DATA ARTIKEL

Judul Artikel	**:**	Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization Approach
Nama Jurnal	**:**	Journal of Engineering Science and Technology Review
Nomor ISSN	**:**	1791-2377
Vol, No., Bln Thn	**:**	Volume 13, 2020 - 2
Penerbit	**:**	Kavala Institute of Technology
DOI Artikel	**:**	https://doi.org/10.25103/jestr.132.22
Terindex	**:**	Scopus, Q3
H-index	**:**	31
SJR	**:**	0,22 (2021)

REKAP BUKTI KORESPONDENSI

Tanggal	Keterangan
9 Desember 2019	Manuscript submission
17 Februari 2020	Revision
24 Februari 2020	Submit revised manuscript
29 Maret 2020	Acceptance notification

International Hellenic University - Kavala Campus Online Journals Editorial Manager

Journal of Engineering Science and Technology Review Hello, Aprilina Purbasari | Logged in as: Author

Paper and review details

- Submission ID: 3376
- Title: Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization Approach
- Corresponding author: Aprilina Purbasari | e-mail:
- Co-author full names: | Co-author e-mails:
- Section: Research Article
- Submitted on: 09/12/2019
- Status: In review (round 2)

Review round 1

- Paper submitted for review on: 09/12/2019
- Paper download link: jestr_sub_1575905666.docx (../uploads/jestr_sub_1575905666.docx)

Review round 1	Assigned on	Result	Comments to author	Review file	Review date
Reviewer 1	14/12/2019	Accept with minor revision	The results are clearly explained and presented in an appropriate format. The findings are properly described in the context of the published literature. However, no significant limitations are discussed.	jestr_rev_1578896542.docx (../uploads/jestr_rev_1578896542.docx)	13/01/2020
Reviewer 2	14/12/2019			Awaiting review (../uploads/)	

Reviewer 3				Awaiting review (../uploads/)	

Decision by the Journal Editor on review round 1

➜ Editor's decision: Accept with minor revision

➜ Editor's comments: Dear author, We have to inform you that there have been some changes recommended by the reviewers of your article. We look forward to your article after these changes have been made.Prof. D.Bandekas Editor in Chief Journal of Engineering Science and Technology Review Kavala Institute of Technology 65 404 St.Lucas, Kavala, Greece

➜ Editor's decision date: 17/02/2020

Review round 2

➜ Paper submitted for review on: 24/02/2020

➜ Paper download link: jestr_sub_1582507044.docx (../uploads/jestr_sub_1582507044.docx)

Review round 2	Assigned on	Result	Comments to author	Review file	Review date
Reviewer 1				Awaiting review (../uploads/)	
Reviewer 2				Awaiting review (../uploads/)	
Reviewer 3				Awaiting review (../uploads/)	

Decision by the Journal Editor on review round 2

➜ Editor's decision: Accept as it is

➜ Editor's comments: Dear author, We are glad to inform you that, your article: "Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization ApproachS" Has been accepted for publication in our journal (Journal of Engineering Science and Technology Review) In order to publish your article, please send us (via email) filled the copyright form, the authors names and the affiliations and the article in wrd format. Kind regards Prof. D. V. Bandekas Editor - in - Chief Journal of Engineering Science and Technology Review

➜ Editor's decision date: 29/03/2020

Research Article

Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization Approach

Abstract

Geopolymer, alumino-silicate inorganic polymer, has the potential to substitute Portland cement because of its lower energy consumption and CO_2 emissions, as well as its raw material can use solid wastes such as fly ash, slag, and biomass ash. Geopolymer as Portland cement substitute in addition to having good mechanical strength must also have resistance to high temperature exposure which can be predicted from its solidus and liquidus temperatures. Solidus temperature indicates the occurrence of melting when the solid is heated, while the liquidus temperature indicates the occurrence of precipitation when the liquid is cooled. Thus geopolymer having high solidus and liquidus temperatures demonstrates its resistance to high temperature exposure. In this paper, composition effect of raw material mixture (fly ash, slag, and biomass ash) on the solidus and liquidus temperatures of geopolymer had been studied using experimental design of 3-components mixture. Solidus and liquidus temperatures of geopolymer in each mixture composition were determined using Gibbs energy minimization approach by FactSage 6.3 software, while the effect of mixture composition on solidus and liquidus temperatures was determined statistically by Minitab 17 software. Phase changes were observed in temperature range of 100-2500 ^oC and simulation results showed that geopolymers had solidus temperatures of 500-972.4 ^oC and liquidus temperatures of 2146.1-2491.5 ^oC. Solidus and liquidus temperatures obtained in each simulation were treated statistically resulting linear regression model for solidus temperature and special cubic regression model for liquidus temperature. Fly ash component had the highest positive effect on both solidus and liquidus temperatures of geopolymer compared to slag and biomass ash components. Therefore, geopolymer product having high solidus and liquidus temperatures was obtained with composition of raw material mixture dominated by fly ash.

Keywords: experimental design of 3-components mixture; geopolymer; Gibbs energy minimization approach; liquidus temperature; solid waste; solidus temperature

1. Introduction

Portland cement is a building material that has been widely used and its use tends to increase. World cement production in 2006 is about 2540 million tons and increase to about 4080 million tons in 2013 [1]. Cement production, which requires temperature of 1400 ^{o}C, is an energy intensive process. The dry process consumes energy about 4.60 GJ per ton of clinker, while for wet process the required energy can reach 5.85-6.28 GJ per ton of clinker [2]. The CO_2 emissions generated in the production of cement around 0.9 ton CO_2 per ton of cement and CO_2 emissions of cement industry has contributed approximately 5% of global CO_2 emissions [3].

Several alternatives to Portland cement with lower energy consumption and CO_2 emissions are calcium sulphoaluminate cement, magnesium-based cement, and geopolymer. Geopolymer is more potential to be developed as a Portland cement substitute because geopolymer production takes place at low temperatures (below 100 °C) and can use waste materials such as fly ash, biomass ash, and slag [4]. Geopolymerisation process involves complex reactions between materials containing alumino-silicate oxide with alkali hydroxide/silicate at temperature below 100 °C. This produces Si-O-Al polymeric bond with the empirical formula of $M_n(-(SiO_2)_z-AlO_2)_n.wH_2O$, where: M = cation Na^+/K^+; z = 1,2,3 ; n = degree of polycondensation. Reaction of geopolimerisation is as follows [5]:

$$\underset{\text{(Si–Al material)}}{(Si_2O_5,Al_2O_2)n + 3nH_2O} \xrightarrow{NaOH/KOH} \underset{\text{Orthosialate}}{n(OH)_3\text{-}Si\text{-}O\text{-}Al^{-}\text{-}(OH)_3} \quad (1)$$

$$\underset{\text{Orthosialate}}{n(OH)_3–Si–O–Al^{-}–(OH)_3} \xrightarrow{NaOH/KOH} \underset{\text{(Na,K)-poly(sialate)}}{(Na,K)\begin{pmatrix} | & & | & \\ –Si–&O–&Al^{-}–&O– \\ | & & | & \\ O & & O & \\ | & & | & \end{pmatrix}n + 3n\,H_2O} \quad (2)$$

Three-dimensional structure of geopolymer products are amorphous to semi-crystalline and can be poly(sialate)/(-Si-O-Al-O-) for Si:Al = 1:1, poly(sialate-siloxo)/(-Si-O-Al-O-Si-O-) for Si:Al = 2:1, or poly(sialate-disiloxo)/(-Si-O-Al-O-Si-O-Si-O-) for Si:Al = 3:1 [5].

Sources of alumino-silicate material are natural mineral (for example: kaolin), waste from combustion of coal (fly ash) and biomass, and waste from steel industry (slag). Fly ash from coal combustion and slag has been used extensively in the cement production. In addition to improving the cement quality, fly ash or slag usage would reduce the amount of clinker in cement so that the energy for clinker production could also be reduced [2]. Utilization of waste products of combustion, i.e. fly ash and biomass ash, and slag for geopolymer as a Portland cement substitute is an attempt to reduce the burden on the environment and can also contribute to the reduction of CO_2 emissions.

Geopolymer as a Portland cement substitute in addition to having good mechanical strength must also have resistance to high temperature exposure. Geopolymer has shown better resistance to fire than Portland cement [4]. Exposure of Portland cement-based mortars and concretes to temperature above 300 ^oC can decompose $Ca(OH)_2$ into CaO and H_2O which causes mortar shrinkage [6]. Furthermore CaO may react with water vapour in air to form $Ca(OH)_2$ having greater volume than CaO so that mortar will crack resulting in mortar damage.

To determine the resistance of geopolymer to high temperature exposure, it can be predicted from its solidus and liquidus temperatures. Solidus temperature indicates the occurrence of melting when the solid is heated, while the liquidus temperature indicates the occurrence of precipitation when the liquid is cooled [7]. Thus geopolymer having high solidus and liquidus temperatures demonstrates its resistance to high temperature exposure.

This paper studies the composition effect of raw material mixture (fly ash, slag, and biomass ash) on high temperature behavior of geopolymer product, i.e. solidus and liquidus temperatures. Determination of solidus and liquidus temperatures was conducted using Gibbs energy minimization approach with FactSage 6.3 software, whereas determination of the composition effect of raw material mixture statistically was conducted with Minitab 17 software.

2. Experimental

Determination of solidus and liquidus temperatures by FactSage software uses phase equilibrium calculation with minimization of the Gibbs energy change.

$$\Delta G < 0 \tag{3}$$

$$G - \sum n_m G_m < 0 \tag{4}$$

$$G = \sum n_m G_m = minimum \tag{5}$$

where: ΔG = Gibbs energy change, n_m = mole numbers of component *m*, and G_m = Gibbs energy of component *m*. One of the models used in FactSage software for oxides, salts, and metal alloys with short-range-ordering is modified quasi-chemical [8].

The Gibbs energy for solution is:

$$G = \sum n_m g_m^o - T\Delta S^{config} + \sum_{n>m} \sum n_{mn} (\frac{\Delta g_{mn}}{2}) \tag{6}$$

where: g_m^o = Gibbs energy of pure component *m*, *T* = temperature, ΔS^{config} = configurational entropy of mixing, n_{mn} = mole numbers of *m*-*n* pair, and Δg_{mn} = nonconfigurational Gibbs energy change for formation of 2 moles of *m*-*n* pair.

For multicomponent solution [9]:

$$G = (n_{11}g_{11}^o + n_{12}g_{12}^o + n_{22}g_{22}^o + n_{13}g_{13}^o + \cdots) - T\Delta S^{config} + \sum_{n>m} \sum \left(\frac{n_{mn}}{2}\right) (\Delta g_{mn} - \Delta g_{mn)}^o \tag{7}$$

with:

$$\Delta S^{config} = -R \sum n_m \ln X_m - R(\sum n_{mm} \ln(X_{mm}/Y_m^2) + \sum_{m>n} \sum n_{mn} \ln(X_{mn}/2Y_m Y_n)) \tag{8}$$

$$\Delta g_{mn} = \Delta g_{mn}^o + \sum_{(i+j)\geq 1} g_{mn}^{ij} X_{mm}^i X_{nn}^j \tag{9}$$

where: *R* = universal gas constant , X_m = mole fraction of component *m*, X_{mn} = mole fraction of *m*-*n* pair, and Y_m = coordination-equivalent fraction of component *m*.

Module of calculation used in FactSage software was Equilib with SLAGE solution phase, namely an oxide mixture of Al, Ca, Cu, Fe, K, Mg, Mn, Na, Si, Ti with H_2O/OH, Cl, SO_4, PO_4. Data required to determine solidus and liquidus temperatures were oxide compositions of geopolymer raw material, in this case fly ash, slag, and biomass ash (palm oil fuel ash) as presented in Tab. 1.

In each simulation run by FactSage software, it was used 100 grams mixture of fly ash, slag, and biomass ash as alumino-silicate material with certain composition reacted with 5 N KOH as alkaline activator with weight ratio of 2:1 to form geopolymer. The composition of raw material (fly ash, slag, biomass ash) used in each simulation was based on experimental design of 3-components mixture generated by Minitab software with 10 compositions as shown in Fig. 1. Phase changes of formed geopolymer were observed in temperature range of 100-2500 ^oC.

Solidus and liquidus temperatures obtained in each simulation then statistically were treated by Minitab software. Regression model of mixture experiment can be linear, quadratic, full cubic, or special cubic equation [11]. By analysis of variance (ANOVA) the adequate equations for solidus and liquidus temperatures could be determined. These equations could be used to predict solidus and liquidus temperatures of geopolymer with fly ash, slag, and biomass ash as raw material. Furthermore, the composition effect of raw material mixture on solidus and liquidus temperatures could be determined from the equations.

3. Result and Discussion

3.1 Solidus and liquidus temperatures of geopolymer

Solidus and liquidus temperatures of geopolymer resulted by simulation using FactSage software on each mixture composition of raw material are presented in Tab. 2. The range of the solidus temperature of geopolymer is 500-972.4 ^oC, while the liquidus temperature is 2146.1-2491.5 ^oC.

At various temperature ranges geopolymer can undergo dehydration of free water (100-300 ^oC); dehydroxylation (250-600 ^oC); densification by viscous sintering (550-900 ^oC); and crystallization, expansion due to cracking, further densification (>900 ^oC) [12]. Thus at temperature of 550-900 ^oC

it begins to form liquid. This range is not much different with the solidus temperatures obtained by FactSage (500-972.4 ^{o}C) where at that temperature molten slag begins to be formed.

Mineral phases that occur from FactSage calculation are presented in Tab. 3 on simulation with a mixture of fly ash:slag:biomass ash = 1/3:1/3:1/3 (M7). This agrees with the results of XRD (X-Ray Diffraction) analysis to geopolymer exposed to high temperatures [12]. Leucite ($KAlSi_2O_6$) is a major phase encountered in geopolymer synthesized with alkaline activator containing potassium at temperature about 1000 ^{o}C, while hematite (Fe_2O_3) at temperature about 1200 ^{o}C. Garnet ($Ca_3Fe_2Si_3O_{12}$) and wollastonite ($CaSiO_3$) will be found in geopolymer with slag as raw material due to high calcium content [13].

The liquidus temperature which indicates geopolymer in wholly liquid form is obtained above 2000 ^{o}C. Mineral formed or start precipitated at liquidus temperature generally is $(SrO)(SiO_2)$ or $(SrO)_2(SiO_2)$, but for geopolymer with slag composition = 1 (M2), slag:biomass ash = 1/2:1/2 (M6), and fly ash:slag:biomass ash = 1/6:2/3:1/6 (M9) mineral formed is $Ca_3(PO_4)_2$. This is possible because of the high content of CaO in the slag compared to that in the fly ash and in the biomass ash.

Among the raw materials of fly ash, slag, and biomass ash, solidus and liquidus temperatures of geopolymer from fly ash is the highest. This can be explained by observing the oxides content in raw materials. The oxides composition of silica, alumina, alkali oxide, and water forming geopolymer can affect the mechanical strength of geopolymer, as well as the solidus and liquidus temperatures of geopolymer. To obtain strong geopolymer products, ratios of silica, alumina, alkali oxide, and water are in the following ranges: SiO_2/Al_2O_3 = 3.0-4.5; M_2O/SiO_2 = 0.2-0.5; H_2O/M_2O = 10-25; and M_2O/Al_2O_3 = 0.6-1.6 [14]. Result of research in [15] showed that the ratio of alkali (K_2O) on alumina (Al_2O_3) had the most effect on the mechanical strength of geopolymer and geopolymer with ratio of K_2O/Al_2O_3 = 0.8 had the highest mechanical strength. In this simulation, ratio of K_2O/Al_2O_3 in the fly ash is 0.79 or close to 0.8, while for slag and biomass ash 1.52 and 4.91, respectively, or greater than 0.8, likewise ratio of K_2O/Al_2O_3 in all mixture of fly ash-slag-biomass ash are greater than 0.8 (Tab. 2). The greater the ratio of K_2O/Al_2O_3 or more K_2O in geopolymer, the lower solidus and liquidus temperatures of geopolymer due to the lowest melting point of K_2O (740 ^oC) compared to SiO_2 (1600-1725 ^oC) and Al_2O_3 (2072 ^oC). Thus the ratio of K_2O/Al_2O_3 in addition affects the mechanical strength of geopolymer also solidus and liquidus temperatures of geopolymer.

3.2 The composition effect of raw material mixture on solidus and liquidus temperatures of geopolymer

The composition effect of raw material on solidus and liquidus temperatures of geopolymer can be observed from regression models generated by Minitab software. Analysis of variance (ANOVA) for each regression model obtained for the solidus and liquidus temperatures is presented in Tab. 4 and Tab. 5, respectively. The regression model for solidus temperature of geopolymer that has P-value <0.05 is linear model with R^2-value of 69.91% and R^2_{Adj}-value of 61.31%. Meanwhile regression model for liquidus temperature of geopolymer that has P-value <0.05 with the highest value of R^2 and R^2_{Adj} is special cubic.

Adequacy checking for each regression model is conducted from normal probability plot and residual versus fitted value as shown in Fig. 2 for linear model of geopolymer solidus temperature and Fig. 3 for special cubic model of geopolymer liquidus temperature. The normal probability plots of residuals in Fig. 2(a) and Fig. (3a) show that residuals are distributed normally. Furthermore, plots of residuals versus fitted value in Fig. 2(b) and Fig. (3b) indicate that residuals do not form a specific pattern. Thus, it can be concluded that each regression model is adequate.

Equation with linear model to predict the solidus temperature of geopolymer indicated by Eq. 10 and equation with special cubic model to predict the liquidus temperature of geopolymer indicated by Eq. 11.

$$T_{sol}(\,^{o}C) = 935.2x_1 + 536.9x_2 + 619.9x_3 \quad (10)$$

$$T_{liq}(\,^{o}C) = 2488x_1 + 2148x_2 + 2132x_3 - 83x_1x_2 + 472x_1x_3 + 290x_2x_3 - 1506x_1x_2x_3 \quad (11)$$

where: T_{sol} = solidus temperature of geopolymer; T_{liq} = liquidus temperature of geopolymer; x_1 = fly ash fraction , x_2 = slag fraction, and x_3 = biomass ash fraction in the mixture.

At both Eq. 10 and Eq. 11, fly ash fraction (x_1), slag fraction (x_2), and biomass ash fraction (x_3) have positive coefficients or positive effects on solidus and liquidus temperatures of geopolymer. Fly ash component has the highest positive effect compared to slag and biomass ash components. Equation 11 denotes that mixing of fly ash-biomass ash or slag-biomass ash provides positive effect on the liquidus temperature, while mixing of fly ash-slag or mixing of fly ash-slag-biomass ash provides negative effect.

From the contour plots of solidus temperature and liquidus temperature as shown in Fig. 4 and Fig. 5, we can determine the composition of the raw material mixture (fly ash, slag, and biomass ash) that produce geopolymer with expected solidus temperature and liquidus temperature. Higher solidus temperatures in Fig. 4 and higher liquidus temperatures in Fig. 5 are indicated by darker shades, obtained in mixtures with fly ash as the dominant component.

Geopolymer as a Portland cement substitute is expected having resistance to high temperature exposure or fire. In general, temperature will reach 800 °C quickly in about 30 minutes during fire. After that, temperature will increase more slowly from 900 °C to 1200 °C within 6 hours [16]. Therefore geopolymer having solidus temperatures above 800 °C indicates having better resistance to fire. From Fig. 4 geopolymer with solidus temperatures above 800 °C is obtained at mixture of fly ash, slag, and biomass ash with slag composition not more than ±30% and biomass ash composition not more than ±40%.

4. Conclusions

Results of FactSage simulation indicate that geopolymers with raw material mixture of fly ash, slag, and biomass ash have solidus temperatures of 500-972.4 ^{o}C and liquidus temperatures of 2146.1-2491.5 ^{o}C. Using a mixture experimental design, the effect of raw material composition on solidus and liquidus temperatures of geopolymer can be determined. Fly ash has the highest positive effect on solidus and liquidus temperatures of geopolymer compared to slag and biomass ash so that geopolymer having high solidus and liquidus temperatures can be obtained at raw material mixtures with fly ash as the dominant component.

Acknowledgments

The authors are grateful to Laboratory of Mineral and Inorganic Material Technology, Bandung Institute of Technology for providing access to software used in this study.

References

[1] Y. Yang, L. Wang, Z. Cao, C. Mou, L. Shen, J. Zhao, and Y. Fang, J. Geogr. Sci., 27(6), p. 711-730 (2017).

[2] A. Naqi and J.G. Jang, Sustainability, 11(2), 537 (2019).

[3] R.M. Andrew, Earth Syst. Sci. Data, 10, p. 195-217 (2018).

[4] J.L. Provis, Cem. Concr. Res., 114, p. 40-48 (2018).

[5] J. Davidovits, J. Ceram. Sci. Technol., 8(3), p. 335-350 (2017).

[6] F.N. Degirmenci, Ceram.-Silik., 62(1), p. 41-49 (2018).

[7] O. Martinik, B. Smetana, J. Dobrovska, A. Kalup, S. Zla, M. Kawulokova, K. Gryc, P. Dostal, L. Drozdova, and B. Baudisova, J. Min. Metall. Sect. B-Metall., 53(3B), p. 391-398 (2017).

[8] C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R.B. Mahfoud, J. Melançon, A.D. Pelton, and S. Petersen, Calphad, 26(2), p. 189-228 (2002).

[9] A.D. Pelton and P. Chartrand, Metall. Mater. Trans., 32A, p. 1355-1360 (2001).

[10] A. Islam, U.J. Alengaram, M.Z. Jumaat, and I.I. Bashar, Mater. Design., 56, p. 833-841 (2014).

[11] D.C. Montgomery, Design and analysis of experiments, 9th ed., John Wiley & Sons, Inc., New York (2017).

[12] A. van Riessen and W. Rickard in Geopolymers: Structure, processing, properties and industrial applications, J.L. Provis and J.S.J. van Deventer, Eds., Woodhead Publishing Limited and CRC Press LLC, Cambridge p. 315-342 (2009).

[13] G. Kovalchuk, and P.V. Krivenko in Geopolymers: Structure, processing, properties and industrial applications, J.L. Provis and J.S.J. van Deventer, Eds., Woodhead Publishing Limited and CRC Press LLC, Cambridge p. 227-266 (2009).

[14] J. Davidovits, Geopolymer: Chemistry and applications, 2nd ed., Institut Géopolymère, Saint-Quentin (2008).

[15] Y. Zhang, W. Sun, and Z. Li, J. Cent. South Univ. T., 16, p. 906-913 (2009).

[16] ASTM, ASTM E119-18: Standard Test Methods for Fire Tests of Building Construction and Materials, American Society for Testing and Materials, West Conshohocken (2018).

NOMENCLATURE

ΔG	Gibbs energy change
Δg_{mn}	nonconfigurational Gibbs energy change for formation of 2 moles of *m*-*n* pair
ΔS^{config}	configurational entropy of mixing
Adj MS	adjusted mean squares
Adj SS	adjusted sum of squares
DF	degrees of freedom
G_m	Gibbs energy of component *m*
g_m^o	Gibbs energy of pure component *m*
n_m	mole numbers of component *m*
n_{mn}	mole numbers of *m*-*n* pair
R	universal gas constant
T	temperature
T_{liq}	liquidus temperature of geopolymer

T_{sol}	solidus temperature of geopolymer
X_m	mole fraction of component *m*
X_{mn}	mole fraction of *m*-*n* pair
Y_m	coordination-equivalent fraction of component *m*
x_1	fly ash fraction
x_2	slag fraction
x_3	biomass ash fraction

E-mail @che.undip.ac.id

Aprilina Purbasari <aprilina.purbasari@che.undip.ac.id>

New round of reviews

1 message

International Hellenic University - Kavala Campus online Journals Editorial Manager <konsster@teiemt.gr> Mon, Feb 17, 2020 at 8:03 PM
To: editor@jestr.org, aprilina.purbasari@che.undip.ac.id

Dear author of Journal of Engineering Science and Technology Review,
A new round of reviews has been initiated by the Journal Editor for the paper with ID: **3376**.

Submission details

Submission ID: 3376
Author: Aprilina Purbasari
Title: Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization Approach
Section: Research Article
Review round: 2
Please log in International Hellenic University - Kavala Campus online Journals Editorial Manager in order to answer to the reviewer(s) and upload a revised paper.
Warning: For the new round of reviews, you need to upload only the revised paper using the upload field that will be available at the submission history page. **Do not start a new paper submission**.

This is an automated e-mail, please do not reply.

Introduction

The introduction provides a good, generalized background of the topic with the wide range of applications. However, to make the introduction more substantial, the author may provide more references to substantiate the claim made in introduction (that is, provide references that have done research in this area). The literature cited is relevant to the study.

Motivation

In order to make motivation clearer and to differentiate the paper from other papers, the author may provide some of the applications of this technology, along with appropriate references. I think the motivations for this study need to be made clearer.

The main focus of the paper is the determination of solidus and liquidus temperatures using Gibbs energy minimization approach with FactSage 6.3 software and the composition effect of raw material mixture with Minitab 17 software.

Methods

The experimental works is quite standard, and is appropriate for the study, especially determination of solidus and liquidus temperatures by FactSage software uses phase equilibrium calculation with minimization of the Gibbs energy change.

Results/ Discussion

The results are clearly explained and presented in an appropriate format. The findings are properly described in the context of the published literature. However, no significant limitations are discussed.

Comments

The paper sufficiently has the novelty for possible publication. The paper provides an excellent technique for validation of experimental work.

Introduction

The introduction provides a good, generalized background of the topic with the wide range of applications. However, to make the introduction more substantial, the author may provide more references to substantiate the claim made in introduction (that is, provide references that have done research in this area). The literature cited is relevant to the study.

Answer:
In Introduction section, some similar studies about application of FactSage 6.3 software have been added, for example: determination of phase compositions in manganese ores calcination, determination of liquidus temperature in Portland clinker, determination of liquidus temperature in copper smelting, and prediction of ash behavior and ash fusion temperature.

References that have been added:

- B. Sorensen, S. Gaal, E. Ringdalen, M. Tangstad, R. Kononov, and O. Ostrovski, Int. J. Miner. Process., 94, p. 101-110 (2010).
- M.-N. de Noirfontaine, S. Tusseau-Nenez, C. Girod-Labianca, and V. Pontikis, J. Mater. Sci., 47(3), p. 1471-1479 (2012).
- B. Zhao, P. Hayes, and E. Jak, J. Min. Metall. Sect. B-Metall., 49(2) B, p. 153-159 (2013).
- P. Pintana and N. Tippayawong, WSEAS Trans. Environ. Dev., 10, p. 202-210 (2014).

Motivation

In order to make motivation clearer and to differentiate the paper from other papers, the author may provide some of the applications of this technology, along with appropriate references. I think the motivations for this study need to be made clearer.

The main focus of the paper is the determination of solidus and liquidus temperatures using Gibbs energy minimization approach with FactSage 6.3 software and the composition effect of raw material mixture with Minitab 17 software.

Answer:
Some of the applications of the technology have been added in Introduction section.

Methods

The experimental works is quite standard, and is appropriate for the study, especially determination of solidus and liquidus temperatures by FactSage software uses phase equilibrium calculation with minimization of the Gibbs energy change.

Answer:
Thank you.

Results/ Discussion

The results are clearly explained and presented in an appropriate format. The findings are properly described in the context of the published literature. However, no significant limitations are discussed.

Answer:

In the result and discussion section, the results of solidus and liquidus temperatures from simulation with FactSage software on various raw material mixture (fly ash, slag, biomass ash) have been discussed and compared to the literatures. Meanwhile the results of the composition effect of raw material on the solidus and liquidus temperatures statistically with Minitab software have been discussed. The results obtained can be used to determine the composition of raw material mixture (fly ash, slag, biomass ash) so that geopolymer can be predicted to have high solidus and liquidus temperatures or have good resistance to high temperature exposure or fire.

Comments

The paper sufficiently has the novelty for possible publication. The paper provides an excellent technique for validation of experimental work.

Answer:
Thank you.

Research Article

Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization Approach

Abstract

Geopolymer, alumino-silicate inorganic polymer, has the potential to substitute Portland cement because of its lower energy consumption and CO_2 emissions, as well as its raw material can use solid wastes such as fly ash, slag, and biomass ash. Geopolymer as Portland cement substitute in addition to having good mechanical strength must also have resistance to high temperature exposure which can be predicted from its solidus and liquidus temperatures. Solidus temperature indicates the occurrence of melting when the solid is heated, while the liquidus temperature indicates the occurrence of precipitation when the liquid is cooled. Thus geopolymer having high solidus and liquidus temperatures demonstrates its resistance to high temperature exposure. In this paper, composition effect of raw material mixture (fly ash, slag, and biomass ash) on the solidus and liquidus temperatures of geopolymer had been studied using experimental design of 3-components mixture. Solidus and liquidus temperatures of geopolymer in each mixture composition were determined using Gibbs energy minimization approach by FactSage 6.3 software, while the effect of mixture composition on solidus and liquidus temperatures was determined statistically by Minitab 17 software. Phase changes were observed in temperature range of 100-2500 ^oC and simulation results showed that geopolymers had solidus temperatures of 500-972.4 ^oC and liquidus temperatures of 2146.1-2491.5 ^oC. Solidus and liquidus temperatures obtained in each simulation were treated statistically resulting linear regression model for solidus temperature and special cubic regression model for liquidus temperature. Fly ash component had the highest positive effect on both solidus and liquidus temperatures of geopolymer compared to slag and biomass ash components. Therefore, geopolymer product having high solidus and liquidus temperatures was obtained with composition of raw material mixture dominated by fly ash.

Keywords: experimental design of 3-components mixture; geopolymer; Gibbs energy minimization approach; liquidus temperature; solid waste; solidus temperature

1. Introduction

Portland cement is a building material that has been widely used and its use tends to increase. World cement production in 2006 is about 2540 million tons and increase to about 4080 million tons in 2013 [1]. Cement production, which requires temperature of 1400 ^{o}C, is an energy intensive process. The dry process consumes energy about 4.60 GJ per ton of clinker, while for wet process the required energy can reach 5.85-6.28 GJ per ton of clinker [2]. The CO_2 emissions generated in the production of cement around 0.9 ton CO_2 per ton of cement and CO_2 emissions of cement industry has contributed approximately 5% of global CO_2 emissions [3].

Several alternatives to Portland cement with lower energy consumption and CO_2 emissions are calcium sulphoaluminate cement, magnesium-based cement, and geopolymer. Geopolymer is more potential to be developed as a Portland cement substitute because geopolymer production takes place at low temperatures (below 100 °C) and can use waste materials such as fly ash, biomass ash, and slag [4]. Geopolymerisation process involves complex reactions between materials containing alumino-silicate oxide with alkali hydroxide/silicate at temperature below 100 °C. This produces Si-O-Al polymeric bond with the empirical formula of $M_n(-(SiO_2)_z\text{-}AlO_2)_n.wH_2O$, where: M = cation Na^+/K^+; z = 1,2,3 ; n = degree of polycondensation. Reaction of geopolimerisation is as follows [5]:

$$\underset{\text{(Si–Al material)}}{(Si_2O_5,Al_2O_2)n + 3nH_2O} \xrightarrow{NaOH/KOH} \underset{\text{Orthosialate}}{n(OH)_3\text{-Si-O-Al}^{-}\text{-(OH)}_3} \tag{1}$$

$$\underset{\text{Orthosialate}}{n(OH)_3\text{–Si–O–Al}^{-}\text{–(OH)}_3} \xrightarrow{NaOH/KOH} \underset{\text{(Na,K)-poly(sialate)}}{(Na,K)\left(\begin{array}{c} | \quad\quad | \\ \text{–Si–O–Al}^{-}\text{–O–} \\ | \quad\quad | \\ O \quad\quad O \\ | \quad\quad | \end{array}\right)n + 3n\,H_2O} \tag{2}$$

Three-dimensional structure of geopolymer products are amorphous to semi-crystalline and can be poly(sialate)/(-Si-O-Al-O-) for Si:Al = 1:1, poly(sialate-siloxo)/(-Si-O-Al-O-Si-O-) for Si:Al = 2:1, or poly(sialate-disiloxo)/(-Si-O-Al-O-Si-O-Si-O-) for Si:Al = 3:1 [5].

Sources of alumino-silicate material are natural mineral (for example: kaolin), waste from combustion of coal (fly ash) and biomass, and waste from steel industry (slag). Fly ash from coal combustion and slag has been used extensively in the cement production. In addition to improving the cement quality, fly ash or slag usage would reduce the amount of clinker in cement so that the energy for clinker production could also be reduced [2]. Utilization of waste products of combustion, i.e. fly ash and biomass ash, and slag for geopolymer as a Portland cement substitute is an attempt to reduce the burden on the environment and can also contribute to the reduction of CO_2 emissions.

Geopolymer as a Portland cement substitute in addition to having good mechanical strength must also have resistance to high temperature exposure. Geopolymer has shown better resistance to fire than Portland cement [4]. Exposure of Portland cement-based mortars and concretes to temperature above 300 ^{o}C can decompose $Ca(OH)_2$ into CaO and H_2O which causes mortar shrinkage [6]. Furthermore CaO may react with water vapour in air to form $Ca(OH)_2$ having greater volume than CaO so that mortar will crack resulting in mortar damage.

To determine the resistance of geopolymer to high temperature exposure, it can be predicted from its solidus and liquidus temperatures. Solidus temperature indicates the occurrence of melting when the solid is heated, while the liquidus temperature indicates the occurrence of precipitation when the liquid is cooled [7]. Thus geopolymer having high solidus and liquidus temperatures demonstrates its resistance to high temperature exposure.

This paper studies the composition effect of raw material mixture (fly ash, slag, and biomass ash) on high temperature behavior of geopolymer product, i.e. solidus and liquidus temperatures. Determination of solidus and liquidus temperatures was conducted using Gibbs energy minimization approach with FactSage 6.3 software, whereas determination of the composition effect of raw material mixture statistically was conducted with Minitab 17 software. Several studies related to the use of FactSage software have been carried out such as determination of phase compositions in manganese ores calcination [8], determination of liquidus temperature in Portland clinker [9], determination of liquidus temperature in copper smelting [10], and prediction of ash behaviour and ash fusion temperature [11].

2. Experimental

Determination of solidus and liquidus temperatures by FactSage software uses phase equilibrium calculation with minimization of the Gibbs energy change.

$$\Delta G < 0 \quad (3)$$

$$G - \sum n_m G_m < 0 \quad (4)$$

$$G = \sum n_m G_m = minimum \quad (5)$$

where: ΔG = Gibbs energy change, n_m = mole numbers of component *m*, and G_m = Gibbs energy of component *m*. One of the models used in FactSage software for oxides, salts, and metal alloys with short-range-ordering is modified quasi-chemical [12].

The Gibbs energy for solution is:

$$G = \sum n_m g_m^o - T\Delta S^{config} + \sum_{n>m} \sum n_{mn} (\frac{\Delta g_{mn}}{2}) \quad (6)$$

where: g_m^o = Gibbs energy of pure component *m*, *T* = temperature, ΔS^{config} = configurational entropy of mixing, n_{mn} = mole numbers of *m*-*n* pair, and Δg_{mn} = nonconfigurational Gibbs energy change for formation of 2 moles of *m*-*n* pair.

For multicomponent solution [13]:

$$G = (n_{11}g_{11}^o + n_{12}g_{12}^o + n_{22}g_{22}^o + n_{13}g_{13}^o + \cdots) - T\Delta S^{config} + \sum_{n>m} \sum \left(\frac{n_{mn}}{2}\right) (\Delta g_{mn} - \Delta g_{mn}^o) \quad (7)$$

with:

$$\Delta S^{config} = -R \sum n_m \ln X_m - R(\sum n_{mm} \ln(X_{mm}/Y_m^2) + \sum_{m>n} \sum n_{mn} \ln(X_{mn}/2Y_m Y_n)) \quad (8)$$

$$\Delta g_{mn} = \Delta g_{mn}^{o} + \sum_{(i+j)\geq 1} g_{mn}^{ij} X_{mm}^{i} X_{nn}^{j} \quad (9)$$

where: R = universal gas constant , X_m = mole fraction of component m, X_{mn} = mole fraction of m-n pair, and Y_m = coordination-equivalent fraction of component m.

Module of calculation used in FactSage software was Equilib with SLAGE solution phase, namely an oxide mixture of Al, Ca, Cu, Fe, K, Mg, Mn, Na, Si, Ti with H_2O/OH, Cl, SO_4, PO_4. Data required to determine solidus and liquidus temperatures were oxide compositions of geopolymer raw material, in this case fly ash, slag, and biomass ash (palm oil fuel ash) as presented in Tab. 1.

In each simulation run by FactSage software, it was used 100 grams mixture of fly ash, slag, and biomass ash as alumino-silicate material with certain composition reacted with 5 N KOH as alkaline activator with weight ratio of 2:1 to form geopolymer. The composition of raw material (fly ash, slag, biomass ash) used in each simulation was based on experimental design of 3-components mixture generated by Minitab software with 10 compositions as shown in Fig. 1. Phase changes of formed geopolymer were observed in temperature range of 100-2500 ^{o}C.

Solidus and liquidus temperatures obtained in each simulation then statistically were treated by Minitab software. Regression model of mixture experiment can be linear, quadratic, full cubic, or special cubic equation [15]. By analysis of variance (ANOVA) the adequate equations for solidus and liquidus temperatures could be determined. These equations could be used to predict solidus and liquidus temperatures of geopolymer with fly ash, slag, and biomass ash as raw material. Furthermore, the composition effect of raw material mixture on solidus and liquidus temperatures could be determined from the equations.

3. Result and Discussion

3.1 Solidus and liquidus temperatures of geopolymer

Solidus and liquidus temperatures of geopolymer resulted by simulation using FactSage software on each mixture composition of raw material are presented in Tab. 2. The range of the solidus temperature of geopolymer is 500-972.4 ^{o}C, while the liquidus temperature is 2146.1-2491.5 ^{o}C.

At various temperature ranges geopolymer can undergo dehydration of free water (100-300 ^oC); dehydroxylation (250-600 ^oC); densification by viscous sintering (550-900 ^oC); and crystallization, expansion due to cracking, further densification (>900 ^oC) [16]. Thus at temperature of 550-900 ^oC it begins to form liquid. This range is not much different with the solidus temperatures obtained by FactSage (500-972.4 ^oC) where at that temperature molten slag begins to be formed.

Mineral phases that occur from FactSage calculation are presented in Tab. 3 on simulation with a mixture of fly ash:slag:biomass ash = 1/3:1/3:1/3 (M7). This agrees with the results of XRD (X-Ray Diffraction) analysis to geopolymer exposed to high temperatures [16]. Leucite ($KAlSi_2O_6$) is a major phase encountered in geopolymer synthesized with alkaline activator containing potassium at temperature about 1000 ^oC, while hematite (Fe_2O_3) at temperature about 1200 ^oC. Garnet ($Ca_3Fe_2Si_3O_{12}$) and wollastonite ($CaSiO_3$) will be found in geopolymer with slag as raw material due to high calcium content [17].

The liquidus temperature which indicates geopolymer in wholly liquid form is obtained above 2000 ^oC. Mineral formed or start precipitated at liquidus temperature generally is $(SrO)(SiO_2)$ or $(SrO)_2(SiO_2)$, but for geopolymer with slag composition = 1 (M2), slag:biomass ash = 1/2:1/2 (M6), and fly ash:slag:biomass ash = 1/6:2/3:1/6 (M9) mineral formed is $Ca_3(PO_4)_2$. This is possible because of the high content of CaO in the slag compared to that in the fly ash and in the biomass ash.

Among the raw materials of fly ash, slag, and biomass ash, solidus and liquidus temperatures of geopolymer from fly ash is the highest. This can be explained by observing the oxides content in raw materials. The oxides composition of silica, alumina, alkali oxide, and water forming geopolymer can affect the mechanical strength of geopolymer, as well as the solidus and liquidus temperatures of geopolymer. To obtain strong geopolymer products, ratios of silica, alumina, alkali oxide, and water are in the following ranges: SiO_2/Al_2O_3 = 3.0-4.5; M_2O/SiO_2 = 0.2-0.5; H_2O/M_2O = 10-25; and M_2O/Al_2O_3 = 0.6-1.6 [18]. Result of research in [19] showed that the ratio of alkali (K_2O) on alumina (Al_2O_3) had the most effect on the mechanical strength of geopolymer and geopolymer with ratio of K_2O/Al_2O_3 = 0.8 had the highest mechanical strength. In this simulation, ratio of K_2O/Al_2O_3 in the fly ash is 0.79 or close to 0.8, while for slag and biomass ash 1.52 and 4.91, respectively, or greater than 0.8, likewise ratio of K_2O/Al_2O_3 in all mixture of fly ash-slag-biomass ash are greater than 0.8 (Tab. 2). The greater the ratio of K_2O/Al_2O_3 or more K_2O in geopolymer, the lower solidus and liquidus temperatures of geopolymer due to the lowest melting point of K_2O (740 ^oC) compared to SiO_2 (1600-1725 ^oC) and Al_2O_3 (2072 ^oC). Thus the ratio of K_2O/Al_2O_3 in addition affects the mechanical strength of geopolymer also solidus and liquidus temperatures of geopolymer.

3.2 The composition effect of raw material mixture on solidus and liquidus temperatures of geopolymer

The composition effect of raw material on solidus and liquidus temperatures of geopolymer can be observed from regression models generated by Minitab software. Analysis of variance (ANOVA) for each regression model obtained for the solidus and liquidus temperatures is presented in Tab. 4 and Tab. 5, respectively. The regression model for solidus temperature of geopolymer that has P-value <0.05 is linear model with R^2-value of 69.91% and R^2_{Adj}-value of 61.31%. Meanwhile regression model for liquidus temperature of geopolymer that has P-value <0.05 with the highest value of R^2 and R^2_{Adj} is special cubic.

Adequacy checking for each regression model is conducted from normal probability plot and residual versus fitted value as shown in Fig. 2 for linear model of geopolymer solidus temperature and Fig. 3 for special cubic model of geopolymer liquidus temperature. The normal probability plots of residuals in Fig. 2(a) and Fig. (3a) show that residuals are distributed normally. Furthermore, plots of residuals versus fitted value in Fig. 2(b) and Fig. (3b) indicate that residuals do not form a specific pattern. Thus, it can be concluded that each regression model is adequate.

Equation with linear model to predict the solidus temperature of geopolymer indicated by Eq. 10 and equation with special cubic model to predict the liquidus temperature of geopolymer indicated by Eq. 11.

$$T_{sol}(\,^{o}C) = 935.2x_1 + 536.9x_2 + 619.9x_3 \quad (10)$$

$$T_{liq}(\,^{o}C) = 2488x_1 + 2148x_2 + 2132x_3 - 83x_1x_2 + 472x_1x_3 + 290x_2x_3 - 1506x_1x_2x_3 \quad (11)$$

where: T_{sol} = solidus temperature of geopolymer; T_{liq} = liquidus temperature of geopolymer; x_1 = fly ash fraction , x_2 = slag fraction, and x_3 = biomass ash fraction in the mixture.

At both Eq. 10 and Eq. 11, fly ash fraction (x_1), slag fraction (x_2), and biomass ash fraction (x_3) have positive coefficients or positive effects on solidus and liquidus temperatures of geopolymer. Fly ash component has the highest positive effect compared to slag and biomass ash components. Equation 11 denotes that mixing of fly ash-biomass ash or slag-biomass ash provides positive effect on the liquidus temperature, while mixing of fly ash-slag or mixing of fly ash-slag-biomass ash provides negative effect.

From the contour plots of solidus temperature and liquidus temperature as shown in Fig. 4 and Fig. 5, we can determine the composition of the raw material mixture (fly ash, slag, and biomass ash) that produce geopolymer with expected solidus temperature and liquidus temperature. Higher solidus temperatures in Fig. 4 and higher liquidus temperatures in Fig. 5 are indicated by darker shades, obtained in mixtures with fly ash as the dominant component.

Geopolymer as a Portland cement substitute is expected having resistance to high temperature exposure or fire. In general, temperature will reach 800 °C quickly in about 30 minutes during fire. After that, temperature will increase more slowly from 900 °C to 1200 °C within 6 hours [20]. Therefore geopolymer having solidus temperatures above 800 °C indicates having better resistance to fire. From Fig. 4 geopolymer with solidus temperatures above 800 °C is obtained at mixture of fly ash, slag, and biomass ash with slag composition not more than ±30% and biomass ash composition not more than ±40%. Thus geopolymer from solid wastes can be predicted to have solidus temperatures above 800 °C with maximum slag composition of 30% and maximum biomass ash composition of 40%.

4. Conclusions

Results of FactSage simulation indicate that geopolymers with raw material mixture of fly ash, slag, and biomass ash have solidus temperatures of 500-972.4 ^oC and liquidus temperatures of 2146.1-2491.5 ^oC. Using a mixture experimental design, the effect of raw material composition on solidus and liquidus temperatures of geopolymer can be determined. Fly ash has the highest positive effect on solidus and liquidus temperatures of geopolymer compared to slag and biomass ash so that geopolymer having high solidus and liquidus temperatures can be obtained at raw material mixtures with fly ash as the dominant component.

Acknowledgments

The authors are grateful to Laboratory of Mineral and Inorganic Material Technology, Bandung Institute of Technology for providing access to software used in this study.

References

[1] Y. Yang, L. Wang, Z. Cao, C. Mou, L. Shen, J. Zhao, and Y. Fang, J. Geogr. Sci., 27(6), p. 711-730 (2017).

[2] A. Naqi and J.G. Jang, Sustainability, 11(2), 537 (2019).

[3] R.M. Andrew, Earth Syst. Sci. Data, 10, p. 195-217 (2018).

[4] J.L. Provis, Cem. Concr. Res., 114, p. 40-48 (2018).

[5] J. Davidovits, J. Ceram. Sci. Technol., 8(3), p. 335-350 (2017).

[6] F.N. Degirmenci, Ceram.-Silik., 62(1), p. 41-49 (2018).

[7] O. Martinik, B. Smetana, J. Dobrovska, A. Kalup, S. Zla, M. Kawulokova, K. Gryc, P. Dostal, L. Drozdova, and B. Baudisova, J. Min. Metall. Sect. B-Metall., 53(3B), p. 391-398 (2017).

[8] B. Sorensen, S. Gaal, E. Ringdalen, M. Tangstad, R. Kononov, and O. Ostrovski, Int. J. Miner. Process., 94, p. 101-110 (2010).

[9] M.-N. de Noirfontaine, S. Tusseau-Nenez, C. Girod-Labianca, and V. Pontikis, J. Mater. Sci., 47(3), p. 1471-1479 (2012).

[10] B. Zhao, P. Hayes, and E. Jak, J. Min. Metall. Sect. B-Metall., 49(2) B, p. 153-159 (2013).

[11] P. Pintana and N. Tippayawong, WSEAS Trans. Environ. Dev., 10, p. 202-210 (2014).

[12] C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R.B. Mahfoud, J. Melançon, A.D. Pelton, and S. Petersen, Calphad, 26(2), p. 189-228 (2002).

[13] A.D. Pelton and P. Chartrand, Metall. Mater. Trans., 32A, p. 1355-1360 (2001).

[14] A. Islam, U.J. Alengaram, M.Z. Jumaat, and I.I. Bashar, Mater. Design., 56, p. 833-841 (2014).

[15] D.C. Montgomery, Design and analysis of experiments, 9th ed., John Wiley & Sons, Inc., New York (2017).

[16] A. van Riessen and W. Rickard in Geopolymers: Structure, processing, properties and industrial applications, J.L. Provis and J.S.J. van Deventer, Eds., Woodhead Publishing Limited and CRC Press LLC, Cambridge p. 315-342 (2009).

[17] G. Kovalchuk and P.V. Krivenko in Geopolymers: Structure, processing, properties and industrial applications, J.L. Provis and J.S.J. van Deventer, Eds., Woodhead Publishing Limited and CRC Press LLC, Cambridge p. 227-266 (2009).

[18] J. Davidovits, Geopolymer: Chemistry and applications, 2nd ed., Institut Géopolymère, Saint-Quentin (2008).

[19] Y. Zhang, W. Sun, and Z. Li, J. Cent. South Univ. T., 16, p. 906-913 (2009).

[20] ASTM, ASTM E119-18: Standard Test Methods for Fire Tests of Building Construction and Materials, American Society for Testing and Materials, West Conshohocken (2018).

NOMENCLATURE

ΔG	Gibbs energy change
Δg_{mn}	nonconfigurational Gibbs energy change for formation of 2 moles of *m*-*n* pair
ΔS^{config}	configurational entropy of mixing

Adj MS	adjusted mean squares
Adj SS	adjusted sum of squares
DF	degrees of freedom
G_m	Gibbs energy of component *m*
g_m^o	Gibbs energy of pure component *m*
n_m	mole numbers of component *m*
n_{mn}	mole numbers of *m*-*n* pair
R	universal gas constant
T	temperature
T_{liq}	liquidus temperature of geopolymer
T_{sol}	solidus temperature of geopolymer
X_m	mole fraction of component *m*
X_{mn}	mole fraction of *m*-*n* pair
Y_m	coordination-equivalent fraction of component *m*
x_1	fly ash fraction
x_2	slag fraction
x_3	biomass ash fraction

E-mail
@che.undip.ac.id

Aprilina Purbasari <aprilina.purbasari@che.undip.ac.id>

Acceptance of article by JESTR (132)

2 messages

Editor JESTR <editor@jestr.org> Sun, Mar 29, 2020 at 4:32 PM
To: aprilina.purbasari@che.undip.ac.id

Dear author,

We are glad to inform you that, your article:

"Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization ApproachS"

Has been accepted for publication in our journal (Journal of Engineering Science and Technology Review)

In order to publish your article, please send us (via email) filled the copyright form, the authors names and the affiliations and the article in wrd format.

Kind regards

Prof. D. V. Bandekas
Editor - in - Chief
Journal of Engineering Science and Technology Review

Copyright.doc
32K

Aprilina Purbasari <aprilina.purbasari@che.undip.ac.id> Mon, Mar 30, 2020 at 2:55 PM
To: Editor JESTR <editor@jestr.org>

Dear Editor,

Thank you very much for the information.
Hereby I send the copyright and the article.

Best regards,
Aprilina Purbasari
[Quoted text hidden]

2 attachments

Copyright_JESTR_AprilinaPurbasari_etal.PDF
420K

FullPaper_JESTR_AprilinaPurbasari_etal.docx
83K

Journal of Engineering Science and Technology Review

Copyright Licensing Agreement

By submitting to the Journal of Engineering Science and Technology Review the manuscript entitled:

Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization Approach

I declare (on behalf of me and my co-authors) that the said manuscript has never been published and that I am (we are) the sole owner(s) of the manuscript thereof and of all rights, title, and interest therein. I agree (on behalf of me and my co-authors) to the following: 1) Assignment: I (we) hereby assign to the publisher of the Journal of Engineering Science and Technology Review the right to electronically publish and distribute the said manuscript and to create a derivative print work from said manuscript. The assignment shall be effective so long as the Journal of Engineering Science and Technology Review is available on computer networks; 2) Certain Rights Reserved to Author: I (we) shall remain the owner of the copyright in said manuscript. I (we) may publish the manuscript in any other journal or medium but such publication must include the notice that the manuscript was first published by the Journal of Engineering Science and Technology Review including reference to the corresponding issue; 3) Infringement of Copyright: I (we) agree to hold the publisher of the Journal of Engineering Science and Technology Review harmless for any unauthorized use of the paper by the Journal of Engineering Science and Technology Review subscribers. The Journal of Engineering Science and Technology Review subscribers may copy or download the paper from the network.
This Copyright Licensing Agreement comes into force the day of sending this completed electronic form. Please enter your name, address, and e-mail address (and the names of your co-authors):

Name of corresponding author: **Aprilina Purbasari**

Affiliation address: **Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. Soedarto, Semarang 50275, Indonesia**

E-mail address: **aprilina.purbasari@che.undip.ac.id**

Names of co-authors:
- **Tjokorde Walmiki Samadhi (Department of Chemical Engineering, Faculty of Industrial Technology, Bandung Institute of Technology, Jl. Ganesha 10, Bandung 40132, Indonesia)**
- **Yazid Bindar (Department of Chemical Engineering, Faculty of Industrial Technology, Bandung Institute of Technology, Jl. Ganesha 10, Bandung 40132, Indonesia)**

Date and signature of corresponding author: March 30, 2020

Print out the completed form and send per fax/post to:

Journal of Engineering Science and Technology Review
Kavala Institute of Technology
65 404 St.Lucas, Kavala, Greece
Tel & Fax: ++30 2510-462272

Research Article

Prediction of High Temperature Behavior of Geopolymer from Solid Wastes Using Gibbs Energy Minimization Approach

Aprilina Purbasari[1,*], Tjokorde Walmiki Samadhi[2], Yazid Bindar[2]

[1]Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. Soedarto, Semarang 50275, Indonesia

[2]Department of Chemical Engineering, Faculty of Industrial Technology, Bandung Institute of Technology, Jl. Ganesha No. 10, Bandung 40132, Indonesia

[*]E-mail: aprilina.purbasari@che.undip.ac.id

Abstract

Geopolymer, alumino-silicate inorganic polymer, has the potential to substitute Portland cement because of its lower energy consumption and CO_2 emissions, as well as its raw material can use solid wastes such as fly ash, slag, and biomass ash. Geopolymer as Portland cement substitute in addition to having good mechanical strength must also have resistance to high temperature exposure which can be predicted from its solidus and liquidus temperatures. Solidus temperature indicates the occurrence of melting when the solid is heated, while the liquidus temperature indicates the occurrence of precipitation when the liquid is cooled. Thus geopolymer having high solidus and liquidus temperatures demonstrates its resistance to high temperature exposure. In this paper, composition effect of raw material mixture (fly ash, slag, and biomass ash) on the solidus and liquidus temperatures of geopolymer had been studied using experimental design of 3-components mixture. Solidus and liquidus temperatures of geopolymer in each mixture composition were determined using Gibbs energy minimization approach by FactSage 6.3 software, while the effect of mixture composition on solidus and liquidus temperatures was determined statistically by Minitab 17 software. Phase changes were observed in temperature range of 100-2500 ^oC and simulation results showed that geopolymers had solidus temperatures of 500-972.4 ^oC and liquidus temperatures of 2146.1-2491.5 ^oC. Solidus and liquidus temperatures obtained in each simulation were treated statistically resulting linear regression model for solidus temperature and special cubic regression model for liquidus temperature. Fly ash component had the highest positive effect on both solidus and liquidus temperatures of geopolymer compared to slag and biomass ash components. Therefore, geopolymer product having high solidus and liquidus temperatures was obtained with composition of raw material mixture dominated by fly ash.

Keywords: experimental design of 3-components mixture; geopolymer; Gibbs energy minimization approach; liquidus temperature; solid waste; solidus temperature

1. Introduction

Portland cement is a building material that has been widely used and its use tends to increase. World cement production in 2006 is about 2540 million tons and increase to about 4080 million tons in 2013 [1]. Cement production, which requires temperature of 1400 ^oC, is an energy intensive process. The dry process consumes energy about 4.60 GJ per ton of clinker, while for wet process the required energy can reach 5.85-6.28 GJ per ton of clinker [2]. The CO_2 emissions generated in the production of cement around 0.9 ton CO_2 per ton of cement and CO_2 emissions of cement industry has contributed approximately 5% of global CO_2 emissions [3].

Several alternatives to Portland cement with lower energy consumption and CO_2 emissions are calcium sulphoaluminate cement, magnesium-based cement, and geopolymer. Geopolymer is more potential to be developed as a Portland cement substitute because geopolymer production takes place at low temperatures (below 100 °C) and can use waste materials such as fly ash, biomass ash, and slag [4]. Geopolymerisation process involves complex reactions between materials containing alumino-silicate oxide with alkali hydroxide/silicate at temperature below 100 °C. This produces Si-O-Al polymeric bond with the empirical formula of $M_n(-(SiO_2)_z-AlO_2)_n.wH_2O$, where: M = cation Na^+/K^+; z = 1,2,3 ; n = degree of polycondensation. Reaction of geopolimerisation is as follows [5]:

$$(Si_2O_5,Al_2O_2)n + 3nH_2O \xrightarrow{NaOH/KOH} n(OH)_3\text{-}Si\text{-}O\text{-}Al^-\text{-}(OH)_3 \qquad (1)$$

(Si–Al material) Orthosialate

| |

$$n(OH)_3–Si–O–Al^-–(OH)_3 \xrightarrow{NaOH/KOH} (Na,K)(–Si–O–Al^-–O–)n + 3n\ H_2O \qquad (2)$$

| |

O O

| |

Orthosialate (Na,K)-poly(sialate)

Three-dimensional structure of geopolymer products are amorphous to semi-crystalline and can be poly(sialate)/(-Si-O-Al-O-) for Si:Al = 1:1, poly(sialate-siloxo)/(-Si-O-Al-O-Si-O-) for Si:Al = 2:1, or poly(sialate-disiloxo)/(-Si-O-Al-O-Si-O-Si-O-) for Si:Al = 3:1 [5].

Sources of alumino-silicate material are natural mineral (for example: kaolin), waste from combustion of coal (fly ash) and biomass, and waste from steel industry (slag). Fly ash from coal combustion and slag has been used extensively in the cement production. In addition to improving the cement quality, fly ash or slag usage would reduce the amount of clinker in cement so that the energy for clinker production could also be reduced [2]. Utilization of waste products of combustion, i.e. fly ash and biomass ash, and slag for geopolymer as a Portland cement substitute is an attempt to reduce the burden on the environment and can also contribute to the reduction of CO_2 emissions.

Geopolymer as a Portland cement substitute in addition to having good mechanical strength must also have resistance to high temperature exposure. Geopolymer has shown better resistance to fire than Portland cement [4]. Exposure of Portland cement-based mortars and concretes to temperature above 300 ºC can decompose $Ca(OH)_2$ into CaO and H_2O which causes mortar shrinkage [6]. Furthermore CaO may react with water vapour in air to form $Ca(OH)_2$ having greater volume than CaO so that mortar will crack resulting in mortar damage.

To determine the resistance of geopolymer to high temperature exposure, it can be predicted from its solidus and liquidus temperatures. Solidus temperature indicates the occurrence of melting when the solid is heated, while the liquidus temperature indicates the occurrence of precipitation when the liquid is cooled [7]. Thus geopolymer having high solidus and liquidus temperatures demonstrates its resistance to high temperature exposure.

This paper studies the composition effect of raw material mixture (fly ash, slag, and biomass ash) on high temperature behavior of geopolymer product, i.e. solidus and liquidus temperatures. Determination of solidus and liquidus temperatures was conducted using Gibbs energy minimization approach with FactSage 6.3 software, whereas determination of the composition effect of raw material mixture statistically was conducted with Minitab 17 software. Several studies related to the use of FactSage software have been carried out such as determination of phase compositions in manganese ores calcination [8], determination of liquidus temperature in Portland clinker [9], determination of liquidus temperature in copper smelting [10], and prediction of ash behaviour and ash fusion temperature [11].

2. Experimental

Determination of solidus and liquidus temperatures by FactSage software uses phase equilibrium calculation with minimization of the Gibbs energy change.

$$\Delta G < 0 \qquad (3)$$

$$G - \sum n_m G_m < 0 \qquad (4)$$

$$G = \sum n_m G_m = minimum \qquad (5)$$

where: ΔG = Gibbs energy change, n_m = mole numbers of component m, and G_m = Gibbs energy of component m. One of the models used in FactSage software for oxides, salts, and metal alloys with short-range-ordering is modified quasi-chemical [12].

The Gibbs energy for solution is:

$$G = \sum n_m g_m^o - T\Delta S^{config} + \sum_{n>m} \sum n_{mn} (\frac{\Delta g_{mn}}{2}) \quad (6)$$

where: g_m^o = Gibbs energy of pure component m, T = temperature, ΔS^{config} = configurational entropy of mixing, n_{mn} = mole numbers of m-n pair, and Δg_{mn} = nonconfigurational Gibbs energy change for formation of 2 moles of m-n pair.

For multicomponent solution [13]:

$$G = (n_{11}g_{11}^o + n_{12}g_{12}^o + n_{22}g_{22}^o + n_{13}g_{13}^o + \cdots) - T\Delta S^{config} + \sum_{n>m} \sum \left(\frac{n_{mn}}{2}\right) (\Delta g_{mn} - \Delta g_{mn)}^o \quad (7)$$

with:

$$\Delta S^{config} = -R \sum n_m \ln X_m - R(\sum n_{mm} \ln(X_{mm}/Y_m^2) + \sum_{m>n} \sum n_{mn} \ln(X_{mn}/2Y_m Y_n)) \quad (8)$$

$$\Delta g_{mn} = \Delta g_{mn}^o + \sum_{(i+j)\geq 1} g_{mn}^{ij} X_{mm}^i X_{nn}^j \quad (9)$$

where: R = universal gas constant, X_m = mole fraction of component m, X_{mn} = mole fraction of m-n pair, and Y_m = coordination-equivalent fraction of component m.

Module of calculation used in FactSage software was Equilib with SLAGE solution phase, namely an oxide mixture of Al, Ca, Cu, Fe, K, Mg, Mn, Na, Si, Ti with H_2O/OH, Cl, SO_4, PO_4. Data required to determine solidus and liquidus temperatures were oxide compositions of geopolymer raw material, in this case fly ash, slag, and biomass ash (palm oil fuel ash) as presented in Tab. 1. In each simulation run by FactSage software, it was used 100 grams mixture of fly ash, slag, and biomass ash as alumino-silicate material with certain composition reacted with 5 N KOH as alkaline activator with weight ratio of 2:1 to form geopolymer. The composition of raw material (fly ash, slag, biomass ash) used in each simulation was based on experimental design of 3-components mixture generated by Minitab software with 10 compositions as shown in Fig. 1. Phase changes of formed geopolymer were observed in temperature range of 100-2500 ^{o}C.

Table 1. Composition (wt-%) of fly ash, slag, and biomass ash [14]

Component	Fly ash	Slag	Biomass ash
SiO_2	55.30	32.68	63.49
Al_2O_3	27.28	13.71	5.55
Fe_2O_3	5.15	0.76	4.19
CaO	5.31	45.83	4.34
MgO	1.10	3.27	3.74
Na_2O	0.43	0.25	0.16
K_2O	1.00	0.48	6.33
TiO_2	1.82	0.73	0.33
MnO	0.10	0.35	0.17
P_2O_5	1.12	0.04	3.78
SO_3	1.01	1.80	0.91
SrO	0.36	0.08	0.02
Cl	0.01	0.02	0.45
CuO	0.01	-	6.54

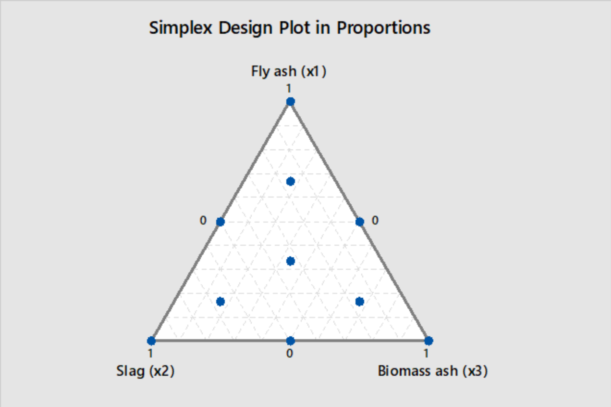


Fig.1. Experimental design of 3-components mixture

Solidus and liquidus temperatures obtained in each simulation then statistically were treated by Minitab software. Regression model of mixture experiment can be linear, quadratic, full cubic, or special cubic equation [15]. By analysis of variance (ANOVA) the adequate equations for solidus and liquidus temperatures could be determined. These equations could be used to predict solidus and liquidus temperatures of geopolymer with fly ash, slag, and biomass ash as raw material. Furthermore, the composition effect of raw material mixture on solidus and liquidus temperatures could be determined from the equations.

3. Result and Discussion

3.1 Solidus and liquidus temperatures of geopolymer

Solidus and liquidus temperatures of geopolymer resulted by simulation using FactSage software on each mixture composition of raw material are presented in Tab. 2. The range of the solidus temperature of geopolymer is 500-972.4 ^{o}C, while the liquidus temperature is 2146.1-2491.5 ^{o}C. At various temperature ranges geopolymer can undergo dehydration of free water (100-300 ^{o}C); dehydroxylation (250-600 ^{o}C); densification by viscous sintering (550-900 ^{o}C); and crystallization, expansion due to cracking, further densification (>900 ^{o}C) [16]. Thus at temperature of 550-900 ^{o}C it begins to form liquid. This range is not much different with the solidus temperatures obtained by FactSage (500-972.4 ^{o}C) where at that temperature molten slag begins to be formed.

Table 2. Solidus and Liquidus temperatures of geopolymer, calculated using Factsage software

Mixture No.	Component			K_2O/Al_2O_3 ratio	Responses	
	Fly ash (x_1)	Slag (x_2)	Biomass ash (x_3)		$T_{Solidus}$ (^{o}C)	$T_{Liquidus}$ (^{o}C)
M1	1	0	0	0.79	972.4	2491.5
M2	0	1	0	1.52	500	2146.1
M3	0	0	1	4.91	600	2124.4
M4	1/2	1/2	0	1.03	851.1	2298.6
M5	1/2	0	1/2	1.48	700	2423.8
M6	0	1/2	1/2	2.50	700	2202.8
M7	1/3	1/3	1/3	1.50	700	2256.8
M8	2/3	1/6	1/6	1.04	750	2391.6
M9	1/6	2/3	1/6	1.51	500	2223.0
M10	1/6	1/6	2/3	2.40	700	2277.3

Mineral phases that occur from FactSage calculation are presented in Tab. 3 on simulation with a mixture of fly ash:slag:biomass ash = 1/3:1/3:1/3 (M7). This agrees with the results of XRD (X-Ray Diffraction) analysis to geopolymer exposed to high temperatures [16]. Leucite ($KAlSi_2O_6$) is a major phase encountered in geopolymer synthesized with alkaline activator containing potassium at temperature about 1000 ^{o}C, while hematite (Fe_2O_3) at temperature about 1200 ºC. Garnet ($Ca_3Fe_2Si_3O_{12}$) and wollastonite ($CaSiO_3$) will be found in geopolymer with slag as raw material due to high calcium content [17].

Table 3. Equilibrium phases in geopolymer (M7) at temperature of 900-1200 ºC, calculated using Factsage software

Temperature (ºC)	Phases
900	Leucite ($KAlSi_2O_6$), merwinite ($Ca_3MgSi_2O_8$), andradite (garnet) ($Ca_3Fe_2Si_3O_{12}$), K_2SO_4, Cu_2O, perovskite-a ($CaTiO_3$), hydroxyapatite ($Ca_5HO_{13}P_3$), wollastonite ($CaSiO_3$), (SrO)(TiO_2), Mn_3O_4
1000	Leucite ($KAlSi_2O_6$), merwinite ($Ca_3MgSi_2O_8$), andradite (garnet) ($Ca_3Fe_2Si_3O_{12}$), K_2SO_4, (Cu_2O)(Fe_2O_3), perovskite-a ($CaTiO_3$), hydroxyapatite ($Ca_5HO_{13}P_3$), wollastonite ($CaSiO_3$), (SrO)(TiO_2)
1100	Leucite ($KAlSi_2O_6$), merwinite ($Ca_3MgSi_2O_8$), andradite (garnet) ($Ca_3Fe_2Si_3O_{12}$), (Cu_2O)(Fe_2O_3), perovskite-a ($CaTiO_3$), hydroxyapatite ($Ca_5HO_{13}P_3$), (SrO)(TiO_2)
1200	Leucite ($KAlSi_2O_6$), $Ca_3(PO_4)_2$, hematite (Fe_2O_3), akermanite ($Ca_2MgSi_2O_7$), (SrO)(TiO_2)

The liquidus temperature which indicates geopolymer in wholly liquid form is obtained above 2000 ºC. Mineral formed or start precipitated at liquidus temperature generally is (SrO)(SiO_2) or $(SrO)_2$(SiO_2), but for geopolymer with slag composition = 1 (M2), slag:biomass ash = 1/2:1/2 (M6), and fly ash:slag:biomass ash = 1/6:2/3:1/6 (M9) mineral formed is $Ca_3(PO_4)_2$. This is possible because of the high content of CaO in the slag compared to that in the fly ash and in the biomass ash.

Among the raw materials of fly ash, slag, and biomass ash, solidus and liquidus temperatures of geopolymer from fly ash is the highest. This can be explained by observing the oxides content in raw materials. The oxides composition of silica, alumina, alkali oxide, and water forming geopolymer can affect the mechanical strength of geopolymer, as well as the solidus and liquidus temperatures of geopolymer. To obtain strong geopolymer products, ratios of silica, alumina, alkali oxide, and water are in the following ranges: SiO_2/Al_2O_3 = 3.0-4.5; M_2O/SiO_2 = 0.2-0.5; H_2O/M_2O = 10-25; and M_2O/Al_2O_3 = 0.6-1.6 [18]. Result of research in [19] showed that the ratio of alkali (K_2O) on alumina (Al_2O_3) had the most effect on the mechanical strength of geopolymer and geopolymer with ratio of K_2O/Al_2O_3 = 0.8 had the highest mechanical strength. In this simulation, ratio of K_2O/Al_2O_3 in the fly ash is 0.79 or close to 0.8, while for slag and biomass ash 1.52 and 4.91, respectively, or greater than 0.8, likewise ratio of K_2O/Al_2O_3 in all mixture of fly ash-slag-biomass ash are greater than 0.8 (Tab. 2). The greater the ratio of K_2O/Al_2O_3 or more K_2O in geopolymer, the lower solidus and liquidus temperatures of geopolymer due to the lowest melting point of K_2O (740 ºC) compared to SiO_2 (1600-1725 ºC) and Al_2O_3 (2072 ºC). Thus the ratio of K_2O/Al_2O_3 in addition affects the mechanical strength of geopolymer also solidus and liquidus temperatures of geopolymer.

3.2 The composition effect of raw material mixture on solidus and liquidus temperatures of geopolymer

The composition effect of raw material on solidus and liquidus temperatures of geopolymer can be observed from regression models generated by Minitab software. Analysis of variance (ANOVA) for each regression model obtained for the solidus and liquidus temperatures is presented in Tab. 4 and Tab. 5, respectively. The regression model for solidus temperature of geopolymer that has P-value <0.05 is linear model with R^2-value of 69.91% and R^2_{Adj}-value of 61.31%. Meanwhile regression model for liquidus temperature of geopolymer that has P-value <0.05 with the highest value of R^2 and R^2_{Adj} is special cubic.

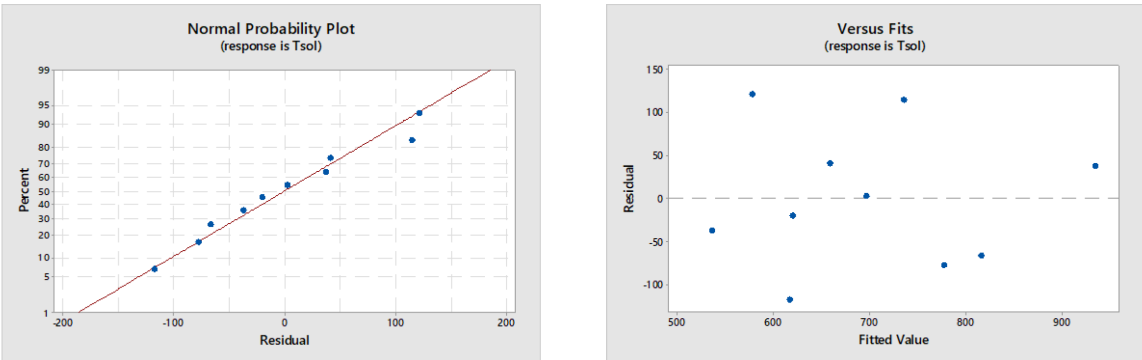
Table 4. Anova for regression model of geopolymer solidus temperature, calculated using Minitab software

Model	DF	Adj SS	Adj MS	DF Error	Adj SS Error	Adj MS Error	F	P	R^2 (%)	R^2_{Adj} (%)
Linear	2	132439	66219.7	7	57007	8143.9	8.13	0.015	69.91	61.31
Quadratic	5	154916	30983.3	4	34530	8632.6	3.59	0.120	81.77	58.99
Special cubic	6	163274	27212.3	3	26173	8724.4	3.12	0.189	86.18	58.55
Full cubic	8	182684	22835.5	1	6763	6763.2	3.38	0.399	96.43	67.87

Table 5. Anova for regression model of geopolymer liquidus temperature, calculated using Minitab software

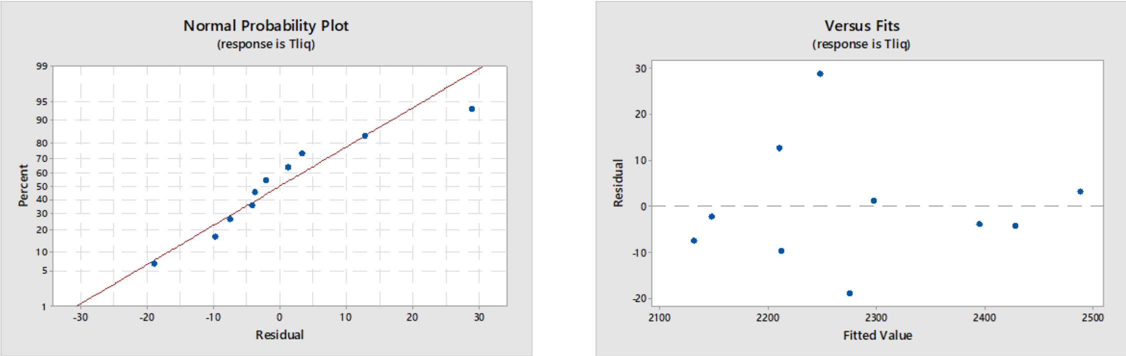
Model	DF	Adj SS	Adj MS	DF Error	Adj SS Error	Adj MS Error	F	P	R^2 (%)	R^2_{Adj} (%)
Linear	2	115420	57709.9	7	14564	2080.6	27.74	0.000	88.80	85.59
Quadratic	5	126230.9	25246.2	4	3753.1	938.3	26.91	0.004	97.11	93.50
Special cubic	6	128435.4	21405.9	3	1548.6	516.2	41.47	0.006	98.81	96.43
Full cubic	8	129086.5	16135.8	1	897.5	897.5	17.98	0.181	99.31	93.79

Adequacy checking for each regression model is conducted from normal probability plot and residual versus fitted value as shown in Fig. 2 for linear model of geopolymer solidus temperature and Fig. 3 for special cubic model of geopolymer liquidus temperature. The normal probability plots of residuals in Fig. 2(a) and Fig. (3a) show that residuals are distributed normally. Furthermore, plots of residuals versus fitted value in Fig. 2(b) and Fig. (3b) indicate that residuals do not form a specific pattern. Thus, it can be concluded that each regression model is adequate.



(a) (b)

Fig. 2. Adequacy checking for linear model of geopolymer solidus temperature: (a) normal probability plot and (b) residual versus fitted value



(a) (b)

Fig. 3. Adequacy checking for special cubic model of geopolymer liquidus temperature: (a) normal probability plot and (b) residual versus fitted value

Equation with linear model to predict the solidus temperature of geopolymer indicated by Eq. 10 and equation with special cubic model to predict the liquidus temperature of geopolymer indicated by Eq. 11.

$$T_{sol}(\,^{o}C) = 935.2x_1 + 536.9x_2 + 619.9x_3 \quad (10)$$

$$T_{liq}(\,^{o}C) = 2488x_1 + 2148x_2 + 2132x_3 - 83x_1x_2 + 472x_1x_3 + 290x_2x_3 - 1506x_1x_2x_3 \quad (11)$$

where: T_{sol} = solidus temperature of geopolymer; T_{liq} = liquidus temperature of geopolymer; x_1 = fly ash fraction, x_2 = slag fraction, and x_3 = biomass ash fraction in the mixture.

At both Eq. 10 and Eq. 11, fly ash fraction (x_1), slag fraction (x_2), and biomass ash fraction (x_3) have positive coefficients or positive effects on solidus and liquidus temperatures of geopolymer. Fly ash component has the highest positive effect compared to slag and biomass ash components. Equation 11 denotes that mixing of fly ash-biomass ash or slag-biomass ash provides positive effect on the liquidus temperature, while mixing of fly ash-slag or mixing of fly ash-slag-biomass ash provides negative effect.

From the contour plots of solidus temperature and liquidus temperature as shown in Fig. 4 and Fig. 5, we can determine the composition of the raw material mixture (fly ash, slag, and biomass ash) that produce geopolymer with expected solidus temperature and liquidus temperature. Higher solidus temperatures in Fig. 4 and higher liquidus temperatures in Fig. 5 are indicated by darker shades, obtained in mixtures with fly ash as the dominant component.

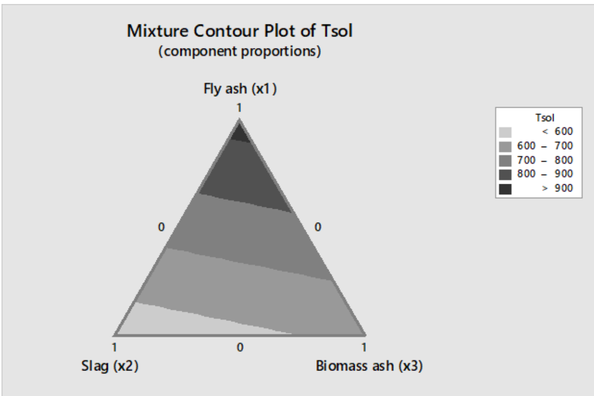


Fig. 4. Contour plot of geopolymer solidus temperature

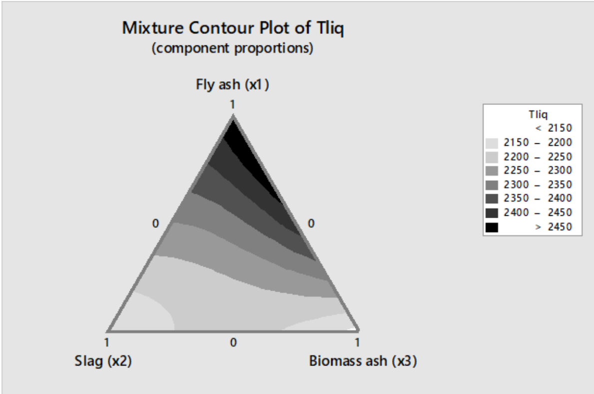


Fig. 5. Contour plot of geopolymer liquidus temperature

Geopolymer as a Portland cement substitute is expected having resistance to high temperature exposure or fire. In general, temperature will reach 800 °C quickly in about 30 minutes during fire. After that, temperature will increase more slowly from 900 °C to 1200 °C within 6 hours [20]. Therefore geopolymer having solidus temperatures above 800 °C indicates having better resistance to fire. From Fig. 4 geopolymer with solidus temperatures above 800 °C is obtained at mixture of fly ash, slag, and biomass ash with slag composition not more than ±30% and biomass ash composition not more than ±40%. Thus geopolymer from solid wastes can be predicted to have solidus temperatures above 800 °C with maximum slag composition of 30% and maximum biomass ash composition of 40%.

4. Conclusions

Results of FactSage simulation indicate that geopolymers with raw material mixture of fly ash, slag, and biomass ash have solidus temperatures of 500-972.4 ºC and liquidus temperatures of 2146.1-2491.5 ºC. Using a mixture experimental design, the effect of raw material composition on solidus and liquidus temperatures of geopolymer can be determined. Fly ash has the highest positive effect on solidus and liquidus temperatures of geopolymer compared to slag and biomass ash so that geopolymer having high solidus and liquidus temperatures can be obtained at raw material mixtures with fly ash as the dominant component.

Acknowledgments

The authors are grateful to Laboratory of Mineral and Inorganic Material Technology, Bandung Institute of Technology for providing access to software used in this study.

References

[1] Y. Yang, L. Wang, Z. Cao, C. Mou, L. Shen, J. Zhao, and Y. Fang, J. Geogr. Sci., 27(6), p. 711-730 (2017).
[2] A. Naqi and J.G. Jang, Sustainability, 11(2), 537 (2019).
[3] R.M. Andrew, Earth Syst. Sci. Data, 10, p. 195-217 (2018).
[4] J.L. Provis, Cem. Concr. Res., 114, p. 40-48 (2018).
[5] J. Davidovits, J. Ceram. Sci. Technol., 8(3), p. 335-350 (2017).
[6] F.N. Degirmenci, Ceram.-Silik., 62(1), p. 41-49 (2018).
[7] O. Martinik, B. Smetana, J. Dobrovska, A. Kalup, S. Zla, M. Kawulokova, K. Gryc, P. Dostal, L. Drozdova, and B. Baudisova, J. Min. Metall. Sect. B-Metall., 53(3B), p. 391-398 (2017).
[8] B. Sorensen, S. Gaal, E. Ringdalen, M. Tangstad, R. Kononov, and O. Ostrovski, Int. J. Miner. Process., 94, p. 101-110 (2010).
[9] M.-N. de Noirfontaine, S. Tusseau-Nenez, C. Girod-Labianca, and V. Pontikis, J. Mater. Sci., 47(3), p. 1471-1479 (2012).
[10] B. Zhao, P. Hayes, and E. Jak, J. Min. Metall. Sect. B-Metall., 49(2) B, p. 153-159 (2013).
[11] P. Pintana and N. Tippayawong, WSEAS Trans. Environ. Dev., 10, p. 202-210 (2014).
[12] C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R.B. Mahfoud, J. Melançon, A.D. Pelton, and S. Petersen, Calphad, 26(2), p. 189-228 (2002).

[13] A.D. Pelton and P. Chartrand, Metall. Mater. Trans., 32A, p. 1355-1360 (2001).
[14] A. Islam, U.J. Alengaram, M.Z. Jumaat, and I.I. Bashar, Mater. Design., 56, p. 833-841 (2014).
[15] D.C. Montgomery, Design and analysis of experiments, 9th ed., John Wiley & Sons, Inc., New York (2017).
[16] A. van Riessen and W. Rickard in Geopolymers: Structure, processing, properties and industrial applications, J.L. Provis and J.S.J. van Deventer, Eds., Woodhead Publishing Limited and CRC Press LLC, Cambridge p. 315-342 (2009).
[17] G. Kovalchuk and P.V. Krivenko in Geopolymers: Structure, processing, properties and industrial applications, J.L. Provis and J.S.J. van Deventer, Eds., Woodhead Publishing Limited and CRC Press LLC, Cambridge p. 227-266 (2009).
[18] J. Davidovits, Geopolymer: Chemistry and applications, 2nd ed., Institut Géopolymère, Saint-Quentin (2008).
[19] Y. Zhang, W. Sun, and Z. Li, J. Cent. South Univ. T., 16, p. 906-913 (2009).
[20] ASTM, ASTM E119-18: Standard Test Methods for Fire Tests of Building Construction and Materials, American Society for Testing and Materials, West Conshohocken (2018).

Nomenclature

ΔG	Gibbs energy change
Δg_{mn}	nonconfigurational Gibbs energy change for formation of 2 moles of *m*-*n* pair
ΔS^{config}	configurational entropy of mixing
Adj MS	adjusted mean squares
Adj SS	adjusted sum of squares
DF	degrees of freedom
G_m	Gibbs energy of component *m*
g_m^o	Gibbs energy of pure component *m*
n_m	mole numbers of component *m*
n_{mn}	mole numbers of *m*-*n* pair
R	universal gas constant
T	temperature
T_{liq}	liquidus temperature of geopolymer
T_{sol}	solidus temperature of geopolymer
X_m	mole fraction of component *m*
X_{mn}	mole fraction of *m*-*n* pair
Y_m	coordination-equivalent fraction of component *m*
x_1	fly ash fraction
x_2	slag fraction
x_3	biomass ash fraction