Application of Organic Additives as Pore Forming Agents for Geopolymer Composites

Suresh K. Kaliappan, Ahmer A. Siyal, Zakaria Man, Mark Lay, Rashid Shamsuddin

Abstract: Geopolymer is a relatively new type of material derivable from aluminosilicate precursors such as fly-ash, clays and mining slags is often regarded as a green material. The structure of geopolymer consists of a negatively charged aluminosilicate network where the charge balancing cations (Na^+, K^+, or Ca^{2+}) can be exchanged from solution, therefore offers adjustable properties. Due to its porosity, geopolymer is a good adsorbent material. The porosity can be enhanced using pore forming agents, however research in this field remains limited. This work investigated the potential of corn oil, waste cooking oil (palm) and starch as organic pore forming agents (POF) for fly-ash geopolymers to create pores of various size ranges in the matrices. Highlights of results include pristine geopolymer had a compressive strength of 30.93 MPa, corn oil as PFA induced the highest porosity of 26.6% with compressive strength of 9.9 MPa, followed by palm oil at 21.3 % and 9.0 MPa and starch at 17.9 % and 20.41 MPa. The pores were combination of voids and tunnels in the composites as confirmed by SEM.

Keywords: Geopolymer, aluminosilicate, fly-as, ($Na+$, $K+$, or $Ca2+$).

I. INTRODUCTION

A few years ago, World Board of Commerce for Sustainable Development's (WBCSD) in its initiative into greening the concrete industry, included the use of geopolymer binders in its strategy for reducing greenhouse and volatile gas emissions associated with cement production [1].A new growing interest on recycling these secondary inputs have made the production of geopolymer material more popular than ever. Geopolymer as the term coined by Davidovits in 1978, is an ecologically natural material that is synthesized in both cost effective and safe manner possesses superior mechanical properties.Depending on the raw material selection and processing conditions, geopolymers can exhibit a wide variety of properties including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity [2].

Suresh K. Kaliappan, Chemical Engineering Department, UniversitiTeknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia

Ahmer A. Siyal, Chemical Engineering Department, UniversitiTeknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia.

Zakaria Man, Chemical Engineering Department, UniversitiTeknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia.

Mark Lay, School of Engineering, Faculty of Science and Engineering, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand

Rashid Shamsuddin, Chemical Engineering Department, UniversitiTeknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia. Center for Biofuel and Biochemical Research (CBBR), Institute for Sustainable Living, UniversitiTeknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia. mrashids@utp.edu.my

Despite the potential application of geopolymer adsorbents as membrane, the porosity of the material must be tailored to enable removing contaminants of various sizes and physical states.

Current application of geopolymer as water filtration membrane is limited due to its rigid pore openings [3]. Therefore, there is a need to find a reliable technique to synthesize geopolymer at specific pore size ranges to remove contaminants in water filtration. One potential approach is to introduce organic additives during geopolymerization to induce pores formation. Because the pore alteration will influence the mechanical properties, the compressive strength was determined to serve as a baseline value to ensure its suitability for industrial applicationsthat involves high flowrate and high driving force. In this project, three organic additives of corn oil, waste cooking oil from palm oil (WCO) and starch were studied as pore inducing agents to improve porous characteristics of geopolymer in relation to the change of the composites' mechanical properties.

II. LITERATURE REVIEW

Geopolymerization

Inorganic polymer concrete or geopolymer is an eco-friendly material that is formed by alkali activation of aluminosilicate materials. Potential precursors include industrial waste materials such as fly ash and slags with the aid of an alkali activator of sodium hydroxide. During geopolymerization, the Si and Al species of the aluminosilicate materials go through condensation, nucleation, oligomerization and polymerization giving an amorphous three-dimensional network. The Si/Al ratio alters the three-dimensional network of the composite and therefore changing the mechanical strength and porosity of the geopolymer[4].

Pore Forming Method Using Foaming Agents

To produce geopolymer materials for adsorption or membranes application, addition of pore forming agents (PFA) are commonly appliedto induce gas formation during geopolymerization reaction. The release of gas will create voids and tunnel during curing process of geopolymer. Pore forming agents such as aluminium, graphite and silica fume have been widely used previously[5]. These additives

however could be unsuitable for geopolymer intended as water purifier due to toxicity. Suitable additives should be harmless to human, effective, abundant and low cost.

The idea of "complementing" adsorption should also be prioritized where the additives used could be beneficial for the intended end applications of the geopolymer composites. For example, naturally abundant and low cost bentonite was utilized to remove dissolved protein from meat rendering plant stickwater, was successfully used as a filler material in bioplastics, eliminating the need to regenerate the adsorbent[6].

Base solutions as alkaline activators

In the production of a geopolymer, alkaline activator plays a very important role in the geopolymerization process. The alkaline activation on fly ash which is the reactant material that contains the Si and Al bonds or aluminosilicate bond will break and thus release Al and Si ion species. These ions will further react to form a different structure beginning with formation of nuclei and aluminosilicate oligomers consisting of a tetrahedral structure of both the elements. According to [7], the alkaline activators play a part where the negative charge in the aluminosilicate chain is balanced by the alkali cations, in most cases potassium cation as KOH is widely used as the alkaline activator. Different alkaline activators contribute different cations in the reaction thus, it will influence the geopolymerizationstructure at the end as different cations have different charge density and different sizes[8].

Summary on previous research works on geopolymers

In summary, the main methods of producing of porous geopolymer were by using a pore forming agent and direct fuming. In terms of foaming agent, aluminum was most preferred as it gives high overall porosity of above 50 % compared to hydrogen peroxide and other gas forming additives. Studies involving limestone based foaming agents also proved to be performing well as PFA as resulting in high total porosity at maximum, 70% and low thermal conductivity. Inorganic additives somehow would harm the environment in the end if not managed properly whereas for application in waste water treatment system for instance, a safe organic pore forming agent is always preferable. Despite this, there also has been a lack of attention given in studying organic additives such as corn oil and vegetable oils as compared to inorganic and metallic foaming agents. Following that, freeze casting, which is also a good pore forming technique but is less investigated probably because proper operational condition and a specific equipment is required to control the ice growth for pore formation. Almost all previous studies suggested that by increasing the drying period and increasing curing temperature, the pore formation was improved.

Application of geopolymer materials.

As geopolymer is getting attention in terms of its green production method, its utilization in the industry is also encouraged. Fly ash based geopolymer concrete for instance, has paved way to decreased CO_2 emission. Fly-ash geopolymer is known as a good binder that can be mixed with aggregates to produce geopolymer cement in construction industry[9].Apart from that, geopolymer is also extensively studied for use as adsorbent material in wastewater treatment. Geopolymerization produces a three-dimensional structure of fly ash matrix that will bind hazardous materials such as Co, Cr, Cu, and Nb[10].

The concept of separation dealing with membrane relies hugely in the characteristic of the pore. Geopolymer technology application widely depend on the mechanical properties such as compressive strength, flexural strength and on the chemical composition as it leads to a more cost effective and innovative application. Despite existence of strong economic and environmental advantages, many potential applications of geopolymer and related composites remain unexplored largely because the research and development community still has a limited understanding of the properties of the material influenced by the gap of technology. With time, this is expected to change and these materials can then be expected to find innovative applications within various field.

III. METHODOLOGY

Materials

Fly ash was obtained from a local coal-fired power plant inManjung, Perak. Food-grade starch powder, corn oil and waste cooking oil (palm) were used as pore forming agents. Research-grade sodium hydroxide (NaOH)was purchased from Merck used as the alkaline activator.

Preparation of Pore Forming Agents

Thecorn oil and waste cooking oil were used as supplied while a 1M starch solution was prepared by mixing starch with tap water. NaOH solution at 8M concentration, fly ash, and PFA were added into pre-weighed water in a beakerat a ratio of 30 parts fly ash, 12.5 parts NaOH and 1 part PFA by weight at the concentrations of PFA listed in Table 1.

Table. 1 PFA dosages in geopolymer samples (wt.%)

PFA	Corn Oil	Waste Cooking Oil (Palm)	Starch Solution
Dosage 1	4	4	4
Dosage 2	8	8	8
Dosage 3	12	12	12

Synthesis of Fly Ash Based Geopolymer

The prepared fly ash was mixed with alkaline activator in the ratio of 3:1 respectively. The mixture was stirred until visibly homogeneous. Then, PFA was added into mixture and stirred for 2 minutes to form a paste.The geopolymer paste was then poured into an iron cast of 5cm x 5cm x 5cm dimension and cured in an oven for 24 hours at 60ºC. The samples were stored in a desiccator prior for analysis.

Characterization of Geopolymer Composites

The resulting geopolymer composites were characterized for porosity, mechanical properties, morphology and surface area and pore size according to methods reported below.

i)   Porosity Test

Bulk density of the geopolymer was determined using the Archimedes' principle by immersing a pre-weighed sample into a known volume of water. The displacement of water volume was recorded and divided from the sample weight to obtain the bulk density in kg/m^3. Powder density was measured using Powder Density Tester AU-300P. Equation 1 was used to calculate the percentage of porosity in the sample[11].

$$Porosity\ \% = \frac{Bulk\ density\ - Powder\ density}{Bulk\ density} \times 100 \quad (1)$$

ii)   Compressive Strength Test

Compression test was carried out using an ADR-Auto compression machine operating at 3000 kN load and compression rate of 0.9 s/m. The analysis was done in triplicate[12].

iii)   Scanning Electron Microscopy (SEM) Analysis

The morphology of the crushed specimens after the compression test were examined using SEM by following the standard SEM procedure for composite materials [13].

iv)   Brunauer–Emmett–Teller (BET) Surface Area Analysis

The surface areas of geopolymer samples were determined by nitrogen adsorption using an ASAP Plus 2020 BET analyzer. Powder samples were degassed under vacuum at 80°C for 2 hours and nitrogen adsorption was measured across 35 points of relative pressure (P/P_o) for 6 hours. The mean surface area was determined using the Multi-Point BET method.

IV.   RESULTS AND DISCUSSION

Results for bulk and powder density and porosity are summarized in Table 2. Corn oil as PFA at 12 wt.% loading resulted in the highest porosity at 26.6 % with the lowest bulk and powder density. Waste cooking oil, showed high porosity percentage of about 21.3 % followed by starch at 17.9 %, compared to 4.49 % porosity of the control sample (geopolymer without PFA). Highly porous materials generally resulted in lower density due to higher presence of voids except for geopolymer with 12 wt.% WCO. The high density values could reflect human error that needs further investigation.

Density and Porosity

Table. 2 PFA dosages in geopolymer samples (wt.%)

Sample	Bulk density (kg/m^3)	Powder density (kg/m^3)	Porosity (%)
Control	2304	2795	4.49
12 wt. % Corn Oil	1139	1442	26.6
12 wt. % WCO	1292	1350	21.3
2.5 wt. % Starch	1450	1710	17.9

Compressive Strength

The average compressive strength for the control sample was 30.93 MPa, which is generally higher compared to geopolymers with PFA. The compressive strength of PFA-geopolymers is inversely proportional to the loading dosage where samples with 1 wt.% loading gave higher strength than at 12 wt.%. Geopolymer with PFAs recorded the highest compressive strength at 1 wt.% loading, corresponding to 29.7 MPa for starch followed by 27.6 MPa for waste palm oil and 26.7 MPa for corn oil. Addition of corn oil and waste palm oil at the highest dosage of 12 wt.% reflected a drop of about 70 % strength value compared to the control sample. SEM analysis revealed that samples with higher PFA dosages had higher particle dispersion and void formation and hence, the mechanical strength of the sample was compromised compared to less porous samples at lower PFA dosages.

Starch solution at dosages of more than 4 wt.% failed to form geopolymers because the resulting slurry become very viscous and dried off during mixing. The condition might be a result of starch hydrolysis during geopolymerization that consumed more water from the starch slurry than normally. In the presence of alkaline activator, further stirring caused the equilibrium to be reached faster and the mixture was gelled into a network of starch and fly ash. This behaviour is termed as anti-trixotropy or time dependent viscosity where further stirring causes an increase in viscosity or even solidification. This trend was absent in the other two PFAs as they are oil-based and hydrophobic. Graphical results for starch at dosages above 4 wt.% were therefore absent in Fig. 1.
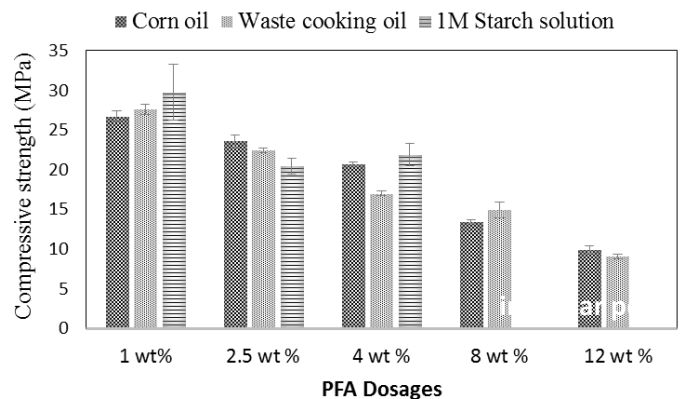

**Fig. 1 Compressive strength comparison of control and PFA-added geopolymers.**

Scanning Electron Microscopy Analysis (SEM)

From Fig. 2 and Fig. 3, the presence of irregular pores can easily be seen in both samples resulting from gases released during the geopolymerization reaction. Clumps of fly ash on the surface (Fig. 2a) signify incomplete reaction between the raw materials and the alkaline activator either due to incomplete mixing or excess of fly ash for the amount of NaOH used. From Fig. 2b, the surface of geopolymer with

12 wt.%corn oil seems to be loosely packed with oil residue visible compared to the control sample. This is attributed to the corn oil being immiscible with the mixture. Pore formation and excess of oil weakened the samples,

explaining the sizeable difference in the compressive strength between the PFA-geopolymer and the control. SEM analysis for the rest of samples showed similar trends of highly porous geopolymers with higher dosages of PFAs. All morphological features are more visible under higher magnification as depicted in Fig. 3.
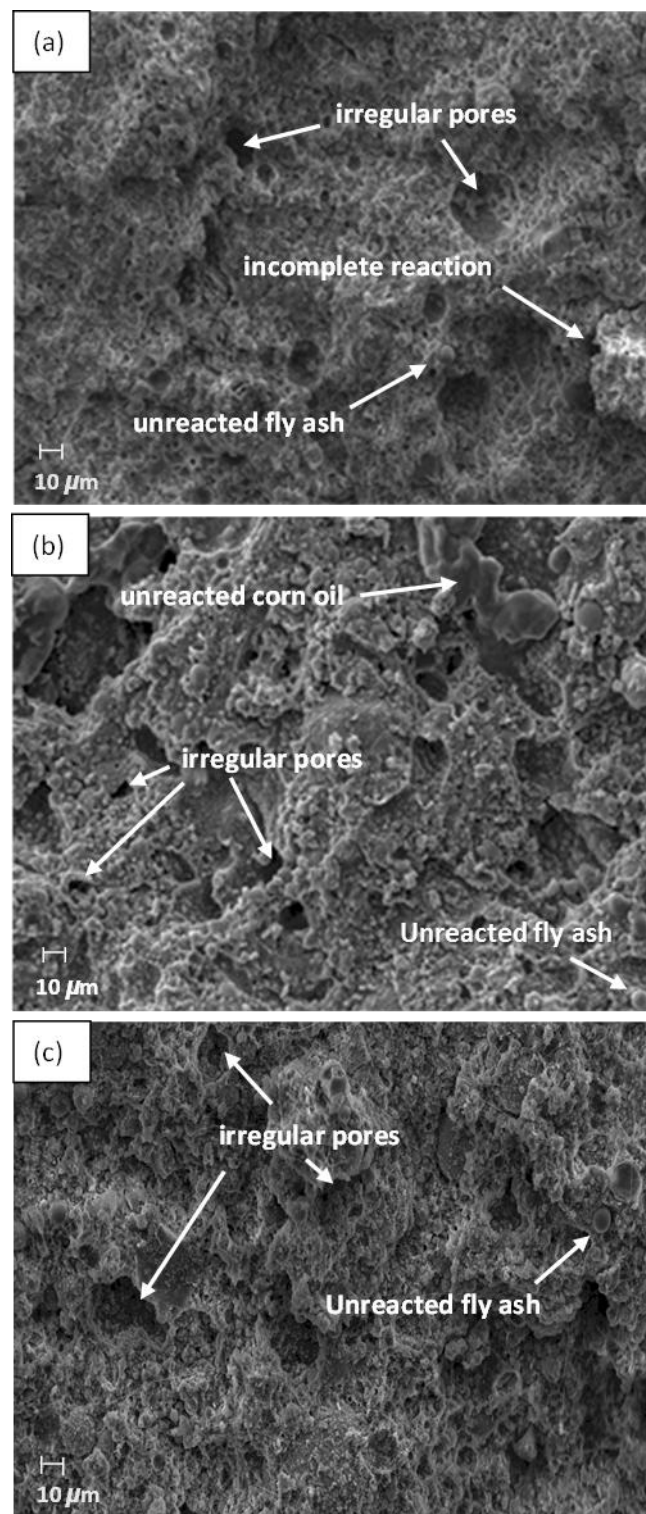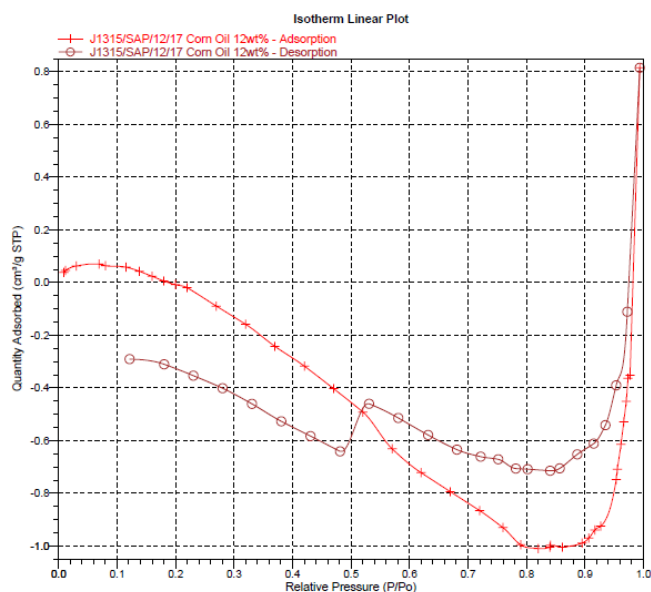

Fig. 2 SEM imagesof geopolymer samples at 300X for a) control sample, b) with 12 wt.% corn oil and c) with 12 wt.% WCO.
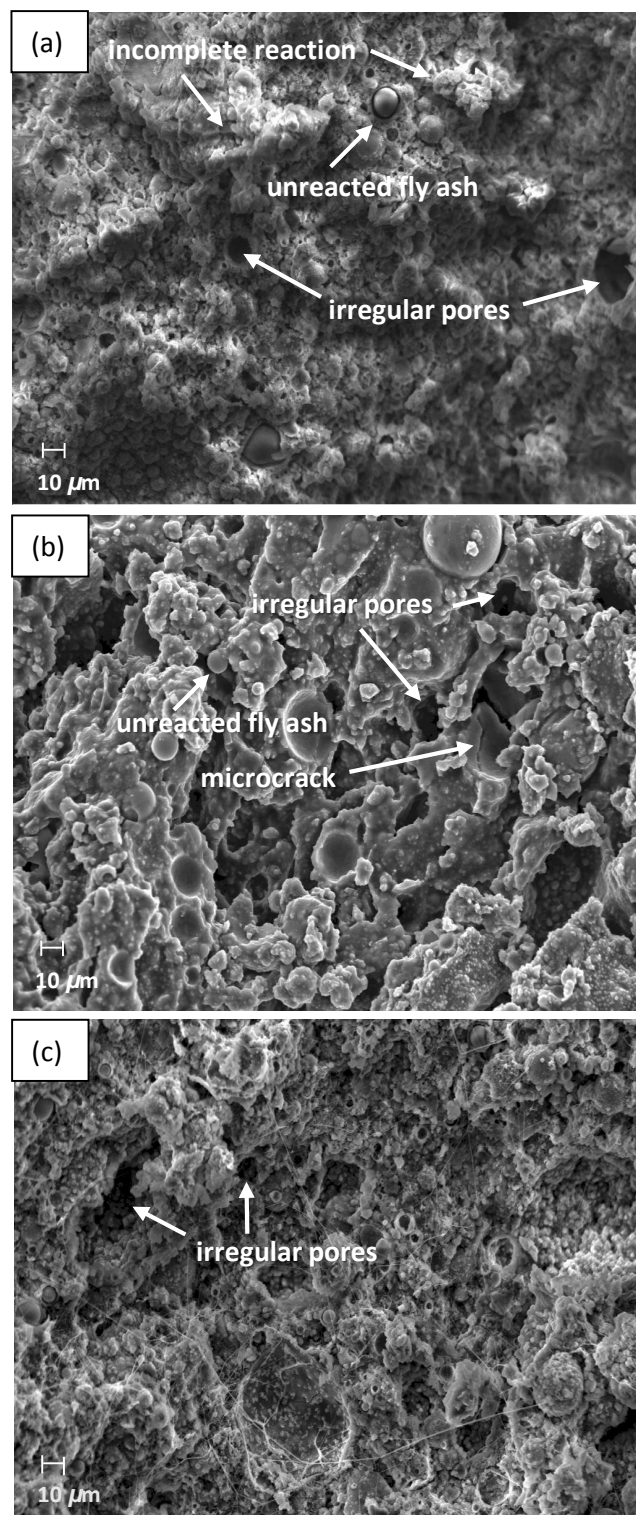
Fig. 3 SEM imagesof geopolymer samples at 500X for a) control sample, b) with 12 wt.% corn oil andc) with 12 wt.% WCO.

BET Surface Area Analysis

Fig. 4 BET isotherm plot for geopolymer sample with 12 wt.% corn oil.

The surface area of the control geopolymer wasbetween 50 to 60 m^2/g. BET analysis on geopolymer with 12 wt.% corn oilyielded an unusual isotherm with negative adsorption up to relative pressures of 0.8 (Fig. 4), and an unexpectedly low surface area of 0.0307 m^2/g. This was despite a high volume of pores recorded from the density test and SEM. It is possible the oil was volatilising during the BET test resulting in the poor result. The corn oil probably contained a large number of fatty acids and odour compounds that would volatilise while under vacuum. Therefore, BET would need to be repeated with the samples degassing for longer and at higher temperatures for example at smoke point of corn oil at 270°C and above.

V. CONCLUSION AND FUTURE WORKS

This work has revealed the inverse relationship of geopolymers porosity and compressive strength. The highest porosity at 26.6% was achieved with the highest PFA addition of 12 wt.%of corn oil, which corresponds to the lowest compressive strength of 9.9 MPa. This strength value is considered high for a material with such high percentage of porosity. This finding is consistent with other PFAs used at different dosages. SEM analysis confirmed the initial hypothesis of void and tunnel formation behind the composites porosity. However, the sizes of the pores were not consistent for all PFA loadings. From BET analysis, nitrogen gas was prohibited access to the binding sites on geopolymer surface due to the presence of residual oil, therefore degassing the samples at higher temperature for longer should be investigated.

Though there has been a progressive effort in fly ash application as a precursor material for geopolymer,there are vast areas of geopolymer remain unexplored. Chief amongst all is to establish a standard geopolymer formulation agreeable by the leading scientists. That way any improvement work can be seen as a concerted effort towards a common development in this field. Secondly, other PFAs should be explored emphasizing on the effectiveness for the

immediate goals to enhance porosity as well as the being advantageous for the final intended use of the products. Lastly, trials on water treatment to remove contaminants should be conducted as a verification step.

VI. ACKNOWLEDGMENT

REFERENCES

1. Esther Obonyo , E.K., Uphie C. Melo and Cristina Leonelli Advancing the Use of Secondary Inputs in Geopolymer Binders for Sustainable Cementitious Composites: A Review. Sustainability, 2011. 3(2): p. 410-423.
2. Tang, Q., et al., Study on synthesis and characterization of ZSM-20 zeolites from metakaolin-based geopolymers. Applied Clay Science, 2016. 129: p. 102-107.
3. Helmut Foll, J.C., and Stefan Frey, Porous and Nanoporous Semiconductors and Emerging Applications. Journal of Nanomaterials, 2006. Volume 2006: p. Pages 1–10.
4. Badanoiu, A.I., et al., Preparation and characterization of foamed geopolymers from waste glass and red mud. Construction and Building Materials, 2015. 84: p. 284-293.
5. Obradović, N., et al., Formation of Porous Wollastonite-based Ceramics after Sintering With Yeast as the Pore-forming Agent. Vol. 49. 2017. 235-246.
6. Shamsuddin, R.M., C.J.R. Verbeek, and M.C. Lay, Settling of Bentonite Particles in Gelatin Solutions for Stickwater Treatment. Procedia Engineering, 2016. 148: p. 194-200.
7. Böke, N., et al., New synthesis method for the production of coal fly ash-based foamed geopolymers. Construction and Building Materials, 2015. 75: p. 189-199.
8. Zhang, J., et al., Synthesis of a self-supporting faujasite zeolite membrane using geopolymer gel for separation of alcohol/water mixture. Materials Letters, 2014. 116: p. 167-170.
9. Alsafi, S., et al., Collapsibility potential of gypseous soil stabilized with fly ash geopolymer; characterization and assessment. Construction and Building Materials, 2017. 137: p. 390-409.
10. Zhuang, X.Y., et al., Fly ash-based geopolymer: clean production, properties and applications. Journal of Cleaner Production, 2016. 125: p. 253-267.
11. Bai, C. and P. Colombo, High-porosity geopolymer membrane supports by peroxide route with the addition of egg white as surfactant. Ceramics International, 2017. 43(2): p. 2267-2273.
12. Rashid, K. and R. Waqas, Compressive strength evaluation by non-destructive techniques: An automated approach in construction industry. Journal of Building Engineering, 2017. 12: p. 147-154.
13. Krause, F.F., et al., Atomic resolution elemental mapping using energy-filtered imaging scanning transmission electron microscopy with chromatic aberration correction. Ultramicroscopy, 2017. 181: p. 173-177.