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## WHAT HAPPENS TO 5-YEAR OLD METAKAOLIN GEOPOLYMERS? THE EFFECT OF THE ALKALI CATION

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### ABSTRACT

In this study we report X-ray diffraction and dilatometry results of metakaolin (MK) geopolymers produced with Na, K, Rb or Cs silicate solutions, and cured for 7 days and 5 years, with the aim of identifying variations in structure and performance (dimensional stability at elevated temperature) over an extended curing period at ambient temperature. All of the geopolymers studied are mainly X-ray amorphous after 5 years of curing; however, in Rb-based and Cs-based geopolymers formation of aluminosilicate crystalline phases was identified. As the alkali cation radius increases, so does the thermal stability of the MK-geopolymer, potentially as a consequence of the combined effect of the higher degree of ordering of the geopolymer itself, which might retard the dehydration of the geopolymers upon heating, and the reduced energy of hydration of larger alkali cations. The 7-day and 5-year cured samples produced with Rb and Cs silicate solutions do not exhibit significant dimensional changes above 300°C, with a maximum shrinkage of < 2% after exposure to 1100°C. This shows that increasing the radius of the alkali cation during geopolymerisation of MK has an effect on the thermal stability of these materials, and promotes the formation of a highly densified and rigid structure at advanced curing ages.

### 1. INTRODUCTION

Metakaolin (MK), derived from dehydroxylation of kaolinite clays upon thermal treatment, is one of the main aluminosilicate precursors used in the production of geopolymers [1]. These materials are produced via a chemical reaction of a poorly crystalline aluminosilicate source and a highly concentrated alkaline solution, forming a hardened solid with a disordered pseudo-zeolite type structure [2]. MK-geopolymers have been extensively studied over the past 50 years, however, most studies have been focussed in the performance of these materials over a short period of curing (days to weeks), and limited attention has been paid to their longer-term structural evolution.

The kinetics of reaction and microstructural features of MK-geopolymers are strongly dependent on the characteristics of the MK used [3], along with the overall SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of the system [4], and the type and concentration of the alkaline activator. Specifically, the alkali metal cation present in the activator influences the dissolution, polycondensation kinetics, and the consequent geopolymer gel and crystal formation processes. This is a

consequence of the role of the alkali cations in the ordering of water and dissolved Al and Si complexes in solution, as well as their structural directing role in geopolymerisation.

The most widely used activators are solutions of sodium and/or potassium hydroxides and/or silicates [5]. Na<sup>+</sup> and K<sup>+</sup> have the same overall electric charge, but different charge densities as a result of their different radii, and so they have different effects in the geopolymerisation process and the microstructure of the material formed. This is associated with the different ionic sizes of these cations, which affects charge density and hydration [6]. It has been identified [7] that potassium-based geopolymers have greater compressive strength compared with sodium-based geopolymers synthesised from alkali-feldspar/kaolinite matrices, as a consequence of a higher polymerising activity between silicate and aluminosilicate species when using K-based activators. In a NaOH solution compared with KOH, it is expected that Na<sup>+</sup> with a smaller cation size will be more active in inducing dissolution than K<sup>+</sup>, resulting in a higher extent of reaction of silicate and aluminate precursors. However, it has been demonstrated [8] that there is also an ion pairing effect taking place in these systems. Metal cations with a smaller size and a higher positive charge favour ion pairing with smaller silicate oligomers such as monomers, dimers or trimers [8]. Therefore, Na<sup>+</sup> has a greater ability to stabilise silicate monomers, while the larger K<sup>+</sup> cation will stabilise silicate oligomers.

The effects of larger alkaline cations such as Cs and Rb on the structure of MK-geopolymers have attracted less attention than Na<sup>+</sup> and K<sup>+</sup>, mainly due to the high cost of the hydroxide solutions containing these alkalis. However, MK-geopolymers have been identified as one of the most promising immobilisation matrices for alkali metal radionuclides such as <sup>135</sup>Cs and <sup>137</sup>Cs, which are highly leachable from Portland cement based wastefoms. Therefore, it is of great interest to understand the role of Cs in these systems. The few reports on activation of MK with CsOH or Cs silicate demonstrate that the chemical binding of Cs to the geopolymer network is feasible, favouring the formation of crystalline phases including pollucite [9, 10]. On the other hand, no information is recorded in the literature regarding rubidium hydroxide activation of MK geopolymers.

In the contexts of nuclear waste disposal, cementitious matrices must retain performance for decades and even centuries, and therefore it is important to evaluate aged materials to understand the changes in phase assemblage and binder structure that can take place over a period of years after casting. In this study Na, K, Cs and Rb metakaolin geopolymers after 7 days and 5 years of curing were evaluated through X-ray diffraction and dilatometry.

## 2. EXPERIMENTAL METHODOLOGY

A commercial metakaolin (Metastar 402, Imerys UK) was used to produce geopolymers. The BET surface area of the metakaolin was 12.7 m<sup>2</sup>/g, and the mean particle size (d<sub>50</sub>) was 1.58 μm. Reagent-grade alkali hydroxides (NaOH, KOH, RbOH and CsOH) were purchased from Sigma-Aldrich (Australia), and alkaline silicate solutions with a molar ratio SiO<sub>2</sub>/M<sub>2</sub>O (M= Na, K, Cs or Rb) of 1.0 and H<sub>2</sub>O/M<sub>2</sub>O = 11 were prepared by dissolving fumed silica (Aerosil 200) in appropriate hydroxide solutions until clear. Solutions were stored for a minimum of 24 hours before use. All geopolymer samples were formulated with an overall Al<sub>2</sub>O<sub>3</sub>/M<sub>2</sub>O molar ratio of 1.0 and Si/Al = 1.5, considering the chemical composition of the MK and the alkaline solution used. The geopolymer pastes were produced by mechanically mixing the MK with the activator for 15 minutes, using a high shear mixer. Samples were

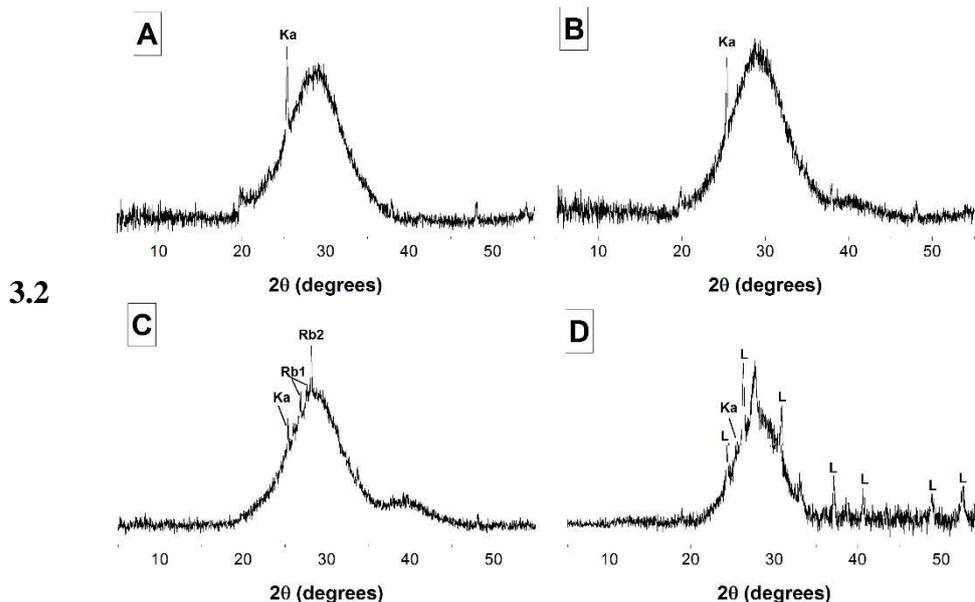
transferred to polymeric moulds and vibrated for 15 minutes to remove entrained air. All samples were cured in a laboratory oven at 40°C for 20h, and then transferred into sealed containers for storage at ambient temperature (20°C-25°C) until testing.

After 7 days and 5 years of curing, samples were crushed and sieved (<67 µm). A Philips PW 1800 diffractometer with Cu K $\alpha$  radiation was used for studying 7-day cured samples, while 5-year cured samples were analysed using a Bruker D8 Advance instrument with Cu K $\alpha$  radiation and a nickel filter. All data were collected with a step size of 0.020°, over a 2 $\theta$  range of 5° to 70°. Dilatometry measurements were performed on a Perkin Elmer Diamond Thermomechanical Analyser (TMA), using cylindrical samples with 5 mm diameter and 10mm height, at a constant heating rate of 10°C/min, a constant load of 50 mN, and a nitrogen purge rate of 200 mL/min.

### 3. RESULTS AND DISCUSSION

#### 3.1 X-ray diffraction

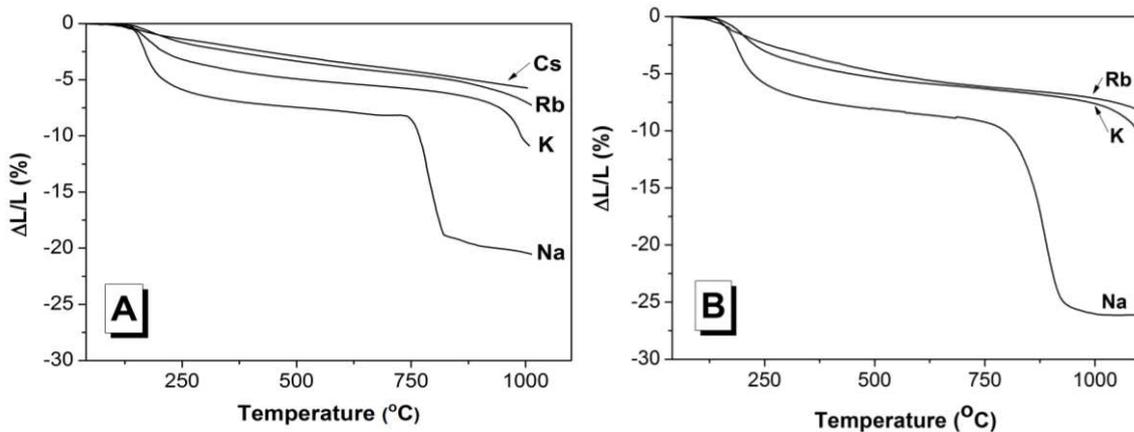
All 7-day cured samples were X-ray amorphous, with the exception of remnant crystalline components in the commercial metakaolin (data not shown). In all 5-year old samples (Fig 1) an amorphous hump between 18 < 2 $\theta$  < 45° is identified, consistent with the literature for metakaolin geopolymers. In the Na-based (Fig 1A) and K-based (Fig 1B) geopolymer the only crystalline phase present is kaolinite-1A (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>; powder diffraction file, PDF, # 014-0164, marked Ka in Fig 1A,B). Conversely, in the Rb-based geopolymer, the crystalline phases RbAlSi<sub>2</sub>O<sub>6</sub> (marked Rb1 in Fig 1C) (PDF#028-1077) and RbAlSiO<sub>4</sub>·H<sub>2</sub>O (Rb2 in Fig 1C) (PDF#030-1043) are present, while in the Cs-based geopolymers formation pollucite (CsAlSi<sub>2</sub>O<sub>6</sub>) (PDF#04-013-2101, L in Fig 1D) is observed. These results elucidate that the use of activating solution with larger alkali cations promotes the formation of crystalline products in MK-geopolymers during an extended period of curing.



**Figure 1.** X-ray diffractograms of 5-year cured MK geopolymers formulated with a Si/Al ratio of 1.5, activated with (A) Na, (B) K, (C) Rb and (D) Cs silicate solutions

### 3.2 Dilatometry

Consistent with previously studies [11-13], the 7 day cured Na-geopolymer shows (Fig 2A) a slight shrinkage between approximately 100 and 300°C, corresponding to the collapse of some of the pores as the pore water evaporates. This is followed by a period of slow and constant shrinkage from 300-700°C corresponding to the physical contraction resulting from dehydroxylation, with condensation of silanol or aluminol groups on the surface of the geopolymeric gel leading to the release of water and the creation of Si-O-T (T: tetrahedral Si or Al) linkages [12, 14]. Thermal shrinkage then accelerates significantly at temperatures above 700°C, via viscous sintering.

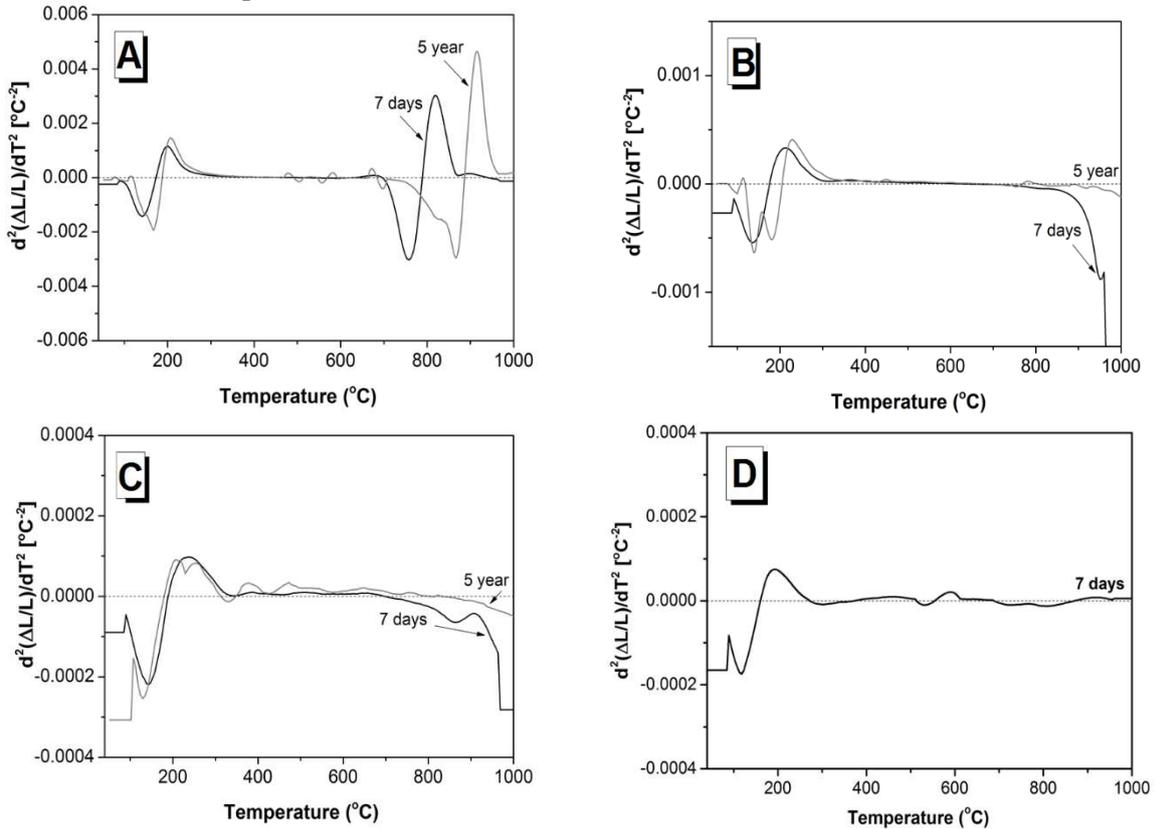


**Figure 2.** Dilatometry curves of MK geopolymers formulated with a Si/Al ratio of 1.5, as a function of the alkali cation used, assessed after (A) 7 days and (B) 5 years of curing

As the radius of the alkali cation increases, a significant reduction in the initial shrinkage (100- 300°C) is observed (Fig 2A), so that Cs and Rb geopolymers show less than 2% shrinkage in this temperature range. The onset of viscous sintering also shifts towards higher temperatures as the alkali radius increases, and it is not detected for Cs and Rb-containing geopolymers within the range of temperatures evaluated (up to 1000°C). This demonstrates that early age Cs and Rb geopolymers are highly dimensionally stable at elevated temperatures. In aged samples, the Na-geopolymers (Fig 2B) shrinks more at temperatures above 600°C than is observed in specimens with 7 days of curing (Fig. 2A). This could be associated with changes in the pore structure, overall Si/Al ratio and fraction of remnant unreacted MK present, which modifies the viscous sintering process that is taking place in these samples. Both K and Rb aged geopolymers exhibit comparable shrinkage to that identified in 7-day cured samples, indicating that limited structural changes are occurring in these specimens with maturity, and that the physical and chemical distribution of hydroxyl sites in these samples are comparable.

The second derivatives of the dilatometry traces are reported in Fig 3, and provide further clarity regarding the onset and nature of shrinkage phenomena. In Na based geopolymers (Fig 3A), the onset temperature (~700°C) remains similar between 7 days and 5 years of curing, but the rate of initial shrinkage is much more gradual in the more mature samples, which could be associated with the densification of the geopolymer gel skeleton over the time of curing, as a consequence of pore refinement. There is a slight indication of an expansion phenomenon prior to the onset of shrinkage in this sample at 7 days and 5 years, just below

700°C, which differs from the other samples studied. Conversely, in the K-based geopolymer (Fig 3B) at early age initiation of shrinkage is observed above 800°C, but almost no dimensional change is detectable in the mature sample. A similar effect is observed in the Rb-based geopolymer (Fig 3C), which at early age showed slightly less shrinkage below 500°C but more at temperatures between 600 and 700°C, compared with the K-based formulation. Cs-based geopolymers only show dimensional changes below 300°C (Fig 3D), associated with the dehydration of loosely bonded water in the geopolymer gel, and are dimensionally stable from this temperature to above 1000°C.



**Figure 3.** Second derivative of the dilatometry curves of MK geopolymers formulated with a Si/Al ratio of 1.5, activated with (A) Na, (B) K, (C) Rb and (D) Cs silicate solutions, as a function of the curing time

#### 4. CONCLUSIONS

Production of metakaolin geopolymers using rubidium and cesium silicate solutions is feasible. All geopolymers studied are predominantly X-ray amorphous after 5 years of curing; however, in Rb-based and Cs-based geopolymers the formation of additional aluminosilicate crystalline phases is taking place. The thermal stability of MK-geopolymers is influenced by the alkali cation present in the material, so that different thermal shrinkage profiles are observed when using different silicate solutions as activators. There seems to be a direct correlation between the alkali radius and the onset of the viscous sintering process identified in Na-geopolymers above 600°C, so that geopolymers produced with Rb and Cs show negligible dimensional changes in the range of temperatures evaluated. This cannot solely be attributed to the alkali cation, and might be consequence of the combined effect of the higher

ordering identified in the Rb and Cs geopolymers compared with Na and K geopolymers, which may retard the dehydration of the geopolymers upon heating; the reduced energy of hydration of larger alkali cations, favouring water removal at reduced temperatures from the hydration shell of alkali cations associated with aluminium; and the differences in the amount of remnant MK present in the samples, associated with different degrees of reaction. These results elucidate that small microstructural changes are taking place in MK-geopolymers, independent of the alkali cation, over an extended period of curing, demonstrating the high stability of appropriately formulated MK geopolymers upon aging.

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