

CRITICAL THINKING ON EFFLORESCENCE IN ALKALI ACTIVATED CEMENT (AAC)

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ABSTRACT

Alkali-activated cement (AAC), also known as “geopolymer”, has been extensively investigated over the past 40 years and has been developed from laboratory mock ups to real structural usage in construction in the last decade. While numerous life cycle analyses and carbon accounting studies show the “green potential” of this material compared to Portland cement, some authors state that the high alkali concentration in AAC is a potentially unstable factor which may lead to, for example, efflorescence. This paper presents a critical thinking on the literature and some new experimental work regarding the possibility of efflorescence in AAC products. Subjects of the discussion include: (1) the role of alkalis in AACs, (2) the effect of alkali concentration on efflorescence, (3) the effect of solid precursor selection on efflorescence, (4) the effect of curing scheme and chemical additives on efflorescence, and (5) the impacts of efflorescence on the microstructural properties of AACs. Particular attention is given to the relationship between pore structure and efflorescence behaviour, and consequently the mechanical properties of AACs suffering from either efflorescence or alkali loss (by leaching). The changes in sodium aluminosilicate hydrate (N-A-S-H) gels due to efflorescence or alkali loss are critical to the durability of AACs. This paper emphasizes that the nature of the solid precursor and the pore structure of the resulting AAC are the two most important factors that control efflorescence rate. However, considering its alkaline nature, it seems difficult or impossible to avoid this issue in AAC products, although kinetically controlled diffusion of alkalis using phase transformation techniques may help to mitigate efflorescence. Efflorescence in AAC is a “skin issue” that needs to be carefully treated. It is recognized to be different from the visually similar, but chemically distinct, efflorescence that occurs in Portland cement based materials.

KEYWORDS

Alkali-activated cement (AAC), geopolymer, efflorescence, carbonation, durability.

INTRODUCTION

Alkali-activated cement (AAC) technology has shown potential in converting solid industrial wastes into greener cement. The environmental benefit of applying AAC technology mainly lies in the reduction of CO₂ emissions and energy consumption, which are issues of wide concern for the sustainable development of the cement and concrete industries (Damtoft *et al.* 2008). McLellan *et al.* (2011) pointed out that the unit emissions of greenhouse gas in making AAC binder depend on the source location, the energy source and the mode of transport. The counting of the four mixtures using typical Australian fly ashes indicated potential for a 44–64% reduction in greenhouse gas emissions. More recently, Heath *et al.* (2014) showed that AAC manufacture can reduce CO₂ emissions by about 40% when clay minerals are used to replace the widely used fly ash and slag. These have been the main forces driving the current research and development of AAC.

The use of AAC to fabricate concretes is still rare in industry compared to normal Portland cement concretes. Apart from the challenges in supplying consistent raw materials and the cost issues, there are still a variety of technical problems remaining, either unclear or un-solved (van Deventer J.S.J. *et al.*, 2012). Efflorescence is one such problem which has been raised as a concern in some AAC formulations and this has been discussed briefly by Bernal *et al.* (2014), and more recently, systematically investigated by Zhang *et al.* (2014).

Looking back to efflorescence occurring in Portland cement based masonry and concrete, the most common efflorescence is formation of calcium carbonate, which involves six basic and coupled processes: dissolving of $\text{CO}_2(\text{g})$ in H_2O at air-water interface on the surface of products, conversion of CO_2 to aqueous species, release of alkali(s), dissolution of $\text{Ca}(\text{OH})_2$, diffusion of reactants through solution and precipitation of calcium carbonate (Dow *et al.* 2003). The products are whitish, structurally harmless but aesthetically undesirable. To avoid and mitigate efflorescence, the first principle is to reduce the alkali concentration of cements so as to reduce the solubility and absorption rate of CO_2 from the ambient environment (Dow *et al.* 2003). However, in AAC systems, the concentrations of Na and K usually contain much higher soluble alkali metal concentrations than conventional cement. Burciaga-Díaz *et al.* (2010) mentioned that alkali-activated slag based materials show significant efflorescence and some have also shown negative impacts on the mechanical properties of the binders. It must be noted that alkali-activated slag contains higher concentration of calcium than alkali-activated metakaolin and fly ash systems, and this may lead to certain differences in the specific effects of efflorescence. Škvára *et al.* (2012) reviewed 25 fly ash-based mixes and reported that the total alkali content required in fly ash based AAC binders to meet reasonable workability and mild curing ($>50^\circ\text{C}$) for strength development mainly ranges from 30 to 150 g/kg (expressed as Na_2O to total mass of paste), which is 8.4 to 42 times higher than in Portland cement paste (assuming 0.5% Na_2O in cement and $w/c = 0.4$ for paste). This raises particular attention to the efflorescence issue in the application of AAC.

In literature and in our previous investigation, observations of many AAC mixes did find efflorescence that rapidly occurred on drying surfaces when samples were in contact with water and under highly humid atmosphere conditions. A number of factors have been reported to affect the extent of efflorescence in AAC: alkali metal type (Škvára *et al.* 2009; Škvára *et al.* 2012), raw materials (Temuujin *et al.* 2009; Najafi Kani *et al.* 2012) and reaction conditions (Burciaga-Díaz *et al.* 2010; Najafi Kani *et al.* 2012; Zhang *et al.* 2014).

The aim of this paper is to briefly discuss the results found in literature and our current experiments (not yet published). The role of alkalis in AACs (low calcium systems) and the effect of alkali concentration on efflorescence are discussed. Particular interest is given to the different efflorescence behaviours of AACs that were prepared with fly ashes sourced from different power stations. The suggestions are made based on the understanding of the effect of the curing scheme and chemical additives on efflorescence. The importance of this issue is highlighted by the observations of the microstructural properties of AACs which were subjected to efflorescence.

FACTORS AFFECTING EFFLORESCENCE

Roles and States of Alkalis in AACs

An AAC is usually formed by the reaction between the two parts of materials: an alkali activator and a reactive aluminosilicate precursor, which are usually metakaolin and fly ash or their blends. Slag is also very common in AAC manufacture but it can form high calcium gels, which are substantially different to low calcium gels that are formed in the AAC systems discussed. In this paper we mainly focus on the low calcium systems. There have been plenty of research into the molecular structure of AAC gels, a three-dimensional alumino-silicate network configured with SiO_4 and AlO_4 tetrahedrons and by oxygen bridges, with positive ions (Na^+ , K^+) present to compensate the negative charge of Al that is present in coordination 4. This role is widely accepted and generally agreed on in most literature. However, there are some differences regarding the state of alkali metals.

According to Duxson *et al.* (2005), sodium has two states, with one present with aluminium inside gel structures and the other present in pore solutions, neutralizing the charge of $\text{Al}(\text{OH})_4^-$ group. In other words, sodium can partially form Na-O-Al(Si) in gel structure, in which the Na-O bond is relatively intense, and partially form $\text{Na}(\text{H}_2\text{O})_n^+$, in which Na is weakly associated with water molecules. This is in agreement with the leaching result and deconvolution of ^{23}Na MAS NMR spectra for alkali activated fly ash (Fernández-Jiménez *et al.* 2009). If it is assumed that the Na-O in gel structure is relatively stable in hydration conditions (contact with water molecules), similar to the Na-O in dehydrated zeolite, the soluble sodium must be limited, i.e. a certain fraction of sodium ions cannot be readily leached. Najafi Kani *et al.* (2012) ground AAC pastes (could be very fine) and used the stable leaching method at a water to solid ratio of 20:1 and reported that after 24 h the leached alkali is 1-7%, depending on the Si/Na and Na/Al ratios. Zhang *et al.* (2014) crushed alkali activated fly ash pastes into 1.25-1.5 mm particles, used the stable leaching method at water/solid ratio of 25:1 and found that after 24 h the leached sodium is 12-16%, depending on the activator type, curing temperature and slag replacement. These results are in agreement with the above hypothesis.

Škvára *et al.* (2012) crushed AAC pastes into particles under the size of 0.5 mm and used the dynamic leaching method (regularly change leaching solution with fresh water) and found that the alkalis can be almost completely leached from the binder after 150 days. In comparison with zeolite leaching behaviour (usually extremely slow in water), they concluded that the alkalis (Na and K) were only weakly bonded in the form of $\text{Na}(\text{H}_2\text{O})_n^+$. This might not be true. Lloyd *et al.* (2010) measured the alkali concentration in the extracted pore solutions of typical alkali activated binders with 7% Na_2O provided from activator. If we assume that all of the sodium presents in the form of $\text{Na}(\text{H}_2\text{O})_n^+$ in pore solution, and furthermore we assume that in 100 g binder, the pore water (free water) is 10 g and the structural water is 5 g, the sodium concentration is estimated to be higher than 20000 mM, which is far from the measured values of Lloyd *et al.* (2010), 600 to 1600 mM for the alkali activated fly ash systems. In fact, it is well known that the alkalis bound in zeolite frame structure may have different states, and each state having its own ion exchange capacity. Therefore, we state here the hypothesis that alkalis in AAC have different states (more than the two discussed above), and each state has its own leaching rate.

Nevertheless, a large amount of the alkalis are highly moveable, either due to the excessive utilization of activator or the inherent neutralization of $\text{Al}(\text{OH})_4^-$ in pore solution, or both; hence the efflorescence can be potentially intense for AACs.

Effect of Alkali Concentration on Efflorescence

The results obtained by Najafi Kani *et al.* (2012) showed that the extent of leaching alkalis increased with Na/Al increasing from 0.61 to 1.23, and the severity of efflorescence of dry samples after immersion also increased. Fig.1 shows our current experiments of examining efflorescence rate on two fly ash-based AACs, GP(L) and GP(H), which were prepared by the activation of sodium silicate solution at different dosages: GP(L) contained 3.9% Na_2O (expressed as Na_2O to fly ash mass ratio, excluding the Na_2O originating from fly ash) while GP(H) contained 4.6% Na_2O . In GP(L) mixing a small amount of additional water was used to achieve similar workability as GP(H). The samples were cured in sealed moulds, initially 24 hours at $\text{RH} = 90 \pm 10\%$, $25 \pm 1^\circ\text{C}$, followed by 12 hours curing at $75 \pm 1^\circ\text{C}$ and naturally cooled down to $25 \pm 1^\circ\text{C}$ and allowed further 7 days of ageing. Specimens were removed from the moulds and put in ambient air with the bottom immersed in water at a depth of 0.5-1 mm. Efflorescence occurs on the surface of GP(L) more rapidly. Tiny white products were observed after 1.5 hours (not presented here), and after only 2 hours, evidently efflorescence products could be seen on its surface above the wet line. In comparison, GP(H) started to exhibit visible efflorescence after 2 hours. The leaching analysis of the crushed samples, as a quantitative method of assessing efflorescence potential (Zhang *et al.* 2014), showed that the two AACs have very close sodium releasing rate and fraction (not shown). It means that GP(H) has higher efflorescence potential as the absolute amount of leached alkali is higher. This result indicates that lowering the alkali concentration in an AAC by reducing the amount of sodium silicate activator may not be a good practical method to mitigate efflorescence. In fact, other factors, such as gel composition (as a result of varied reaction extent of fly ash due to the change of activation conditions) and pore features (size and volume), can also influence the efflorescence rate.

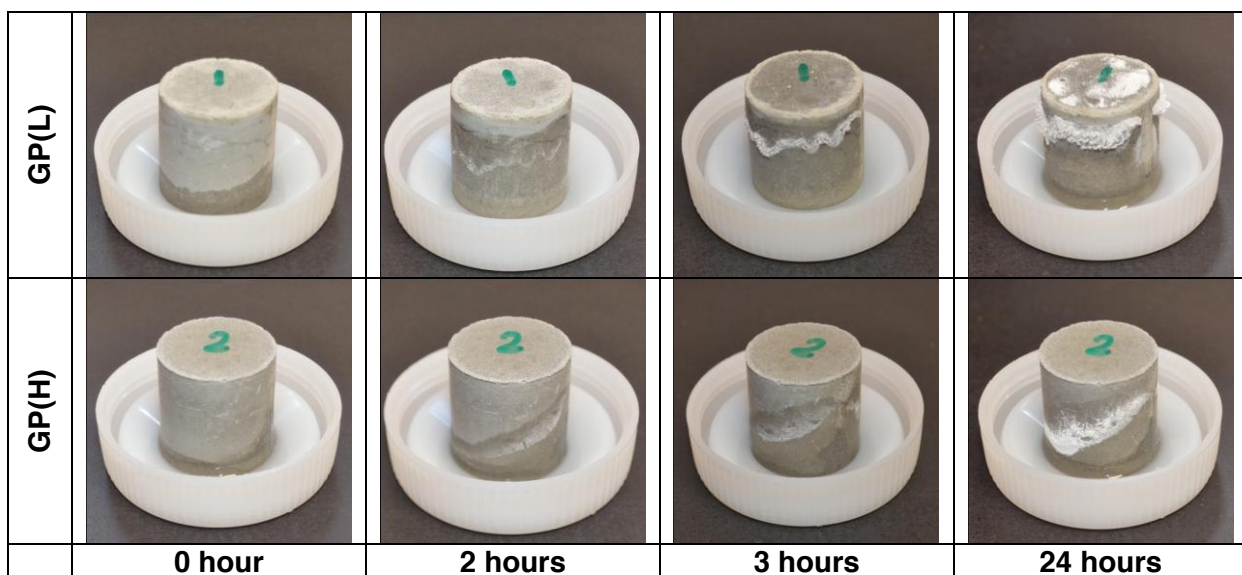
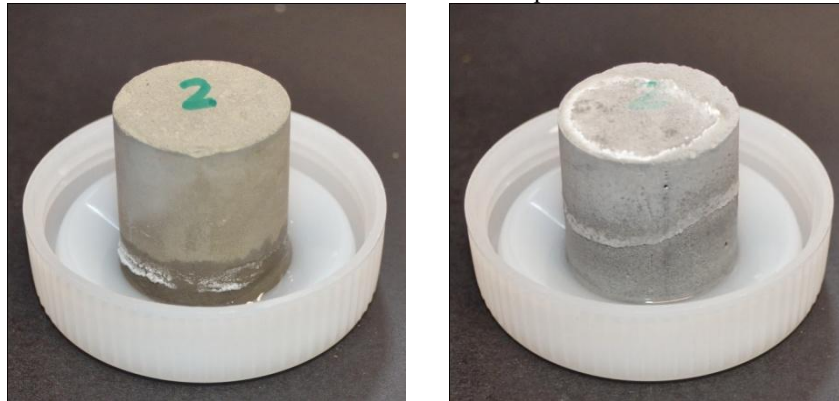


Figure 1 Efflorescence of hardened alkali-activated fly ash pastes in contact with water

Effect of Solid Raw Materials and Curing Scheme

Fly ashes collected from different power stations vary substantially in their chemistry and physical nature, and the slow reaction of some fly ash sources leads to temptation to add excessive alkali to the mix to accelerate hardening, which can then lead to efflorescence. Figure 2 shows the efflorescence behaviour of AACs GPG and GPM, which were prepared by 12 M NaOH solution activation of fly ashes obtained from Gladstone and Millmerran power stations (Queensland, Australia), respectively. The curing conditions were the same as described earlier. GPG shows much slower efflorescence rate compared to GPM.



(a) GPG

(b) GPM

Figure 2 Efflorescence of hardened AAC pastes in contact with water for 24 hours

The addition of slag into fly ash-based AACs has been shown to significantly reduce the efflorescence rate; however, it does not alter the efflorescence potential (Zhang *et al.* 2014). In fact it increases the total amount of leached alkali. Similar results were reported for natural pozzolan-based AAC (Najafi Kani *et al.* 2012). The addition of 6-8% slag increased the extent of alkali leaching. Therefore, the blending of slag is most likely to provide beneficial reductions in permeability rather than changing the binding nature of alkalis. Najafi Kani *et al.* (2012) suggested using alumina-rich admixtures, such as calcium aluminate cement, to reduce the efflorescence. This is probably because of the high reactivity of these additives and the high concentration of Al in the derived gels, which may require increased amount of alkali ions for charge balance. This mechanism is supported by the previous work by Temuujin *et al.* (2009). They reported that the efflorescence was more intensive in AACs that were prepared by preliminarily heated (500°C and 800°C) fly ashes, in which the quantities of amorphous phases were slightly reduced.

Curing scheme is one of the most critical factors that affects efflorescence of AACs. Najafi Kani *et al.* (2012) have shown that curing at $\geq 65^{\circ}\text{C}$ provided a significant effect in efflorescence reduction. This was verified in a previous investigation (Zhang *et al.* 2014). This is because hydrothermal curing can change the local structure and improves the crystallinity of AAC gels. The transition of amorphous gels into more ordered or crystallized zeolite seems to reduce the alkali release rate and extent (Fernández-Jiménez *et al.* 2009). From this point of view, the use of some fine crystalline particles in raw materials as seeds to induce crystallization may help to reduce the efflorescence.

IMPACT OF EFFLORESCENCE

The Evolution of Microstructure

The effect of efflorescence on the microstructure of AACs GP(L) and GP(H) is shown in Figure 3. The observed areas are the surface parts of each sample after 28 days of ambient ageing (in air) and accelerating efflorescence (with bottom immersed in water as described above). The crushed particles near the surface were solidified using resin, polished and washed in acetone using an ultrasonic washer to remove loose particles.

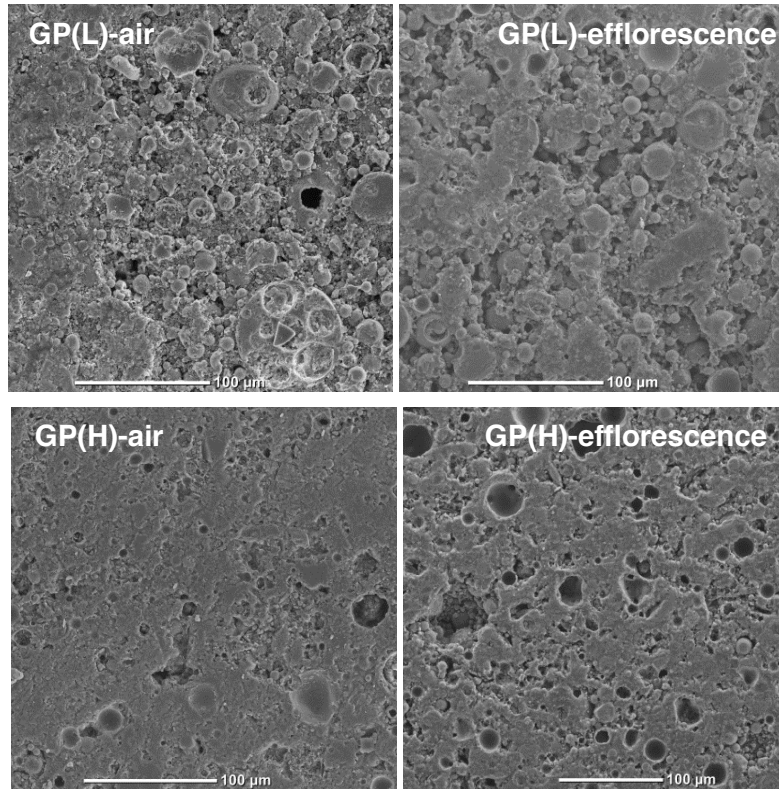


Figure 3 Scanning electron micrograph of AACs after 28 days of ageing under ambient air and accelerating efflorescence conditions

After the accelerating efflorescence procedure, GP(L) becomes more porous when compared to its corresponding samples after ageing in ambient air. Given that the same polishing and washing procedures were used for all the samples, the porous microstructure in cross-section implies the binder may be softer or less strong after efflorescence. The loss of alkalis due to the intensive efflorescence in these two binders is likely to be harmful for strength development. The cross-section of GP(H) after the accelerating efflorescence programme shows the same microstructural feature.

Compressive Strength Development

To date, there is very limited information about the effect of efflorescence on the mechanical properties of AACs. Burciaga-Díaz *et al.* (2010) have shown the degradation of alkali-activated slag binders due to efflorescence (mainly carbonation of excessive Na_2O) after 360 days of curing. Škvára *et al.* (2012) proposed that the leaching of alkalis from well matured AACs does not affect the strength significantly; they attributed the observed slight strength loss to the 'lower cohesion forces between the gel particles' when samples were immersed. We made direct comparison by measuring the specimens after demoulding, air-ageing and accelerating efflorescence recently. Figure 4 shows the compressive strengths of GP(L) and GP(H). After 28 days of ageing, the compressive strengths of the pastes in air all increase by 20 to 35% from their demoulding strengths, while the efflorescence samples show much less increase in strength compared to their strength at demoulding.

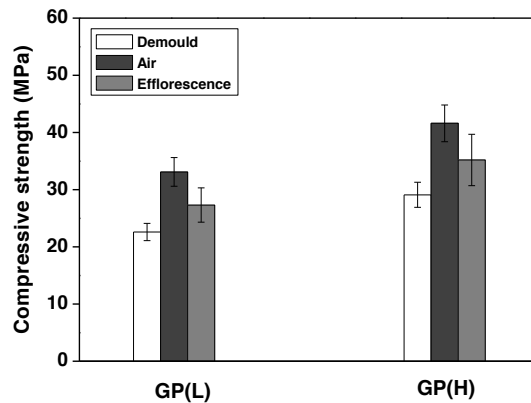


Figure 4 Compressive strengths of well-matured AACs after demoulding, air-aging and accelerating efflorescence for 28 days

It is evident that efflorescence has a negative influence on strength development. When an AAC paste is placed in simulated efflorescence conditions, water can be drawn into the pores of the solid matrix by capillary suction, and evaporate from the sample surface. The internal alkalis are able to diffuse towards the surface, providing Na^+ for the precipitation of sodium carbonates, until an equilibrium (saturation) condition between the pore solution and the crystals is reached. The reduced alkali concentration in the matrix due to diffusion will affect or suppress the later activation of residual precursors. In addition, the crystallization pressure due to the precipitation of sodium carbonates in the pores of the binder may also introduce inner stress, and affect the mechanical properties of AAC. Further investigation is required to make a comparison of fully-matured specimens (strength remains constant in air) and specimens subjected to efflorescence, to reveal the exact mechanical impact of efflorescence.

CONCLUSIONS

In this brief review paper we discussed efflorescence occurring in fly ash-based AACs. This phenomenon is distinct from that which occurs in Portland cement based materials. The high concentration and high mobility of alkalis in normal AAC systems make efflorescence an inborn process. Some progress has been made to understand these efflorescence mechanisms and the factors that influence them. It must be highlighted that the addition of Al-rich additives and the adoption of hydrothermal curing have been confirmed to be effective methods to reduce efflorescence rate. Other aspects, such as how efflorescence will affect the microstructure and properties, remain to be established.

ACKNOWLEDGMENTS

This study was sponsored by the Halok Geopolymer research project and Australian Research Council project (LP130101016). The support of the joint research project that funded by Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory (14zxnk01) is also acknowledged.

REFERENCES

- Bernal S.A., Bilek V., Criado M., et al. Durability and testing - Degradation via mass transport, in: J.L. Provis, J.S.J. van Deventer (eds.) Alkali-Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM, Springer/RILEM, Dordrecht; 2014. pp. 223–276.
- Burciaga-Díaz O., Escalante-García J. I., Arellano-Aguilar R., et al., 2010. Statistical analysis of strength development as a function of various parameters on activated metakaolin/slag cements. *Journal of American Ceramic Society* 93, 541–547.
- Damtoft J.S., Lukasik J., Herfort D., et al., 2008. Sustainable development and climate change initiatives. *Cement and Concrete Research* 38, 115–127.
- Dow C., Glasser F.P., 2003. Calcium carbonate efflorescence on Portland cement and building materials. *Cement and Concrete Research* 33, 147–154.
- Duxson P., Lukey G.C., Separovic F., et al., 2005. Effect of alkali cations on aluminum incorporation in geopolymeric gels. *Industrial & Engineering Chemistry Research* 44 (4), 832–839.

- Fernández-Jiménez A., Palomo A. Nanostructure/microstructure of fly ash geopolymers. In J.L. Provis and J.S.J. van Deventer (Eds.) *Geopolymers: Structure, Processing, Properties and Industrial Applications*. Woodhead, Cambridge, UK; 2009. pp. 89–117.
- Heath A., Paine K., McManus M., 2014. Minimising the global warming potential of clay based geopolymers. *Journal of Cleaner Production* 78, 75–83.
- Lloyd R.R., Provis J.L., van Deventer J.S.J., 2010. Pore solution composition and alkali diffusion in inorganic polymer cement. *Cement and Concrete Research* 40, 1386–1392.
- McLellan B.C., Williams R.P., Lay J., et al., 2011. Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement. *Journal of Cleaner Production* 19, 1080–1090.
- Najafi Kani E., Allahverdi A., Provis J.L., 2012. Efflorescence control in geopolymer binders based on natural pozzolan. *Cement and Concrete Composites* 34, 25–33.
- Škvára F., Kopecký L., Šmilauer V., et al. 2009. Aluminosilicate polymers – influence of elevated temperatures, efflorescence. *Ceramic–Silikáty* 53, 276–282.
- Škvára F., Šmilauer V., Hlaváček P., et al., 2012. A weak alkali bond in (N, K)-A-S-H gels: evidence from leaching and modeling. *Ceramics–Silikáty* 56, 374–382.
- Temuujin J., van Riessen A., 2009. Effect of fly ash preliminary calcination on the properties of geopolymer. *Journal of Hazardous Materials* 164, 634–639.
- van Deventer J.S.J., Provis J.L., Duxson P., 2012. Technical and commercial progress in the adoption of geopolymer cement. *Minerals Engineering* 29, 89–104.
- Zhang Z., Provis J.L., Reid A., et al., 2014. Fly ash-based geopolymers: the relationship between composition, pore structure and efflorescence. *Cement and Concrete Research* 64, 30–41.