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Characterizations of Polyester-Cement Composites Used for the Immobilization of Radioactive Wastes

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/45751>

1. Introduction

Radioactive waste is the ethical issue facing the development of peaceful applications of nuclear technology all over the world. It poses a serious threat to human health and dangerous impact to his environment. Hence, the problem needs early global cooperative solutions. Almost all the International Atomic Energy Agency's member states produce some types of radioactive wastes from their applications e.g. industrial, agricultural, medical, educational, nuclear power production plants, defenses aspects, accidents...

Solidification/stabilization (s/s) of radioactive waste is an attractive technology to reduce their risks and facilitate their handling prior to disposal. The transformation of those materials into monolithic homogeneous solid forms by immobilization in inert matrices; cement, polymer, polymer-cement composite, is essential to preserve man and his surrounding from the dispersion of these radioactive hazardous wastes (Tawfik et al., 2005). Owing to its advantage, cement matrices have been practiced for many years in different places for the immobilization of waste materials. Based on long experience on the suitability of cement for immobilization of numerous low and intermediate level waste residues, it is recommended to be used as an appropriate matrix for safe handling, transport, storage and disposal (Drace & Ojovan, 2009; Sobolev et al., 2006; Varlakova et al., 2009).

Cement and cement based materials have been successfully applied in multi barrier system of a repository. The first chemical and physical barrier is the cement matrix used for the immobilization of waste materials. The second important barrier is the cement container for packaging of waste forms. Among the advantages of the cement used, as engineering barrier, are low cost, simplicity of the process, abundance of raw materials, fire resistance, pronounced shielding effect, radiation and heat stability in addition to satisfactory mechanical properties (Burns, 1971; IAEA, 1983, 1993).

The high porosity of cement materials facilitates water percolation resulting in pronounced high leach rates of the radionuclides to the surrounding. To overcome this main disadvantage, polymer-cement composites have been developed as candidate matrices for radioactive waste incorporation.

The main component of liquid waste concentrates generated from the pressurized water reactor is boric acid (H_3BO_4). Such reactors generate about 50,000 gallons of the boric acid evaporator bottom yearly. Boric acid waste is mostly neutralized by using sodium hydroxide and then concentrated by evaporation. The resulted borate slurry should be immobilized usually in cement, polymer, bitumen or polymer-cement composites (Eskander et al., 2006; Greenhalgh, 1986; Huang & Yang, 1999). Direct solidification of borate waste with Portland cement is complicated through the retarding effect of both acidity of the waste (H_3BO_3) and specification of the borate ions ($B_4O_7^{2-}$ and BO_3^{3-}) (Tawfik et al., 2005).

2. Theoretical background

The polymer-cement composite is a combination between cement and polymers. Hence, it is essential to have a short theoretical background for those two key materials, i.e. cement and polymer.

Cement has been described as adhesive substance capable of uniting fragments of solid matter to compact solid blocks (Holcomb, 1978). There is a wide range in composition of cement materials used for the solidification of radioactive wastes and in the construction of various barriers in a repository. Their common feature is that the main constituents are lime (CaO), silica (SiO_2) and alumina (Al_2O_3). Portland cement is the most commonly used type in radioactive waste management applications (Peter C, 2003). It has lime as principal constituent which is obtained by mixing calcareous and argillaceous or other silica-alumina and iron oxide-bearing materials. The principal compositions and oxides percentages of Portland cement used in this study are represented in Table 1.

Chemical compositions, %		Compounds compositions, %	
SiO_2	19.84	C_3S	53.11
Al_2O_3	4.74		
Fe_2O_3	4.0	C_2S	16.89
CaO	61.01		
MgO	2.5	C_3A	5.81
K_2O	0.6		
SO_3	2.4	C_4AF	12.16
Insoluble residue	0.95		

-Loss on ignition = 3.96%.
 -Lime saturation factor = 96%by wt.

Table 1. Chemical and mineral composition (%w/w) of Portland cement

Polyester is a category of polymers which contain ester functional group in their main chain (at least 85% by the weight). Although there are many types of polyester, the term "polyester" as a specific material most commonly refers to polyethylene terephthalate (PET). Polyesters include naturally occurring chemicals, such as in the cutin of plant cuticles, as well as synthetics through step-growth polymerization such as polycarbonate and polybutyrate. Natural polyesters and a few synthetic ones are biodegradable, but most synthetic polyesters are not. Depending on the chemical structure, polyester can be a thermoplastic or thermoset; however, the most common polyesters are thermoplastics (Rosato et al., 2004). Polyesters as thermoplastics may change shape after exposing to heat. While combustible at high temperatures, polyesters tend to shrink away from flames and self-extinguish upon ignition. Saturated polyesters refer to that family of polyesters in which the polyester backbones are saturated. Unsaturated polyesters refer to that family of polyesters in which the backbone consists of alkyl thermosetting resins characterized by vinyl unsaturation. On the other hand, unsaturated polyester resin (UPR) is thermosetting material. There are several reasons for the importance of polyester such as the relatively easy accessible raw materials, the very well understood and described simple chemical process of polyester synthesis, the low toxicity level of all raw materials and side products during polyester production and processing, the outstanding mechanical and chemical properties of polyester and the recyclability. Polyester is very durable: resistant to most chemicals, stretching and shrinking, wrinkle resistant, mildew and abrasion resistant. Polyester is hydrophobic in nature and quick drying.

This study is based on a large body of researches carried out at Inorganic and Applied Chemistry Unit, Radioisotope Department, Egyptian Atomic Energy Authority for nearly 5 decades. These published work, in addition, to that contained in literatures reviewed the development and applications of polyester-cement composite (PCC) in the field of solidification/stabilization of radioactive wastes. Throughout this review, it can be concluded that the proposed PCC, especially which based on the recycled PET, as a matrix for immobilizing the borate waste, is economic and safe.

3. Preparation of some polyester-cement composites

3.1. Water extended polyester (WEP)

The used water extended polyester is obtained either based on the virgin raw components or the recycled polyethylene terephthalate (PET).

3.1.1. Synthesis of water extended polyester from virgin raw components

Unsaturated polyester was prepared from high purity ingredients by adding 2 moles of maleic anhydride to 2.2 moles diethylent glycol in a round bottom three necks flask provided with a constant thermometer, a stirrer and a condenser. The reaction mixture was heated in an oil bath and maintained at 80°C for 1 hour, then to 190°C for 4 hours. The unreacted monomer and other products were removed from the reaction mixture under vacuum using oil pump and the acid number was adjusted at 50 mg of KOH/g. The

temperature was then lowered and maintained at 170°C until an acid number of 50 or less was reached. Water extended polyester emulsions were prepared by dispersing water or waste solution samples containing 1.03% by weight triethanolamine as an emulsifier into the prepared unsaturated polyester containing 30% by weight styrene. The stable emulsion of polyester was cured by the addition of 2% by weight benzoyl peroxide (BP) as an initiator. More experimental details for the preparation of water extended polyester are given in previous publication (Saleh et al., 2005).

3.1.2. Synthesis of water extended polyester based on recycling of poly(ethylene terephthalate) (PET)

The overall annual consumption of PET, for packaging only, had increased by mid-2000 to about 30% compared to 1990. Over the last decades, PET consumption has increased tremendously due to its ever-increasing use in fibre manufacturing and in packaging. At present, the global yearly PET production is approximately 13 million of metric tons (Tawfik et al., 2005). PET is a synthetic semi-crystalline thermoplastic polymer, which has long life due to almost complete resistance to biodegradation and as a result large amounts of PET waste are accumulated. Physical, mechanical and chemical recycling processes have been developed even to industrial scales. Due to the well-known disadvantages of both mechanical and physical processes, chemical recycling has been the subject of interest all over the world. This technique is the most acceptable one, following the principles of sustainable development, since it leads to the formation of raw materials from polymer as well as to the secondary value-added products. PET is known to be attacked in chemical recycling by different alkalis, glycols, alcohols, ammonia and amines by making use of processes such as hydrolysis, glycolysis, alcoholysis, ammonolysis and aminolysis, respectively. The degradation of the main backbone of PET is supposed to take place through chain scission. The challenging disadvantage, accompanied with these processes, is the relatively high consumption of energy (Tawfik et al., 2005).

3.1.2.1. Glycolysis of PET waste

PET waste was depolymerized by diethylene glycol (DEG)/propylene glycol (PG) mixture at a ratio of 1:0.5:0.5 by weight, in the presence of lead acetate as a catalyst (0.5% by weight of PET) at the reflux temperature of the glycols. The mixture was charged into a four-necked round bottom flask, which was fitted with a stirrer, reflux condenser, nitrogen inlet and thermometer. The flask was immersed in oil bath, and the temperature was brought up to 200°C for 5 hours. In order to check the extent of depolymerization, the glycolized product was analyzed for hydroxyl number value, and it was found to be 617 mg KOH/g.

3.1.2.2. Preparation of unsaturated polyester (UP)

Unsaturated polyester (UP) was prepared by the esterification of the glycolized PET oligomers with maleic anhydride (MA) and adipic acid (AA) at a molar ratio of 1.1:0.7:0.3 for hydroxyl to carbonyl groups, respectively. The polyesterification reaction was carried out in a four-necked round bottom flask, having a stirrer, reflux condenser, an inert gas inlet

and thermometer. A Dean–Stark trap was used for measuring the water amount, which was removed throughout the reaction. The reactants were heated in oil bath, and its temperature raised to 150°C. The temperature was then increased to 210°C at a rate of 10°C/h until the acid number value reached nearly 45 ± 2 mg KOH/g.

3.1.2.3. Preparation of water extended polyester (WEP)

The obtained UP was dissolved in a styrene (S) monomer at a ratio of 60:40% by weight at room temperature ($25 \pm 5^\circ\text{C}$). WEP emulsion was prepared by dispersing with continuous stirring of 20% water by weight, containing 0.2 mmole DEA/g prepolymer as an emulsifier, into 10 g of the obtained styrenated polyester. The stable emulsion was cured by addition of 2% from the prepared WEP by weight benzoyl peroxide (Bz_2O_2) as a catalyst.

The obtained water extended polyester mixture was mixed with cement paste at various water/cement ratios to prepare either the final waste form by incorporating a predetermining weight of borate waste simulate or polyester-cement composite container.

3.1.3. Polyester-cement waste form

The final waste forms were prepared by mixing predetermined weight of powdered radioactive borate waste simulates with polymer-cement composite paste. This mixture was poured in a polyethylene moulds and allowed to set and harden at room temperature in its humid atmosphere for 28 days. At the end of curing time, the obtained blocks were demoulded giving solid cylindrical blocks of 60 ± 2 mm height and 31 ± 0.5 mm diameter. Various factors that may affect the physicochemical stability of the formed composite specimens were studied.

3.1.4. Polyester-cement container

Portland cement was thoroughly mixed with pure water at constant water/cement ratio of 1:2.8 by weight. Water extended polyester was mixed with cement paste to form a polymer-cement composite paste. The polymer-cement composite paste was poured in a special closed moulds and was left to solidify in a humid atmosphere for 28 days. The obtained solid samples were in the form of small containers having the dimensions of 7.6 ± 0.4 cm height, 5.92 ± 0.20 cm diameter and various wall thicknesses. A given weight of labeled powder simulating waste samples was introduced into these containers. The containers were closed with cover and then introduced to subsequent investigations.

4. Characterization of unsaturated water extended polyester (WEP)

4.1. Water extended polyester (WEP) based on virgin raw ingredients

Both IR and NMR analyses of the WEP prepared from its virgin raw materials illustrate the expected formula of the polyester given in the literature and determine the main characteristic groups of the prepared polyester used as an additive to the cement waste forms (Figs. 1,2)(Shatta, 1996).

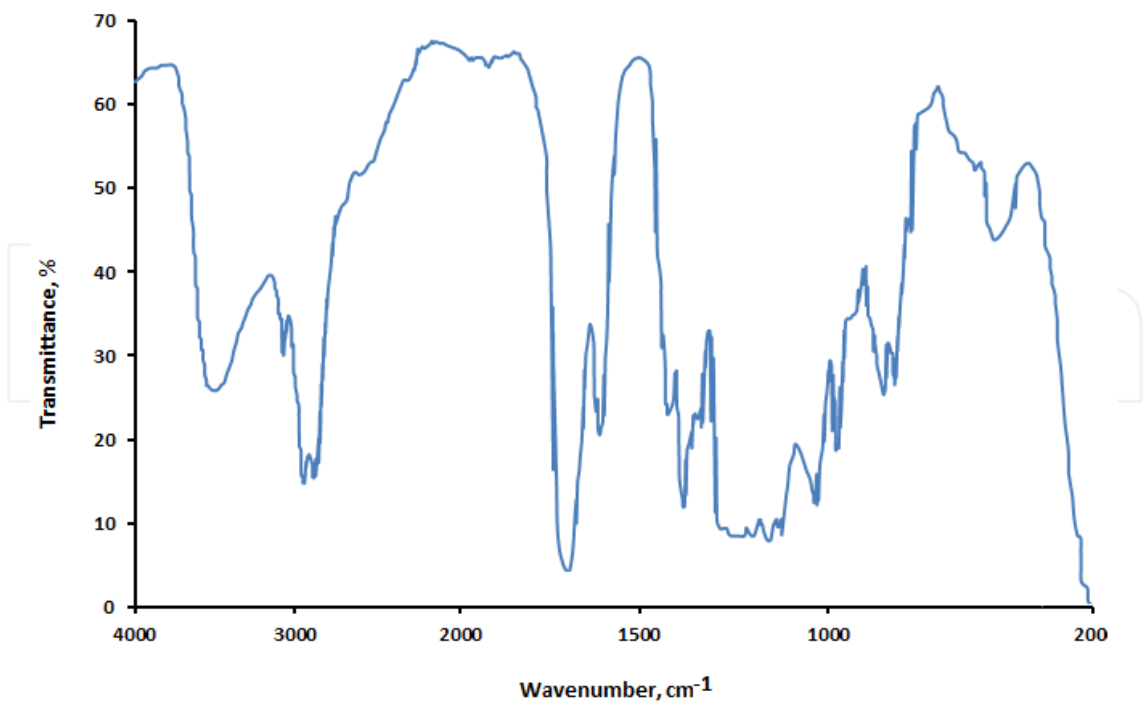


Figure 1. FTIR spectrum of the water extended polyester prepared from virgin raw ingredients

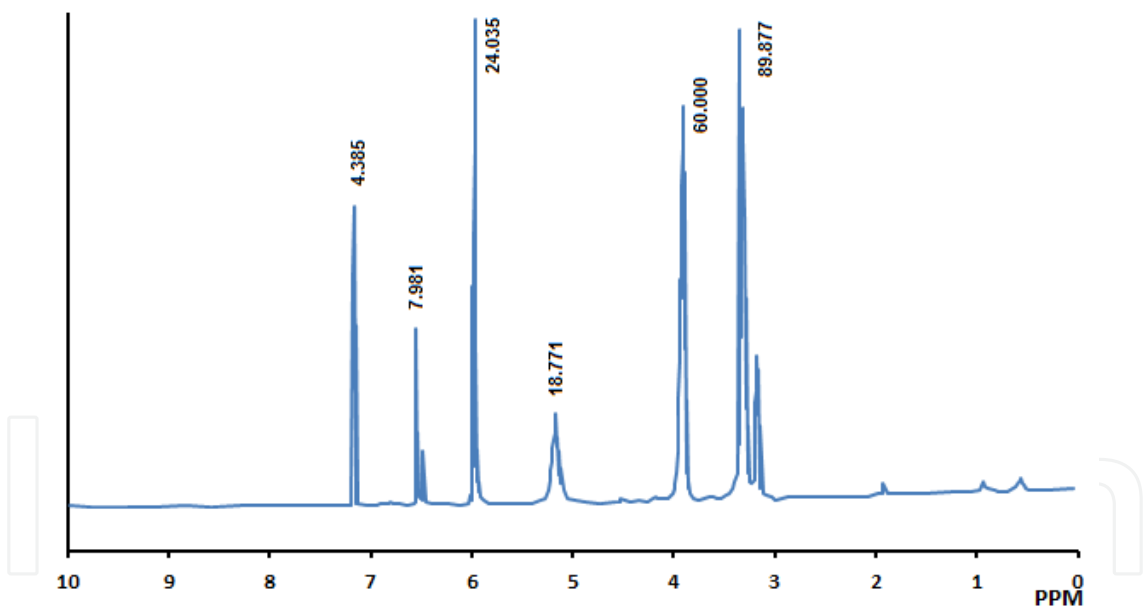


Figure 2. NMR spectrum of the water extended polyester prepared from virgin raw ingredients

4.2. Water extended polyester (WEP) based on recycled PET

WEP is used as an organic additive to improve the properties of cement waste forms. The resulting PCC products show a good mechanical integrity, enhanced physical properties, acceptable radiation stability, low leachability of radionuclide, and withstand relatively high temperatures. However, it could be stated that the characters of the prepared PCC depend mainly on the properties of UP used. Nuclear magnetic resonance (NMR, ppm) analysis for

the UP based on PET was carried out using a Bruker AC-400 spectrometer and deuterated chloroform as a solvent. The spectrum represented in Fig. 3 shows the obtained signals for the UP analysis and their corresponding assignments represented the following groups; at 8.07–8.08 (4H, C₆H₄), at 6.85–6.89 (olefinic protons in the CO-CH=CH=CO chromophore of maleic and fumaric acid residues), at 5.2–5.6 (methine proton of PG residue), at 3.58–4.68 (-O-CH₂-CH₂-O and -O-C-CH₂-O), at 1.63–2.14 (adipic acid residue), and at 1.27–1.48 (methyl group in PG residue) (Tawfik et al., 2005).

The IR spectrum of unsaturated polyester (UP) obtained from recycled soft drink bottles of PET shows that the broad band that appeared around 3500 cm⁻¹ is due to the stretching vibrations of the OH terminal in the hydroxyl group in the hard polymer. The band at 3020 cm⁻¹ may be assigned to the aromatic CH while bands at 2950 cm⁻¹ and 2880 cm⁻¹ may refer to the stretching of CH in methylene and methyl olefinic groups, the stretching frequencies of the ester carbonyl group (C=O) in the polymer appeared near 1720 cm⁻¹ and 1640 cm⁻¹ while that for olefinic -C=C- appeared at 1580 cm⁻¹. The band in the region 1450–1380 cm⁻¹ may be attributed to the bending vibration of CH₂ and CH₃ in propylene glycol. The curve shows also the bending in trans -CH=CH- groups, which appears at 980 cm⁻¹. On the other hand, bands at 880 cm⁻¹, 750 cm⁻¹, and 650 cm⁻¹ may be attributed to cis olefinic and aromatic residues (Eskander et al., 2006). It could be clearly stated that there were non-significant differences between the WEP based on the recycled PET and that prepared from its virgin raw ingredients. However, it is worth mention that the economical and environmental aspects favored the preparation of WEP based on the recycled PET.

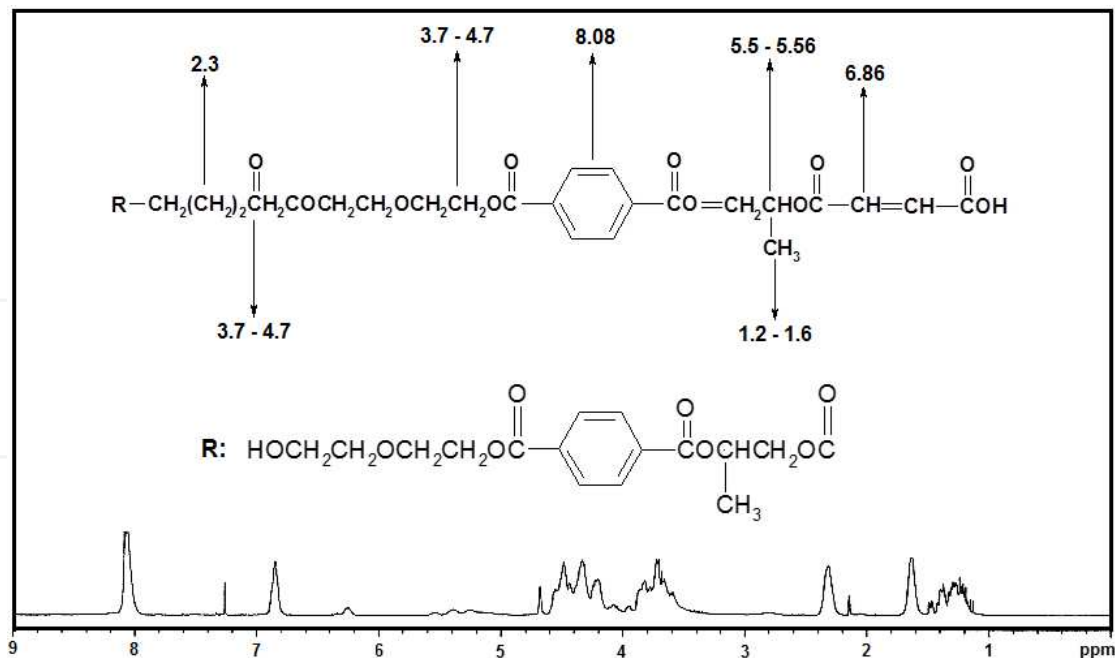


Figure 3. NMR spectrum of polyester based on glycolized PET waste

On the other hand, styrenated unsaturated polyester products based on both the recycled PET and poly(oxy-diethylene maleate) mixed with styrene monomer showed mechanical and physical characterizations closely similar to each other as reported in Table 2.

Composition	WEP based on recycled PET	WEP based on virgin raw ingredients
Styrene monomer	30 %	30 %
Specific gravity at 25°C	1.45	1.45
Appearance	Light yellow	Yellowish white
Water of emulsion	50 %	50 %
Initiator (Benzoyl peroxide)	2 %	2 %
Compressive strength, MPa	9.57	9.95

Table 2. Chemical, physical and mechanical characterizations of WEP

5. Evaluation of the final waste form

Transformation of borate wastes from pressurized water reactor into homogeneous monolithic solid waste forms was achieved using cement and polymer-modified cement as an inert matrices. The aim was to reduce the potential migration and dispersion of radionuclides from waste forms to the environment, the primary objectives were to provide possible options helping in choosing the proper immobilization media, to improve the quality of the final waste forms and process technology.

Compressive strength is generally given for the description of structural stability of the final waste forms. To evaluate the mechanical integrity of the solid PCC containing the borate waste simulate, compressive strength measurements were carried out for PCC solid blocks under variable factors that may affect e.g., polymer/cement ratio, water content, or borate waste simulate concentration. A remarkable change in compressive strength values for PCC samples containing an increasing ratio of WEP premixed with cement paste having different water/cement ratios were recorded, as shown in Fig. 4. Premixing cement with WEP affected the final properties of the final waste forms in two contradicting ways depending on the WEP/PC ratio used. In the case of low polymer content (up to 3% of hydrated cement), the compressive strength values were increased by increasing the WEP content, as shown in Fig. 4. On the other hand, increasing the polymer content, more than 3 weight percent, the mechanical integrity of the final waste forms diminished clearly. The improvement in mechanical integrity of the blocks containing low WEP concentration may be attributed to the positive effect of the organic WEP on the final waste forms. When premixing the polymer with the cement and water, it becomes uniformly dispersed within the fresh paste. On hardening, the polymer particles coalesce and gradually build up together to form a three-dimensional cross-linked network that contributes to the toughness and durability of the PCC-system (Tawfik et al., 2005). In other words, the WEP additives act as binding materials improving adhesion of the different heterogeneous cement components. Moreover, the WEP dispersion during hardening seals the pores of the cement matrix and, hence, diminishes the porosity of the products reflecting improvement of the mechanical integrity of the final waste forms. Also, the WEP may act as a filler material that has a plasticizing effect and results in a detectable increase in the durability of the final waste forms.

On the other hand, the high WEP contents negatively affected on the mechanical properties of the final solid blocks, as shown in Fig. 4. This may be due to the fact that the dispersion of the excess organic polymer materials in the paste restricts the access of water in cement grains by forming a thin coating skin over them and also enhanced the ettringite formation. In addition, the hydration process of cement could also be negatively affected by the interaction of excess polymer with Ca^{++} in the cement materials. The carboxylate anions (COO^-) produced by the hydrolytic reaction of esters combine chemically with Ca^{++} cations released from cement grains during the hydration of cement material to form a molecular structure that prevents the scission of the polymer chain.

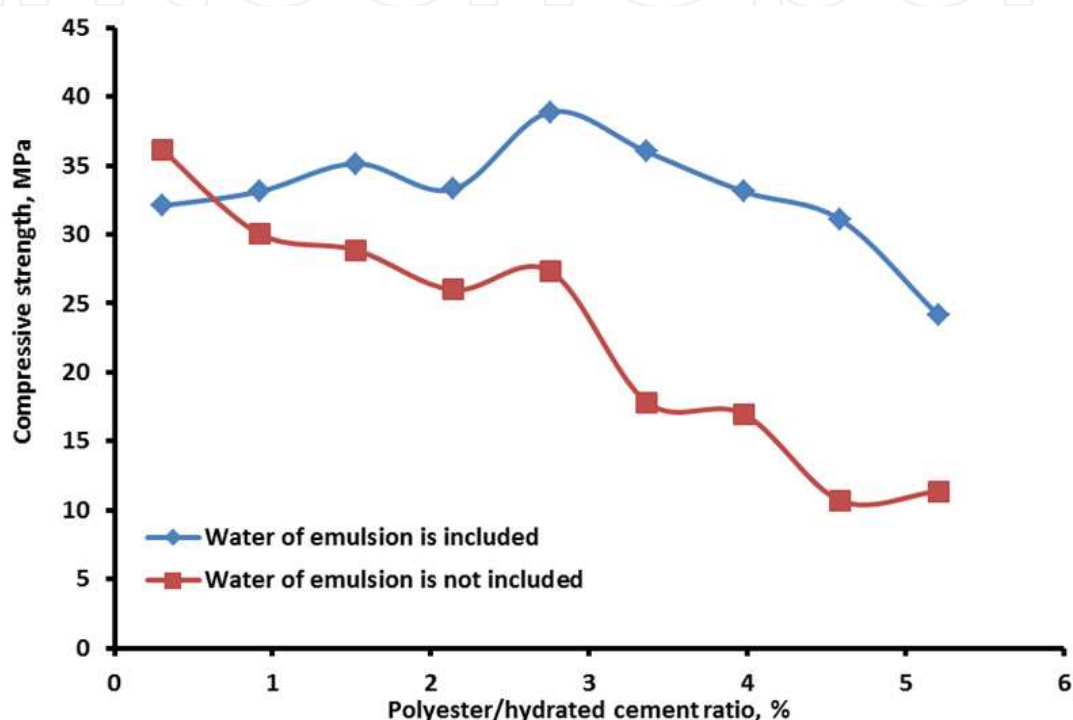


Figure 4. Mechanical integrity of the final polymer-cement composite waste form; Effect of the water content on the compressive strength of the final waste form

Basically, in the cementation process, the anhydrous tricalcium silicate (C_3S) and dicalcium silicate (C_2S), which contribute with the most abundant constituents of PC, commences the hydration reaction very rapidly. Water reacts chemically with the cement constituents to form hydrate silicate and aluminate compounds, which normally contribute to setting and hardening of cement (Tawfik et al., 2005). Figs 4 and 5 describe the effect of water content on the mechanical properties of PCC. Two sets of PCC solid blocks were prepared having different water contents. In the first set, the water of emulsion was included in the water of hydration, while in the second set the water of emulsion was not included in the water of hydration. It is clear from Fig. 4 that when the water of emulsion was not included in cement hydration water, solid blocks with higher compressive strength values were obtained, compared to that of the solid blocks in which the water of emulsion was included in the cement hydration water. This may be attributed to the fact that in the second set, part of the water was used for emulsion formation and at this low water content, the hydration

reaction of cement may be stopped in the presence of significant amounts of non-reactive cement materials due to the lack of sufficient amounts of water needed for the hydration process. Therefore, it is recommended to calculate the cement hydration water separately from the polymer emulsion water. It is worth mentioning that the same trend was exhibited for different w/c ratio, i.e., 35 wt% or 45 wt% which was not including the water of emulsion. The ratio of 35 wt% of higher mechanical integrity was obtained compared to that at the ratio 45 wt%, but the workability at the w/c ratio 45 wt% was better than that at 35 wt% (Fig. 5) (Tawfik et al., 2005).

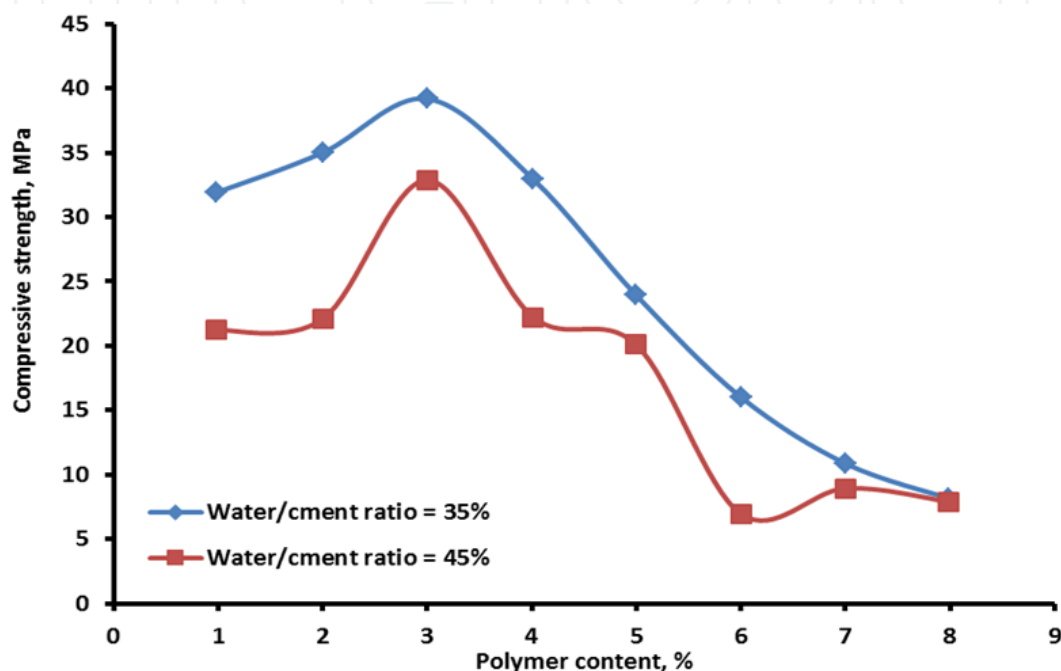
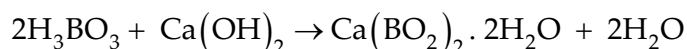


Figure 5. Mechanical integrity of the final polymer-cement composite waste form; effect of polymer content on the compressive strength of the final waste form

The effect of borate content on the mechanical integrity of PCC final waste forms were followed by increasing the waste simulate percentages that premixed with WEP/PC mixture containing 3% polymer (WEP) and at water/cement ratio 40%. After the curing period, the compressive strength measurements were performed for the solid blocks and the data obtained were represented in Table 3. Increasing the borate content premixed with the PCC caused a remarkable decrease in the mechanical integrity of the final waste forms.

Borate waste simulate mainly includes a large percentage of boric acid H_3BO_3 (i.e., 180 g/l) and some borates, e.g., BO_3^{3-} and $B_4O_7^{2-}$ are known as cementation inhibitors. Boric acid reacts with calcium hydroxide during cementation as follow:



Calcium borate is sparingly soluble and is assumed to create a barrier at the cement particles and the solution interface. This barrier retards the diffusion of water and colloidal particles. Acceptable compressive strength values for solid blocks containing up to 3% borate waste

simulate were achieved for PCC waste forms containing 3% WEP and w/c ratio 40%. At higher borate levels, a sharp deterioration in the mechanical integrity was detected (Tawfik et al., 2005).

Borate, wt.%	Compressive strength of blocks, MPa	
	Containing 3%, by wt WEP	Containing 6%, by wt WEP
0	33.6	32.74
1	30.06	28.74
2	19.0	0.38
3	20	brittle
4	2.5	brittle
5	brittle	—

Table 3. Compressive strength values of the final PCC waste forms containing, different percentages of borate waste simulates

6. Frost resistance of the polymer-cement composite immobilizing borate waste simulate

To evaluate the suitability of PCC to solidify and stabilize (S/S) radioactive borate waste resulting from pressurized water reactors (PWRs) under the aggressive frost conditions, experimental studies have been undertaken on a laboratory scale, aiming at the determination of the influence of freezing and thawing cycle (FTC) on the mechanical strength, structural deformation, and porosity of the candidate PCC after 115 cycles (Eskander et al., 2006).

The objective of immobilization of radioactive wastes is to convert the wastes into a form that is mechanically, physically, and chemically stable during handling, transport, and disposal. During the long term disposal, and at very low temperature, the frost resistance of the final solid waste form should be assessed. The adequacy of resistance of PCC, based on recycled poly (ethylene terephthalate) from postconsumed soft drink bottles as a candidate matrix for solidification of radioactive borate liquid wastes to frost attack can be determined by a freezing/thawing test. The repeated cycles of freezing and thawing have a cumulative effect rather than the single occurrence frost that causes damage (Eskander et al., 2006).

One of the classical criteria of frost resistance is the weight change of the casted specimens after a number of freezing and thawing cycles. Therefore, a simple formula was postulated to calculate the weight durability percent (Kw) for the candidate PCC subjected to 115 repeated FTC. $Kw = W_n/W_o \times 100$ Where; W_o is the weight of solid specimen before FTC and W_n is the weight of solid specimen subjected to n FTC.

The data obtained for PCC and plain cement subjected to 115 freezing-thawing cycles were represented in Table 4. The Kw for the plain cement decreases by about 14% after 14 cycles and more than 17% after 115 cycles while the Kw for PCC decreases only 13.3% after 115

cycles (230 days) of freezing and thawing at -19°C and $+60^{\circ}\text{C}$. It is also worth mentioning that the weight durability indices for the PCC exhibit constant value ($87.5\% \pm 0.2$) starting from the 28 cycles up to 115 cycles (i.e., end of the treatment). This indicates that the PCC shows acceptable frost resistance compared to the plain cement (Table 4).

FTC	Kw Durability index, %	
	PC	PCC
1	96.6	96.7
4	94.5	95.3
7	93.3	93.1
14	86.4	90.2
28	85.1	87.6
54	84.5	87.3
90	84.5	87.5
115	82.9	86.7

Table 4. The weight durability index (Kw) for plain cement and polymer-cement composite (PCC) subjected to 115 freezing-thawing cycles

Generally, the cement-water extended polyester system consists of three main interacting components: polymer, cement, and water. The polymer-cement modification is initiated in the presence of water to form the polymer phase and simultaneously the cement hydration occurs. Consequently, a co-matrix phase is formed with a network structure of interpenetrating polymer and cement hydration phase. As a result of this intrinsic structure, the mechanical strength and other properties of the modified polymer-cement matrix is improved (Eskander et al., 2006).

Table 5 represents the results of volume of open pores (cm^3), apparent porosity (%), and water absorption (%) for PC (w/c ratio = 40%) as well as PCC that are nominated for processing the borate waste (WEP/PC ratio = 3% and w/c ratio = 40%) and subjected to freezing/thawing treatment up to 115 cycles. It is clear that the PCC matrices have improved resistance to freezing and thawing, based on the improvement in the intrinsic properties, namely volume of open pores, water absorption, and apparent porosity compared to the conventional cement matrix Table 5. This may be attributed to filling the pores of cement matrix in PCC and air entrainment introduced by the WEP (Eskander et al., 2006). The apparent porosity percent for the PCC matrix decreased after the first cycle and then a very slight increase was detected (+4%) after 90 cycle, (Table 5). This may be explained on the basis that: the polyester-styrene binder is a thermoplastic resin and due to the heating effect during the thawing cycles ($+60^{\circ}\text{C}$) enhancement in the polymerization may take place and, consequently, lower porosity is reached (Table 5). The slight increase in the apparent porosity after four FTC may be attributed to the deterioration that may start in the polymer-cement composite due to the repeated freezing and thawing effect.

The advantages of the addition of polymers to PC is reducing the water absorption, total porosity, and volume of open pores. Both water absorption and apparent porosity percentages were improved for PCC after 115 cycles compared to the plain cement. It is thought that this comes about by the effect of polymer on the size of the calcium hydroxide (CH) crystals formed during the hydration of C_3S , which in turns reduces this formation during the crystallization process, as well as the air entrainment and/or the filling effect introduced by the polymer and surfactants as previously stated (Eskander et al., 2006).

FTC	Composition	Exterior volume, (cm ³)	Impervious Volume, (cm ³)	Volume of open pores (cm ³)	Apparent Porosity, %	Water absorption, (%)	Apparent specific gravity	Bulk density, (g/cm ³)
0	PCC	26.85	18.05	8.8	32.77	20.28	2.4	1.62
	PC	26.40	16.55	9.18	35.67	21.8	2.54	1.47
1	PCC	25.55	18.74	6.81	26.67	15.08	2.41	1.77
	PC	25.44	16.56	8.89	34.95	21.17	2.53	1.65
4	PCC	25.7	18.28	7.42	28.25	16.68	2.43	1.73
	PC	25.86	16.85	9.00	34.82	20.99	2.54	1.66
7	PCC	24.94	17.51	7.43	29.81	16.61	2.56	1.8
	PC	26.04	16.96	9.08	34.87	20.8	2.57	1.66
14	PCC	26.02	18.34	7.57	29.2	16.43	2.46	1.74
	PC	26.09	17.28	8.82	33.8	20.17	2.6	1.68
28	PCC	25.32	17.69	7.63	30.13	17.3	2.49	1.74
	PC	25.65	16.19	9.46	36.87	20.4	2.6	1.65
54	PCC	25.09	17.34	7.65	30.52	17.41	2.52	1.75
	PC	25.54	16.55	8.98	35.78	20.96	2.59	1.68
90	PCC	25.54	17.17	7.36	30.76	18.71	2.61	1.75
	PC	25.84	16.52	9.33	36.09	21.69	2.64	1.67
115	PCC	24.89	17.83	7.05	30.3	18.36	2.40	1.82
	PC	24.71	16.72	9.98	36.31	21.04	2.51	1.7

Table 5. Some physical properties of PC and PCC subjected to freezing/thawing test

Certain minimum values of the mechanical integrity are required during long term stress of storage and disposal. An improvement in the compressive strength measurements was observed for polymer-modified cement candidate matrix up to 54 FTC, i.e., more than 35% compared to unmodified specimens (Table 6). On the other hand, after 115 FTC a slight decrease in the compressive strength values $\approx 12\%$ of the candidate matrix was recorded, (Table 6). However, it should be mentioned that even after 115 cycles of freezing-thawing treatment at -19°C and $+60^\circ\text{C}$, the compressive strength figures reached by the proposed matrix are still higher than that recommend by the Nuclear Regulatory Commission (NRC) for transport and disposal requirements (Eskander et al., 2006). On the other hand, obvious deterioration in the plain cement blocks was recorded due to the freezing/thawing treatment (Table 6). Similar trends were obtained previously in the literature. This improvement in mechanical integrity of the cementitious system is usually controlled by pore structure,

especially porosity. The addition of polymer to the cement has the entrained air effect in the mixture that stabilized as small bubbles. The latter have a reproducible pore structure as well as good dispersion of air in the modified cementitious system and reflects a good frost resistance character. On the other hand, the increase in the compressive strength measurements of the candidate polymer-cement matrix up to 54 cycles (Table 6), can be attributed to the increase in the cross-linking of the polyester-styrene during the thawing cycles as previously stated (Eskander et al., 2006).

FTC	Compressive strength, MPa	
	PC	PCC
0	34.4	33.2
1	33.8	33.2
4	31.3	33.4
7	24.2	33.5
14	25.7	35.6
28	25.8	37.3
54	25.6	40.1
90	26.7	35.4
115	25.3	34.3

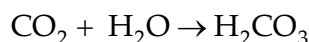
Table 6. Effect of freezing-thawing cycles on the compressive strength values of PC and PCC

7. Behavior of solid waste form during a scenario of flooding accident in the disposal site

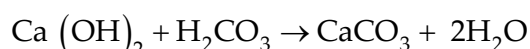
The behavior of the PCC waste form during an accident of flooding disposal sites with any of three different types of water (tapwater, groundwater and seawater) was followed. Mechanical integrity, weight change, porosity, bulk density, water absorption, specific gravity, . . . were selected for laboratory testing under the immersion conditions in any of the three different types of water during a period of 260 days (Tawfik & Eskander, 2007).

Water is at the heart of most of the physical and chemical causes underlying the deteriorations of concrete structures. Cement-based solid products exposed to water undergo carbonation process that refers to the reaction of the carbon dioxide, in the surrounding, with water to form carbonic acid, which then combined with calcium ions leached from the hydrated cementitious materials to form insoluble calcium carbonate salts (CaCO_3). A white thin layer (≈ 0.1 mm thickness) started to appear very clearly on the surface of solid PCC blocks immersed statically in seawater after 30 days. On the other hand, by the visual examination of PCC blocks immersed in groundwater, this layer was less obviously seen, while for those immersed in tapwater this layer was hardly detected even after 260 days of immersion. This may be due to the high salt contents of both seawater

and groundwater that affect highly the leaching of lime $[\text{Ca}(\text{OH})_2]$ from the surface of the PCC and its reaction with the carbon dioxide, of surrounding, forming the thin layer of calcite (CaCO_3). To confirm this finding, this thin layer was scratched from the surface of PCC blocks that immersed in seawater for 260 days, and subjected to XRD and the obtained diffractogram is represented in Fig. 6. Peaks at $d = 1.63, 1.93, 2.63, 5.42 \text{ \AA} \dots$ are refer to the lime $[\text{Ca}(\text{OH})_2]$ leached from the PCC blocks, while that at $d = 4.91 \text{ \AA}$ may attributed to the formed calcite (CaCO_3). The proposed reactions for the formation of this layer can be illustrated as follows. The slight acidity of naturally occurring water is generally due to the dissolved carbon dioxide (CO_2), which is found in significant concentration in mineral, seawater, and groundwater as previously stated (Tawfik & Eskander, 2007).



A cation exchange reaction between carbonic acid and calcium hydroxide $\text{Ca}(\text{OH})_2$ leached from the hydrated PCC processed as follows:



This leads to the precipitation of the insoluble calcium carbonate salts (CaCO_3) and step further ingress of water into the interior of PCC products through reduction in permeability. This kind of protection would be available under static conditions. Nearly, similar behavior for the carbonation of concrete components was discussed in the literature (Tawfik & Eskander, 2007).

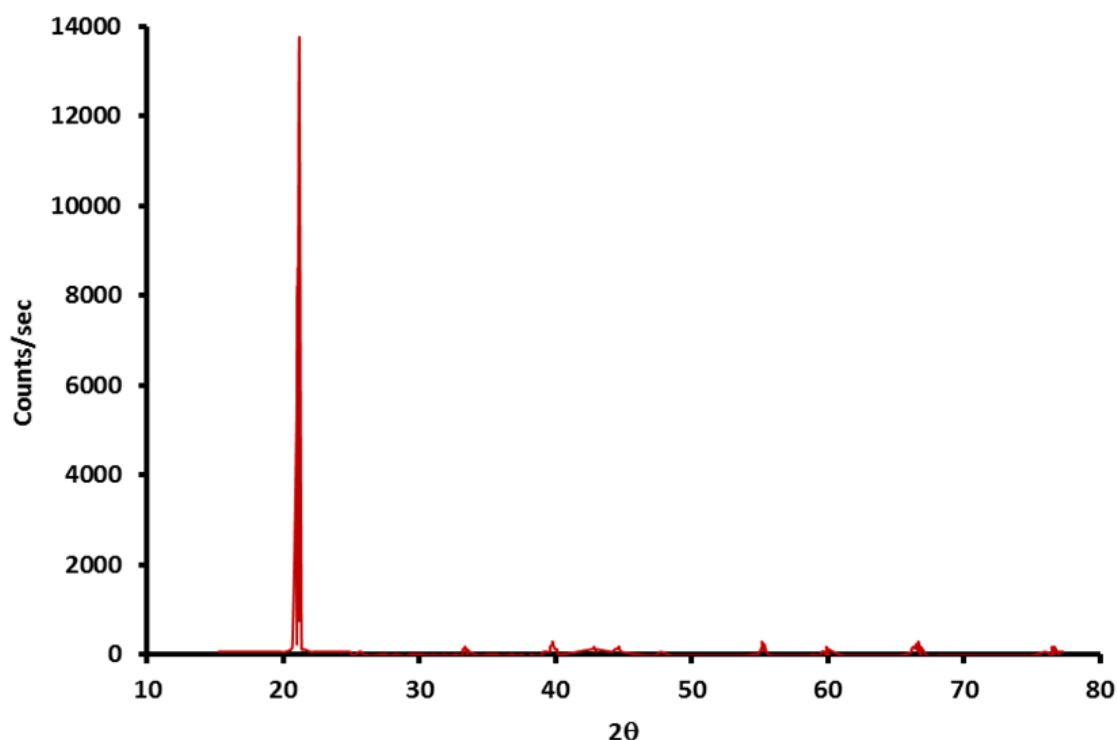


Figure 6. X-ray diffraction of the white thin layer scratched from the surface of polymer-cement composite (PCC) blocks immersed in seawater after 260 days

Porosity and other relating parameters for PCC blocks immersed in the three different types of water and for different periods were determined according to ASTM C20-74 based on BWS technique (Tawfik & Eskander, 2007) and the data obtained are represented in Table 7 for tapwater, seawater and ground water, respectively. Generally, it was observed that both porosity and water absorption percentages were increased for the PCC waste form immersed in tapwater to reach 39.55 and 24.44%, respectively, after 260 days of immersion at $30 \pm 5^\circ\text{C}$ compared to 32.77 and 20.28% for control non-immersed specimens (Table 7).

Immersion period, day	Immersion media	Exterior volume, (cm ³)	Impervious Volume, (cm ³)	Volume of open pores (cm ³)	Apparent Porosity, %	Water absorption, (%)	Apparent specific gravity	Bulk density, (g/cm ³)
0	----	26.85	18.05	8.8	32.77	20.28	2.4	1.62
7	Tapwater	27.32	18.12	9.20	33.67	20.99	2.42	1.60
	Seawater	26.32	16.68	9.68	36.78	22.54	2.58	1.63
	Groundwater	28.17	20.2	7.97	34.71	20.84	2.18	1.56
30	Tapwater	24.99	16.47	8.52	34.09	19.96	2.59	1.71
	Seawater	25.55	16.87	8.68	33.50	20.15	2.55	1.69
	Groundwater	23.7	15.54	8.16	34.43	19.24	2.73	1.79
45	Tapwater	25.16	16.40	8.99	35.41	20.58	2.66	1.72
	Seawater	25.53	17.66	7.87	30.83	17.62	2.53	1.75
	Groundwater	25.55	17.04	8.72	33.85	19.81	2.58	1.71
60	Tapwater	25.19	16.02	9.17	36.4	21.5	2.66	1.69
	Seawater	26.58	18.26	8.32	31.30	19.31	2.36	1.62
	Groundwater	26.64	17.92	8.72	32.73	19.82	2.45	1.65
260	Tapwater	25.26	15.59	10.2	39.55	24.44	2.68	1.62
	Seawater	26.63	19.66	6.97	26.17	15.36	2.31	1.7
	Groundwater	24.96	16.99	7.97	31.93	18.12	2.59	1.76

Table 7. Physical properties of polymer-cement composite (PCC) subjected to immersion test at different periods and in different leachants

On the other hand, very slight increase in the two parameters was detected for the PCC specimens immersed in groundwater at the same conditions of immersion up to 30 day. However, it should be noted that the values of porosity and water absorption percentages were declined again to reach 31.93 and 18.12%, respectively, after 260 days compared to 32.77 and 20.28% for non-immersed blocks. For the PCC blocks immersed in seawater, slightly different trend was observed where a detectable increase in porosity and water absorption percentages were occurred within the first 7 days, then a high decrease took place to reach a minimum value after 260 days (i.e. 26.17 and 15.36%, respectively) (Table 7). Generally speaking, the increase in the porosity values may refer to the leaching of the cementitious materials due to the diffusion of water into the pores of PCC specimens and removing lime and calcium sulfate components (Tawfik & Eskander, 2007). While the reduction in porosity values for the PCC blocks immersed in both groundwater and

seawater afterwards can be attributed to the carbonization process where the calcite protective layers claim to be formed and fill the pores of immersed blocks as previously described. The pronounced reduction in the porosity and water absorption percentages for the PCC immersed in seawater may be due to the high salinity of the sea leachant solution compared to tapwater and groundwater. A direct relationship can describe the mechanical integrity of the concrete composite from the knowledge of its pore system characteristics (Tawfik & Eskander, 2007). The results obtained from the porosity and pore parameters measurements were confirmed by the compressive strength measurements for the PCC cured waste forms immersed in the three different leachants for different immersion periods and their strength were measured at the end of each period up to 260 days.

Fig. 7 represents the change in compressive strength of PCC blocks immersed in different types of water for different periods compared to non-immersed ones. It is clear that loss in compressive strength was observed for all PCC specimens immersed in the three leachants for 7 and 30 days. This result confirmed the result obtained from porosity measurements. Similar trend was reached for similar concrete products immersed in groundwater. The loss in compressive strength for blocks immersed in tapwater was continued while gain in compressive strength was obtained for blocks immersed in seawater and groundwater after 45 and 260 days, respectively (Fig. 7). The initial drop, as previously explained, may be due to the leaching of the cement constituents, which results in formation of microvoids, while the gain in compressive strength can refer to the deposition of the insoluble calcite (CaCO_3) salt inside the PCC pores leading to its filling. These results are in a satisfactory agreement with previously published work and are confirmed by porosity measurements (Tawfik & Eskander, 2007). However, it is worth mentioning that, in the case of PCC blocks immersed in tapwater even with the loss in compressive strength integrity, the PCC waste forms still had compressive strength values largely greater than that recommended for transportation, handling, and disposal of final radioactive solid waste form. Porosity and mechanical integrity measurements affirm that the PCC waste form made from PC and WEP based on recycled PET candidate for borate waste incorporation can withstand the different disposal environments even in case of flooding the disposal site for long periods.

Theoretically, any environment at pH less than 12.5 is aggressive to the cementitious products due to the reduction in the alkalinity of the pore fluids, which would eventually led to destabilization of the hydration products (Tawfik & Eskander, 2007). However, our candidate PCC waste form shows acceptable properties, visually and experimentally, in the three immersion solutions even at pH values less than 12.5 (Table 8).

The change in chemical constituents of the cementitious waste forms due to leaching has been intensively studied because it is assumed to affect the release of radioactive nuclides to surrounding environment in the repository. The leaching of soluble calcium from 28 days cured PCC blocks immersed in the three leachants for 260 days is shown in Fig. 8. It is clear from the Fig. 8 that the highest release of soluble calcium was detected for PCC blocks immersed in seawater and reached ≈ 360 ppm after 45 days. This value represents nearly 0.37% of the Ca added as CaO in PC. It is worth mentioning that the release of soluble

calcium declines after 45 days to reach only 320 ppm at 60 days showed a tendency to coverage into a constant value for the next 260 days. The decrease in the Ca release may be due to the carbonation process that takes place for the PCC blocks during the immersion in the seawater. However, it could be predicted that, supposing the permanent flooding condition in the disposal site, more than 200 years are needed for the complete depilation of calcium from the PCC blocks. However, it should note that, although the PCC blocks immersed in groundwater and tapwater exhibited the same trend, the released Ca in both cases were less than that released from PCC blocks immersed in seawater (Fig. 8). These results lead to the suggestion that the proposed PCC made from PC at w/c ratio 40% and containing 3% WEP based on recycling PET waste could withstand the worst conditions of flooding in the disposal site.

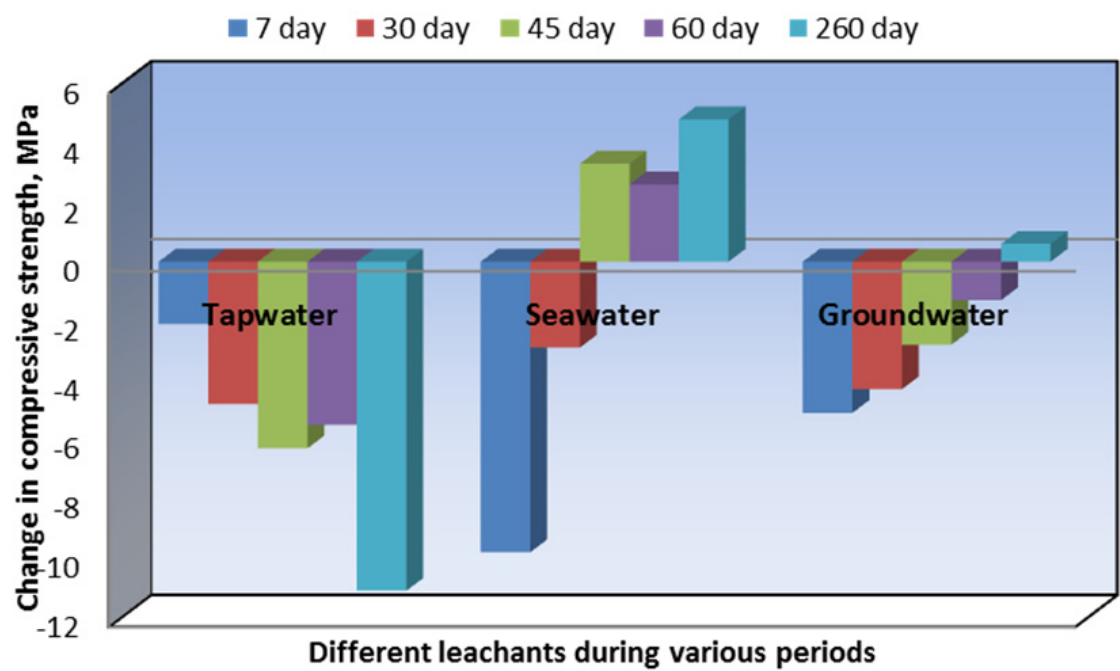


Figure 7. The variation in compressive strength integrity of polymer-cement composites (PCC) due to the immersion period in the different leachants

Immersion period, days	Tapwater	Seawater	Groundwater
0	6.72	8.02	7.2
7	11.1	10.7	10.9
30	11.1	10.9	10.9
45	11.1	11.0	11.0
60	11.1	11.0	11.0
260	11.1	11.0	11.0

Table 8. The pH of leachant solutions at the end of different immersion periods

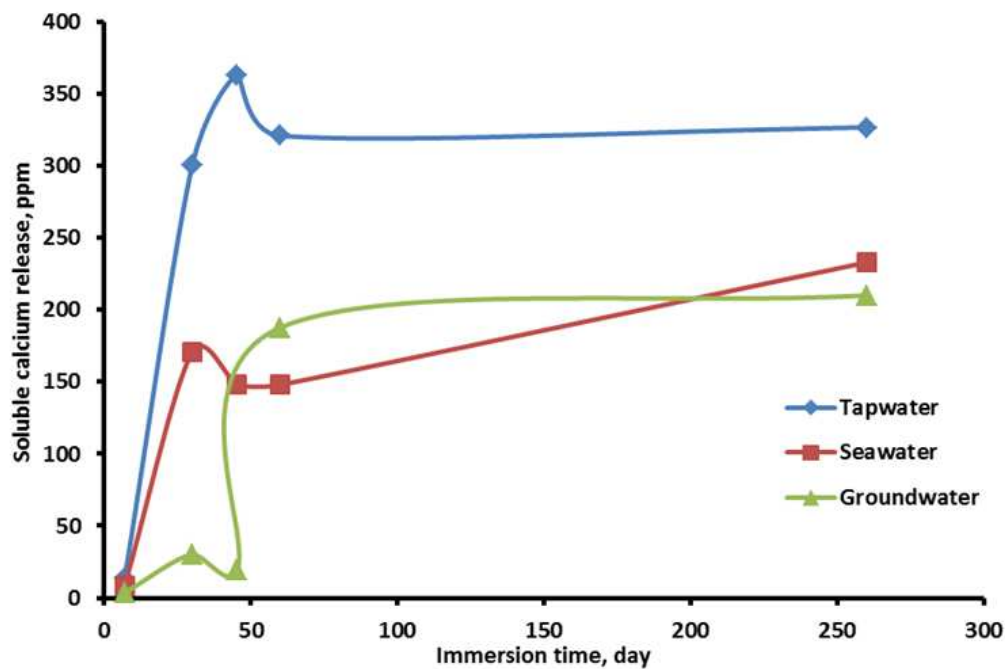


Figure 8. The release of calcium from polymer-cement composite blocks immersed in the leachant solutions versus the immersion periods

Fig. 9(a,b) shows the scanning electron micrographs (2500x magnification) of portion of a laboratory scale non-immersed plain cement, ($w/c = 0.40$) and polymer-cement composites ($w/c = 0.40$ and $c/p = 3\%$) samples. Fig. 9(c–e) represents scanning electron micrograms of polymer-cement composite specimens, having the same composition but immersed in tapwater, groundwater and seawater, respectively for 260 days. C-S-H, which represents the main hydration product of the PC, has foil and plate like crystals (Fig. 9(a)). On the other hand, portlandite (CH), i.e. crystalline calcium hydroxide, which represents the second most abundant product in the hydrated cement paste, appears in the form of relatively large crystalline aggregate and supposed to be intimately mixed with the C-S-H. Their entanglement makes it hard to define their exact shape (Fig. 9(a)). It is clear from Fig. 9(b) that the surface of the non-immersed PCC based on PET waste is characterized by a continuous large polymer, mutually intergrown with considerable number of compact points and areas connecting the cement paste and forming the binding phase of the product (Tawfik & Eskander, 2007). Therefore, the hydration products of cement formed in the polymer layers cannot be distinguished out right by their appearance (Fig. 9(b)). The fracture of the polymer-cement composite samples after immersion in tapwater is characterized by porous surface (Fig. 9(c)), and its feature after that is comparable to the analogous sample before immersion (Fig. 9 (b)). On the other hand, the PCC specimens immersed for the same period in groundwater and seawater described by peculiar qualities to each other (Fig. 9(d,e)) but differ from these immersed in tapwater (Fig. 9(c)), in the predominant presentation of calcite crystals. However, it is worth mentioning that the calcium carbonate crystals in the micrograph of samples immersed in seawater (Fig. 9(e)) are abundant, widespread and lump. SEM imaging gives detailed information about the structure of the specimens of PCC before and after immersion in the three leachants, and

consequently confirms the physicommechanical results obtained for the behavior of the PCC waste forms in the disposal environment.

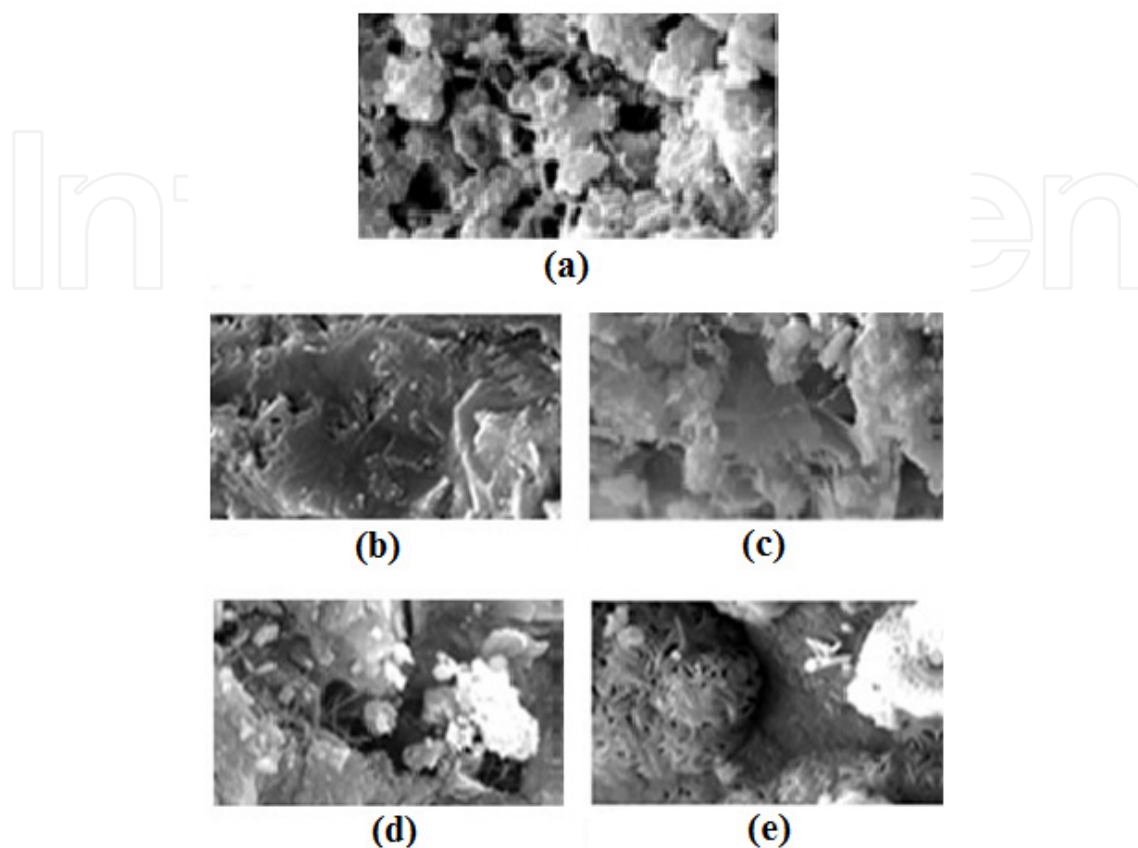


Figure 9. Scanning electron micrographs of Portland cement (PC), polymer-cement composite (PCC) before and after immersion in different leachants for 260 days. (a) PC non-immersed; (b) PCC non-immersed; (c) PCC in tapwater; (d) PCC in groundwater; (e) PCC in seawater

8. Performance of physical and chemical stability of aged polyester-cement composite containing borate waste simulate

8.1. Mechanical and physical characterizations

Much attention has been paid to study the long-term performance of polymer-cement composite from the point of view of durability related to mechanical characterizations. Fig. 10 represents the variation in compressive strength values of the aged final waste form specimens immersed in different water compositions. After 260 days of water exposure, the 7 years aged specimens exhibited a decrease in their mechanical durability through fluctuations in strength. The samples immersed in both seawater and groundwater showed greater fluctuations in strength compared to that dipped in tapwater. Loss of strength could be attributed to the formation of gypsum and ettringite in the pores of specimens (Thokchom et al., 2010). However, it is worth mentioning that the candidate polymer-cement composite immobilizing the borate waste simulate had compression strength greatly exceeds the value specified by the Nuclear Regulatory Commission (NRC) technical position

paper for stabilized low-level radioactive waste forms even after 7 years aging and nearly 260 days of immersion in different compositions of water (Eskander et al., 2012).

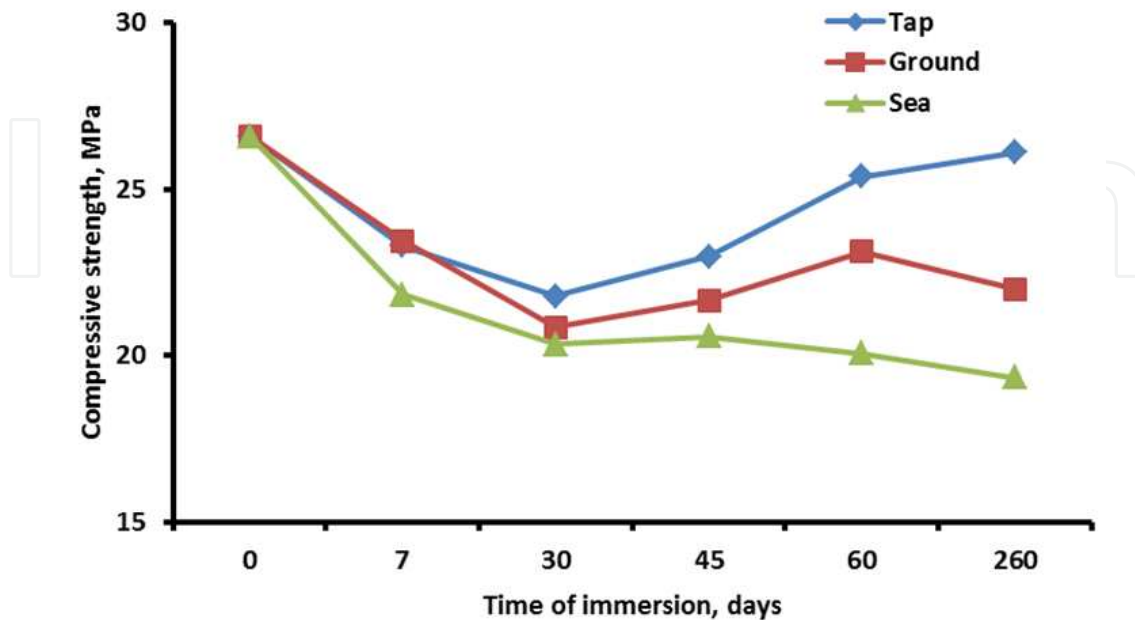


Figure 10. Compressive strength of aged PCC specimens immersed in different water compositions

The performance of plain polymer-cement composite [Portland cement (PC) and the recycled Poly(ethylene terephthalate)] incorporated borate waste simulates, which aged for 7 years immersed into the three types of water for 260 days was assessed. The internal microstructures and morphology of the aged polymer-cement composite incorporating borate waste simulate before and after immersions in various water types are represented in Figs 11, 12, respectively. Fig. 11 shows the plate like crystals of $\text{Ca}(\text{OH})_2$, which found in parallel towards each other, and they are almost undistorted (Fig. 11a). The crystals are arranged in some sort of stack. The polymer films stretched and covered the C-S-H phases (Fig. 11b), giving them a more smooth texture.

Fig. 11c,d exhibits pronounced randomly oriented calcite crystals. At the end of the immersion period for the aged final waste form in various leachants, abundant C-S-H phases coated by thin polymer film were detected (Fig. 12a). The thin polymer film was also observed around the needle-like structure of ettringite that assumed to be recrystallized inside the final waste form holes due to the immersion in seawater and groundwater (Fig. 12b). Even after 260 days of immersion process, polymer was detected between $\text{Ca}(\text{OH})_2$ crystals and may act as a glue bonding for the crystals together. In addition, a large amount of ettringite crystals was distributed in-between. It is worthwhile mention that, the solubility of the ettringite was much lower than that of portlandite and hence the former is predominant in the immersed samples (Fig. 12c).

Gypsum crystals could be distinguished in final waste forms immersed in seawater and groundwater due to their measurable contents of sulfate ions (Fig. 12d). Furthermore, this Fig. shows the gluing action of the polymer. Gypsum and ettringite are known by causing

expansion in the polymer-cement composite immersed in groundwater or seawater and accordingly, some internal cracks could be present, (Fig. 12b). The compressive strength could be decreased due to the expansion cracks in the final waste forms. Similar trend was described by Thokchom et al. (Thokchom et al., 2010). The data recorded by SEM could confirm the adequate performance of the proposed polymer-cement composite based on the recycled PET waste to incorporate the borate waste up to 4% even for long time and under flooding condition for 260 days.

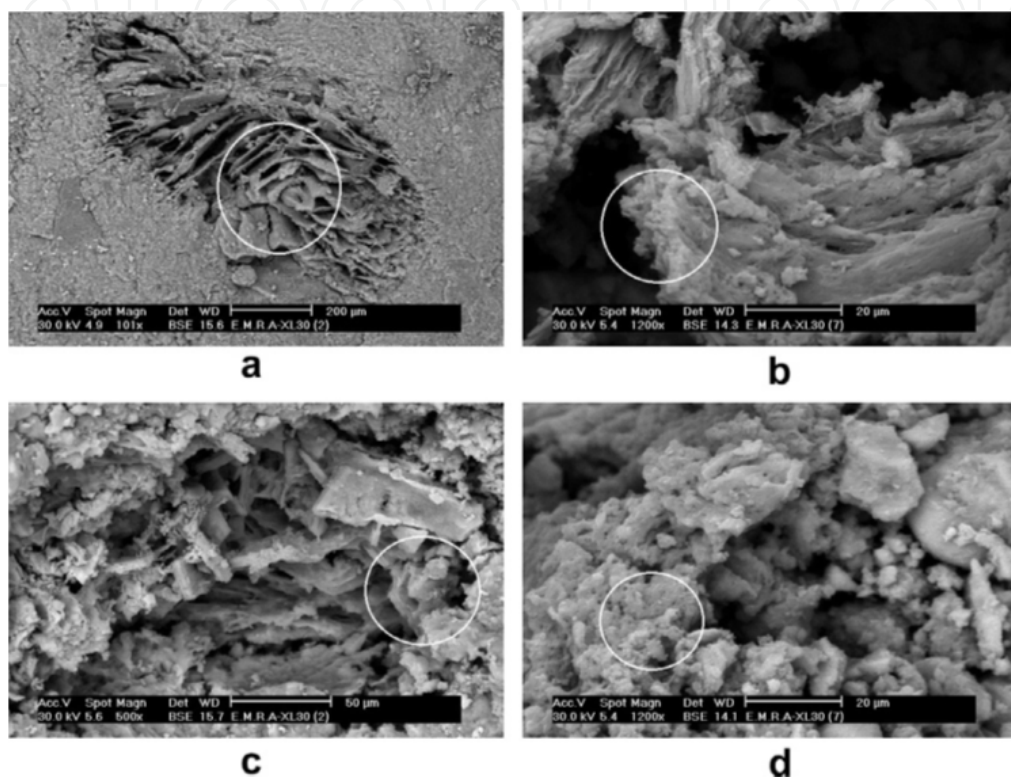


Figure 11. Scanning electron photomicrograph of the internal microstructure of 7 years aged polymer-cement composite incorporating borate waste simulate

Aged polymer-cement composite incorporating borate waste simulate did not show any changes in its shape and remained structurally intact without visible cracks even after immersion in the three types of leachants for 260 days. Specimen's surfaces received white deposits throughout the water exposure period while rare and minimum white deposits were appeared in case of tapwater. On the other hand, the maximum deposits were observed on the blocks dipped in seawater. These deposits were powdery and harden with time. The typical images of such structural formations are shown in Fig. 13, which revealed the photographs of the specimens after 260 days exposure to different water types tap (a), ground (b) and sea (c), respectively.

8.2. Chemical characterization

The long-term chemical stability of the polymer-cement composite waste (PCC) aged for 7 years under normal weather conditions and then exposed to different leachants was

studied. Cumulative fraction leached of radiocontaminants and mass changes of the waste form during leaching periods were addressed (Saleh et al., 2011).

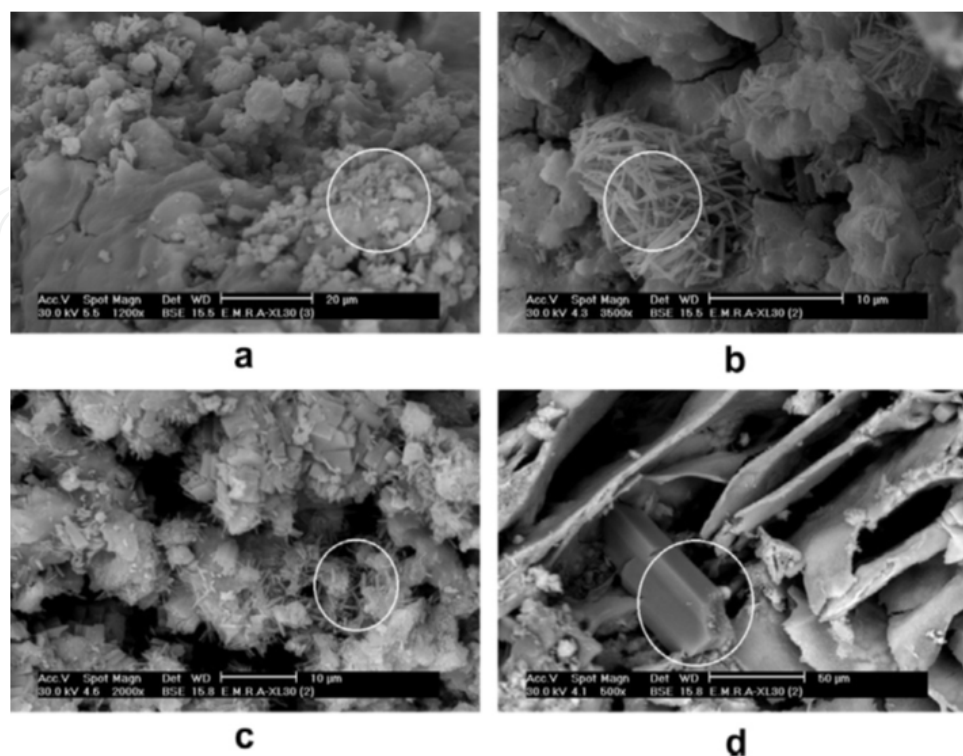


Figure 12. Scanning electron photomicrograph of the internal microstructure of 7 years aged polymer-cement composite incorporating borate waste simulate and immersed in different leachants for 260 days

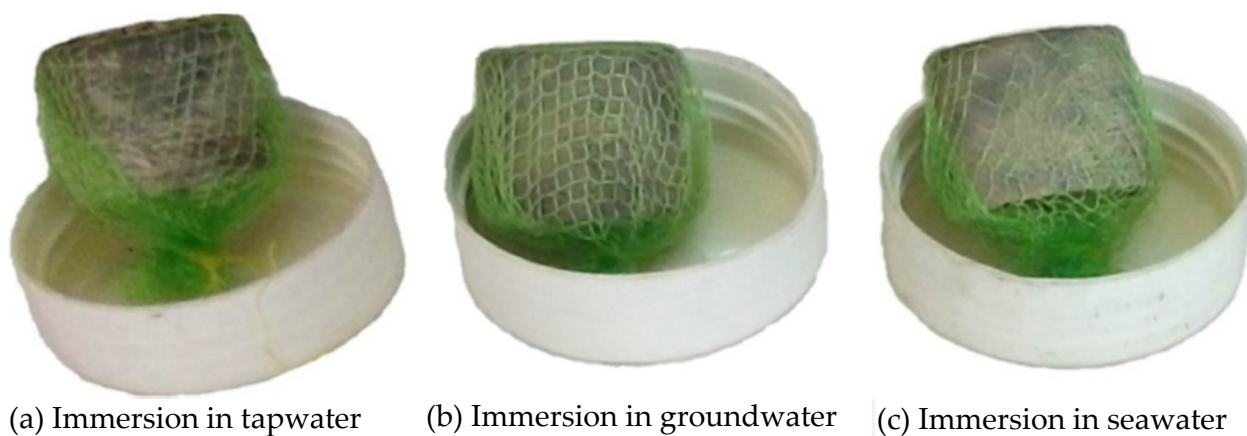


Figure 13. The 7 years aged polymer-cement composite incorporating borate waste simulate after immersion in different leachants for 260 days

Development of leach resistant waste forms is a major area of research in the field of radioactive waste management in order to minimize the environmental impact through the back release of the hazardous materials. The leaching mechanisms of simulated low and intermediate level radioactive waste forms immobilized in polymer-cement composite are being determined as a support for the development of their chemical stability under different leaching parameters such as static and dynamic conditions, various dipping media,

environment temperatures, etc. However, it should be noticed, and to the best of our knowledge, that no data have been published, which provides a basis and direct comparison of the leaching behavior of the candidate final waste form aged for 7 years before subjected to leachants flooding under previously stated conditions, which is supposed to play a role in the long-term durability of the prepared composite.

8.2.1. Static and dynamic leaching conditions

PCC samples spiked with ^{137}Cs and ^{60}Co were suspended in the center of a closed leaching jar containing groundwater (leachant volume of 150 ml) under static conditions (i.e. no agitation, no movement and the leachant was not replaced by fresh one during the whole test period). The whole volume of the leach solution was periodically withdrawn out of the leaching jar, (Fig. 14), subjected to counting and then returned back again. While in dynamic experiments, similar PCC blocks were treated in the same manner, except, the leaching solution was replaced periodically by fresh one at time intervals parallel to the sampling in a static test.

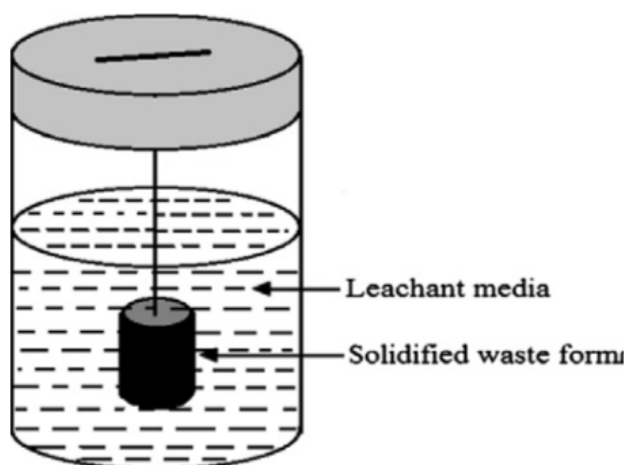


Figure 14. Schematic diagram of suspended solidified waste form during leaching test

The leachability, of ^{137}Cs and ^{60}Co radionuclides from the PCC monolith waste form, was calculated based on the upcoming relations.

Cumulative fraction leached (CFL) which is the sum of all fractions leached during the time intervals $\sum A_n/A_0 \cdot S/V$, was plotted versus the square root of time in days ($t^{1/2}$) where; A_n is the activity of radionuclides released during the particular leaching period with index n , A_0 is the initial activity of radionuclides present in the borate waste immobilized in PCC and t_n is the elapsed time of the leaching period n in days. S and V are the surface area and volume of the tested block, respectively (Saleh et al., 2011). The counts of radionuclides were determined using multichannel analyzer, PCAP, USA. From the plot of the cumulative fraction leached as a function of the square root of time in the diffusion region of leaching, slopes were calculated and applied to determine the diffusion coefficient using the following formula: $De = \pi(mV/2S)^2$ where; De is the apparent diffusion coefficient (m^2/s), m is the slope of the curve demonstrating the $\sum A_n/A_0$ versus the square root of leaching time in seconds, V is the sample volume (cm^3) and S is the sample surface area (cm^2).

On the other hand, leach index (L_x) which denotes a direct measure of the extent of leaching of radionuclides from the candidate polymer-cement composite, was computed based on the relation, $L_x = \log(1/D_e)$.

For all leaching curves, it should be notified that the leaching behavior of radionuclides from the monolith waste forms revealed two distinguished performances. The first initial period characterized by a high leachability of radionuclides relative to the second final one. This may be explained by the fact that up to nearly 25 days from the starting time, the high release may be attributed to the washout of loose radioactivity from the surface of PCC waste form (Saleh et al., 2011). This can be due to the relatively rapid washing process occurred when the blocks were firstly exposed to the leaching solution. This was followed by nearly a steady state diffusion controlling periods that persist. Leaching solution velocity (m) is defined by the volume (v) of the leachant contacted with solid waste per unit of surface area (S) and unit of time (t) given as: $v = v / (S \cdot t)$.

At a low leaching solution velocities, i.e. static condition, where the leachant was not replaced by fresh one, the amount leached approaches the saturation limit and leaching solution allowed to equilibrate with waste forms. On the other hand, under dynamic conditions where the leachant was periodically replaced maximum saturation limits were not obtained (Saleh et al., 2011) and consequently, higher leach rate was reached as presented in Fig. 15a,b. In the forthcoming leaching experiments, the dynamic condition will be performed.

8.2.2. Chemical behavior of PCC in various leaching media

The long-term durability of the polymer-cement composite under the imposed disposal conditions is a key factor controlling whether the proposed PCC can be accepted as a solidification matrix for borate waste or not. One of the major concerns that meets the cementitious waste form products in the disposal site is the exposure to an aggressive flooding environment. The leaching test was used to predict the long-term durability of the waste forms when exposed to aqueous media.

Polymer-cement waste forms are alkali in nature, and they are vulnerable to acid attack either from acid rains, seawater or groundwater that may be reached the disposal environment.

Seven years aged PCC blocks, spiked with ^{137}Cs and ^{60}Co , were suspended in separate jars each of which contains one of the following leachants, 0.1 M H_2SO_4 , groundwater, seawater or tapwater. Cumulative fractions leached of the two radionuclides in the different leaching solutions were plotted as a function of leaching time and the data obtained are shown in Fig. 16a,b. Both ^{137}Cs and ^{60}Co recorded the highest leachability in 0.1 M H_2SO_4 followed by seawater and then groundwater while the leachability in tapwater was the lowest.

In sulfuric acid medium, the dissolution of calcium hydroxide crystals and the highly decalcified calcium silicate hydrate (CSH) gels due to the acid attack result in increasing porosity and enlarged capillary pores in the leached specimens. This causes self-accelerating leaching (Saleh et al., 2011). Due to exposure to sulfuric acid for 260 days, the 7 years aged

PCC solidified waste forms showed some swelling and corrosion due to the formation of a gypsum layer on the surface. It is worth mentioning that the visual appearance of the blocks, shown in Fig. 17 is in consistence with the leaching rate results and confirms the data obtained for the high leachability of both radionuclides in sulfuric acid (Fig. 16a,b).

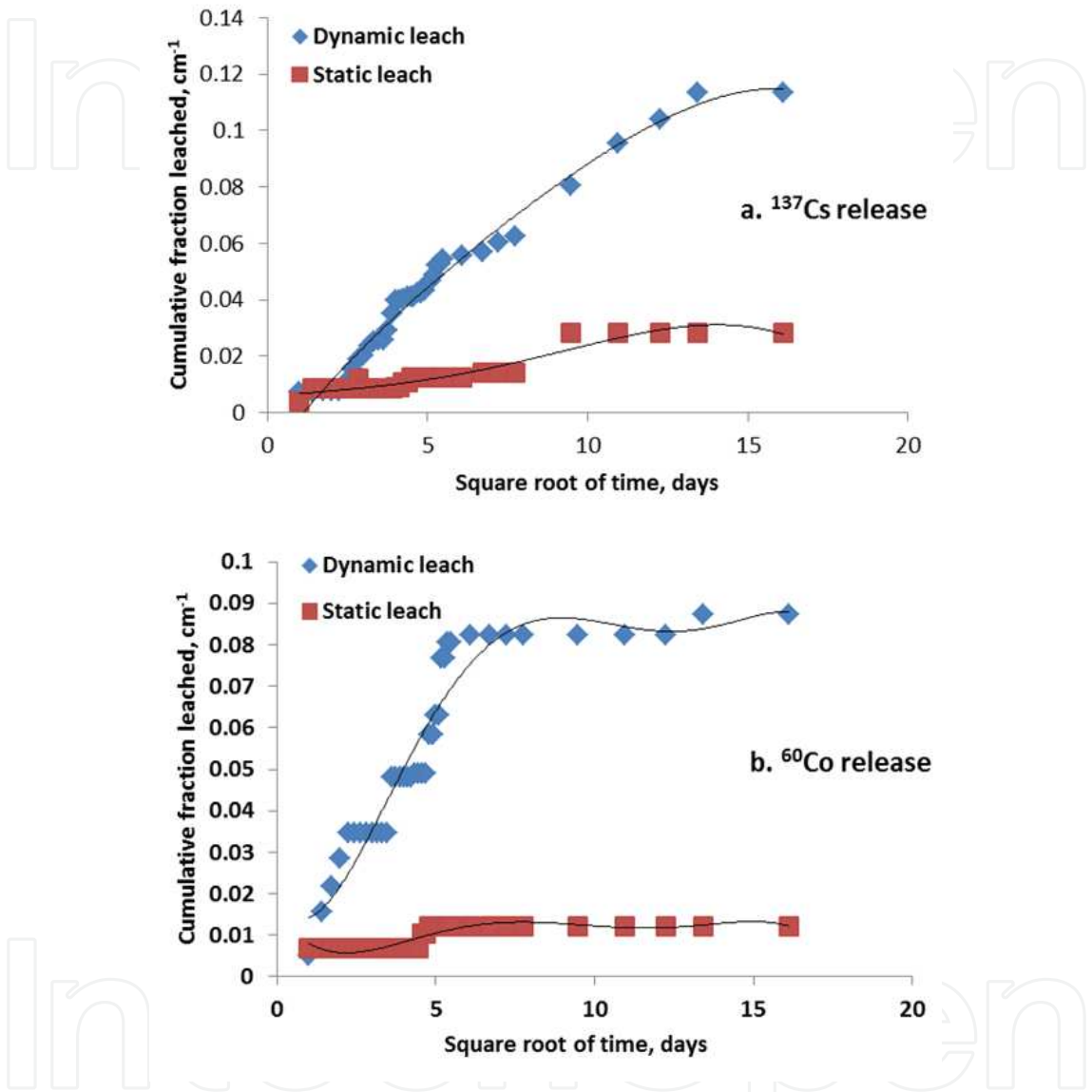
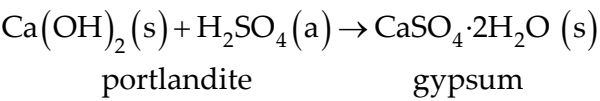


Figure 15. Cumulative fraction leached of ¹³⁷Cs and ⁶⁰Co released in groundwater under static and dynamic leach conditions at room temperature (25 ± 5°C)

The attack caused by solutions containing sulfate, e.g. seawater or groundwater can have the same diverse effects on the cementitious-base waste form. The effect of sulfate in both media may be associated mainly with the expansion of the gypsum and ettringite that can be formed as a result of contact with such leachants, as shown in the following formula:



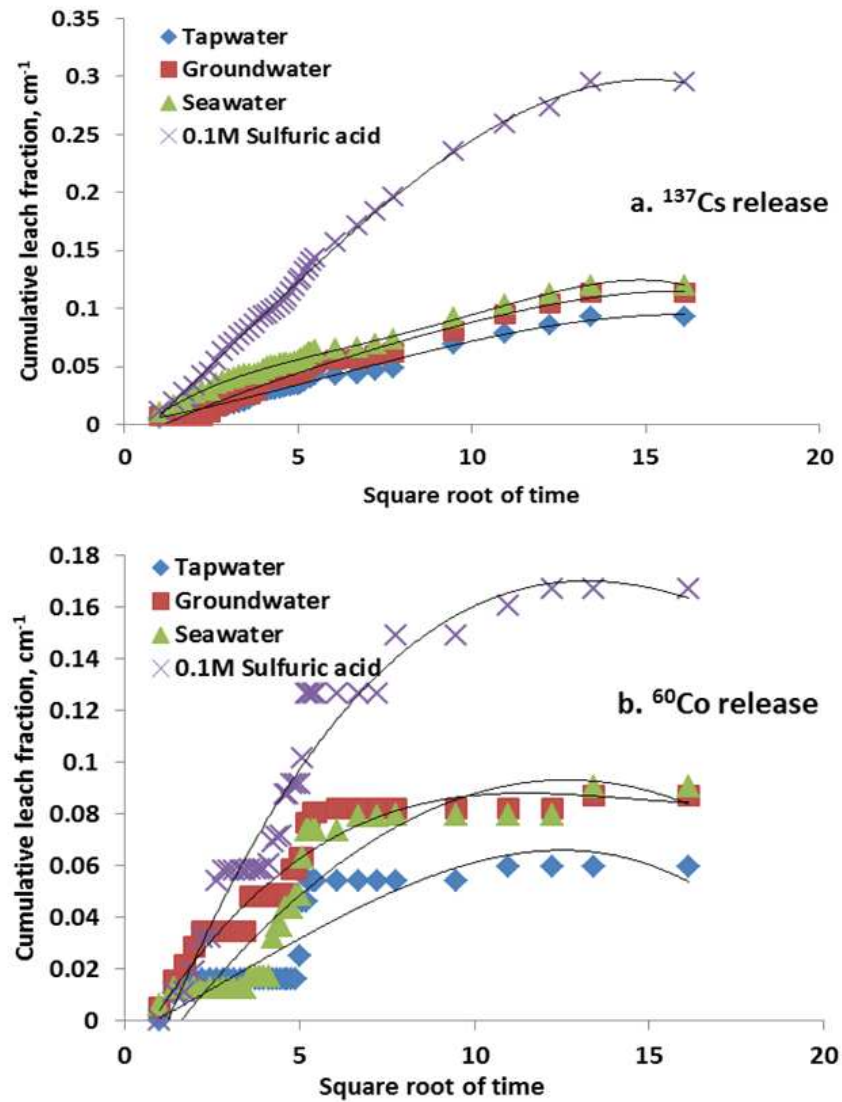


Figure 16. Cumulative fraction leached of ¹³⁷Cs and ⁶⁰Co released in different leachants at room temperature (25 ± 5°C)

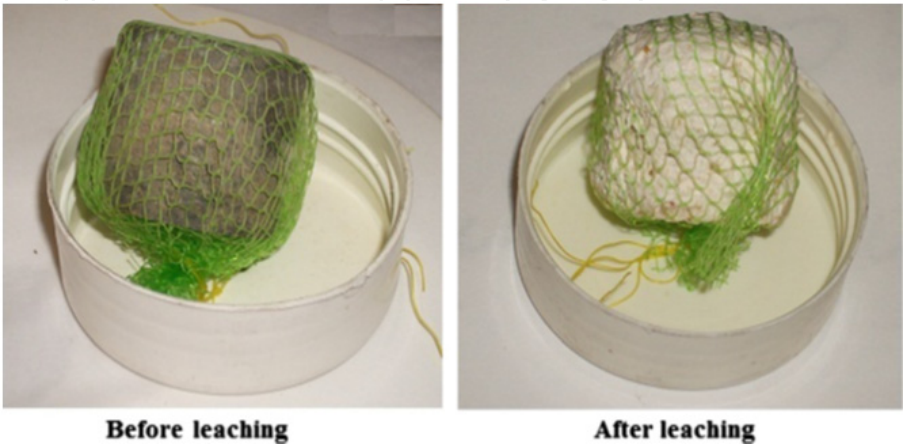
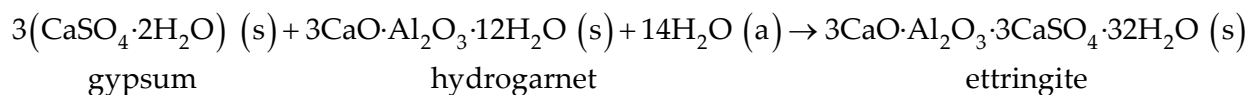


Figure 17. Polymer-cement composite waste form (PCC) before and after immersion in 0.1 M H₂SO₄ for 260 days



The expansion of these two abrasive salts can cause cracking and consequently, increase in the exposed surface area of the PCC blocks to the leaching solution and accordingly results in higher leach rates (Saleh et al., 2011). Due to the absence of the most aggressive components (e.g. sulfate or chloride) in tapwater, the ^{137}Cs and ^{60}Co leachability represented the lowest rate even after more than 260 days (Fig. 16a, b). Hence, when PCC present in places flooded by tapwater or non-acidic rain water, reasonable leaching performance could be expected.

8.2.3. Effect of temperature on the leaching performance of the PCC

Waste forms may be subjected to severe changes in temperature during transport, storage or final disposal. The variation in temperature may affect the degradation of structural integrity of the final waste forms and consequently, their chemical stability. Fig. 18 describes the cumulative fraction leached, (cm^{-1}) of ^{137}Cs (a) and ^{60}Co (b) for PCC blocks aged for 7 years and then dipped separately in groundwater. The leaching process was performed at three different temperatures, namely, at $4 \pm 1^\circ\text{C}$ (in a refrigerator), room temperature ($25 \pm 5^\circ\text{C}$) and at $60 \pm 2^\circ\text{C}$ (in an oven). The obtained data showed that, as the temperature was increased from 4°C to 60°C , the fractions leached for both radiocesium and radiocobalt were escalated. This effect of the temperature is in a good agreement with the results reported in previous reported work (Saleh et al., 2011). The high temperature may cause an increase in pore diameter dimension of the polymer-cement composite and consequently, raise their porosity that leads to elevation in the effective diffusion coefficient of both radionuclides from the final waste forms. On the other hand, when leaching was carried out at a lower temperature (4°C), the water within the pores of the waste forms may be nearly frozen and consequently, the infiltration of groundwater leachant inside the PCC microstructures was highly slowed down and accordingly, the leachability of both radiocesium and radiocobalt was decreased (Fig. 18a,b).

8.2.4. Effect of volume of leachant to surface area of specimens on chemical durability of PCC

Leachant volume to surface area of PCC, (V/S), is an additional important factor that influences the leachability of radiocesium and radiocobalt from the final waste forms and consequently, their chemical long-term stability in the disposal site. Two of 7 years aged PCC similar specimens dopped with ^{137}Cs and ^{60}Co were hang in two leaching jars having various volumes of groundwater leachant. The duration of the leaching process was more than 260 days and the cumulative fractions leached for ^{137}Cs and ^{60}Co were calculated periodically and shown in Fig. 19a,b. The V/S ratio in repository environment will certainly affect the leaching behavior of radionuclides from waste form monolith. This was clearly illustrated by the data obtained where leaching of ^{137}Cs and ^{60}Co radionuclides was directly proportional to V/S values.

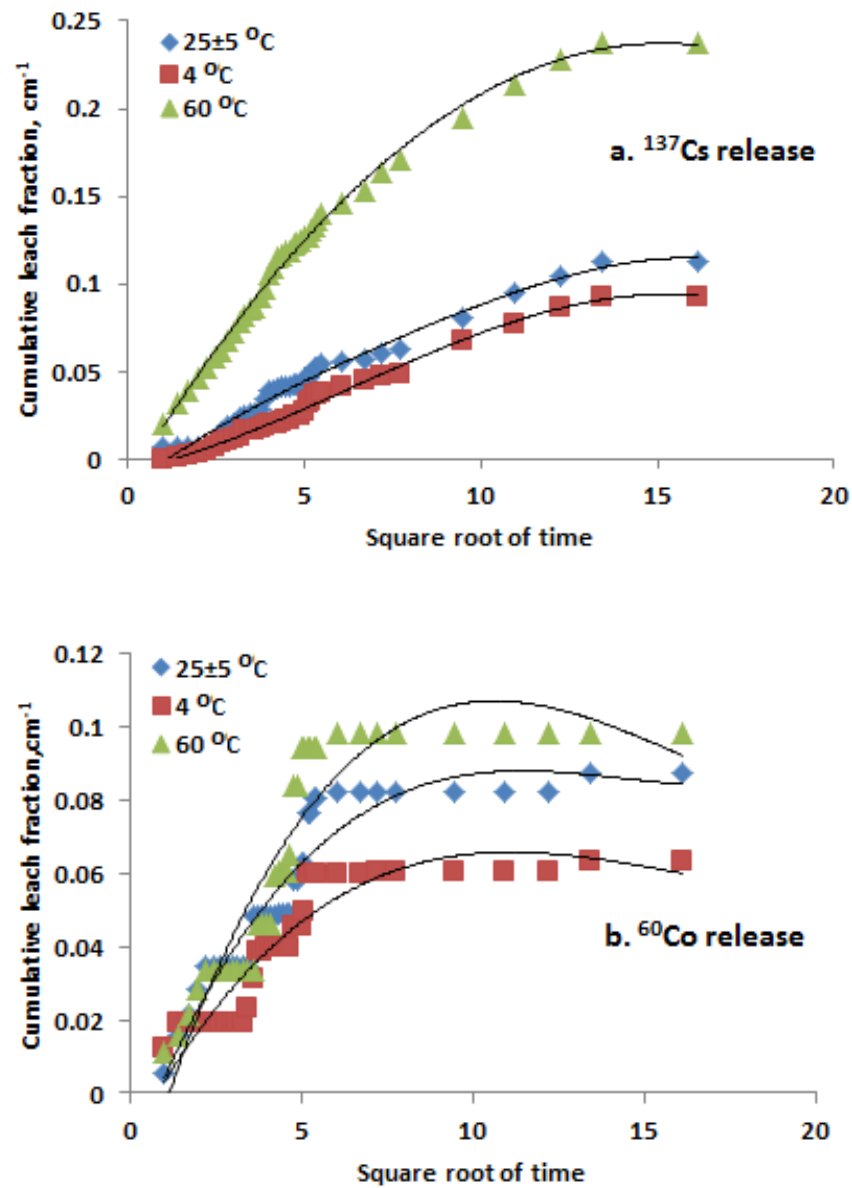


Figure 18. Cumulative fraction leached of ^{137}Cs and ^{60}Co released in groundwater as a function of leaching time at different temperatures

8.2.5. Mass changes and structural stability of PCC

The mass changes of the 7 years aged polymer-cement composite specimens during the immersion in the three leachant solutions are represented in Fig. 20. All the blocks recorded an increase in their masses over 260 days of exposure. The pattern of the mass gain was nearly identical to the three various immersion solutions. The highest gain in mass was recorded for blocks dipped in groundwater (10% after 260 days). While the lowest increase in mass was occurred for the specimens sank in tapwater. Insignificant difference in mass gain was observed for blocks immersed in seawater and those in groundwater (Fig. 20). Generally speaking, the increase in the mass of the specimens due to dipping in different

leachants may be referred to the water absorbed by the slightly porous polymer-cement composite. On the other hand, the relatively high increase in mass of the PCC samples due to immersion in groundwater or seawater may be attributed to white salt deposits formed on the surface of the specimens. Similar trend was reported by Thokchom et al. (Thokchom et al., 2010). However, it is worth noting that even with this relatively high mass gain (about 10%) all the 7 years aged blocks sustained their formal structure under complete dipping in the aggressive leachant solutions where no microcrakings were observed for all tested blocks for more than 260 days of immersion. It is worth mentioning that, when the final waste form maintained their dimensional integrity, during leaching, it was indicated that internal bulk diffusion is the most likely rate determining mechanism during the phases of the leaching process (Saleh et al., 2011).

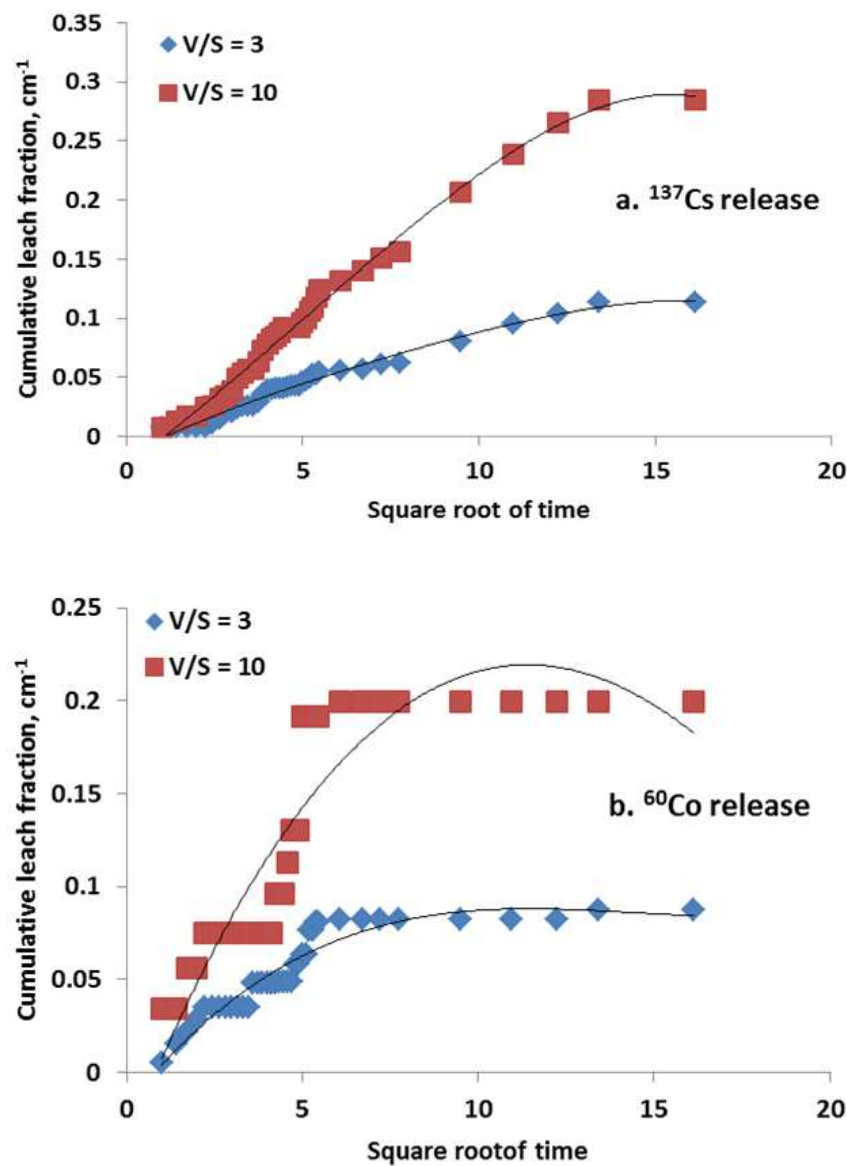


Figure 19. Cumulative fraction leached of ^{137}Cs and ^{60}Co released in groundwater at different ratios of leachant volume to surface area of waste form (V/S), under the room temperature ($25 \pm 5^\circ\text{C}$)

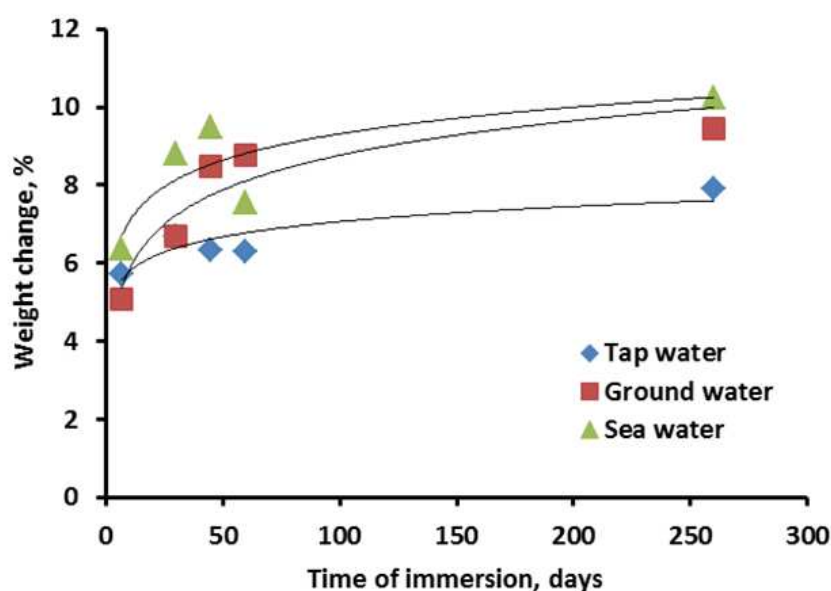


Figure 20. Mass change percent due to immersion period in various media

8.2.6. Diffusion coefficient and leach index

It is clear from all leaching curves that, after nearly 30 days a plateau of stabilization of the cumulative fraction leached is reached for the PCC blocks under all various studied conditions, which shows that the only leaching mechanism of the two radionuclides is controlled by diffusion mechanism.

Based on the diffusion coefficient (D_e), the leachability index (L_x) is calculated to characterize the efficiency of the candidate matrix to solidify the problematic borate waste concentrate. The value 6 of leach index is the threshold value to accept a given formulation as adequate for certain solidification/stabilization of nuclear wastes (Saleh et al., 2011). The higher values of the leachability index represent the lower release of the radionuclides from the monolith waste forms. The diffusion coefficients (D_e) in (m^2/s) together with leach indices data for the various leaching conditions are represented in Table 9.

Cesium, being the most mobile waste soluble species in the nuclear waste stream, is poorly adsorbed in the basic environment of cement (Saleh et al., 2011). On the other hand, cobalt may form insoluble hydroxide at this higher pH condition. Therefore, the leachability of ^{137}Cs was greater than that of ^{60}Co from the PCC-waste form immersed in the same leachants. The data in Table 9, indicated that all leach indices of either ^{137}Cs or ^{60}Co in various leachants and under different conditions were usually greater than the value of 6 (Saleh et al., 2011). The relative high L_x values may be attributed to the role played by polymers within the PCC in reducing the porosity of the final waste forms and hence retarding the release of radiocontaminants. Recently, it was reported that more than 60% of cesium activity was released from immersed PCC-waste form cured for 28 days only (Saleh et al., 2011). This value can be easily compared to 11.3% of radiocesium leached after 260 days from the aged PCC under investigation. This assures the task achieved by the polyester

based on the recycled PET waste in increasing the chemical stability of the proposed PCC even after 7 years of aging and immersion for 260 days.

Based on all leach tests data obtained, it could be stated that the candidate polymer-cement composite is an acceptable solution for immobilizing the radioactive borate waste even after 7 years of aging and under a breakthrough of water into the disposal site.

Leaching Conditions	¹³⁷ Cs		⁶⁰ Co	
	De (m ² /s)	L _x	De (m ² /s)	L _x
0.1M acid*	1.02E-13	8.99	2.105E-14	9.67
Seawater*	1.29E-14	9.89	7.255E-15	10.14
Groundwater*	1.24E-14	9.91	2.786E-16	11.56
Tapwater*	9.49E-15	10	2.232E-16	11.65
4°C*	1.06E-14	9.98	6.509E-17	12.19
60°C*	3.48E-14	9.46	3.935E-17	12.41
Static condition*	1.03E-15	11	7.32E-15	10.14
V/S = 10	9.6E-14	9.02	3.327E-18	13.48

* leachant volume/surface area of waste form (V/S) =3

Table 9. Diffusion coefficients and leach indices at different leaching conditions

9. Conclusion

In conclusion, it could be stated that the polymer-cement composite prepared from PC premixed with WEP based on the recycled poly(ethylene terephthalate) wastes is a promising and economical matrix for incorporating borate waste solution originating from the primary coolant circuit of the pressurized water reactors. Also, the proposed treatment process serves in saving the environment from two types of wastes at the same time, namely the hazardous radioactive borate waste and PET solid waste.

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