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Metakaolin-based geopolymers for nuclear waste encapsulation

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Abstract

The UK nuclear industry has a significant and challenging stockpile of nuclear wastes, and geopolymers produced from activation of the calcined clay metakaolin offer a valuable alternative to Portland cement-based systems. The characteristics of different formulations of metakaolin-based geopolymers, reacted with sodium and potassium silicate, are therefore of interest. As preliminary steps, the compressive strength and rheology of some metakaolin geopolymer grouts have been studied. This work showed that a potassium silicate-based geopolymer binder, with a sufficiently high water content can be produced to be highly workable. These grouts have a shear stress of approximately 80 Pa at a shear rate of 110 s^{-1} and can achieve compressive strengths of up to 40 MPa after 7 days of curing. This study is to be expanded in future and compared to the results produced from further analysis performed on the chemical structure of the geopolymer, as well as the overall physical characteristics achieved, to support the immobilisation, incorporation and retention of metal and oil based nuclear wastes.

1. Introduction

Since the introduction of nuclear power to the UK in the 1950s, the question of how to safely handle the potentially harmful radioactive waste produced has always been posed. The UK nuclear industry continues to develop and produce new ideas and concepts for dealing with the diverse waste streams that are produced in operational and decommissioning phases of the lifecycle of a nuclear power plant, as well as the complex legacy wastes resulting from experimental and historical operations.

The UK has three basic classifications of nuclear waste: High-level waste (HLW), Intermediate-level waste (ILW) and Low-level Waste (LLW). ILW is by far the most diverse and problematic of these waste types; it is defined as waste that does not generate significant heat but emits radioactivity greater than 4 GBq per tonne of alpha activity or 12 GBq per tonne of beta/gamma activity. This waste can be generated from many sources across the operational lifecycle of a nuclear reactor. This includes, but is not limited to, plant maintenance and decommissioning, fuel cladding, effluents from plant operation, and sludges formed from liquid effluents and corrosive metallic elements [1]. Geopolymers based on calcined clays, produced through the reaction of the calcined clay powder with an alkali source, could be ideal for the encapsulation and immobilisation of ILW due to the possibility of tailorable chemistry, such as alkalinity and corrosion resistance, and physical properties, such as the refined pore structure and adaptable viscosity in the fresh state [2].

The gel chemistry of metakaolin (MK) is based on a highly disordered, highly cross-linked structure containing high levels of Si and Al, and low levels of Ca. This leads to the formation of a $(Na,K)_2O$-Al_2O_3-SiO_2-H_2O (or in abbreviated notation (Na,K)-A-S-H) gel, where Na and/or K are alkali cations supplied by the activating solution. The chemical characteristics of the gel can be closely related to the Si/Al ratio and mineralogy of the aluminosilicate precursor [2].

An (Na,K)-A-S-H gel is formed of Al- and Si-centred tetrahedra, bridged by oxygen [3], with the alkali cations present in a charge balancing role associated with the Al-centred tetrahedra. The initial setting of a geopolymer takes a few hours, and a relatively strong microstructure takes around 1-7 days to form depending on the precursor characteristics and curing temperature [4]. As the reaction advances over longer time periods, the structure begins to rearrange, and allows the formation of zeolites [5]. The formation of zeolites generates host sites in the crystal structure that are ideal hosts for some of the metal cations present within nuclear waste.

The International Atomic Energy Agency (IAEA) has examined the use of clays for the encapsulation of ILW: natural clays, including kaolinite, were used to encapsulate Cs contaminated liquid waste streams [6], with moderate success. However, after many years of intermittent research in the use of calcined clay-based geopolymers in the nuclear industry, Kuenzel et al. [7-10] and Frizon et al. [11-13] have produced useful data that has generated much interest within the nuclear sector.

Kuenzel et al. demonstrated some initial success for the encapsulation of Cs/Sr [7] and Al [9], and studied how composition can affect the shrinkage and cracking characteristics of geopolymers [10]. Their work has shown that the metallic Al present in some ILW streams has the potential to be encapsulated in MK-based geopolymers [9]. Cs can also be bound tightly to the aluminosilicate phase replacing Na, while Sr has a limited degree of uptake; beyond 0.4 mol of Sr per mol of Al in the geopolymer, the Sr was observed to precipitate out [7].

Frizon et al. have also moved towards the solidification/stabilisation of oil-based waste streams in geopolymers. This work was carried out by producing an emulsion of oil and sodium silicate, mixing this with the MK and allowing to set. This produced very limited oil leaching and a retention of the mechanical properties at up to 20 vol.% oil fraction [12]. Oil is incompatible with Portland cement, and so if a valid alternative arose this could provide the answer to many problems, not just within the nuclear sector. Work from the same group also focused on Mg-Zr waste streams, showing that a sodium silicate activated MK-geopolymer with appropriate fluoride corrosion inhibitors can reduce the release of hydrogen as a product of Mg metal corrosion [13].

The brief summary, presented above shows that the use of MK-based geopolymers to encapsulate materials of specific interest to the nuclear sector is viable. This report demonstrates that the work that has been undertaken can be used and advanced to promote the use of geopolymers within the nuclear industry. A discussion will be provided showing how the results from the literature can be used in conjunction with new results to provide key formulations for immobilisation of problematic nuclear waste streams in clay-based geopolymers.

2. Experimental Programme

Flash-calcined MK (Argeco, France), with a particle size (d_{50}) of 25 µm and a SiO_2/Al_2O_3 of 5.1 (elevated due to the presence of quartz in the pre-calcined kaolin), was used to produce geopolymers using sodium or potassium silicate solutions (provided by PQ Silicates) blended with reagent grade MOH (M = Na or K; Sigma Aldrich UK). The activating solutions were designed with SiO_2/M_2O molar ratios of 0.5, 1 and 1.5, and H_2O/M_2O molar ratios of 11 and 13. The geopolymers were produced with $Al_2O_3/M_2O = 1$, by high shear mixing of the MK and activating solution, at 20 °C.

The geopolymer grouts were cast in 50 mm cubes for compressive strength analysis. Compressive strength tests were performed using a Control 5000 kN Compression Tester, at 3, 7 and 28 days after casting. The rheological experiments were undertaken using a Haake Viscotester with a 6-bladed vane impeller and a sample volume sufficient to approximate an infinite medium.

3. Results and Discussion

This section will describe some characteristics that must be understood, to determine the suitability of geopolymers for the solidification and stabilisation of waste from the nuclear industry.

The compressive strengths of sodium and potassium silicate activated MK geopolymers are shown in Figure 1a and Figure 1b, respectively. These strength curves show that binders where the activator contains more silica, up to an $SiO_2/(Na,K)_2O$ molar ratio of 1.5, tend to have greater compressive strengths. The low compressive strength determined for the sodium silicate formulation, H_2O/Na_2O = 11 and SiO_2/Na_2O = 0.5, is believed to be due to the formation of sodium metasilicate crystals within the activating solution before or during shear mixing. This has been described by Provis et al. [14], where low modulus sodium silicate solutions, $SiO_2/Na_2O \leq 1$, crystallised and solidified during storage. This formulation has therefore been removed from further studies. A compressive strength of 75 MPa was reached after 28 days for the lowest alkalinity potassium-based system, H_2O/K_2O = 11 and SiO_2/K_2O = 1.5. When the $H_2O/(Na,K)_2O$ ratio is increased to 13, the compressive strength is approximately 40 MPa for both formulations. This is well within the acceptable range for nuclear waste immobilisation.

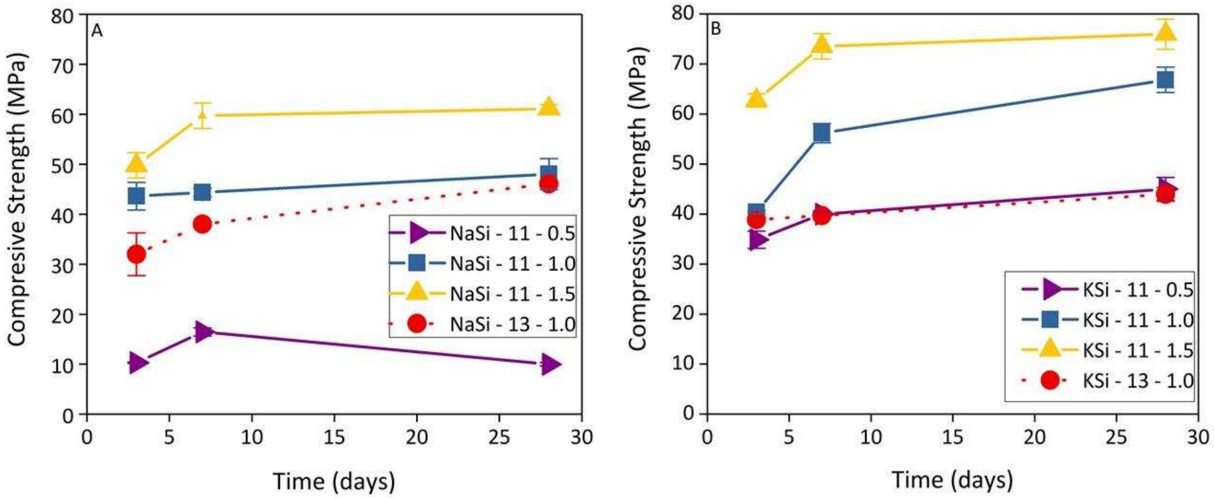

Figure 1 - Compression strength curves showing a comparison between sodium silicate (A) and potassium silicate (B) activated geopolymers. The legends show the activator, H2O/(Na,K)2O molar ratio and activator SiO2/(Na,K)2O ratio for each formulation. The curves for $H_2O/(Na,K)_2O$ ratios of 11 and 13 are shown with solid and dotted lines, respectively. Error bars show the standard deviation among triplicate samples.

The next step in explaining this geopolymer system is to perform rheological analysis on the different grouts produced. These grouts are described by the Herschel-Bulkley (H-B) Model, which states that shear stress (τ) of these materials are related to the shear rate ($\dot{\gamma}$) by a power law, Equation 1. This is different from Portland cement based systems that often follow the Bingham model (constant plastic viscosity once the yield stress is overcome) [15].

$$\tau = \tau_0 + K\dot{\gamma}^n \tag{1}$$

The viscosity data and the calculated theoretical H-B curve are given in Figure 2a and Figure 2b for sodium and potassium silicate activated solutions, respectively. The rheology curve for the grout with SiO_2/Na_2O = 1.0 and H_2O/Na_2O = 11 was unable to be obtained as the paste formed was too stiff to be measured, and formed a solid skin-like layer on the top of the grout mix upon exposure to air, possibly through a combination of carbonation and drying effects. This is therefore not a valid formulation for the applications outlined in this study.

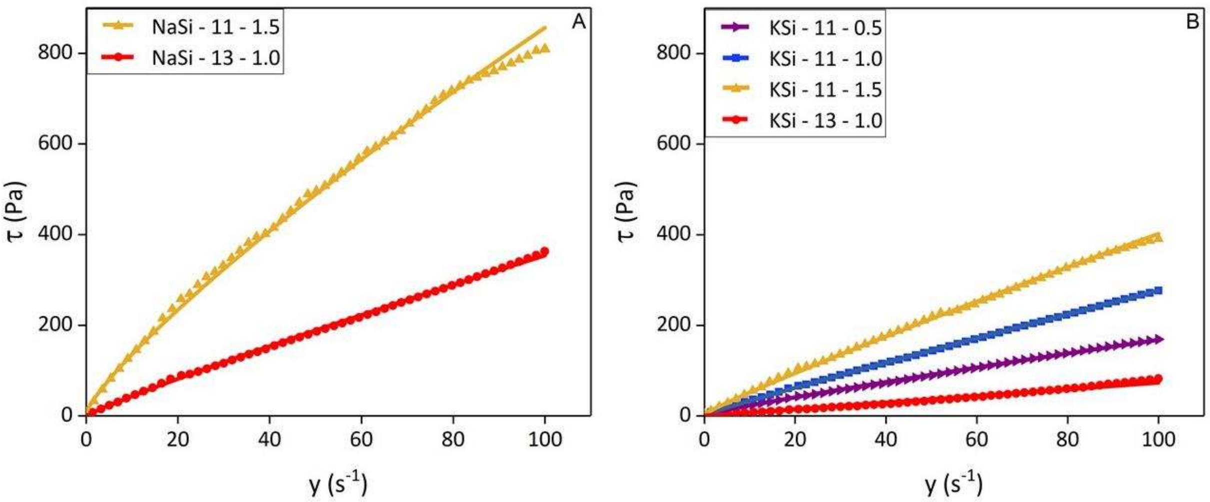

Figure 2 - Flow curves for the alkali-activated MK grouts. The sodium and potassium activated systems are given in A and B, respectively, and the solid lines represent the H-B model fits to each data set.

All the grouts produced appear to show some degree of shear thinning in this shear rate range (H-B parameter $n < 1$), which can be of use in and beyond the nuclear industry. The potassium-activated systems show a lower viscosity than the sodium-activated systems, and particularly when the water content of the grout is increased to $H_2O/K_2O = 13$, low to negligible yield stress and highly fluid behaviour is observed. This is therefore the ideal formulation to examine further, both chemically and structurally, to determine its ability to encapsulate nuclear waste streams whilst complying with the relevant UK guidelines for waste management and disposal.

4. Conclusions and Future Work

It has been demonstrated that the production of MK-based geopolymers using sodium and potassium silicate activation can yield desirable material characteristics for the encapsulation of nuclear waste streams: sufficient strength and high flowability. A moderate activator $SiO_2/(Na,K)_2O$ ratio of 1.5 gives the highest overall compressive strength at low water content, but the viscosity of the sodium silicate-activated composition at the studied water content is too high to give the high fluidity needed for nuclear wasteform grouts. Two effective ways of reducing the viscosity were to use an increased water ratio, $H_2O/M_2O = 13$, or to replace sodium silicate with a potassium silicate activator. A combination of these parameters yielded high fluidity whilst keeping a compressive strength of 40 MPa. This is a good formulation on which to base further studies of the key physical and chemical characteristics of geopolymers for nuclear waste immobilisation, to allow ideal formulations for different problematic waste streams to be validated.

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