Novel Alternative Cementing Systems for Waste Immobilisation

By **Y. Bai, A. Connelly and N. B. Milestone**

Immobilisation Science Laboratory, Department of Engineering Materials, The University of Sheffield, U.K.

1. Introduction

UK currently uses Portland cement composite blends to encapsulate intermediate and low level radioactive wastes. However, there are several disadvantages with the Portland cement system, notably its high pH and significant heat generation during hydration. The high pH causes the corrosion of some metals leading to expansion and generation of dangerous hydrogen gas while the significant heat generation during setting can cause cracking due to thermal stresses. Therefore, this project centres around developing new methods and systems for radioactive waste immobilisation using a range of novel cementing systems, as well as determining the engineering properties and durability of such systems.

2. Objectives

- To develop a novel cementing system with a high fluidity, low heat of hydration, low pH, low water permeability, low free moisture content and high heavy metal immobilisation efficiency for immobilising low to medium level nuclear wastes.
- To investigate the engineering properties and long-term durability of the novel cementing system.
- To investigate the corrosion behaviour of Al embedded in the novel cementing system.

3. Potential Alternative Systems

Alkali-activated slag

Alkali-activated slag (AAS) is a novel cementing system which was invented in 1957 in USSR. Typically, the hydration of ground granulated blast furnace slag is activated with sodium silicate or/and hydroxide. Compared with the OPC system, the AAS generally provides a superior system with reduced water demand, lower permeability, low heat of hydration and good resistance to chemical attacks. In particular, the formation of the thermodynamically stable low CaO CSH together with a self-generated zeolitic phase can fix nuclide ions in its cage-like structures As a result, AAS has been successfully used as a matrix for immobilising Hg^{2+}, Zn^{2+}, Cr^{6+}, Cd^{2+}, Pb^{2+}, Cs^{+} and Sr^{2+} from various wastes.

Geopolymer

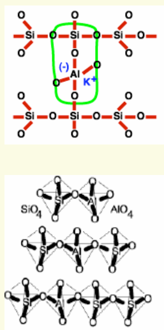

Fig. 1 Structure of Geopolymer

Geopolymers are amorphous analogues of natural zeolitic materials, synthesised by polymerising a variety of alkaline silicates with silico-aluminates. Geopolymers consist of a polymeric silicon-oxygen-aluminium framework with alternating silicon and aluminium tetrahedra joined together in three directions by sharing all the oxygen atoms (as shown in Fig. 1). The aluminium is four co-ordinated creating a negative charge imbalance. Therefore, the presence of cations such as K^+ and Na^+ is essential to maintain electric neutrality in the matrix.

The advantages of geopolymers over OPC are their low permeability, fire resistance and acid resistance. Heavy metals also can be immobilised within their unique structure by means of ion exchange, in addition to the physical encapsulation. Up to date, geopolymers have been successfully used in immobilising Pb^{2+}, Cu^{2+}, Zr^{4+}, HPO_4^{2-} and Cl^-.

4. Challenge of the Alternative Systems

- **Alkali-activated slag**: high pH of the activator used for activating the slag.
- **Fly ash-based geopolymer**: high pH of the activator, high free moisture content, high curing temperature and variation of fly ash.
- **Metakaolin-based geopolymer**: high pH of the activator and high free moisture content.

5. On-going Projects

- Immobilisation of toxic metals within a fly ash-based geopolymer matrix.
- Effect of properties of metakaolin and water/solid on workability, setting time, strength, microstructure, free moisture content and leaching of geopolymer.
- Development of a novel waste immobilisation matrix by activating slags with low pH alkali salts (being developed jointly with Chongqing University in China).
- Modification of metakaolin-based geopolymers for immobilising nuclear wastes by addition of Ca^{2+}ions (being developed jointly with Chongqing University in China).
- Optimisation of pulverised fuel ash, ggbs and metakaolin-based geopolymeric cements to immobilise toxic industrial wastes (being developed jointly with The Queen's University Belfast).

6. Preliminary Investigation on Fly Ash-based Geopolymer

6.1 Materials

- Class F Pulverised Fuel Ash (PFA). Table 1 shows its chemical composition.
- Sodium silicate solution (8.9% Na_2O, 27.3% SiO_2, 63.8% H_2O).
- Analytical grade sodium hydroxide pearl.
- Analytical grade caesium chloride (CsCl), tin chloride ($SnCl_4.5H_2O$), sodium dichromate ($Na_2Cr_2O_7.2H_2O$), sodium orthophosphate ($Na_3PO_4.12H_2O$) and lead nitrate [$Pb(NO_3)_2$].

Elements (% as oxide)	Percent (by mass)
SiO_2	48.64
Na_2O	1.91
CaO	1.44
Al_2O_3	25.88
MgO	1.42
Fe_2O_3	7.57
TiO_2	0.92
K_2O	2.83
CO_2 (from TGA)	0.05
C (CO_2)	3.06
SO_3	1.20
H_2O	1.05
Total	95.97

Table 1 Chemical composition of PFA

6.2 Formulas details

The composition and oxide-mole ratio of the formulas used in this study are shown in Tables 2 and 3, respectively.

Table 2. Composition of the geopolymer (% of total mass)

	Matrix F	Matrix H
PFA	54%	56%
$NaO.SiO_2$ Solution	32%	33%
NaOH	11%	8%
Metal ion	3%	3%

Matrix	F	H
$SiO_2:Al_2O_3$	2.50	2.50
$Na_2O:SiO_2$	0.33	0.25
$Na_2O:Al_2O_3$	0.82	0.62
$H_2O:Al_2O_3$	1.45	1.45
$H_2O:Na_2O$	1.76	2.32
H_2O:Solid	0.26	0.28

Table 3. Oxide-mole ratio of the geopolymerization

6.3 Results and discussion

SEM examination shows that many of the PFA particles do not fully react but are firmly imbedded in the geopolymeric matrix. (Fig. 2)

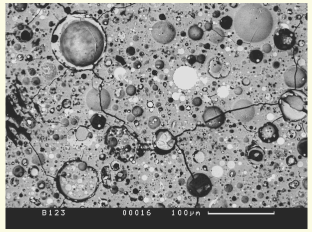

Fig. 2 SEM image of matrix H

Addition of metal ions such as Pb or Sn to the silicate solution resulted in an initial precipitation of metal silicates but these suspensions were added directly to the mix. It is not clear how these ions are immobilised, whether as insoluble silicates or as counter cations in the substitutes aluminosilicate structure. However, the presence of these heavy metal ions as well as Cs resulted in small amounts of zeolite formation in the samples with high NaOH concentration (Fig 3). Zeolite formation has been reported previously but in this work it appears only associated with the presence of heavy metal ions so does raise questions as to durability.

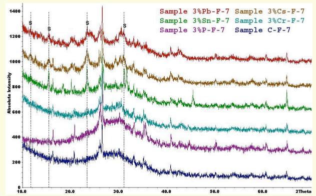

Fig. 3 XRD of matrix F after 7 days

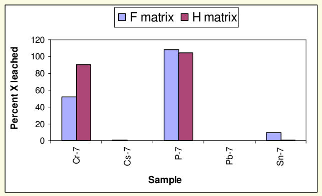

Fig. 4 Results of leaching at 7 days

(Note: X is a toxic metal)

The results of leaching after 7 days curing are shown in Fig 4. It is clear that anions such as CrO_4^{2-} and PO_4^{3-} are not retained in the matrix whereas metal ions such as Cs, Pb, Sn are strongly held. Although not shown, considerable quantities of sodium and silica leached from matrix F indicating incomplete polymerisation which may be due to the extra sodium present.

6.4 Conclusions

- A hardened geopolymer matrix can be formed from BNFL fly ash. Curing at 80°C is needed to harden the formulation which was determined by experiment.
- The matrix will immobilise large cations such as Cs, Sn and Pb.
- The presence of a significant amount of heavy metal cations can provide nucleation for zeolite crystallisation within the geopolymer.
- The geopolymer matrix has limited effectiveness in the immobilisation of anions such as PO_4^{3-} and CrO_4^{2-}.

6.5 Acknowledgements

Thanks to Martin Hayes, NSTS for support and discussion.