

INSITU SAXS/WAXS STUDY OF THE DEVELOPING PROCESS OF GEOPOLYMER STRUCTURES

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Abstract

Geopolymers with different chemical composition have been prepared at 70°C. The processes of geopolymerization have been investigated insitu by simultaneous WAXS and SAXS measurements. WAXS shows that the developed structure of the geopolymers is mostly amorphous, and its structural arrangement strongly depends on the chemical composition of the used suspension. During the evaluation process the SAXS data were analyzed by using a fractal approach. The fractal dimensions are in the range from 2.2-3.3. The developed geopolymeric structure was confirmed by FTIR.

1 Introduction

During the last decade a new kind of material called geopolymer has emerged as a viable alternative for many conventional cements and concrete. Geopolymer is an inorganic polymer usually derived by mixing metakaoline (MK), fly ash (FA) or/and granulated blast furnace slag (GBFS) with an the alkali activation solution (AAS). AAS is composed from sodium/potassium silicate solution (water glass) and sodium/potassium hydroxide.

Geopolymers may be synthesized at ambient or elevated temperature [1-3]. The main characteristics of the geopolymers which attract many scientists to study them are very good mechanical properties, excellent thermal resistance as well as good resistance to the influence of acids and alkali solution [2-5]. The thermal stability up to 1150°C gives an advantage to geopolymers which can be used as building materials, instead of ordinary Portland cement which loses its mechanical properties above 500°C [5-7]. The preparation of geopolymers from waste materials like FA and GBFS at low temperature results in lower costs, and has a positive influence on the environment by reducing waste materials.

The process of geopolymerization is very complex. All developed models of geopolymerization suppose that the process starts with the dissolution of amorphous aluminosilicate and silica species present in the raw material, which requires a high pH value (8-12) and is "time consuming". An extra addition of soluble silicate from water glass has a catalytic role in the process of geopolymerization [8,9].

Geopolymers, also called polysilates, are amorphous to semi-crystalline three-dimensional aluminosilicate polymers. They are also referred to as alkali-activated aluminosilicate binders and comprise three classes of inorganic polymers that, depending on the silica to alumina ratio, are based on the following three different monomeric units: (-Si-O-Al-O-) polysilicate (PS), $\text{SiO}_2/\text{Al}_2\text{O}_3=2$; (-Si-O-Al-O-Si-O-) polysilatesiloxo (PSS), $\text{SiO}_2/\text{Al}_2\text{O}_3=4$; and (-Si-OAl-O-Si-O-Si-O-) polysilatedisiloxo (PSDS), $\text{SiO}_2/\text{Al}_2\text{O}_3=6$. The general formula to describe the chemical composition of these mineral polymers is $M_n[-(\text{SiO}_2)_z-\text{AlO}_2]_n \cdot w\text{H}_2\text{O}$ where z is 1, 2 or 3 and M is an alkali cation (such as Na^+ or K^+), n is the degree of polymerization and w is the water content[9-13].

In this experimental work the geopolymeric reaction has been conducted in a polydispersion heterogeneous system of metakaoline - solution silicate (water glass) - water - alkali hydroxide. The materials were characterized by simultaneous insitu SAXS/WAXS, and the developed structure and microstructure was investigated also by Scanning Electron Microscopy (SEM) and Fourier Transformed Infrared Spectroscopy (FTIR).

2 Materials and testing methods

2.1 Metakaoline

The used metakaoline was prepared by calcination of kaolin (Carlo Erba). The calcination of kaolin was performed in a laboratory furnace at 750°C for 8 hours. The obtained metakaoline was kept in a plastic bottle up to the beginning of the experiment. X-Ray powder diffraction pattern of the produced metakaoline (Figure 1.) show the diffuse diffraction maximum centred at $2\theta=24.3^\circ$ due to presence of the amorphous phase of the aluminosilicate, which is the main reactant in the preparation process of geopolymers. According to the chemical analysis the chemical composition of the metakaoline can be expressed by the element composition, and is 45.09 % (O), 23.00 % (Al), 29.50 % (Si), 1.74 % (K) and 0.68 % (Fe).

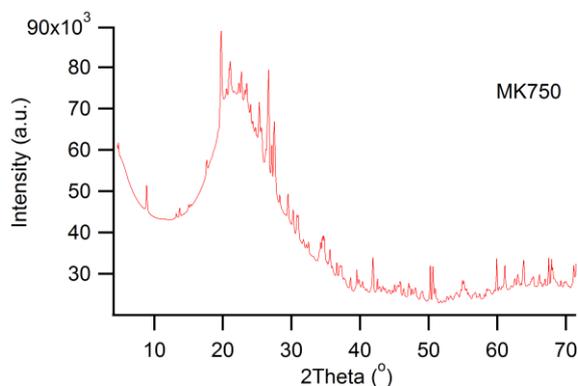


Figure 1. XRD powder pattern of metakaoline

2.2 Alkaline activator solutions

Alkaline activator solutions were prepared by mixing sodium hydroxide and sodium silicate together. The sodium silicate solution used in the experiment is the commercially available sodium silicate produced by Matrix co. The chemical composition of sodium silicate was: SiO_2 (26.5 %), Na_2O (12 %) and H_2O (62%) with specific mass of 1.41 g/cm^3 . The NaOH concentration in sodium silicate solution, determined by titration, was 3 mol/dm^3 . The sodium hydroxide solution was prepared by dissolving NaOH pellets in ultra-pure water in order to achieve a concentration of 16 mol/dm^3 in the solution.

2.3 Geopolymer samples preparation

Geopolymers have been prepared by mixing powder of metakaoline, alkaline activator solution and water. The sample series D1 was prepared from a suspension composed to satisfy the concentration of sodium hydroxide ($c(\text{NaOH})=9.85 \text{ mol/dm}^3$) and the ratios of $\text{SiO}_2 / \text{Al}_2\text{O}_3 = 3.31$, $\text{Na}_2\text{O} / \text{Al}_2\text{O}_3 = 0.90$, $\text{Na}_2\text{O} / \text{SiO}_2 = 0.27$ and $\text{H}_2\text{O} / \text{Na}_2\text{O} = 5.44$. The series D14 was prepared from a suspension composed to satisfy the concentration of sodium hydroxide ($c(\text{NaOH})=10.31 \text{ mol/dm}^3$) and the ratio of $\text{SiO}_2 / \text{Al}_2\text{O}_3 = 4.13$, $\text{Na}_2\text{O} / \text{Al}_2\text{O}_3 = 1.72$, $\text{Na}_2\text{O} / \text{SiO}_2 = 0.42$ and $\text{H}_2\text{O} / \text{Na}_2\text{O} = 5.10$. Freshly prepared samples have been kept at room temperature in sealed polyethylene cups, for at least 6 hours. Just before the SAXS/WAXS measurement on the SAXS beamline, the samples were mounted on a thermostated sample holder. This sample holder maintained the temperature during the thermal activation process of geopolymerization at the constant value of 70°C .

2.4 Methods used in the characterization of geopolymers

In situ time resolved SAXS/WAXS measurements have been performed at the Austrian SAXS beamline at the Sincrotrone Trieste. The sample to detector distance has been 2082 mm and the used photon energy 8 keV ($\lambda=1.5 \text{ \AA}$). The SAXS and WAXS data have been collected simultaneously by a MAR300 Image Plate and a Pilatus 100k detector, respectively. The exposition time for the SAXS signal was 1-2 seconds and for WAXS 10 seconds.

The FTIR spectrums have been performed with a Perkin Elmer spectrophotometer (Spectrum One model). The spectrums have been obtained with the KBr method in the wavenumber range $4000 - 400 \text{ cm}^{-1}$ and with resolution of 4 cm^{-1} . The microstructure of the geopolymer samples was investigated by Scanning Electron Microscopy (SEM).

3 Results and discussion

SEM investigation shows that the microstructure of the prepared geopolymers is heterogenic and mostly build-up from smallest particles which possess an irregular spherical shape; but also larger structures with irregular shape which look like sheets (Figure 2).

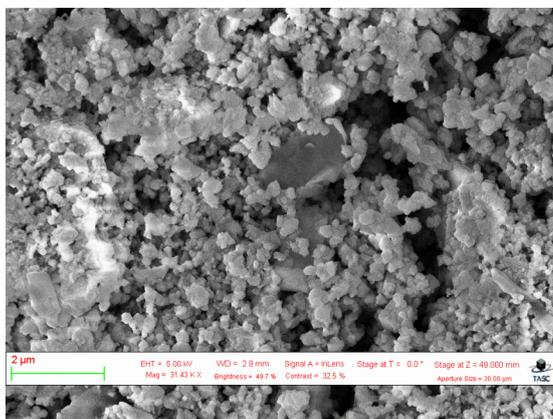


Figure 2. SEM microphotograph of the developed geopolymer structure

The progress of the geopolymerization process was observed in situ by simultaneous WAXS and SAXS performed on the same sample. The obtained WAXS results are shown in Figure 3 for two series denoted as D1 and D14. In the same figure is presented the WAXS pattern of metakaoline (MK750). From the first frame obtained (immediately after the start of the SAXS/WAXS experiments) it becomes clear that the curing period of the mixture (at room temperature) was long enough that the process of geopolymerization had progressed so far that a new amorphous geopolymer phase had developed. This observation was expected, and the main purpose why freshly prepared mixtures have to be kept at room temperature (or

lower) is to give time for dissolving the solid amorphous aluminosilicate phase from the metakaoline. Only when we have enough dissolved aluminosilicate and enough solution of water glass the geopolymerization can start in the right direction, and this observation is in agreement with the literature.[1] The WAXS pattern of the sample denoted as MK750 is characterized by a very diffuse diffraction maximum centred at 2Theta 24.3° which arises from amorphous aluminosilicate. A second diffuse diffraction maximum which belongs to the product of geopolymerization is centred at 29.4° (in the series D1) and 30.6° (in the series D14).

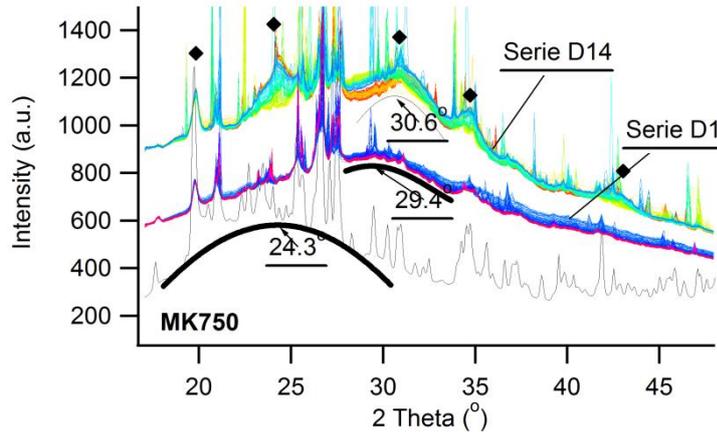


Figure 3. WAXS patterns of the geopolymers series denoted as D1 and D14, prepared at 70°C (with up to 12 hours of geopolymerization). The black line shows the WAXS pattern of metakaoline, and the peaks marked with ♦ are characteristic for Sodalite (PDF 037-0476)

The different positions of the diffuse diffraction maxima indicate different structural arrangements for the series D1 and D14. Another difference in the WAXS pattern is that only the D14 series shows in addition to the dominant diffuse diffraction maximum at 2Theta =30.6 another three correlated diffuse diffraction maximums at the positions 2Theta=24.2°, 34.9°, 42.9°. The positions of these diffraction peaks suggest the presence of structural forms, which are isostructural with the sodalite crystal form (empirical formula Na₄Al₃Si₃O₁₂Cl). This observation is in agreement with a previous observation [11].

The final plotted SAXS data, i.e. the so-called scattering curves, are actually the dependences of the macroscopic differential scattering cross-section:

$$\frac{d\Sigma}{d\Omega}(q) = I(q) \quad (1)$$

where dΣ is the area, dΩ the solid angle, I is the scattering intensity and q is the modulus of the scattering vector.

$$q = \frac{4\pi \sin\theta}{\lambda} \quad (2)$$

Where λ is wave length, 2θ is the scattering angle.

The interpretation of the scattering curves relies, among others, on their analytical behaviour in different q regions. The SAXS measurements can determine whether the scatterers are fractal, and allow the estimation of the fractal dimension D by analysing the scattering power law. In Figure 4 and 5 are shown the scattering curves obtained for the series D1 and D14. These scattering curves were analysed in terms of fractals with the following relation:

$$I(q) \sim \frac{d\Sigma}{d\Omega}(q) = C \cdot q^{-\alpha} \quad (3)$$

where C is the Pareto constant (for the fractal region), and α is the slope of the scattering curve in the log-log plot of the intensity $I(q)$ versus q .

The magnitude of the exponent α is directly related to the value of D. The value of the exponent alpha in (3) allows us to distinguish whether there are volume ($D_v = \alpha$, $2 < \alpha < 3$) or surface ($D_s = 6 - \alpha$, $3 < \alpha < 4$) fractals, respectively [14-16].

The analysis of the SAXS scattering curves indicates two areas that correspond to two different surface fractals dimensions, in both series D1 and D14. For the series D1, the characteristic of q -value ranges for the two fractal dimensions are denoted as A1 ($0.10 \leq q \leq 0.20 \text{ nm}^{-1}$) and A2 ($0.34 \leq q \leq 0.64 \text{ nm}^{-1}$) in Figure 4. The change of the fractal dimensions in dependence of the reaction time indicates that a major change of the fractal dimension has happened in the early phase of the geopolymerization process (up to 4 hours), while after this period the fractal dimensions remain almost constant. The final values for the fractal dimensions $D_s(A1) = 2.4$ and $D_s(A2) = 2.2$.

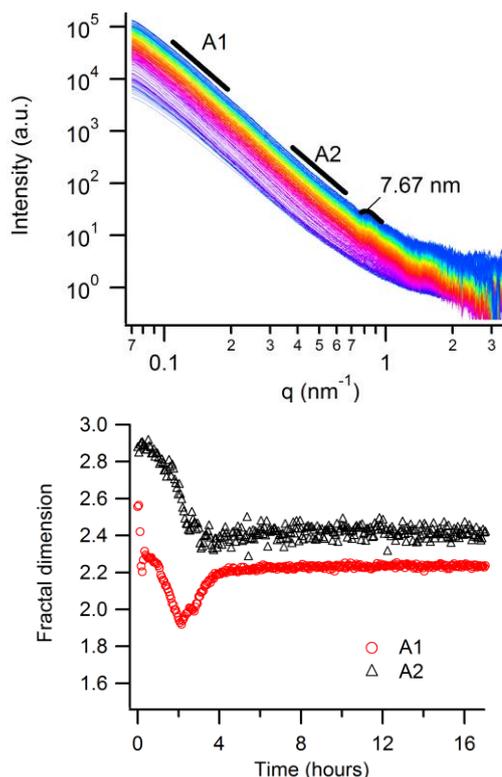


Figure 4. SAXS curves (top), and fractal dimensions in the range of A1 and A2 (below) in dependence of the geopolymerization time for the series D1

In Figure 5 are shown the SAXS curves of the series D14: the first fractal denoted as B1 appears in the region $0.09 \leq q \leq 0.18 \text{ nm}^{-1}$ and the second fractal denoted as B2 in the region $0.36 \leq q \leq 0.80 \text{ nm}^{-1}$. Compared to series D1, the series D14 shows much more fluctuations of the fractal dimension, and has a longer period of the geopolymerization process (up to 11 hours). The final value of the fractal dimensions are $D_s(B1)=2.8$ and

$D_s(B2)=2.3$. The SAXS curves show further, that after 8 hours starts to appear a new phase at the position $d=7.67\text{nm}$ (series D1), and $d=7.32$ and 6.42 nm in series D14.

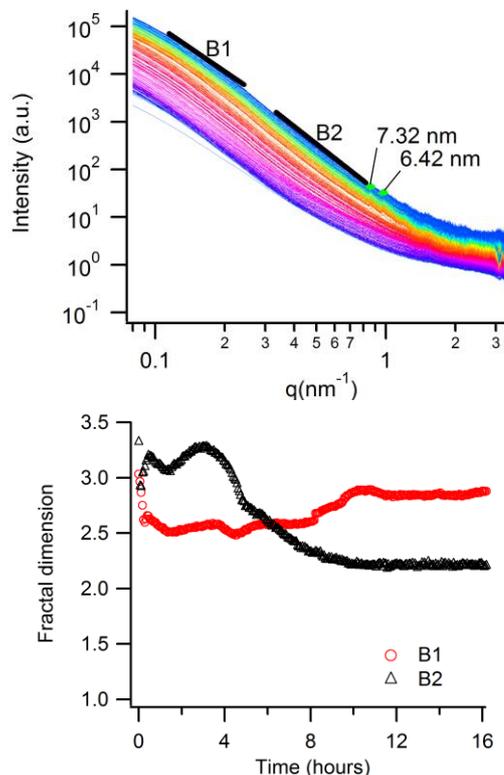


Figure 5. SAXS curves (top), and fractal dimensions in the range of B1 and B2 (below) in dependence of the geopolymerization time for the series D14

FTIR spectra of the geopolymers series D1 and D14 and also from the pure metakaoline are shown in Figure 6. The results indicate that all geopolymer samples are showing almost the same spectroscopic behaviour. These FTIR confirm the presence of the geopolymer phase in all samples. The very broad absorption band centred in the range $3450\text{--}3454\text{ cm}^{-1}$ is associated to stretching of H-O-H also followed by a strong absorption band centred at $1647\text{--}1655\text{ cm}^{-1}$ which arises from the free and bound water.

In the low-wavenumber region, for the spectrum of MK750 (Figure 6), the bands around 475 and 800 cm^{-1} are assigned to the T-O (T = tetrahedral Al or Si) bending modes in the TO_4 tetrahedra [17]. The band at 701 cm^{-1} in the geopolymer spectra indicates the formation of Al^{IV} as the main Al environment in the polymer. The most intensive band in the geopolymeric materials which appears in the range $979\text{--}991\text{ cm}^{-1}$ represents the asymmetric vibration of the oxygen linkages between the tetrahedra in the geopolymeric structure, whereas the band at 1055 cm^{-1} is assigned to the stretching mode of the internal tetrahedra. A weak band around 840 cm^{-1} was observed in all geopolymer mixtures and is assigned to the bending vibration of Si-OH, this same band was not found in the FTIR spectrum of metakaoline [18].

In the mid-wavenumber region ($600\text{--}1400\text{ cm}^{-1}$), after the geopolymerization of the metakaoline, appear two new bands at 1055 cm^{-1} and $979\text{--}991\text{ cm}^{-1}$ which are the most notable changes in the spectra. The very broad bands from MK750, with the principle band centered at 1082 cm^{-1} are associated with the Si-O-T asymmetric stretching mode of the original metakaoline (MK750), and are shifted in the process of geopolymerization to a lower frequency, and appear as boarded bands with the principle band at $979\text{--}991\text{ cm}^{-1}$. The absorption band in the region of $979\text{--}991\text{ cm}^{-1}$ is assigned to the asymmetric stretching

vibration of the Si–O–T links in the geopolymer framework. This band shifting is usually considered to be due to the formation of geopolymers and is considered as finger print for the determination of the process of geopolymerization. The presence of the absorption band at 1050 cm^{-1} means that probably one part of the unreacted metakaoline still remains in the hardened material but under different surroundings. The shift in the Si–O–T component peak to a lower wavenumber indicates a higher degree of Al conversion from non-tetrahedral environments in metakaoline to tetrahedral environments bonded to Si in the geopolymer framework. The very weak absorption band at about 1438 cm^{-1} that appears in geopolymers is characteristic for the C–O carbonate asymmetric stretching and indicates the presence of Na_2CO_3 , which is forming under atmospheric influence on geopolymer samples [12].

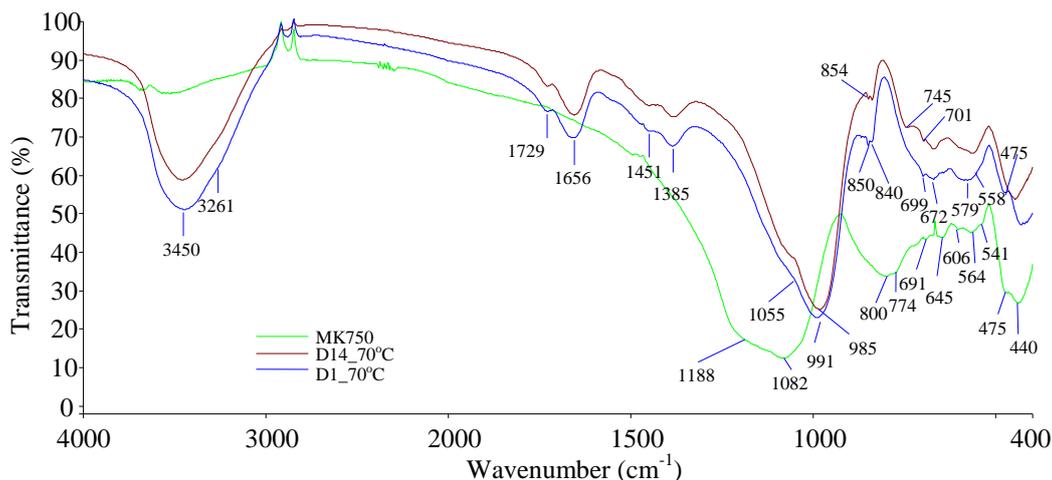


Figure 6. FTIR spectrums of MK750, and the geopolymers D14 and D1.

4 Conclusions

Metakaoline obtained from kaolin at 750°C by calcination is a suitable material for preparing geopolymers. WAXS measurements confirm that the period of the suspension precondition at room temperature, before of thermal activation, contributes to the formation of geopolymers and further that the thermal activation accelerates it. The geopolymers D1 and D14, synthesized at 70°C , are amorphous, but the different 2θ positions of the diffuse diffraction maxima show that their structural arrangements are different. Although the geopolymers in the series D14 are amorphous they possess a small amount of crystalline phase the content of which increases with the reaction time. This crystalline phase is isostructural with sodalite form. The SAXS analysis confirmed that the geopolymerization process is quite dynamic at the beginning of the thermal activation and that major changes occur in the systems D1 up to 4 hours after thermal activation and in D14 up to 11 hours. The obtained geopolymers are amorphous, but have a fractal structure with different fractal dimensions in the range of 2.2-3.3. Further after 8 hours appear in the SAXS images different new phases with dimensions of 7.67 nm in the series D1 and 7.32 and 6.42 nm in the series D14.

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