Optimizing Geopolymer-Based Material for Industrial Application with Analytic Hierarchy Process and Multi-Response Surface Analysis

Ana Karmela R. Sumabat[a], Aristotle J. Mañalac[a], Hoc Thang Nguyen[a,c], Martin Ernesto Kalaw[b], Raymond R. Tan[a], Michael Angelo B. Promentilla*[a]

[a]Chemical Engineering Department, De La Salle University 2401 Taft Ave, Manila, 1004 Metro, Philippines
[b]Mechanical Engineering Department, De La Salle University 2401 Taft Ave, Manila, 1004 Metro, Philippines
[c]Faculty of Materials Engineering, Ho Chi Minh City University of Technology, Vietnam
michael.promentilla@dlsu.edu.ph

High CO_2 emission and energy intensity from the Portland cement industry has prompted many researchers to develop cleaner and low-emission technologies for a sustainable built environment. Geopolymer technology is one promising solution to produce an alternative cementitious material with lower carbon footprint, and reduce the global consumption of Portland cement. Geopolymer can use waste such as red mud, coal ash, rice hull ash, among others, as raw materials for reactive alumina-silicates. At high alkaline condition, these alumina-silicates form a geopolymer cement binder system that hardens at room temperature like Portland cement. However, optimal mix formulation of these raw materials is necessary to produce materials with desired specification for a specific application. This work thus presents a systematic method that integrates the statistical design of experiment, multiple response optimization technique and analytic hierarchy process for product design of geopolymer-based materials. The method is demonstrated using a case study involving a geopolymer from a ternary blend of red mud, rice hull ash, and diatomaceous earth. Aside from the mechanical and thermal properties, production cost, embodied energy and carbon footprint were considered in modeling the product desirability.

1. Introduction

Geopolymer-based material is recognized as a sustainable alternative to Portland cement-based materials because of its waste valorization potential, lower embodied energy and carbon footprint. Geopolymer is an inorganic polymer formed from the reaction of alumino-silicates at high alkaline condition. Typically, the alkaline activator could be either alkali hydroxides or alkali silicates (Davidovitz, 1989). Industrial wastes such as coal ash and red mud waste, and agricultural waste such as rice hull ash are used as alumino-silicate resource for geopolymerization. Use of performance-based approach to optimize geopolymer products in comparison to Ordinary Portland Cement (OPC) is being done to standardize material specifications (Provis et al., 2014). However, criteria such as cost and ecological impact are considered in the later portion of development—limiting possibility of adjustment in material composition or process change to meet these standards. Hence, methods in optimizing geopolymer products are explored to provide a sustainable approach to geopolymer product development (Weil, et al., 2005).

The overall product performance of a geopolymer can be determined by considering several properties such as its mechanical and thermal properties as well as sustainability criteria (production cost, embodied energy and carbon footprint. These properties have already been widely studied as influenced by various factors (Sung Ryu et al., 2013) including the source of alumina-silicate resource such as coal ash (Miccio et al., 2014), red mud, and rice husk ash (Nguyen et al., 2014), among others.

In this paper, we present a methodology that integrates the statistical design of experiment, multiple response optimization technique and Analytic Hierarchy Process (AHP) for product design of geopolymer-based materials. An illustrative case study is discussed for the production of a geopolymer from a ternary blend of red mud, rice hull ash, and diatomaceous earth.

2. Methodology

The optimization model used in this study is as follows, a list of nomenclature is given at the end:

Maximize $D = \prod_j^m (dU_j + dL_j)^{W_j}$ (1)

$$\mathrm{dU_j} = \mathrm{if}\left(\frac{(\mathrm{Y_j}-\mathrm{L_j})}{(\mathrm{U_j}-\mathrm{L_j})} > 1, 1, if\left(\frac{(\mathrm{Y_j}-\mathrm{L_j})}{(\mathrm{U_j}-\mathrm{L_j})} < 0, 0.001, \frac{(\mathrm{Y_j}-\mathrm{L_j})}{(\mathrm{U_j}-\mathrm{L_j})}\right)\right) * UF_j \qquad \forall j \tag{2}$$

$$\mathrm{dL_j} = \mathrm{if}\left(\frac{(\mathrm{U_j}-\mathrm{Y_j})}{(\mathrm{U_j}-\mathrm{L_j})} > 1{,}1, if\left(\frac{(\mathrm{U_j}-\mathrm{Y_j})}{(\mathrm{U_j}-\mathrm{L_j})} < 0{,}0.001, \frac{(\mathrm{U_j}-\mathrm{Y_j})}{(\mathrm{U_j}-\mathrm{L_j})}\right)\right) * LF_j \quad \forall j \tag{3}$$

$$\mathrm{Y_j} = \mathrm{f}(\mathrm{X_1}, \mathrm{X_2}, \ldots, \mathrm{X_n}) \;\; \forall j \tag{4}$$

$$0 \le \mathrm{X_i} \le 1 \quad \forall i \tag{5}$$

$$0 \le \mathrm{w_j} \le 1 \quad \forall j \tag{6}$$

$$\textstyle\sum_{\mathrm{i}}^{\mathrm{n}} \mathrm{X_i} = 1 \tag{7}$$

$$\textstyle\sum_{\mathrm{j}}^{\mathrm{m}} \mathrm{w_j} = 1 \tag{8}$$

$$\mathrm{dU_j} \ge 0.01 * \mathrm{UF_j} \quad \forall j \tag{9}$$

$$\mathrm{dL_j} \ge 0.01 * \mathrm{LF_j} \quad \forall j \tag{10}$$

The model is based on the modified Derringer and Suich (1980) method used for multiple response surface optimization with desirability function. D is the overall desirability of the product and the objective function as shown in Eq(1) is to maximize this value by finding the optimal mix formulation of the raw materials. It is the weighted geometric mean of all the individual desirability function of the product based on a specific attribute. If the predicted attribute value is outside the acceptable range, the desirability value is 0 whereas if the predicted value has the optimal value, the desirability value is 1. In the case of larger-the-better type of attribute, the desirability function is to be maximized as shown in Eq(2). As for the smaller-the-better type of attribute, the desirability function is to be minimized as shown in Eq(3). The $\mathrm{dU_j}$ and $\mathrm{dL_j}$ are multiplied by factor $\mathrm{UF_j}$ and $\mathrm{LF_j}$ which are binary parameters (either 1 or 0) to indicate if the attribute is to be maximized or minimized.

Note that each desirability function is developed from a mathematical model of the attribute as a function of mix proportions (X_i) of the *n* raw materials. For example, appropriate model for Eq(4) can be obtained from regression model of response surface analysis using statistical mixture design of experiment.

The weights (w_j) used in aggregating the individual desirability function are associated with the relative importance of the attributes to the overall desirability. The eigenvector method of Analytic Hierarchy Process (AHP) was then used to derive the importance weights of the *m* attributes. The AHP, originally developed by Saaty (1979) integrate subjectivity within a rigorous mathematical framework, rather than trying to exclude it from the decision-making process (Bernasconi et al., 2013). The AHP framework thus provides a systematic approach to decompose and structure the problem, and derive the priority weights that reflect the subjective judgements of the stakeholder or domain expert.

The nonlinear optimization model was implemented in MS Excel 2007 environment using the Solver add-in that employs the generalized reduced gradient (GRG) algorithm. Eqs(9) and (10) were used as additional constraint to ensure that individual desirability $\mathrm{dU_m}$ and $\mathrm{dL_m}$ will not become zeros. In Eqs(2) and (3), the *if* function was used to control the range of the predicted values and prevent it from exceeding the value of 1. In addition, the lowest value is fixed at 0.001 to prevent the desirability from resulting to a value of zero.

3. Case Study: ternary-blended geopolymer from rice hull ash, red mud, diatomaceous earth for refractory material

A sodium silicate-activated geopolymer using red mud (RM), rice husk ash (RHA) and diatomaceous earth (DE) as raw materials for alumina-silicates is presented as an illustrative example. The said geopolymer is considered to act as a replacement for refractory service building material. The objective then is to find an optimal mix formulation of these raw materials with the desired properties for this specific industrial application. Specific attributes were selected based on common engineering properties required in the industry including the sustainability aspect as shown in Figure 1. This is an example of an AHP decision structure that decomposes the overall desirability of the geopolymer product to mechanical properties, thermal properties, and sustainability attributes. The Mechanical Properties to be considered are: Compressive Strength, Volumetric Weight and Water Absorption; while Thermal Properties considered are: Thermal Conductivity, Volumetric Shrinkage and Coefficient of Thermal Expansion. On the other hand, the Sustainability Criteria are Embodied Energy, CO_2 emissions and Cost.

Five respondents representing experts from the academe and industry were elicited for value judgment to derive weights in terms of the relative importance of the nine attributes to the overall desirability of the product. Table 1 summarizes the results from the eigenvector computation of the weights. AHP results show high preference on compressive strength (0.609), thermal conductivity (0.470) and cost (0.748) for each category (level 2) of desirability attribute. Thermal property is considered as top priority for the main attributes resulting in a weight value of 0.740 of the overall.

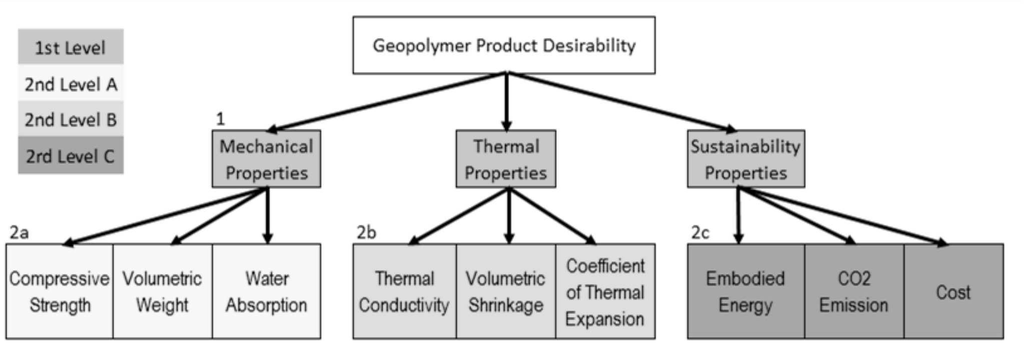

Figure 1: Hierarchical structure for the geopolymer product desirability

Table 1: Priority weights of attributes for the geopolymer-based refractory material

Level 1	Level 2	weight (w_j)
Mechanical Properties (0.164)	Compressive Strength (0.609)	0.100
	Volumetric Weight (0.278)	0.046
	Water Absorption (0.113)	0.019
Thermal Properties (0.740)	Thermal conductivity (0.470)	0.348
	Volumetric Shrinkage (0.213)	0.158
	Coefficient of thermal expansion (0.317)	0.234
	Embodied Energy (0.183)	0.017
Sustainability Criteria (0.096)	CO_2 Emissions (0.069)	0.007
	Cost (0.748)	0.071

In developing the individual desirability functions, the following predictive models for the nine attributes as a function of the mix proportion of red mud (X_1), rice husk ash (X_2) and diatomaceous earth (X_3) were used as shown in Eqs(11) - (19).

$$\mathrm{Y_1: Compressive\ Strength, MPa} = 5.78X_1 + 13.52X_2 + 7.13X_3 + 98.76X_1X_2X_3 \quad (11)$$

$$\mathrm{Y_2: Volumetric\ weight, kg/m^3} = 1{,}710.80X_1 + 1150.80X_2 + 1{,}316.80X_3 \quad (12)$$

$$\mathrm{Y_3: Water\ absorption}, \frac{\mathrm{kg}}{\mathrm{m^3}} = 347.76X_1 + 309.07X_2 + 389.22X_3 - 561.84X_1X_2X_3 - 530.53X_2X_3 \quad (13)$$

$$\mathrm{Y_4: Thermal\ Conductivity}, \frac{\mathrm{W}}{\mathrm{m{-}K}} = 0.811X_1 + 0.345X_2 + 0.466X_3 - 0.931X_1X_2 - 1.065X_2X_3 \quad (14)$$

$$\mathrm{Y_5: Volumetric\ Shrinkage, \%} = 7.53X_1 + 0.49X_2 + 22.75X_3 + 24.17X_1X_2 + 57.24X_1X_3 - 27.47X_2X_3 \quad (15)$$

$$\mathrm{Y_6: Coefficient\ of\ Thermal\ Expansion,}\ \alpha\ \left(\frac{1}{\mathrm{K}}\right) = 9.62\ \mathrm{x}10^{-6}X_1 + 1.17\ \mathrm{x}10^{-5}X_2 + 6.42\ \mathrm{x}10^{-6}X_2 - 1.22\ \mathrm{x}10^{-5}X_2X_3 \quad (16)$$

$$\mathrm{Y_7: Embodied\ energy}, \frac{\mathrm{MJ}}{\mathrm{kg}} = 0.29\ X_1 + 0.29X_2 + 0.527X_3 + 1.98 \quad (17)$$

$$\mathrm{Y_8:\ CO_2\ emissions}, \frac{\mathrm{CO_2}}{\mathrm{kg\ product}} = 6.32\ \mathrm{x}10^{-4}\ X_1 + 1.15\ \mathrm{x}10^{-3}X_2 + 6.3\ \mathrm{x}10^{-4}X_3 + 0.114 \quad (18)$$

$$\mathrm{Y_9: Cost}, \frac{\$}{\mathrm{kg}} = 0.0229\ X_1 + 0.0975\ X_2 + 0.829\ X_3 + 0.06 \quad (19)$$

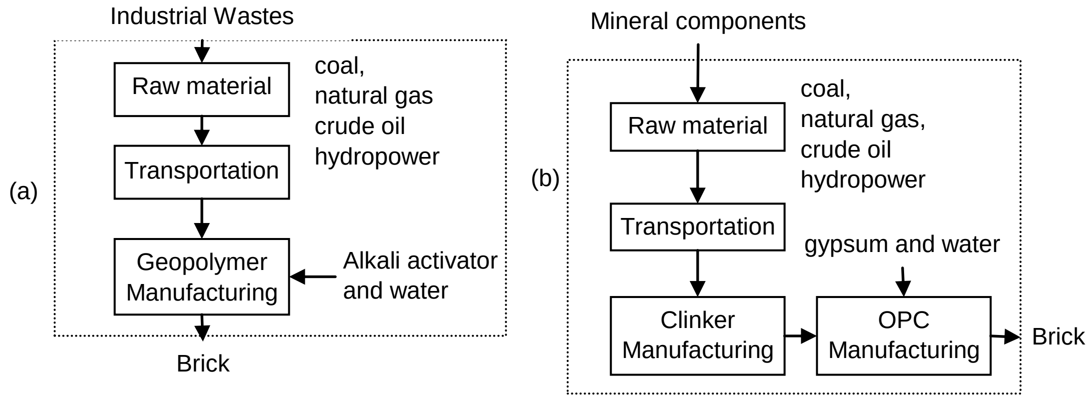

Figure 2: System boundary assumptions for (a) geopolymer and (b) OPC brick case study

The attributes for mechanical and thermal properties were obtained from response surface analysis of the experimental data of a statistical mixture design reported in Nguyen et al. (2014). On the other hand, the embodied energy and CO_2 emissions models are generated through analysis of ternary blend geopolymer processing conditions. System boundary for consideration is shown in Figure 2.

Embodied energy calculations for geopolymer include transportation for raw material, excluding CO_2 generation from burning waste material. This is based on the assumption that production of GHG is done for power generation purposes which is outside the scope of the analysis. Alkaline activator considered is sodium silicate as per data source consideration (Nguyen et al, 2014). Variability in costs for activator used is excluded as it may vary depending on the source location of the chemical. This is in consideration that the expected drastic increase in energy consumption is attributed to transportation. Location dependency in the assessment of sustainability properties allow for upper limit assumptions accounts for variability. The same assumptions apply for source material for OPC brick production to ensure that there is a good comparison between two materials.

Table 2 shows the summary of optimization parameters in computing the desirability function for the nine attributes. Only the compressive strength is considered the larger-the-better type of attribute as indicated by a UF_j of 1.0 whereas the rest such as cost are smaller-the-better type of attribute as indicated by LF_j of 1.0. Thus, compressive strength will be maximized whereas the rest of the attributes will be minimized. As shown in Table 3, some of the technical specifications were based from a typical lightweight heat-resistant and insulating material specification according to ASTM standards. These specifications were used as either the lower or upper limit in computing the individual desirability (see Eqs. 2 and 3) depending on whether the attribute is maximized or minimized. The other set limits for mechanical and thermal properties were then based on the experimental values of mix design obtained in Nguyen et al., 2014. For example, the lower limit of the 28-day compressive strength was set to 11.70 MPa according to ASTM specification (ASTM Standards, 2013). It means a geopolymer product with a compressive strength lower than this value will have an individual desirability value of zero. On the other hand, the upper limit in Eq(2) was set to 14.30 MPa as this will be the lowest reasonable value for the compressive strength of a geopolymer product from a ternary blend of red mud, rice hull ash and diatomaceous earth (Nguyen et al., 2014). In other words, a compressive strength of equal or more than 14.30 MPa will yield a desirability value of one. Thus, values in between the lower and upper limit of the set properties will give a desirability value between zero and one associated with that property.

Embodied energy upper limit is based on OPC embodied energy estimate at 7.8 MJ/kg OPC (Ramezanianpour, 2013), while the lower limit is based on the lowest expected embodied from the projection model in Eq(7) (2.78 MJ/kg). For CO_2 emissions, 70 % of the reference OPC data (0.94 kg CO_2/kg) is the expected maximum CO_2 reduction possible based on projected target by International Energy Agency (2009) whereas the lower limit is the lowest value (0.115 kg CO_2/kg) attributed to the mix design with the projection model in Eq(8). The product manufacturing cost's upper and lower limit is set at 0.158 and 0.082 USD/kg, based on the highest and lowest possible value from the cost model in Eq(19).

Table 2: Optimization parameters for desirability function

Attribute	U_j	UF_j	L_j	LF_j

Y_1:Compressive Strength (MPa)	14.30	1	11.70	0
Y_2:Volumetric Weight (kg/m^3)	1,680	0	1,104	1
Y_3:Water Absorption (kg/m^3)	288	0	165	1
Y_4:Thermal Conductivity (W/m-K)	0.43	0	0.33	1
Y_5:Volumetric Shrinkage (%)	10	0	0.84	1
Y_6:Coefficient of Thermal Expansion, α x10^6 (1/K)[a]	12.42	0	5.71	1
Y_7:Embodied Energy (MJ / kg)	7.80	0	2.78	1
Y_8:GHG Emissions (kg CO_2 /kg product)	0.94	0	0.115	1
Y_9:Cost (USD/kg)	0.158	0	0.082	1

[a] $\alpha\times10^6 = 12.42$; $\alpha = 12.42 \times 10^{-6}$

Table 3 summarizes the results of the optimization using the desirability function. A geopolymer with mix formulation of 11.56 % RM, 67.20 % RHA and 21.24 % DE obtained the highest overall desirability of 0.621. The desirability calculation was also performed with LINGO 14 and yielded the same results with that of MS Excel 2007.

Table 3: Optimization results for the ternary-blended geopolymer

	Optimal values	Desirability function (D = 0.621)	Desired Specification
Compressive strength (MPa)	12.90	0.461	>11.70 (ASTM C109/C109M)
Volumetric Weight (kg/m^3)	1,251	0.745	<1,680 (ASTM C55-99)
Water Absorption (kg/m^3)	211	0.625	<288 (ASTM C140)
Thermal Conductivity (W/m-K)	0.33	1.000	< 0.43 (ASTM C332)
Volume Shrinkage (%)	5.39	0.503	< 10 (ASTM C210-95)
Coefficient of Thermal Expansion, $\alpha\times10^6$ (1/K)[a]	8.63	0.564	<12.42
Embodied Energy (MJ/kg product)	2.33	1.000	<7.80
CO_2 Emissions (kg CO_2/kg product)	0.115	1.000	<0.94
Cost ($/kg product)	0.146	0.155	<0.158

[a] $\alpha\times10^6 = 8.63$; $\alpha = 8.63 \times 10^{-6}$

4. Conclusion

The proposed methodology using multiple objective optimization with desirability function and AHP allows us to find an optimal mix formulation of raw materials to produce a geopolymer product with desired specifications. The method not only accounts for ASTM materials specifications but also considers attributes relevant to product preference. This has been illustrated in the refractory material application of a ternary-blended geopolymer from red mud (RM), rice hull ash (RHA) and diatomaceous earth (DE). Based on the desirability function in terms of thermal, mechanical and sustainability properties, the desired properties were obtained with an optimal mix formulation of 11.56 % red mud, 67.20 % rice hull ash and 21.24 % diatomaceous earth. Predicted values from the model of each attribute are: compressive strength, 12.90 (MPa); volumetric weight, 1,251 (kg/m^3); water absorption, 211 (kg/m^3); thermal conductivity, 0.33 (W/m-K); volume shrinkage, 5.39 (%); coefficient of thermal expansion, 8.63×10^{-6} (1/K); embodied energy, 2.33 MJ/kg; CO_2 emissions 0.115 kg CO_2/kg; and cost 0.146 $/kg. Future studies will extend this work to other geopolymer binder system and include qualitative aspects that are relevant to product design.

Acknowledgements:

We are grateful for the financial support of the Philippine Commission on Higher Education (CHED) via the PHERNet Sustainability Studies Program.

Nomenclature

i	Geopolymer mix components
j	Geopolymer product attributes
X_i	Mass fraction of component i in the mix of raw materials
w_j	Importance of weight of attribute
m	Total number of attribute

n	Total number of components
D	Overall desirability of geopolymer product
Y_j	Attribute value for the given mix of X_i
L_j	Lower limit of the attribute value
U_j	Upper limit of the attribute value m_D

References

ASTM C210-95, 2014, Standard Test Method for Reheat Change of Insulating Firebrick, ASTM International, West Conshohocken, PA, <www.astm.org/Standards/C210.htm>, DOI: 10.1520/ C0210-95R14, accessed 25.02.2015.

ASTM Standards, 2013, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens). 904.04.01 - Volume 04.01 - Cement; Lime; Gypsum. ASTM International, West Conshohocken, PA,<www.astm.org/Standards/C109>, DOI: 10.1520/C0109_ C0109M-02. accessed 25.02.2015.

ASTM C140-12, 2013, Standard Test Methods for Sampling and Testing Concrete Masonry Units and Related Units , ASTM International, West Conshohocken, PA, <www.astm.org/DATABASE.CART /HISTORICAL/C140-12.htm> DOI: 10.1520/C0140-12. accessed 25.02.2015.

ASTM C55-99, 2001,Standard Specification for Concrete Brick, ASTM International, West Conshohocken, PA, <www.astm.org/DATABASE.CART/HISTORICAL/C55-99.htm> DOI: 10.1520/C0055-14A. accessed 25.02.2015.

ASTM C332-09, 2010, Standard Specification for Lightweight Aggregates for Insulating Concrete., ASTM International, West Conshohocken, PA, <www.astm.org/Standards/C332.htm>, DOI 10.1520/C0332-09. accessed 25.02.2015.

Bernasconi M., Choirat C., Seri R., 2014, Empirical properties of group preference aggregation methods employed in AHP: Theory and evidence. European Journal of Operational Research, 232, 584-592.

Davidovitz J., 1989, Geopolymers and geopolymeric materials, Journal of Thermal Analysis, 35(2), 429-441.

Derringer G., Suich R.,1980. Simultaneous optimization of several response variable. Journal of Quality Technology, 12, 214–219.

International Energy Agency, 2009, Cement Technology Roadmap 2009: carbon emissions reductions up to 2050 <www.iea.org/publications/freepublications/publication/Cement.pdf>, accessed 25.02.2014

Miccio F., Medri V., Papa E., Natali Murri A., Landi E., 2014, Geopolymerization as effective measure for reducing risks during coal ashes handling, storage and disposal, Chemical Engineering Transactions, 36, 133-138.

Nguyen H.T., Do Q.M., Hinode H., Gallardo S.M., Bacani F.T., Promentilla M.A.B., 2014, Development of geopolymer-based materials from a ternary blend of red mud, rice husk ash and diatomaceous earth using the statistical mixture design modelling, Journal of Philippine Institute of Chemical Engineers (PIChE), 15(2), 33-45.

Provis J.L., van Deventer J., 2014, Conclusions and Future of Alkali Activated Technology. Alkali Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM Alkali Activated Materials, RILEM State-of-the-art-reports, New York, US, 384-387.

Ramezanianpour A.A., 2013, Cement Replacement Materials: Properties, Durability and Sustainability., Geochemistry Mineralogy, 328, Springer Geochemistry/Mineralogy, London, UK.

Saaty T.L., 1979, Application of analytical hierarchies, Mathematics and Computers in Simulation, 21(1), 1-20.

Sung Ryua G., Bok Leeb Y., Taek Koha K., Soo Chungb Y., 2013, The mechanical properties of fly ash-based geopolymer concrete with alkaline activators. Construction and Building Materials, 47, 409–418. DOI:10.1016/j.conbuildmat2013.05.069.

Weil M., Buchwald A., Dombrowski K., 2005, Development of geopolymers supported by system analysis. Proceedings of the 2nd International Symposium of Non-traditional Cement and Concrete, ed. by Bilek and Kreshner. <www.uni-weimar.de/projekte/geton/Downloads/BrnoMW.pdf>, accessed 25.02.2015.