

## Geopolymers for the encapsulation of solid nuclear waste

C. Künzel<sup>1</sup>, L. Vandeperre<sup>2</sup>, A.R. Boccaccini<sup>3</sup> and C.R. Cheeseman<sup>1</sup>  
<sup>1</sup>Civil and Environmental Engineering Department, Imperial College London  
<sup>2</sup>Materials Department, Imperial College London  
<sup>3</sup>Materials Department, Universität Erlangen-Nürnberg  
(correspondence: c.cheeseman@imperial.ac.uk)

### ABSTRACT

Geopolymers are cementitious materials synthesized by a polycondensation reaction between aluminate and silicate. This study has investigated using geopolymers as an encapsulation matrix for solid nuclear waste. For this application geopolymers ideally have to meet several criteria including low viscosity, low pH, high compressive strength, high thermal stability and low porosity. It is shown that pure geopolymers exhibit shrinkage cracking when they are exposed drying at 110°C. This cracking can be controlled by replacing the precursor metakaolin with fillers. Viscosity measurements showed that up to 35 wt. % filler could be added without changing the flow properties. Samples with high filler additions show an increase in compressive strength and decrease in porosity.

### INTRODUCTION

Geopolymers are cementitious materials in which aluminate and silicate groups are tetrahedrally linked [1]. Due to the tetrahedral coordination of aluminate, Al has a negative charge which can be neutralised by a cation, normally an element from the first group of the periodic table [2]. This type of mineral polymers has been known since the 1940s [3]. The polymerisation reaction is a geosynthesis which involves a naturally occurring silico-aluminate mineral such as kaolin or metakaolin and an activation solution [4]. The synthesis is similar to organic condensation polymerisation [5, 6, 7].

A wide range of applications have been proposed for geopolymers because they can have similar properties to Portland cement such as high flowability, fast setting, high strength, and fire and blast resistance [8]. Many of these applications are in construction, but the nuclear industry has also shown interest in geopolymers to encapsulate liquid and solid intermediate nuclear waste. Currently, a mixture of blast furnace slag/Portland cement (BFS/OPC) is used for this purpose [9, 10]. However, a wider range of binders is needed to accommodate the widely varying waste streams produced by the nuclear industry [11].

The main advantages of geopolymers compared to BFS/OPC is the acid resistance and the rapid setting while still achieving high final strengths [12, 13, 14].

Initial research investigated the immobilisation of liquid ILW in geopolymers, where heavy radioactive metals are dissolved in water [15, 16, 17, 18]. Later encapsulation of Cs and Sr ions has been demonstrated [19, 20, 21]. Moreover, an inorganic polymer similar to geopolymers is already being used to encapsulate nuclear sludges in Slovakia [22]. To date the encapsulation of solids using geopolymers has not been extensively investigated. Encapsulating solid wastes rather than liquids involves different constraints on the binder characteristics. For example when liquid waste is encapsulated leaching is one of the most important criteria whereas for solid wastes porosity, heat resistance and fluidity are also important.

The objective of this work was to investigate whether pure geopolymers can be used as the encapsulation matrix for solid nuclear waste. For this, fluidity was optimised and the use of fillers to improve the physical properties was investigated. Previous studies have shown that an effective molar ratio for the geopolymer mix is 1:2:1 of Al:Si:Na [23, 24, 25]. Therefore this mixture was chosen. The effect of water content on fluidity and physical properties was investigated followed by a study of the effect of filler content. In all cases the flow properties of the mix were determined and samples prepared for measurement compressive and flexural strength, hardness and porosity.

## MATERIALS AND METHODS

### Preparation of geopolymers

Samples were prepared at room temperature ( $25 \pm 2$  °C) by mixing metakaolin (MK) (Metastar 501, Imerys, UK) with sodium silicate solution (VWR International, Philadelphia, , USA), NaOH (Fischer, Pittsburgh, USA) and distilled water to give a molar ratio of Al/Si/Na/H<sub>2</sub>O of between 1:2:1:7.5 and 1:2:1:10.5. The chemical composition of the metakaolin used was 59.5 wt.% SiO<sub>2</sub>, 34.0 wt.% Al<sub>2</sub>O<sub>3</sub>, 6.5 wt.% other minerals, with a median particle size was 3.9 μm. Sand was obtained from Sibelco, UK with the particle size distribution given in Figure 1. All components were mixed for 15 minutes and vibrated simultaneously to remove remaining air bubbles. After casting in moulds, the samples were cured in sealed containers.

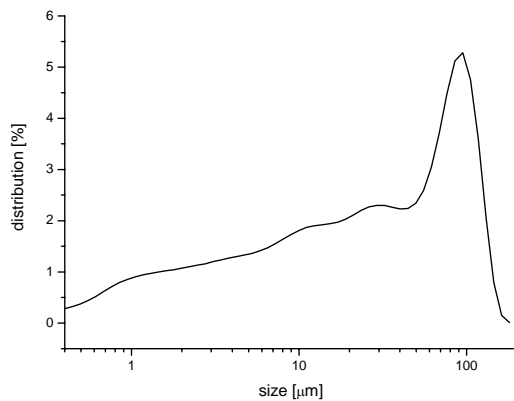


Figure 1 Particle size distribution of the sand

### Investigation of the viscosity

To investigate the viscosity of geopolymer slurries, samples were placed on a Paar Physica UDS200 rheometer and measured 15 minutes after mixing. The shear rate was increased from 0.1 to 75 s<sup>-1</sup>.

### Determination of the pH during polymerisation

Two techniques were used to determine the pH. Until setting, the pH was measured *in-situ*. Thereafter, samples were dried at 105°C for 24h, Tema milled for 30s and mixed with water to obtain a water/solid ratio of 1.6 [26]. The slurry was mixed for 24h and the pH measured (Fischerbrand Hydrus 500 pH-meter, with an Inlab Routine Pro electrode from Mettler Toledo).

### Determination of the compressive and flexural strength

The compressive strength was measured using a Zwick/Roell Z010 on cubic samples of edge length 8 mm. The crosshead speed was set to 0.2 mm/min. The unconfined compressive strength ( $\sigma$ ) was calculated using Equation 1.

$$\sigma = \frac{F}{A} \quad (1)$$

where F is the maximum applied force [N], and A the cross section area [mm<sup>2</sup>].

The flexural strength was measured using three point bending using a Zwick/Roell Z2.5. The distance between the support points was 30±1 mm and the crosshead speed was set to 0.5 mm/min. The specimen had a rectangular shape with a length of 40 mm and a height and width of 8 mm. The flexural strength was calculated using following Equation (2):

$$\sigma_f = \frac{3Fl}{2bd^2} \quad (2)$$

where F is the maximum applied force [N], l is the distance between the support points, b the width and d the thickness of the test beam [mm].

### Shrinkage

The shrinkage was determined using a dilatometer (Netzsch 402E) with a heating rate of 10 °C min<sup>-1</sup>.

### Porosity

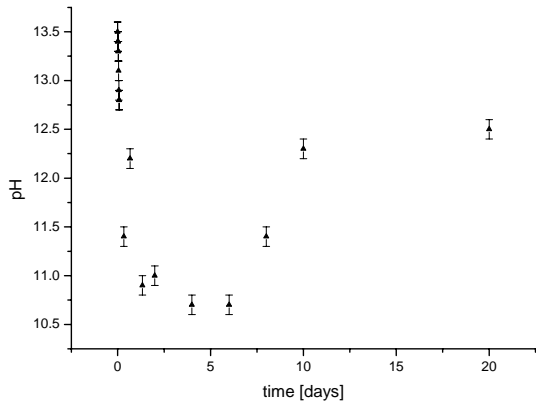
The porosity [P] was measured using Archimedes' principle. The samples were dried at 110 °C for 24 h, weighed and then soaked in water for 24 h. The height of the water above the samples was 100 mm. The porosity was calculated using Equation (3 and 4):

$$P_{open} = \frac{V_{open}}{V_{total}} = \frac{(m_{soaked} - m_{dry})}{\rho_{fluid} * V_{total}} \quad (3)$$

$$P_{total} = 1 - \left( \frac{\rho_{fluid} m_{dry}}{[(m)_{soaked} - m_{elevated}]} \right) \quad (4)$$

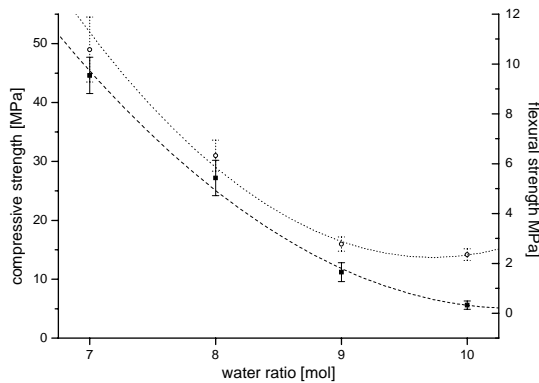
## RESULTS AND DISCUSSION

Figure 2 shows the variation of pH with time for a molar ratio Al:Si:Na:H<sub>2</sub>O of 1:2:1:10.5. Similar results were obtained using lower water contents. During the dissolution process of MK the pH decreased to a minimum of ~10.5. As the polycondensation reaction proceeds the pH eventually increases to 12. These results are consistent with those obtained elsewhere [27, 28].

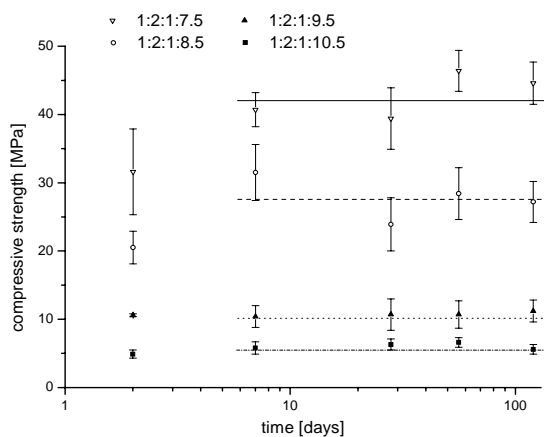


**Figure 2** pH value over time for a molar ratio of Al:Si:Na:H<sub>2</sub>O 1:2:1:10.5

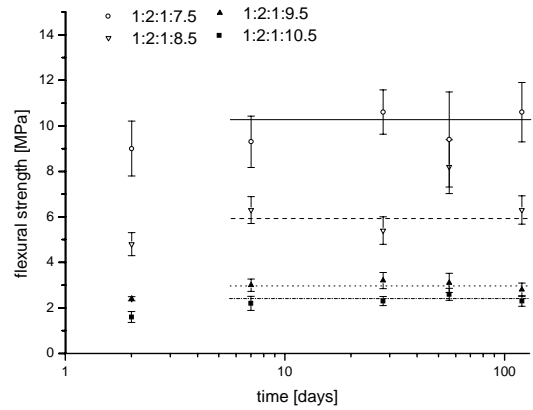
To investigate the influence of water on mechanical properties, compressive and flexural strengths were measured. As shown in Figure 3, higher water contents reduce the strength. Water is only necessary for the dissolution process, after which it remains in the material and weakens the structure. Figures 4 and 5 show that the maximum strength is reached after 7 days.



**Figure 3** Flexural/compressive strength of mixes with a molar ratio of Al:Si:Na from 1:2:1 after 28 days curing

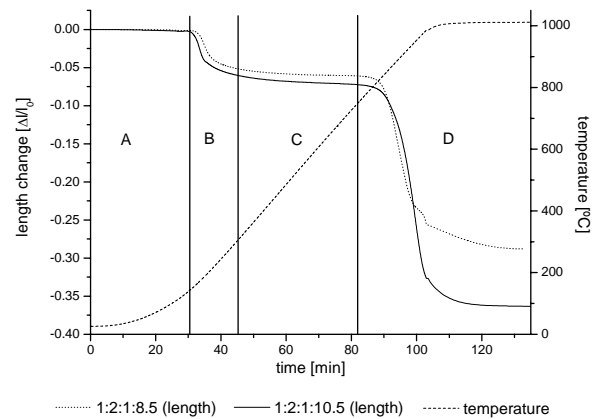


**Figure 4** Compressive strength versus time, molar ratio of Al:Si:Na is 1:2:1



**Figure 5** Flexural strength versus time, molar ratio of Al:Si:Na is 1:2:1

When samples were dried, extensive cracking occurred, even under mild drying conditions in a desiccator. This is due to shrinkage of the geopolymers as can be seen from the dilatometer trace shown in Figure 6.

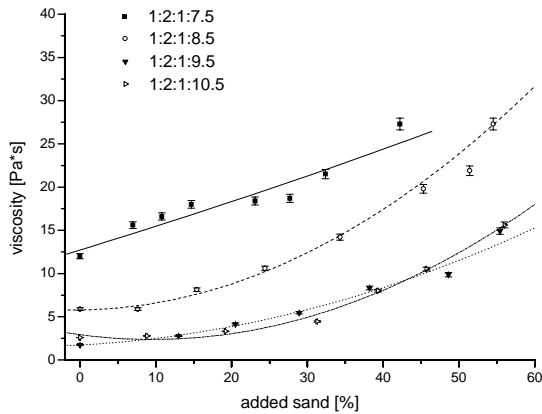


**Figure 6** Shrinkage of geopolymers after 28 days curing

Figure 6 indicates that the temperature behaviour of geopolymers can be separated into four zones A-D. In region A, geopolymers are stable and any free water evaporating does not cause dimensional instability. In region B, further removal of water causes a first shrinkage step. Region C is characterised by a flat slope and region D by sintering and densification [24]. The results indicate that cracking only occurs if geopolymers are heated beyond region B. The initial water content does not affect the overall shrinkage in the first step and this suggests that much of the excess water is present in large pores, from which the water can be removed without causing the material to shrink. The higher level of porosity in samples with higher water content results in a larger densification step during sintering.

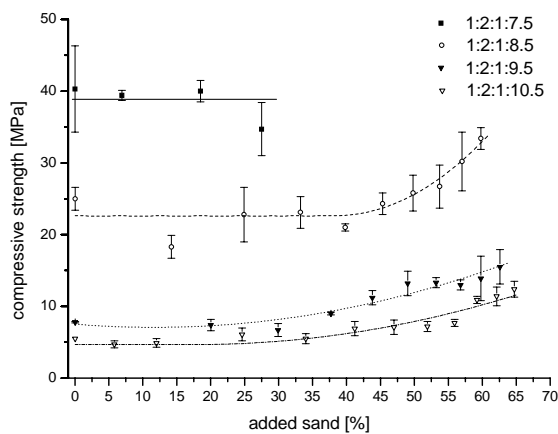
Despite a wide range of compositions investigated it was not possible to produce pure geopolymer samples which did not show drying cracking. However the shrinkage can be reduced by adding

inert fillers to replace MK. In this study sand was used because it has been used in previous research [14, 29, 30]. As this increases the solids loading of the paste, a possible drawback could be an increase in viscosity. Measurements of the viscosity shown in Figure 8 indicate that adding sand has almost no influence on the viscosity up to a concentration of 40 wt%. The viscosity reported in Figure 7 was taken at a shear rate of  $40 \text{ s}^{-1}$  as this is the point where a constant viscosity independent of shear rate is reached. For lower shear rates, the viscosity is a strong function of shear rate.



**Figure 7** Viscosity of geopolymer/sand mixed at a shear rate of  $40 \text{ s}^{-1}$

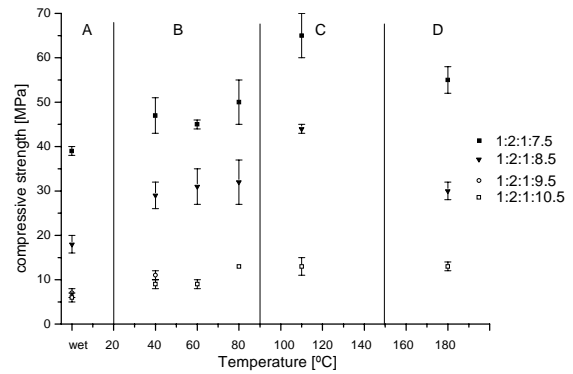
Compressive strength data on 75 day samples kept in humid conditions is given in Figure 8. This shows that sand contents which increase the viscosity improve the compressive strength.



**Figure 8** Compressive strength of wet geopolymer/sand samples after curing for 75 days

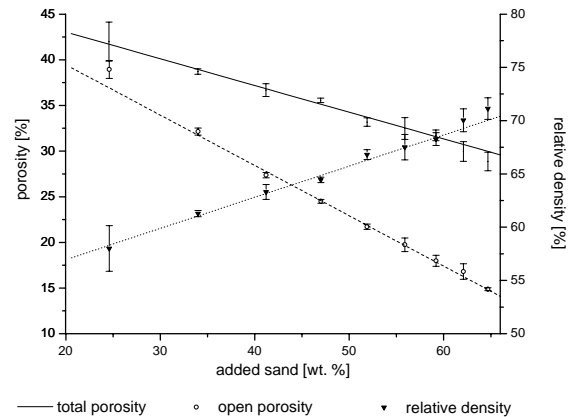
To investigate whether adding sand eliminates drying cracking, the geopolymer/sand mixtures were dried at a range of temperatures for 24 hours and compressive strengths measured. Samples with a w/s ratio above 0.518 cracked at temperatures above  $40^\circ\text{C}$ . Figure 9 shows the results for a w/s ratio of 0.518. It can be seen that the compressive strength increases after drying at  $40^\circ\text{C}$  for 24h. A further increase can be seen

between  $80^\circ\text{C}$  and  $110^\circ\text{C}$ . If, however, samples are heated to  $180^\circ\text{C}$  directly, the compressive strength decreases. The first increase is believed to result from evaporation from larger pores, and the subsequent increase is due to water evaporating from smaller pores. The decrease at  $180^\circ\text{C}$  is believed to be due to shock heating and the formation of micro-cracks.



**Figure 9** Compressive strength of geopolymer/sand mixture with a w/s 0.518 at different temperatures

Another important criteria to use a material as an encapsulation matrix is porosity. Figure 10 shows the result for a geopolymer/sand mix with a molar ratio for Al:Si:Na:H<sub>2</sub>O of 1:2:1:10.5. Similar results were obtained using a lower water ratio. It can be seen that increasing the sand content decreases the total and open porosity. Therefore addition of sand filler is beneficial because cracking due to drying is suppressed, porosity is reduced and the viscosity is not significantly altered.



**Figure 10** Porosity measurement of a geopolymer/sand mixture with a molar ratio Al:Si:Na:H<sub>2</sub>O of 1:2:1:10.5

## CONCLUSION

This study suggests that pure geopolymers cannot be used as an encapsulation matrix for solid nuclear waste because of shrinkage cracking. However, the formation of cracks in geopolymers can be reduced by adding an inert filler. When the w/s ratio is below 0.518, geopolymers can be produced which do not crack on drying. In addition up to 35 wt.% of filler can be added without

increasing the viscosity or decreasing the compressive strength. Replacing MK with sand has only minor effects on the porosity.

A drawback with using MK based geopolymers is likely to be the pH, which is relatively high during the whole reaction and only decreases during the dissolution process. As a result only wastes which are inert under high pH conditions have potential to be encapsulated.

Further research will focus on understanding the influence of the Si ratio on shrinkage, viscosity and pH. The effect of optimizing the particle size distribution of the filler and establishing the suitability of other fillers than sand is also being investigated. Future work will also investigate using different minerals to replace metakaolin and to produce a geopolymer which react at lower pH.

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