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Investigation on Cement/Polymer Waste Packages Containing Intermediate Level Waste and organic Exchange Resins

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خلاصة

الغرض من هذا البحث هو دراسة تأثير إضافة البلمرات إلى الإسمنت البورتلاندي المستخدم في تصليد النفايات المشعة على تحسين خواص القوالب الإسمنتية الحاوية للنفايات المشعة. ويجذب هذا الإتجاه أنظار الباحثين ويحتاج بالتالي إلى دراسات مستفيضة. وفي هذا البحث، أضيفت أنواع مختلفة من البلمرات إلى الإسمنت البورتلاندي العادي بغرض تصليد النفايات متوسطة المستوى الإشعاعي وكذلك المبادلات الأيونية العضوية. وقد تبين من هذا البحث أن إضافة بلمرات الايبوكسي تخفض من معدل ارتشاح عنصر السيزيوم.

Abstract

Polymers can be added to cements to improve its nuclear waste immobilization properties. This trend in cementation processes is attracting attention and requiring thorough investigations. In this work, polymers of different kinds were added to ordinary portland cement for the purpose of solidifying intermediate level liquid wastes and organic ion exhange resins. Epoxy polymer such as Kemapoxy-150 reduced the leaching rate of cesium compared to cement alone. Latex to cement ratio less than 4% caused an increase in leaching rate of cesium. When cesium was absorbed to an organic resin its leachability was improved.

Introduction

The disposal of low and intermediate-level radioactive wastes requires two major preparation processes. First, the treatment of the waste, and second the solidification or immobilization into a solid matrix.

The main objective of treatment is to achieve a reasonable volume reduction factor.This leads to substantial improvements in safety and economic aspects associated with the further handling, transport, storage and disposal process [1].

The incorporation of radioactive wastes into cement matrices has been widely practiced due to the positive charactristics of the resulting waste forms. Among the advantages of the cementation process are the simplicity and low cost of the process and raw material, fire resistance, ..etc. However, there are some disadvantages [2,3] associated with the cementation process. Addition of epoxy resins to cement may improve leach resistance of the waste forms. The epoxy system may be visulized as network crosslinked in all three dimensions [4]. Polymer impregnated cement matrix (PIC) is a new type of solidifying agents characterized with high mechanical stength, low porosity and their leachability is by far better than plain cement [5,6].

Polymer-modified cement systems, the relative advantages and disadvantages of these new immobilizing media have recently been reviewed[7,8]. Laboratory studies have been carried out [9] to test various embedding matrices, such as hydraulic binders, bitumen, epoxy, ...etc. Johnson [10,11] investigated the properties of polymer modified cements and studied in details the modification of OPC with styrene, butadiene, bitumen emulsion, epoxide and polyurethane resins.

The aim of the present study, is to modify the Inshas ILW and ILSW waste packages by adding some new additives to improve both the compressive strength and leachability.

Experimental

All chemicals used in the present work are Analar Grade Reagents.

The chemical and radioactive recipe of the simulated waste solutions of Inshas [12] intermediate-level liquid waste (ILLW) used in this work is shown in Table 1.

Table 1 : Radiochemical Composition of Inshas ILLW

Radionuclide	Quantity Bq/m³	Ci/l
Total Radioactivity	3.7E9	1E-4
β and γ-emitters including:		
Cesium-137	1.85E9	5E-5
Cobalt-60	3.7E7	1E-6
Strontium-90		
+ Yttrium-90	7.4E8	2E-5
Ruthenium-106		
+ Rhodium-106	3.7E7	1E-6
Europium-154	3.7E8	1E-5
Zirconium-95		
+ Niobium-95	3.7E8	1E-5

Organic ion exchange resins were used as an intermediate-level solid waste (ILSW). They were mixed with OPC and Kemapoxy-150 (epoxy) resin. The properties of organic ion exchange resins are shown in Table 2.

Table 2: Specifications of the Organic Ion Exchange Resins

Name	Type	Ionic form	Mesh size	Product of
Permutite	Organic anion exchanger	Cl^-	14-52	UK
Amberlite IRA-=900	Organic anion exchanger	Cl^-	16-50	Aldrich
Dowex-50W	Organic cation exchanger	H^+	200-400	DOW, USA
Dowex-3	Organic weakly basic anion exchanger	OH^-	20-50	DOW, USA

Kemapoxy-150, is an organic polymer, consists of two components, the resin and the hardner. The kemapoxy-150 (epoxy) was prepared by self polymerization at room temperature. In this respect, the resin and the hardner were obtained from Chemicals for Modern Buildings Company, Egypt, and mixed according to the ratio 2:1 to produce the epoxy as a viscous colourless polymer. Specifications of the kemapoxy-150 (epoxy) are shown in Table 3 [13].

Table 3: Specifications of Kemapoxy-150

Density (kg/cm^3)	**Compressive strength (kgf /cm^2)**	**Bending resistance (kgf /cm^2)**	**Tensile strength (kgf /cm^2)**	**Heat resistance (C^o)**
1.8-2.1	500-1000	200-400	150-250	60 (wet) 140 (dry)

Latex, is a natural polymer milk emulsion, of pH 10. It contains about 60 wt% solid material. It was brought from Alexandria's Chemical and Medical Industries Company, Egypt [14].

Radioactive isotope used in this work was Cs- 137, it was obtained from Amersham (England) in the solution with a specific activity form of CsCl aqueous solution with a specific activity of 1-10 mCi/mg Cs. The half-life of Cs-137 is known to be 30 years [15].

Ordinary Portland Cement (OPC) was used for incorporating Inshas ILLW, and ion-exchange resin. OPC produced by the National Cement Company at Helwan, Egypt. The composition of cement materials used is made according to British Standard Specifications (B.S.S) [16].

Samples were prepared starting from the raw materials involved. Triplictes were prepared and the results given are the average. Details of sample preparation procedures are given by Zaki [17].

Among the properties of materials to be used for the solidification of radioactive wastes, the leaching of radioactivity is undoubtedly the most important one. The knowledge of it can estimate the hazards arising when solidified waste comes into contact with water, under given conditions during other stages or shipping or even after disposal. The IAEA recommends that leach test results be reported as a plot of [(cumulative fraction of the radioactivity leached from the specimen). (specimen volume to exposed surface ratio)] as a function of total time of leaching,

$[\Sigma\, an/ A_o]\, [V / S]$ versus $\Sigma\, tn$

where

Σan = sum of radioactivity lost during leaching periods

A_o = initial radioactivity

V = volume of specimen in cm^3

S = exposed surface area of specimen in cm^2

Σtn = sum of all leaching periods in days.

The radioisotope used in long-term leaching studies is Cs-137. The samples were cured for 28 days before leaching test using distilled water.

The chemical properties of the final cement grout were studied by subjecting the different specimens to leach tests. The leachants were then radiochemically analyzed. Leaching tests were performed according to the International Atomic Energy Agency (IAEA)'s standard test [18]. Cs-137 was the radioactive isotope studied in these tests. Cement grout were prepared as previously described by Zaki [17]. Distilled water was the leachant used for all samples. The recipe for all samples is shown in Table 4.

In epoxy/cement samples W/C ratio was kept at 0.25 by weight. For all the rest samples W/C ratio was kept at 0.35 by weight. The volume of leachant was 10 times the surface area of the sample (600 ± 20 ml).

Result and Discussion

1. Compressive strength

The compressive strength of the solidified waste packages were measured after curing for 28 days. the waste packages were cracked using the Challenger range of compression testing machine (2000 KN) calibrated at BS 1610 Grade A. The corrected cylinder strength and estimated cube strength have been calculated from the measured values using the appropriate correction factor for 30mm right cylinder[19].

The effect of epoxy addition to the OPC/ILLW on the compressive strength is shown in Fig. 1. This figure can be divided into two steps, the first reveals a direct increase in compressive strength with the increase in EP/OPC ratio in the range (10-50 wt%); and the second step reveals a constant value of compressive strength with the increase of EP/ OPC ratio in the range (50-90 wt%). These results could be attributed to the addition of epoxy to OPC/ ILLW paste which leads to decrease the

Table 4 : Composition of Cement Grout Samples Used in Leaching Tests

Sample No.	Cement material	Waste	Additive	Additive cement (wt%)	Surface area (cm^2)	Volume (cm^3)	Volume surface area (cm^3)	Density (g/cm^3)	Weight (g)	Initial activity (count/min)
1	OPC	ILLW	Latex	1	61.02	35.48	0.59	1.79	63.50	271073
2	OPC	ILLW	Latex	2	59.86	34.61	0.59	1.81	62.50	125395
3	OPC	ILLW	Latex	3	58.81	37.63	0.61	1.65	62.30	263827
4	OPC	ILLW	Latex	4	62.19	37.66	0.61	1.76	66.30	297159
5	OPC	ILLW	Epoxy	30	62.20	41.08	0.62	1.56	64.10	298171
6	OPC	ILLW	Epoxy+ permutite	OEX / EP+OPC 10 wt%	65.90	44.45	0.64	1.52	67.70	240971
7	OPC	ILSW	Expoxy + Amberlite IRA-900	OEX / EP+OPC 15 wt%	69.53	41.45	0.63	1.57	65.00	297377
8	OPC	ILSW	Epoxy+ Dowex-50w	OEX / EP+OPC 20 wt%	66.37	43.61	0.65	1.53	66.70	271891
9	OPC	ILLW	Dowex-3+ Epoxy	OEX / EP+OPC 35 wt%	66.67	54.01	0.683	1.78	96.39	28528

porosity of the paste which in turn leads to increase the compressive strength [20]. The constant compressive strength values obtained in the range (50-99 wt%) of EP/OPC can be attributed to the approximate closing of the paste pores and therefore the elasticity properties of epoxy is predominating in this range.

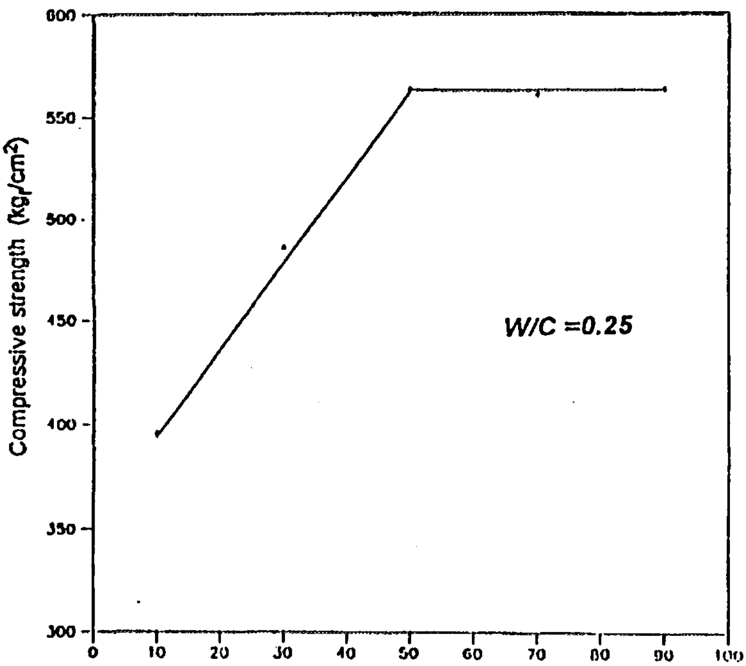

Fig. 1 : Effect of Epoxy / cement ratio on the compressive strength of OPC/ILLW waste forms.

Fig. 2 shows the effect of the addition of latex to OPC/ILLW system on the compressive strength. It is clear from this figure that the compressive strength of OPC/ILLW decreases with the increase of La/OPC ratio. This could be attributed to the pH effect of the added latex, OPC is stable at pH=13 [21]. Addition of relatively lower pH latex (10.5) may result in final pH value of about 11.5 for the La/OPC/ILLW system. In spite of the decrease of the absolute value of compressive strength due to the addition of latex, it is still acceptable from the practical point of view; the compressive strength of the produced packages after the addition of latex to OPC is still higher than 125 kgf/cm^2.

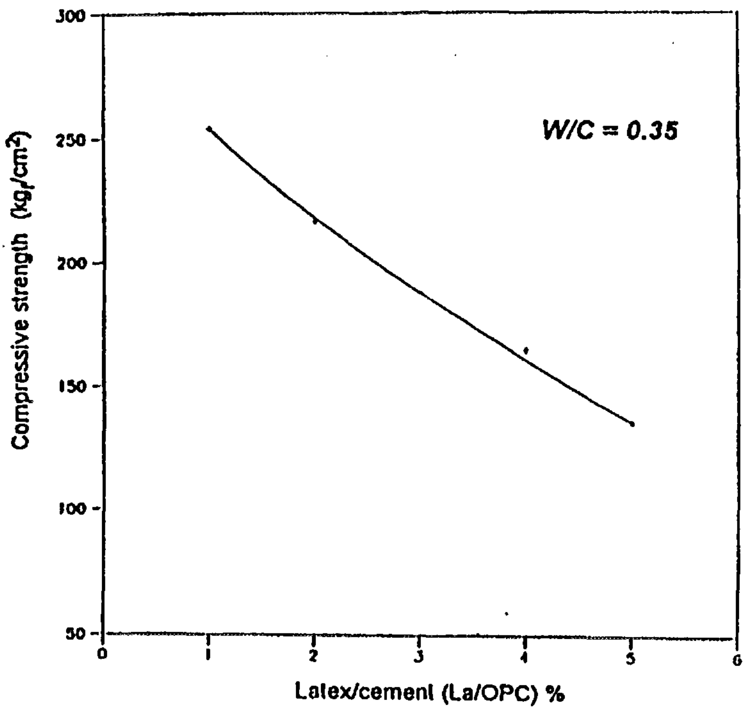

Fig. 2 : Effect of Epoxy / cement ratio on the compressive strength of OPC/ILLW waste forms.

Effect of OEX/ (OPC+EP) ratio on the compressive strength of organic exchanger resin/OPC/Epoxy system is shown in Fig.3. It is clear from this figure that the compressive strength decreases with the increase in OEX / (OPC+EP) ratio. Dowex-3 achieved the highest compressive strength, however, a wide range of OEX / (OPC+EP) loading. Dowex 50/ Epoxy / OPC packages revealed the lowest range of loading ratio for OEX / (EP+OPC) of about 25 wt%. Permutite/Epoxy/OPC packages gave the lowest compressive strength; while Dowex-50W and Amberlite-IRA-900 lies in between compared to the other three exchangers under investigation.

The decrease in compressive strength with the increase in the OEX / (OPC+EP) ratio may be attributed to the decrease of polymer/cement (Epoxy + OPC) ratio. The decrease of the conditioned quantity of Dowex-50W (OEX / (OPC+EP) =25 wt% may be due to the small specific density of Dowex-50W. On the other hand Dowex-3 achieve a large (EX/ (OPC+EP) ratio (430 kgf/cm2 at 50 wt% OEX/ (OPC+EP).

This may be attributed to the OH^- group of Dowex-3 cross - linking with epoxy compared with that of plain OPC.

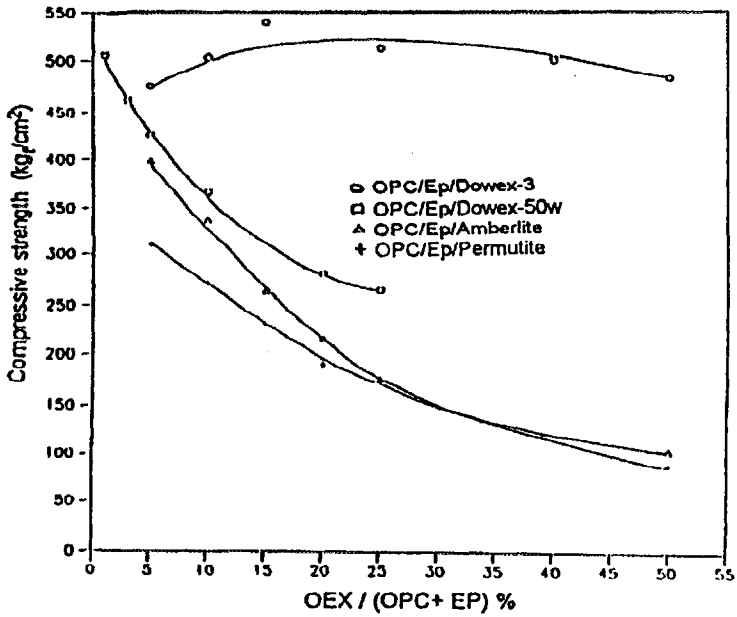

Fig. 3 : Effect of organic exchanger on the compressive strength of OPC/Epoxy waste forms at 28 days.

2.Leachability

Among the properties of materials to be used for the solidification of radioactive wastes, the leachability of radioactivity is undoubtedly the most important one. The organic polymer latex (La) was mixed with OPC/ILLW with La/ OPC ratio: 1,2,3 and 4 wt%.

The leached cumulative fraction of CS-137 from OPC/ILLW/ La waste forms is clear from this figure that, the 2 wt% La/OPC waste packages have a lower cumulative fraction followed by 4 wt% in comparison with plain OPC, while a high leaching fraction was observed for 3 wt% and 1 wt%. The low leaching rate of Cs-137 from 2 wt% La/OPC may be attributed to the formation of epoxy polymer which coated the constituents of the hardned cement paste retarding cesium diffusion to the outer surface of the waste package [5,22].

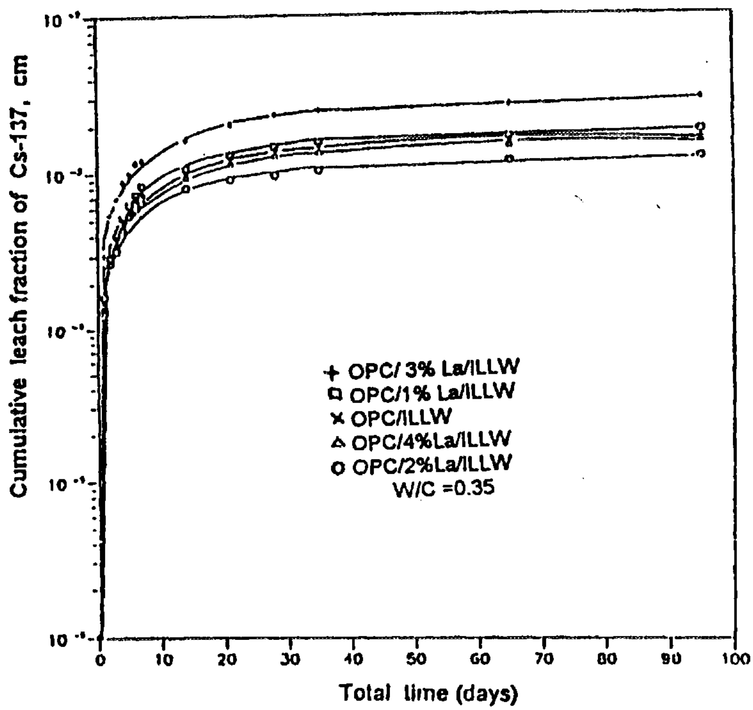

Fig. 4 : Product of cumulative fraction of Cs-137 leached and the volume - to - surface ratio plotted against total time of different OPC/ Latex / ILLW waste samples

The Cs-137 leaching rate of the solidified OEX/OPC/EP waste packages of different organic exchangers are shown in Fig.5. It is clear from this figure that all the conditioned resins exhibit higher leaching rates than that of OPC/EP matrix. The leaching rates have the following order: (OPC/EP) < (Dowex-3/OPC/EP) < (permutite/ OPC/EP) < (Dowex-50W/OPC/EP) < (amberlite-IRA-900/ OPC/EP). This sequence reveals that Dowex-3 achieves the lowest leaching arte, whereas Amberlite-IRA-900 achieves the highest leaching rate. This sequence can be attributed to the low porosity (W/C=0.25)and that the epoxy polymer may close the hardned cement pores decreasing cesium diffusion for OPC/EP waste package system. The low leaching rate of the waste packages containing Dowex-3 may be attributed to the adsorption of cesium on the Dowex-3 ion - exchanger resin; inspite of its high OEX/OPC ratio.

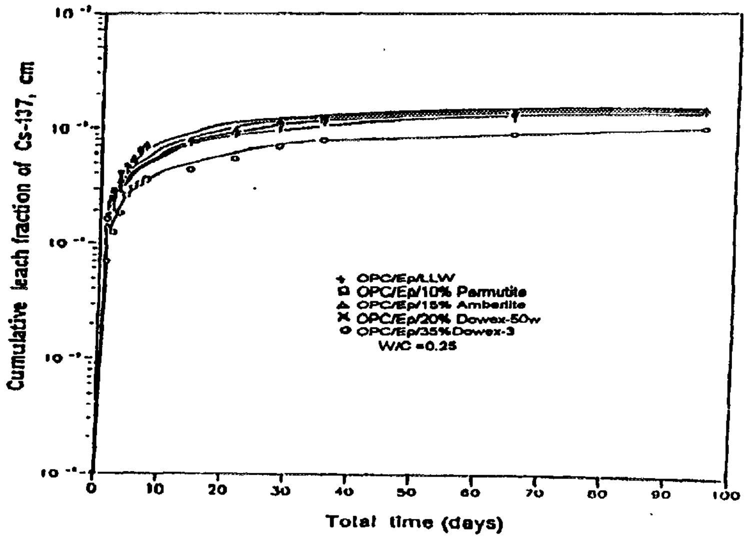

Fig. 5 : Product of cumulative fraction of Cs-137 leached and the volume -to- surface ration plotted against total time of different OPC/ Epoxy/ Organic exchanger waste samples.

The effect of different additives on the Cs-137/ OPC leachability are shown in Fig.6. It is clear from this figure that the addition of epoxy decreases the leachability of Cs-137/ OPC. On the other hand, the Cs-137 leachability of Dowex- 3/ OPC/ Epoxy and 2 wt% of La/ OPC/ ILLW are higher than that of the plain OPC (Cs-137/ OPC).

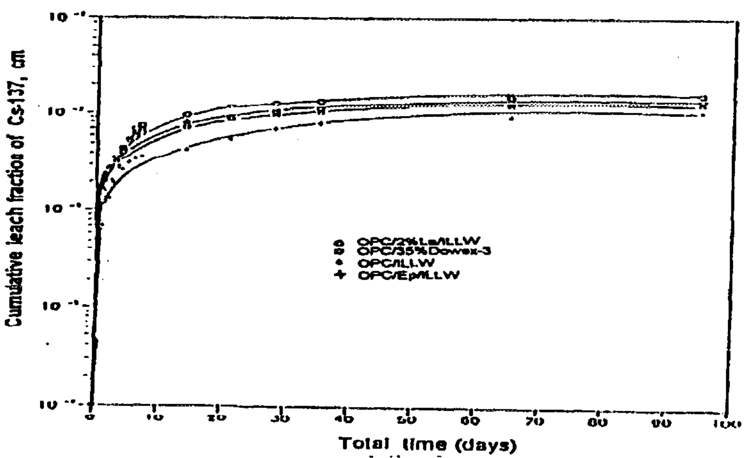

Fig. 6 : Product of cumulative fraction of Cs-137 leached and the volume -to- surface ratio plotted against total time of different cement waste samples.

Conclusion

It is possible to condition the organic exchangers Dowex-3 in OPC/Epoxy matrix up to 35 wt% with a low Cs-137 leach rate. The compressive strength can be increased by the addition of epoxy polymer to OPC up to 560 kgf/cm2. On the other hand,the addition of latex to OPC decreased the compressive strength by about 66% compared to OPC.

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