Aluminosilicate polymers - geopolymers (influence of temperatures 20 - 1000 ^{o}C, efflorescences)

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Introduction

New materials composed of 2-D to 3-D-structure of the type $M_n[-(Si\text{-}O)_z - Al - O]_n \cdot wH_2O$ are formed when aluminosilicate bodies are exposed to the action of a strong alkaline environment (hydroxides, silicates). Inorganic aluminosilicate polymers (geopolymer) represent a new type of materials on the border line between vitreous, ceramic materials and those based on classic (traditional) inorganic binders and building materials made of rejects as, for instance, slags, fly ashes, kaolinitic materials, etc./1-7 / The present investigation has been focused on the influence of temperatures ranging from 20 to 1000 ^{o}C on properties of aluminosilicate polymers (further ASP) materials based on brown coal fly ash from the Czech Republic and on problem of efflorescences.

Experimental Part

A fly ash rejected in a Czech power plant using brown coal was used for investigation; its specific surface area is 210 m^2/kg (Blaine).

Table 1: Chemical composition of the fly ash

Oxide (wt %)	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	TiO_2
Fly ash	53.52	32.87	0.33	2.05	1.80	0.85	5.89	1.89

The slurries (suspensions) were prepared by mixing the fly ash and other ingredients with a solution of an alkaline activator (NaOH + Na water glass, KOH + K water glass). The mortars were obtained by mixing the slurry with aggregate (silica sand) at a ratio (fly ash–to-aggregate) of 1 : 2. The SiO_2-to-$Na(K)_2O$ ratio (M_S modulus) in the alkaline activator was modified by a NaOH, KOH addition to water glass so that the final M_S modulus would range from 1 to 1.6. The water coefficient (the ratio of the water mass to that of the fly ash) w/s ranged from 0.23 to 0.37. After the preparation of slurries or mortars, the test specimens (in steel molds) were subjected to a thermal process under “dry conditions” in a dryer at a temperature of 80 ^{o}C (in the open air atmosphere) for a period of time lasting 12 hours. The specimens were then kept in air with a relative humidity of 40 to 50 % till the moment of the strength determination. The compressive strength was determined after 2, 7 and 28 days, or after 90 and 360 days. The compressive strength of specimens fired at 200 - 1000 ^{o}C at a heating rate of 5 ^{o}C/min and with a soak time of 2 hours at the maximum temperature was also determined. Fragments remaining after the strength tests were investigated with the aid of x-ray diffraction analysis, thermal analysis and high-pressure mercury porosimetry as well as by measuring the BET isothermal lines. Furthermore NMR MAS (^{29}Si, ^{27}Al, ^{29}Na) spectra were determined. The ESEN microstructure was studied on fracture or polished surfaces and selected zones were analyzed by an ED spectrometer. The Na, K leaching was determined by analyzing leaching liquids obtained by keeping the specimens in water for 24 hours and using a procedure specified in the decree of the Czech Ministry of Environment. The evolution in the efflorescence formation was monitored qualitatively by means of a procedure recommended for articles made by the brick industry: the bottom half of the specimen was immersed in water for more than 14 days (procedure described in the Czech Standard CSN 72 2608).

Results

The ASP prepared by alkaline activation of brown coal fly ash contains a phase of the type Mn$[-(Si\text{-}O)_z - Al - O]_n \cdot wH_2O$, parts of unreacted fly ash and pores.

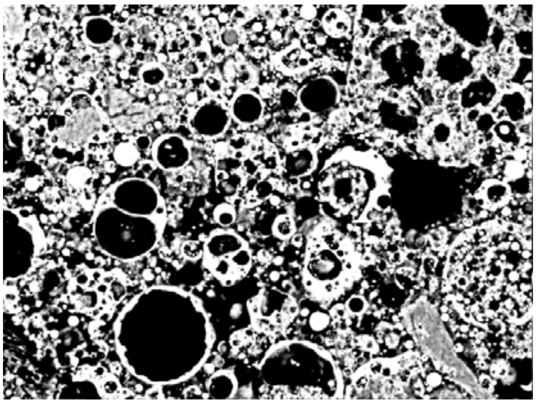


Fig.1 Polished section of ASP (BSE imaging), Na activator

The porosity of the ASP (determined by Hg porosimetry) consists of closed spherical pores formed as a result of the dissolution of inner sections of the fly ash or by air entrapment during the preparation. Spherical pores caused by the fly ash residues exhibit a thin coating made of Si, Al glass with a high Fe content. The solubility of this glass with a higher Fe content in an alkaline environment /8/ is very low and, hence, it remains in the body of the ASP phase as an unreacted residue.

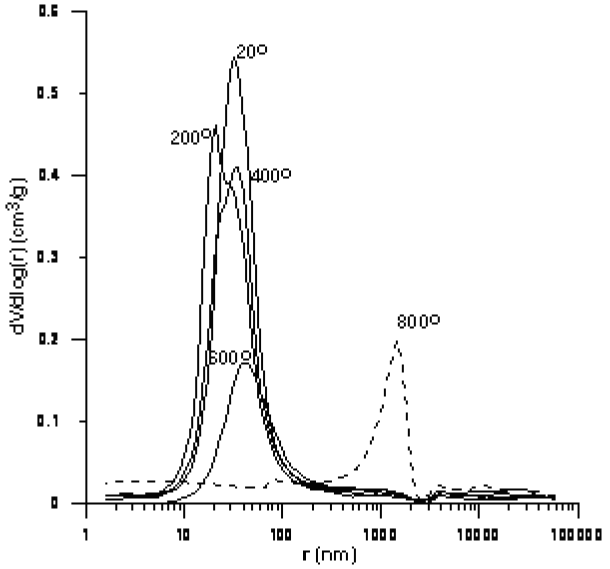


Fig.2 Pore size distribution in a geopolymer fired at a temperature of 20 – 800 °C (Hg porosimetry)

ASP porosity (determined by BET) also develops pores in the nanometric region (2 to 5 nm) /11/ as found in a metakaolin-based ASP /12/. The ASP porosity in the nanometric region is not particularly dependent on the preparation conditions. The differences in the porosity in the micron range are due to the preparation technique and H_2O content (water coefficient) during the preparation process.

The strength of ASP slurries, mortars (and even of concretes) prepared from fly ashes and kept at a temperature of 20 – 25 °C for 2 – 520 days /9,10,11,19/ exhibits an increasing trend. The values of the compressive strength of slurries, mortars (and even of concretes) range from 15 to 70 MPa after 28 days in dependence on the preparation conditions and composition. The highest values of the compressive strength ranging from 130 to 160 MPa after 28 days from the moment of their preparation (ASP prepared from fly ash and blast-furnace slag) /11/ could be obtained in ASP.

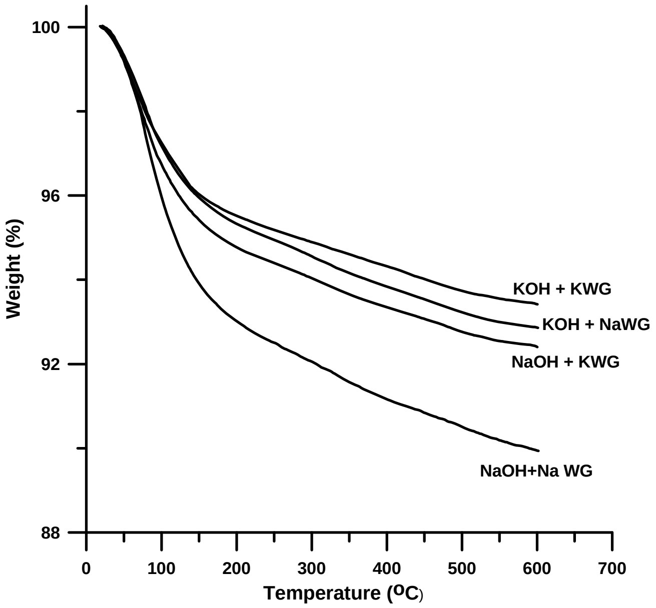


Fig.3. GTA curves of ASP (Na, K activator)

The ASP loses continuously its mass (the water content drops) on heating up to a temperature of 400-600° C (GTA curves). The water is probably present in the ASP as “free” water in micro-pores, then in gel pores and as OH groups at the end of Si-O-Al chains. The water may be bonded as Na, K $(H_2O)^+_n$ in gel pores (as this is evident from NMR spectra). More than 60 % of H_2O are lost on heating at temperatures below 200 °C. The residual water is lost, or OH groups are split off on heating at temperatures above 600 °C. A similar character of the thermal decomposition could also be observed in a aluminosilicate gel (prepared by sol-gel method without alkali activation) /25/ and in a metakaolin-based ASP /12/.

The strength values of ASP (determined at room temperatures after firing) increase after the heating to 200 °C but they exhibit a decreasing tendency afterwards. Contrary to the Portland cement, no gradual loss in strength takes place on firing that eventually finishes with a complete decomposition. The values of the residual strength of the ASP after the firing are substantially higher than those of Portland cement.

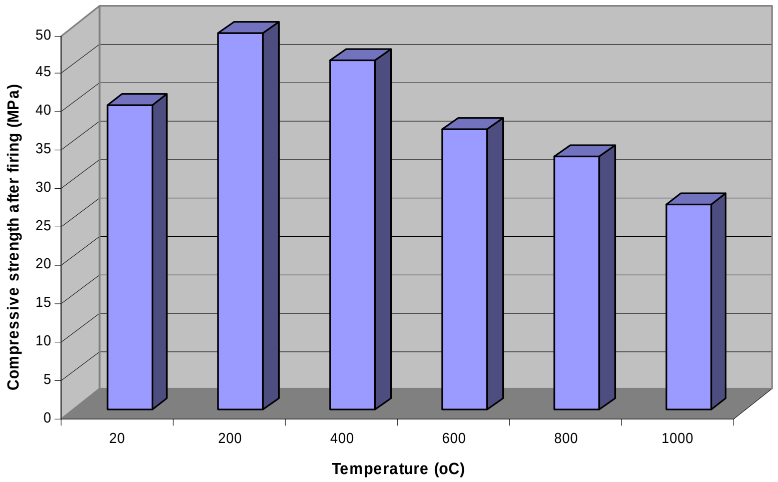


Fig.4 Strength values of the ASP (mortar, Na activator) after firing (determined at 20 °C)

The porosity of the ASP drops on firing at temperatures below 1000 °C and the material density increases (fig.2). The microporosity almost disappears at 600 °C; new pores form at 800 °C and thermal fissures are obviously originated. The same densification character of the ASP material could also be observed in a metakaolin-based ASP /13/.The firing of the ASP at temperatures above 500 °C results in the changes in its microstructure as this is evident from the following pictures (Na activator).

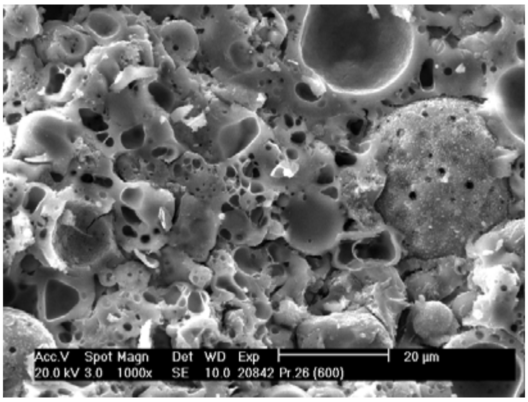


Fig.5 ASP after firing at 600 °C

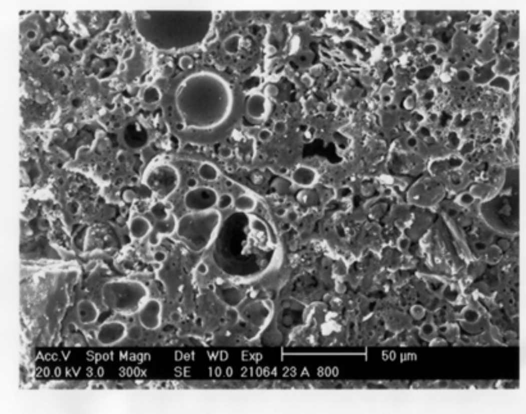


Fig.6 ASP after firing at 800 °C

The ^{29}Si NMR MAS spectra of the ASP subjected to the heat treatment in the temperature range of 200 – 800 °C do not change significantly. The $SiQ_4(4Si)$ and $SiQ_4(3Al)$structures predominate and there is a peak bloc at -85 to -95 ppm. The Q_4(1-2Al) structure is poorly represented. Structures remaining after the residues of mullite from the original fly ash are visible in the spectra. The ^{27}Al NMR MAS spectra of the ASP subjected to the heat treatment in the temperature range of 200 – 800 °C do not change significantly. The Al^{IV} $AlQ_4(4Si)$ coordination predominates while the Al^{VI} coordination from the mullite residues in the original fly ash is in minority. However, the firing temperature affects the character of ^{23}Na NMR MAS spectra. It is evident from the ^{29}Na NMR MAS spectra at temperatures below 400 °C that Na occurs in the structure in the form of $Na(H_2O)_n$ where n = 2 – 8 /14/.^{39}K NMR of potassium ASP show a similar effect /18/. A shift towards a $Na(H_2O)_2$ structure becomes apparent at higher temperatures. There is a series of peaks in the spectrum at 600 °C that correspond to an overall re-arrangement of the structure. At 800 °C, there is a dominant -14ppm peak in the spectrum that corresponds to the structure of a sodium silicate glass /15, 16/.

Na, K present in the ASP compensates the negative charge of Al in the Si-O-Al structure. It is probable that Na,K is rather bonded in the ASP in the form of $Na,K(H_2O)_n^+$ than as Na^+, K^+. The $Na,K(H_2O)_n{}^+$ bond is weaker than that of Na^+, K^+. Hence, this fact creates favourable conditions for the Na leaching from the ASP structure thus favoring the ASP tendency to the formation of efflorescences.

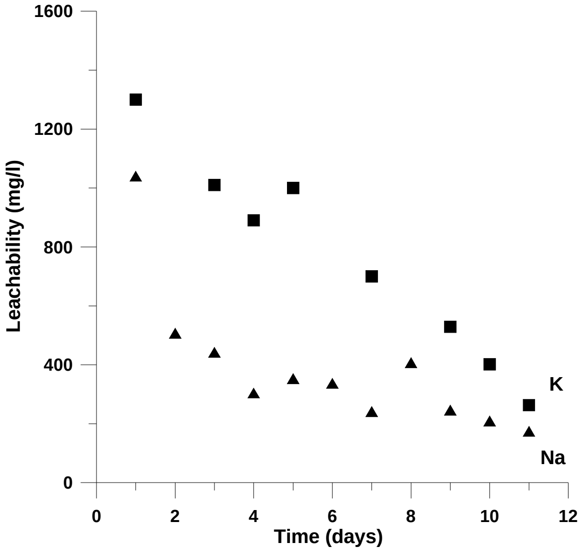
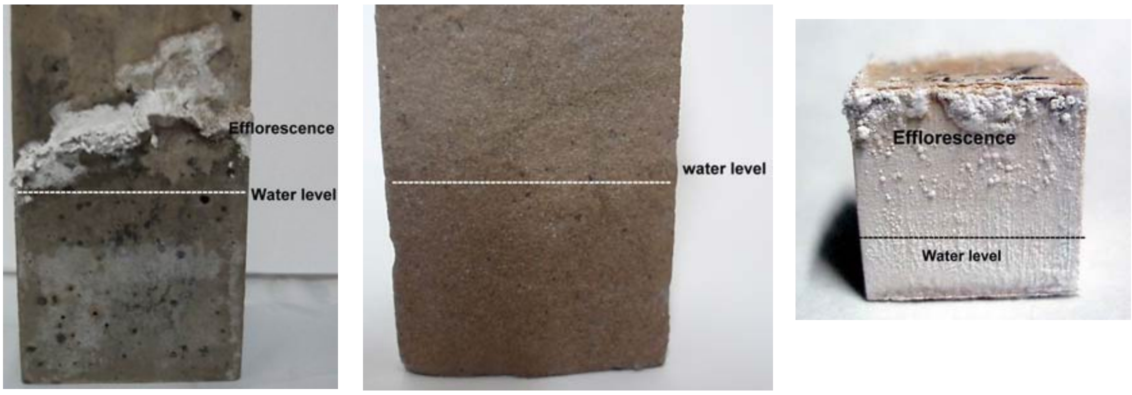


Fig.7 Leachability of Na, K (mortar)



a.ASP fly ash basis aa.ASP after firing at 800 ^{o}C b.ASP metakaoline basis

Fig.8 Efflorescences on the ASP (Na activator) surface kept in a humid environment. The efflorescences are composed of hydrates of the type Na_2CO_3 . n H_2O, $NaHCO_3$.n H_2O, seldom $Na_6(SO_4)(CO_3, SO_4)$. n H_2O.

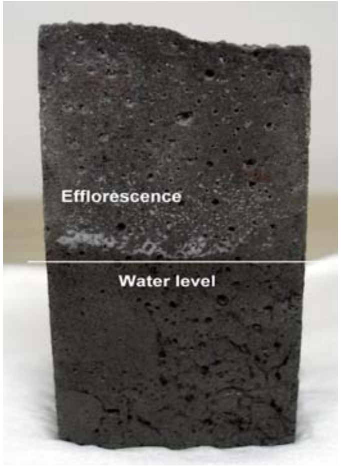


Fig.9 Efflorescences on the ASP (K activator) surface kept in a humid environment. The efflorescences are composed of K_2CO_3.

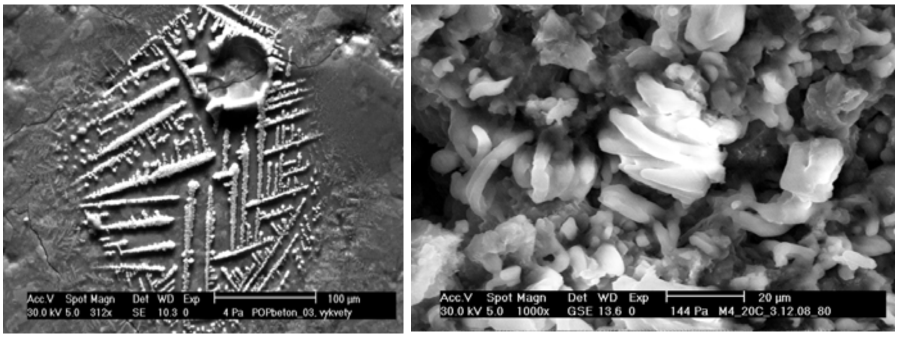


Fig.10 Initial stage of efflorescence on the ASP surface (fly ash basis)

Na activator, effl.$Na_2CO_3.nH_2O$ K activator, efflorescence K_2CO_3

The Na leaching will only decline substantially (up to hundredfold) after the elimination of H_2O from the structure (on firing) and the transformation of the Na bond.

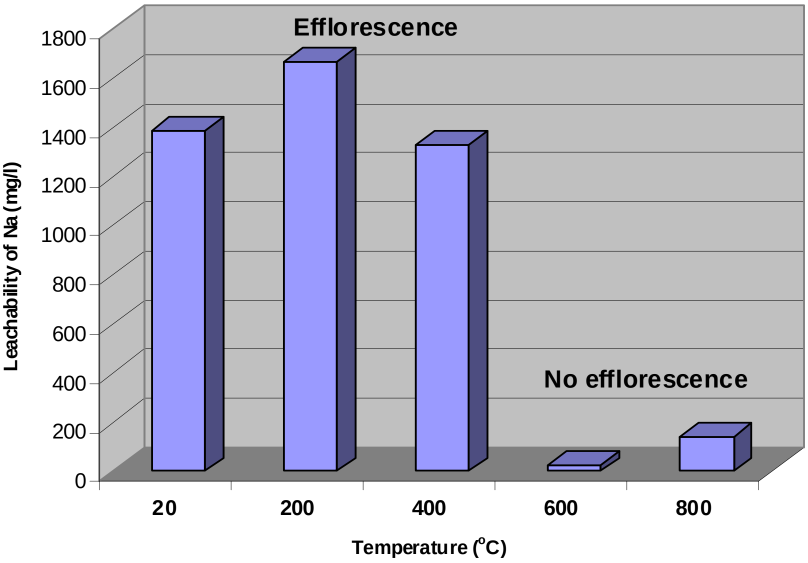


Fig.11 Na leaching from ASP (mortar) in dependence on firing temperature

A visible formation of efflorescence can be partially prevented by replacing Na with K during the alkaline activation because K_2CO_3 does not give rise to visible hydrates. The water solubility of K_2CO_3 that forms on the surface of the aluminosilicate polymer is significantly larger than that of $Na_2CO_3.n\ H_2O$; therefore, in contact with aqueous environment, it dissolves practically without any formation of visible efflorescences. Nevertheless, the K leaching from the ASP structure is comparable or even larger (in dependence on the preparation conditions of ASP) than that of Na, as this is demonstrated on Fig.7, and by results obtained by other workers /17, 18/. Furthermore, the strength values of fly ash-based ASP subjected to a potassium-containing activating agent are substantially smaller than those obtained with a sodium-containing one /19/.
Amorphous aluminosilicate polymers and crystalline zeolites have a similar chemical composition. The chemical composition of the ASP phase is similar to that of the

mineral analcime $Na_{16}((AlO_2)_{10}(SiO_2)_{26}).2H_2O$ (point analysis). However, the Na^+ and K^+ ions are not bonded so strongly by ion bonds in aluminosilicate polymers as this happens in the case of crystalline zeolites the leachability of which (Na, K) is very small. The leaching of Na and K from zeolites takes place in negligible amounts only under long-term hydrothermal conditions /20/. The character of the Na, K bond in crystalline zeolites is affected by the presence of water that weakens the Na, K bond in zeolites /21, 22/. The model submitted by Rowles /24/ and others is also in agreement with these results.

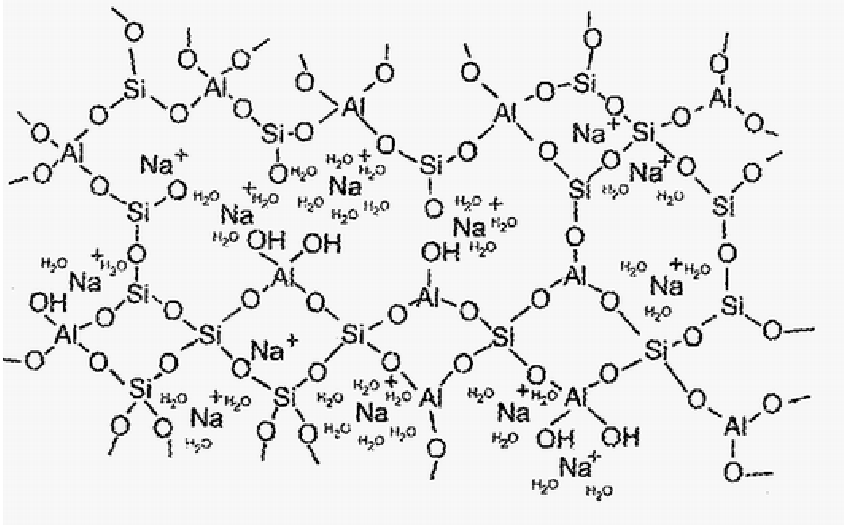


Fig. 12. Model of ASP /24/

The geopolymerization process (the formation of the aluminosilicate polymer) occurring in a strong alkaline environment characterized by a high pH value (above 12-13) begins, first, as a dissolution process of aluminosilicate bodies (the sources of Si and Al). The solution transforms into an aluminosilicate gel; the ions of Na^+, K^+ and OH^- , respectively $(SiO_4)_n^{m-}$ together with H_2O molecules remain in the pores in the gel (in nano- and micro-pores). This fact was demonstrated by Herr /23)/ with his experiments when aluminosilicate polymers were molded at a pressure of 350 MPa. The alkaline activating agent remains enclosed in the body of the aluminosilicate polymer after the polymerization process (essentially as ballast).

The structure of aluminosilicate inorganic polymers synthesized at temperatures ranging from 20 to 200 °C is obviously similar to that of glass. It can be assumed that the structure of the polymer is ordered over short distances and randomly ordered over larger distances, which corresponds to their amorphous character. The possibility of leaching easily Na (K) from the body of the aluminosilicate polymer is obviously in relation with this unordered structure.

4 Conclusions

The ASP prepared by alkaline activation of brown coal fly ash is a porous body containing an aluminosilicate polymer of the type $M_n[-(Si-O)_z - Al - O]_n . wH_2O$. Sodium is obviously bonded in the ASP structure as $Na(H_2O)_n$ and not as Na^+. The Na bond in the ASP structure is weak and this fact explains the tendency of ASP material to the formation of efflorescences in a humid environment. The strength values of the ASP fired at temperatures in the range of 200 – 1000 C attain their maximum at 200 C; they decline gradually afterwards. The ASP strength after firing is substantially higher than the residual strength of Portland cement.. The Na bond in the structure suffers a fundamental change and, starting from 600 C, the character of the Na bond is the same as that in vitreous materials. The Na leaching declines in a very significant way after firing at temperatures above 600 C and the tendency to the formation of efflorescences disappears.

Inorganic polymer aluminosilicate materials exhibit excellent material properties as, for instance, a fast increase in strength, an excellent durability in contact with corrosive environments (salts, acids, bases), refractoriness, an excellent resistance to abrasion, etc. These materials offer promising potentials in areas where the utilization of rejects from the processing of inorganic raw materials is envisaged. Nevertheless, there are also some drawbacks associated with their application. They are, first of all, an easy leaching of alkaline components and the formation of efflorescences.

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