Araştırma Makalesi / Research Article

Development of Efflorescence Control Methods of Fly Ash Based Foam Geopolymers

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Abstract

Since the environmental impacts of carbon emissions due to the cement production have started to be discussed, an alternative material has been sought. Geopolymers are new generation materials that are good candidates to be used instead of cement in the structures. Within the scope of geopolymer technology, the reuse of industrial by-products such as fly ash and blast furnace slag enable reuse of both the reduction of waste stock and the production of new generation material which excites the scientific world. However, various problems that have been focused on preventing the advancement of this technology. Efflorescence is a critical problem for the development of geopolymer technology. White residues formed on the surfaces of the materials produced from geopolymer wetting are referred to as efflorescence. Although it may seem like a visual problem in the initial stage, it may cause structural problems in later stages. Therefore, it is an issue that needs to be addressed. In this study, studies were made to prevent or minimize this problem. Efflorescence behavior of geopolymer foam samples prepared in different molarities and cured at different temperatures were investigated. It was determined that the samples prepared at high molarities and the samples cured at lower temperatures are more prone to the problem of efflorescence.

Uçucu Kül Tabanlı Jeopolimerlerin Çiçeklenme Kontrol Yöntemlerinin Geliştirilmesi

Anahtar Kelimeler:
Çiçeklenme; Uçucu Kül; Jeopolimer; Hidrojen Peroksit

Öz

Çimento üretiminden kaynaklanan karbon emisyonlarının çevresel etkileri tartışılmaya başlandığından beri, çimentoya alternatif bir malzeme aranmaktadır. Jeopolimerler, binada çimento yerine kullanılmaya uygun yeni nesil malzemelerdir. Jeopolimer teknolojisi kapsamında, uçucu kül ve yüksek fırın cürufu gibi atık malzemelerin yeniden kullanılması, hem atık stokunun azaltılmasını hem de bilim dünyasını heyecanlandıran yeni nesil malzemenin üretimini sağlamaktadır. Fakat çeşitli sorunlar bu teknolojinin ilerlemesini engellemektedir. Çiçeklenme jeopolimer teknolojisinin geliştirilmesinin önünde önemli bir problemdir. Jeopolimerlerin ıslanması sonucu yüzeyleri üzerinde oluşan beyaz kalıntılara çiçeklenme denir. İlk aşamada yalnızca görsel bir sorun gibi görünse de, sonraki aşamalarda yapısal sorunlara neden olabilir. Bu nedenle, ele alınması gereken bir konudur. Bu çalışmada, bu sorunu önlemek veya en aza indirmek için çalışmalar yapılmıştır. Farklı molaritelerde hazırlanan ve farklı sıcaklıklarda kürlenen jeopolimer köpük numunelerin çiçeklenme davranışı incelenmiştir. Yüksek molaritelerde hazırlanan numunelerin ve daha düşük sıcaklıklarda kürlenen numunelerin çiçeklenme problemine daha yatkın olduğu tespit edilmiştir.

1. Introduction

Cement is of great importance in developing technology for housing, which is one of the most basic needs of human beings. It is known that the CO_2 emitted by the cement produced by the heating of limestone and clay mixtures constitutes 8% of the CO_2 emission in the world and this is a very high rate. Davidovits emphasized that one ton of portland cement produced anywhere in the world causes CO_2 emissions between 0.85 and 1 tonnes (Davidovits 2015). In order to limit or completely stop the use of cement, he has synthesized geopolymeric materials and continues to work on the subject. (Davidovits 1994).

Geopolymer is the name given to products obtained by reaction of raw materials containing aluminosilicate in highly alkali medium and produces interconnected –Si–O–Al–O–Si– bonds (Davidovits 2008). Geopolymer term usually used to measure amorphous alkali aluminosilicates. The terms alkali-activated cements, geocements alkali bonded ceramics and hydroceramics have the same meaning as the term geopolymer, also (Thakur et al. 2017). The aluminosilicates can be obtained from natural sources or from industrial byproducts such as fly ash and blast furnace slags (Duxson et al. 2007). The geopolymer reacts at very low temperatures (40-100°C), the fact that waste raw materials do not require any pretreatment and the easy preparation method facilitates the development of this technology (Duxson et al. 2007). These materials may exhibit close properties performance with conventional cementitious binders in various applications and can therefore be nominated as substitutes for cement in many areas. The point where geopolymer is more advantageous than cement is less CO_2 emissions (Damtoft et al. 2008; Van Deventer, Provis, and Duxson 2012; McLellan et al. 2011; Thaarrini and Dhivya 2016).

Geopolymer technology can utilize many by-product materials, such as fly ash, granulated blast furnace slag and mining wastes or they can be produced from thermally activated materials such as metakaolin. Compared to other thermally activated natural raw materials, industrial by-products are both cost-effective and environmentally beneficial, since they have a lower combined energy level and then lower CO_2 emissions (Srinivasan and Sivakumar 2013).

The popular main precursor by-product for geopolymer production is fly ash. Fly ash refers to inorganic, non-combustible material present in coal that is fused to a glassy, amorphous structure during the combustion (Davidovits 2008). Depending upon the source of the burned coal, the fly ash components vary considerably. In general, the fly ash contains SiO_2, Al_2O_3, CaO and Fe_2O_3 components. Fly ashes are divided into two classes as C and F. Class C fly ash has a total SiO_2, Al_2O_3 and Fe_2O_3 content from 50% to 70 % by weight and CaO content more than 20% by weight. Class F fly ash contains low calcium and is obtained by the combustion of anthracite or bituminous coal. Class F fly ash has a total SiO_2, Al_2O_3 and Fe_2O_3 content over 70 % by weight and CaO content less than 10%.

For structural applications of materials, pores are generally what to be eliminated because they act as fracture defects and degrade the structural reliability, and therefore, ceramic engineers tried to sinter ceramics to full density to attain high mechanical strength. On the other hand, there have been various industrial applications where pores are taken advantage of positively, from filtration, absorption, catalysts and catalyst supports to lightweight structural components and thermal insulator. In these decades, a great deal of research efforts have been devoted for tailoring deliberately sizes, amounts, shapes, locations and connectivity of distributed pores, which have brought improved or unique properties and functions of porous materials (Bai & Colombo, 2018). Many studies are carried out for porous geopolymer materials to be used in areas such as insulation applications and filtering applications (Hajimohammadi et al., 2017; Novais et al., 2016, 2019; Ohji & Fukushima, 2012; Strozi Cilla et al., 2014). Although there are many methods in the production of porous geopolymer, the direct foaming method is the most preferred method because it is cheap and easy. Foaming is generally done by adding H_2O_2 (Vaou & Panias, 2010), metallic Al (Zhang et al., 2014), metallic Si (Medri et al., 2013) and sodium perborate to the geopolymer sludge and mechanically mixing. As a result of the decomposition of the additives in the alkaline sludge, bubble is formed and a porous structure is formed.

Most studies of alkali-activated geopolymer mixture have focused on microstructure and mechanical properties (Neupane, Chalmers, and Kidd 2018; Lecomte et al. 2006; Liew et al. 2013; Subaer 2004; Gatti and Prasad 2017; Kaur, Singh, and Kaur 2018). However, there are not many publications on the problems of geopolymers. The lack of research on main problems such as shrinkage, efflorescence and cracking may actually result in some difficulties for practical applications.

Efflorescence is a common problem in concrete structure surfaces. The main cause of white deposits on the surface as a result of efflorescence is the formation of $CaCO_3$ during drying by the reaction of dissolved and diffused Ca^{2+} with CO_2 dissolved in the surface liquid (Dow and Glasser 2003). It is stated that efflorescence mainly results from a combination of three main factors. This problem occurs; in the availability of soluble components in the environment, the existence of water to dissolve the components and the solution with a capillary action to move to the surface when a capillary force is encountered (Allahverdi et al. 2014). In both Portland cement and alkali-activated cements, efflorescence is mainly caused by carbonates. Geopolymer sludge contains little or no Ca, but similar problems have been encountered in the studies conducted on geopolymer (Zhang et al. 2013, 2018). While calcium carbonates cause efflorescence in portland cement, sodium carbonates in geopolymers cause this problem. Skvara et al. discloses that unreacted sodium reacts with CO_2 to cause efflorescence and the resulting compound is sodium carbonate (Škvara, Svoboda, and Dolezal 2008) eqs (1) and (2).

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \qquad (1)$$
$$2Na^+ + CO_3^{2-} + nH_2O \rightarrow Na_2CO_3 \cdot nH_2O \qquad (2)$$
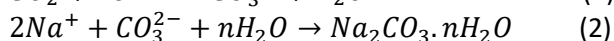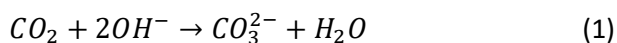
The availability of OH^- and Na^+ is crucial for the deposition of sodium carbonate hydrates; high alkalinity accelerates the reaction of CO_2 with the aqueous environment (Dow and Glasser 2003). Furthermore, the fact that Na cations are able to move faster in the aluminosilicate network than K^+ cations leads to more destructive efflorescence problems due to the increase of unreacted Na ions at high molarities (Allahverdi et al. 2014). This situation is described by Szklorzova et al weak bond of sodium cations to the aluminosilicate network structure (Szklorzová and Bílek 2008).

Although efflorescence is considered to the mainly as an aesthetic flaw, if not controlled, white deposits continue to form affects integrity of the material. In this study, the variables of molarity and temperature were used to analyze the efflorescence problem.

2. Material and Method

Fly ash supplied from Seyitömer Thermal Power Plant (Kütahya/Turkey) was used in this study. Metakaolin powder (MEFISTO L05) was purchased from Czech Republic. Compositional analysis using X-Ray fluorescence (XRF) analysis is presented in Table 1.

Table 1. Chemical content of Fly ash and Metakaolin

	Fly Ash	Metakaolin
SiO_2	50,30	54,10
Al_2O_3	19,10	41,10
CaO	4,55	0,13
Fe_2O_3	12,40	1,10
MgO	4,67	0,18
K_2O	2,16	0,80

NaOH and Na_2SiO_3 (Na_2O = 35.47%, SiO_2 = 64.10%, and water = 45%) were used as an alkaline activator. 6M and 10M alkali solutions were prepared and used without waiting for cooling. Hydrogen peroxide was used as a chemical foaming agent. An equal amount of hydrogen peroxide was used to ensure uniform pore size distribution in all samples. Experimental design of the study is given in Table 2. Firstly, 6M and 10M alkaline solutions was prepared by using water, NaOH pellets and sodium silicate. Subsequently, alkaline solution was added to the mixture of metakaolin and fly ash, which was homogeneously mixed, and stirred for 5 minutes to form a geopolymer mixture. The geopolymer mixture was mixed with hydrogen peroxide for an additional 1 minute to ensure foam formation and poured into 10x10x10 cm^3 molds and cured at three different temperatures of 60°C, 70°C and 80°C for 24h. Bulk densities of the prepared samples were measured by Archimedes principle. Compressive strength test, efflorescence test and water absorption tests were performed on the prepared samples. Test details are explained in the results and discussion section.

Table 2. Experimental Design

Sample Code	Fly Ash (%)	Metakaolin (%)	Molarity (M)	Foaming Agent (%)	Curing Temperature (°C)
1	90	10	10	6	80
2	90	10	10	6	70
3	90	10	10	6	60
4	90	10	6	6	80
5	90	10	6	6	70
6	90	10	6	6	60

3. Results and Discussion

3.1. Compressive Strength

Table 3 shows the results of the compressive strength of geopolymer foams. Compressive strengths were performed on 10x10x10 cm^3 concrete specimens. The compressive strength of specimens were tested at after 28 days of curing.

When the samples prepared at the same molarity were examined according to the curing temperatures, changes in temperature-dependent strength values were observed. Significant increases in strength values of geopolymer samples were observed with temperature increase. When the strength values of the samples with different molarity at equal temperature values were examined, it was seen that the samples with higher molarity had higher strength values.

Density values vary between approximately 444 – 478 kg /m^3 but there is no relation found between density value and strength.

Table 3. Compressive strength results of geopolymer foams

Sample Code	Compressive Strength (MPa)	Density (kg/m^3)	Curing Temperature (°C)	Molarity
1	1.78	468	80	10
2	1.67	463	70	10
3	1.65	458	60	10
4	1.43	444	80	6
5	1.22	478	70	6
6	1.14	454	60	6

3.2. Water Absorption Analysis

Absorption tests were applied on 10x10x10cm^3 specimens. First, 28 day samples were dried in the oven at 105°C during 48 hours and then cooling was carried out to achieve constant moisture level. During the tests, samples were sealed with four surfaces of 1cm height with wax to ensure uniaxial water flow. Then dry weights were noted before samples were placed in water. Afterward, only one surface of specimens was kept in direct contact with water and was weighted in proportion of square root of time.

The water absorption behavior was calculated by the following expression:

$$S = \left(\frac{Q}{A}\right)/\sqrt{t} \qquad (3)$$

Where S is sorptivity (cm/min$^{1/2}$), Q is the volume of water absorbed (cm^3), and A is the surface area in contact with water (cm^2) and t is the time (min).

The water absorption capillarity coefficients are shown in Fig 1. In samples prepared with 10M alkaline solution, it was observed that the capillaries decreased with increasing curing temperature. However, the same could not be seen for samples prepared with the aid of 6M alkaline solution. In addition, samples prepared in 10M alkaline solution were observed to absorb more water in quantities and were interpreted to contain more capillariy spaces inside.
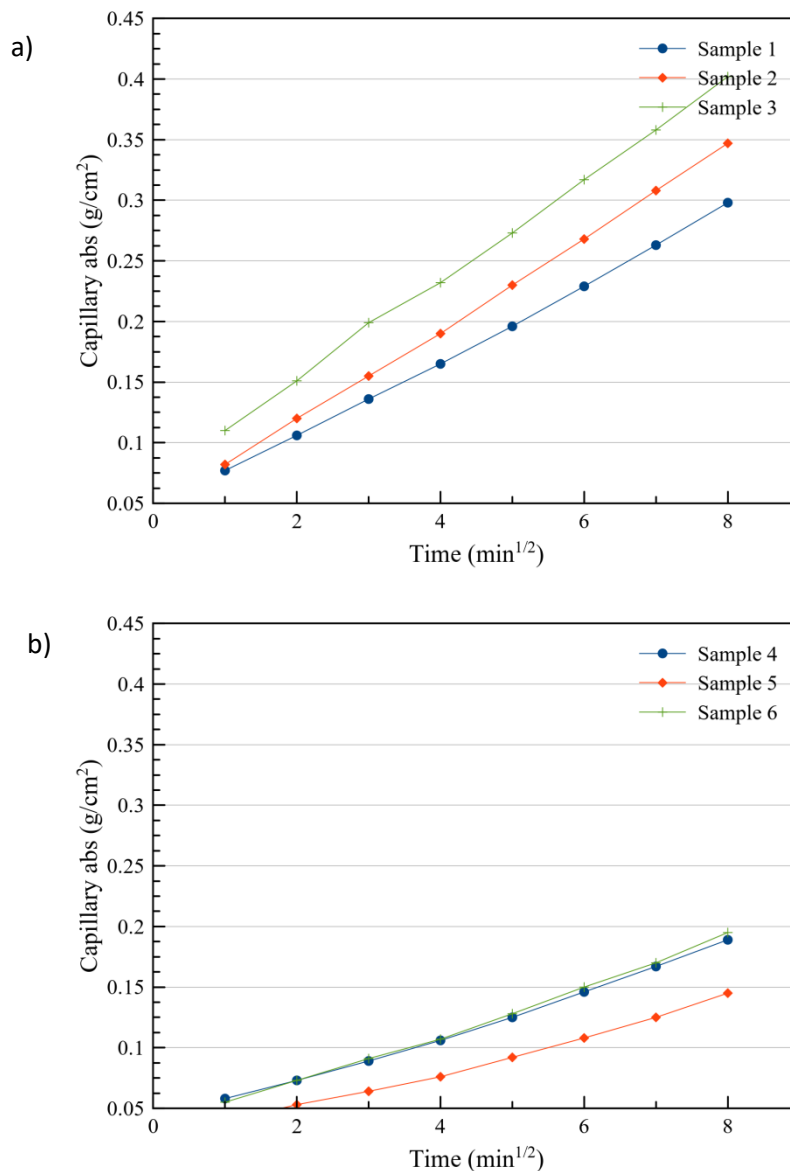
Figure 1. Variation of capillarity (a)10M geopolymer compositions (b) 6M geopolymer compositions. Samples 1 and 4 were cured at 80°C, 2 and 5 were cured at 70°C, 3 and 6 were cured at 60°C

3.3. Efflorescence

To observe an efflorescence, samples stored at room temperature for 28 days were contacted with water at the under part for 6 days. The white salt deposits on the samples were observed and photographed at regular intervals for 6 days (Figure 2).

First three samples prepared with 10M solution were examined visually, it was experienced that the efflorescence changes depending on the temperature difference. The amount of efflorescence in the sample cured at 80°C was seen to be less than 70°C and 60°C respectively. In the samples prepared with 6M solution, it was observed that the amount of white salt deposit was inversely proportional to the temperature as in the 10M solution.

Also, it was found that efflorescence started after 12h and gradually increased with waiting time. Initial efflorescence can only be described as aesthetic problems, but in service conditions, they

create destructive effects on the samples. At the end of 6 days, it was determined that all samples were cracked and even separated from many areas because of expansion in regions close to the surfaces (Figure 2).

In order to analyze efflorescence in geopolymer materials, the white product collected from the surface of the samples was analyzed by XRD. (Figure 3). In Figure 3 it was observed that mainly sodium based compounds were formed. The presence of unreacted sodium cations is the main cause of efflorescence formation.
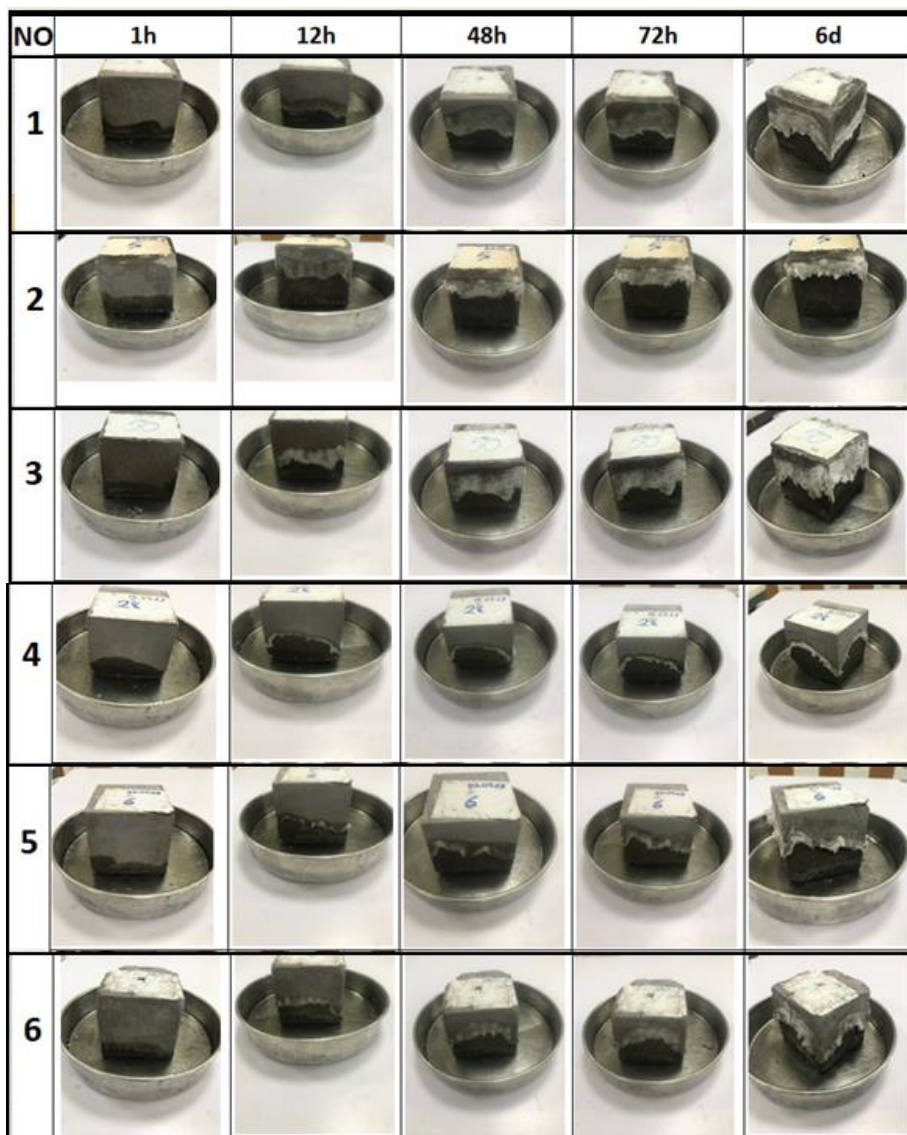

Figure 2. Visual analysis of efflorescence behavior of geopolymer samples by contact with water
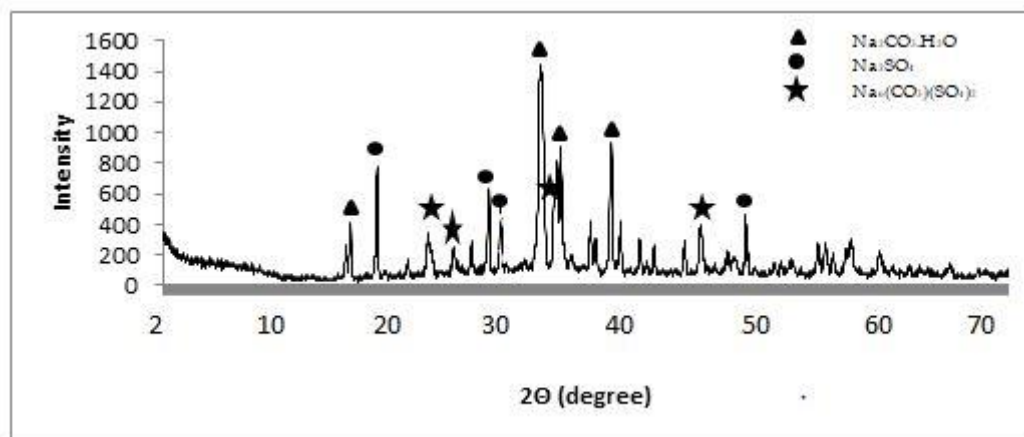
Figure3. XRD analysis of white residues collected from samples

4. Conclusion

This study investigates the efflorescence behavior of fly ash based geopolymers. During the experimental study, geopolymers were cured at three different curing temperatures and at two different alkalinity geopolymer pastes were prepared, and it is found out that these variables affect effloresence rate and potential prominently. However, only the change in molarity and temperature cannot completely hinder the efflorescence, but only reduce it.

Although the curing temperature and the decrease in molarity diminish the efflorescence problem, a significant decrease in strength was also experienced. Although the aim of this study is to develop geopolymer foams for insulation purposes, strength values below 1.5 MPa are not acceptable. In addition, it can be stated that as the capillarity increases the efflorescence behavior of the samples increases in general meaning.

In conclusion, it can be deduced that efflorescence is not only a visual problem, but it can cause destructive effects when the effect of the efflorescence problem is not eliminated. Since it is known that the efflorescence problem in geopolymers is mainly caused by free sodium ions, a system should be established to bind sodium ions.

References

Allahverdi, A., Najafi K., Hossain, K.M.A. and Lachemi, M., 2014. *Methods to Control Efflorescence in Alkali-Activated Cement-Based Materials*. *Handbook of Alkali-Activated Cements, Mortars and Concretes*. Woodhead Publishing Limited, 463-483.

Bai, C., Colombo, P. 2018. Processing , Properties and Applications of Highly Porous Geopolymers : A review. *Ceramics International*, **44**(14), 16103–16118.

Damtoft, J.S., Lukasik, J., Herfort, D., Sorrentino, D. and Gartner, E.M., 2008. Sustainable Development and Climate Change Initiatives. *Cement and Concrete Research* **38** (2): 115–27.

Davidovits, J., 1994. Global Warming Impact on the Cement and Aggregates Industries. *World Resource Review* **6** (2): 263–78.

Davidovits, J., 2008. Geopolymer Chemistry and Applications. Saint-Quentin: Institut Géopolymère, 102-18.

Davidovits, J., 2015. *False Values on CO_2 Emission For Geopolymer Cement/Concrete*. *Scientific Papers*, Technical Paper 24.

Deventer, J., Van, S.J., Provis, J.L. and Duxson, P., 2012. Technical and Commercial Progress in the Adoption of Geopolymer Cement. *Minerals Engineering* **29**:89–1

Dow, C., Glasser, F.P., 2003. Calcium Carbonate Efflorescence on Portland Cement and Building Materials. *Cement and Concrete Research* **33** (1): 147–54..

Duxson, P., Fernández-Jiménez, A., Provis, J.L., Lukey, G.C., Palomo, A., Van Deventer, J.S.J. 2007. Geopolymer Technology: The Current State of the Art. *Journal of Materials Science* **42** (9): 2917–33.

Gatti, S. and Prasad, D.S.V., 2017. A Comparative Study on Compressive Strength of Geo Polymer Concrete Using Partial Replacement of Cement With Ggbs. *International Journal of Recent Trends in Engineering and Research* **3** (8): 267–81.

Hajimohammadi, A., Ngo, T., Mendis, P., Sanjayan, J., 2017. Regulating the chemical foaming reaction to control the porosity of geopolymer foams. *Materials and Design*, *120*, 255–265.

Kaur, M., Singh, J., Kaur, M., 2018. Microstructure and Strength Development of Fly Ash-Based Geopolymer Mortar: Role of Nano-Metakaolin. *Construction and Building Materials* **190:** 672–79.

Lecomte, I., Henrist, C., Liégeois, M., Maseri, F., Rulmont, A., Cloots, R., 2006. (Micro)-Structural Comparison between Geopolymers, Alkali-Activated Slag Cement and Portland Cement. *Journal of the European Ceramic Society* **26** (16): 3789–97.

Liew, Y.M., Nizar, I.K., Kamarudin, H., Heah, C.Y., Bnhussain, M., Mustafa Al Bakri, A. M., Ruzaidi, C. M., Luqman, M., 2013. Kaolin-Based Geopolymers with Various NaOH Concentrations. *International Journal of Minerals, Metallurgy, and Materials* **20** (3): 313–22.

McLellan, B.C., Williams, R.P., Lay, J., Riessen, A V., Corder, G.D., 2011. Costs and Carbon Emissions for Geopolymer Pastes in Comparison to Ordinary Portland Cement. *Journal of Cleaner Production* **19** (9–10): 1080–90.

Medri, V., Papa, E., Dedecek, J., Jirglova, H., Benito, P., Vaccari, A., Landi, E. 2013. Effect of metallic Si addition on polymerization degree of in situ foamed alkali-aluminosilicates. *Ceramics International*, *39*(7), 7657–7668.

Neupane, K., Chalmers, D., Kidd, P., 2018. High-Strength Geopolymer Concrete- Properties , Advances in Materials **7** (2): 15–25.

Novais, R. M., Buruberri, L. H., Ascensão, G., Seabra, M. P., Labrincha, J. A. 2016. Porous biomass fly ash-based geopolymers with tailored thermal conductivity. *Journal of Cleaner Production*, **119:** 99–107.

Novais, R.M., Pullar, R.C., Labrincha, J.A. 2019. Geopolymer foams: an overview of recent advancements. *Progress in Materials Science*, 100621.

Ohji, T., Fukushima, M. 2012. Macro-porous ceramics: processing and properties. *International Materials Reviews*, **57**(2), 115–131.

Škvara, F., Svoboda, P., Dolezal, J., 2008. Geopolymer Concrete-an Ancient Material Too? *Ceramics – Silik{á}ty* **52** (4): 296–98.

Srinivasan, K., Sivakumar, A., 2013. Geopolymer Binders: A Need for Future Concrete Construction. *ISRN Polymer Science* 1–8.

Strozi Cilla, M., Colombo, P., Raymundo Morelli, M. (2014). Geopolymer foams by gelcasting. *Ceramics International*, **40**(4), 5723–5730.

Subaer, S., 2004. Influence of Aggregate on the Microstructure of Geopolymer, PhD Thesis, Curtin University, pp 226.

Szklorzová, H., Bílek, V., 2008. Influence of Alkali Ions in the Activator on the Performance of Alkali Activated Mortars. *Proceedings of the 3rd International Symposium on Non-Traditional Cement and Concrete*, 777–84.

Thaarrini, J., Dhivya, S., 2016. Comparative Study on the Production Cost of Geopolymer and Conventional Concretes. *International Journal of Civil Engineering Research* **7** (2): 2278–3652.

Thakur, V.K., Thakur, M. K., Kessler, M.R., 2017. *Handbook of Composites from Renewable Materials. Physico-Chemical and Mechanical Characterization*, **3**:563-580.

Vaou, V., Panias, D. 2010. Thermal insulating foamy geopolymers from perlite. *Minerals Engineering*, **23(**14), 1146–1151.

Zhang, Z., Provis, J.L., Reid, A., Wang, H. 2014. Geopolymer foam concrete: An emerging material for sustainable construction. *Construction and Building Materials*, **56:** 113–127.

Zhang, Z., Provis, J. L., Ma, X., Reid, A., Wang, H., 2018. Efflorescence and Subflorescence Induced Microstructural and Mechanical Evolution in Fly Ash-Based Geopolymers. *Cement and Concrete Composites* **92:** 165–77.