Kinetics of Fly Ash Geopolymerization using Semi Quantitative Fourier-Transform Infrared Spectroscopy (FTIR); Corr Data

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Abstract. Fly ash utilization is very urgent to be conducted alas contaminating the environment. One of the promising utilizations is geopolymer formation for material construction. In this study, geopolymer formation was studied using fly ash from PLTU Tanjung Jati Jepara. This study included kinetics prediction using solid state isoconversion kinetics that has been developed based on nucleation, geometric contraction, and diffusion models. Semi quantitative FTIR analysis (corr) has been applied to predict the kinetics of the fly ash geopolymerization in curing temperature of 30° and 90°C. In order to be able to verify the kinetics model time series data were taken in interval of 1,3,5,14,21, and 28 days. It is the diffusion model that represents the fly ash geopolymerization with R² of 0.9437.

1. Introduction
The needs of energy cannot be avoided nowadays. The increase of energy needs will be significant with the increase of population. Fig. 1 shows the increase of electricity consumption worlwide in many sectors.
In the year of 2015, it was recorded that the world’s electricity needs reached the value of 24.255 TWh supplied with coal based power generation as it can be seen in Fig. 2. Indonesia is facing similar condition at which of about 50% of the energy supply will be generated from the coal burning power generation in order to fulfill the 35 GW in 2025. Along with this coal based energy supply increases there will be of about 8.31 million tonnes of fly ash in 2019 with predicted increase of about 5% per year [2].

Due to its potential danger to the environment, some research on fly ash utilization have been developed, i.e., cenospheres recovery using both wet and dry separation methods [3]-[5]; adsorbent [6]-[10]; and material construction in the form of pozzolanic [11]; concrete [12]-[14]; and geopolymer [15]-[16]. Among other utilizations, geopolymer possesses some advantages due to its possibility to overpower the regular concrete, i.e., the hardening time is faster, the tensile strength as well as compressive strength are higher, and most of all geopolymer has good resistance to corrosion. Although many studies on geopolymer have been conducted, the kinetics study has not been well developed. One of the methods to observe the growth of geopolimerization is by using FTIR [17]. Thus, in this study we would like to predict the kinetics of fly ash geopolymerization using semi quantitative approach from FTIR Corr data.

2. Materials and Method
A. Materials.
Fly ash from the coal burning electricity plant generation in PLTU Tanjung Jati Jepara has been obtained and used as the raw material for the geopolymer through all the experiments. Other materials, such ash NaOH and sodium silicate, were supplied by PT. Brataco Chemical with analytical grade concentration.

B. Method

1. Raw material preparation
Fly ash was dried in an oven with temperature of 50°C for 5 hours. It was then milled and sieved to result product below 300 mesh. The over 300 mesh product will be remilled and sieved.

2. Chemical composition analysis
Chemical composition of fly ash is crucial to distinguish due to certain proportion of SiO$_2$ and Al$_2$O$_3$ should be fulfilled for geopolimerization. In order to provide chemical composition of the fly ash used in this experiment, energy dispersive X-ray spectroscopy (EDX) was conducted. The chemical composition of the fly ash is shown in Fig. 3.

Fig. 3. Chemical composition of fly ash

From Fig. 3, it can be seen that the composition of fly ash from PLTU Tanjung Jati Jepara is dominated with silica. The ratio of SiO$_2$/Al$_2$O$_3$ is 3.01 in the range value that is optimum for geopolymerization in the range of 3.00 – 3.80 [18]-[20].

3. Geopolimerization
The -300 mesh fly ash was thoroughly mixed with NaOH and natrium silicate (alkaline activator) forming paste. The concentration of NaOH used in this geopolymerization is 12 M. Ensuring the homogenized geopolymer paste by agitation, the paste was then poured into cubical cast with the size of 5x5x5 cm$^3$ and let it solidify for 2 days. Each cubical cast would consumed 50 mL of alkaline activator.

Further treatment was conducted by curing the samples for 8 hours at certain temperature (30°C and 90°C). The samples were prepared and taken for further analysis using compresive strength and Fourier-transform infrared spectroscopy (FTIR) in certain time interval of 1,3,5,14,21, and 28 days. Three geopolymer samples were prepared for each data point to ensure the reliability.

4. Analytical methods
Geopolymer samples were analyzed using Universal Testing Machine Avery-Denison to measure the compresive strength of each data point. After compresive strength analysis, the sample was then milled to have powdery sample and further analyse using FTIR to observed the growth of geopolymer bonding. The fingerprint of geopolymerization reaction is similar to that of zeolite which is determined by the Si-O-Al formation (aluminosilicate). The wavelength for the Si-O-T (T: Si or Al) bonding is detected in the range of 900-1300 cm$^{-1}$. However there are 2 other peaks showing the growth of the geopolymer as shown in Table 1.
Table 1. FTIR spectra for geopolymerization of fly ash [21]

| Wavelength (cm⁻¹) | Functional groups                                      |
|-------------------|--------------------------------------------------------|
| 900-1300          | Si-O-T (T: Si, Al Tetrahedral) asymmetric stretching   |
| 1650              | H-OH bending                                           |
| 3400-3650         | -OH symmetric and asymmetric stretching                |

Based on the peak of the aluminosilicate wavelength the correlation value (Corr) will be calculated relative to the zeolit peaks in accordance with equation 1 and 2 [22].

\[
\begin{align*}
    r &= \frac{\sum(a_i - \bar{a})(b_i - \bar{b})}{\sqrt{\sum(a_i - \bar{a})^2(b_i - \bar{b})^2}} \\
    \text{Corr} &= \frac{999(r + 1)}{2}
\end{align*}
\]

5. Kinetics approach

Kinetics of fly ash geopolymerization will be verified using iso-conversion approach on solid state reaction as formulated in equation 3.

\[
\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha)
\]

\[
\alpha = \frac{x_0 - x_t}{x_0 - x_m}
\]

\(\chi\) can represent any quantitative value showing the physical change phenomenon. In this study the \(\chi\) value will be represented by the semi-quantitative FTIR data (Corr) [23]. There are several derivations of isoconversion approach based on the background phenomenon as tabulated in Table 2.

Table 2. Derivative model of solid state reaction [23]

| Kinetics                       | Differential \(f(\alpha) = 1/k \frac{da}{dt}\) | Integral \(g(\alpha) = kt\) |
|--------------------------------|-----------------------------------------------|-----------------------------|
| **Nucleation Model**           |                                               |                             |
| Avrami-Erofejev (A2)           | \(2(1-\alpha)[-\ln(1-\alpha)]^{1/2}\)      | \([-\ln(1-\alpha)]^{1/2}\) |
| Avrami-Erofejev (A3)           | \(3(1-\alpha)[-\ln(1-\alpha)]^{2/3}\)      | \([-\ln(1-\alpha)]^{1/3}\) |
| Avrami-Erofejev (A4)           | \(4(1-\alpha)[-\ln(1-\alpha)]^{3/4}\)      | \([-\ln(1-\alpha)]^{1/4}\) |
| Prout-Tompkins (B1)            | \(\alpha(1-\alpha)\)                         | \(\ln[\alpha/(1-\alpha)] + c^\alpha\) |
| **Geometry Contraction Model** |                                               |                             |
| Contracting area (R2)          | \(2(1-\alpha)^{1/2}\)                       | \(1 - (1-\alpha)^{1/2}\) |
| Contracting volume (R3)        | \(3(1-\alpha)^{2/3}\)                       | \(1 - (1-\alpha)^{1/3}\) |
| **Diffusion Model**            |                                               |                             |
| 1-D diffusion (D1)             | \(1/(2\alpha)\)                             | \(\alpha^2\)                |
| 2-D diffusion (D2)             | \(-[1/\ln(1-\alpha)]\)                     | \((1-\alpha)\ln(1-\alpha) + \alpha\) |
| 3-D diffusion-Jander (D3)      | \([3(1-\alpha)^{2/3}]/[2(1-(1-\alpha)^{1/3})]\) | \((1-(1-\alpha)^{1/3})^2\) |
| Ginstling-Brounshtein (D4)     | \(3/[2((1-\alpha)^{-1/3} - 1)]\)            | \(1 - (2/3)\alpha - (1-\alpha)^{2/3}\) |
| **Order Reaction Model**       |                                               |                             |
The corr semi quantitative FTIR data will be calculated in accordance with the kinetics models that have been developed. The kinetics of fly ash geopolymerization will be determined by the most fitted model for solid state reaction as tabulated in Table 2.

### 3. Results and Discussion

Raw material characterization is an important stage that has to be accomplished in order to predict the potential utilization of the fly ash. As it has been discussed previously that fly ash from PLTU Tanjung Jati Jepara has SiO$_2$/Al$_2$O$_3$ ratio in the order of 3.01 which is potential to utilize as geopolymer raw material. Further, analysis using FTIR it shows that the existence of Si-O-Al in the fly ash matrix is relatively low in comparison to the standard zeolite used in this experiment, as seen in Fig. 4.a.

![FTIR characterization of fly ash and geopolymer samples](image)

Fig. 4. FTIR characterization of fly ash and geopolymer samples (curing temperature of 30°C and 90°C) in comparison with zeolite.

After treatment with curing temperature of 30°C and 90°C it can be seen that the absorbance of the peaks showing the existence of aluminosilicate (Si-O-Al) increases along with the higher curing temperature (Fig. 4.b.). The increase of this absorbance representing the higher conversion of aluminosilicate formation is in line with the increase of compressive strength of the geopolymer samples (Fig. 5)
The compressive strength of fly ash geopolymer sample represents the degree of geopolymerisation at where formation of aluminosilicate takes place (Olivanas et al., 2017(b)). It can be seen from Fig. 5.a, the compressive strength increases from 29 MPa to 58 MPa along with the increase of curing temperature from 30\(^{\circ}\)C to 90\(^{\circ}\)C. The increase of compressive strength is in accordance with the corr from the FTIR from 989.5 to 992.8. This phenomenon shows that the physical characteristic of geopolymer is affected by the degree of polymerization or formation of aluminosilicate matrix. Having this supportive macro and micro-phenomenon on fly ash geopolymer, we would like to understand the mechanism of fly ash geopolymerization by fitting the existing solid state reaction as tabulated in TABLE II with time series data that we have conducted on fly ash geopolymerization in two curing temperatures (30\(^{\circ}\)C and 90\(^{\circ}\)C) (Fig. 6).

The highest corr for any FTIR data is 1000 showing that the correlation with the associated peaks is at the maximum value similar to that of 100\% of conversion. As it can be seen in Fig. 6, the corr value increases with time in both curing temperature of 30\(^{\circ}\)C and 90\(^{\circ}\)C. These data series of corr was then calculated to fit the kinetic model of fly ash geopolymerization. In solid state reaction, there are several kinetic models that have been developed. Eliminating the reaction controlling model due to its fast reaction step [24], the avrami, contracting volume, and diffusion model were analyzed to fit the corr data shown in Fig. 6.
Fig. 6. Corr for each data point taken as a function of time sequence (both curing temperature 30° and 90°C)

From the kinetic model fitting as shown in Fig. 7, it is found that the diffusion model fits the fly ash geopolymerization model with average $R^2$ of 0.9437. In comparison to that of the avrami model with $R^2$ of 0.9409 and the contracting volume with $R^2$ of 0.9427. The finding is actually aligned with the mechanism of the geopolymerization proposed by Davidovits (1999), in which the steps of geopolymerization includes dissolution, reaction, gel formation, and solidification. Indeed the proposed mechanism merely includes diffusion in the process.
Fig. 7. Kinetic model of fly ash geopolymer (a) Avrami model (b) volume contraction model and (c) diffusion model.

4. Conclusion
Geopolymer has successfully formed using fly ash from PLTU Tanjung Jati Jepara with the highest compressive strength of 58 MPa resulted in curing temperature of 90°C for 28 days. The increase of compressive strength as a function of temperature and series of time sequence is in accordance with the semi quantitative FTIR analysis represented by corr value. The kinetics of fly ash geopolymerization has fitted with the diffusion model resembled with the proposed geopolymer mechanism by Davindovits (1999) in which diffusion control in the process including dissolution, gel formation, and solidification. The diffusion model fits the phenomenon with $R^2$ of 0.9437.

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6. References
[1] International Energy Agency (IEA). (2017, September). Key World Energy Statistics in 2017. Dipetik July 1, 2018, dari https://www.iea.org/publications/freepublications/publication/KeyWorld2017.pdf
[2] Direktorat Jenderal Ketenagalistrikan. (2016, February 16). Kementerian Energi dan Sumber Daya Mineral, Direktorat Jenderal Ketenagalistrikan. Dipetik April 12, 2017, dari Pemerintah Dorong Pemanfaatan Limbah PLTU: http://www.djk.esdm.go.id/index.php/detail-berita?ide=4060
[3] Hirajima, T., Oosako, Y., Nonaka, M., Petrus, H., Sasaki, K., and Ando, T., Recovery of hollow and spherical particles from coal fly ash by wet separation process, Journal of MMIJ 124 (12), 2008, pp. 878-884
[4] Hirajima, T., Petrus, H., Oosako, Y., Nonaka, M., Sasaki, K., and Ando, T., Recovery of cenospheres from coal fly ash using a dry separation process: Separation estimation and potential application, International Journal of Mineral Processing 95 (1-4), 2010, pp. 18-24.
[5] Petrus, H., Hirajima, T., Oosako, Y., Nonaka, M., Sasaki, K., and Ando, T., Performance of dry-separation processes in the recovery of cenospheres from fly ash and their implementation in a recovery unit, International Journal of Mineral Processing 98 (1-2), 2011, pp. 15-23.
[6] Davini, P., 1996, Investigation of the SO$_2$ adsorption properties of Ca(OH)$_2$-fly ash systems, Fuel, vol. 75, 1996, pp. 713–716.
[7] Lu, G.Q., and Do, D. D., 1991, Adsorption properties of fly ash particles for NOx removal from flue gases, Fuel Process Technol., vol. 27, 1991, pp. 95–107.

[8] Dasmahapatra, G. P., Pal, T. K., Bhadra, A. K., and Bhattacharya, B., 1996, Studies on separation characteristics of hexavalent chromium from aqueous solution by fly ash, Sep. Sci. Technol., vol. 31, 1996, pp. 2001–2009.

[9] Alinnor, I. J., 2007, Adsorption of heavy metal ions from aqueous solution by fly ash, Fuel, vol. 86, 2007, pp. 853–857.

[10] Kapoor, A., and Viraraghavan, T., 1992, Adsorption of mercury from wastewater by fly ash, Adsorpt. Sci. Technol., vol. 9, 1992, pp. 130–147.

[11] Siddique, R., 2004, Performance characteristics of high-volume Class F fly ash concrete, Cem. Concr. Res., vol. 34, 2004, pp. 487–493.

[12] Bouzoubaa, N., Zhang, M. H., and Malhotra, V. M., 2001, Mechanical properties and durability of concrete made with high-volume fly ash blended cements using a coarse fly ash, Cem. Concr. Res., vol. 31, 2001, pp. 1393–1402.

[13] Wilson, M., Cabrera, J. G., and Zou, Y., 1994, The process and mechanism of alkali-silica reaction using fused silica as the reactive aggregate, Adv. Cem. Res., vol. 6, 1994, pp. 117–25.

[14] O’Connor, A. K., and Yildiz, R., 2005, An experimental study on strength development of concrete containing fly ash and optimum usage of fly ash in concrete, Cem. Concr. Res., vol. 35, 2005, pp. 1165–1171.

[15] Varmuza, K., Demuth, W., and Karlovits, M., 2002, Structural and Spectral Similarity, CHEM 02 - Biannual Conference on Chemistry. Cairo: Chemistry Department Cairo University, 2002.

[16] Khawam, A., and Flanagan, D., Solid-State Kinetic Models: Basics and Mathematical Fundamentals, J. Phys. Chem. B, 110(35), 2006, pp. 17315-17328.

[17] Xu, H., and Van Deventer, J., The Geopolymerisation of Alumino-Silicate Minerals, International Journal of Mineral Processing, 2000, pp. 247-266.