

Application of Metakaolin-slag Binders to Solidify Rad-waste Glass Sharps: Leaching of ^{137}Cs and $^{152+154}\text{Eu}$ Radionuclides

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METAKAOLIN (MK) and blast furnace slag (BFS) were utilized to design alkali activated binders suitable for solidification of waste glass (WG sharps contaminated with ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides). Two forms of WG, powdered and fused, were utilized. Effects of WG forms and BFS addition on the ability of formulations to withstand compression were preliminary studied. When cold powdered WG was solidified the corresponding compressive strength (MPa) values were decreased by increasing the loading percentages. While fused forms were positively affected MPa values till 10.0% loading. Positive relations between BFS addition and MPa values were also detected. Leaching of ^{137}Cs and $^{152+154}\text{Eu}$ from MK-based formulations was followed as affected by WG forms, BFS addition and early age (2hr) curing temperatures. Both studied radionuclides were cumulatively leached in larger fractions from solidified powdered WG than from fused one. The obtained results reflected the ability of the designed formulations to retain ^{137}Cs in greater extents than $^{152+154}\text{Eu}$. The lowest diffusion coefficient values (2.01×10^{-11} and $3.92 \times 10^{-10} \text{cm}^2/\text{s}$) were recorded when fused forms of WG containing ^{137}Cs and $^{152+154}\text{Eu}$, respectively, were solidified into slag seeded MK-based formulations, early aged cured at 40°C . Slope values of $\log(\text{CLF})$ vs. $\log(\text{time})$ plots were < 0.35 indicating that the controlling leaching mechanisms for all studied leaching systems were predicted to be wash-off.

Keywords: Alkali activated binders, Non-combustible rad-waste, Glass, ^{137}Cs , $^{152+154}\text{Eu}$.

Introduction

As a result of different operations in nuclear facilities such as plants of nuclear power and fuel reprocessing, research reactors and centers, ...etc., different radioactive wastes are produced (IAEA, 2001). The nature of these wastes varies considerably from facility to facility and can be differentiated according to physical forms into four basic types: Liquid, solid absorbed liquids, dry combustible or compactible solids and dry non-combustible or non-compactible solids. The primary constituent of non-combustible solid waste is glass, metal (including fuel cladding) and concrete which are significant (Efremenkov, 1989). Rad-waste glass sharps are kinds of sharps contaminated with radioactive materials capable of cutting or piercing and may cause internal contamination to workers. As fission products, both cesium (^{134}Cs and ^{137}Cs ; $t_{1/2}$ of 2.06 and 30.17 y, respectively) and europium radionuclides (^{152}Eu and ^{154}Eu ; $t_{1/2}$ of 13.54 and 8.69 y, respectively) can be presented in such solid wastes. For disposal

options, it is better for all radioactive waste to be in a relatively insoluble solid form which is less susceptible to dispersion from a disposal site. Thus, where possible, the waste can be crushed or melted for volume reduction. Smaller units of noncombustible wastes, such as incineration ash, ion-exchange resins, and sludges and residues from the treatment of intermediate- and low-level liquid wastes are incorporated in concrete and bitumen (Lennemann, 1992). Ordinary Portland cement (OPC) is the traditional material to solidify rad-wastes (El-Kamash et al., 2006) in which glass powders can be utilized as supplementary cementitious material (Federico & Chidiac, 2009). However, most cement-based materials are porous causing radionuclides to be easily leached, combined with low thermal stability and poor acid corrosion resistance (Santanu & Pak, 2006; Malviya & Chaudhary, 2006 and Zhou et al., 2006). Thus, the retention of radionuclides in the cement matrix is not ideal (Zhou et al., 2006) making the investigation of other alternatives is of a paramount concern.

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DOI: 10.21608/ejrsa.2019.13301.1072

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Nowadays, alkali activated binders (AABs) are considered efficient alternatives to OPC due to their superior properties in terms of high mechanical strength, acid and fire resistances, thermal and radiation stabilities and solidification of hazardous wastes with low energy consumption (Palomo et al., 1999; Yao et al., 2009; El-Naggar, 2014; El-Naggar et al., 2018). AABs are polymeric silicon-oxygen-aluminum three-dimensional materials containing various amorphous to semi-crystalline phases and the fundamental structure of geopolymers are tetrahedral coordination of Si and Al linked by oxygen bridges and the negative charges on tetrahedral Al sites were balanced by alkali cations (typically Na⁺ and/or K⁺) (Palomo et al., 2004; Jimenez & Palomo, 2005 and Huang & Han, 2011). The large reserves of kaolin in Egypt (Abdel-Khalek, 1999) beside an annual production of blast furnace slag of about 300,000 tons could make such geopolymer technology applicable. Considerable efforts were performed to evaluate the solidification of different kinds of rad-wastes into AABs (Fletcher & Rima, 2012; Li et al., 2013; El-Naggar, 2014; Cantarel et al., 2015 and El-Naggar et al., 2018). Recently, Liu and co-workers overviewed the reuse of waste glasses in AABs (Liu et al., 2019). They abstracted that fusion method of waste glass which proposed by El-Naggar and El-Dessouky (El-Naggar & El-Dessouky, 2017) is among the three methods which can be applied to use waste glass to manufacture alternative activators. They also observed limited research in the employment of waste glasses in alkali activated materials.

Thus, the present study was constructed to investigate slag seeded metakaoline based alkali activated binders to solidify rad-waste glass sharps. Assessments were focused on the mechanical integrity of waste forms, in terms of 28-days compressive strength, and 90-days static leaching tests of both ¹³⁷Cs and ¹⁵²⁺¹⁵⁴Eu radionuclides from the solidified hot WG. Leaching results were kinetically analyzed to determine diffusion coefficients, leachability indexes and mechanism of leaching of radionuclides.

Materials and Methods

Materials

Metakaolin (MK) and blast furnace slag (BFS) constituted the raw materials which applied in the alkali activated binders synthesis. Kaolinite clay and BFS (Table 1; El-Naggar, 2014) were obtained locally from El-Teeh plateau (Sinai, Egypt) and Egyptian Iron and Steel Co, respectively. Segregated radioactive (hot; HWG) and non-radioactive (cold; CWG) waste glass sharps were collected as by-products of the research activities at Hot Laboratories Center, Atomic Energy Authority, Egypt. HWG sharps were further radiometrically segregated into sharps which contaminated were with either ¹³⁷Cs (HWG-¹³⁷Cs) or ¹⁵²⁺¹⁵⁴Eu (HWG-¹⁵²⁺¹⁵⁴Eu) radionuclides. Analytical grades of sodium hydroxide (SH) and sodium metasilicate pentahydrate (SSH) pellets were products of Sigma-Aldrich Co. Fumed silica (FS) (SiO₂; 99.8%) was a product of A. Johnson Mathey Co. Reactive MK was produced by the *In-Lab* calcinations of kaolinite clay for 4hr at 750°C (5°C/min.).

Elaboration of powders

Individual milling of MK, BFS and both kinds of WG sharps were carried out for 6hr in a ball mill (U.S. Stoneware, Eastpalestine 44413) having zirconia balls of ¼" radius end cylinder. Particle sizes of the milling powders were estimated and were less than 75µm each. Powders of WG were divided into two portions where one of which was directly immobilized into the designed AAB while the other was immobilized after the fusion of 5, 10 and 30% WG with definite amounts of NaOH pellets (heating in crucibles in the air at temperature of 550°C). Each fusion product was air cooled, ground and mixed with a definite amount of bi-distilled water, followed by vigorous shaking at room temperature for 30min. The fusion products were filtered where three WG residues were obtained, followed by drying and the subsequent immobilization into the designed formulations.

TABLE 1. Oxide compositions of local Sinai kaolinite clay and local blast furnace slag (El-Naggar, 2014).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Na ₂ O	CaO	MnO	K ₂ O	MgO	P ₂ O ₅	SO ₂	LOI
Sinai kaolinite	51.13	32.40	2.06	1.40	0.10	0.09	0.01	0.01	--	--	--	12.80
Blast furnace slag	33.25	12.23	1.65	--	0.88	45.42	0.90	0.12	2.47	0.07	1.68	1.33

Alkaline silicate solutions

Four types of alkaline silicate solutions (ASS) were prepared. ASS1 having $\frac{SiO_2}{Na_2O}$, $\frac{SiO_2}{H_2O}$ and $\frac{Na_2O}{H_2O}$ of 1.35, 0.44 and 0.33, respectively, was prepared by dissolving adequate amounts of SH, SSH and FS into the definite volume of bi-distilled water. ASS2, ASS3 and ASS4 were prepared by dissolving the aforementioned amounts of SSH and FS in filtrates resulted from fusion of 5, 10 and 30% WG, respectively.

Designs of different binders

Four groups of alkali activated binders were designed (Table 2). The first group (G1) was designed to preliminary investigate the mechanical integrity of different matrices as affected by waste glass forms (powder or fusion residues). The three other groups were designed to evaluate leaching parameters of ^{137}Cs and $^{152+154}Eu$ radionuclides. Factors affecting leaching of radionuclides such as waste glass form (G2 and G3) and curing temperature (25, 40 and 70°C; G4) were investigated.

Preliminary compressive strength investigations

Waste form failure under load may lead to great problems in its disposal sites due to a larger

effective surface area from which activity can be leached. Hence, the mechanical properties of such forms are of great concern. Preliminary compressive strength investigations, expressed as the maximum applied load divided by the cross-sectional area of a specimen, were performed as a measure of mechanical integrity. Measurements were achieved by a load compression machine (model WF, Eng., UK) according to the British Standards, with a test data accuracy of $\pm 1\%$. All pastes of the first group (G1) were prepared by placing the desired binders on smooth non-absorbent surfaces, and craters were formed into centers. Appropriate volumes of ASS_(s) were poured into craters (according to Table 2), at S/L of 0.8, and then the vigorous mixing operations were completed using a helix grout mixer (1500rpm for 4min). Pastes were cast into acrylic molds (40 × 40 × 40mm i.d.), vibrated for 2min to remove entrained air and covered with a polyethylene thin sheet to prevent water evaporation. The prepared formulations were kept at ambient conditions for 24hr then were demolded and were kept for 28-days curing time. A good binder is expected to withstand the maximum achievable compression (MPa) which accompanied by good workability with suitable setting time.

TABLE 2. Experimental conditions of geopolymerized rad-waste glass.

Group	Symbol	Raw materials ratios						Radionuclide(s)	ASS	Curing temp., °C
		Binder(s), %		Waste glass, %						
		MK	BFS	CWG		HWG				
				Powder	Fused	Powder	Fused			
<u>Preliminary investigations</u>										
	P5CWG	95.0	-----	5.0	-----	-----	-----	-----	ASS1	Ambient
	P10CWG	90.0	-----	10.0	-----	-----	-----	-----	ASS1	Ambient
	P30CWG	85.0	-----	30.0	-----	-----	-----	-----	ASS1	Ambient
	F5CWG	95.0	-----	-----	5.0	-----	-----	-----	ASS2	Ambient
G1	F10CWG	90.0	-----	-----	10.0	-----	-----	-----	ASS3	Ambient
	F30CWG	85.0	-----	-----	30.0	-----	-----	-----	ASS4	Ambient
	S5/F10CWG	85.0	5.0	-----	10.0	-----	-----	-----	ASS3	Ambient
	S10/F10CWG	80.0	10.0	-----	10.0	-----	-----	-----	ASS3	Ambient
	S30/F10CWG	60.0	30.0	-----	10.0	-----	-----	-----	ASS3	Ambient
<u>Leaching investigations</u>										
G2	G2HWG- ^{137}Cs	90.0	-----	-----	-----	10.0	-----	^{137}Cs	ASS3	Ambient
	G2HWG- $^{152+154}Eu$	90.0	-----	-----	-----	10.0	-----	$^{152+154}Eu$	ASS3	Ambient
G3	G3HWG- ^{137}Cs	90.0	-----	-----	-----	-----	10.0	^{137}Cs	ASS3	Ambient
	G3HWG- $^{152+154}Eu$	90.0	-----	-----	-----	-----	10.0	$^{152+154}Eu$	ASS3	Ambient
	G4- ^{137}Cs -25°C	60.0	30.0	-----	-----	-----	10.0	^{137}Cs	ASS3	25°C
	G4- ^{137}Cs -40°C	60.0	30.0	-----	-----	-----	10.0	^{137}Cs	ASS3	40°C
	G4- ^{137}Cs -70°C	60.0	30.0	-----	-----	-----	10.0	^{137}Cs	ASS3	70°C
G4	G4- $^{152+154}Eu$ -25°C	60.0	30.0	-----	-----	-----	10.0	$^{152+154}Eu$	ASS3	25°C
	G4- $^{152+154}Eu$ -40°C	60.0	30.0	-----	-----	-----	10.0	$^{152+154}Eu$	ASS3	40°C
	G4- $^{152+154}Eu$ -70°C	60.0	30.0	-----	-----	-----	10.0	$^{152+154}Eu$	ASS3	70°C

ASS= Alkaline silicate solution, BFS= Blast furnace slag, CWG= Cold waste glass, HWG= Hot waste glass, MK= Metakaolin

Leachability investigations

Leaching of ^{137}Cs and $^{152+154}\text{Eu}$ from the designed binders into bi-distilled water were comparatively performed by the IAEA's standard static leaching test proposed by Hesper (Hesper, 1971). Acrylic cylinders ($20 \times 10\text{mm}$ i.d.) were used to cast pastes of groups 2, 3 and 4 given in Table (2). Effects of BFS addition, WG forms and early age curing temperatures on leaching of the studied radionuclides were investigated. After 28 curing time, cylinders were demolded and were directly immersed in the leaching medium. The ratio between the volume of leachant and the exposed surface area of a formulation was not more than 10cm (Hesper, 1971). Samples of the leaching solution were withdrawn at the frequency of: daily during the first week, once per week for the following four weeks and once per month during the following three months. Radiological analyses were carried out using a multichannel analyzer coupled with a high purity germanium coaxial detector (Model GX 2518, Canberra Series, USA). Calibration was done using a mixed sealed source of the radioisotopes; ^{155}Eu (86.5 and 105.3keV), ^{57}Co (122.1 and 136.5keV), ^{137}Cs (661.6keV), ^{54}Mn (834.8keV) and ^{65}Zn (1115.5keV). The radionuclidic assessments were conducted by tracing the net area under the respective gamma-ray peaks. Results were obtained in terms of the cumulative leach fractions (CLF, cm) which were calculated according to **Eq. 1 (Hesper, 1971)**:

$$CLF = \left(\frac{\sum A_n}{A_0} \right) \left(\frac{V}{S} \right) \quad (1)$$

where, $\sum A_n$ is the cumulative radioactivity leached (count/min.), A_0 is the radioactivity initially present in the alkali activated specimen (count/min.), V is the volume of the specimen (cm^3), and S is the exposed surface area of the specimen (cm^2).

Results may also be expressed by a plot of the incremental leaching rate, R_n , as a function of the time, t_n (days) of leaching (Hesper, 1971), as expressed by:

$$R_n = \frac{A_n V}{A_0 S t_n} \quad (2)$$

Results and Discussion

Preliminary compressive strength investigations

Figure 1 presents preliminary investigations about the influence of the solidified waste glass forms and blast furnace slag addition on

compressive strength (MPa) of metakaolin-based formulations. When the cold powdered waste glass was solidified (Fig. 1 a), the corresponding MPa values were decreased by increasing the loading percentages. Tan and Du attributed this influence to the smooth surface (weakened binding to the matrix) and microcracks of glass cullet (Tan & Du, 2013). In contrary to powdered WG, Fig. 1 (b) illustrates that fused forms positively affected MPa values till 10.0% loading (F10CWG; 42.64 MPa). This can be interpreted through the expected high Si-modulus of ASS3 which was prepared from the filtrate product of the fused WG (El-Naggar & El-Dessouky, 2017). Tchakouté and co-workers stated the formation of geopolymeric gels with high cross-linking structure when MK-based geopolymers were activated by waste glass activators (Tchakouté et al., 2014). Further preliminary investigations were carried out onto F10CWG formulations using different addition percentages of a high calcium system (BFS; 5.0, 10.0 and 30.0%) (Fig. 1 c). Positive relations between BFS addition percentages and MPa values were detected which may be attributed to the expected high calcium silicate hydrate products (El-Naggar et al., 2019). S30/F10CWG formulation recorded the highest compressive strength (49.49MPa) which beside P10CWG and F10CWG was selected for leaching examinations of ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides.

Leaching investigations

Cumulative and incremental leached fractions

Effect of waste glass form: Experiments were designed according to the IAEA's standard leaching test (Hesper, 1971). Figure 2 illustrates that the CLFs (Fig. 2 a) that leached from the solidified WG as well as the corresponding incremental leached fractions (Fig. 2 b) were varied according to WG form as well as the type of the studied radionuclide. Figure 2 (a) reveals that both studied radionuclides were cumulatively leached in larger fractions from solidified powdered WG cullet than from fused one. For the solidified powdered WG, $^{152+154}\text{Eu}$ radionuclides recorded cumulative and incremental leached fractions of $7.84 \times 10^{-7}\text{cm}$ and $2.18 \times 10^{-6}\text{cm/day}$, respectively, at the time where ^{137}Cs radionuclide recorded $1.78 \times 10^{-3}\text{cm}$ and $5.85 \times 10^{-7}\text{cm/day}$, respectively. When WG was solidified in its fused form, the cumulative and incremental leached fractions of ^{137}Cs radionuclide were

reduced by 25.0% recording 1.32×10^{-3} cm and 4.41×10^{-7} cm/day, respectively. Also, the cumulative and incremental leached fractions of $^{152+154}\text{Eu}$ radionuclides were reduced by about 26.0% recording 5.90×10^{-3} cm and 1.66×10^{-6} cm/day, respectively, when WG was solidified in its fused form. The superiority of formulations containing fused WG form in reducing the leached fractions of both radionuclides may be due to their higher MPa values, comparing to those containing powdered WG. El-Naggar and Amin stated that Na-MK based geopolymers showed distinctive sorption capacity toward Cs radionuclide that could interpret the low leached fractions of ^{137}Cs , in the present study, compared to $^{152+154}\text{Eu}$ radionuclides (El-Naggar & Amin, 2018).

Effect of curing temperature with slag addition: Figures 3 and 4 depict the effects of curing temperature of the optimized slag seeded

MK-based formulations on cumulative (Fig. 3 a, Fig. 4 a) and incremental (Fig. 3 b, Fig. 4 b) leached fractional activities of ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides when fusion residues of hot WG were solidified. Data reflected the ability of the designed formulations to retain ^{137}Cs on the expense of $^{152+154}\text{Eu}$. Figures 3 and 4 reveal also that curing at 25°C (ambient temperature) reduced CLF and R_n to values lower than those recorded in Fig. 2. This may be attributed to the sorption capabilities of calcium silicate hydrates (C-S-H) that were suggested to be formed due to BFS addition (El-Naggar et al., 2019). Further reduction in CLF and R_n values, for both radionuclides, were observed when curing temperatures were raised to reach 40°C . Early age curing at 70°C led to more leached fractions for both studied radionuclides which may be due to an increased geopolymerization rate leading to irregular increasing trends of compressive strength (Rovnanik, 2010).

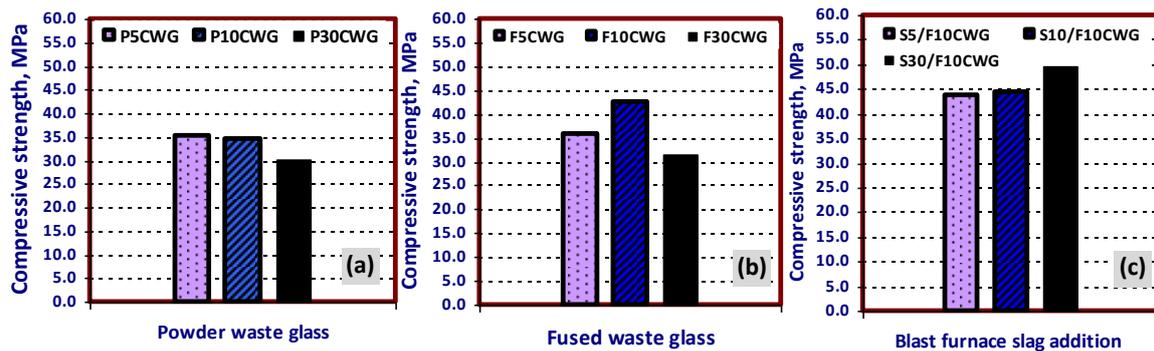


Fig. 1. Effects of waste glass forms and blast furnace additions on 28-days compressive strength (MPa) of metakaolin-based alkali activated binders; (a) 5.0, 10.0 and 30.0% solidified cold powder waste glass, (b) 5.0, 10.0 and 30.0% solidified fused cold waste glass and (c) 5.0, 10.0 and 30.0 % blast furnace slag.

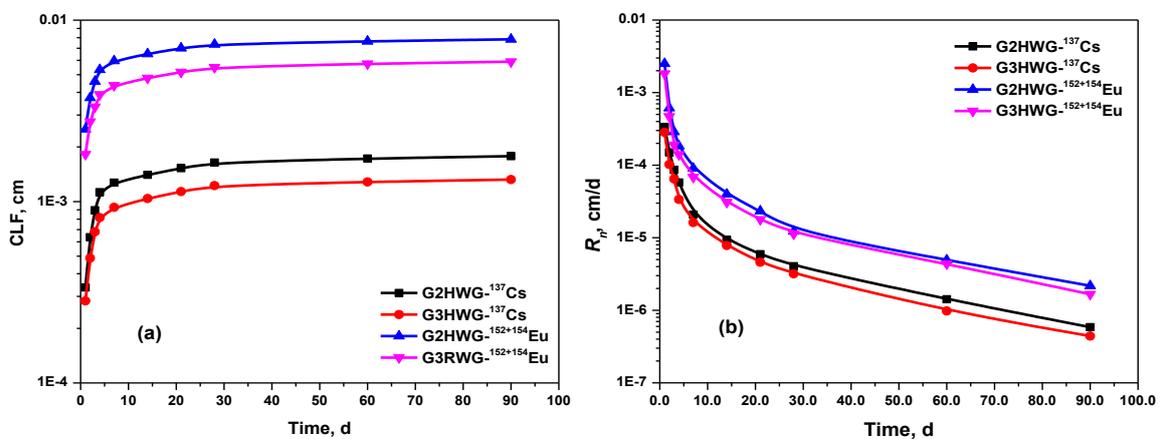


Fig. 2. Effect of waste glass form on (a) cumulative and (b) incremental leached fractions of ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides solidified into metakaolin-based alkali activated binders, after 28-days curing time.

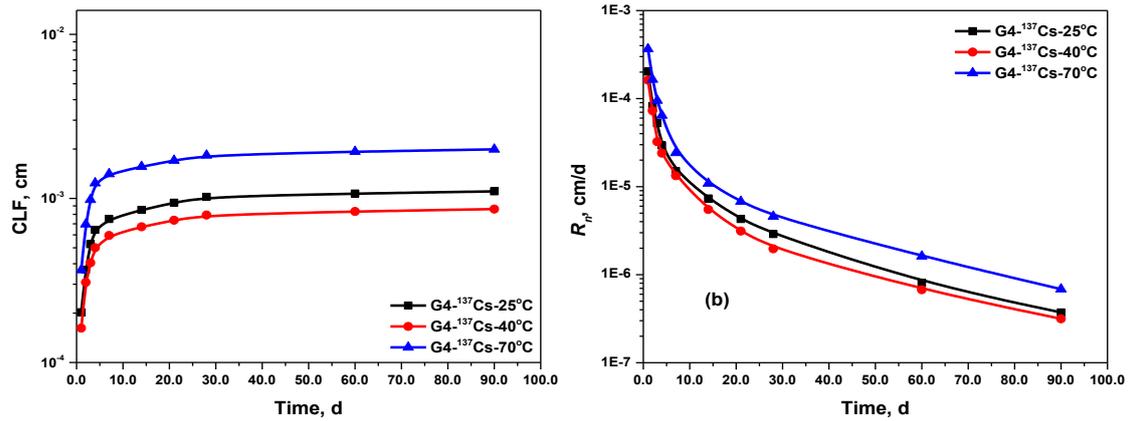


Fig. 3. Effect curing temperatures on (a) cumulative and (b) incremental leached fractions of ¹³⁷Cs radionuclide from hot waste glass fusion residues solidified into slag seeded metakaolin-based alkali activated binders, after 28-days curing time.

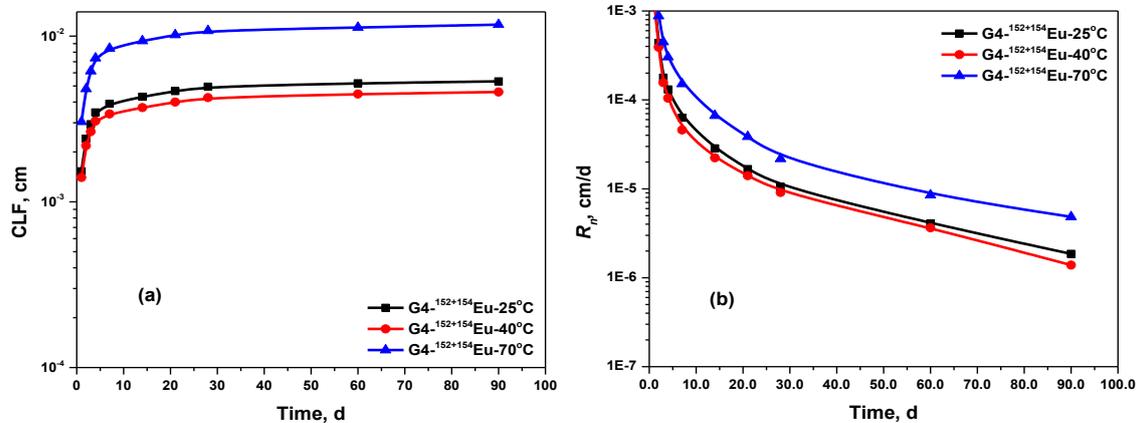


Fig. 4. Effect curing temperatures on (a) cumulative and (b) incremental leached fractions of ¹⁵²⁺¹⁵⁴Eu radionuclide from hot waste glass fusion residues solidified into slag seeded metakaolin-based alkali activated binders, after 28-days curing time.

Effective diffusion coefficients

Since the diffusion is a well-established mechanism depicting leaching and its coefficient as a material constant for rad-waste form, IAEA suggested that these coefficients may be used to compare leaching data (Nickerson, 1988). The quantity of radionuclide leached out from a unit surface area during time, t_n is given by:

$$A_n = 2A_o \sqrt{\frac{Dt_n}{\pi}} \tag{3}$$

where, A_n is the activity leached out after time t_n (count/min.), A_o the initial activity in the composite (count/min.) and D is the diffusion coefficient (cm²/s). Hence, the cumulative leached fractions can be expressed as:

$$\left[\frac{\sum A_n}{A_o} \right] \left[\frac{S}{V} \right] = \frac{2SA_o \sqrt{D \sum t_n}}{A_o V} \tag{4}$$

$$\frac{\sum A_n}{A_o} = 2 \left(\frac{S}{V} \right) \sqrt{\frac{D \sum t_n}{\pi}} \tag{5}$$

Values of D can be calculated from the slopes m of the linear plots of $(\sum A_n/A_o)$ vs. $\sqrt{t_n}$:

$$D = \frac{\pi m^2 V^2}{4S^2} \tag{6}$$

The American National Standards Institute (ANSI) defines a material parameter of the leachability of diffusing species. This parameter is called the leachability index, L , and is defined as (ANSI, 1986):

$$L = \log \left(\frac{\beta}{D} \right) \tag{7}$$

where, β is a defined constant (1.0cm²/s) and D is the diffusion coefficient of the species (cm²/s) assumed to be independent of time during the course of leaching.

Effect of waste glass form: The effect of waste glass forms which were solidified into MK-based AABs on plots of $(\sum A_n/A_0)$ vs. $\sqrt{t_n}$ were explored (Fig. 5) for the subsequent calculation of diffusion coefficients (D , cm^2/s) and leachability indexes (L) (Table 3). Data in Table 3 indicated that both radionuclides were diffused faster when the powdered waste glass was solidified. However, formulations containing fused waste glass performed better in the prevention of the diffusion of both radionuclides. The lowest D value was observed when ^{137}Cs was diffused from formulations containing fused WG ($4.35 \times 10^{-11} \text{cm}^2/\text{s}$) with the subsequent higher L value, of near twice the waste acceptance criteria (10.36) (ANSI, 1986). This may be attributed to the improved mechanical properties caused by the activation of metakaolin using alternative alkaline solution (ASS3) based on fusion of waste glass (Liu et al., 2019). While the highest D value was recorded when $^{152+154}\text{Eu}$ radionuclides were diffused from formulations containing powdered waste glass with the corresponding lowest L value (8.96).

Effect of curing temperature with slag addition: Figure 6 showed the effect of early age curing temperature on the variation of fractional activities vs. square root of time of ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides leached from solidified waste glass residues into slag seeded metakaolin-based formulations. The D values and their corresponding L values were calculated and were given in Table 4. The influence of BFS seeding was obvious where D value of ^{137}Cs was reduced to $3.42 \times 10^{-11} \text{cm}^2/\text{s}$ with the corresponding increase of L value (10.47) when early age curing at 25°C (relatively ambient) was applied. A further reduction in such D value ($2.01 \times 10^{-11} \text{cm}^2/\text{s}$) was observed when early age

curing temperature was raised to 40°C . Therefore, curing at 70°C made un-desired influence where the D value of ^{137}Cs was increased again to reach ($1.04 \times 10^{-10} \text{cm}^2/\text{s}$). Diffusion of $^{152+154}\text{Eu}$ behaved in a similar manner of ^{137}Cs as affected by BFS seeding and curing temperatures, with greater D values and the subsequent L values. The expected C-S-H products, due to BFS addition, may play crucial adsorptive roles in retaining the diffusion of the fixed radionuclides (El-Naggar et al., 2019). Additionally, early age curing temperature at 40°C made the desired influence as reported by El-Naggar and El-Dessouky who examined the microstructure of the geopolymeric products. They stated that regular surface structures with lesser cracking can be obtained when early age pastes of WG/MK were cured at a temperature range of $25\text{--}40^\circ\text{C}$ (El-Naggar & El-Dessouky, 2017).

Controlling leaching mechanism

Various reported studies indicated that the determination of the controlling leaching mechanism could be conducted based on the linear regression of the logarithm CLF versus the logarithm of time (Abdel Rahman & Zaki, 2009 and El-Naggar et al., 2018). If the slope is less than 0.35 the controlling leaching mechanism will be the surface wash-off, for the slope values ranging from 0.35 to 0.65, the controlling mechanism will be the diffusion, and higher slope values represent the dissolution mechanism. The plots of $\log(\text{CLF})$ versus $\log(\text{time})$ are illustrated in Fig. 7 and 8. Results of the linear regression for the studied ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides leaching data were given in Tables 3 and 4. It is clear that the slope values for all the studied systems were < 0.35 indicating that the wash-off mechanism is the controlling leaching mechanism.

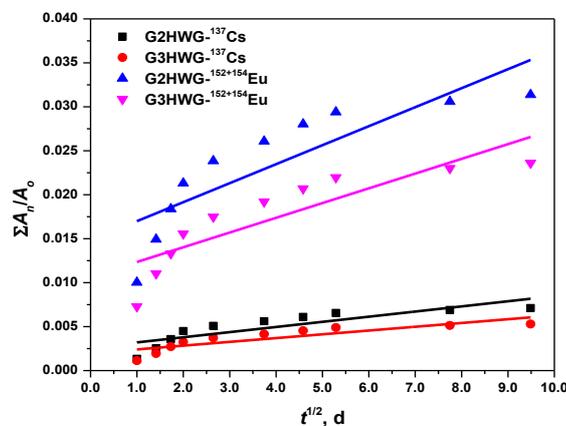


Fig. 5. Effect of waste glass form solidified into metakaolin-based formulations on variation of fractional activities vs. square root of time for ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides.

TABLE 3. Values of diffusion coefficients and leachability indexes for ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides leached from powdered and fused waste glass solidified into MK-based alkali activated binders.

Waste glass form	Formulation	Diffusion coefficient, D (cm ² /s)	Leachability index, L	Slopes of linear fitting of $\log(\text{CLF})$ vs. $\log(t)$
Powder	G2-HWG- ^{137}Cs	8.07×10^{-11}	10.09	0.319
	G2-HWG- $^{152+154}\text{Eu}$	1.09×10^{-9}	8.96	0.227
Fusion residue	G3-HWG- ^{137}Cs	4.35×10^{-11}	10.36	0.302
	G3-HWG- $^{152+154}\text{Eu}$	6.65×10^{-10}	9.18	0.235

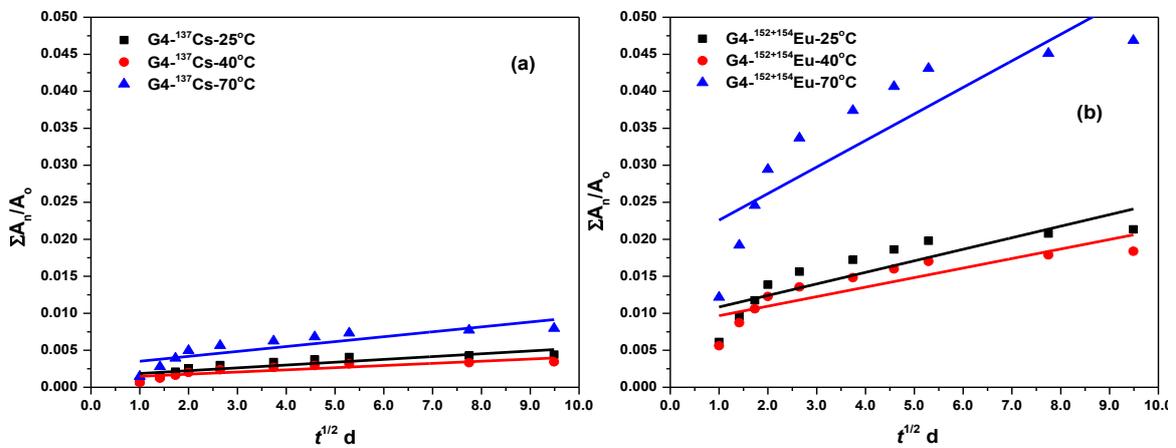


Fig. 6. Effect of early age curing temperature on variation of fractional activities vs. square root of time of (a) ^{137}Cs and (b) $^{152+154}\text{Eu}$ radionuclides leached from solidified waste glass residues into slag seeded metakaolin-based formulations.

TABLE 4. Effect of early age curing temperature on values of diffusion coefficients and leachability indexes for ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides leached from fused waste glass solidified into slag seeded MK-based alkali activated binders.

Radionuclide	Temp., °C	Formulation	Diffusion coefficient, D (cm ² /s)	Leachability index, L	Slopes of linear fitting of $\log(\text{CLF})$ vs. $\log(t)$
^{137}Cs	25	G4- ^{137}Cs -25°C	3.42×10^{-11}	10.47	0.335
	40	G4- ^{137}Cs -40°C	2.01×10^{-11}	10.69	0.326
	70	G4- ^{137}Cs -70°C	1.04×10^{-10}	9.98	0.325
$^{152+154}\text{Eu}$	25	G4- $^{152+154}\text{Eu}$ -25°C	5.74×10^{-10}	9.24	0.249
	40	G4- $^{152+154}\text{Eu}$ -40°C	3.92×10^{-10}	9.41	0.232
	70	G4- $^{152+154}\text{Eu}$ -70°C	3.04×10^{-09}	8.52	0.269

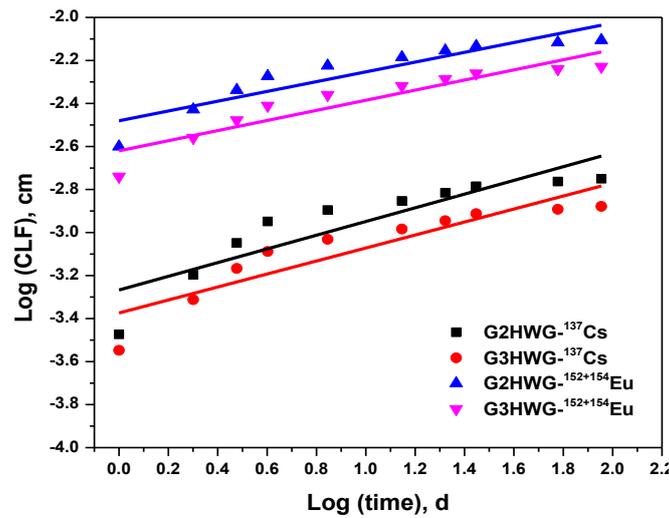


Fig. 7. Determination of the controlling leaching mechanism of ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides as affected by waste glass forms which solidified into metakaolin-based formulations.

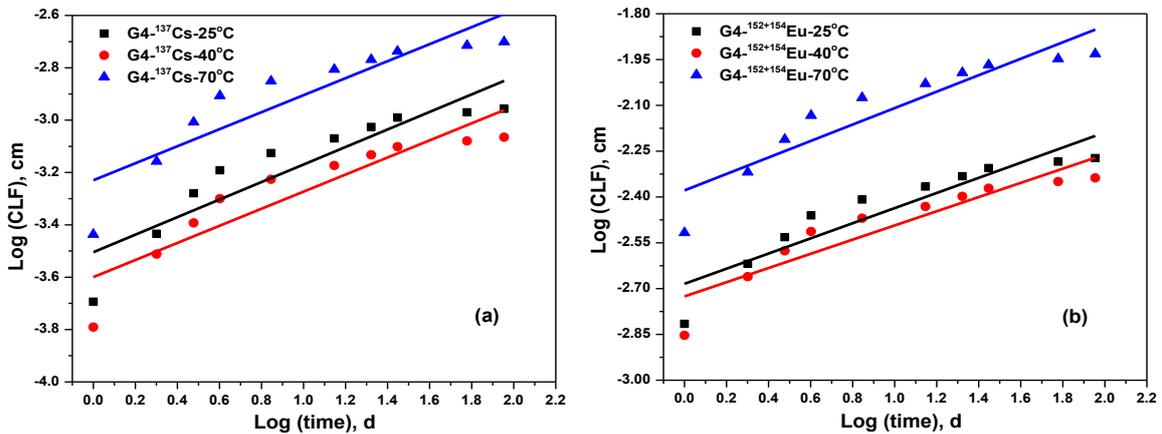


Fig. 8. Determination of the controlling leaching mechanisms of (a) ^{137}Cs and (b) $^{152+154}\text{Eu}$ radionuclides from waste glass residues solidified into slag seeded metakaolin-based formulations, as affected by early age curing temperatures.

Conclusions

The present work has been established to investigate the applicability of local Egyptian raw materials (metakaolin and blast furnace slag) to synthesize alkali activated binders suitable for solidification of radioactive waste glass sharps contaminated with ^{137}Cs and $^{152+154}\text{Eu}$ radionuclides. To achieve this goal, factors affecting the mechanical integrity of the constructed binders, in terms of compressive strength, were preliminarily investigated. Leaching of the fixed radionuclides from the designed binders was followed and kinetically analyzed in order to predict their diffusion coefficient values. It can be concluded that when

the cold powdered waste glass was solidified, the corresponding MPa values were decreased by increasing the loading percentages. While fused forms positively affected MPa values till 10.0% loading. Also, positive relations between blast furnace slag addition percentages and MPa values were detected. Leaching investigations revealed that both studied radionuclides were cumulatively leached in larger fractions from solidified powdered WG than from fused one. Data reflected the ability of the designed formulations to retain ^{137}Cs on the expense of $^{152+154}\text{Eu}$. Raising the early age curing temperature to 40°C made the desired influence on cumulative leached fractions of both studied radionuclides and their corresponding diffusion coefficient values. The controlling

leaching mechanisms were predicted to be wash-off. Thus, the performance of the studied alkali activated binders regarding the solidification of rad-waste glass sharps indicated that it can be utilized as an alternative binder to ordinary Portland cement.

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(Received 29/5/2019;
accepted 8/7/2019)

تطبيق خليط من الميتاكاولين وخبث الحديد كمواد أسمنتية في تصليد نفايات الزجاج المشعة ذات الحواف الحادة: تسريب نويدات السيزيوم-¹³⁷ والأوروبيوم-¹⁵²⁺¹⁵⁴ المشعة

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تم في هذا البحث دراسة إمكانية تطبيق خليط من مادتي الميتاكاولين وخبث الحديد المنشطة قاعدياً (جيوپوليمرات) كمواد أسمنتية بديلة لإستخدامها في تصليد نفايات الزجاج (حادة الحواف) الملوثة إشعاعياً بنويدات السيزيوم-¹³⁷ والأوروبيوم ¹⁵²⁺¹⁵⁴ المشعة. تم تجميع بعض من تلك النفايات وتصنيفها إلى زجاج ملوث وآخر غير ملوث إشعاعياً، كما تم تجهيز كلا النوعين بإجراء عمليات الطحن لتحويلهما إلى مساحيق يتم تصليدها إما مباشرة أو بعد صهرها عند درجة حرارة مرتفعة مع هيدروكسيد الصوديوم. تم إجراء تجارب مبدئية حول إضافة كميات مختلفة من الزجاج غير الملوث إشعاعياً بنوعيه (مسحوق أو منصهر) إلى عينات الجيوپوليمرات لدراسة مدى تأثيرها على قدرة العينات على تحمل الضغط الميكانيكي (ميغا باسكال). أوضحت النتائج التأثير السلبي لإضافة مسحوق الزجاج على قدرة العينات على تحمل الضغط الميكانيكي، بينما عند إضافة نفايات الزجاج في الشكل المنصهر أدى إلى زيادة قدرة العينات على تحمل الضغط الميكانيكي حتى نسبة 10%. عُيِّنَت الدراسة بالأساس بتتبع معدلات تسريب النويدات المشعة من نفايات الزجاج المُصلدة داخل عينات الجيوپوليمرات في ضوء تأثير شكل نفايات الزجاج المُصلدة (مسحوق أو منصهر) وكذلك تأثير إضافة خبث الحديد بالإضافة إلى المعالجة الحرارية المبكرة لعينات الجيوپوليمرات المُحضرة عند عمر ساعتين. أوضحت النتائج مدى قدرة عينات الجيوپوليمرات المُحضرة على منع تسريب نويدة السيزيوم-¹³⁷ بدرجة أكبر من نويدات الأيوبيوم-¹⁵²⁺¹⁵⁴. تم حساب معاملات إنتشار النويدات المشعة حيث سجلت عينات الجيوپوليمرات المُصلدة بداخلها 10% نفايات زجاج في شكل صهير والمعالجة حرارياً عند 40°م أقل معاملات إنتشار بالنسبة للسيزيوم-¹³⁷ ($10^{-11} \times 2.01$ سم²/ثانية) ولأيوبيوم-¹⁵²⁺¹⁵⁴ ($10^{-10} \times 3.92$ سم²/ثانية). تم استنتاج ميكانيكية تسريب النويدات المشعة ولو غار يتم الزمن الذي استغرقته ميل العلاقة الخطية بين لو غار يتم التسريب التراكمي لأجزاء النويدات المشعة ولو غار يتم الزمن الذي استغرقته تلك النويدات لكي تتسرب من عينات الجيوپوليمرات المُحضرة. أوضحت النتائج المتحصل عليها أن ميكانيكية تسريب النويدات المشعة هي الغسيل السطحي لعينات الجيوپوليمرات المستخدمة في عمليات التصليد مما يعطي دلائل جيدة حول إمكانية استخدام خليط الميتاكاولين وخبث الحديد المنشط قاعدياً كمادة أسمنتية بديلة يمكن تطبيقها في تصليد نفايات الزجاج الملوثة إشعاعياً بالنويدات محل الدراسة.