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Journal of Nuclear Materials 299 (2001) 199–204

**Journal of
nuclear
materials**

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New aluminium-rich alkali slag matrix with clay minerals for immobilizing simulated radioactive Sr and Cs waste

Guangren Qian^{*}, Darren Delai Sun, Joo Hwa Tay

*School of Civil and Structural Engineering, Environmental and Engineering Research Center,
Nanyang Technological University, Singapore*

Received 10 June 2001; accepted 3 October 2001

Abstract

A new aluminium-rich alkali-activated slag matrix (M-AAS) with clay absorbents has been developed for immobilization of simulated radioactive Sr or Cs waste by introducing metakaolin, natural zeolite and NaOH-treated at-pulgite clay minerals into alkali-activated slag matrix (AAS). The results revealed that the additions of metakaolin and clay absorbents into the cementitious matrixes would greatly enhance the distribution ratio, R_d , of selective adsorption whether the matrix was OPC matrix or AAS matrix. The new immobilizing matrix M-AAS not only exhibited the strongest selective adsorption for both Sr and Cs ions, but also was characterized by lower porosity and small pore diameter so that it exhibited the lowest leaching rate. Hydration product analyses also demonstrated that (Na+Al)-substituted C–S–H(I) and self-generated zeolite were major hydration products in the M-AAS matrix, which provided this new immobilizing matrix with better selective adsorption on Sr and Cs and lower leaching rate. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Portland cement or modified blend Portland cement was the most common matrix for immobilizing low or medium radioactive waste such as ^{137}Cs and ^{90}Sr . This matrix had many disadvantages such as high porosity, poor adsorption and poor durability in practical application. Caesium and strontium as dangerous radionuclides in nuclear waste cannot be well immobilized in the matrix of Ca-rich C–S–H during the hydration of Portland cement [1,2]. Alkali-activated binder is a non-traditional cementitious system that relies on the alkali activation of aluminosilicate materials. In the past decade, alkali-activated aluminosilicate binders have shown great potential in disposal of low or medium

radioactive waste [3,4]. When used as barriers or for encapsulation, they can both effectively reduce the permeability of the matrix and fix nuclide ions in the structure with large cage-like crystals. This excellent properties is attributed to the formation of hydrates such as CaO-low C–S–H(I) [5,6] and zeolitic minerals [7].

It has also been realized that (Al+Na)-substituted C–S–H(I) has much bigger cation exchange capacities and selectivity for Cs ion than normal C–S–H(I) [8,9]. Whether zeolitic hydrate products exist in the matrix of alkali-activated binder is still argued [10,11], however, it has been confirmed that the reaction of aluminium-rich aluminosilicate materials such as metakaolin and fly ash with alkali would favour the formation of zeolitic minerals [12,13].

Additionally, introduction of clay minerals such as natural zeolite and montmorillonite, into the matrix of cementitious materials has been proved to be a very effective means to improve the immobilizing ability of the matrix for low or medium radioactive wastes [14,15].

^{*} Corresponding author. Permanent address: Southwest University of Science and Technology, Mianyang 621002, Sichuan, People's Republic of China. Fax: +65-861 5254.

E-mail address: cgrqian@ntu.edu.sg (G. Qian).

Attapulgite clay is the same magnesium hydroxide–silicate compound as montmorillonite. It appeared to have the greatest promise as potential sorbent for capturing hazardous constituent trace metals and was used for the immobilizing of low-level radioactive waste in the matrix of Portland cement [16,17].

The objective for this work is to constitute a new and highly effective immobilizing matrix, in which (Al+Na)-substituted C–S–H(I) and self-generated zeolitic minerals are created together with natural attapulgite and zeolite by addition of metakaolin.

2. Experiments

2.1. Raw materials

Blast furnace slag (BFS) was used as the main raw material to synthesize an alkali-activated slag matrix. The hydraulic modulus of this slag, $K = (\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3) / (\text{SiO}_2 + \text{MnO} + \text{TiO}_2) = (46.74 + 5.52 + 9.71) / (36.27 + 0.52 + 2.80)$, was 1.56. The surface area of the slag was $520 \text{ M}^2/\text{Kg}$.

After evaluating the adsorption and cation exchange ability of different clays on Cs or Sr ion, the clays with optimal adsorption behaviour were selected for the absorbents of alkali-activated slag matrix. Six clays in Table 1 were tested in total. They included natural montmorillonite (XJMO), illite (YX), kaolinite (Kao),

zeolite (XJZ), attapulgite (JB) and NaOH-treated attapulgite clay (JB–Na). NaOH-treated attapulgite was made by a process, in which the natural powdered attapulgite was immersed in 2 M NaOH solution for 24 h and then washed and dried.

Metakaolin clay (MK) was used as a source of aluminium. It was produced from the decomposition of kaolinite clay burned at $650 \text{ }^\circ\text{C}$ for 2 h and then ground into powder.

2.2. Preparation of immobilizing matrixes

Four immobilizing matrixes were made from different raw materials as listed in Table 2. The cement pastes containing 0.5 wt% Cs^+ (CsCl) or Sr^{2+} ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) were cast in a cylinder module with diameter of 2.5 cm and height of 5 cm, and cured in a fog room at $25 \text{ }^\circ\text{C}$ for 28 days. Ratio of water to solid in the pastes was 0.3. The alkali activators were water glass and sodium carbonate. The addition of alkali activator was adjusted to 5% (by Na_2O) of slag in weight.

2.3. Determination of cation exchange and selective adsorption capacity

Cation exchange capacities were measured by using a method as described by Komarneni and Roy [18]. Selective Cs or Sr adsorption by the various clay absorbents and synthesized matrixes without Sr or Cs ion

Table 1
Cation exchange capacities and distribution ratio R_d for clay minerals

No.	Sample	Main phase	CEC (meq/100 g)	R_d (mol/g)	
				Cs	Sr
JB	Untreated attapulgite	Palygorskite	17.7	7.8×10^2	1.1×10^3
JB–Na	NaOH-treated attapulgite	Palygorskite	–	3.7×10^3	2.7×10^3
XJZ	Zeolite	Clinoptilolite modernite	74.4	4.4×10^3	1.5×10^4
XJMO	Bentonite	Montmorillonite	105.8	4.8×10^3	3.8×10^3
YX	Illite	Illite	3.5	7.5×10^2	8.2×10^2
Kao	Kaolinite	Kaolinite	5.9	1.4×10^3	7.2×10^2
Z4A	Synthesized NaA–zeolite	NaA–zeolite	236.4	1.4×10^4	8.2×10^4

Table 2
Mix proportion of immobilizing matrixes and distribution ratio R_d

Samples	Proportion (wt%)					Distribution ratio R_d (mol/g)	
	OPC	Slag	MK	XJZ	JB–Na	Cs	Sr
OPC	100					1.5×10^3	4.7×10^3
M-OPC	70		10	5	15	2.8×10^3	6.1×10^3
AAS		100				3.9×10^3	6.4×10^3
M-AAS		70	10	5	15	6.4×10^3	1.2×10^4

were determined by adding 25 ml 0.002 M CsCl or SrCl₂ solution to 50 mg of samples, equilibrating for 7 days in glass vials, separating the solid and solution phases by centrifugation and analysing Cs or Sr in solution by atomic adsorption spectroscopy.

2.4. Hydration products, porosity and leachability analysis

After various pastes cured for 28 days, one part of each specimen was employed for hydration product analysis by XRD, DTA–TG and porosity analysis by Quantachrome scanning mercury porosimeter. The leach rates of immobilizing matrixes were determined according to GB7023-86. The method is to place the specimen into deionized water solution in a Teflon container at 25 °C for different times. The volume of solution was 100 ml. The size of cylinders used for leach test was 2.5 × 5 cm². The concentration of Sr or Cs ion in the leachate was analysed by atomic adsorption spectroscopy.

3. Results and discussion

3.1. Cation exchange capacity and distribution ratio of adsorption

3.1.1. Clay minerals

The cation exchange capacity is an important index reflecting clay properties. There are three causes that control the cation exchange capacity of clay minerals: broken bonds around the edges of the silica–alumina units, lattice substitution and the hydrogen of exposed hydroxyls [19]. Table 1 lists the cation exchange capacity of six samples. For kaolinite, illite and attapulgite minerals, broken bonds are the major cause of their exchange capacity [19]. As a result, they had poor cation exchange capacity of less than 20 meq/100 g. Natural bentonite and zeolite minerals have a high cation exchange capacity over 70 meq/100 g. This feature was controlled by the crystal structure of either montmorillonite in bentonite or clinoptilolite in zeolite, in which there are a lot of lattice substitutions of different valent ions or a framework of a molecular sieve [19,20]. Synthesized NaA–zeolite was made from the reaction between metakaolin and NaOH. Its dominant mineral is NaA–zeolite [21]. This NaA–zeolite exhibited much higher cation exchange capacity of 236 meq/100 g than natural zeolite. It was attributed to have much larger specific surface area in addition to lattice substitution [22].

The cation exchange capacities predominate over selective adsorption of clay minerals with respect to uptake of Sr or Cs ions. Sr or Cs adsorption ability of adsorbents was evaluated by their distribution ratio R_d

[9]. The distribution ratio R_d was expressed in terms of the amounts of ions adsorbed by a unit mass of solid sorbent, divided by the equilibrium ion concentration of aqueous phase. Table 1 also shows results of distribution ratio R_d for different clays. The distribution ratio R_d of bentonite for Cs is 4.8×10^3 mol/g and that of zeolite XJZ for Sr is 1.5×10^4 mol/g, both the highest among six natural clays. Similar to cation exchange capacity, synthesized NaA–zeolite presented an excellent adsorption for both Cs and Sr. The distribution ratio R_d was 1.4×10^4 mol/g for Cs and 8.2×10^4 mol/g for Sr, respectively, 2.2–4.5 times higher than that of natural zeolite XJZ. In this work, natural attapulgite clay was treated with NaOH solution. The result shows that the distribution ratio R_d for Sr or Cs ion for NaOH-treated attapulgite is enhanced by 1.4–3.7 times than natural attapulgite. Attapulgite is a dioctahedral mineral with some substitution of Al³⁺ for Si⁴⁺. This mineral is formed by shortened sheets of octahedral–tetrahedral linkages which are alternatively inverted. The alternation of the sheet orientations creates open a cavity in the structure similar to zeolite, in which water and exchange ions can be accommodated [23]. Yi's results [24] showed NaOH-treated attapulgite is negative-charged and has much larger surface area than natural attapulgite.

3.1.2. Immobilizing matrixes

In this work, a new immobilizing matrix was derived from a modification to the traditional alkali-activated slag system. Expected hydration products in this matrix are (Al+Na)-substituted C–S–H(I) and self-generated zeolite. To get to this goal, two ways are adopted. Firstly, metakaolin was added into an alkali-activated slag system as the source of aluminium. Wang [10] established that the ratios of both Al/Si and Ca/Si are the key to control the formation of zeolite in an alkali-activated slag system. Secondly, based on selective adsorption results for clay minerals with Cs and Sr ion, natural zeolite, bentonite and NaOH-treated attapulgite appeared to have excellent potential to adsorb both Sr or Cs ion. The mechanical test results of immobilizing matrixes with clay absorbents, however, showed addition of bentonite clay would cause the compressive strength of matrixes to be greatly reduced [25]. For this reason, only metakaolin, zeolite and NaOH-treated attapulgite were selected for supplementary absorbents in the designed matrix. It is also expected the addition of natural zeolite would favour the formation of self-generated zeolite by providing a nucleation site.

To compare the adsorption behaviour of different immobilizing matrixes on Sr or Cs ion, three immobilizing matrixes were designed and OPC matrix was used as a controlled sample according to Table 2. The distribution ratios R_d of four matrixes for Sr or Cs ion were also listed in Table 2. Traditional OPC matrix had the

lowest distribution ratio R_d for both Sr and Cs. In contrast to this, the distribution ratio R_d of alkali-activated slag matrix AAS was greater and reached 6.4×10^3 mol/g for Sr and 3.9×10^3 mol/g for Cs. The additions of metakaolin and clay absorbents into matrixes had strong positive effects on enhancing the distribution ratio R_d , whether the matrix was OPC matrix or AAS matrix. As listed in Table 2, the distribution ratio R_d of M-OPC sample, OPC matrix with clay absorbents, was about the same as that of the AAS matrix. Comparatively, AAS matrixes with clay absorbents showed the strongest adsorption capacity among the four matrixes and its distribution ratio R_d was 1.2×10^4 for Sr and 6.4×10^3 mol/g for Cs, 1.5–3 times larger than that of the OPC matrix and 67–88% higher than that of the AAS matrix without clay absorbents.

3.2. The hydration products of immobilizing matrix

The excellent adsorption behaviour of AAS matrix with clay absorbents was well correlated with its hydration products. The hydration products were determined by XRD and DTA. Fig. 1 shows the XRD results and Fig. 2 is the DTA–TG results. There existed a broad and diffuse hump around $30\text{--}31^\circ 2\theta$, which arises from the original slag reflecting the short-range order of slag glass structure. After being alkali-activated for 28 days, a new peak was superimposed on the amorphous hump, at 3.03 \AA can be identified in the samples AAS and M-AAS. It can be attributed to the (110) reflection of poorly crystalline C–S–H(I) [10]. This C–S–H(I) phase gave a steeper endothermic peak with bigger weight loss at 130°C and a broad exothermic peak at $800\text{--}900^\circ \text{C}$ in DTA curve (Fig. 2), which correspond to the gradual dehydration of the C–S–H(I) interlayer and the decomposition of C–S–H(I) into wollastonite. The exothermic peak of AAS matrix stood at 810°C while that of M-AAS matrix was shifted to a higher temperature lying at 860°C . M-AAS matrix was added with metakaolin, belonging to the Al_2O_3 -rich $\text{NaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaO-H}_2\text{O}$ system. Diamond and others [26,27] proved that the position shift of the exothermic peak in

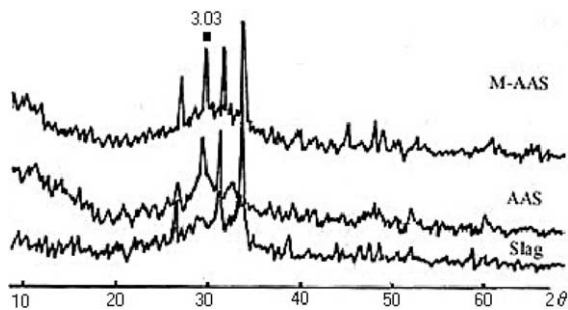


Fig. 1. XRD patterns of slag and immobilizing matrixes.

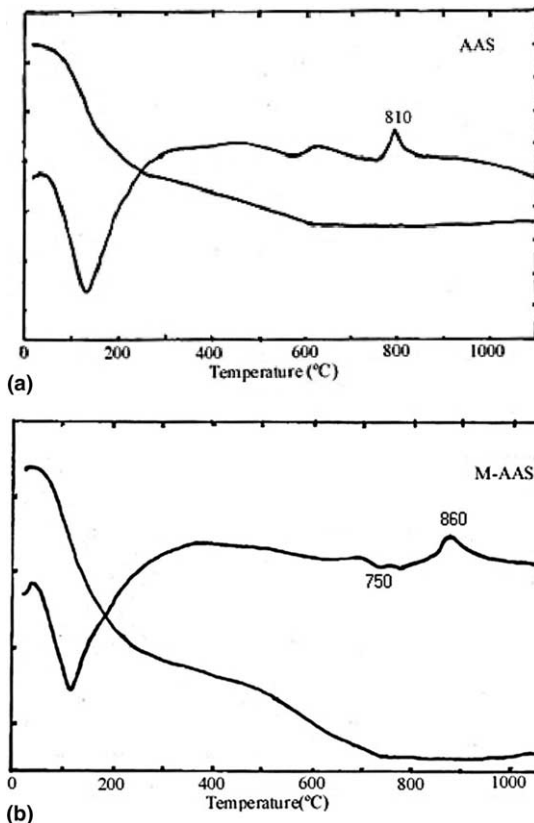


Fig. 2. DTA and TG curves of immobilizing matrixes: (a) AAS; (b) M-AAS.

DTA was due to the corporation of Al^{3+} into C–S–H(I) to replace Si^{4+} . The non-equilibrium charge balance induced by replacement of Al^{3+} for Si^{4+} would be compensated by Na^+ . It indicates that C–S–H(I) formed in the M-AAS matrix is (Na+Al) substituted C–S–H(I). (Na+Al) substituted C–S–H(I) showed high cation exchange capacity and very high selectivity for Cs ion [8,9].

Although Glukhovskiy [7] found in 1959 that zeolite is a major hydration product formed in the AAS system, it has not been verified by later researches. However, it has been accepted that addition of aluminium-rich materials such as metakaolin and fly ash into AAS would accelerate the formation zeolite-like products, which was confirmed by NMR [12]. For the sample M-AAS added with metakaolin, no trace of newly formed zeolite was found in XRD, as the product formed under normal ambient condition is amorphous [11]; but a poor endothermic peak at 750°C and small weight loss can be detected in DTA curve (Fig. 2(b)), which are absent from the AAS matrix (Fig. 2(a)). This endothermic peak is matched with that of phillipsite zeolite. This fact suggests that metakaolin addition favours the formation of self-generated zeolite.

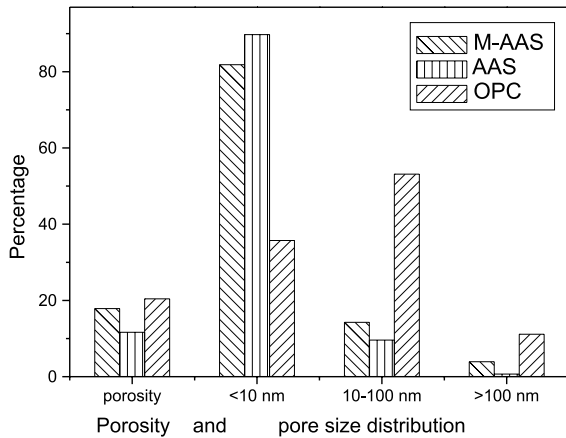


Fig. 3. Porosity and pore size distribution of immobilizing matrixes.

3.3. Porosity and leachability

The pore structure characteristics of three matrixes are summarized in Fig. 3. OPC matrix has the largest porosity 20.41% among three matrixes and its porosity consists of mainly 53% medium pores (10–100 nm) and 11% large pores (>100 nm). M-AAS matrix and AAS matrix had similar pore structures. Their pore size distributions were concentrated among small pores (<10 nm), which represent over 80% of the porosity. The quantities of medium pores and large pores in the M-AAS matrix were slightly larger than that in the AAS matrix.

The leachability of three matrixes containing 0.5 wt% Sr^{2+} or Cs^+ was expressed by the leaching rate R ($\text{g}/\text{cm}^2 \text{d}$) as Eq. (1):

$$R_n^i = \frac{a_n^i}{Ft_n}, \quad (1)$$

where i is Sr^{2+} or Cs^+ , a_n is mass of leached Sr^{2+} or Cs^+ at certain period (g), F is surface area of the specimens (cm^2), and t_n is leach time (d).

Figs. 4 and 5 list the leaching rate of three immobilizing matrixes with simulated radioactive nuclide Sr or Cs at 25 °C. The leaching rate of three matrixes for Sr or Cs decreased in the order OPC > AAS > M-AAS, that is to say, M-AAS matrix exhibited the lowest leaching rate while the OPC matrix was the highest at any time. Although the porosity and quantities of pore with over medium pore size in M-AAS were slightly higher than that in AAS, the former had less leaching rate than the later. This reason may be from two aspects. On the one hand, the addition of metakaolin into the M-AAS matrix promoted the formation of hydration products (Al+Na)-substituted C-S-H(I) and self-generated zeolite. As discussed above, these hydrate products had

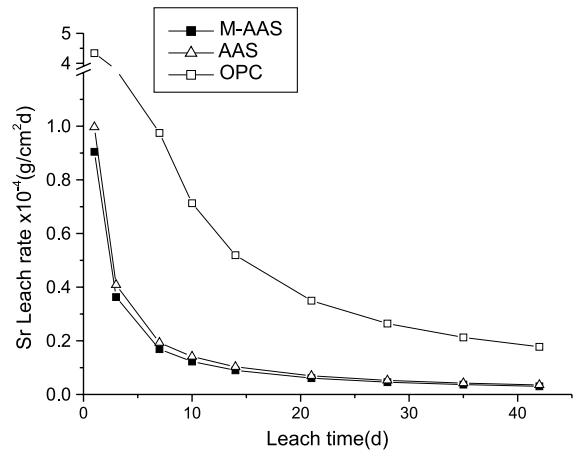


Fig. 4. Sr^{2+} leach rate of immobilizing matrixes.

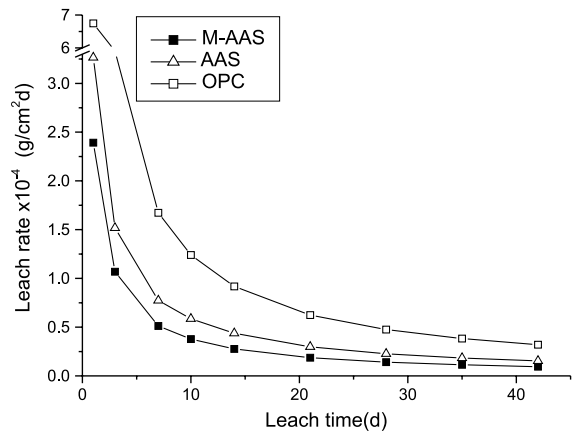


Fig. 5. Cs^+ leach rate of immobilizing matrixes.

excellent adsorption capacities for Sr or Cs. Saki et al. [28] also found similar results for OPC matrix with metakaolin. On the other hand, additions of clay minerals such as zeolite and NaOH-treated attapulgite were helpful to enhance the adsorption capacities of the M-AAS matrix for Sr or Cs so that its leaching rate became the lowest.

4. Conclusions

1. Natural bentonite and zeolite minerals exhibit a high cation exchange capacity over 70 meq/100 g in natural clay minerals. They also had strong selective adsorption for Sr or Cs. Synthesized NaA-zeolite not only had a much bigger cation exchange capacity of 236 meq/100 g but also had the strongest selective

adsorption for Sr and Cs ions. In addition, the selective adsorption capacity of NaOH-treated attapulgite was largely improved.

2. Addition of metakaolin, natural zeolite and NaOH-treated attapulgite clay into immobilizing matrixes enhances the distribution ratio R_d . Comparative to the OPC matrix and the AAS matrix, M-AAS matrix exhibits the highest distribution ratio R_d and lowest leaching rate for both Sr and Cs ions.
3. (Na+Al)-substituted C–S–H(I) and self-generated zeolite were major hydration products in the M-AAS matrix.

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