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# Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements

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#### Abstract

This paper reviews progresses on the use of alkali-activated cements for stabilization/solidification of hazardous and radioactive wastes. Alkaliactivated cements consist of an alkaline activator and cementing components, such as blast furnace slag, coal fly ash, phosphorus slag, steel slag, metakaolin, etc., or a combination of two or more of them. Properly designed alkali-activated cements can exhibit both higher early and later strengths than conventional portland cement. The main hydration product of alkali-activated cements is calcium silicate hydrate (C–S–H) with low Ca/Si ratios or aluminosilicate gel at room temperature; C–S–H, tobmorite, xonotlite and/or zeolites under hydrothermal condition, no metastable crystalline compounds such as  $Ca(OH)_2$  and calcium sulphoaluminates exist. Alkali-activated cements also exhibit excellent resistance to corrosive environments. The leachability of contaminants from alkali-activated cement stabilized hazardous and radioactive wastes is lower than that from hardened portland cement stabilized wastes. From all these aspects, it is concluded that alkali-activated cements are better matrix for solidification/stabilization of hazardous and radioactive wastes than Portland cement.

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### 1. Introduction

Solidification/stabilization (S/S) is a process that involves the mixing of a waste with a binder to reduce the contaminant leachability by both physical and chemical means and to convert the hazardous waste into an environmentally acceptable waste form for land disposal or construction use. The S/S of contaminants by cements includes the following three aspects: (a) chemical fixation of contaminants–chemical interactions between the hydration products of the cement and the contaminants; (b) physical adsorption of the contaminants on the surface of hydration products of the cements and (c) physical encapsulation of contaminated waste or soil (low permeability of the hardened pastes) [1,2]. The first two aspects depend on the nature of the hydration products and the contaminants, and the third aspect relates to both the nature of the hydration products and the pore structure characteristics of the paste. S/S has been widely used to dispose of low-level radioactive, hazardous, and mixed wastes, as well as remediation of contaminated sites. According to the US Environment Protection Agency (USEPA), S/S is the bestdemonstrated available technology (BDAT) for 57 hazardous wastes [3]. About 30% of the superfund remediation sites used S/S technologies according to a USEPA report in 1996 [4]. Of all the binders, hydraulic cements are the most widely used for S/S of wastes.

In later 1957, Glukhovsky first discovered the possibility of producing binders using solutions of alkali metal and a low basic calcium or calcium-free aluminosilicate (clays) [5]. He called the binders "soil cements" and the corresponding concretes "soil silicates". Depending on the composition of starting materials, the binders can be divided into two groups: (a) alkalineearth alkali binding system Me<sub>2</sub>O–MeO–Me<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O and (b) alkaline binding system Me<sub>2</sub>O–Me<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O. Alkali-activated blast furnace slag cement is a typical example for the first group and alkali-activated metakaolin or fly ash cement for the second group. Davidovits called the second

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group geopolymer since they have polymeric structure [6]. During the past decade, these two types of cement also generally known as alkali-activated cements (AACs) and have attracted a lot of attention from all over the world due to some of their special characteristics. The book by Shi et al. has discussed the detailed composition, properties and applications of alkaliactivated cements and concretes [7]. This paper reviews the use of alkali-activated cements for stabilization and solidification of hazardous and radioactive wastes.

#### 2. Structural characteristics of alkali-activated cements

Two important characteristic attracted attentions to alkaline activated cements as host phase for radwaste: (i) these materials are set at low temperature  $(10-100 \,^{\circ}\text{C})$  to give amorphous of semi-crystalline structure, (ii) the product material have some properties superior to cement Portland as chemistry stabilized from acid medium.

#### 2.1. $Me_2O-MeO-Me_2O_3-SiO_2-H_2O$ system

The main hydration product of alkali-activated slag cement is calciumsilicate hydrate (C-S-H) with a low Ca/Si ratio, and no Ca(OH)<sub>2</sub> exists. According with RMN MAS techniques the model proposes was based on formation of disordered calcium silica hydrate with a "deierketten" structure, in witch tetrahedral lineal chains of silicate ( $Q^1$  chain end and  $Q^2$  units, see Fig. 1(a)) are linked to Ca-O layer. In these structures, association of three members units forms tetrahedral chains, two tetrahedra bound to the Ca-O layer and the third one called "bridging" tetrahedron, pointing out of the layer. An important part of bridging tetrahedra are occupied by aluminum tetrahedral (Al<sub>T</sub>) as  $Q^2(1Al)$ units [8,9]. It is found that when the slag fineness, nature and dosage of alkaline activator, and curing temperature change, the Ca/Si ratio of C-S-H, amount of Al incorporated and the chain means length change very little. The minor hydration products also vary with the characteristics of the raw materials used [10]. Thus, alkali-activated slag cements show much better resistance in aggressive environments than Portland cement.

Alkali-activated cements also exhibit much less porous structure and higher stability than Portland cement at high temperatures. For example, the main hydration products of alkaliactivated slag cements at 150 °C are CSH (B) and tobmorite or xonotlite, which give the hardened pastes a much less porous and more stable structure than Portland cements [11]. As the curing temperature was increased to 300 °C, well crystallized tobermorite and xonotlite were detected [12]. At the same time, a more porous microstructure with lower strength was obtained. Thus, it is important to understand how the temperature will affect the hydration products and the structural characteristics of the cements. CSH (B), tobmorite or xonotlite has an obvious cation ion exchange capacity and enhances the chemical fixation of contaminants [13–16]. This means that alkali-activated slag cement is better than Portland cement for S/S of wastes.

#### 2.2. $Me_2O-Me_2O_3-SiO_2-H_2O$ system

The main hydration product of alkaline binding system  $Me_2O-Me_2O_3-SiO_2-H_2O$  is semicrystalline aluminosilicate gel, which is essentially amorphous to X-rays but NMR studies have revealed a three-dimensional short-range structure in which the Si is found in a variety of environments, with a predominance of Q<sup>4</sup>(3Al) and Q<sup>4</sup>(2Al) units (see Fig. 1(b)) [17,18]. The characteristics of the aluminosilicate used, the nature and concentration of activators, and the curing temperature have the most significant effects on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the hydration products [19].

It is noticed that alkali-activated fly ash cement have quite different microstructures when different alkaline activator are used [20,21]. The OH<sup>-</sup> ion catalyzes the reaction, whereas the alkaline metal (Na<sup>+</sup>) and the other ions present in the alkali activator are structure-forming elements. N–A–S–H contains tetrahedral Si and Al in its structure, randomly distributed along the crosslinked polymeric chains; the gaps so formed are large enough to house the charge-balancing hydrated sodium ions. When the alkali activator is a NaOH solution, the "sodium aluminosilicate gel" presents a Si/Al ratio of 1.8–2.0 and a Na/Al ratio of 0.46–0.68. In the presence of silicate ions, the Si ion content in

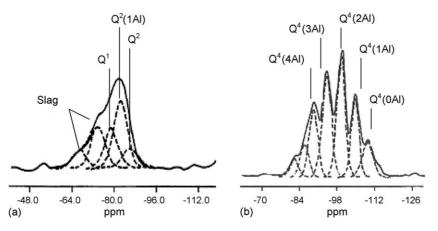


Fig. 1. (a) Alkali-activated slag with NaOH solution (4% of Na<sub>2</sub>O in mass respect to slag) 7 days at room temperature [9]; (b) alkali-activated fly ash with 8M NaOH, 20 h at 85  $^{\circ}$ C [18].

N-A-S-H rises substantially (Si/Al = 2.7 and Na/Al = 1.5). Condensation and mechanical strength are likewise greater under these conditions.

Under hydrothermal conditions, the amorphous or semicrystalline hydration products may be crystallized and converted to zeolites. Many researchers [22–25] have mixed coal fly ashes or metakaolin with alkaline solutions to synthesize zeolites under hydrothermal conditions. The nature of the raw materials, hydration time and curing temperature of alkali-activated fly ash or metakaolin dictate the nature of the zeolites formed [25].

#### 3. Resistance to corrosive environments

Many publications have reported that alkali-activated cements have a much better resistance to corrosive environments than Portland cement. Figs. 2 and 3 show the corroded depth of alkali-activated slag and Portland cement pastes with time in pH 3 nitric and acetic acid solutions [26,27]. Alkali-activated slag cement showed much less corroded depths than the Portland cement pastes.

After 580 days of immersion in pH 3 nitric acid solutions, the Portland cement pastes were corroded approximately 2.5 mm,

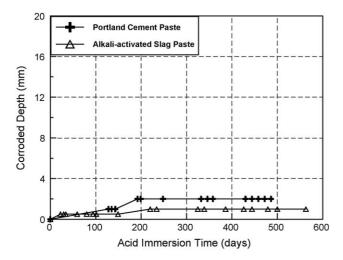


Fig. 2. Corrosion of cement pastes in pH 3 nitric acid solution [27].

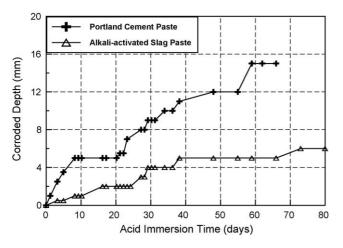


Fig. 3. Corrosion of cement pastes in pH 3 acetic acid solution [27].

while the alkali-activated slag cement pastes were corroded only about 1.3 mm. High aluminum cement is well known for its good resistance to acid corrosion. Alkali-activated cement can even show much better corrosion resistance in HCl and  $H_2SO_4$  solutions than high aluminum cement [6].

It appears that acetic acid is much more aggressive than nitric acid the difference in acid corrosion resistance became more obvious. After 60 days of immersion, 15 mm of Portland cement and but only 5 mm of alkali-activated slag cement pastes were corroded. This is further confirmed by Bakharev et al. [28]. However, it has been reported that, at the same concentration, mineral acids are more corrosive to hardened cement pastes than weak acids [29]. The contradiction can be attributed to the different testing conditions—constant pH was used in this study and a constant concentration was used by Pavlik [29].

Immersion in various aggressive liquids such as deionized water, sea water, sodium sulphate solution (4.4 wt.% and sulphuric acid solution (0.001 M)) indicated that alkali-activated fly ash or metakaolinite had much better stability than Portland cement [30]. Their microstructure was characterized and their physical, mechanical, and microstructural properties were measured. It was observed that the nature of the aggressive solution had little negative effect on the evolution of microstructure and the strength of these materials. The long-term immersion did result in the transformation of the amorphous aluminosilicate network structure into a crystalline one. Small amounts of these crystals have the faujasite structure, account for the continuing development of the mechanical strength of the material after 90 days of immersion. Faujasite crystal appears to act as reinforcement of the cement matrix.

Bakharev [31] suggested that the stability of alkali-activated fly ash pastes in aggressive environment depends on the intrinsic order of aluminosilicate gel. More crystalline hydration products formed in sodium hydroxide-activated fly ash pastes than in the sodium silicate-activated fly ash pastes. Also, the former is more stable in sulphuric and acetic acid solutions than the latter. This can be attributed to a more stable cross-linked aluminosilicate polymeric structure forms when sodium hydroxide is used as the activator. In any case, the performance of alkali-activated fly ash mortar exposed to 5% acetic or sulphuric acid solution is superior to ordinary Portland cement pastes.

### 4. Stabilization/solidification of hazardous wastes with alkali-activated cements

Portland cement-based binders have been widely used for stabilization/solidification of wastes due to its availability and low cost. However, they are not very effective in stabilizing some heavy metals such as Pb, Cu, Cr, As, Hg, etc. An alternative to Portland cement is alkali-activated cements, which have *technical*, environmental and economical advantages over traditional Portland cement. However, there is a need to understand how the raw materials of alkali-activated cements affect mechanisms and efficacy of stabilisation/solidification of different contaminants. The following sections reviews some published results on stabilization/solidification of wastes with alkali-activated cements.

### 4.1. Stabilization/solidification of hazardous wastes with alkali-activated slag cements

Many substances can significantly interfere with the hydration of cement as discussed in the book [32]. This is the basic principle for the use of different cement chemical admixtures such as retarders, accelerators, superplasticizers, etc. to obtain some special properties of cements and concrete. It has been reported that heavy metals show much less interference with the hydration of alkali-activated slag cements than with Portland cement. Shi et al. [33,34] investigated S/S of an electrical arc furnace dust (AFD) with Portland cement (PC) and an alkaliactivated slag cement (ASC) using an adiabatic calorimeter, as shown in Fig. 4. In Fig. 4, ASC0 consists of no AFD, 30% ASC, ASC30 consists of 30% AFD, 70% ASC, and so on.

The AFD is from the production of a specialty steel, which contains a variety of highly concentrated heavy metals. When 30% AFD was added, it retarded the hydration of the Portland cement, but did not show an obvious effect on the hydration of cement at later ages. As the AFD content was increased from 30 to 60%, it retarded the hydration of Portland cement very significantly and the solidified waste forms did not show measurable strength after 6 months of hydration. When the AFD was mixed with alkali-activated slag based cement, the early hydration of the cement was retarded more obviously as the AFD content increased. However, the cement continued to hydrate with time and released more heat as the AFD content increases. It seems that the presence of the AFD retarded the early hydration but was beneficial to the later hydration of the slag [35]. A full-scale demonstration indicated that the alkali-activated slag worked well during the field operation [34,36]. Although the solidified waste form cured in laboratory behaved better that that in the field, the latter still demonstrated very less porous structure and low leachability [36–38]. If the waste material is acidic, it may need to be neutralized before alkali-activated cements are used [39].

Heavy metals, such as  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Cr^{6+}$  can be well stabilized in NaOH-, Na<sub>2</sub>CO<sub>3</sub>- and sodium silicate-activated slag cements [40,41]. These alkali-activated slag cements could

immobilize these heavy metals very well regardless of activators. Cho et al. [42] investigated the leachability of  $Pb^{2+}$  and  $Cr^{6+}$  immobilized in NaOH and sodium silicate-activated slag cement pastes. They noticed that the leachability of  $Pb^{2+}$  and  $Cr^{6+}$  in alkali-activated slag cement pastes varied with curing conditions, but was very small. There is a very good relationship between the diffusion coefficient of  $Cr^{6+}$  and the pore volume with a radius less than 5 nm.

Qian et al. [43] found that low concentrations of  $Hg^{2+}$  ions had little effect on the compressive strength, pore structure and degree of hydration of alkali-activated slag cements, however, the addition of 2%  $Hg^{2+}$  ions into the alkali-activated slag cement showed an evident retardation on early hydration and reduction of early compressive strength, but no negative effects were noticed after hydration for 28 days. The results also show that up to 2% of  $Hg^{2+}$  ions can be effectively immobilized in the alkali-activated slag cement matrix, with the leaching meeting the TCLP mercury limit. Two mechanisms, physical encapsulation and chemical fixation, are assumed to be responsible for the immobilization of mercury in the alkali-activated slag cement matrix.

The effects of  $Zn^{2+}$  on the AAS matrix depend on  $Zn^{2+}$  ion concentrations [44]. At low  $Zn^{2+}$  ion concentrations, little negative influences on the compressive strength, setting time and distribution of pore structure were observed. Moreover, low concentrations of  $Zn^{2+}$  ion could be effectively immobilized in the AAS matrix. For 2% Zn-doped AAS matrix, the hydration of AAS paste was greatly retarded and leaching from this matrix was higher than TCLP zinc limit even at 28 days. Based on the analyses of hydration products, the chemical fixation mechanisms are considered responsible for the immobilization of  $Zn^{2+}$ ions in the AAS matrix.

### 4.2. Stabilization/solidification of hazardous wastes with alkali-activated metakaolin or fly ash cements

Several studies have reported the use of alkali-activated calcined metakaoline or fly ash cements as effective binders for S/S of wastes [45–53]. Lead inhibits the hydration of Port-

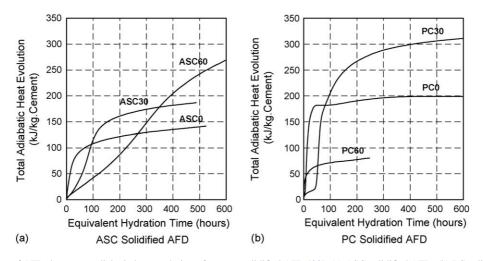


Fig. 4. Effect of AFD dosage on adiabatic heat evolution of cement solidified AFD [33]. (a) ASC solidified AFD. (b) PC solidified AFD.

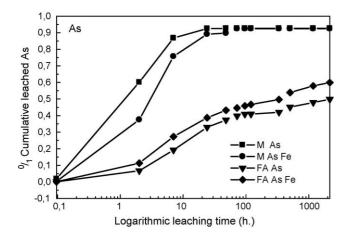


Fig. 5. 0/1 cumulative leached As in alkali-activated matrices (ANS 16.1 method) [53]; M, metakaolin matrices; FA, fly ash matrices; As = 1% of As added; Fe = 5% of  $Fe_2O_3$  added.

land cement. However, it was found that alkali-activated fly ash cements could effectively immobilize lead because it is precipitated as a highly insoluble silicate Pb<sub>3</sub>SiO<sub>5</sub> [48,49]. This has been confirmed by various leaching tests and the determination of the amount of lead fixed by activated fly ash systems. Bankowskia et al. [54] used alkali-activated metakaolin for stabilization of brown coal ash containing high concentrations of heavy metals. Phair and Van Deventer [55] noticed that the immobilization of Cu is generally less effective than lead.

In Portland cement based systems, chromium can be stabilized in the form of  $Ca_2CrO_4$ , which also enhances the strength of the cement. However, it was found [48] that all  $Cr^{6+}$  in alkaliactivated fly ash matrix could be leached out due to the formation of Na<sub>2</sub>CrO<sub>4</sub>·4H<sub>2</sub>O, which is highly soluble. The formation of Na<sub>2</sub>CrO<sub>4</sub>·4H<sub>2</sub>O also has a negative effect on the activation of fly ashes.

In any case, the efficiency of immobilization of these heavy metals in geopolymeric matrices is dominated by physical micro-encapsulation mechanisms and the degree of permeability in the matrix. The nature of the fly ash used does have a significant impact on the effectiveness of lead fixation in these systems.

Fernández-Jiménez et al. [52,53] examined alkali-activated fly ash and metakaolin matrices containing arsenic using a combination of scanning and transmission electron microscopy along with energy-dispersive X-ray analysis of argon-milled sections. The leaching behavior was tested following TCLP and ANS 16.1 methods. The activated metakaolin matrices retain less As than activated fly ash matrices (see Fig. 5). It was found that the arsenic incorporated in hydration product of alkaliactivated fly ash matrix, was apparently associated with iron derived from the hydration of the fly ash. There was no association of As with added  $Fe_2O_3$ .

Soluble boron salts retard the setting and hardening of Portland cement, and negatively affect its durability characteristics as well. It was found that a high concentration of boron salts did not affect the properties of alkali-activated fly ash cements [56]. Experimental results indicated that leaching indexes and diffusion coefficients of boron in activated fly ash based matrix was 100 times lower than those in Portland based matrix. The authors felt that the boron present in the system would precipitate as compounds such as NaB(OH)<sub>4</sub> or other kinds of sodium borates, which would fill the voids in the matrix. The main factor affecting the leaching degree was the solubility of these compounds in the usually rather high alkaline matrix.

## 5. Stabilization/solidification of radioactive wastes with alkali-activated cements

Radioactive wastes are generated in most nuclear fuel cycle processes, in some other industries such as hospitals, research facilities, etc. According to the IAEA classification most of these wastes can be classified as low-level wastes (LLW) or intermediate level wastes (ILW). Stabilization/solidification has been widely used to treat LLW and ILW. The leaching resistance of treated products is dependent on the characteristics of the matrix binder, contaminant being leached and leaching environment.

## 5.1. Stabilization/solidification of radioactive wastes in alkali-activated slag cements

Cs is the most difficult radionuclide to be stabilized in radioactive wastes. Several laboratory studies have confirmed that the cesium leachability from alkali-activated slag pastes is much lower that that from Portland cement pastes [1,10,57–59]. To evaluate the leachability of Cs<sup>+</sup> in alkali-activated slag cements, monolithic specimens were suspended in deionized water in Teflon containers at testing temperature, were transferred to other containers with fresh deionized water at specified intervals, and the concentration of Cs<sup>+</sup> in original solutions was measured [1,10]. The cesium leachability  $L_t$  (cm<sup>-1</sup>) at time t was calculated by the following equation:

$$L_t = \left(\frac{a_t}{A}\right) \left(\frac{F}{V}\right)$$

where  $a_t$ —mass of leached Cs<sup>+</sup> at time *t* (g); *A*—total original mass of Cs<sup>+</sup> in the specimens (g); *F*—total surface area of the monolithic specimens (cm<sup>2</sup>); *V*—volume of the monolithic specimens (cm<sup>3</sup>).

Fig. 6 shows the leached fraction of Cs<sup>+</sup> in Portland cement and alkali-activated slag cement pastes containing 0.5% CsNO<sub>3</sub> after 28 days of moist curing at 25 °C. The results indicate that the Cs<sup>+</sup> in Portland cement pastes shows much higher leached fraction than that in alkali-activated slag cement pastes at the same temperature. As the temperature increases from 25 to 70  $^{\circ}$ C, the leached fraction of Cs<sup>+</sup> in both pastes escalates. The leached fraction of Cs<sup>+</sup> in Portland cement pastes at 25 °C is even higher than that from alkali-activated slag cement pastes at 70 °C. The calculation using Arrhenius' equation indicated that the Cs<sup>+</sup> leaching activation energy of Portland cement pastes is 19 kJ/mol compared with 25 kJ/mol for alkali-activated slag cement pastes. The lower leached fraction and higher leaching activation energy of Cs<sup>+</sup> in alkali-activated slag cement pastes than in Portland cement pastes can be attributed to the less porous structure and lower C/S ratio in C-S-H.

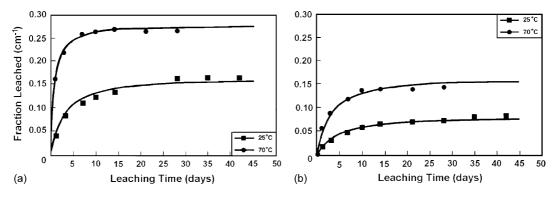


Fig. 6. Leached fraction of Cs<sup>+</sup> in hardened Portland and alkali-activated slag cement pastes [2]. (a) Portland cement pastes. (b) Alkali-activated slag cement pastes.

A partial replacement of slag with zeolites or metakaolin increases the porosity of the hardened cement pastes, but decreases the leached fraction of  $Cs^+$  and  $Sr^{2+}$  in the hardened pastes [59,60]. The decrease in leached fraction may be attributed to the formation and adsorption properties of (Al + Na) substituted C–S–H and self-generated zeolite precursor.

### 5.2. Stabilization/solidification of radioactive wastes in alkali-activated fly ash cement

The presence of CsNO<sub>3</sub> or Cs(OH)·H<sub>2</sub>O in the alkaliactivated fly ash cement pastes, prepared using 8 M NaOH solution as activator, showed no significant adverse effects on mechanical strength or microstructure [61]. Leaching tests following TCLP and ANSI/ANS-16.1 indicated that the leachability of Cs in the solidified waste form is also very low. Microstructural analysis shows Cs associated with the main reaction product in the AAFA (see, Fig. 7) suggesting that cesium is chemically bound rather than physically encapsulated. It is proposed that cesium is incorporated into the alkaline aluminosilicate gel, a precursor for zeolite formation.

Similar result was obtained by Khalil and Merz [46] for immobilization of intermediate-level wastes (Cs, Mo and Sr

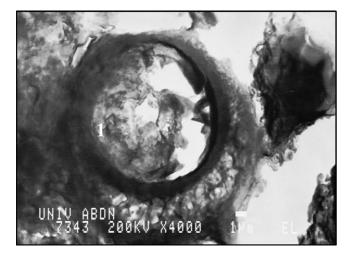


Fig. 7. TEM picture [61]. Point 1: alkaline aluminosilicate gel with the following compositional ratios: Si/Al = 2.3, Na/Al = 0.32 and Na + Cs/Al = 0.45. The lower level of Na and Cs detected are due to the high volatility of these elements with this type of analysis.

together) in commercial geopolymer. The static leaching tests were performed in two media: distilled water and Q-brine. Results indicated that Sr was reasonably immobilized but Cs was leachated more rapidly in water. Almost constant concentrations were found after one week at room temperature (Sr = below the detection limit, Cs = 1-11 wt.% and Mo = 20-40 wt.% as function of composition of the matrix). In Q-brine, the leaching rate became slow after the leached fraction reached Sr = 1-6 wt.%, Cs = 14-28 wt.% and Mo = 4-18 wt.%, in about 120 days. They concluded that these elements are part of the solid structure, in others words, geopolymer act like a zeolite in retaining certain cations.

### 6. Stabilization/solidification of wastes under hydrothermal conditions

Under hydrothermal conditions, C–S–H (B) and tobmorite or xonotlite are the hydration of alkali-activated slag cements, and zeolites form when coal fly ashes or metakaolin is mixed with alkaline solutions under hydrothermal conditions. Zeolites are a family of complex aluminosilicates having a three-dimensional network structure containing channels and cavities. They are thermodynamically stable and their channels and cavities can immobilize a variety of contaminants.

In one study, cementitious materials with high fly ash contents were used to solidify highly alkaline low-level radioactive waste solutions [62]. The temperature of the solidified materials during adiabatic curing reached up to 90 °C. Zeolites were identified in the solidified waste materials.

Hydroceramics are hydrous materials consisting mainly of zeolites and have been design for the treatment of sodium bearing wastes [50,51]. The raw materials include waste (typically 30% dry-mass basis), metakaolin or Class F fly ash, ~5% powdered vermiculite (to enhance <sup>137</sup>Cs fixation), ~0.5% sodium sulfide (redox buffer and heavy metal precipitant), plus ~10% sodium hydroxide dissolved in enough water to produce a stiff paste.

The hydroceramic waste forms are then autoclaved at 90 or  $190 \,^{\circ}$ C, then a dense matrix having sufficient strength to withstand the rigors of stacking in a repository environment. But best of all, the matrix is extremely insoluble. The primary load-limiting characteristic of the hydroceramic waste forms is that cancrinite (or sodalite) represents maximal waste loading; i.e.,

no more than 25% of the formulation's sodium can be in forms other than hydroxide, silicate, or aluminate.

The hydroceramic waste forms were specifically developed to deal with the reprocessing waste at the Idaho National Engineering and Environmental Laboratory (INEEL). INEEL waste is uniquely suited for cementitious solidification because of its overwhelming amounts of sodium. A portion of the reprocessing waste generated at other DOE (Department of Energy, US) fuel reprocessing facilities could be directly processed into hydroceramic waste forms, but the majority (the "supernates" and "salt cakes") is unfit unless they are pretreated in a way that re-speciates the sodium.

#### 7. Summary and future research needs

The performance and microstructure of alkali-activated cements are dependent upon the characteristics of the raw materials and the dosage of activators used. Properly designed alkaliactivated cements exhibit excellent mechanical properties, less porous microstructure and good resistance to attacks by aggressive solutions.

At room temperature, the main hydration product of alkaliactivated cement is C–S–H with low C/S ratio or aluminosilicate gel; there is no readily soluble Ca(OH)<sub>2</sub>. Under autoclaving conditions, the main hydration products are C–S–H with a low C/S ratio, tobermorite, xonotlite and/or zeolites. C–S–H, tobermorite, xonotlite and zeolites show ion-exchange properties.

Wastes show much less interferences with the hydration of alkali-activated cements that that of Portland cement. Extensive published results have confirmed that alkali-activated cements can be effectively used for stabilization/solidification of a variety of hazardous and radioactive wastes.

Alkali-activated cements usually exhibit higher shrinkage than Portland cement when they hydrate at room temperatures, which may result in the cracking of monolithic waste forms. Some alkalis may leach out of the waste forms and enter into the environment if they are immersed in solution. Although the hydration and microstructure development mechanisms of alkali-activated cements are still not clear, it will be very helpful to establish the relationship between the nature of contaminants to be fixed and the nature of raw materials used in the alkaliactivated cements.

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