High-temperature properties of geopolymers based on brown fly ash

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1 Introduction

Geopolymers 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 determination of the influence of temperatures ranging from 20 to 1,000 ^oC on properties of geopolymer materials based on brown coal fly ash from the Czech Republic.

2 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). The chemical composition of the fly ash is given in Table 1.

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 + sodium water glass). The mortars were obtained by mixing the slurry with aggregate (silica sand) at a ratio (fly ash –to-aggregate) of 1 : 2 to 1 : 4. The SiO_2-to-Na_2O ratio (M_S modulus) in the alkaline activator was modified by a NaOH addition to water glass (having the M_S modulus equal to 2.5) so that the final M_S modulus would range from 1 to 1.6. The overall concentration of the alkaline activator amounted to 6-10 % Na_2O of the fly ash mass. The water coefficient (the ratio of the water mass to that of the fly ash) w/s ranged from 0.23 to 0.37. In some cases, agents containing calcium as, for instance, ground blast-furnace pelletized slag or ground limestone were added; their addition amounted to 5 - 20 % of the fly ash mass. 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 60 to 90 ^oC (in the open air atmosphere) for a period of time lasting 4 to 16 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 - 1,000 ^oC at a heating rate of 5 ^oC/minute and with a soak time of 2 hours at the maximum temperature was also determined. The refractoriness under load and the firing shrinkage were measured and used for the characterization of thermal properties.

3 Results

The geopolymer prepared by alkaline activation of brown coal fly ash contains a geopolymer phase of the type $M_n[-(Si-O)_z - Al - O]_n . wH_2O$, parts of unreacted fly ash and pores.

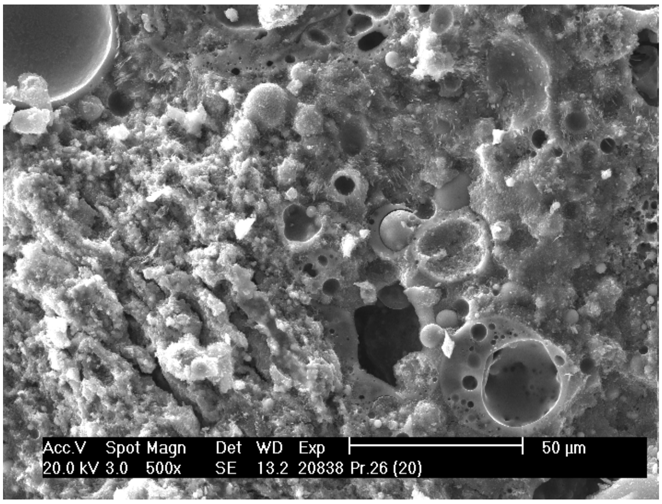

FIG. 1 Fracture surface of a geopolymer

The chemical composition of the geopolymer phase is similar to that of the mineral analcime $Na_{16}((AlO_2)_{10}(SiO_2)_{26}). 2 H_2O$ (point analysis of the geopolymer phase). The porosity of the geopolymer (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 geopolymer phase as an unreacted residue.

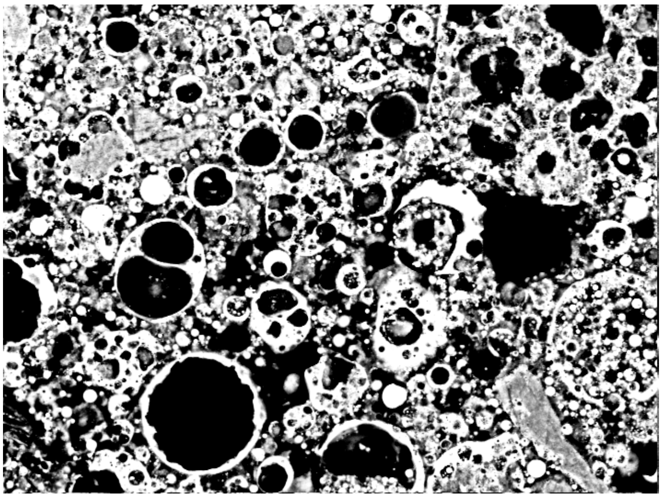

FIG. 2 Polished section of a geopolymer (BSE imaging)

Geopolymer porosity (determined by BET) also develops pores in the nanometric region (2 to 5 nm)[11] as found in a metakaolin-based geopolymers [12].

The geopolymer 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 geopolymer slurries, mortars (and even of concretes) prepared from fly ashes and kept at a temperature of 20 – 25 °C for 2 – 520 days [9,10,11,12] 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 (geopolymers prepared from fly ash and blast-furnace slag) [11] could be obtained in geopolymers.
The geopolymer 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 geopolymers 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 $Na(H_2O)^+$ in gel pores (as this is evident from NMR spectra, see below). More than 60 % of H_2O are lost on heating at temperatures below 200 ^oC. The residual water is lost, or OH groups are split off on heating at temperatures above 600 ^oC. A similar character of the thermal decomposition could also be observed in a metakaolin-based geopolymer [12] .

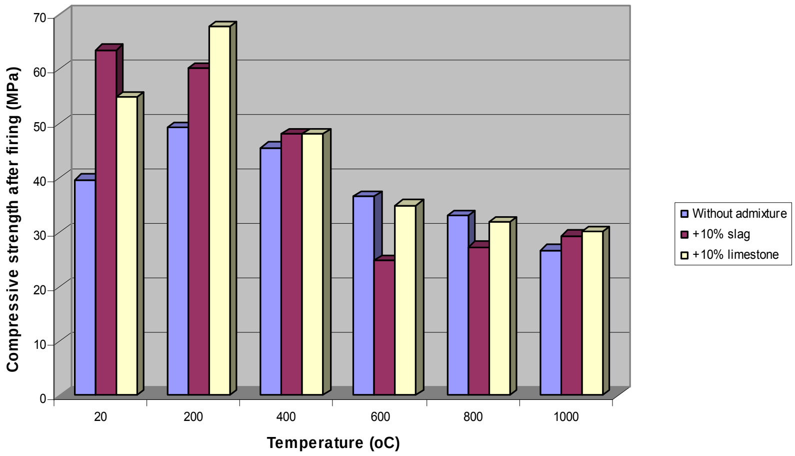

Fig.3.

The strength values of geopolymers (determined at room temperatures after firing) increase after the heating to 200 ^oC 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 geopolymer after the firing are substantially higher than those of Portland cement.

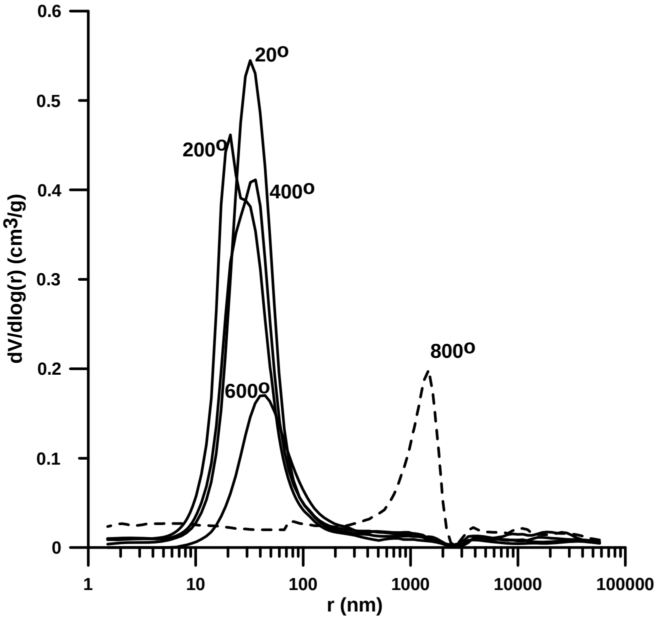

FIG. 4 Pore size distribution in a geopolymer fired at a temperature of 20 – 800 ^oC (mercury porosimetry).

The porosity of the geopolymer drops on firing at temperatures below 1,000 °C and the material density increases. The micro-porosity almost disappears at 600 °C; new pores form at 800 °C and thermal fissures are obviously originated. The same densification character of the geopolymer material could also be observed in a metakaolin-based geopolymer [13].

The determination of the refractoriness under load indicates that the $T_{0.5}$ temperature ranges from 630 to 700 °C. The addition of Ca-containing materials increases the $T_{0.5}$ temperature as this could also be found by other workers [14].

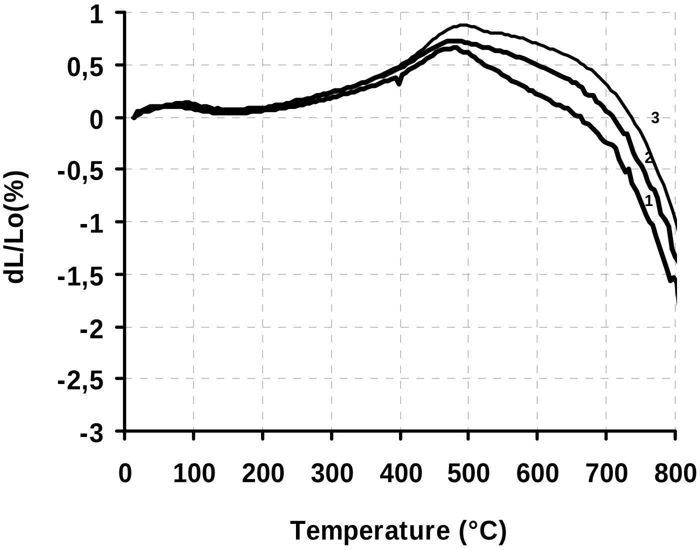

FIG. 5 Geopolymer deformation on heating (under a load of 2MPa)

Curve 1…Geopolymer
Curve 2…Geopolymer with a 10-percent addition of dolomitic limestone
Curve 3…Geopolymer with a 10-percent addition of dolomitic limestone

The firing of the geopolymer at temperatures above 400 °C results in the changes in its microstructure as this is evident from fig. 6,7.

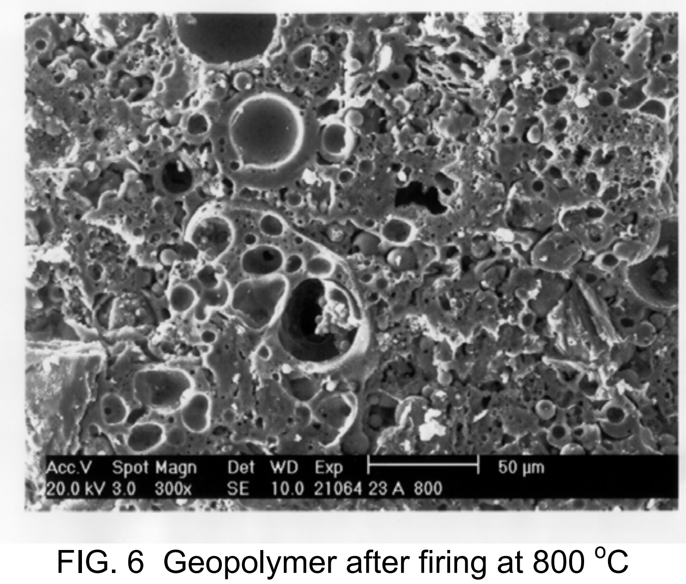

FIG. 6 Geopolymer after firing at 800 °C

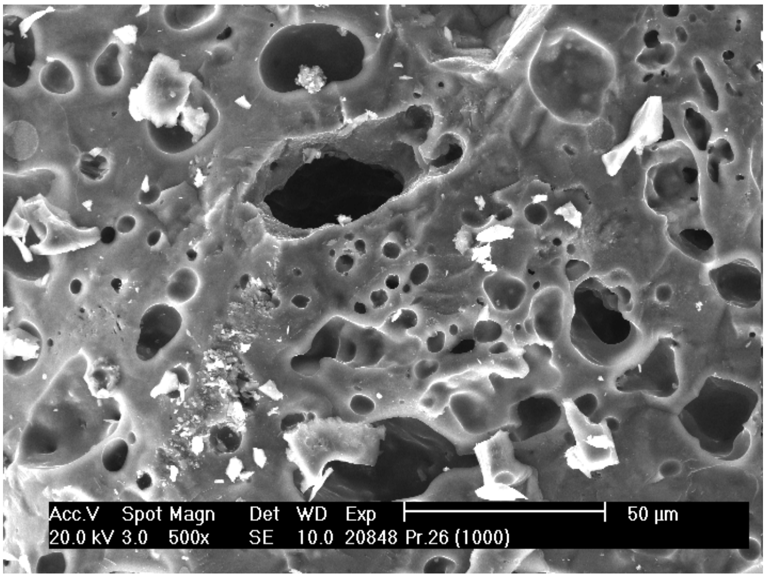

FIG. 7 Geopolymer after firing at 1000 ^{o}C

The ^{29}Si NMR MAS spectra of the geopolymers subjected to the heat treatment in the temperature range of 200 – 800 ^{o}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 ispoorly represented. Structures remaining after the residues of mullite from the original fly as are visible in the spectra.

The ^{27}Al NMR MAS spectra of the geopolymers subjected to the heat treatment in the temperature range of 200 – 800 ^{o}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 ^{o}C that Na occurs in the structure in the form of $Na(H_2O)_n$ where n = 2 – 8 [15]. 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 ^{o}C that correspond to an overall re-arrangement of the structure. At 800 ^{o}C, there is adominant -14ppm peak in the spectrum that corresponds to the structure of a sodium silicate glass [16, 17].

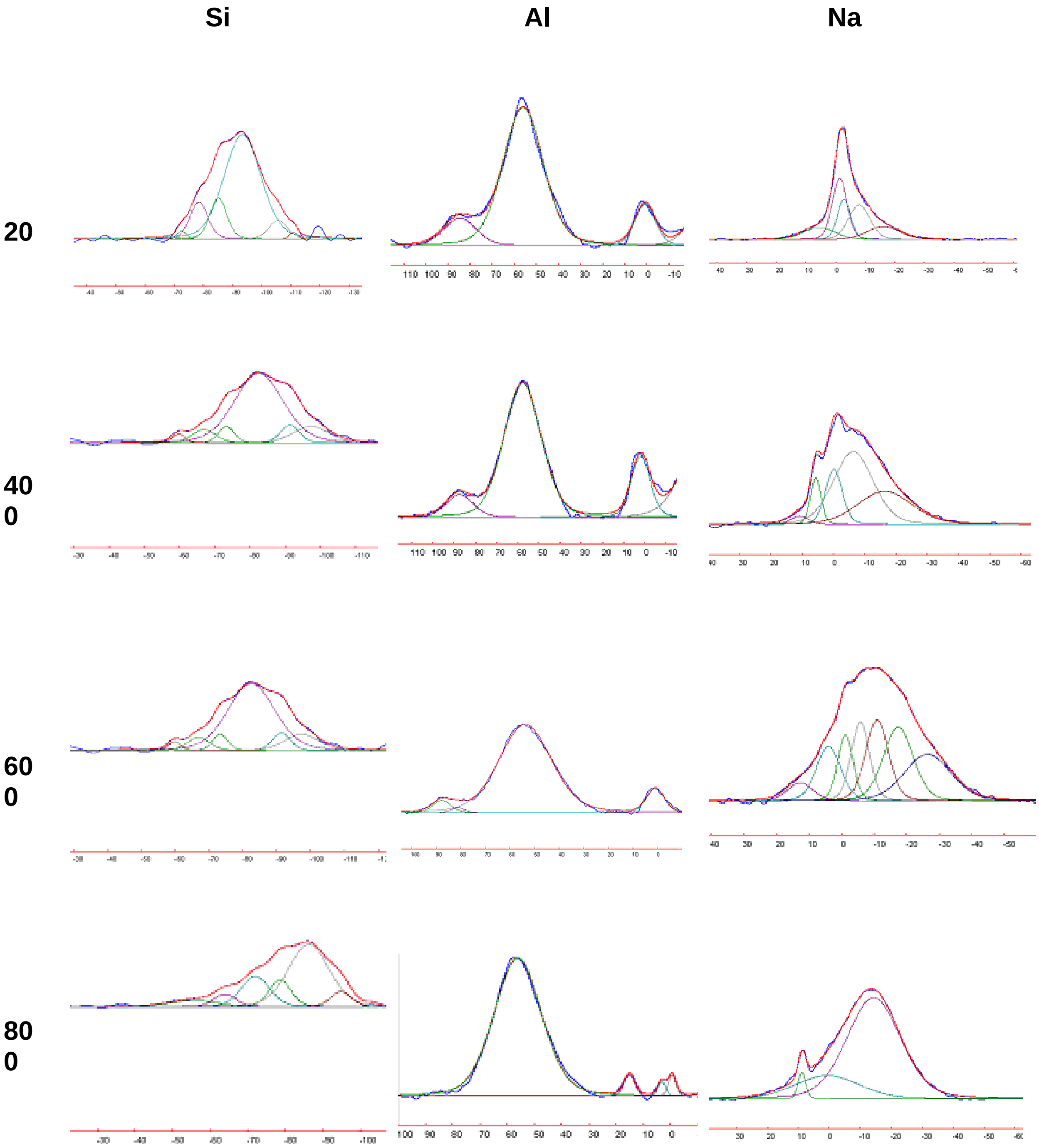

FIG. 8 NMR MAS spectra of the geopolymer in dependence on temperature

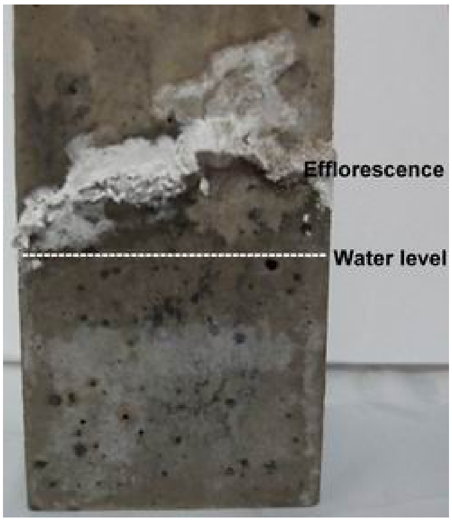

FIG. 9 Typical efflorescences on the geopolymer surface kept in a humid environment.
The efflorescences are composed of hydrates of the type $Na_2CO_3 \cdot n\,H_2O$, $Na_6(SO_4)(CO_3, SO_4) \cdot n\,H_2O$.

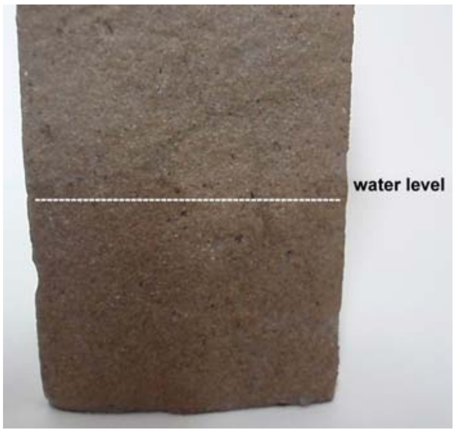

FIG. 10 Geopolymer after firing at 800 C, without any efflorescences formed in a humid environment

Na present in the geopolymer compensates the negative charge of Al in the Si-O-Al structure. It is probable that Na is rather bonded in the geopolymer in the form of $Na(H_2O)_n^+$ than as Na^+. The $Na(H_2O)_n^+$ bond is weaker than that of Na^+. Hence, this fact creates favourable conditions for the Na leaching from the geopolymer structure thus favoring the geopolymer tendency to the formation of efflorescences. 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. The formation of efflorescences is thus prevented as this is demonstrated in fig 9., 10.

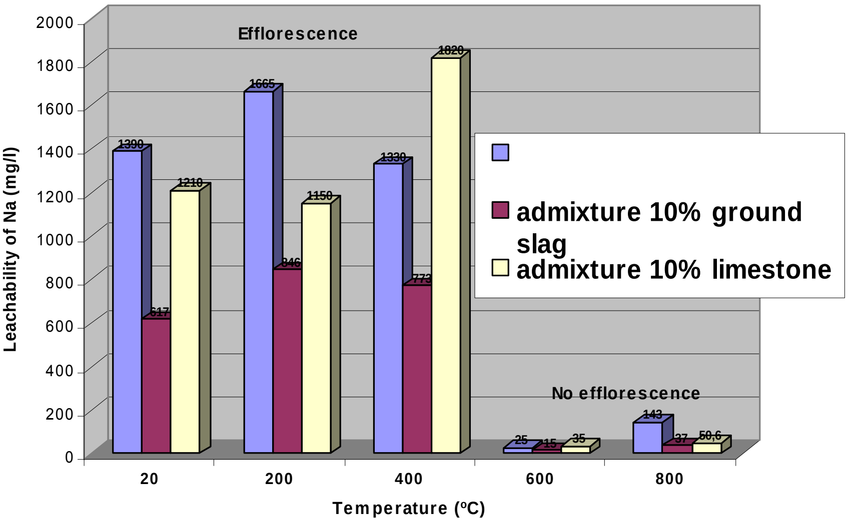

FIG. 11 Na leaching from a geopolymer (mortar) in dependence on firing temperature

A visible formation of efflorescences can be prevented by replacing sodium with potassium during the alkaline activation because K_2CO_3 does not give rise to visible hydrates. Nevertheless, the K leaching from the geopolymer structure is comparable or even larger (in dependence on the preparation conditions of geopolymers) than that of Na as this is demonstrated by results obtained by other workers [18, 19]. Furthermore, the strength values of fly ash-based geopolymers subjected to a potassium-containing activating agent are substantially smaller than those obtained with a sodium-containing one [20].

Acknowledgements

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