

## Immobilization of simulated evaporator concentrate waste in low density polyethylene

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### A B S T R A C T

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Simulated evaporator concentrate was prepared by pre-treating sodium borate with calcium hydroxide to produce an insoluble, ulexite-like borate salt. The resultant solid waste was blended by extrusion with virgin and recycled low density polyethylene (LDPE) at 30 and 50 wt% load. Samples were evaluated to homogeneity by density determinations (ASTM D792-91), compressive strength (ASTM D695-91) and leaching behavior by accelerated leaching tests (ASTM C1308-95). Coefficient of variation of density was lower than 5% for all evaluated waste forms, indicating a satisfactory homogeneity. Compressive strengths have complied to U.S.NRC standard and were above CNEN standard limit for cement waste products if 5% strain could be considered a reasonable limit to assure the structural integrity of the material. Cumulated fraction leached after 11 days of accelerated leach test was found to be lower than 10%, and diffusion coefficients of boron have varied between  $3.86 \times 10^{-10}$  and  $9.06 \times 10^{-10}$  cm<sup>2</sup>/s. Boron concentrations for all materials have shown a tendency to reach an asymptotic value at the end of the test (around 0.25 and 0.7 mg/L for 30 and 50% waste load, respectively). Measured cumulated fraction leached (CFL) data with time have shown a tendency of becoming asymptotic sooner than it was predicted by the diffusion model.

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### 1. Introduction

Radioactive waste immobilization aims to obtain a waste form suitable to be transported, storage and disposal. Cement and bitumen are materials commonly used as matrices to immobilize radioactive wastes. The main goal of the process is to transform waste in a monolithic block with reduced leaching potential.

Low density polyethylene (LDPE) as an immobilization matrix was firstly evaluated by the Brookhaven National Laboratory (BNL) (Kalb et al., 1996; Lageraen and Kalb, 1997; U.S.EPA, 1997) in a process called polymer microencapsulation. The processes of extrusion and kinetic mixing were investigated to melt and mix the polymer (virgin and recycled) with different types of waste (radioactive, hazardous and mixed) in both laboratory and pilot-scale.

These studies demonstrated that the use of polymeric materials for waste immobilization can be very promising due to several factors, such as chemical resistance to a variety of chemical agents and solvents; degradation resistance due to soil saturated conditions, thermal cycles, microorganisms and radiation; matrix solidification is assured by the polymer cooling, dispensing chemical reactions; best leaching performance if compared to cemented waste forms with equivalent waste loads; and capability of loading great amounts of waste.

BNL studies also showed that polyethylene matrices can be applied to different kinds of waste since chemical characteristics of the waste do not affect thermoplastic solidification. However, physical characteristics of the waste, such as particle size, humidity level and presence of volatile substances, can be problematic during the extrusion process. Another limiting factor is the thermal degradation of the waste related to the application of relatively high temperatures during the process (as high as 200 °C).

This paper goal is to present the evaluation of waste forms resulting from the immobilization of a simulated evaporator concentrate, containing mainly boron, in two LDPE matrices (virgin and recycled), blended by extrusion (in laboratory scale) in the proportion of 30 and 50 wt%. Samples were evaluated for homogeneity using density determinations, mechanical (compressive) strength and leachability for boron by accelerated leach test.

### 2. Materials and methods

Simulated evaporator concentrate was prepared by the pre-treatment of sodium borate with calcium hydroxide to produce an insoluble borate salt (Awwal et al., 1996). The boron concentration in the evaporator concentrate was around 44,000 ppm and the reaction was carried out at a temperature of 85–87 °C for a period of 7 h with mechanical agitation. Solid samples dried at 60 °C for 3 h were analyzed by X-ray diffraction and presented a predominant crystalline phase identified as NaCaB<sub>5</sub>O<sub>9</sub>·8H<sub>2</sub>O, as well as minor

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amorphous phase. This new compound is similar to ulexite, which is a hydrate boron mineral composed of sodium and calcium. The equilibrium concentration of boron in water at the borate saturation condition (at 25 °C) was about 650 mg/L of boron. Borate salt was also dehydrated at 170 °C to avoid vapor release during extrusion.

Waste immobilization was carried out in a 35 mm, simple screw laboratory scale extruder, with length to diameter ratio (L/D) equal to 32 and five heating zones. Two types of low density polyethylene were applied, a virgin LDPE with melt index (MI) of 30 g/10 min and density of 0.917 g/cm<sup>3</sup> (referred as PV30) and a recycled LDPE (referred as PR16) with MI of 16.2 g/10 min and 0.93 g/cm<sup>3</sup> density (MI at 190 °C and 2.16 kg, according to ASTM D1238-90, 1990). Table 1 shows the extruder temperature configuration used during the process. The extruder rotation was set as 80 rpm.

Polymer and simulated waste were pre-mixture before feeding in the extruder. Batches of 500 g were prepared with 30/70 and 50/50 waste/polymer ratio and 1% (weight basis) of mineral oil to help fixing the waste powder on the surface of the polymer pellets. Care was taken to avoid the segregation of the components in the feeder funnel and keep the waste/polymer ratio as constant as possible. The melted material leaving the extruder was collected into cylindrical molds of 6 cm of diameter and 10 cm of height and allowed to cool down in room temperature under slight load (3 tons) using a hydraulic press. After cooling, samples were removed from molds and cut to produce suitable samples for being used in characterization tests. Summary description of each evaluated material and the respective material code is given in Table 2.

The homogeneity of each mixture was investigated by determining the density of each one of three consecutive cylindrical samples and evaluating the variability of the measurements for the three samples as a whole. Density values were determined by displacement (ASTM D792-91, 1991). For each sample, a representative value of density (arithmetic average) was determined by sectioning it in four pieces and evaluating the density of each piece. Each piece weight was measured to check for conformity with maximum weight allowed by the standard test (50 g). Temperatures were controlled to comply with standard requirements of 23 ± 2 °C.

Mechanical strength was evaluated through determination of compressive strength (ASTM D695-91, 1991), using an Instron Universal Testing Machine. For each determination, five prismatic samples (12.5 × 12.5 × 25.4 mm) were used. Load was applied longitudinally at constant rate of 1 mm/min. Tests were conducted at room temperature. Results were compared to the value for the pure polymer and with limits established by CNEN-NN-6.09 standard for cement waste forms and by U.S. Nuclear Regulatory Commission (U.S.NRC, 1991).

Three cylindrical samples (2.5 cm diameter and 2.5 cm height) for each mixture were tested to determine the leach rate of the immobilized waste by the accelerated leach test method (ASTM C1308-95, 1995). Three liters of deionized water were used as leachant for each one of the 13-leachant replacements required by the standard. Leachant replacement was made using the specified time intervals: 24 h of interval during 11 consecutive days plus two additional changes in the first day, 2 and 7 h after the beginning of the test. Samples of the pure polymers were also evaluated to allow checking for contamination. Tests were conducted at room temperature. After each interval, samples of the leachant were taken and analyzed for boron by Inductively Coupled Plasma Mass

**Table 1**  
Temperature configuration for the temperature zones of the extruder.

Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)	Matrix (°C)
175	180	185	190	190

**Table 2**  
Characteristics of the evaluated mixtures<sup>a</sup>.

Material	Polymer	Polymer (wt%)	Waste (wt%)
PV30	Virgin LDPE; MI 30	100	0
PV30B30	Virgin LDPE; MI 30	70	30
PV30B50	Virgin LDPE; MI 30	50	50
PR16	Recycled LDPE; MI 16.2	100	0
PR16B30	Recycled LDPE; MI 16.2	70	30
PR16B50	Recycled LDPE; MI 16.2	50	50

<sup>a</sup> Melt index (MI) reported at 190 °C and 2.16 kg, according to ASTM D1238-90 (1990).

Spectrometry (ICP-MS). Boron concentration data were introduced in the accelerated leach test (ALT) computer program in order to fit a leaching model and estimate the model parameters.

### 3. Results and analysis

Processing of the materials in the extruder was successful. The melted material was homogeneous, with few bubbles due to polymer and/or waste degradation. The small size of the waste particles (a powder-like material) has reduced polymer wettability and made feeding more difficult. Applying slight pressure during cooling with a hydraulic press has produced more homogeneous and bubbles-free samples.

Statistics of the density determinations for each evaluated material are given in Table 3. The homogeneity of each material can be measured by calculating the coefficient of variation for the determinations. This parameter was lower than 5% to all materials, suggesting that the process is able to mixture properly melted polymer and waste and produce a homogeneous material. However, pre-mixing and feeding the extruder manually are not feasible in large scale processes and these aspects of the process must be improved.

Values of compressive strength properties of the pure polymers and the waste forms are listed in Table 4. Data of strength at yield point, at 5 and 10% deformation and the maximum strength (when failure by fracture was observed) showed that these values increase as waste is added to the polymers, resulting in a stronger material. This was already expected since fillers are commonly used in polymer industry as additive in order to improve the mechanical strength properties. Failure by fracture was only observed for the materials containing recycled polymers (PR16B30 and PR16B50).

Comparing the values of mechanical strength obtained with the requirements of waste form acceptance criteria is a difficult task due to the lack of compressive strength values for waste incorporated in polymers. CNEN regulation (CNEN-NN-6.09, 2002) requires that cemented waste forms must support 10 MPa strength in order to satisfy the criteria of structural integrity of a repository. U.S.NRC requires a minimum value of 60 psi (0.4 MPa), independently of the matrix, but also requires that efforts must be applied to achieve the higher possible mechanical resistance within practical limits (U.S.NRC, 1991). All values of compressive strength

**Table 3**  
Results of the homogeneity evaluation<sup>a</sup>.

Material	Density (average ± 95% confidence interval) (g/cm <sup>3</sup> )	Standard deviation (g/cm <sup>3</sup> )	Coefficient of variation (%)
PV30B30	1.04 ± 0.06	0.02	1.9
PV30B50	1.2 ± 0.1	0.04	3.3
PR16B30	1.05 ± 0.03	0.01	1.0
PR16B50	1.2 ± 0.1	0.03	2.5

<sup>a</sup> Density average and 95% confidence interval for pure polymers: PV30 density = 0.916 ± 0.002 g/cm<sup>3</sup> and PR16 density = 0.93 ± 0.01 g/cm<sup>3</sup>.



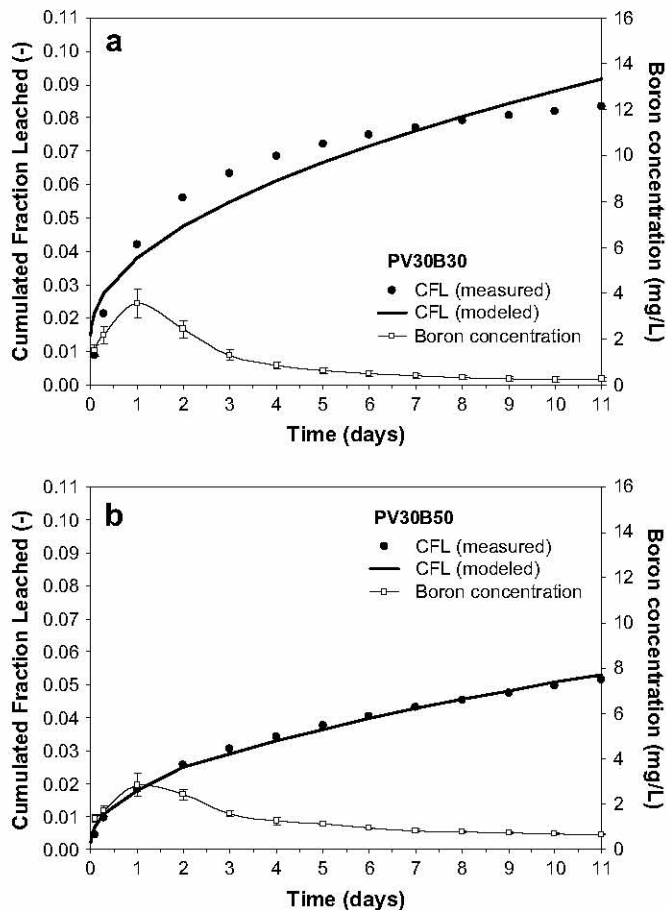
**Table 4**  
Results of the compressive strength tests<sup>a</sup>.

Material	Strength at yield point (MPa)	Strength at 5% deformation (MPa)	Strength at 10% deformation (MPa)	Maximum strength (MPa)	Deformation at maximum strength (%)
PV30	3.3 ± 0.4	9.5 ± 0.2	12.4 ± 0.3	NO	NO
PV30B30	4.4 ± 0.5	10.9 ± 0.2	13.3 ± 0.2	NO	NO
PV30B50	5.9 ± 0.8	13.6 ± 0.6	16.2 ± 0.6	NO	NO
PR16	7.1 ± 0.5	15.2 ± 0.2	18.6 ± 0.3	NO	NO
PR16B30	8.6 ± 0.4	16.1 ± 0.4	18.7 ± 0.5	18 ± 2	12 ± 5
PR16B50	11.0 ± 0.6	19 ± 1	20.8 ± 0.7	21 ± 3	13 ± 8

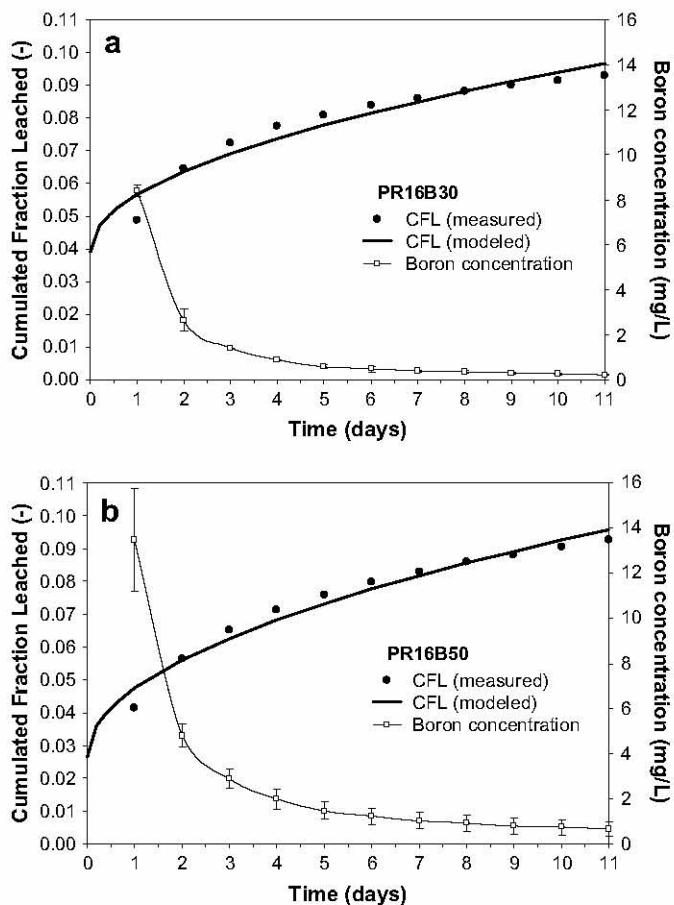
<sup>a</sup> All data are expressed as average ± 95% confidence interval. NO = not observed.

obtained for the waste forms using both polymers comply with U.S.NRC requirement. According to CNEN criteria, if 5% deformation can be considered low enough to assure structural integrity, the evaluated waste forms can also be considered acceptable.

Boron concentration data resulting from accelerated leach test are shown in the right vertical axis of Figs. 1 and 2, for virgin and recycled LDPE matrices, respectively. These values were introduced in ALT program and used to match a leaching model. The mass of boron in each sample, a parameter required by the model matching process, was estimate as 516 and 974 mg for 30 and 50% load, respectively, considering sample geometry, sample density and that the waste molecular weight is the same as ulexite molecular weight (calcium and sodium borate salt; 405.11 g/mol). Measured and modeled cumulated fraction leached (CFL) are also shown in the left vertical axis of Figs. 1 and 2. Table 5 shows the parameters and error for the fitting process of CFL data.



**Fig. 1.** Results of accelerated leach tests versus time for virgin LDPE matrix at 30% (a) and 50% (b) waste load.



**Fig. 2.** Results of accelerated leach tests versus time for recycled LDPE matrix at 30% (a) and 50% (b) waste load.

Among the possible leaching models included in ALT program (diffusion, dissolution and partitioning), diffusion model has provided the best match with experimental data for all materials. Diffusion coefficients of boron in the polymeric matrices were found to vary between  $3.86 \times 10^{-10}$  and  $9.06 \times 10^{-10}$  cm<sup>2</sup>/s. Maximum CFL after 11 days of test was lower than 10%. Literature has reported similar values for 50% load of sodium in virgin and recycled LDPE ( $4.40 \times 10^{-10}$  and  $1.91 \times 10^{-10}$  cm<sup>2</sup>/s, respectively) and a maximum CFL of 8% at 11 days (Lageraen and Kalb, 1997).

Poor results of the fitting process for some materials (mainly, for PV30B30) might be an indication of an inadequate representation of the leaching mechanisms which take place in polymeric matrix. As the ASTM C1308 standard limits the estimation error to 0.5% to allow data extrapolation using the fitted model, diffusion model cannot be used to predict the leaching behavior of the waste form for longer times. Partitioning model could also be suitable for describing leaching from waste forms, but data fitting to this model did not show to be significantly better in comparison to diffusion model. Another possible reason can be pointed as uncertainties related to the actual amount of boron within the samples. ALT leach

**Table 5**  
Results of the accelerated leach tests and fitting process with ALT program.

Material	Measured CFL (after 11 days)	Diffusion coefficient (cm <sup>2</sup> /s)	Error (%)
PV30B30	0.085	$9.06 \times 10^{-10}$	8.32
PV30B50	0.051	$3.86 \times 10^{-10}$	0.77
PR16B30	0.095	$5.34 \times 10^{-10}$	1.44
PR16B50	0.092	$7.51 \times 10^{-10}$	0.94

models and the fitting process have shown to be very sensitive to the initial amount of boron in the source term.

Due to operational problems, leachant replacement for the first two changes for the recycled LDPE materials was not possible and the first actual change was made after 24 h of the beginning of the test. An increase of boron concentration in the first leachant with respect to the observed in virgin LDPE materials was the result of this problem and data input in ALT program was altered to account for the change in time intervals for this materials.

Boron concentrations for all materials have shown a tendency to reach an asymptotic value at the end of the test. Final boron concentration (at 11 days) was  $0.25 \pm 0.06$  and  $0.24 \pm 0.01$  mg/L for PV30B30 and PR16B30 (30% waste load) and  $0.65 \pm 0.04$  and  $0.7 \pm 0.3$  mg/L for PV30B50 and PR16B50 (50% waste load), respectively. The proportionality between waste load and final boron concentration indicates that the performance of both polymers with respect to the amount of boron released after 11 days is similar. Also, measured CFL data with time show a tendency of becoming asymptotic sooner than it was predicted by the diffusion model, implying that the actual leach behavior of polymeric waste forms is more favorable than predicted.

#### 4. Conclusions

A preliminary evaluation of the waste form resulting of the immobilization of a simulated evaporator concentrate containing boron in virgin and recycled LDPE matrix was presented. Simulated solid waste was blended by extrusion with the polymeric matrices in the proportion of 30 and 50 wt%. Samples were evaluated by homogeneity (using density determinations), mechanical strength (compressive strength) and leaching behavior (accelerated leaching test).

Coefficient of variation of density of three consecutive samples was lower than 5% for all evaluated waste forms, indicating a satisfactory homogeneity of the material. Improvements on the feeding process of the extruder must be introduced in order to increase the homogeneity and guarantee the homogeneity of the waste forms in larger scales.

Compressive strength for all materials has increased after the mixture with the simulated waste, indicating an increase of the material strength with the increase of waste load. Ductile fracture was observed for recycled polymer when mixed with waste. Estimated compressive strengths comply to U.S.NRC standard and were above CNEN standard limit for cement waste products if 5% strain could be considered a reasonable limit to assure the structural integrity of the material.

Cumulated fraction leached after 11 days of accelerated leach test was found to be lower than 10%, and diffusion coefficients of boron have varied between  $3.86 \times 10^{-10}$  and  $9.06 \times 10^{-10}$  cm<sup>2</sup>/s. Boron concentrations for all materials have shown a tendency to reach an asymptotic value at the end of the test (around 0.25 and 0.7 mg/L for 30 and 50% waste load, respectively). Measured CFL

data with time have shown a tendency of becoming asymptotic sooner than it was predicted by the diffusion model, implying that the actual leach behavior of polymeric waste forms is more favorable than predicted.

The good results obtained in this study have demonstrated that this immobilization method could effectively become an alternative to current employed matrices for low level wastes. Some possible restrictions of using this technology already pointed by the literature could be verified during the development of the research: waste must be inert to thermal degradation within the range of temperatures used during the extruder operation; water and volatile substances content in the waste must be kept to a minimum, and waste particle size distribution must be controlled. Improvements in the extruder feed system, an evaluation of higher waste/polymer ratios and a more detailed study about the involved leaching mechanisms could be considered during further developments in this issue.

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