Aluminosilicate polymers

Škvára, F., Šmilauer V., Kopecký L.

Prof. RNDr.František Škvára DrSc, ICT Prague, Faculty of Chemical Technology,
Department of Glas and Ceramics, 16628 Praha 6 , Technická 5,
skvaraf@vscht.cz

The inorganic material prepared by alkali activation (mixture of NaOH and Na silicate) of the Al,Si raw material (brown-coal fly ash) is a porous body containing aluminosilicate polymer (N-A-S-H gel, geopolymer). The heterogeneous microstructure of the N-A-S-H gel that forms during the alkaline activation was examined by means of XRD, TGA, DSC, BET, MIP, FTIR, NMR MAS (^{29}Si, ^{27}Al, ^{23}Na), ESEM, EDS, EBSD and microcalorimetry.

Composition of N-A-S-H gel, determined by EDS analysis is represented by Na_2O/SiO_2 ratio in range from 0.1-0.3 and Al_2O_3/SiO_2 ratio from 0.25-0.35. The ^{29}Si NMR spectrum of N-A-S-H gel has the shifts at −85.2, −78.5ppm revealing the coordination of SiQ_4(3Al) and the shift at −93.5ppm of SiQ_4(2–3Al) coordination. The shift at −105.7ppm as a coordination of SiQ4(0Al) is less represented; thus in fact it reveals the penetration of Al atoms into the $[SiO_4]^{4-}$ network structure. The ^{27}Al NMR spectrum displays a dominant peak at 56ppm corresponding to AlQ_4(4Si) and minor shifts at 84.6ppm and 1.5ppm. The latter corresponds to octahedral Al, revealing the remnants of mullite incorporated into the N-A-S-H gel from fly ash. The main shifts of the ^{23}Na NMR spectrum occur at −1.4, −2.8 and −8.0 ppm, plus weaker shifts at 5.6, −16.2ppm. These shifts of Na are very similar to that of the structures of hydrated Na-aluminosilicate glasses. We can deduce that the bond of Na in N-A-S-H gel is in the form of $Na(H_2O)_n^+$, where n = 2–8. The Na bond in the N-A-S-H gel structure is weak, which is reflected in the tendency of N-A-S-H gel materials to the formation of efflorescence's in humid environments.

The X-ray diffraction analysis revealed no additional crystalline phases associated with N-A-S-H gel formation. The N-A-S-H gel loses continuously its mass (the water content drops) on heating up to a temperature of 400-600^o C. The water is probably present as "free" water in micropores, then in gel pores and as OH^- groups at the end of Si-O-Al chains. The porosity of the N-A-S-H gel 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. ASP porosity (determined by BET) also develops pores in the nanometric region (2 to 5 nm). Total porosity of N-A-S-H gel is between 20% and 40%. Alkali-activation of the fly-ash is perceived as the volumetric evolution of elastically-invariant components. Nanoindentation technique identified the intrinsic Young's modulus of N-A-S-H gel as ~18 GPa, which was further downscaled to the solid gel particles.

As^{3+}, As^{5+} and Cr^{6+} are weakly bonded in the N-A-S-H gel matrix, while excellent immobilization of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Cr^{3+} are reported.

Aluminosilicate polymer materials exhibit excellent material properties, The values of the compressive strength 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.