feldspar	Frit
F0	45	44	11	0
F2	45	44	9	2
F4	45	44	7	4
F6	45	44	5	6
F8	45	44	3	8
F10	45	44	1	10

### 3. Results and Discussion

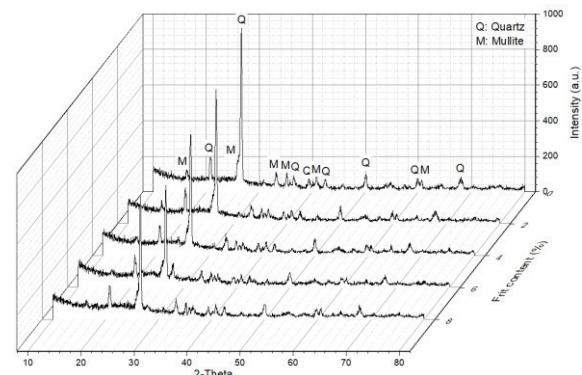
Differential scanning calorimetry (DSC) shows the glass transition point ( $T_g$ ) at approximately 600 °C (Figure 1). Following this transition is crystallization, represented by an exothermic peak at 634 °C. However, due to the dominance of melting, this exothermic peak is relatively small, and a deep heat absorption due to melting was evident at 767 °C. Along with heat absorption, possible oxidation of ferrous oxide causes a continuous increase in weight between 400 – 800 °C. These observations suggest that the frit might be an effective flux for liquid sintering.

Two crystalline phases, quartz (PDF # 96-900-9667 ) and mullite (PDF # 96-900-5503), are evident in all of the sintered ceramic samples (Figure 2 and Figure 3). X-ray diffraction analysis on samples sintered at 1170 °C showed that the crystallinity of quartz decreases with increasing frit content, indicated by a decrease in diffraction intensity. In addition, the amount of amorphous phase also increased with frit content, as indicated by the increase of diffraction peak tails height in the range of 2-theta below 40 degrees. These observations suggest that the frit had provided an additional liquid phase content during the sintering and caused partial melting of quartz. Frit does not seem to affect the crystallinity of the mullite phase.

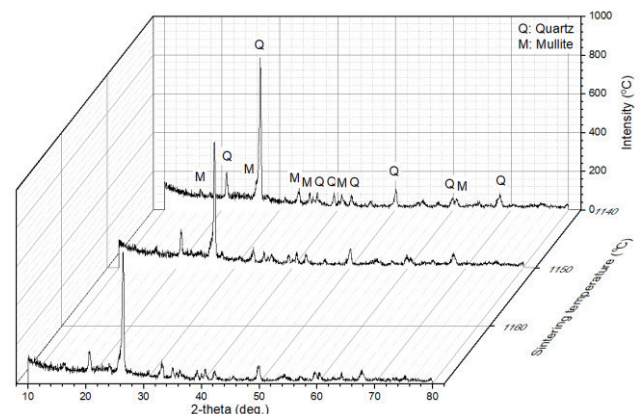


**Figure 1.** TG-DSC analysis of fly ash-based frit.

X-ray diffraction patterns of samples with four weight percent being frit (F4) are shown in Figure 3. As the sintering temperature decreases from 1170 °C to 1140 °C, there is an increase in the crystallinity of quartz and a decrease in the diffraction peak tails height, indicating a reduction in the liquid phase content during sintering.



**Figure 2.** X-ray diffraction patterns of the ceramic bodies with different frit content.



**Figure 3.** X-ray diffraction patterns of F4 sintered at 1140, 1150, and 1170 °C.

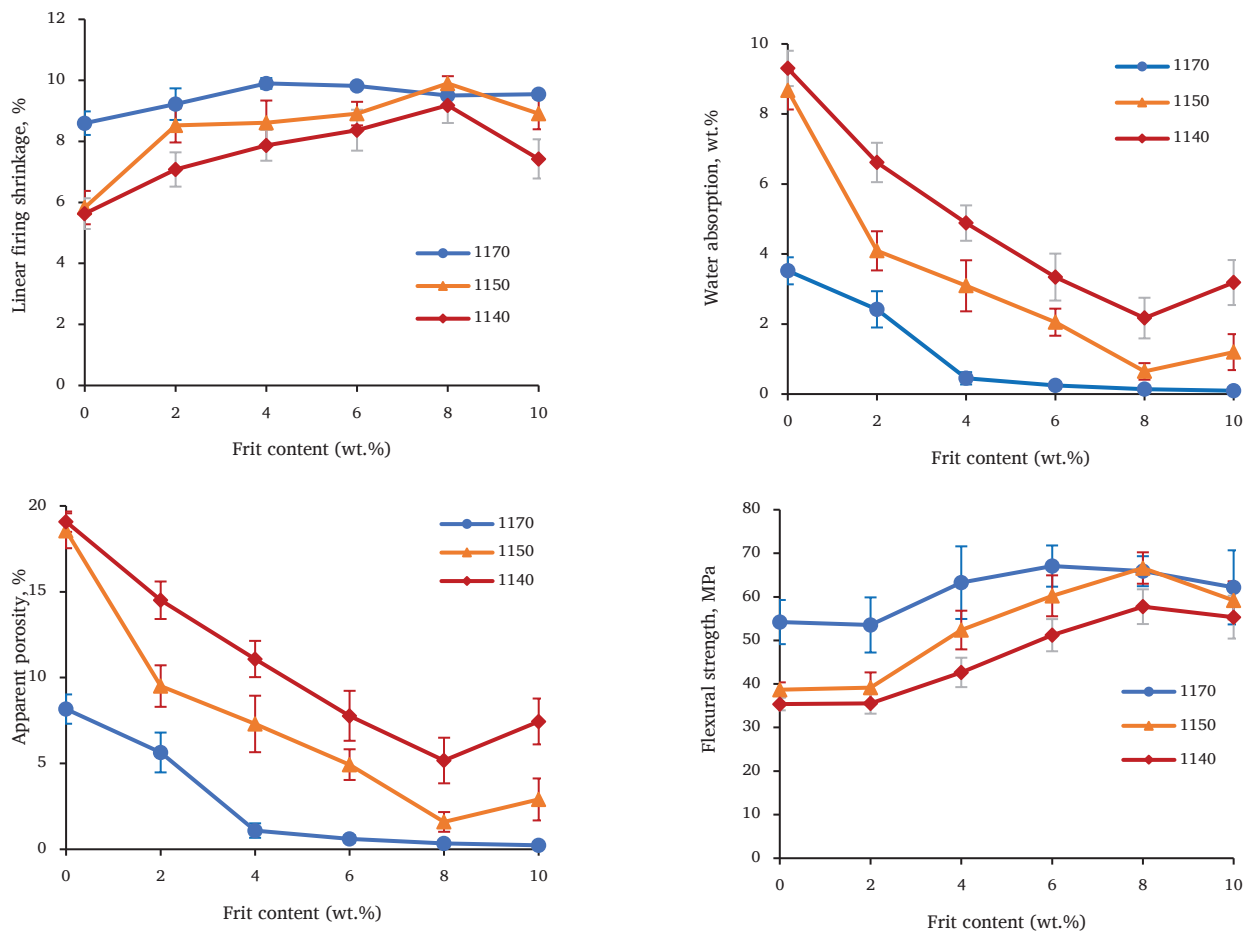
Notably, no black core, crack, or swelling was found in all the studied ceramic samples. In addition, the porosity of the frit-added samples is comparable and even lower than that of the reference (F0, sintered at 1700 °C)

Frit positively affects the physical properties of the sintered ceramic samples. As presented in **Figure 3**, the 1170 °C-sintered series exhibits a decrease in the water absorption and apparent porosity and an increase in the flexural strength as the frit content increase from 2 to 8%. The turning point of this trend occurred at the frit content of 8%, above which the flexural strength decreases even though a decrease in water absorption and apparent porosity is evident. The excessive glass phase in the sintered sample, suggested by X-ray analysis, explains this phenomenon.

Observation from the 1170 °C-sintered series suggests that it is possible to reduce the sintering temperature with frit addition. For the 1140 and 1150 °C-sintered series, with 2% of the raw mix being frit, a

significant decrease in water absorption and porosity was observed, but no improvement in flexural strength was seen. For the 1150 °C-sintered series, the flexural strengths of F4 (52.4 MPa), F6 (60.2 MPa), and F10 (59.2 MPa) are comparable to that of the reference (54.2 MPa), while flexural strength of F8 is 12 MPa higher than that of the reference. For the 1140 °C-sintered series, the flexural strengths of F6 (51.2 MPa), F8 (57.7 MPa), and F10 (55.3 MPa) are compared to that of the reference. The abnormality of F10 is explained by a greater amount of the glass phase caused by excessive flux. Besides, there might be a co-existence of closed pore openings under pressure and high liquid phase viscosity at a low sintering temperature, making pore filling difficult.

Fly ash-based frit melting process consumes heat, but in return, it provides an ability to reduce the sintering temperature of ceramic tiles by 20–30 °C at low frit contents. This possibility of reducing sintering temperature offers an effective solution for fly ash recycling.



**Figure 4.** Physical properties of ceramic samples sintered at 1400, 1500, and 1700 °C.

#### 4. Conclusion

Fly ash-based glass prepared by the frit synthesis technique has a glass transition point of approximately 600 degrees C. It behaves as

an effective sintering aid for ceramic tile without creating black cores, swelling, or cracking. The synthesis of frit is energy-consuming. However, adding 4-6 wt % frit to ceramic tile raw mix makes it possible to reduce the sintering temperature by 20-30°C while

maintaining the flexural strength above 40 MPa. Detail calculations on the heat balance between frit synthesis and ceramic tile sintering are needed to promote fly ash-based frit as a ceramic sintering aid.

### Acknowledgment

This study was financially supported by the Vietnam Ministry of Training and Education under grant number B2020-BKA-017. The authors wish to thank Mr. Mai Van Vo and Ms. Bui Thi Thu Ha, Department of Silicate Material technology, Hanoi University of Science and Technology, for their valuable technical support.

### References

- [1]. CEA, "Report on Fly Ash Generation at Coal/Lignite Based Thermal Power Stations and its Utilization in the Country for the Year 2020-2021," Central Electricity Authority, Ministry of Power, Government of India, New Delhi, India, 2021. Accessed: 29/04/2022. [Online]. Available: [https://cea.nic.in/wp-content/uploads/tcd/2021/09/Report\\_Ash\\_Yearly\\_2020\\_21.pdf](https://cea.nic.in/wp-content/uploads/tcd/2021/09/Report_Ash_Yearly_2020_21.pdf)
- [2]. Y. Luo, Y. Wu, S. Ma, S. Zheng, Y. Zhang, and P. K. Chu, "Utilization of coal fly ash in China: a mini-review on challenges and future directions," *Environmental Science and Pollution Research*, vol. 28, no. 15, pp. 18727-18740, 2021, doi: <https://doi.org/10.1007/s11356-020-08864-4>.
- [3]. *ASTM C618 - 19 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, ASTM, West Conshohocken, PA, USA, 2019. [Online]. Available: <https://www.astm.org/c0618-19.html>
- [4]. U. E. P. Agency, "Human and Ecological Risk Assessment of Coal Combustion Wastes," ed: RTI International NC, USA, 2007.
- [5]. P. Sandeep, S. Sahu, P. Kothai, and G. Pandit, "Leaching behavior of selected trace and toxic metals in coal fly ash samples collected from two thermal power plants, India," *Bulletin of environmental contamination and toxicology*, vol. 97, no. 3, pp. 425-431, 2016, doi: <https://doi.org/10.1007/s00128-016-1864-x>.
- [6]. S. Zhao *et al.*, "Chemical speciation and leaching characteristics of hazardous trace elements in coal and fly ash from coal-fired power plants," *Fuel*, vol. 232, pp. 463-469, 2018, doi: <https://doi.org/10.1016/j.fuel.2018.05.135>.
- [7]. A. Al-Shawabkeh, H. Maisuda, and M. Hasatani, "Comparative reactivity of treated FBC-and PCC-Fly ash for SO<sub>2</sub> removal," *The Canadian Journal of Chemical Engineering*, vol. 73, no. 5, pp. 678-685, 1995, doi: <https://doi.org/10.1002/cjce.5450730511>.
- [8]. H. Tsuchiai, T. Ishizuka, H. Nakamura, T. Ueno, and H. Hattori, "Removal of sulfur dioxide from flue gas by the absorbent prepared from coal ash: Effects of nitrogen oxide and water vapor," *Industrial & engineering chemistry research*, vol. 35, no. 3, pp. 851-855, 1996, doi: <https://doi.org/10.1021/ie950322p>.
- [9]. Z. Aksu and J. Yener, "The usage of dried activated sludge and fly ash wastes in phenol biosorption/adsorption: comparison with granular activated carbon," *Journal of Environmental Science & Health Part A*, vol. 34, no. 9, pp. 1777-1796, 1999, doi: <https://doi.org/10.1080/10934529909376928>.
- [10]. M. Ugurlu, A. Gurses, M. Yalcin, and C. Dogar, "Removal of phenolic and lignin compounds from bleached kraft mill effluent by fly ash and sepiolite," *Adsorption*, vol. 11, no. 1, pp. 87-97, 2005, doi: <https://doi.org/10.1007/s10450-005-1096-6>.
- [11]. V. K. Gupta and I. Ali, "Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste," *Water Research*, vol. 35, no. 1, pp. 33-40, 2001, doi: [https://doi.org/10.1016/S0043-1354\(00\)00232-3](https://doi.org/10.1016/S0043-1354(00)00232-3).
- [12]. X. Lingling, G. Wei, W. Tao, and Y. Nanru, "Study on fired bricks with replacing clay by fly ash in high volume ratio," *Construction and building materials*, vol. 19, no. 3, pp. 243-247, 2005, doi: <https://doi.org/10.1016/j.conbuildmat.2004.05.017>.
- [13]. M. S. Başpınar, E. Kahraman, G. Görhan, and İ. Demir, "Production of fired construction brick from high sulfate-containing fly ash with boric acid addition," *Waste management & research*, vol. 28, no. 1, pp. 4-10, 2010, doi: <https://doi.org/10.1177/0734242X08096529>.
- [14]. S. Yürüyen and H. Ö. Toplan, "The sintering kinetics of porcelain bodies made from waste glass and fly ash," *Ceramics International*, vol. 35, no. 6, pp. 2427-2433, 2009, doi: <https://doi.org/10.1016/j.ceramint.2009.02.005>.
- [15]. Y. Luo, S. Ma, C. Liu, Z. Zhao, S. Zheng, and X. Wang, "Effect of particle size and alkali activation on coal fly ash and their role in sintered ceramic tiles," *Journal of the European Ceramic Society*, vol. 37, no. 4, pp. 1847-1856, 2017, doi: <https://doi.org/10.1016/j.jeurceramsoc.2016.11.032>.
- [16]. Y. Dong, X. Feng, X. Feng, Y. Ding, X. Liu, and G. Meng, "Preparation of low-cost mullite ceramics from natural bauxite and industrial waste fly ash," *Journal of alloys and Compounds*, vol. 460, no. 1-2, pp. 599-606, 2008, doi: <https://doi.org/10.1016/j.jallcom.2007.06.023>.
- [17]. R. Goren, C. Ozgur, and H. Gocmez, "The preparation of cordierite from talc, fly ash, fused silica and alumina mixtures," *Ceramics International*, vol. 32, no. 1, pp. 53-56, 2006, doi: <https://doi.org/10.1016/j.ceramint.2005.01.001>.
- [18]. J. Bai, X. Yang, S. Xu, W. Jing, and J. Yang, "Preparation of foam glass from waste glass and fly ash," *Materials Letters*, vol. 136, pp. 52-54, 2014, doi: <https://doi.org/10.1016/j.matlet.2014.07.028>.
- [19]. M. Erol, S. Küçükbayrak, and A. Ersoy-Mericboyu, "Comparison of the properties of glass, glass-ceramic and ceramic materials produced from coal fly ash," *Journal of Hazardous Materials*, vol. 153, no. 1-2, pp. 418-425, 2008, doi: <https://doi.org/10.1016/j.jhazmat.2007.08.071>.
- [20]. D. H. Vu, K.-S. Wang, J.-H. Chen, B. X. Nam, and B. H. Bac, "Glass-ceramic from mixtures of bottom ash and fly ash," *Waste management*, vol. 32, no. 12, pp. 2306-2314, 2012, doi: <https://doi.org/10.1016/j.wasman.2012.05.040>.
- [21]. J. Zhang, W. Dong, J. Li, L. Qiao, J. Zheng, and J. Sheng, "Utilization of coal fly ash in the glass-ceramic production," *Journal of hazardous materials*, vol. 149, no. 2, pp. 523-526, 2007, doi: <https://doi.org/10.1016/j.jhazmat.2007.07.044>.
- [22]. R. M. Vasić, Ž. Lalić, Z. Radojević, and L. Nešić, "Possibilities of producing solid bricks from mixtures of plastic brick clay and fly ash," in *Key Engineering Materials*, 2004, vol. 264: Trans Tech Publ, pp. 1669-1672, doi: <https://doi.org/10.4028/www.scientific.net/KEM.264-268.1669>.
- [23]. R. Sokolar and L. Vodova, "The effect of fluidized fly ash on the properties of dry pressed ceramic tiles based on fly ash-clay body," *Ceramics International*, vol. 37, no. 7, pp. 2879-2885, 2011, doi: <https://doi.org/10.1016/j.ceramint.2011.05.005>.
- [24]. H. Wang, Y. Sun, L. Liu, R. Ji, and X. Wang, "Integrated utilization of fly ash and waste glass for synthesis of foam/dense bi-layered insulation ceramic tile," *Energy and Buildings*, vol. 168, pp. 67-75, 2018, doi: <https://doi.org/10.1016/j.enbuild.2018.03.018>.
- [25]. P. Chindaprasit, A. Srisuwan, C. Saengthong, S. Lawanwadeekul, and N. Phonphuak, "Synergistic effect of fly ash and glass cullet additive on properties of fire clay bricks," *Journal of Building Engineering*, vol. 44, p. 102942, 2021, doi: <https://doi.org/10.1016/j.jobbe.2021.102942>.