

## Research Article

# Immobilization of Simulated Borate Radioactive Waste Solution in Cement-Poly(methylmethacrylate) Composite: Mechanical and Chemical Characterizations

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Solidified cured cement blocks containing different concentrations of the borate waste simulate were impregnated using methyl methacrylate monomer having 0.3% by weight benzoyl peroxide as initiator. Then, the polymerization process was completed by heating the impregnated blocks at  $\approx 40^{\circ}\text{C}$ . To define the suitability, range of applicability, and compatibility of the inert matrix used, relevant to the borate waste immobilized, the final radioactive borate waste forms are evaluated on the basis of their mechanical and chemical properties. Some factors that may affect the characterization of the obtained final waste form, for example, concentration of the incorporated borate waste solution simulate, aging of the solid waste form, before immersion, immersion in various leachants, and time of immersion, were followed systematically. It could be stated that cement-poly(methylmethacrylate) composite exhibited better mechanical and chemical characters compared to the cement as a unique matrix for immobilization of borate waste concentrates.

## 1. Introduction

The principle waste materials generated from the pressurized water reactors (PWRs) consist of hot ( $\approx 77^{\circ}\text{C}$ ) aqueous concentrates of boric acid. In this part of the work, cement-poly(methylmethacrylate) (PMMA) composite was used for incorporation of these wastes to overcome the retarding effect of borate salts in case of their direct cementation.

Radioactive wastes generated from nuclear power plants are one of the main issues underlying the difficulties in developing a nuclear power program if not adequately treated and conditioned [1, 2].

Cement materials have been used on a large scale as immobilization matrices for radioactive wastes to minimize release of radionuclides [3, 4]. Among the disadvantages of cement waste forms is pronounced high porosity, which in aqueous medium leads to the release of radionuclides from the waste materials to the environment. Poly(methylmethacrylate) (PMMA), as an organic polymer, has been used as an effective additive to improve the properties of the cement waste forms [5, 6]. The polymer increases

durability and strength and decreases capillary flow of water of the final waste forms.

The present study is part of a comprehensive research program, carried out in Radioisotope Department, Atomic Energy Authority, aiming at reducing the potential migration and dispersion of radionuclides from the solidified waste forms to the environment. The work deals with the impregnation of the cement blocks with methylmethacrylate monomer having 0.3% by weight benzoyl peroxide as initiator, and the polymerization process is completed by heating at  $\approx 40^{\circ}\text{C}$ . Mechanical and chemical properties of the final waste form were evaluated under various experimental conditions.

## 2. Experimental Approach

### 2.1. Materials and Solutions Used

**Cement Materials.** Ordinary Portland Cement (OPC) is the available local cement manufactured according to BSS [7]. The chemical analysis of the cement type used in the present

TABLE 1: Oxides (wt. %) and compounds compositions (%) of the cement used.

Oxides, wt. %		Compounds composition, %	
SiO <sub>2</sub>	19.84	C <sub>3</sub> S	53.11
Al <sub>2</sub> O <sub>3</sub>	4.74	C <sub>2</sub> S	16.89
Fe <sub>2</sub> O <sub>3</sub>	4.0	C <sub>3</sub> A	5.81
CaO	61.01	C <sub>4</sub> AF	12.16
MgO	2.5		
K <sub>2</sub> O	0.6		
SO <sub>3</sub>	2.4		
Insoluble residue	0.95		

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

TABLE 2: Chemical composition of simulated borate waste solution concentrate (g/L).

NaOH	H <sub>3</sub> BO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	NaCl	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
29	180	30	5	5	5

study as well as the Bogue calculation [8] for its four major compounds are given in Table 1.

**Simulated Waste Solution.** Borate waste concentrates generated from pressurized water reactors (PWRs) vary in their content, ratios, and amounts of their salts according to conditions of operation, pretreatment, and coolant constituents [9]. A simulated borate waste solution concentrate was used in the present study, representing its average chemical composition in g/L. Table 2. Part of this simulated waste solution was spiked with radioactive Cs-137 and was used to evaluate the chemical characterization, while a cold part was used for the mechanical properties measurements.

**Cement-Waste Form.** Predetermined concentrations of the simulated borate waste solution were thoroughly mixed with OPC powder. The water/cement (w/c) ratio was kept constant at 35% (wt/wt) in all experiments. The homogenous cement-waste mixture was poured in standard closed molds and left to solidify in humid atmosphere. Free standing solid cylindrical blocks were obtained after 28 days having the dimensions of  $6.20 \pm 0.10$  cm height and  $3.13 \pm 0.01$  cm diameter. Borate-free cement blocks were also prepared at the same w/c ratio for the sake of comparison.

**Cement-Poly(methylmethacrylate) Composite Waste Forms (Heat-Suction Technique).** Methylmethacrylate monomer (MMA) (AR grade) was freed from inhibitor by distillation under reduced pressure and was polymerized using benzoyl peroxide (BP) as initiator. Solidified cement-waste forms were dried in oven at  $\approx 60^\circ\text{C}$  for two hours, followed by suction (0.1 mm Hg) for another two hours. The blocks were then flooded with sufficient MMA monomer containing 0.3% by weight BP. After complete immersion, the system was allowed to return slowly back to atmospheric pressure, as shown in Figure 1. After 24 hours of immersion at room

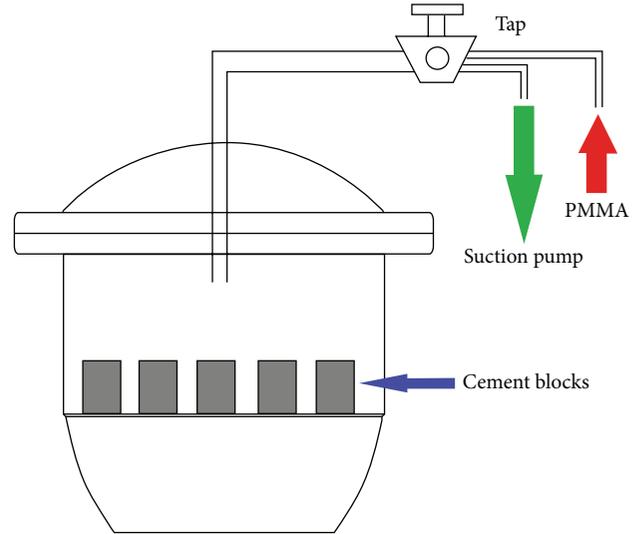


FIGURE 1: Schematic diagram of the apparatus used in impregnation process.

temperature ( $25 \pm 5^\circ\text{C}$ ), samples were taken and allowed to polymerize at  $\approx 40^\circ\text{C}$ .

**Leaching Solution.** The ground water used as immersion media for the radionuclides release test is obtained from Abu-Zaabal (well no. 202), which is one of the nearest ground water wells to Inshas-Reactor site where storage and disposal facilities of radioactive wastes are found. The chemical composition of the ground water used is shown in Table 3.

The prepared solidified waste specimens spiked with Cs-137 were suspended in leaching jars. The whole surface area of the specimen was exposed to the immersion water. Care was taken to keep the leaching solution surrounded the samples with equal depth from all sides.

Hespe's leaching test [10] proposed by the International Atomic Energy Agency was chosen and followed in the present study. All leach data obtained were prepared by plotting the cumulative leach fraction ( $\sum a_n/A_o$ )/(S/V) (cm) versus square root of total leachant period, ( $\sqrt{\sum t_n}$ ), where  $A_o$  is the radioactivity initially in the specimen,  $A_n$  is the radioactivity leached during the leachant renewal period  $n$ ,  $t_n$  is the duration in days of leachant renewal period, S is the exposed surface area of specimen ( $\text{cm}^2$ ) and V is the volume of the specimen ( $\text{cm}^3$ ).

## 2.2. Characteristics of Solidified Waste Form

- (1) Mechanical properties were studied by measuring the compressive strength of cold solid samples. The compressive load required to cause failure (damage) was determined for 3–5 cylindrical blocks. Instron Universal Testing Instrument Mode 1178 (ASTM-D-695) was used for compressive strength measurements.

TABLE 3: Chemical composition of ground water leachant.

Total dissolved salts (g/L)	pH	Soluble cations (ppm)				Soluble anions (ppm)		
		K <sup>+</sup>	Na <sup>+</sup>	Mg <sup>++</sup>	Ca <sup>++</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>--</sup>	HCO <sub>3</sub> <sup>-</sup>
1.05	7.2	23	149	13	74	137	317	272

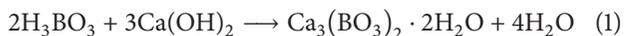
(2) Chemical tests were performed by subjecting spiked solidified specimens, having similar dimensions to those used for mechanical properties evaluation, either to the ground or distilled water. The Cs-137 contents in the leachant solutions were analyzed using Ortic-Single Channel Analyzer (USA). The leach coefficients (Lc) and leach indices (Li) of Cs-137 for cement-PMMA composite waste form and cement waste form were also calculated.

### 3. Results and Discussion

In order to improve the cement-waste form and reduce the potential migration and dispersion of radionuclides from this waste form to the environment, PMMA was used to impregnate the cement-waste form. The good understanding of the mechanical and chemical characterizations of the solidified waste form is based on the interpretation of the experimental results obtained as well as the long-term behavior and durability of polymer impregnated cement.

**3.1. Mechanical Properties.** Mechanical integrity of the waste form is an important consideration in the safe handling, transportation and disposal of radioactive wastes. Hence, the mechanical characters of the cement-PMMA composite waste form were evaluated under different borate concentrations, immersion in different leachants, and various periods of immersion.

**3.1.1. Changing of Borate Waste Concentrations.** Increasing borate content in cement and cement-PMMA composite waste forms decreased remarkably the compressive strength values (Table 4). Borate waste contains mainly boric acid (H<sub>3</sub>BO<sub>3</sub>) and some borate ions, for example, BO<sub>3</sub><sup>-3</sup> and B<sub>4</sub>O<sub>7</sub><sup>-2</sup>, known as cementation inhibitors [11–13]. Boric acid and calcium hydroxide (produced during cementation process) react as follows:



Calcium borate is fairly insoluble, so it acts as a barrier at the cement particles and solution interface. This barrier retards the diffusion of water and colloidal particles across the boundary, which was in good agreement with results obtained from X-ray diffraction and thermal analysis data previously published [14–16].

Table 4 indicates also that impregnation of cement with PMMA improves the mechanical properties of all cement borate waste form due to the decrease in the porosity of cement-PMMA composite waste forms [5, 17].

From the data obtained, the optimum amount of borate waste should not exceed 6% by weight as far as the mechanical

TABLE 4: Compressive strength values of cement and cement-PMMA composite waste forms incorporating different concentrations of borate waste.

Borate waste concentrations, %	Compressive strength (kg/cm <sup>2</sup> )	
	Cement	Cement-PMMA composite
0	256	298
2	201	221
3	185	245
4	186	230
5	135	147
6	98	146
7	50	63
8	29	38
9	2	8
10	Brittle	Brittle

integrity was concerned, and the value obtained is acceptable for transport, storage, and disposal requirements [18, 19].

**3.1.2. Effect of Immersion.** It is important to establish the behaviour of the solidified waste form under both storage and disposal conditions. Some samples were cured in closed molds, for one month and for 3 months. The obtained blocks were then immersed in distilled water and ground water for different immersion periods. The blocks were subjected to compressive strength measurements at the end of each immersion period, and the obtained data are represented in Tables 5 and 6.

It could be stated from the experimental results that all the samples immersed in both distilled water or ground water show slight increase in compressive strength values compared with that of non-immersed samples, in Table 4. Also, increasing the time of immersion resulted a slight improvement of compressive strength values. Increasing rate of compressive strength values reached the maximum value at early ages due to the increase in the rate of hydration.

The rate of increase in the compressive strength values was decreased with time, due to the low rate of hydration, until a stage was reached when virtually no further hydration takes place [20]. This behavior may be attributed to the formation of a dense layer of calcium sulphate hydrate (CSH) gel around the cement grains [21], but not due to the complete consumption of untreated cement.

Clearly, it could be stated that in case of using cement-PMMA composite and cement-PMMA composite waste form, no deterioration in the final product was observed with increasing time of immersion, but on the contrary, a slight improvement in mechanical properties was observed (Tables

TABLE 5: Compressive strength values of plain cement, cement-waste form, cement-PMMA composite, and cement-PMMA composite waste form immersed in distilled water.

(a) Solid blocks cured for one month before immersion

Immersion times, days	Compressive strength values (kg/cm <sup>2</sup> )			
	Plain cement	Cement waste forms*	Cement-PMMA composite	Cement-PMMA composite waste form*
3	262	177	276	248
7	268	196	305	275
30	270	201	301	250
90	274	206	314	258
365	276	190	301	266

\* Contains 4% by weight borate waste simulate.

(b) Solid blocks cured for 3 months before immersion

Immersion times, days	Compressive strength values (kg/cm <sup>2</sup> )			
	Plain cement	Cement waste forms*	Cement-PMMA composite	Cement-PMMA composite waste form*
3	269	181	291	262
7	272	200	319	281
30	272	211	310	276
90	274	210	321	253
365	281	188	299	262

\* Contains 4% by weight borate waste simulate.

5 and 6). The obtained results were in favour of using cement-PMMA composite materials as immobilization matrices for radioactive borate waste. For the sake of comparison, samples similar to these previously mentioned were prepared, cured for different ages, and then subjected to compressive strength measurements without being immersed in water, and the data obtained are represented in Table 7. The results of compressive strength values show a similar trend to those immersed in water.

3.2. *Chemical Properties.* Leaching is generally considered as the basic criterion to evaluate the safety, acceptability, and chemical behavior of the final waste forms in the disposal sites [22]. Cement-PMMA composite matrices were used in the present study as inert chemical barriers, and chemical stability of immobilized waste forms in ground water and distilled water was studied using radioactive Cs-137 isotope as a tracer. Leaching tests were performed according to Hespé's method [10].

By considering the previously obtained mechanical measurements data, different amounts of simulated radioactive borate waste (0.0%, 4.0%, and 6.6% by weight) spiked by Cs-137 were immobilized in cement and cement-PMMA composite. All the prepared samples were subjected to leaching test in ground water and distilled water, and the results obtained are shown in Figures 2 and 3.

Increasing borate waste content from 4% to 6.6% lowered the chemical integrity of cement waste form, which was reflected in high cumulative leach fractions. Figure 3 shows that using PMMA as an additive polymer decreased cumulative leach fraction of cement and cement-waste forms.

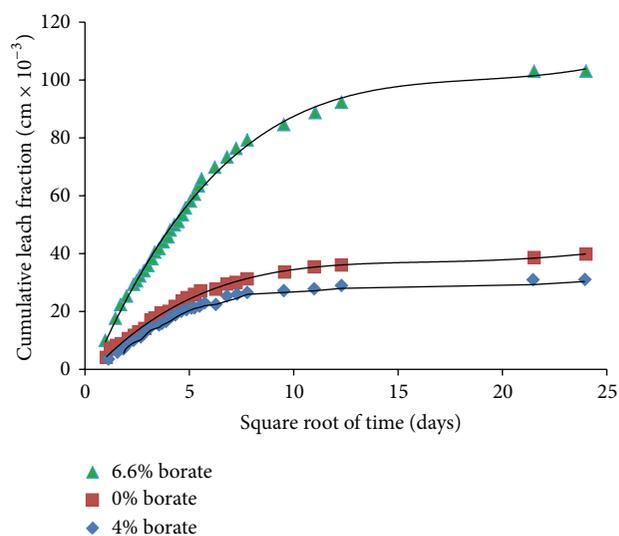


FIGURE 2: Effect of different borate waste concentrations on the release of Cs-137 from the cemented waste forms.

Borate compounds act as an inhibitor by retarding the hydration process of cement due to the formation of insoluble calcium borate, and creation of a barrier at the cement particles/solution interface [23].

It is worth mentioning that little bit significant differences were observed in the chemical behavior of cement-waste form containing 4% borate waste, compared with borate free plain cement specimen. Based on the results obtained

TABLE 6: Compressive strength values of plain cement, cement-waste form, cement-PMMA composite, and cement-PMMA composite waste form immersed in ground water.

(a) Samples cured for one month before immersion

Immersion times, days	Compressive strength values (kg/cm <sup>2</sup> )			
	Plain cement	Cement waste forms*	Cement-PMMA composite	Cement-PMMA composite waste form*
3	275	185	304	236
7	286	190	317	231
30	290	219	290	291
90	295	210	300	278
365	296	216	301	281

\* Containing 4% by weight borate waste simulate.

(b) Samples cured for 3 months before immersion

Immersion times, days	Compressive strength values (kg/cm <sup>2</sup> )			
	Plain cement	Cement waste forms*	Cement-PMMA composite	Cement-PMMA composite waste form*
3	280	192	318	250
7	290	202	324	242
30	292	226	293	300
90	295	216	302	275
365	298	213	299	291

\* Containing 4% by weight borate waste simulate.

TABLE 7: Compressive strength values of plain cement, cement-waste form, cement-PMMA composite, and cement-PMMA composite waste form aged for different periods.

(a) Cement without PMMA

Aging time, month	Compressive strength (kg/cm <sup>2</sup> )	
	Plain cement	Cement waste form*
1	260	164
3	266	187
4	268	186
7	271	197
12	282	194

\* Containing 4% by weight borate waste simulate.

(b) Cement impregnated with PMMA

Aging time, month	Compressive strength (kg/cm <sup>2</sup> )	
	Cement-PMMA composite	Cement-PMMA composite waste form*
1	290	224
3	298	230
4	299	224
7	310	255
12	316	252

\* Containing 4% by weight borate waste simulate.

from both chemical and mechanical properties, it could be concluded that cement-waste form can tolerate up to 4%.

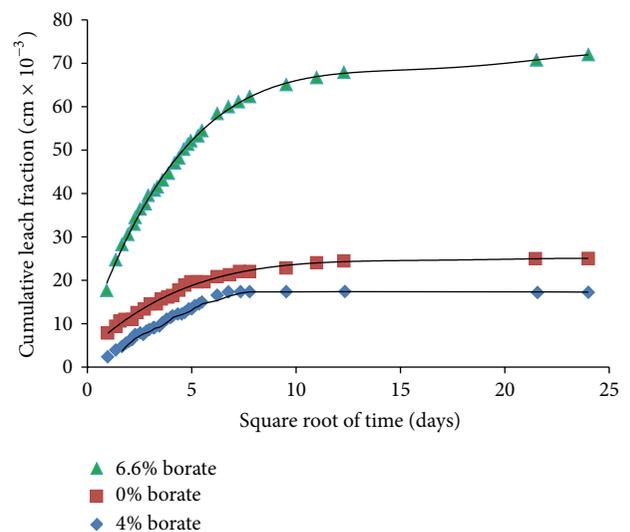


FIGURE 3: Effect of different borate concentrations on the release of Cs-137 from the cement-PMMA composite waste forms.

Figure 4 shows that cumulative leach fraction of Cs-137 for cement and cement borate waste (4%) forms in ground water was lower than in distilled water. This may be due to the formation of an outer protective layer of insoluble compounds on the surface of solid blocks leached [18]. The presence of cement materials in ground water leachant creates an alkaline medium with relatively high pH-value favourable for fixation of different cations present in the ground water

TABLE 8: The leach coefficient (Lc) and leach index (Li) of Cs-137 for cement and cement-PMMA composite containing different borate waste percentages immersed in distilled water and ground water.

Borate waste percentage	Caesium-137			
	Cement waste form		Cement-PMMA composite waste form	
	Lc	Li	Lc	Li
0.0 borate using distilled water	$1.8 \times 10^{-8}$	7.8	$5.0 \times 10^{-9}$	8.3
4.0 borate using distilled water	$1.3 \times 10^{-8}$	7.9	$5.0 \times 10^{-8}$	7.3
6.6 borate using distilled water	$2.5 \times 10^{-7}$	6.6	$1.2 \times 10^{-7}$	6.9
0.0 borate using ground water	$2.8 \times 10^{-8}$	7.6	$7.6 \times 10^{-8}$	7.1
4.0 borate using ground water	$2.2 \times 10^{-8}$	7.7	$7.6 \times 10^{-8}$	7.7
6.6 borate using ground water	$2.9 \times 10^{-7}$	6.8	$1.5 \times 10^{-7}$	7.1

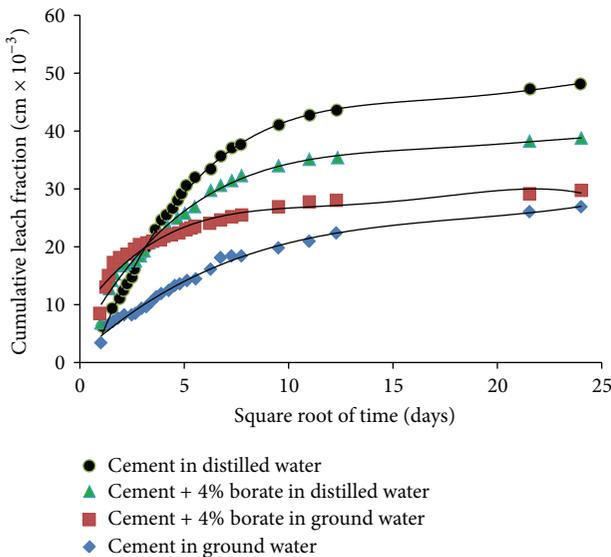


FIGURE 4: Effect of leachant solution on the release of Cs-137 using cement and cement containing 4% borate.

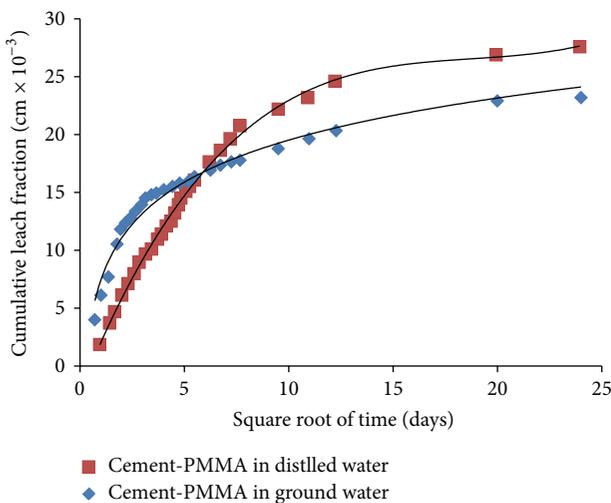


FIGURE 5: Effect of leachant solution on the release of Cs-137 using cement-PMMA composite containing 4% borate waste form.

on the surface of the specimens studied [18]. The same results were obtained for cement-PMMA composite containing 4% borate waste forms (Figure 5).

The leach coefficient (Lc) and leach indices (Li) of radioactive caesium isotope incorporated in cement and cement-PMMA composite containing different percentages of borate wastes were calculated, and the values obtained were found to be within the limits given in the literature of similar cement waste forms [24]. It could be noticed that all leach indices calculated for cement-PMMA composite waste forms were higher than 6 (Table 8).

#### 4. Conclusion

According to both mechanical and chemical characterizations, it could be stated that using poly(methylmethacrylate) as an impregnating matrix, following the heat-suction technique, highly improves the tolerance of the cement matrix for incorporating the borate radioactive waste solution. The results obtained from calculating leach coefficients and leach indices for cement-PMMA composite waste form were optimal and in good agreement with the requirements for transport and disposal processes. Physical and thermal characterizations of solidifying simulated radioactive waste solution in cement-poly(methylmethacrylate) composite could be more attractive point for study.

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