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Structural ordering of aged and hydrothermally cured metakaolin based potassium geopolymers

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Abstract: This study evaluates the potential correlation between natural aging and hydrothermal curing (accelerated aging), related to the crystallisation of zeolites in potassium-based metakaolin geopolymer binders. 5-year old sealed-cured specimens, formulated with varying silicate contents, were evaluated. The effect of different accelerated aging durations on the mineralogy of these potassium-based geopolymers was also assessed. The results show that although zeolite formation is favoured under both natural and accelerated aging in potassium-based geopolymers, different types of zeolites are formed depending on the silicate content added to the mix, and the curing conditions of the specimens.

1. Introduction

Geopolymer materials, produced from the chemical reaction between a poorly crystalline aluminosilicate source and a highly alkaline solution, have been the object of study for over half a century [1]. Metakaolin-based geopolymers were developed as ‘inorganic polymers’ with high fire resistance properties, but they have been gaining acceptance for a wide range of applications including as innovative matrices for radioactive waste cementation [2]. Particularly, geopolymer materials based on calcined clays provide highly desirable performance in the immobilisation of heavy metals, and key radionuclides including ^{137}Cs and ^{90}Sr .

In the context of nuclear waste disposal, cementitious grouts need to withstand hundreds of years of in-service conditions, with high stability under moderate temperature and/or pressure changes, depending on the final method adopted for their disposal. In metakaolin-based geopolymers, it is well known that the main binding phase (an alkali aluminosilicate gel), develops short range ordering with a pseudo-zeolitic structure [3]. Formation of crystalline phases has been identified in these materials over time, and this is accelerated by changes in temperature and/or pressure [4]. The bulk chemical composition of the mix design, and the type and dose of activator, also appear to have a significant influence on the crystalline phase formed. The mechanism of zeolite growth in metakaolin-based geopolymers is likely to resemble a gel-solid transformation via rearrangement of the precursor structure. Therefore, the rates of dissolution and polycondensation within these materials are expected to have a significant impact on the zeolite species present and the degree of crystallisation [5].

In this study, the mineralogy of two K-based metakaolin geopolymers cured for 7 years, under controlled laboratory conditions, is examined, and compared with that of geopolymers produced with similar formulations but cured under hydrothermal conditions, with the aim to simulate accelerated aging of the specimens, and determine potential structural changes in the long-term.

2. Experimental methods:

A commercial grade metakaolin (Metastar 402, Imerys UK) was used in this study, which contains 44.87 wt.% Al_2O_3 and 53.16 wt.% SiO_2 . Potassium hydroxide and silicate solutions (i.e. $\text{SiO}_2/\text{K}_2\text{O}=0.0$ and 0.25 respectively), with $\text{H}_2\text{O}/\text{K}_2\text{O}=11$ were prepared by dissolving potassium hydroxide flake and

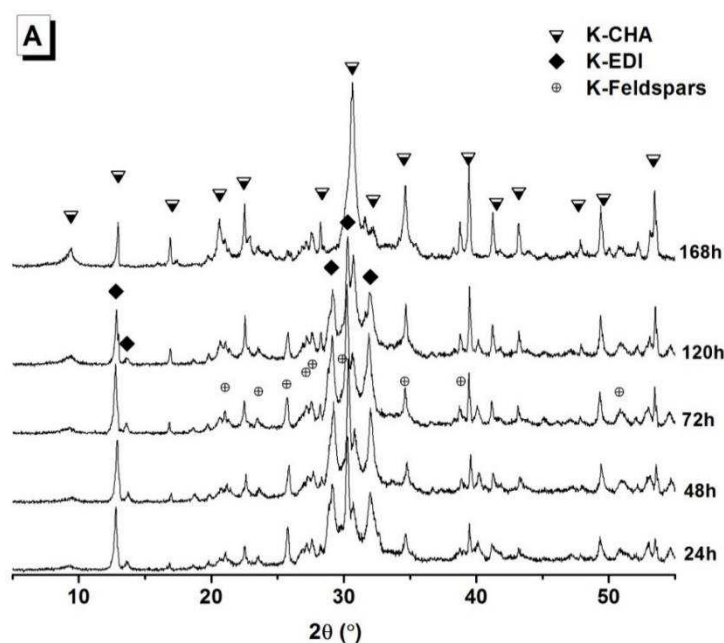
amorphous silica in Milli-Q water until clear. Solutions were stored for a minimum of 24 hours before use. Geopolymer samples were prepared by mixing stoichiometric amounts of metakaolin and activator solution to give a product with bulk $\text{Al}_2\text{O}_3/\text{K}_2\text{O}=1$. For all mix designs, the reagents were mechanically mixed for between 5 to 15 minutes until a homogeneous paste was achieved.

For geopolymers cured under ambient conditions, the freshly prepared geopolymer pastes were cured in a laboratory oven at 40°C first for 20 h, and then transferred into sealed containers for storage at ambient temperature (20-25°C) for 5 years until testing. For hydrothermal curing, a standard pressure cooker was used to achieve an internal temperature of 120°C and an internal pressure of ~2 atm, in a saturated steam environment. The freshly prepared geopolymer samples were firstly sealed in plastic containers containing 100 mL of water (no direct contact with the samples), and then put into the pressure cooker for hydrothermal curing. After 24, 48, 72, 120 and 168 hours of curing, the geopolymer samples were assessed.

Prior to testing, geopolymer samples were crushed and sieved (<67 μm). A Philips PW 1800 diffractometer with Cu $\text{K}\alpha$ radiation generated at 20mA and 40kV was used to evaluate the hydrothermally cured specimens, while a Bruker D8 Advance diffractometer with Cu $\text{K}\alpha$ radiation and a nickel filter was used to evaluate the naturally aged samples. All data were collected with a step size of 0.020°, over a 2 θ range of 5° to 70°.

3. Results and discussion:

Figure 1 shows the diffractograms of two K-based metakaolin geopolymers cured under hydrothermal conditions for different durations. Between the potassium hydroxide ($\text{SiO}_2/\text{K}_2\text{O}=0$) activated geopolymer and potassium silicate ($\text{SiO}_2/\text{K}_2\text{O}=0.25$) activated geopolymer, the structural evolution over the curing time is comparable, where the K-feldspar was formed after 24 hours of curing in both specimens, along with a transition zeolite phase, K-exchanged zeolite F (K-EDI), with a less ordered structure in the samples containing silicate after 48 h of curing. Traces of potassium chabazite (K-CHA) (powder diffraction file (PDF) #00-044-0250 and/or PDF#00-012-0194) are also observed in both specimens.



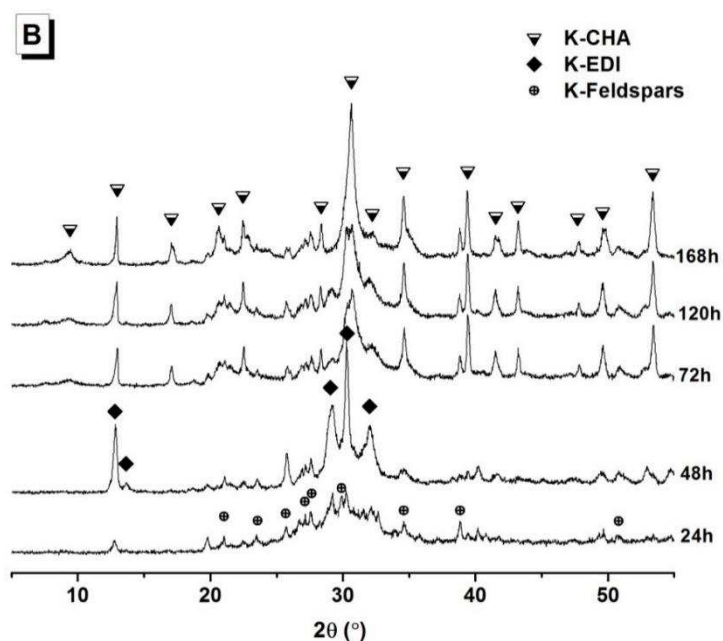


Figure 1 X-ray diffraction patterns of hydrothermally cured potassium-based metakaolin geopolymer with a $\text{SiO}_2/\text{K}_2\text{O}$ of (A) 0, and (B) 0.25; where K-CHA refers to potassium chabazite (similar to PDF#00-044-0250), K-EDI refers to K-exchanged zeolite F (PDF# 00-038-0216), and K-Feldspars refer to either sanidine (PDF# 00-025-0618) or orthoclase (PDF# 00-031-0966), both of which are monoclinic

These results elucidate the important role of silicate in crystallisation kinetics of the geopolymers assessed, where ordered K-EDI and K-Feldspar are observed in the potassium hydroxide activated geopolymer (Figure 1A) after 24 h, while the potassium silicate activated geopolymer remained mostly amorphous at this curing duration, with a small amount of K-Feldspar formed. However, at advanced times of hydrothermal curing, both samples present similar mineralogy. In the silicate-containing samples, the additional amorphous Si dissolved in the activator increases the viscosity of the solution, slowing down the mobility of dissolved ionic species [1]. This might be responsible for the delayed formation of crystalline phases. However at later times in the gel nucleation/growth reaction under hydrothermal curing conditions, the additional monomeric silica together with continuously dissolved ionic species favours the further polycondensation process of the geopolymer gel [5]. The formation of K-EDI (zeolite K-F, $\text{Si}/\text{Al}=1$) as a transient zeolite phase is likely related to the sufficient presence of alkali in the pore solution prior to the fully reaction of metakaolin [7]. Also, the potassium chabazite (zeolite K-G) formed in the two geopolymer specimens is likely to have different Si/Al ratios (Si/Al between 1 and 2) in the aluminosilicate framework of the chabazite phase formed, as a result of the differences in bulk chemical compositions [8].

Under ambient curing conditions for up to 7 years, as shown in Figure 2, zeolite EDI was also identified; however neither K-feldspar nor chabazite was observed. Instead, other zeolite group minerals are formed. Notable differences in crystallinity are observed between the potassium hydroxide and the potassium silicate activated geopolymer; the specimens containing silicate are notably less crystalline. A zeolite-type silica polymorph [9] and K-exchanged zeolite A are identified in the potassium hydroxide activated geopolymer, while leucite is forming in the potassium silicate activated geopolymer. The potassium silicate activated geopolymer also maintained a significant amount of poorly crystalline alkali aluminosilicate type gel ('geopolymer gel') after 5 years, observed as a diffuse hump at $\sim 30^\circ$ (2θ).

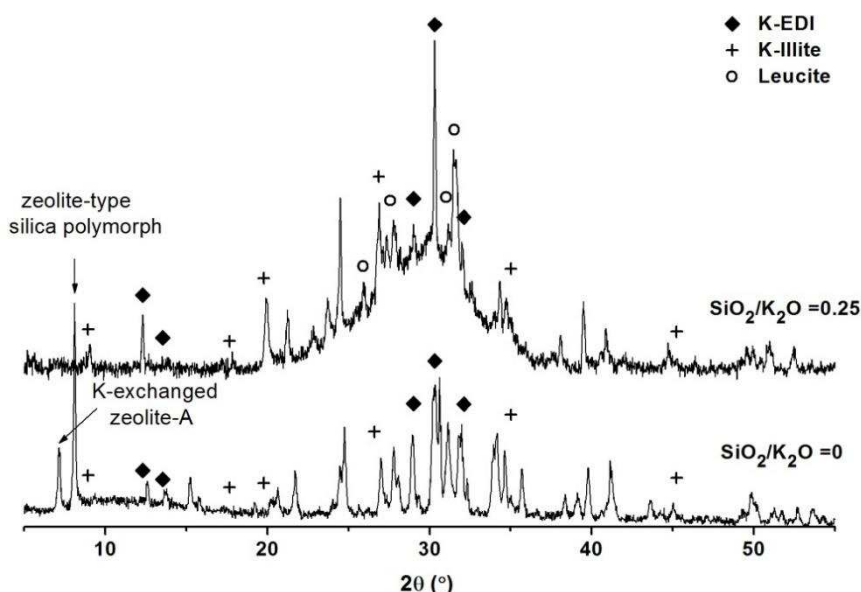


Figure 2 X-ray patterns of potassium geopolymer cured under ambient condition for 7 years, where K-EDI refers to K-exchanged zeolite F (PDF# 00-038-0216), and other phases are K-illite (PDF# 00-026-0911), leucite (PDF# 00-049-0619), K-exchanged zeolite A (PDF# 01-082-2070), and zeolite-type silica polymorph (PDF# 01-085-0462)

4. Conclusion

Formation of zeolite type phases is favoured in potassium-based metakaolin geopolymers, particularly those produced using a hydroxide type activator. Using silicate-containing activators favours formation of a less ordered structure, which remains almost unchanged after 5-years of curing. Under hydrothermal curing conditions, using a silicate activator delays the formation of zeolite type phases. The fact that different types of zeolites were identified in naturally aged and hydrothermal cured samples, indicates the marked influence of differences in time, temperature, and potentially also pressure during curing influencing the nucleation stage of the crystallisation process of these materials, which is of great importance within the context of nuclear waste disposal.

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