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CHARACTERIZATION OF SURROGATE RADIOACTIVE CEMENTED WASTE: A LABORATORY STUDY

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ABSTRACT

Portland cement is commonly used to stabilize intermediate and low level of radioactive wastes. The stabilization/solidification process needs to be well understood as waste constituents can retard or activate cement hydration. The objectives of this project were to prepare surrogate radioactive cemented waste (SRCW), develop a comminution strategy for SRCW, determine its chemical characteristics, and develop processes for long term storage. This paper emphasizes on the characterization of surrogate radioactive cemented waste.

The SRCW produced showed a high degree of heterogeneity mainly due to the method used to add the solution to the host cement. Heavy metals such as uranium and mercury were not distributed uniformly in the pail. Mineralogical characterization (SEM, EDS) showed that uranium is located around the rims of hydrated cement particles. In the SRCW, uranium occurs possibly in the form of a hydrated calcium uranate. The SEM-EDS results also suggest that mercury occurs mainly in the form of HgO although some metallic mercury may be also present as a result of partial decomposition of the HgO.

1. INTRODUCTION

Stabilization/solidification (S/S) is an important tool in the treatment of potentially hazardous waste. S/S processes include chemical, physical and thermal processes. Of these, chemical processes dominate the field, particularly the use of Portland cement (PC), cement/fly ash, cement soluble silicates, lime/fly ash, cement kiln dust and phosphates. Portland cement is the most widely used of all S/S binder reagents [1] for waste containment producing a low permeability product [2]. Portland cement is commonly used to stabilize intermediate and low level radioactive wastes. Large amount of cement is used to stabilize radioactive waste, resulting in low volume-efficiency, high disposal cost, waste handling difficulty and high transportation cost [3]. The stabilization/solidification process needs to be better understood as waste constituents can retard or activate cement hydration. Characterization of the matrix is essential to predict and understand the behaviour of the material under various storage conditions.

The stabilization of low-level of radioactive waste usually involves large quantity of cement and limited mixing operating conditions resulting in significant un-hydrated cement contents in the SRCW. However, a high neutralization potential provided by an excess of un-hydrated cement could promote metal amphoteric leaching. Also, un-hydrated cement in the SRCW increases reagent cost, waste volume and storage footprint. In the case where the SRCW needs to be re-processed for selective metal recovery or restabilized, the quantity of un-hydrated cement may influence the grinding method, metal recovery method and binding agent selection. Within this context, surrogate cemented wastes (SRCW) were produced in order to better characterize the matrix. This paper presents the procedures, bulk characterization, assessment of reproducibility and mineralogical characteristics of the SRCW.

2. METHODOLOGY

Ordinary Portland cement for general use (GU, formerly known as type 10) was used to produce SRCW at a solution-to-cement ratio of 0.29. Ruthenium nitrosyl solution and nitrate salts of metals were added to a 0.36 M nitric acid solution. The total concentration of added metals was 0.07 mole/kg of Portland cement. The chemical composition of the solution is presented in Table 1.

Table 1 – Chemical composition of the solution

Target constituent	Concentration mol/L	Chemical formula of added compound
Aluminum	0.98	$Al(NO_3)_3.9H_2O$
Uranium	0.020	$UO_2(NO_3)_3.6H_2O$
Mercury	0.033	$Hg(NO_3)_2.H_2O$
Rubidium	7.53E-05	$RbNO_3$
Caesium	2.19E-04	$CsNO_3$
Strontium	2.96E-04	$Sr(NO_3)_2$
Barium	2.29E-04	$Ba(NO_3)_2$
Ruthenium	3.02E-04	$RuNO(NO_3)_3$ as 1.5 % solution
Lanthanum	1.44E-04	$La(NO_3)_2.6H_2O$
Cerium	3.89E-04	$Ce(NO_3)_3.6H_2O$
Praseodymium	1.01E-04	$Pr(NO_3)_3.6H_2O$
Neodymium	2.84E-04	$Nd(NO_3)_3.6H_2O$
Samarium	3.40E-05	$Sm(NO_3)_3.6H_2O$
Europium	4.38E-06	$Eu(NO_3)_3.6H_2O$
Gadolinium	1.41E-06	$Gd(NO_3)_3.6H_2O$
Yttrium	1.28E-04	$Y(NO_3)_3.6H_2O$
Iron	1.0E-03	$Fe(NO_3)_3.9H_2O$
Nickel	1.8E-04	$Ni(NO_3)_2.6H_2O$
Chromium	3.3E-04	$Cr(NO_3)_3.9H_2O$
Nitric acid	0.36	HNO_3 (16M)

2.1. SRCW Preparation

A high-density polyethylene pail (20 L) of internal diameter of 29 cm and 39 cm of height was used for the preparation of the SRCW. Exactly 3.5 kg of GU (General Usage) cement were added to the bottom of the pail, forming an even layer approximately 8 cm deep. Additional cement was subsequently introduced through four polyethylene bags (4 mils, ULine, S-1144), each filled with 3 kg of GU cement. The open ends of the polyethylene bags were folded closed and then were placed at the bottom of the pail whereas the sealed ends were accessible from the top of the pail.

A total of 4.5 L of solution (Table 1) was transferred into a 10-L glass beaker, slightly stirred using a Teflon-coated magnetic stirrer bar and heated to 90°C on a hot plate inside a multi-hazardous glove box. The temperature of the solution was monitored using a glass thermometer.

The heated solution was transferred to the pail using a Masterflex pump and Norprene tubing (size 17). The solution was introduced at a flow rate of approximately 1.3L/min. While adding solution, the cement in the polyethylene bags was gradually emptied into the pail by lifting the sealed ends of each of the four bags. The addition of cement was coordinated with the addition of the solution.

2.2. SRCW Characterization

After an ageing period of 28 days, the SRCW were sampled by core-drill at three different locations. Then, each core was divided into three different sections (top, middle and bottom). Prior to characterization, the sample was ground, sieved to 150 μm, and divided into two samples using a splitter. One fraction was air dried for mineralogical characterization by XRD and the other was oven dried for 48 hours at 70°C for chemical characterization. The chemical analyses were done using ICP-MS (Thermo Scientific, X Series II) after microwave total digestion of the cemented waste with HNO_3, HF and HCl for all metals except for mercury. Following the digestion, boric acid was added to neutralize the residual HF. All chemical reagents used during the experiment were laboratory reagent grade. For mercury characterization, the samples were digested using the microwave oven but with HCl only. Total solids, paste pH and paste conductivity were also measured for each sample.

2.3. Mineralogical Analysis

After a curing period of 28 days, drill cores were obtained from the top, the middle and the bottom portions of the SRCW in the pail. The SRCW was generally friable; therefore, most cores were made up of fragmented material. From these, fragments of 20 ± 10 mm were selected for the preparation of polished sections using the following method. The selected fragments were placed into polypropylene moulds of 31 mm in diameter. A mixture of liquid resin and hardener was prepared and degassed using a vacuum oven. The prepared resin mixture was added to the plastic mould to cover the fragment(s) of SRCW. The moulding assembly was placed in a vacuum oven and further degassed until the resin ceased foaming. The resin was left to cure for 24 hrs. The epoxy puck was removed from the polypropylene mould and polished using resin bonded diamond grinding discs of 68 μm and 25 μm. Fine polishing was done in three steps using diamond suspensions of 9, 3, and 1 μm. The lubricant used for the grinding and the diamond suspensions used for the polishing were all propanol-based to avoid unwanted dissolution of the SRCW by water-based products.

The polished sections were examined using a variable pressure scanning electron microscope, VP-SEM (S-3200, Hitachi) equipped with an energy dispersive X-ray analyzer, EDS (Link Pentaflex detector and ISIS analyzing suite, OXFORD). The VP-SEM allowed studying the sections of SRCW without applying any conductive evaporated films.

The VP-SEM analysis was performed at 20 kV of accelerating voltage. Backscattered electron (BSE) imaging was used. The brightness and contrast of BSE images are primarily a function of the average atomic number of the target in the sample. Uranium and mercury have high atomic numbers in the periodic table of elements. This indicates that any compound of uranium and mercury will necessarily have a high average atomic number. Such compounds should appear bright in BSE images. The un-hydrated cement phases and their hydration products are all compounds of elements of low atomic number (e.g. Ca, Si, Al, O). In BSE imaging, these compounds should appear much darker than the U or Hg compounds. Therefore, the strategy for the VP-SEM work was to search for bright areas in a BSE scan. Energy dispersive spectra (EDS) and U $L\alpha$ X-ray dots maps were obtained from the areas of interest.

3. RESULTS AND ANALYSIS

3.1. Chemical Characterization

As described previously, the SRCW was prepared by adding the solution to the cement in a pail. After a curing time of 28 days, each pail was cored at three different locations and sampled at each location at three different depths labeled top (T), middle (M), bottom (B). Table 2 presents the paste pH, paste conductivity (Ec) and % total solids and the chemical composition of the SRCW produced.

Table 2 - Pail physical characterization, SRCW, S/C =0.29

	Paste pH	Paste Ec mS/cm	% Total solids	Cs µg/g	U µg/g	Hg µg/g
U9-T1	12.7	29.4	96.6	3.60	200	318
U9-M1	12.4	26.7	92.5	6.82	600	905
U9-B1	12.4	30.5	93.1	7.90	647	827
U9-T2	12.7	26.5	97.0	2.84	95.9	162
U9-M2	12.5	29.8	89.5	7.42	730	1162
U9-B2	12.2	28.6	86.3	8.98	1362	1890
U9-T3	12.6	26.2	96.8	3.18	224	321
U9-M3	12.2	28.5	89.2	7.06	696	1058
U9-B3	12.1	30.8	85.4	5.75	2064	2857

The uranium vertical profile reflects significant concentration variations. Table 2 indicates that the uranium concentrations vary from a low of 95.9 µg/g to a high of 2064 µg/g at the top and the bottom section, respectively. The mercury concentration in the pail also demonstrated the high degree of heterogeneity in the pail. The amount of solution in contact with the cement in the pail is the principal factor affecting the chemical composition in the pail. During the pail preparation, the solution is pumped into the pail and the solution gets accumulated at the bottom of the pail. As a result, part of the cement in the pail is fully saturated whereas the top section remains unsaturated. The Cs concentrations show some vertical variation but relatively less pronounced. Vertical profile variation was also observed for the paste pH, as more solution remains in the bottom section, the acidity of the solution decreased the paste pH of the matrix.

3.2. Mineralogical Characterization

Understanding the variation in composition and structure of solid phases hosting the uranium and mercury in the SRCW is essential for the recovery and stabilization of these elements. Scanning electron microscopy (SEM) conducted in backscattered electron mode (BSE) sheds light on composition heterogeneity as a result of atomic number contrast. The VP-SEM characterization study clearly confirmed the presence of hydrated and un-hydrated cement particles. Elemental distribution can also be revealed by X-ray dot mapping. Figure 1 shows a BSE image of an area of the section with particles of different brightness. The darkest grains in Figure 1 are hydrated cement phases. The medium grey grains reflect un-hydrated cement phases. Figure 2 presents the result of U Mα X-Ray dot mapping of the same area as in Figure 1. Figure 2 shows that uranium is located in the brighter rims of the hydrated cement. Energy dispersive X-ray spectrometric analyses (EDS) of the rims indicated that uranium is associated with calcium, possibly occurring as calcium uranate phase (Figure 3). In the literature, it has been reported that the primary U(VI) binding mechanism on hardened cement paste was sorption, which could immobilize uranium in a solution of up to about 6 x 10^{-6} mol/L [4]. Above this concentration, immobilization was due to the formation of calcium uranate precipitate. During the hydration of cement, calcium hydroxide is formed mainly from the hydration of alite. Given the high uranium concentration in the solution (0.02 mol/L), the high calcium concentration in the SRCW (350 000 μg/g) and the high solubility of calcium hydroxide, precipitation is most likely the prevalent mechanism for uranium immobilization. Further characterization will provide more details on the uranium binding/precipitation mechanism(s). In general, it was not difficult to find areas enriched with uranium in the samples from the bottom part of the pails. On the other hand, it was difficult to find an area enriched with uranium for the top-section samples. Therefore the VP-SEM/EDS study also indicates a uranium distribution gradient. Less uranium occurs at the top and more uranium in the bottom of the SRCW pails.

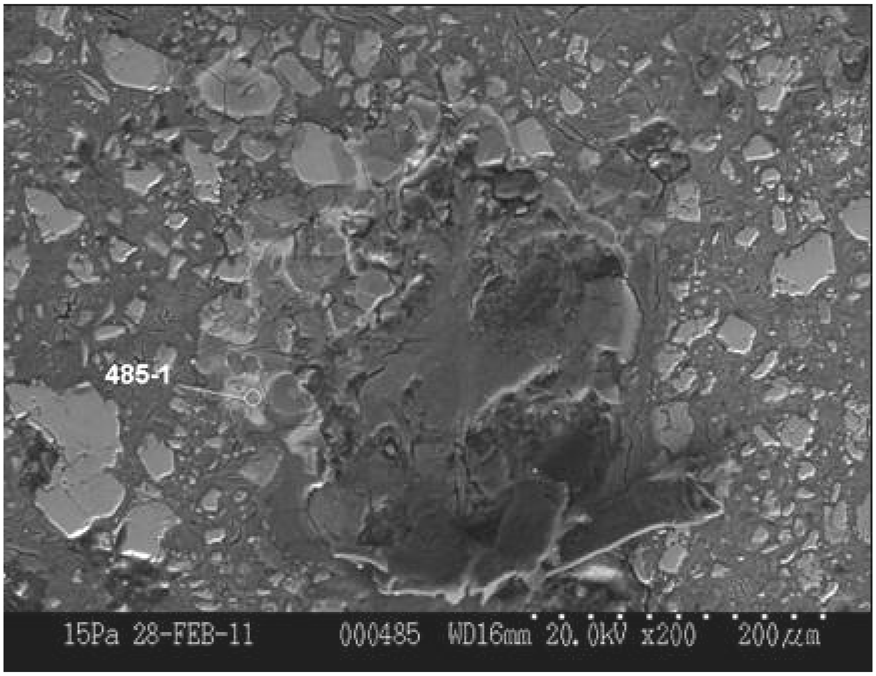

Figure 1 - SRCW bottom section: BSE image of an area showing particles of different brightness (located using U Mα X-ray dot maps)

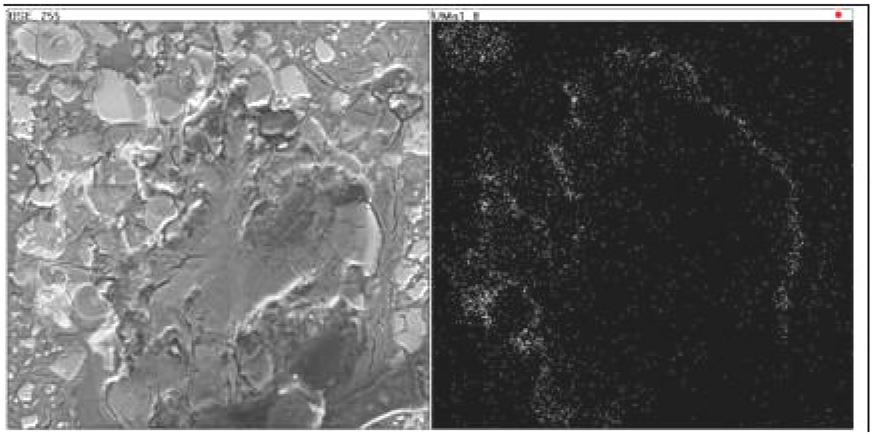

Figure 2 - U Mα Xray dot map (right) shows that an uranium-bearing phase is located at the rims of hydrated cement (bright areas of the BSE image, left)

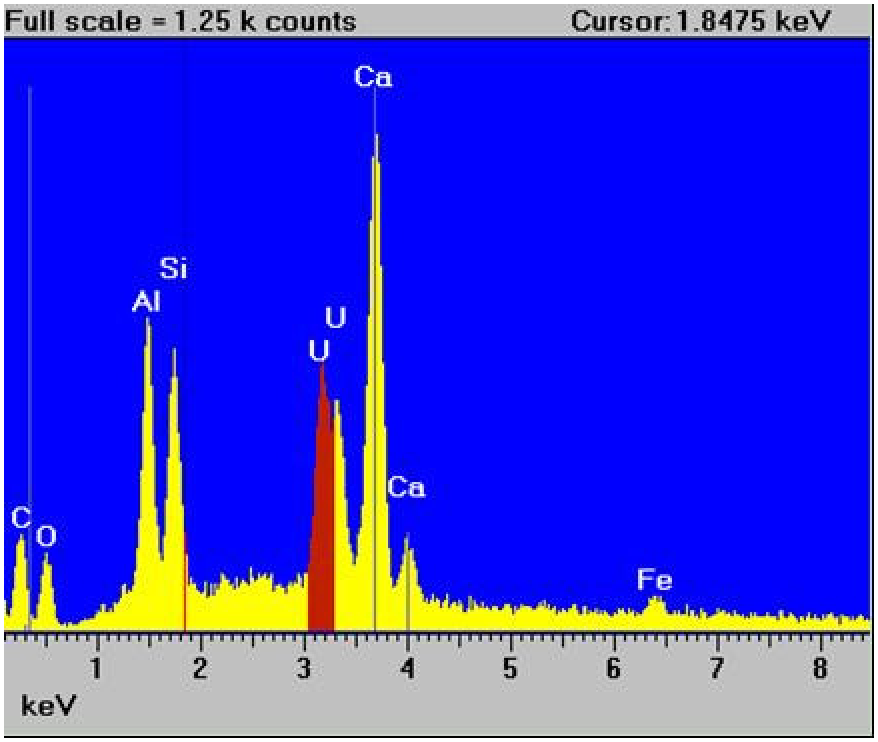

Figure 3 – EDS analysis of uranium located in Figure 2: Indicates a Ca-U phase in the hydrated cement. Possibly calcium uranate

In the presence of a mercury nitrate solution, hydroxide ions produced during cement hydration promote the precipitation of mercury oxide [5]. In the SRCW, mercury was located by SEM in the BSE mode (Figures 4 and 6). The EDS spectra (Figures 5 and 7) show very large peaks of mercury and a very low peak for oxygen, possibly corresponding to a mixture of metallic mercury and mercury oxide. To further clarify this, a sample of pure HgO was acquired and its EDS spectrum was obtained (Figure 8). The EDS spectra of the Hg-phase (e.g. Figure 5) in the

SRCW were very similar to the EDS spectrum for HgO (Figure 8). This indicates that the Hg-phase in the SRCW is mainly HgO. However, the presence of some metallic mercury cannot be completely ruled out because the HgO is not a very stable phase. Under slightly reducing conditions and moderate temperatures it will decompose to metallic mercury and oxygen. The heat generated during cement hydration may be enough to partially reduce the HgO. Therefore particles enriched in Hg in the SRCW must be mainly HgO with some metallic mercury.

The particle size of the Hg-phase was typically in the 5 to 8 µm range. This indicates that the SRCW must be finely ground to ~10-30 µm to expose the Hg phase to leaching solutions. In addition, the possible extraction of mercury by thermal dissociation would also require subjecting the SRCW to fine grinding.

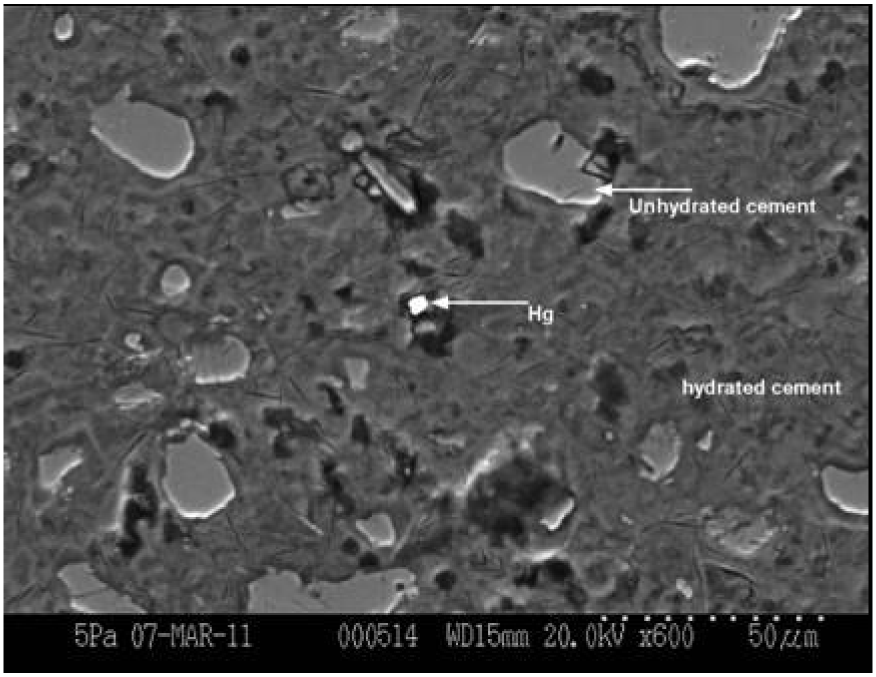

Figure 4 – Pail middle section: mercury, un-hydrated and hydrated cement

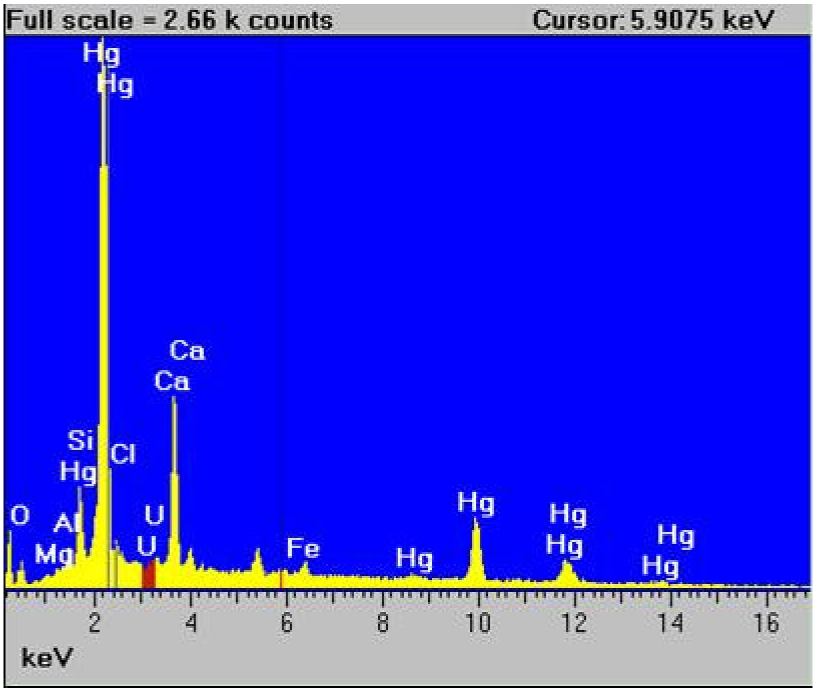

Figure 5 - EDS of the bright grain in the center of Figure 4, suggesting metallic mercury

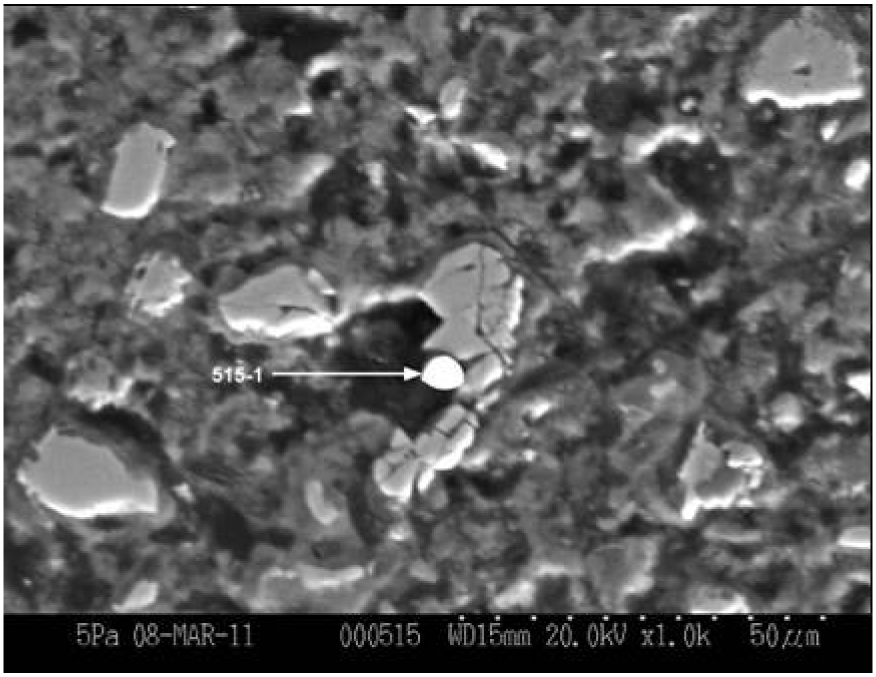

Figure 6 – Pail middle section: Area with bright BSE feature

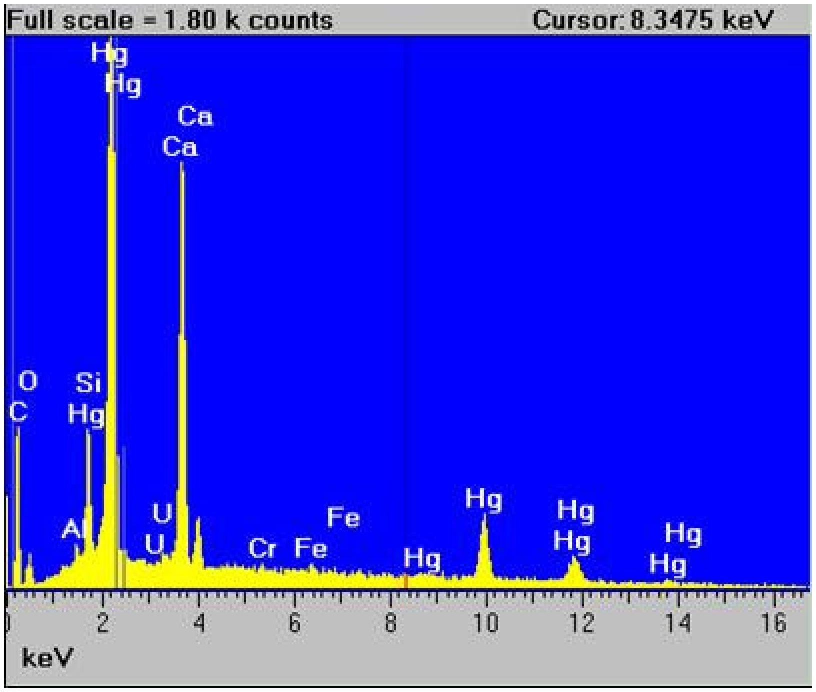

Figure 7 - EDS indicates the bright grain in Figure 6 is rich in Hg, mostly metallic Hg and possibly with some mercury oxide

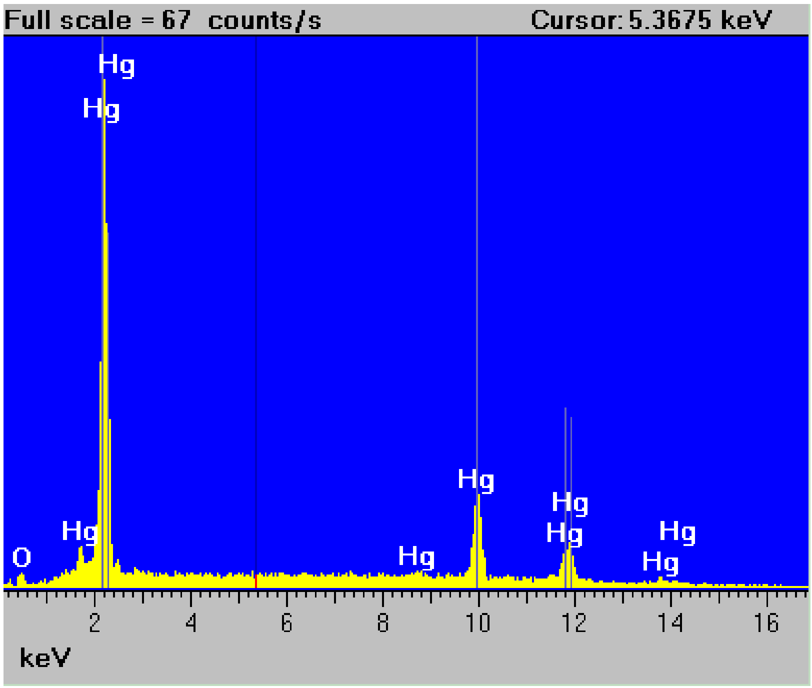

Figure 8 – EDS spectrum of pure HgO (red, hexagonal).

4. CONCLUSIONS

The preliminary characterization of the surrogate radioactive cemented waste revealed that uranium, mercury and cesium are not distributed evenly in the SRCW. The high level of heterogeneity in the SRCW pail is the direct result of the procedure used in preparing the cement pails.

Mineralogical characterization (SEM, EDS) showed that uranium is located at the rims of hydrated cement. It occurs possibly in the form of calcium uranate. Mercury was also found by SEM-EDS and the results suggest that it occurs in the form of mercury oxide. The elevated temperature (> 100°C) reached during the production of the cemented waste pails may lead to a partial decomposition of the HgO. Therefore the mercury in the SRCW is most likely present as HgO with some metallic Hg.

5. REFERENCES

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