Immobilization of Liquid Radioactive Wastes by Hardened Blended Cement - White Sand Pastes

M.S. Sayed[1] and Magdy M. Khattab[2*]

[1] Department of Safety and Radiation Protection, Hot Laboratory Center, Atomic Energy Authority,
[2] Department of Radiation Chemistry, National Center of Radiation Research, Atomic Energy Authority, Cairo, Egypt
Magdass7@hotmail.com

Abstract: A study was undertaken to determine the immobilization performance of blended cement pastes contains different ratios of white sand (WS) loaded with cesium and cobalt radioactive ions. The effect of different ratios of white sand namely 5%, 10% and 20% on the physico-mechanical of the prepared blended cement pastes was also studied. Particle size distribution, X-ray diffraction, thermal stability, and FT-IR analysis of the neat hardened blended cement (OPC) paste and with white sand as additive have been carried out. A pronounced increase of the compressive strength values were observed for the hardened blended cement pastes with different white sand ratios at different hydration time intervals 3, 7, 14, 28 and 90 days comparing to the hardened neat Portland cement (OPC) pastes. The cumulative pore volume becomes much smaller as the percent of white sand increases in the prepared blended cement pastes. The cumulative leach fraction (CLF) for ^{137}Cs and ^{60}Co radioactive ions from the hardened blended cement white sand pastes after 90 days were measured. The examination of the leaching data revealed that adding white sand to cement reduces the leach pattern as OPC+5% white sand < OPC+10% white sand < OPC+20% white sand < OPC only for the studied radionuclides. A simplified mathematical model for analyzing the migration of radioactive ions has been developed. [Journal of American Science 2010;6(7):334-341]. (ISSN: 1545-1003).

Keywords: Cement; white sand; immobilization of radioactive ions; leaching properties.

1. Introduction

Low and intermediated level radioactive wastes are produced from different application such as fuel processing plants, research reactors, activation analysis units, nuclear medicine in hospital as well as industrial activities [1]. The treatment of these wastes is needed to produce a waste product suitable for long term storage and disposal. Many diverse methods are used such as solidification, embedding or encapsulation to immobilize the radioactive wastes in a solidified form. These wastes must be structurally stable to ensure that they does not degrade and/or promote slumping, collapse or other failure [2]. Immobilization technique consists of entrapping within a solid matrix i.e cement, cement-based material, polymer or ceramic [3]. Immobilization in cement has many advantages such as its low volume reduction, compatibility with aqueous waste streams, good mechanical characteristics, radiation, thermal stability, low cost and relatively high leachability [4]. Studies on leaching of alkali metals from cement waste matrices confirm that the solubility of alkali metals are high enough at pH more than 7 [5]. Recently, an extensive array of leaching studies has been addressed to reduce the leachability of different radionuclides from immobilized waste matrices by mixing the cement with different materials having significant sorption capacity such as fly ash, silica fume, sand kaolina and zeolites [6-9]. Additive material is defined as a solid material in powder, granular or fibrous form that is added to cement system to reduce cost, modify the flow and hardness properties [10]. Additive materials have been previously treated for the purpose of removing hazardous ions found in variable wastes, e.g. sand was used as additive material to produce solidified grout with low cost and increasing the strength of this grout by increasing the binder aggregate ratio [11]. The sorptive behavior of different radionuclides as a model of monovalent and divalent cations has been investigated on sand [12]. The International Atomic Energy's (IAEA) standard leach method has been employed to study the leach radionuclides immobilized in cement matrices [13].

In the present work, white sand (WS) known as natural minerals has high sorptive property added to the cement pastes and used to determine their efficiency as cement- based material. The liquid low level radioactive waste (LLRW) used for this study contains ^{137}Csand ^{60}Co with concentrations close to the discharge limits. Also, an evaluation of the cumulative leach fraction (CLF) of the immobilized ions was calculated

2. Experimental and Measurements

2.1. Materials

The materials used in the present work include a freshly powder of ordinary Portland cement (OPC) Type 1 which is provided by National Cement Company (NCC), Cairo, Egypt. The white sand (WS) is a powder material obtained from Sinai desert, Egypt with particles pass through the sieve size 140 i.e., particles smaller than 0.105mm (105µm); specific surface area was 195 $m^2.g^{-1}$ measured by surface area instrument, Nova, 2000. The chemical oxide compositions of the materials used are shown in Table 1

Table 1:Chemical oxide composition (%) of the materials used

Materials / Oxides	CaO	SiO_2	MgO	Na_2O	K_2O	Al_2O_3	SO_3	L.O.I
OPC	**64.50**	**21.56**	**3.34**	**0.20**	**0.70**	**5.40**	**1.48**	**1.25**
WS	**0.04**	**99.30**	**0.005**	**0.009**	**0.0002**	**0.08**	**0.004**	**0.32**

2.2. Preparation and measurements for the blended cement pastes

The hardened blended cement pastes were prepared by adding different ratios of (WS) namely 0, 5, 10 and 20 % by weight to a constant weight of fresh (OPC). The optimum water of consistency was selected and the resulting paste was moulded in cubic moulds (each mould with edge 2.5 cm diameter). The moulds with the specimens were placed at 100% relative humidity for 24 h at 20^{o}C, then the specimens were moulded and cured under tape water for time interval of 3, 7, 28 and 90 days, the curing water changed every 7 days. All the samples are designated as OPC, OPC + 5%WS, OPC + 10%WS, OPC+ 20%WS respectively.

The compressive strength property was carried out on the hardened blended cement pastes according to the ASTM designation [14]. The particle size distributions of the selected specimens in this investigation were determined using a mercury intrusion porosimeter (MIP) technique. It has been supplied from Quantachrome Corp. Boynton Beach, Florida, USA. The effect of white sand (WS) addition on hydrated specimens was studied using X-ray diffraction analysis (XRD) technique. The oriented sample was analyzed using X-ray diffratometer (Shimadzu XRD 490) Japan with nickel filter and a Cu-K_α radiation**.** Infrared spectroscopy was measured using Perkin-Elmer 16 PC Fourier transform spectroscopy (FT-IR). The selected specimens were manually ground with mortar and pestle set inside the N_2 gas chamber and particles with diameter lower than (300-400 µm) were chosen. The spectra were traced in the range 4000- 400 cm^{-1} (wave number), and the band intensities were expressed in absorbance. The thermal stability of the prepared samples was carried out through studying the thermogravimetric analysis TGA and differential thermal analysis DTA which carried out using TA 50 (Shimadzu). The measurements were carried out from room temperature up to 800^{o}C with heating rate 20^{o}C min^{-1}.

For preparing the contaminated WS, a fixed bed column experiments was used through a glass column of 1 cm diameter and 10 cm long. Then, 10 gms of WS as sorbent materials were transferred into the column with the aid of distilled water and adjusted at pH 7 [15]. The radioactive solution was then passed through the column at rate 1 ml/min. The effluent was collected in fractions (5 ml) for radioactive analysis.

2.3 Static leach test

The IAEA standard leach test was applied to determine the leaching characteristic of ^{137}Cs and ^{60}Co radionuclides from the solidified waste [16]. The solidified waste grouts were immersed in beaker containing 300 ml-distilled water. Leachant was exchanged and analyzed for radioactivity after 1, 2, 3, 4, 5, 6, 7, and then after every week, month till 3 months. The ratio of leachant volume to the total exposed surface area of the grout was always kept constant at 10 cm [17]. A known volume was taken from the aqueous solution after contacting with the solid phase and its γ-activity was measured, using a well type NaI crystal connected to a multichannel analyzer which had 256 channel attached with preamplifier (Genee, 2000). All the leachate analyses were carried out on duplicate at room temperature. The cumulative leach fraction CLF (cm) was calculated according to the following equation:

$$CLF = (\sum A_t/A_o). (V/S)$$

where
A_o: initial activity on present in specimen at time zero,
A_t: activity leach out of sample after leaching time t,
t: duration of leaching renewal period (d),
V: volume of specimen, (cm^3) and,
S: surface area of specimen exposed to leachant

3. Results and Discussion

3.1. Compressive strength

On addition of water to blended cement containing different ratios of white sand namely 0, 5, 10 and 20%, the constituent of blended cement (calcium silicate) undergo hydrolysis and the products being less basic calcium silicate hydrate (C-S-H) gel and calcium hydroxide were formed. The final gel fills the spaces between the cement grains and form bridges between them, thereby causes stiffening of the paste and its subsequent hardening. The continuous formation of the gel gradually fills the capillary pores, the porosity of the paste decreased, and its strength is gradually increased which may be attributed to the cohesion force acting between the gel particles or to the inter growing of the crystals and the formation of more chemical bonds. The results also showed that at any hydration time, the compressive strength values of the blended cement pastes containing variable white sand ratios are higher than that of those for Portland cement only Fig.1. This may be due to the interaction between the fine particles of white sand particles and the free calcium hydroxide librated during the hydration process to form new kind of calcium silicate hydrate gel (C-S-H); this kind of gel is strongly hydraulic in nature which leads to an increase in the total content of binding centers leading to an increase in the compressive strength values [18].

3.2. Particle size distribution

Mercury intrusion porosimetry (MIP) is one of the widely methods used to estimate the pore size distribution [19]. It has been demonstrated that, the blended cement pastes contains different ratios of white sand have a lower cumulative intruded pore volume than the paste made of ordinary Portland cement only Fig.2. This may be ascribed due to the fact that, the formation of the new (C-S-H) gel leads to an increase in the total contents of the binding centers in the hardened blended cement paste. Therefore, the pore volume for all the hardened blended cement mixtures with white sand would be filled with the excess (C-S-H) gel, leading to a decrease in the pore diameter between the particles. As a result, the cumulative pore volume becomes much smaller so, the opportunity of mercury intrusion into the pore system becomes difficult.

3.3. X- ray diffraction

XRD was used to study the changes in the crystalline phases of the hardened blended cement pastes after 28 days of curing. The X- ray diffraction pattern of white sand (WS) and the hardened blended cement pastes with different addition of (WS) namely 5 and 20% respectively are shown in Fig.(3a, b). The peaks in Fig.(3a) indicate the main characteristic sharp peaks at 2 θ of 21^o and 26^o, which may be due to the presence of silica in the form of cristobalite and quartz form respectively. Whereas, the X-ray pattern shown in Fig. (3b) also, illustrated the main characteristic peaks of hydration products of cement, calcium silicate hydrate (C-S-H) gel at 2θ of 29.5^o, 32.6^o and 34.5^o respectively [20], and Portlanide phase(calcium hydroxide) was identified at 2θ of 18^o and 47.3^o. Also, it is clear that, as the (WS) content increases in the hardened blended cement pastes up to 20 %, the intensity of the main characteristic peak (C-S-H) gel phases increases. This mainly due to interaction takes place between the active silica in (WS) and $Ca(OH)_2$ librated during hydration process of OPC as a result, more hydrated products formed increasing the compressive strength values [21].

3.4. FT-IR

In Fig.4, the spectrum of white sand (WS) exhibits several strong sharp bands occurred at 3750, 1660, 1480, 1300, 1200, 970, 940 and 860 cm^{-1} respectively. The sharp band at 3750 cm^{-1} may be due to the free silonal group [22]. Also, the band at 1660 cm^{-1} referred to this silonal compound having a carbonyl group attached to the silicon, while the bands around 1300-1000 cm^{-1} means that different acetoxy groups attached to the silica atom. This also identified by a strong doublet band around 970-940 cm^{-1}. The FT-IR spectrum of the hardened blended cement pastes containing 5 and 20 % (WS) are shown in Fig. 4. The main characteristic band appeared around 3500-3200 cm^{-1} due to the hydrogen bond present in the active silica, as well as a strong band around 1600 cm^{-1} due to the consuming or cross linking that takes place between the silicon atom containing the silonal group and calcium silicate present in the hydrated cement phase leading to the formation of more calcium silicate hydrate (C-S-H) gel [23].

3.5. Thermal analysis

The thermal analysis of the tested hardened blended cement specimens with (WS) ratios 0, 5 and 20% was performed. It is considered that an endothermic peak in the temperature range 80-120°C display water loss from the cement gel phase was observed in Fig. (5) when studying the DTA curves. Another intense endothermic peak visible in all DTA curves within the temperature range of 450-485°C; corresponding to the released of trapped water in the crystalline gel form of the hydrated specimens at this temperature [24]. Based on TG curves Fig. (6), it can be stated that the content of water adsorbed on $Ca(OH)_2$ in the hardened cement paste and in the hardened cement paste with different (WS) admixture in the temperature range 80-120°C varied from 8-13% of the total weight of the original prepared specimens. As the percent of (WS) increased in the prepared specimens, the total weight loss percent decreased due to more consumption of the water of hydration to form more gel structure as cleared from the compressive strength tests.

3.6. Leaching Characteristics of ^{137}Cs and ^{60}Co radionuclides

The objective of measuring the cumulative leach fraction (CLF) is to predict the leaching rate of some radionuclides of potential concern from immobilized waste matrix under continuously saturated condition that represent the worst case. The addition of 5% (WS) to the hardened blended cement paste decrease the (CLF) for the studied radionuclides, this due to the low porosity of these constituent paste when compared with that of OPC Fig.(7,8). As the percent of the contaminated (WS) increase the (CLF) increase due to the high sorption capacity of this natural mineral for the studied radionuclides[25].

In general, the leaching character from the solidified material can be explained as a combination of both diffusion and dissolution mechanisms [26]. The value of the apparent diffusion coefficient (D) can be calculated from the slope (m) of the straight line of the plot of $(\sum A_t/A_o)$ versus $(t_n)^{1/2}$ as:

$$(\sum A_t/A_o) = 2\,(S/V)\,(Dt_n/\pi)^{1/2}$$

Where; ΣA_t = cumulative amount of radioactivity leached during cumulative time t_n. The value of the apparent diffusion coefficient (D) can be calculated from the slope (m) of the straight line when plot $(\sum A_t/A_o)$ against $(t)^{1/2}$ as

$$D = \pi\,(mV/2S)^2$$

Figure 9 and 10 represents the plotting of the fraction leached of ^{137}Cs and ^{60}Co from the prepared pastes versus the square root of leaching time. The results from the figures showed an initial fast leaching during the first period followed by slow leaching in the subsequent periods. According to this behavior, the diffusion coefficients D for the fast stages for the prepared pastes were found. The leaching fraction coefficients are listed in Table 2. From these data it was found that the diffusion coefficients values of the studied radionuclides were significantly reduced with (WS) addition of the studied pastes comparing with OPC paste [27]. The leachability index L is a material parameter of the leachability of diffusing species, which used to catalogue the efficiency of the matrix material to solidify a waste and is given by [28]:

$$L = -\log(D)$$

The value of 6 is the threshold to accept a given matrix as adequate for the immobilization of radioactive waste. Table 2, shows the mean leachability indices for the studied leached radionuclides from the prepared pastes and their range from 8.1 to 12 in case of ^{137} Cs and from 6 to 6.8 in case of ^{60} Co which exceed the value of 6. These values indicated that OPC/WS pastes can be used as efficient materials for immobilizing cesium and cobalt for the long term disposal.

Table(2) :The leaching coefficients (D) and the leachabilitiy indices (L) of ^{137}Cs and ^{60}Co radioactive ions from the blended cement pastes at different white sand (WS) ratios.

Prepared Pastes	^{137}Cs D	^{137}Cs L	^{60}Co D	^{60}Co L
OPC+ 5% (WS)	8.5×10^{-13}	12	1.5×10^{-7}	6.8
OPC+ 10% (WS)	1.98×10^{-9}	8.7	2.8×10^{-7}	6.5
OPC+ 20% (WS)	4.65×10^{-9}	8.3	3.9×10^{-7}	6.4
OPC	7.17×10^{-7}	8.1	4.2×10^{-7}	6

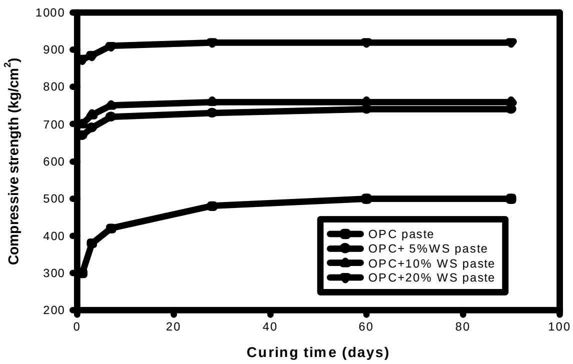

Fig.(1): Compressive strength versus curing time for the hardened blended cement pastes containing different white sand ratios

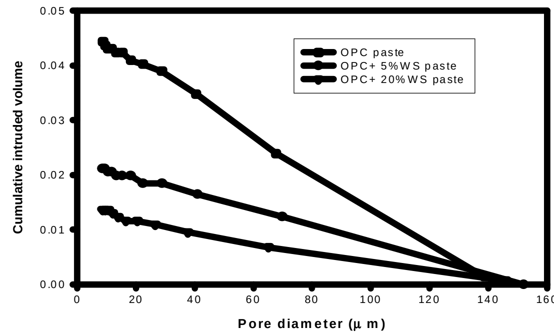

Fig.(2): Cumulative intruded volume versus pore diameter for the hardened cement paste and blended cement pastes contains 5% and 20% of white sand after 28 days of hydration.

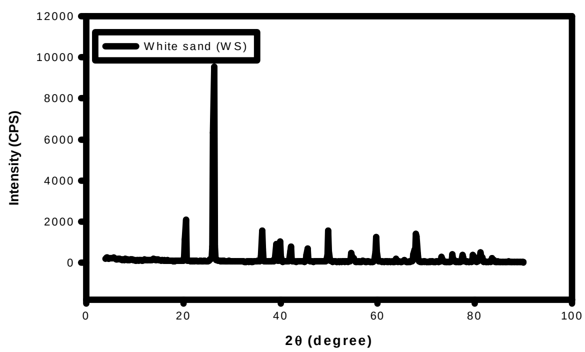

Fig.(3a): XRD pattern of white sand

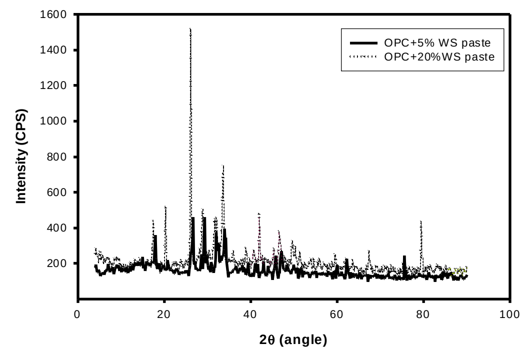

Fig.(3b): XRD patterns of the hardened blended cement pastes contains 5% and 20% white sand after 28 days of hydration.

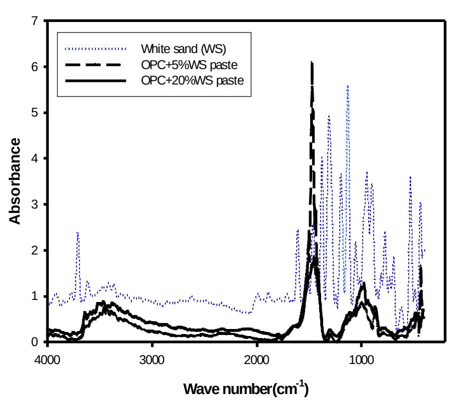

Fig.(4): FT-IR spectrum of white sand and the hardened blended cement pastes contains 5% and 20% white sand after 28 days of hydration.

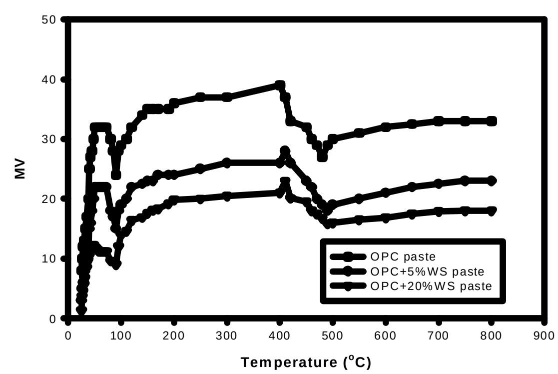

Fig.(5): DTA of the hardened blended cement at different white sand ratios

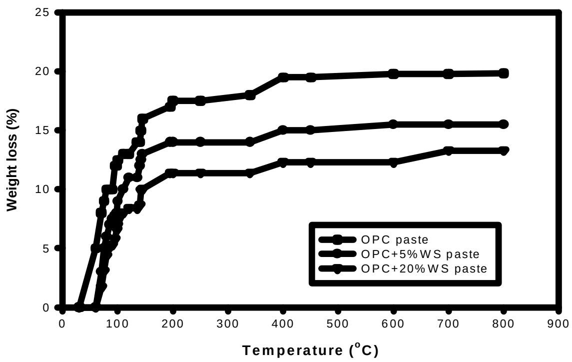

Fig.(6) Weight loss percent of the hardened blended cement pastes at different ratios of white sand.

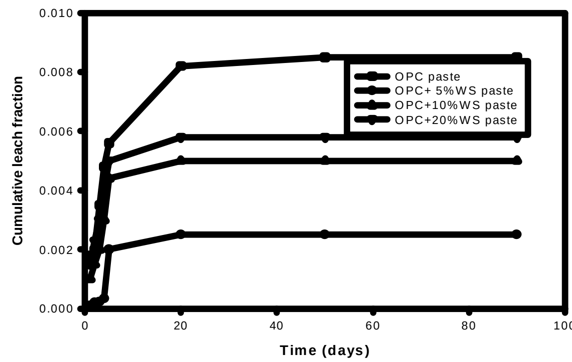

Fig.(7) Cumulative leach fraction of ^{137}Cs from the hardened blended cement pastes at different white sand ratios.

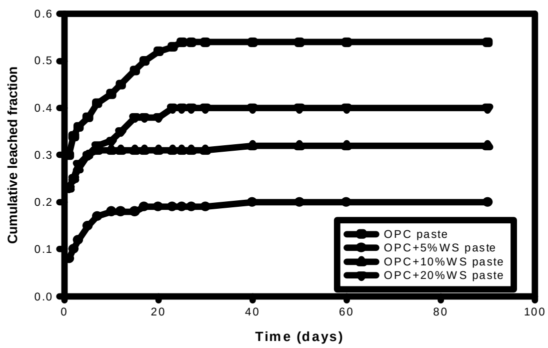

Fig.(8) Cumulative leach fraction of ^{60}Co from the hardened blended cement pastes at different white sand ratios.

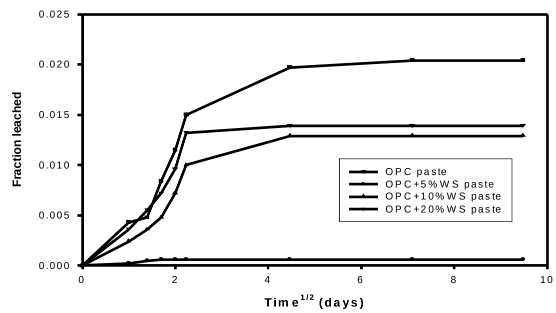

Fig.(9) Variation of fraction leached of ^{137}Cs from the hardened blended cement pastes at different white sand ratios.

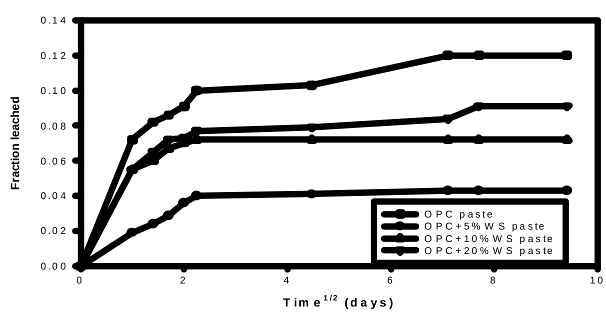

Fig.(10) Variation of fraction leached of ^{60}Co from the hardened blended cement pastes at different white sand ratios.

4. Conclusion

From the above mentioned results, it can be explain that:

- The addition of white sand up to 20% by weight to ordinary Portland cement increases the mechanical properties of the prepared blended cement pastes comparing to the neat ordinary Portland cement paste.
- The pore volume for all the hardened blended cement pastes containing white sand would be filled with the excess calcium silicate hydrate gel, leading to a decrease in the pore diameter between the particles. As a result, the cumulative pore volume becomes much smaller comparing to the neat ordinary Portland cement paste.
- Thermal stability behaviour shows that the hardened blended cement pastes containing white sand are lower in the loss of weight than that of the neat ordinary Portland cement paste.
- From XRD patterns, it has been observed that, the (WS) content increases in the hardened blended cement pastes up to 20 %, the intensity of the main characteristic peaks (C-S-H) gel phases increases. This is mainly attributed to the interaction which takes place between the active silica in (WS) and $Ca(OH)_2$ librated during hydration process of OPC.

Accordingly, The addition of 5% (WS) to the hardened blended cement paste decrease the (CLF), decrease the leaching coefficients (D) and increase the leachabilitiy indices (L) of ^{137}Cs and ^{60}Co radioactive ions from the prepared hardened blended cement pastes.

Corresponding author
Magdy M. Khattab[2*]
Department of Radiation Chemistry, National Center of Radiation Research, Atomic Energy Authority, Cairo, Egypt

5. References

1. El-Dessouky MI, El-Sourougy MR, Aly HF, Investigation on the treatment of low and medium level radioactive liquid waste. Isotopenpraxis 1990; 26: 608-611.
2. Burns RH, Solidification of low and intermediate level waste. At. Energy Rev. 1971; 9: 547-552.
3. Sakr K, Sayed MS, Hafez MB, Immobilization of radioactive waste in mixture of cement, clay and polymer. J. Radio. and Nucl. Chem. 2003; 256(2): 179- 184.
4. Philip J, Philip T, Long–term performance of surface and sub. Surface engineered barriers, US Nuclear Regulatory Commission, National Academy of Science, Washington DC, May 26 (2006).
5. I. Plecas, Dimovic S, Smiciklas I, Utilization of bentonite and zeolite in cementation of dry radioactive evaporator concentrate. Prog. Nucl. Energy 48 495-503 (2006).
6. Plecas IB, Pavlovic RS, Pavlovic SD, Leaching of ^{60}Co and ^{137}Cs from spent ion exchange resins in cement–bentonite clay matrix. Bull. Mater. Sci. 2003; 26(7): 699–701.
7. Osmanlioglu AE, Immobilization of radioactive waste by cementation with purified kaolina clay. Waste Management 2002; 22(5): 481-483.
8. Skripkiunas G, Sasnauskas V, Dauksys M, Dauksys D, Peculiarities of hydration of cement paste with addition of hydrosodalite. Materials Science 2007; 25(3): 627-635.
9. Polettini A, Pomi R, Sirini P, Testa F, Properties of Portland cement-stabilised MSWI fly ashes. J. Hazard. Mater. 2001; 88 (1): 123-138.
10. Koleva M, Vassilev V, Polymer composites containing waste dust from power production. Macedonian J.of Chemistry and Chemical Engineering 2008; 27(1): 47-52.
11. Shawabkeh RA, Solidification and stabilization of Cd^{2+} in sand-cement-clay mixture. J. Hazard. Mater. 2005; 125(1-3): 237-243.
12. Strkalj A, Malina J, Radenoic A, Waste mould sand potential low-cost sorbent for nickel and chromium ions from aqueous solution. Materials and Environment 2009; 56 (2): 118-125.
13. Plećas I, Perić A, Glodić S, Kostadinović A, Comparative leaching studies of ^{60}CO from spent radioactive ion-Exchange resin incorporated in cement. Cem. Concr. Res. 1995; 25(2): 314-318.
14. Ruiz MC, Irabien A, Environmental behavior of cement-based stabilized foundry sludge products incorporating additives. J. Hazard. Mater. 2004; 109(1-3): 45-52.
15. Guerrero A, Goñi S, Allegro VR, Efficiency of fly ash belite cement and zeolite matrices for immobilizing cesium. J. Hazard. Mater. 2006; 137(3): 1608-1617.
16. *Matsuzuru H, Moriyama N, Wadachi Y, Ito A*, Leaching behavior of cesium-137 in cement-waste composites. Health Phys. 1977; 32: 529-534.

17. Abdel Raouf MW, Nowier HG, Assessment of fossil fuel fly ash formulation in the immobilization of hazardous wastes. J. Environ. Eng. 2004; 130(5): 499-507.
18. Ruiz MC, Irabien A, Environmental behavior of cement-based stabilized foundry sludge products incorporating additives. J. Hazard. Mater. 2004; 109(1-3): 45-52.
19. Sohna, D, Johnson DL, Hardening process of cement-based materials monitored by the instrumented penetration test: Part 1: Neat cement paste and mortar. Cem. Concr. Res. 2002; 32(4): 557-563.
20. Shin-ichi Igarashi, Akio Watanabe, Mitsunori Kawamura, Evaluation of capillary pore size characteristics in high-strength concrete at early ages. Cem. Concr. Res. 2005; 35(3): 513-519.
21. Kantautas A, Palubinskaite D, Vaickelionis G, Synthesis and hardening of flouralinite cement. J. Materials Science 2006; 24(2): 385-393.
22. Turanli L, Uzal B, Bektas F, Effect of large amounts natural pozzolan addition on properties on of blended cement. Cem. Concr. Res. 2005; 35(6): 1106-1111.
23. Phenrat T, Marhaba TF, Rachakornkij M, Examination of solidified and stabilized matrices with Portland cement and lime. J. Environmental & Hazrdous Management 2004; 26(1): 65-75.
24. Ben-Dor L, Perez D, Sarig S, Thermal study of the effect of additives on the hydration of tri-calcium silicates. J. of American Ceramic Society 2006; 58(3-4): 87-89.
25. Veronica A, Bucharest SCN, The adaptation of natural (geological) barriers for radioactive low and intermediate level waste near surface disposal in Romania, WM'01 Conference, February 25-March 1, Tucson, AZ, Bucharest University (2001).
26. Plecas I, Immobilization of ^{137}Cs in Concrete. Acta Chim. Slov. 2003; 50(3): 597-600.
27. Abdel Rahman RO, Zaki AA, El-Kamash AM, Modeling the long-term leaching behavior of ^{137}Cs, ^{60}Co and ^{152,154}Eu radionuclides from cement-clay matrices. J. Hazard. Mater. 2007; 145(3): 372-380.
28. Shrivastav PO, Shrivastava R, Cation exchange application of synthetic tobermorite for the immobilization and solidification of cesium and strontium in cement matrix. Bullet. Mater. Soc. 2000; 23: 515-520.

6/6/2010