

Leaching and Mechanical Properties of Cement- Polyacrylamide Composite Developed as Matrices for Immobilization of ^{137}Cs and ^{60}Co Radionuclides.

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Abstract: Low and intermediate level radioactive wastes are produced from diverse applications of radionuclides in industry, medicine, radioisotope production facilities and fuel processing plants. These wastes need treatment to reduce the quantities of radioactive contaminants to the level, which allows safe discharge of the decontaminated liquid to the environment and safe disposal of the concentrated radionuclides according to the international requirements and national regulations. The objectives of the liquid waste processing are to immobilize the radioactive elements and to reduce the volume to be stored. The solidified product must be non-dispersible, insoluble and with good mechanical and structural stability. Portland cements are met the acceptance criteria for immobilizing radioactive wastes because of their low cost, high density, durability and amenability to simple processing techniques. In the present study, immobilization of spent polyacrylamide- zeolite and polyacrylamide-bentonite composites loaded with cesium and/or cobalt radionuclides with Ordinary Portland Cement (OPC) has been carried out. Several factors affecting the characteristics of the final solidified waste product towards safe disposal such as mechanical strength and leaching behavior of the radioisotopes have been studied. The obtained results showed that the presence of polyacrylamide composites in the cemented wastes improve the mechanical characteristics of the solidified cement matrix towards the safety requirements and reduce considerably the radionuclides leach rates.

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1. Introduction

Low and intermediate level radioactive wastes are produced during research activities of the radiochemical laboratories, research reactors, radioisotope and metallurgical laboratories, activation analysis units, nuclear medicine divisions in hospitals, universities and research institutes 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. Chemical precipitation, coagulation, ion exchange and evaporation processes are the most commonly known treatment techniques of radioactive wastes. Ion exchange technique has become one of the most commonly used treatment methods for such aqueous streams due to its simplicity, selectivity and efficiency. A wide range of materials having different chemical and physical properties, which can be naturally occurring or synthetic, is available for this technique. Inorganic ion exchange materials have emerged as an increasingly important replacement or complement for conventional organic ion exchange resins, particularly in liquid radioactive waste treatment due to their radiation stability and greater selectivity for certain radiological important species, such as cesium,

cobalt and strontium. Several inorganic ion exchangers such as zeolites, Bentonite, sodium titanates, silicotitanates and hexacyanoferrates ⁽²⁾ are in use in nuclear sites for the treatment of nuclear wastes. For example polymethylmethacrylate, polystyrene, polyacrylamide has been filled with synthetic or natural inorganic compounds in order to improve their properties or simply to reduce cost ⁽³⁾. Immobilization techniques consist of entrapping the contaminant within a solid matrix i.e. cement, cement-based material, glass, or ceramic. Despite the existence of several disadvantages in the utilization of cement immobilization technique such as its low volume reduction and relatively high leachability, the choice of this technique has been worldwide employed for the immobilization of low and intermediate level radioactive wastes because of its compatibility with aqueous waste streams, capability of activated several chemical and physical immobilization mechanisms for a wide range of inorganic waste species ⁽⁴⁻⁶⁾. Also, cement immobilization possesses good mechanical characteristics, radiation and thermal stability, simple operational conditions, availability, and low cost. Immobilized waste forms can be safely

isolated from the biosphere for a long time in a radioactive waste repository. However, despite the engineering and natural barriers of radioactive waste repositories, the radioactive waste forms would eventually be in contact with ground water, and the releases of radioactive species from the waste forms would occur by the leaching mechanism⁽⁷⁾. Hence, there is a considerable interest in understanding the diffusive transport of radionuclides through cement matrix. Several leaching studies⁽⁸⁻¹⁰⁾ have been reported using different methods to study the temporal distribution of radionuclides in the leachant medium. Also, a significant number of works dealing with the immobilization of different radioisotopes with cement and cement mixed with different additives have been carried out⁽¹¹⁻¹⁷⁾. In the present work, immobilization of spent polyacrylamide- zeolite and polyacrylamide- bentonite composites, loaded with ¹³⁷Cs and/or ⁶⁰Co radionuclides, with Ordinary Portland Cement have been carried out. Several properties such as the effect of composite addition percent on the mechanical strength of the solidified waste package were examined. The leach characteristics of the investigated radionuclides from a simple cement waste form and a heterogeneous waste form consisting of granules of contaminated composite ion exchange in a cement matrix have been also studied using IAEA's standard leach method⁽¹⁸⁻²⁰⁾.

2. Experimental

2.1. Materials

Ordinary Portland cement (OPC) was obtained from National Cement Company, Helwan, Egypt. The chemical composition of Portland cement is given in Table (1). Polyacrylamide- zeolite and polyacrylamide- bentonite composites were prepared using Gamma radiation technique and characterized. Detailed description of the ion exchange procedure needed to prepare loaded composites was presented elsewhere⁽²¹⁾. The radioactive tracers were delivered by Amersham Radioanalytical Center (England).

Table 1: Chemical composition of Ordinary Portland cement.

Chemical	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SiO ₃	Na ₂ O	K ₂ O	Others
Wt %	63	20	6	3	1.5	2	0.5	0.5	1.0

2.2. Preparation of Specimens

The solidified samples prepared by mixing ordinary Portland cement with different weights ranged from 1 to 10% of the prepared composites at water – cement ratio W/C 0.35. The resulting mixtures were stirred for 5 min and the grout was then poured into cubic 7-cm³ Polyethylene mould and vibrated until

any air bubbles present has been removed. After a setting time 24 hrs the samples were demoulded and cured for 28 days at room temp the weight, area and volume of the dried sample was determined⁽²²⁾.

3. Compressive Strength

The mechanical strength test, which is given as applied maximum load divided by a cross-sectional area of a specimen, is performed to confirm the integrity of waste forms. The specimen of a cubic shape with the dimension 7x7x7 cm³ would be desirable for the test because the restriction effect and the increase effect of apparent strength by virtue of friction between loading plate and specimen could be reduced to a minimum.

2.4. Static Leaching Test

Static leaching tests were performed, using distilled water solution, to study the desorption of cesium and cobalt ions from hardened blocks of cement and cement mixed with 5% of Polyacrylamide- zeolite and/or polyacrylamide- bentonite composites. The IAEA's standard test proposed by Hespe⁽²³⁾ was applied. All prepared samples, cubic moulds 2x2x2 cm³ dimensions, were stored in laboratory at ambient temperature (25 ± 2°C) for 28 days curing time. Each sample was immersed in beaker containing 25 ml distilled water for certain time intervals and 1 ml of leachant was taken, dried, and counted. The gamma spectra of studied nuclides were measured using a gamma spectrometer with 4" x 4" NaI crystal activated with Thallium. The crystal is connected to a multichannel analyzer. The cumulative leach fraction was calculated according to the following equation,

$$\text{Cumulative leach fraction} = \left(\frac{\sum A(t)}{A_0} \right) \left(\frac{V}{S} \right) \quad (1)$$

Where, $\sum A(t)$ = Cumulative radioactivity leached

A_0 = Initial radioactivity present in specimen

V = Volume of specimen, cm³

S = Exposed surface area of specimen, cm²

3. Result and Discussion

3.1. Mechanical Characteristics

The incorporation of radioactive waste into cement is the most widely used technique for its practical, technological and economical advantages. Mechanical properties are one of the important factors to be taken into consideration in evaluating the final solidified products. It is worth mentioning that certain minimum values of mechanical properties are required for safe handling of the immobilized waste form during transportation and final disposal⁽²⁴⁾.

Effect of composite Additive Percent

The results of the compressive strength of the hardened cement pastes and cement pastes mixed with different percentages of polyacrylamide- bentonite and / or polyacrylamide- zeolite composites, at 0.35 W/C ratios, are given in Table (2). Results indicated that addition of 5% composite leads to increase the value of the compressive strength from 200 (Kg/cm²) in plain samples to 415, 520 (Kg/cm²) for polyacrylamide- bentonite and polyacrylamide- zeolite composites respectively and beyond this value, the compressive strength is decreased. This increase in compressive strength may be attributed to the increase in silicates present in OPC due to the addition of composites that in consequence increase the rate of hydration and strength the final solid product.

Table (2): Effect of PAM- Bentonite and PAM-Zeolite composites additive percent on compressive strength

Cement matrix	% of additives	Compressive strength, kg/cm ²
Plain cement	0.0	200
OPC+ PAM-Bentonite	1	250
	3	370
	5	415
	7	300
	10	205
OPC+ PAM-Zeolite	1	300
	3	455
	5	520
	7	410
	10	280

3.2. Long Term Leaching Test Leaching Characteristic of ¹³⁷Cs and ⁶⁰Co Radionuclides

The shallow land burial waste forms contain fairly high concentrations of short-lived radionuclides and very low concentrations of long-lived radionuclides. Various radionuclides and salts make chemical bondage with cement components, or they exist dispersively in the state of sole crystals in concrete. When the cemented waste forms come in contact with water, the movement of soluble materials from the waste to the surrounding water is caused by dissolution or chemical reaction with chemical components of water. In this study, the radionuclides chosen for the leach test are intended to represent the desorption (leaching) behavior of some of the typical radionuclides encountered in low-level solid waste forms. The variation of cumulative leach fractions of ¹³⁷Cs and ⁶⁰Co radionuclides incorporated in cement and cement mixed with 5% polyacrylamide- bentonite and polyacrylamide- zeolite are depicted in Fig. (1). The results showed that, addition of 5% composite decreased the leaching rates of cesium and cobalt radionuclides from cement matrix and this may be attributed to the extreme finesse and high surface area of composites which are capable to reduce the volume of large pores and capillaries, which is normally founded in cement pastes, and refinement in pore structure. The magnitude of the cumulative leach fraction is an index for the release of the nuclide from the cement matrix. In both studied cases, cesium has higher values of cumulative leach fraction than cobalt radionuclide.

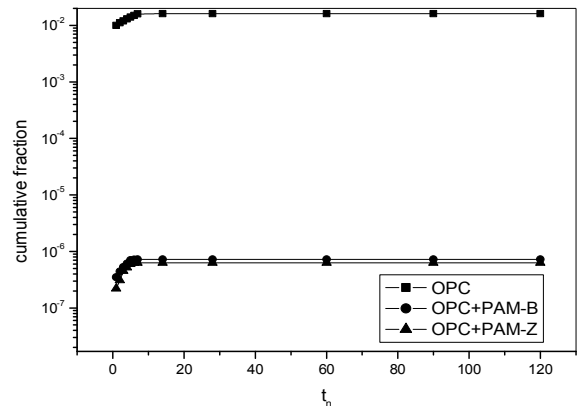
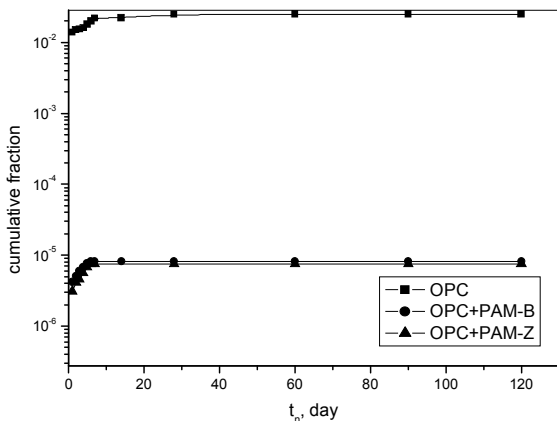


Fig (1): Cumulative fraction of radioactive isotope a) ¹³⁷Cs and b) ⁶⁰Co leached from solidified waste forms.

Controlling leaching mechanism

The examination of the plot of incremental leach fractions from the studied immobilized waste matrices loaded by ¹³⁷Cs and ⁶⁰Co expressed as cm/day on log scale versus time, shown in Fig(2), indicate that the leaching pattern

can be divided into two regions. Region I shows initial rapid release of radionuclides within the first 5 days, then a drastic reduction in the release take place over a longer period of time. From this figure, it is clear that the leaching of the studied radionuclides is due to surface wash-off and diffusion, where the slow portion of dissolution did not take place⁽²⁵⁻²⁷⁾. Results showed also that the incremental fractions of hardened cement pastes mixed with 5% composite were lower than those of plain cement for both radionuclides. This may be attributed to the fact that fineness of composite particles leads to low penetration of caesium and cobalt ions. The determination of the controlling leaching mechanism could be conducted based on the slope of the linear regression of the logarithm of CLF versus the logarithm of time. If the slope is less than 0.35 the controlling leaching mechanism will be the surface wash-off, for the slope values ranging from 0.35-0.65 the controlling mechanism will be the diffusion, and higher slope values represent the dissolution mechanism⁽²⁸⁾. To eliminate interpretative errors in the analysis due to the surface wash off mechanism, the initial leached fraction has been excluded. The result of the linear regression in the second region (5-120 day) is listed in Table (3), it is clearly shown that the slop values less than 0.35 which indicate that the surface wash-off is the controlling leaching mechanism for all studied cases.

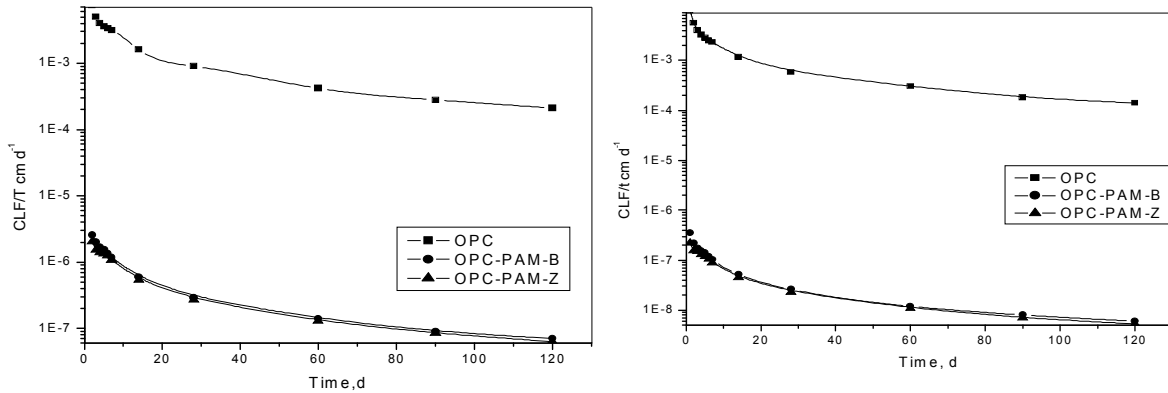


Fig (2): Incremental leach fraction of radioactive isotope a) ¹³⁷Cs and b) ⁶⁰Co leached from solidified waste forms

Table (3): Slope of the linear regression of log (clf) versus log (time) in the second region (7- 120 d).

Radionuclide	OPC	OPC – PAM-B	OPC – PAM-Z
Cs-134	0.11	0.15	0.17
Co-60	0.14	0.20	0.23

Effective Diffusion Coefficient

Leaching is assumed to be diffusion controlled process. The mechanism of this diffusion could not be completely studied due to complex microstructure of composite and the presence of multi variables which affect the rate of leaching such as matrix composition, temperature, chemical nature of leaching solution, chemical nature of the element diffused out, and radiation effects. Several methods are used to measure leaching data and IAEA suggested that diffusion coefficients may be used to compare leaching data⁽²⁹⁾, where the quantity of radionuclide leached out from a unit surface area during time, t_n is given by:

$$A_n = 2A_0 \frac{\sqrt{Dt_n}}{\sqrt{\pi}} \tag{2}$$

Where; A_n = activity leached out after time t_n, Ci
 A₀ = initial activity in the composite, Ci
 D = diffusion coefficient, m² s⁻¹

From the above equation, the cumulative fraction leached out from the composite can be expressed as;

$$\left[\frac{\sum A_n}{A_0} \right] \left[\frac{S}{V} \right] = \frac{2 S A_0 (D \sum t_n)^{0.5}}{A_0 V} \tag{3}$$

$$\frac{\sum A_n}{A_0} = 2 \left(\frac{S}{V} \right) \left(\frac{D \sum t_n}{\pi} \right)^{0.5} \tag{4}$$

Where; $\sum A_n$ = cumulative amount of radioactivity leached during cumulative time t_n

Thus a plot of $[\sum A_n / A_0]$ versus $\sqrt{t_n}$ should give a straight line if D remains constant. The value of D can be calculated from the slope m of the line, i.e.

$$D = \frac{\pi m^2 V^2}{4 S^2} \tag{5}$$

Figure (3) represent the plotting of the fraction leached of cesium and cobalt radionuclides from both studied samples versus square root of

leaching time, respectively. As can be seen from this figure, for all studied leaching tests, the results indicated an initial fast leaching during the first period followed by slow leaching in the subsequent periods. This behavior suggests the presence of two different values of diffusion coefficient for the fast and slow components. So, the calculated diffusion coefficients for all nuclides, as presented in Table (4), are the main average values of their diffusion coefficients. These data indicated that ¹³⁷Cs have

larger value of diffusion coefficients in all waste matrices than ⁶⁰Co nuclide.

Leaching index

As it is shown in Table (5), the mean leachability indices for all radionuclides in all studied matrices are in the range from 8.86 to 9.66, which exceed the value of 6. These values indicated that all studied OPC matrices, especially OPC – PAM- Zeolite, can be catalogued as efficient materials for immobilizing cesium and cobalt from radioactive wastes.

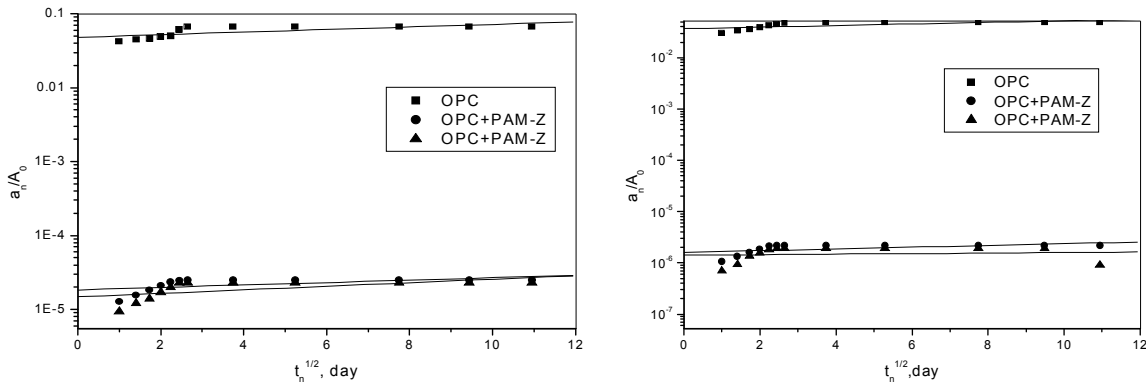


Fig (3): Variation of fraction leached of radioactive isotope a) ¹³⁷Cs and b) ⁶⁰Co leached from solidified waste forms

Table (4): Diffusion coefficient values of cesium and cobalt ions leached from solidified cement matrices.

Cement matrix	Diffusion coefficient cm ² s ⁻¹	
	Cesium	Cobalt
Plain OPC	3.10E-10	2.27E-10
OPC+5%PAM-Bentonite	2.58E-10	2.89E-10
OPC+5%PAM-Zeolite	5.81E-10	3.63E-10

Table (5): Mean Leachability Index of cesium and cobalt ions

Radionuclide	OPC	OPC –PAM-B	OPC –PAM-Z
Cs-137	9.51	9.59	9.24
Co-60	9.64	9.54	9.44

4- Conclusion

This paper presented results of immobilization of cesium and cobalt radionuclides loaded polyacrylamide- bentonite and polyacrylamide-zeolite ion exchange material in a mixture with Ordinary Portland Cement. The results showed that addition of 5% contaminated composite leads to increase the compressive strength of the final matrix form 200 (Kg/cm²) in plain samples to 415, 520 (Kg/cm²) for polyacrylamide- bentonite and polyacrylamide- zeolite composites respectively and behind this percent the compressive strength is decreased. Also, the leaching rates of both studied radionuclides from the cement matrix decreases with that addition and this may be attributed to the

extreme finesse and high surface area of composites which are capable to reduce the volume of large pores and capillaries, which is normally founded in cement pastes, and refinement in pore structure.

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