



Immobilization Of Radioactive And Hazardous Wastes In A Newly Developed Sulfur Polymer Cement (SpC) Matrix

*M. W. Abdel Raouf, *A. I. Husain, and B. El-Gammal*

*Hot Laboratories Center, Atomic energy authority, P. No. 13759,
Cairo, Egypt*

**Polymer Department, Chemistry Division, National Research Center,
Dokki, Cairo, Egypt*

Abstract

Low and Intermediate level radioactive wastes (LILW) and hazardous wastes, presents a waste disposal problem. In this respect, a process to immobilize different radioactive and hazardous wastes, including metals contaminated with radionuclides in a form that is non-dispersible and meet the Environmental Protection Agency (USA, EPA) leaching criteria is a must. In this stabilization and solidification process (S/S), simulated radioactive wastes of Cs, Sr, Ce, Cr, and Pb were immobilized in the stable form of sulfur polymer cement (SPC). In the present work, the mixture of the contaminant(s) and the sulfur mixture which is composed from 95% S and 5% aromatic /or aliphatic hydrocarbons used as polymerizing agents for sulfur (by weight), were added in a stainless steel vessel and primarily heated to 40°C for four hours, this time was sufficient for homogeneous mixing of the metals with sulfur and Na₂S (to convert the metals to their corresponding sulfides). Additional SPC was then added and the temperature of the mixture was raised to 135 ±1°C, resulting in a molten form that was poured into a stainless steel mold where it cooled and solidified.

Durability of the fabricated SPC matrices was assessed in terms of water of immersion, porosity, and compressive strength. The water absorption and open porosity were very low and didn,t exceed 2.5 % for all matrices, whereas the compressive strength ranged between 7 and 14 KN/m² depending on the matrix composition. The immobilized waste forms of SPC were characterized by X-ray diffraction (XRD) technique that showed that the different contaminants were stabilized during the solidification process to form stable sulfides. Lechability of the waste matrices was assessed by the Toxicity Characteristic Leaching Procedure (TCLP) of the EPA, optimized and compared with the new EPA Universal Treatment Standards. The TCLP results showed that the concentration of the most contaminants released were under detection limit of the test. Static leach tests were conducted using the IAEA standard method. The leach index of the prepared materials towards the aforementioned metal ions was high and ranged between about 9-11; and the order of migration of the released ion was

Sr>Cr>Cs>Ce>Pb

Key Words: *Stabilization/Solidification; Sulfur Polymer Cement; Radioactive waste; Water of immersion; Open Porosity; Compressive Strength; Leaching; TCLP and IAEA Standard.*



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

INTRODUCTION

In contrast to organic wastes, hazardous inorganic materials cannot be destroyed, but it can be converted into less soluble or leachable forms to inhibit their migration into the environment after disposal. Encapsulation technologies are based primarily on solidification processes that act to substantially reduce surface exposure to potential leaching media. Encapsulation technologies can also involve a combination of physical entrapment through solidification and chemical stabilization through precipitation, adsorption, or other interactions. This combined treatment approach is sometimes referred to as stabilization/solidification.⁽¹⁻³⁾

Hazardous waste materials can be encapsulated primarily in two ways: microencapsulation or macroencapsulation. Microencapsulation involves mixing the waste together with the encasing material before solidification occurs. Macroencapsulation involves pouring the encasing material over and around a larger mass of waste, thereby enclosing it in a solidified block. Sometimes these processes are combined. For example, Singh et al. (1998) demonstrated the microencapsulation of mercury-contaminated crushed light bulbs in which the glass was crushed and mixed with the encasing material prior to solidification.⁽⁴⁾ Mattus (1998) reported the macroencapsulation of mercury-contaminated lead pipes by pouring the encasing material over and around the lead pipes.⁽⁵⁾

There are a wide variety of materials currently being evaluated in the scientific community and in industry for the encapsulation of hazardous wastes. This review focuses on the performance data related to the solidification/stabilization of hazardous and radioactive inorganic wastes, which have proven to be especially challenging in environmental protection.⁽⁶⁻¹³⁾ Conventional stabilization/solidification methods typically include the fixation of metals using portland cement, and fly ash. This produces an impermeable, solid waste form at a high pH (typically <10) that limits the solubility and leachability of most metals. However, it is very difficult to stabilize all inorganic waste, especially those with high toxicities with cement-based processes because it does not form a low-soluble hydroxide solid. Arsenic and hexavalent chromium are also difficult to stabilize with cement-based processes due to the formation of anionic species that are soluble at high pH.^(14,15) Therefore, a significant work has been done to develop other encapsulation materials that can be used as alternatives to the cement-based process. Sulfur polymer cement (SPC), chemically bonded phosphate ceramic (CBPC's), and polyethylene (PE) encapsulation are currently being used to improve the long-term stability of hazardous and radioactive wastes. The aim of the present work is to fabricate and assess the sulfur polymer stabilization technique for the immobilization of radioactive and hazardous wastes of cesium, cerium, strontium, chromium and lead.

EXPERIMENTAL

Fabrication of the SPC Waste Forms

Sulfur polymer cement matrices (SPC) were prepared by mixing sulfur of Bayer (Germany), and a polymeric material precursors (95:5 wt/wt%). The polymeric material is either composed of butadiene-cyclohexene-cyclopentene aliphatic



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

hydrocarbon mixture, commercially known as Escorase-1101, Axxon, USA or qumaron-indine aromatic mixture, commercially known as Escorase-1137, Axxon, USA.

Simulated radioactive wastes of CsCl (Fluka, Switzerland), SrCl₂ (BDH, UK), Ce(NO₃)₃.6H₂O (Fisher Scientific Co., USA), and hazardous wastes of Pb(NO₃)₂ (Aldrich-Sigma, USA), and Cr(NO₃)₃ (BDH, UK) were used as the contaminants in the present investigation. Each contaminant was mixed together in a single form with the sulfur and polymer powder and then the whole mixture was ground in a ball mill type Fritsch (Germany). To attain homogeneity and to obtain the fine powder, the resulting mixture was screened at 60-mesh sieve size, using a sieving machine, type Retsch (Germany).

To improve the conversion of the contaminants to the sulfide form, Na₂S.xH₂O (Winlab, UK) was added to the reaction mixture.

At first, equal weights of 2g from each contaminant(s) and the sulfur and polymer mixture were mixed into a stainless steel container. Sodium sulfide was added with different ratios. To accelerate for the metal sulfide conversion, the whole mixture was agitated using a mechanical stirrer and heated to 40±1°C using an oil bath. Extra sulfur and polymer mixture was then added to the reaction vessel to obtain different waste loadings of 10-30%, and the temperature was thereafter raised gradually up to 135 ± 1°C, until we have obtained the molten mixture. The molten mixture was then poured into stainless steel molds of inner diameter 1 cm, and cooled gradually to the monolithic form, to obtain the sulfur polymer cement matrices.

Phase Characterization of the Prepared Formulations

The different phases formed during the preparation of SPC matrices were characterized by X-ray diffraction (XRD), using the XRD Spectrophotometer, type Shimadzu (Japan) using Cu K_α filter with a scanning angle from 4 – 80 2θ°, with a scanning speed of 4 degree per minute.

Durability of the Fabricated Matrices

Durability of the prepared SPC matrices was assessed in terms of its water resistance, compression strength, and open porosity.

Water resistance of the prepared matrices was investigated for 28 day immersion in double distilled water at the ambient room temperature (20±1°C). In this experiment, SPC matrices were immersed in double distilled water that was periodically changed to compensate for evaporation loss. At the end of the test, these samples were withdrawn from water, dried with wet cloth, weighed, and their weight change was recorded. This procedure is similar to that outlined in the American Nuclear Society, ANSI / ANS, 16.1. 1986.⁽¹⁶⁾

$$\text{Weight change (\%)} = \frac{W_F - W_I}{W_I} \times 100 \quad (1)$$

where, W_F and W_I are the final and initial weights of the examined samples, after and before water immersion. The concentration of the released cations from the



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

investigated matrices during the whole period of immersion was measured using a Buck Scientific atomic absorption spectrophotometer, model 210.

Compressive strength of the fabricated SPC blocks was measured using the challenger range of the compression-testing machine calibrated at BS 1610 according to the British Standard (BS 1981).

Open Porosity was measured using the Deutsche Institut for Normalization methods, DIN 51056, and the European Norm, EN 178, 159 (1991).⁽¹⁷⁾

Leachability of the Various Matrices

Leachability of the prepared SPC matrices was evaluated by the Toxicity Characteristic Leaching Procedure (TCLP), derivative of the Environmental Protection Agency (EPA),⁽¹⁸⁾ and the long term leach test of the IAEA standard method.⁽¹⁹⁾

The TCLP test is a supplement to the Extraction Procedure (EP) toxicity testing method and is applied inappropriately for environmental assessment purposes. They were developed by the U.S. Environmental Protection Agency (USEPA) under the auspices of the Resource Conservation and Recovery Act (RCRA) of 1976. These tests are considered rigorous (aggressive) tests compared with the adequate ASTM and wash tests (Egemen & Yurteri, 1996).⁽²⁰⁾ In the present work, the toxicity tests were performed in the same way carried out by Parsa et al, (1996).⁽¹⁸⁾

In the TCLP test, acetic acid and sodium hydroxide were used to obtain a buffer solution of pH 4.93. In addition, a TCLP test was performed on replicate samples by an independent laboratory.

In the IAEA standard method, only the upper surface of the examined specimens (disks) was exposed to the leachant, the rest of the disks volume were coated with wax to prevent any water intrusion. In the long-term leach tests, the ratio of the leachant volume to the total volume of the specimen was always kept constant at 10.

The concentration of the released cation(s) of Cs, Sr, Ce, Pb, and Cr in the leachate was measured in mg.l⁻¹, using the Atomic Absorption Spectrophotometer, type Buck scientific 210 VGP (USA).

Leachability could be calculated from the following equations (De Angelis et al 1992)⁽²¹⁾

$$\text{Leach rate, } R_n = [(\Sigma C_n / C_o) \times w \text{ (g)}] / F \text{ (cm}^2\text{)}. \Sigma t_n. \text{ g.cm}^{-2}\text{.s}^{-1}. \quad (2)$$

$$\text{Cumulative fraction released, CFR\% (cm)} = \Sigma C_n / C_o \times V/F \times 100. \quad (3)$$

$$\text{Percentage of cation(s) released (dimensionless)} = \Sigma C_n / C_o \times 100. \quad (4)$$



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

Where, C_0 = initial contamination concentration of the added cation(s) in the solid phase (mg.Kg^{-1}), and/or its initial content in the solid phase in mg, ΣC_n = cumulative concentration of the leached cation(s) in the leachant during the whole test duration, t_n in seconds (s), w is the initial weight of the compressed specimen (g), of volume V (cm^3), and F = the exposed surface of the specimen to the leachant (cm^2).

As demonstrated by the leaching kinetics, the leached cation(s) from the solid phase through a diffusion-controlled mechanism, could be calculated from the empirical formula,

$$C / C_0 = B. t^n \quad (5)$$

Where, C and C_0 are the final and initial cation concentrations, B = value of C / C_0 at $t = 1$ day, n = time exponent. With $n = 0.5$, a relationship drawn from the Fick's law under the condition of a semi-infinite medium can describe the leaching mechanism,

$$C / C_0. (V / F) = 2 (D. t / \pi)^{1/2} \quad (6)$$

$$\therefore D = (C / C_0)^2 (V / F)^2. \pi / 4t \quad (7)$$

Diffusivity D ($\text{cm}^2.\text{s}^{-1}$), could be calculated from Equation (7), only when the cation(s) release is less than 20%.

Leachability index, Li (Cote & Isabel 1983),⁽²²⁾ could be calculated as,

$$Li = - \log D \quad (8)$$

RESULTS AND DISCUSSION

Phase Characterization

Figure (1) shows the physical appearance of some typical formulations composed of sulfur polymer cement that accommodate different contaminants using aliphatic hydrocarbon resin precursors during the preparation process. The appearance of the prepared molds did not change by changing the resin on using aromatic starting material except for slight roughness of the molds was observed

Figure (2) shows the XRD patterns for the prepared matrices that were matched according the Joint Commission of Powder Diffraction Standards (JCPDS), Copyright © 1995; PDF-2 sets 1-45 database. It was found that the blank matrix is crystalline and composed of sharp peaks, which is assigned to the presence of orthorhombic sulfur (JCPDS-ICDD NO. 8-247). This result agrees with the use of other hydrocarbon resins with sulfur during the solidification/stabilization of elemental mercury wastes.⁽¹³⁾

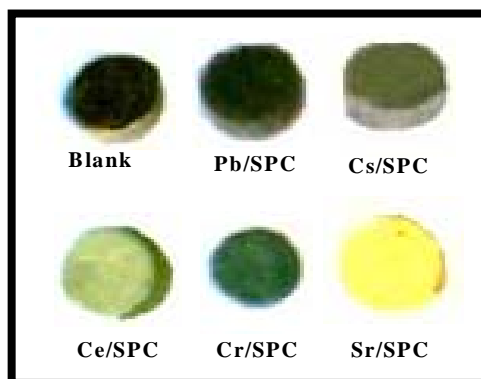


Fig. (1): Typical Sulfur Polymer Cement Formulations, loaded with, Pb, Cs, Ce, Cr and Sr using Aliphatic Hydrocarbon Resin

On immobilizing the aforementioned simulated radioactive waste elements, the sharp crystalline peaks of the orthorhombic sulfur decreases in overall the 2θ range with appearance of metal sulfide peaks corresponding to the different metals. The simulated radioactive cerium forms cubic cerium sulfide with its characteristic peaks at 2θ of 31.35, 43.49 and 73.3 (JCPDS-ICDD NO. 4-688). Also, light yellowish brown cubic strontium sulfide and gray metallic lead sulfide are formed with their own peaks at (29.72, 42.20 and 52.71) (JCPDS-ICDD NO. 8-489) and (30.03, 25.84 and 42.86) (JCPDS-ICDD NO. 5-592) respectively.

On the other hand, crystalline peaks of cesium sulfide corresponding to 19.55, 25.51 and 23.70 $2\theta^\circ$ (JCPDS-ICDD NO. 5-272) are observed, which could be attributed to the formation brownish red triclinic cesium sulfate structure. Finally, black chromium sulfide phase was formed with its hexagonal crystalline structure as a result of reaction with sodium sulfide and the highly excess elemental sulfur with its three strongest peaks at 43.53, 52.84 and 33.70 $2\theta^\circ$ (JCPDS-ICDD NO. 10-344).

The replacement of the used hydrocarbon resin used for the immobilization of the waste elements from aliphatic to aromatic precursor, the intensities of the characteristics peaks are not affected, while their positions remained constant.

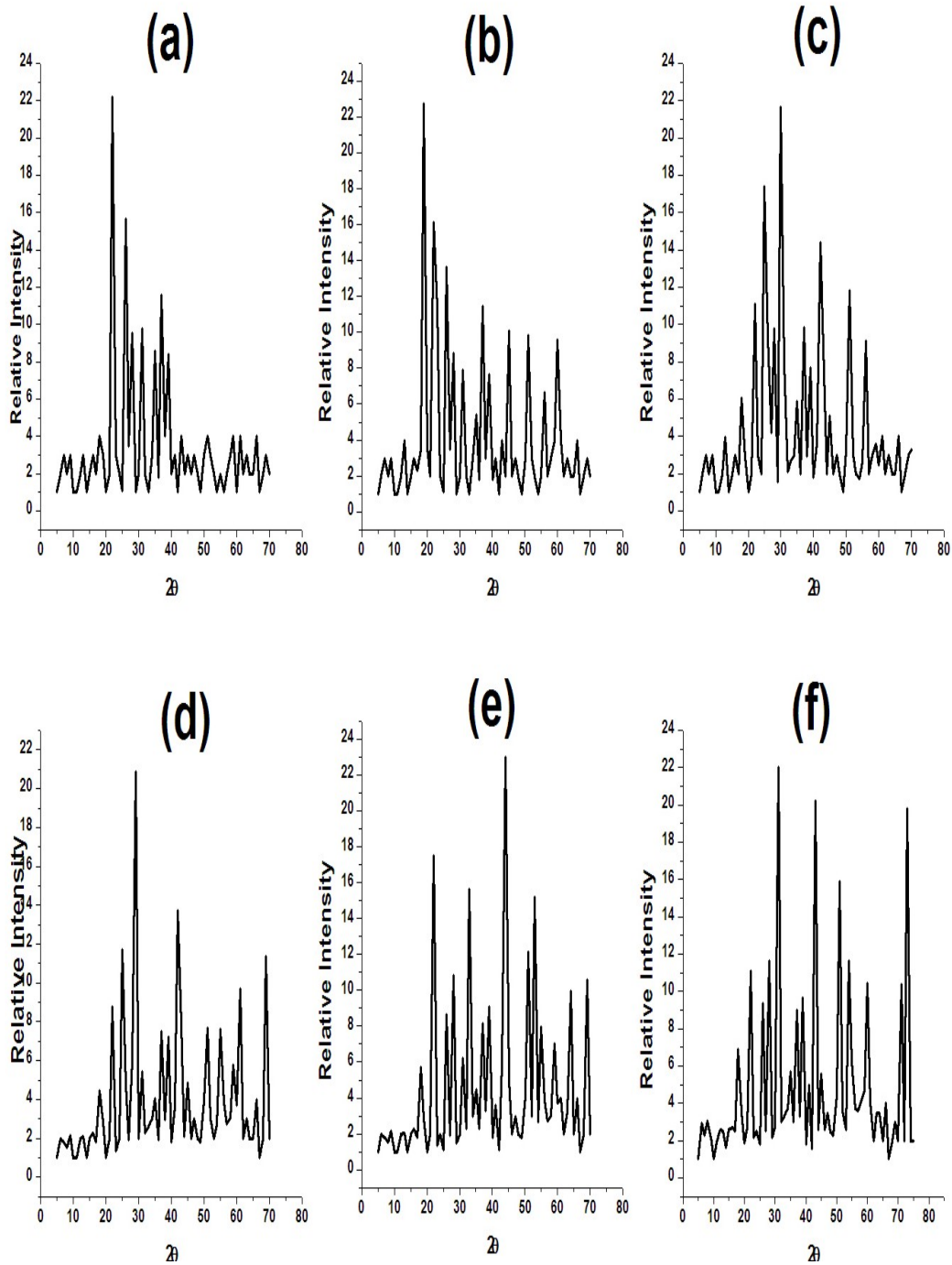


Fig.(2): XRD Patterns for Sulfur Polymer Cement Matrices: Blank Formulation (a), Matrices loaded with Cs (b), Pb (c), Sr (d), Cr (e) and Ce (f) using Aliphatic Hydrocarbon Resin.



Durability of the Fabricated Matrices

Water of Immersion

The water resistance tests of the sulfur polymer cement matrices loaded with different amounts of simulated radioactive nuclides are represented in Tables 1 and 2. The data shows that the prepared matrices accommodate water only to about 2.5 Wt-% of the original samples. This can be attributed to the very high energy required for water molecules to interact with the prepared formulations. In this concern, the ion release of the various loaded metal ions was very low; most of the ions are below the detection limit of the test. However, this technique can be considered very effective in case using of the aliphatic hydrocarbon resin rather than the aromatic one on during the preparation process.

Table 1. Water Resistance Tests for Sulfur Polymer Cement Formulations, Loaded with Cs, Pb, Sr, Cr and Ce, using Aliphatic Hydrocarbon.

Waste Loading (mg.Kg ⁻¹)	Cation(s) Tested	Weight Increase (%)	Ion Release (mg.l ⁻¹)
4130	Cs	0.85	BDL*
4130	Pb	0.64	BDL*
4130	Sr	0.91	BDL*
4130	Cr	0.47	BDL*
4130	Ce	0.35	BDL*
4960	Cs	1.23	BDL*
4960	Pb	0.93	BDL*
4960	Sr	1.45	BDL*
4960	Cr	0.83	BDL*
4960	Ce	0.71	BDL*
5720	Cs	1.97	0.0005
5720	Pb	1.29	BDL*
5720	Sr	2.11	0.0085
5720	Cr	1.23	BDL*
5720	Ce	1.17	BDL*

* BDL = Below Detection Limits



8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT

Table 2. Water Resistance Tests for Sulfur Polymer Cement Formulations, Loaded with Cs, Pb, Sr, Cr and Ce, using Aromatic Hydrocarbon

Waste Loading (mg.Kg ⁻¹)	Cation Tested	Weight Increase (%)	Ion Release (mg.l ⁻¹)
4130	Cs	1.13	BDL*
4130	Pb	0.87	BDL*
4130	Sr	1.53	BDL*
4130	Cr	0.73	BDL*
4130	Ce	0.51	BDL*
4960	Cs	1.48	0.0009
4960	Pb	1.12	BDL*
4960	Sr	1.98	0.0102
4960	Cr	0.96	BDL*
4960	Ce	0.84	BDL*
5720	Cs	2.14	0.0058
5720	Pb	1.62	BDL*
5720	Sr	2.43	0.0487
5720	Cr	1.27	BDL*
5720	Ce	1.38	BDL*

* BDL = Below Detection Limits

Compressive Strength

The mechanical properties of the different formulations were expressed in terms of the compressive strength and tabulated in Tables 3 and 4. The tables indicate that the formulations prepared using aliphatic hydrocarbon resins have slightly higher compressive strength results than the corresponding aromatic formulations. Specifically, these results are higher than the matrices prepared from ordinary Portland cement of 32 – 700 Kg.cm⁻²,⁽²³⁾ and more recent formulations prepared from fly ash as a basic matrix for immobilization of some radioactive and hazardous elements of 18-42 Kg. cm⁻².⁽²⁴⁾

Open Porosity

Tables 3 and 4 show the open porosity measurements was determined according to the procedure described in DIN 51056, EN 178 (1991) and EN 159 (1991).⁽¹⁷⁾ The results indicates that the matrices prepared from aliphatic and aromatic resins and sulfur and loaded with different proportions of hazardous waste materials possessed lower open porosity materials than some matrices prepared from fly ash loaded with different hazardous wastes.⁽²⁴⁾ Also, these results are comparable with some matrices used for the solidification of iron and steel waste slag in some borosilicate glasses and fired high temperatures.⁽¹⁷⁾ Although, the open porosity was found very low and did not exceed 2.5 Vol-% in all cases, the porosity increases with increasing the waste loading. This can be attributed to the roughness of the external surface. On increasing the waste loading over 35 Wt-%, the open porosity was observed to be high and accompanied by low mechanical properties. This



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

phenomenon could be attributed to the formation of microcracks that leads to low energy required for crack propagation on using very low mechanical loads.

Table 3. Mechanical Properties and Open Porosity for Sulfur Polymer Cement Formulations, Loaded with Cs, Pb, Sr, Cr and Ce, using Aliphatic Hydrocarbon

Waste Loading (mg.Kg ⁻¹)	Cation(s)	Open Porosity	Compressive Strength
	Tested	Vol-%	(KN.cm ⁻²)
4130	Cs	0.62	7.5253
4130	Pb	0.51	8.95145
4130	Sr	0.82	6.7245
4130	Cr	0.32	9.1575
4130	Ce	0.34	9.4578
4960	Cs	0.92	8.457
4960	Pb	0.81	10.5467
4960	Sr	0.93	8.1465
4960	Cr	0.67	10.4542
4960	Ce	0.51	11.2386
5720	Cs	0.94	10.7543
5720	Pb	1.31	13.7452
5720	Sr	1.57	9.5327
5720	Cr	1.12	12.7813
5720	Ce	1.01	14.2354

TABLE 4. Mechanical Properties and Open Porosity for Sulfur Polymer Cement Formulations, Loaded with Cs, Pb, Sr, Cr and Ce, using Aromatic Hydrocarbon

Waste Loading (mg.Kg ⁻¹)	Cation(s)	Open Porosity	Compressive Strength
	Tested	Vol-%	KN.cm ⁻²
4130	Cs	0.85	6.2458
4130	Pb	0.67	7.7812
4130	Sr	0.94	5.1246
4130	Cr	0.52	8.9542
4130	Ce	1.01	8.741
4960	Cs	1.21	9.853
4960	Pb	0.94	9.1452
4960	Sr	1.07	7.2583
4960	Cr	0.85	9.1475
4960	Ce	0.92	10.2357



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

5720	Cs	0.99	9.5327
5720	Pb	1.37	12.0257
5720	Sr	1.76	8.6542
5720	Cr	1.39	11.2586
5720	Ce	1.25	13.4257

Leach Test Results

In this work, different leach procedures were used to ensure the chemical performance of the different formulations prepared from sulfur with aliphatic hydrocarbon resins and or aromatic hydrocarbon one, loaded with different amount of simulated radioactive waste salts.

Toxicity leach results (TCLP)

The toxicity characteristic leach procedure (TCLP) results for Cs, Sr, Pb, Cr and Ce with different proportions related to sulfur polymer cement matrix are illustrated in Tables 5 and 6. The TCLP leach results for Ce, Cr and Pb are found to exist below their TCLP limit on using sulfur polymer cement matrices containing aliphatic hydrocarbon. On the other hand, Cs and Sr are found to be very low so that their release% was increasing as the waste loading increases; in all circumstances, they did not exceed 1.52×10^{-10} and 1.68×10^{-8} respectively. On changing the matrix polymer to the aromatic hydrocarbon resin, Ce and Pb remained under the detection level of the TCLP. These results are very promising in comparison with solidification/stabilization using Chemically Bonded Phosphate Ceramics (CBPC) of the low level radioactive waste and hazardous waste.⁽²⁵⁾ Therefore, it could be concluded that Ce, Cr and Pb are well immobilized in the performed sulfur polymer cement matrices..

TABLE 5. Static Leach Test Results for Sulfur Polymer Cement Formulations, Loaded with Cs, Pb, Sr, Cr and Ce, using Aliphatic Hydrocarbon Resin.

Waste Loading (mg.Kg ⁻¹)	Released cations in leachate									
	Cation(s) Concentration (mg.l ⁻¹)					Release (%)				
	Cs	Sr	Pb	Cr	Ce	Cs	Sr	Pb	Cr	Ce
4130	0.00032	0.0063	BDL*	BDL*	BDL*	7.74818×10^{-11}	1.52542×10^{-9}	zero	NA ⁺	NA ⁺
4960	0.00025	0.0345	BDL*	BDL*	BDL*	5.04032×10^{-11}	6.95565×10^{-9}	zero	NA ⁺	NA ⁺
5720	0.00087	0.0965	BDL*	BDL*	BDL*	1.52098×10^{-11}	1.68706×10^{-8}	zero	NA ⁺	NA ⁺



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

* BDL = Below Detection Limits.



TABLE 6. Static Leach Test Results for Sulfur Polymer Cement Formulations, Loaded with Cs, Pb, Sr, Cr and Ce, using Aromatic Hydrocarbon Resin.

Waste Loading (mg.Kg ⁻¹)	Released Cations in Leachate									
	Cation(s) Concentration (mg.l ⁻¹)					Release (%)				
	Cs	Sr	Pb	Cr	Ce	Cs	Sr	Pb	Cr	Ce
4130	0.00075	0.0098	BDL*	0.00023	BDL*	1.81598 x10 ⁻¹⁰	2.37288 x10 ⁻⁹	zero	5.56901 x10 ⁻¹¹	NA ⁺
4960	0.00094	0.0126	BDL*	0.00047	BDL*	1.89516 x10 ⁻¹⁰	2.54032 x10 ⁻⁹	zero	9.47581 x10 ⁻¹¹	NA ⁺
5720	0.00157	0.0358	BDL*	0.00059	BDL*	2.74476 x10 ⁻¹⁰	6.25874 x10 ⁻⁹	zero	1.03147 x10 ⁻¹⁰	NA ⁺

* BDL = Below Detection Limits.

Long Term Leach Results

The long term ISO leach test results of the fabricated sulfur polymer cement loaded with different initial contamination concentrations of Cs, Sr, Pb, Cr and Ce are illustrated in Tables 7 and 8. It is clear that the IAEA leach test results are different according to the specimen type, element loaded and waste loading. Generally, the rate of ion release increases with increasing the waste loading from 20Wt-% to 30Wt-%. On using higher element concentration in the matrix, the formulations failed to prepare due to the formation of non uniform spongy structure with catastrophic cracks. In all experiments, the percentage of ion release is very low; therefore the mechanism of migration of the different metal ions to the environment is basically diffusion, rather than wash-off or dissolution.⁽²⁶⁾ The diffusion coefficient of the different elements was calculated; and hence the leach index of these elements was evaluated; the order of diffusion of the simulated radioactive waste elements was found to be:

$$\text{Sr} > \text{Cr} > \text{Cs} > \text{Ce} > \text{Pb}$$

The long-term test results show that cumulative fraction release was enhanced by changing the precursor polymeric material by using aliphatic hydrocarbon resin instead of the ambient aromatic one.

CONCLUSIONS

There are numerous techniques that can be used in the solidification stabilization of radioactive nuclides. The most recent ones are namely, stabilization/solidification in chemically bonded phosphate ceramics (CBPC), stabilization in sulfur polymer cement matrix and encapsulation in polyethylene



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

polymeric materials. In this work, the solidification/stabilization technologies in sulfur polymer cement matrices for some some radioactive and hazardous nuclides characterized by their presence in the waste streams as well as their toxicities was selected. The prepared formulations were loaded with different concentrations of the metal salts and tested according to the different international standards. The leaching rates are very small compared to other technologies; the percentage of ion release did not exceed 20%. Therefore diffusion mechanism from the matrices predominated rather wash-off or dissolution. The leach index of the prepared materials towards the aforementioned metal ions was high and ranges between about 9-11; and the order of migration of the released ion was



The prepared formulations were subjected to different standard tests of durability, compressive strength, open porosity and water of immersion. The results indicated that the water of immersion was very low compared with other formulations based on different technologies, which could be attributed to the high energy required for water molecules to interact with this type of formulations. These blocks also possessed lower open porosity values and higher compressive strengths compared with less recent formulations. The scanning electron microscopy, energy dispersive X-ray and X-ray diffraction patterns revealed the fixation of the different metal ions in the microstructure of the matrix with the formation of stable sulfide phases. Therefore, this technique can be recommended as it is also characterized by simplicity and economic feasibility for the solidification/stabilization of the different radioactive waste streams.

REFERENCES

- (1) U.S. EPA, Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb EPA/540/S-97/500, U.S. EPA Office of Research and Development, Cincinnati, OH, 1997.
- (2) D. Singh, A.S. Wagh, M. Tlustochowicz, S.Y. Jeong, Phosphate ceramic process for macroencapsulation and stabilization of low-level debris wastes, *Waste Management*, 18, 135-143, 1998.
- (3) C.H. Mattus, Sulfur Polymer Cement for Macroencapsulation of Mixed Waste Debris, in: *Proceedings of the International Conference on Decommissioning and Decontamination and on Nuclear and Hazardous Waste Management*, Denver, Colorado, September 13–18, 1998.
- (4) U.S. EPA, Presumptive Remedy for Metals-in-Soil Sites, EPA/540/F-98/054, U.S. EPA Office of Solid Waste and Emergency Response, Washington, DC, 1999.
- (5) F. Sanchez, D.S. Kosson, C.H. Mattus, M.I. Morris, Use of a New Leaching Procedure for Evaluating Alternative Processes for Mercury Contaminated Mixed Waste (Hazardous and Radioactive), Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, TN, 2001.
- (6) WPI, Got mercury? Mixed Waste Focus Area is Finding Answers, *Initiatives Online*, vol.6, Summer, Internet Website of Waste Policy Institute, <http://www.wpi.org/Initiatives/init/summer99/>, 1999.
- (7) A.S. Wagh, D. Dingh, S.Y. Jeong, Mercury Stabilization in Chemically Bonded Phosphate Ceramics, in: *Invited Paper for Environmental Protection Agency's*



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY**
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT

- Workshop on Mercury Products, Processes, Waste, and the Environment: Eliminating, Reducing and Managing Risks, Baltimore, MD, March 22–23, 2000.
- (8) H.L. Clever, S.A. Johnson, M.E. Derrick, The Solubility of Mercury and some Sparingly Soluble Mercury Salts in Water and Aqueous Electrolyte Solutions, *J. Phys. Chem. Ref. Data* 14 (3), 631–680, 1985.
 - (9) G.R. Darnell, Sulfur Polymer Cement, A Final Waste Form for Radioactive and Hazardous Wastes, in: T. Michael Gilliam, C. Carlton, Wiles (Eds.), *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes: ASTM STP 1240*, vol. 3, American Society for Testing and Materials, West Conshohocken, PA, 1996.
 - (10) DOE, Mixed Waste Integrated Program (MWIP) Technology Summary DOE/EM-0125P, DOE Office of Environmental Management and Office of Science and Technology, Washington, DC, 1994.
 - (11) P.D. Kalb, D. Melamed, B.R. Patel, M. Fuhrmann, Treatment of Mercury Containing Wastes, United States Patent 6,399, 849, 2002.
 - (12) BNL, Brookhaven Lab Licenses its Mercury Waste Treatment Technology to Newmont Mining Corporation, Internet Website of Brookhaven National Laboratory. <http://www.globaltechnoscan.com/6thJune-2thJune01/mercury.htm>, 2002
 - (13) M. Fuhrmann, D. Melamed, P.D. Kalb, J.W. Adams, L.W. Milian, Sulfur polymer Solidification/Stabilization of Elemental Mercury Waste, *Waste Management*, 22, 327-333, 2002.
 - (14) P.D. Kalb, J.W. Adams, M.L. Meyer, H.H. Burns, Thermoplastic Encapsulation Treatability Study for A Mixed Waste Incinerator off-Gas Scrubbing Solution, in: T. Michael Gilliam, C. Wiles Carlton (Eds.), *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes: ASTM STP 1240*, vol. 3, American Society for Testing and Materials, West Conshohocken, PA, (1996).
 - (15) Oak Ridge National Laboratory (ORNL), Demonstration of Mixed Waste Debris Macroencapsulation Using Sulfur Polymer Cement, Internet Website of Oak Ridge National Laboratory. <http://www.ornl.gov/K25/techdemo/macencp.htm>, 1997.
 - (16) American Nuclear Society (ANSI/ANS, 16.1)., American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure, La Grange Park, IL., 1986.
 - (17) B. El-Gammal, PhD Thesis Submitted To Chemistry Dept., Faculty Of Science, Ain Shams University, Cairo, Egypt, 2001.
 - (18) Parsa, J., Stuart, H., Manson.Mc Gee, Steiner, R., Stabilization/Solidification of Hazardous Wastes using Fly Ash. *J. Env. Eng.*, V. 122, No. 10, 935-940, 1996.
 - (19) IAEA, Leach Testing of Immobilized Radioactive Waste Solids, a Proposal for a Standard Method. Special Item, at. *Energy Rev.* 9, 195-207, 1971.
 - (20) Ege Egemen and Coskun Yurteri, Regulatory Leaching Tests for Fly Ash: A Case Study, *Waste Management & Research*, 14, 43-50, 1996.
 - (21) De Angelis, G., Marchetti, A., and Balzamo, S., Leach Studies: Influence Of Various Parameters On The Leachability Of Cesium From Cemented BWR Evaporator Concentrates, Stabilization And Solidification Of Hazardous, Radioactive And Mixed Wastes, 2nd volume, STP 1123, T. M. Illiam and C.C. Wiles, Eds. Gould, JR., and Westberry, C.F., 1992.



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

- (22) L.Cote and D. Isabel, "Application of Dynamic Leaching Test to Solidified Hazardous Wastes", Hazardous and Industrial Waste Management: 3rd Symposium, ASTM STP 856, American Society for Testing and Materials, Philadelphia, pp. 48-60, 1983.
- (23) IAEA, Conditioning Of Low- And Intermediate-Level Radioactive Wastes, Vienna, 1983.
- (24) M.W.Abdel Raouf and H.G.Nowier Assessment of Fossil Fuel Fly Ash Formulations In The Immobilization Of Hazardous Wastes, J Environ. Eng., pp 499-507, 2004
- (25) A. S. Wagh, S. Y. Jeong , D. Singh, R. Strain,. H. No and J. Wescott,. Stabilization of Contaminated Soil and Wastewater with Chemically Bonded Phosphate Ceramics, Paper for Presentation at the Waste Management Annual Meeting, Tucson, AZ, March 2-6, 1997.
- (26) G.J.de Groot, and H. A. Van der Sloot, Determination of Leaching Characteristics of Waste Materials Leading to Environmental Product Certification, Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, 2nd Volume, STP 1123, T.M. Gilliam and C.C. Wiles, Eds. American Society for Testing and Materials, Philadelphia, pp.149-170, 1992.



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

TABLE 7. Static Leach Test Results for Sulfur Polymer Cement Formulations, Loaded with Cs, Pb, Sr, Cr and Ce, using Aromatic Hydrocarbon Resin, after 28 days in bidstilled water.

Waste		Co	∑ Cn		Rn,	D,		C.F.R	
Loading	Cations	(mg)	(mg)	Δ pH	g.cm ⁻² .s ⁻¹	Cm ² .s ⁻¹	L.I	(%)	Release (%)
20 Wt-%	Cs	4130	0.00092	-0.4	8.93982x10 ⁻¹⁶	7.22829x10 ⁻¹²	11.14096	0.000223	2.2276x10 ⁻⁵
20 Wt-%	Pb	4130	0.00064	-0.8	6.21901x10 ⁻¹⁶	5.02838x10 ⁻¹²	11.29857	0.000155	1.5496x10 ⁻⁵
20 Wt-%	Sr	4130	0.00256	-0.6	2.4876x10 ⁻¹⁵	2.01135x10 ⁻¹¹	10.69651	0.00062	6.1985x10 ⁻⁵
20 Wt-%	Cr	4130	0.00052	-0.4	5.05294x10 ⁻¹⁶	4.08556x10 ⁻¹²	11.38875	0.000126	1.2591x10 ⁻⁵
20 Wt-%	Ce	4130	0.00038	-0.5	3.69253x10 ⁻¹⁶	2.9856x10 ⁻¹²	11.52497	9.2E-05	9.201x10 ⁻⁶
25 Wt-%	Cs	4960	0.00325	-0.9	2.62962x10 ⁻¹⁵	2.12618x10 ⁻¹¹	10.6724	0.000655	6.5524x10 ⁻⁵
25 Wt-%	Pb	4960	0.00745	-1.3	6.02789x10 ⁻¹⁵	4.87385x10 ⁻¹¹	10.31213	0.001502	1.5020x10 ⁻⁴
25 Wt-%	Sr	4960	0.07985	-1	6.46077x10 ⁻¹⁴	5.22386x10 ⁻¹⁰	9.282009	0.016099	16.0988x10 ⁻⁴
25 Wt-%	Cr	4960	0.00598	-0.8	4.8385x10 ⁻¹⁵	3.91217x10 ⁻¹¹	10.40758	0.001206	1.2056x10 ⁻⁴
25 Wt-%	Ce	4960	0.00156	-0.9	1.26222x10 ⁻¹⁵	1.02057x10 ⁻¹¹	10.99116	0.000315	3.1452x10 ⁻⁵
30 Wt-%	Cs	5720	0.08523	-1.3	5.97981x10 ⁻¹⁴	4.83498x10 ⁻¹⁰	9.315606	0.0149	14.9003 x10 ⁻⁴
30 Wt-%	Pb	5720	0.01475	-1.8	1.03487x10 ⁻¹⁴	8.36746x10 ⁻¹¹	10.07741	0.002579	2.5787 x10 ⁻⁴
30 Wt-%	Sr	5720	0.12478	-1.6	8.75467x10 ⁻¹⁴	7.07859x10 ⁻¹⁰	9.150053	0.021815	21.8147x10 ⁻⁴
30 Wt-%	Cr	5720	0.09875	-1.3	6.92839x10 ⁻¹⁴	5.60195x10 ⁻¹⁰	9.251661	0.017264	17.264 x10 ⁻⁴
30 Wt-%	Ce	5720	0.03216	-1.4	2.25637x10 ⁻¹⁴	1.82439x10 ⁻¹⁰	9.738882	0.005622	5.6224x10 ⁻⁴



**8th ARAB INTERNATIONAL CONFERENCE ON
POLYMER SCIENCE & TECHNOLOGY
27 – 30 November 2005, Cairo-Sharm El-Shiekh, EGYPT**

TABLE 8. Static Leach Test Results for Sulfur Polymer Cement Formulations, Loaded with Cs, Pb, Sr, Cr and Ce, using Aliphatic Hydrocarbon Resin, after 28 days in Bidstilled Water.

Waste Loading	Cations	Co (mg)	$\sum C_n$ (mg)	Δ pH	R_n , $g.cm^{-2}.s^{-1}$	D , $Cm^2.s^{-1}$	L.I	C.F.R (%)	Release (%)
20 Wt-%	Cs	4130	0.00125	-0.8	1.21465×10^{-15}	9.82105×10^{-12}	11.00784	0.000303	3.0266×10^{-5}
20 Wt-%	Pb	4130	0.00354	-0.7	3.43989×10^{-15}	2.78132×10^{-11}	10.55575	0.000857	8.5714×10^{-5}
20 Wt-%	Sr	4130	0.00935	-0.9	9.08558×10^{-15}	7.34614×10^{-11}	10.13394	0.002264	2.2639×10^{-4}
20 Wt-%	Cr	4130	0.00356	-0.5	3.45932×10^{-15}	2.79703×10^{-11}	10.5533	0.000862	8.6199×10^{-5}
20 Wt-%	Ce	4130	0.00124	-0.6	1.20493×10^{-15}	9.74248×10^{-12}	11.01133	0.0003	3.0024×10^{-5}
25 Wt-%	Cs	4960	0.00658	-1.2	5.32397×10^{-15}	4.30469×10^{-11}	10.36606	0.001327	1.3266×10^{-4}
25 Wt-%	Pb	4960	0.00853	-1.4	6.90174×10^{-15}	5.5804×10^{-11}	10.25333	0.00172	1.7198×10^{-4}
25 Wt-%	Sr	4960	0.01234	-1.3	9.98446×10^{-15}	8.07293×10^{-11}	10.09297	0.002488	2.4879×10^{-4}
25 Wt-%	Cr	4960	0.00732	-1.5	5.92271×10^{-15}	4.78881×10^{-11}	10.31977	0.001476	1.4758×10^{-4}
25 Wt-%	Ce	4960	0.00914	-1.7	7.3953×10^{-15}	5.97947×10^{-11}	10.22334	0.001843	1.8427×10^{-4}
30 Wt-%	Cs	5720	0.00923	-2	6.47585×10^{-15}	5.23605×10^{-11}	10.281	0.001614	1.6136×10^{-4}
30 Wt-%	Pb	5720	0.02365	-2.1	1.6593×10^{-14}	1.34163×10^{-10}	9.872367	0.004135	4.1346×10^{-4}
30 Wt-%	Sr	5720	0.05328	-1.9	3.73817×10^{-14}	3.0225×10^{-10}	9.519634	0.009315	9.3147×10^{-4}
30 Wt-%	Cr	5720	0.08742	-2.1	6.13346×10^{-14}	4.95921×10^{-10}	9.304587	0.015283	15.2832×10^{-4}
30 Wt-%	Ce	5720	0.03458	-2	2.42616×10^{-14}	1.96167×10^{-10}	9.707373	0.006045	6.0455×10^{-5}