CHARACTERIZATION, COMMINUTION, LEACHING AND ENCAPSULATION METHODS OF SURROGATE CEMENTED RADIOACTIVE WASTES

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Abstract

The medical isotope production at Chalk River Laboratory involves the dissolution of irradiated targets prior to extraction of Mo-99. This process generates a liquid that is cemented in a container and transferred to an outdoorwaste-management facility for intermediate storage. Over the past decades, AECL has produced a large number of containers of cemented radioactive waste that are in storage, and must develop a process to convert this material to a form suitable for permanent storage. Two methods were investigated:recovery of element of interests (Hg, Cs and U) and further cement encapsulation.

First, a proper comminution strategy was developed. Among the numerous technologies that were evaluated for unmolding, crushing and grinding the surrogate cemented waste, the high pressure water jet was selected for unmolding and coarse crushing; whereas the attrition mill was selected for fine grinding.

The composition of the surrogated cemented radioactive waste poses significant impediments to the extraction and recovery of uranium using conventional technology. Characterization of the surrogate cemented radioactive waste revealed that the uranium is precipitated as calcium uranate. Mercury exists as a combination of mercury oxide, elementary mercury, and with ageing, mercury sulphide is produced.

This research proved that the use of sulfuric acid withsalts allows the complete dissolutionof U, Cs and Hg by a combination ofacidification, complexation and oxidation. Mercury andcesium were recovered selectively with removal efficiencies reaching 99%respectively. A recovery of 98% for the U in sulfuric liquor was achieved using the chelating resin and high purity yellow cake was obtained by precipitation.

Macro and micro encapsulation formulations were also successfully developed for long term storage. The element recovery process offers the possibility of various waste management options whereas encapsulation methods offer a long term alternative to manage this type of waste.

Keywords: uranium, molybdenum waste, radioactive cemented waste, mercury and cesium

1. Introduction

The National Research Universal (NRU) reactor at Chalk River laboratories generates40% of the world's supply of ^{99m}Tc isotopes used to treat and diagnose several millionsof people every year [1].The isotope production involves the use of a target made from uranium and aluminium that is irradiated for a period of 10 to 15 days in the NRU reactor which produces fission products.One fission product that is produced isthe Molybdenum-99 (^{99}Mo) isotope.It has a half-life of 66 hours, then decays to technetium (^{99m}Tc), which is used for a variety of nuclear medicine and diagnostic procedures.The medical isotope production involves the dissolution of the target using a combination of nitric acid and mercuric nitrate to enhance the process. Then, the ^{99}Mo is extracted using an alumina column and the liquid residue undergoes a cementation process resulting in pails of cemented waste. Once produced, the pails are transferred to an outdoor waste management facility for storage in a concrete tile hole. Over 7,000 containers of cemented waste have been stored for the last 40 years. Investigations are needed to assess the container degradation and find a long term solution to this type of waste. This waste has enriched uranium and several fission products. Approximatively 97% of the uranium present in the targets ends up in the process waste [2]. This enriched uranium can be reused but it is presumably more expensive to reprocess this material compared to the purchase of fresh enriched uranium. However, since the 1990s, Canada has joined global non-proliferation efforts and has furthered this commitment by agreeing to send back used enriched uranium to the U.S. to help consolidate enriched uranium inventories in fewer locations.

The aim of this project is to develop technologies that would offer a long term solutions for this type of waste.CanmetMINING prepared surrogate radioactive cemented waste (SCRW) following procedures and conditions that simulatedthoseused by the Canadian Nuclear Laboratories (CNL). The specimens were also subjected to ageing conditions to simulate the long-term storage conditions in the field. The objectives were to characterize the radioactive cemented waste, define appropriate comminution and sampling strategies, recover the uranium, mercury and cesium, and to develop a suitable encapsulation method.

Characterization of the surrogate is essential to predict and understand the behaviour of the material under various storage conditions and to provide long term solutions either by the recovery of key elements such as the Hg, U and Cs or by developing encapsulation methods. Fragmentation of the surrogate into a size range suitable for characterization, leaching and encapsulation is required.Health and safety is an important issue to be considered during the surrogate fragmentation and large volumes of dust must be avoided. The representativeness of the sample and the impact of the sampling and measurement errors on the study conclusions are very important questions requiring adequate answers and were given full consideration.With the cemented radioactive waste, the design and assessment of the sampling strategy should be given even more attention considering the necessity to keep a very accurate inventory of the three main contaminants of interest, which are Hg, Cs and U.

2. Methodology

2.1 Production of Surrogate Cemented Radioactive Waste (SCRW)

The first step was to produce SCRWthat mimic the waste that is stored at the Chalk River Laboratories. Over decades of production of cemented radioactive waste at Chalk River, variations in the granulometry, mineral phases and chemical composition of the cement are most likely possible. Portland cement finesses have generally increased over the years to accelerate the strength development of concrete in the construction industry. To simulate variations of the cement granulometry, two different types of cement were used in this project. Portland cement for General Use (GU, formerly known as type 10) and High-Early strength cement (HE, formerly known as type 30) were obtained from Lafarge.A total of 40 SCRWwere produced from a solution containing U, Al, Hg and several other elements (Rb, Cs, Sr, Ba, Ru, La, Ce, Pr, Nd, Sm, Eu, Gd, Y, Fe, Ni and Cr) at trace level. The solution was added to cement to produce the SCRWas described by Fiset et al. [3]. Details of the solution used to prepare the SCRW are given in Table 1.

Table 1 Summary of constituents for solution

Constituent	**Concentration mol/L**	**Chemical form**	**Formula weight**	**Amount required for 4.5L**
			g/mol	g
Aluminum	0.98	$Al(NO_3)_3.9H_2O$	375.13	1650
Uranium	0.020	$UO_2(NO_3)_3.6H_2O$	502.13	45.2
Mercury	0.033	$Hg(NO_3)_2.H_2O$	342.61	50.9
Rubidium	7.53E-05	$RbNO_3$	147.47	0.05
Caesium	2.19E-04	$CsNO_3$	194.91	0.192
Strontium	2.96E-04	$Sr(NO_3)_2$	211.63	0.281
Barium	2.29E-04	$Ba(NO_3)_2$	261.35	0.269
Ruthenium	3.02E-04	$Ru(NO_3)_3$ (1.5% solution)		9.16
Lanthanum	1.44E-04	$La(NO_3)_2.6H_2O$	433.02	0.281
Cerium	3.89E-04	$Ce(NO_3)_3.6H_2O$	434.23	0.76
Praseodymium	1.01E-04	$Pr(NO_3)_3.6H_2O$	435.03	0.198
Neodymium	2.84E-04	$Nd(NO_3)_3.6H_2O$	438.35	0.561
Samarium	3.40E-05	$Sm(NO_3)_3.6H_2O$	444.46	0.068
Europium	4.38E-06	$Eu(NO_3)_3.6H_2O$	446.07	0.009
Gadolinium	1.41E-06	$Gd(NO_3)_3.6H_2O$	451.36	0.003
Yttrium	1.28E-04	$Y(NO_3)_3.6H_2O$	383.01	0.22
Iron	1.0E-03	$Fe(NO_3)_3.9H_2O$	404.0	1.82
Nickel	1.8E-04	$Ni(NO_3)_2.6H_2O$	290.81	0.23
Chromium	3.3E-04	$Cr(NO_3)_3.9H_2O$	400.15	0.59
Nitric acid	0.36	HNO_3 (16M)		100 mL

2.2 SCRWCharacterization

After an ageing period of 28 days, the SCRW were sampled by core-drill at three different locations.Then, each core was divided into three different sections (top, middle and bottom). The

SCRW was generally friable; therefore, most cores were made up of fragmented material. Total solids, paste pH and paste conductivity were also measured for each sample. 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 analysis 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 a microwave oven but with HCl only.Fragmentsof 30 ± 10 mm from the top, middle and bottom were selected for the preparation of polished sections. The polished sections were examined using a variable pressure scanning electron microscope, VP-SEM (S-3200, Hitachi) equipped with an energy dispersive X-ray analyser, EDS (Link Pentaflex detector and ISIS analysing suite, OXFORD).The VP-SEM allowed studying the sections of SCRW 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 Lα X-ray dots maps were obtained from the areas of interest.

2.3 Comminution

Hardness of the surrogate waste was characterized by the Bond Work Index and the JKTECK abrasion index. Efficiencies of four comminution mechanisms were compared: compression (jaw and cone crushers, rod mill), impact (ball mill), attrition and high voltage fragmentation. Health, safety and waste water management capabilities were given high consideration in this comminution technology assessment study.

Pressure Water Jet technology was the technology retained for unmoulding the waste and for coarse fragmentation. Wet attrition grinding was the technology retained for fine comminution. A less sturdy grinding chamber was built that could serve for unmoulding, grinding, leaching and as a disposal vessel. Two alternative attrition milling methods, basket milling and attrition milling in the absence of grinding media (autogenous), were evaluated for simplifying the process operation. A pail holder was designed, built and tested for manipulating the pail and for separating the plastic and metal. Cryogenic fragmentation was also tested as a possible alternative to wet grinding.

A laboratory comminution process, aiming to provide representative and suitable samples to the lixiviation testwork, was designed based on the selected comminution technologies. The laboratory process sampling scheme and a process monitoring methodology were designed based on P. Gy's sampling theory [4], its variant proposed by D. François-Bongarçon, and the material balance data adjustment technique BILMAT, which was developed in the 80's for assessment, diagnostic and

improvement of process measurement estimates in the mineral processing industry. A pilot scale version of the laboratory process was designed, built and tested. For some trials, surrogate cemented waste (SCW) were produced only using aluminium nitrate and nitric acid (Table 1).

2.4 Leaching AndRecovery Of Key Elements

The leaching experiments were done by mixing 50 g of the SCRW with 500 mL of solution to obtain a pulp density (PD) of 10% v/w. Agitation was performed using an immersed axial impeller or by magnetic stirring set at 300 rpm. The solution was filtered onto Whatman No. 4 cellulose paper (porosity = 20–25 μm). The residue and filter were dried at room temperature. The recovery experiments using ion exchange were conducted using an Omnifit column (Diba Inc.) with a bed volume of 12 mL.The leachate was passed through the resin using a peristaltic pump (Masterflex) at a flow rate of 3 BV/h. An automatic fraction collector (Eldex Laboratories) was used to take samples of the column effluent. Uranium was eluted from the resin with 1 M Na_2CO_3 and precipitated using sodium hydroxide.

2.5 Micro-encapsulation Methods

For micro-encapsulation, the SCW was simply reduced to a particle size suitable for mixing with cementing material and water to form a homogeneous solid matrix. In a first phase, using dry-processed SCW, a range of suitable mixture proportions was identified based on mechanical properties and resistance to cesium leaching.The “General Use” (GU) Portland cement as defined in the CSA standards [5] was used in most of the experiments.Different supplementary cementing materials (SCMs) were used: two types of fly ash, one type of ground granulated blast-furnace slag and two types of silica fume.Fly ash is a very fine particulate residue that results from the combustion of pulverized coal in power plants.Both an ASTM Class F (low calcium) fly ash and an ASTM Class C (high calcium) fly ash were used [6].Ground granulated blast-furnace slag is a by-product from the production of pig iron.Silica fume, a very fine material, is a by-product of the production of metallic silicon or ferrosilicon.The chemical analysis and the physical properties of the cements and of the various SCMs are presented elsewhere [7].Zeolites were also used in some mortars.Zeolites are microporous aluminosilicate minerals that have the ability to selectively sort molecules based primarily on the size exclusion process.Based on the size of the molecules, the zeolites can capture some ions while allowing others to pass freely.It is believed that the zeolites in the mortars could capture some of the cesium and thus reduce the leaching of that element from the mortar.Three different zeolites, two natural (Clinoptilolite and Chabazite) and one artificial (Molecular Sieve 3A) were used in the study.

3. Results

3.1 Characterization

SCRWspecimens were produced according to the specification of CNL using a containment glove box.The solution used to generate the SCRW contained uranyl nitrate, mercury nitrate, aluminium nitrate and several others (Rb, Cs, Sr, Ba, Ru, La, Ce, Pr, Nd, Sm, Eu, Gd, Y, Fe, Ni and Cr) at trace levels.The characterization revealed that the added metals are not distributed evenly in the SCRW.The high level of heterogeneity of the SCRW is the direct result of the procedure used in making the cement pails[3].Mineralogical characterization by SEM-EDS revealed that the uranium

in the SCRWis present as a Ca-U-O compound that has variable composition and is amorphous.This compound is the product of a reaction between the calcium hydroxide (from the hydration of cement) (Figure 1)and the uranium in the solution.

After the passage of extremely long times, these compounds reach equilibrium, get a fixed composition and a crystalline structure.For the purpose of this report, the Ca-U-O compound found in the SCRW is referred to as calcium uranate. The calcium uranate in the SCRW can be found as small grains of ~20 μm and as long layers of ~1x5 mm. In fresh SCRW prepared with GU cement, the calcium uranate is mostly small grains dispersed in the matrix, whereas when HE cement is used, the calcium uranate is present in very well defined reaction layers.

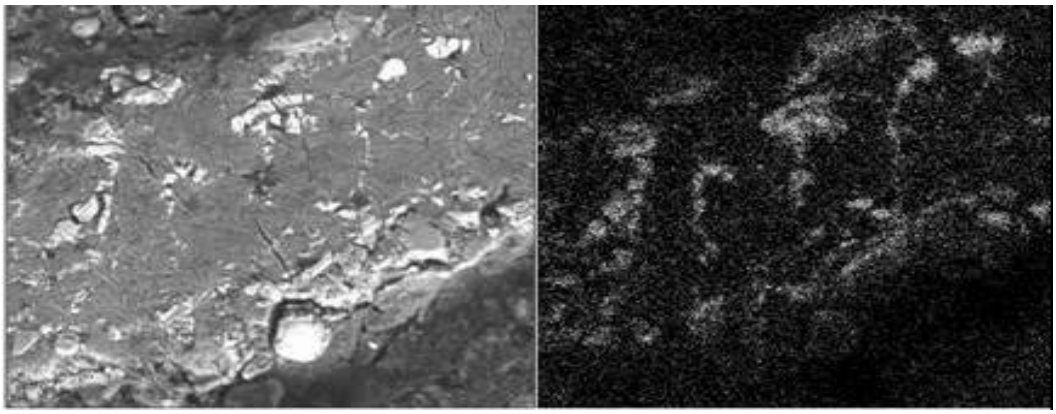
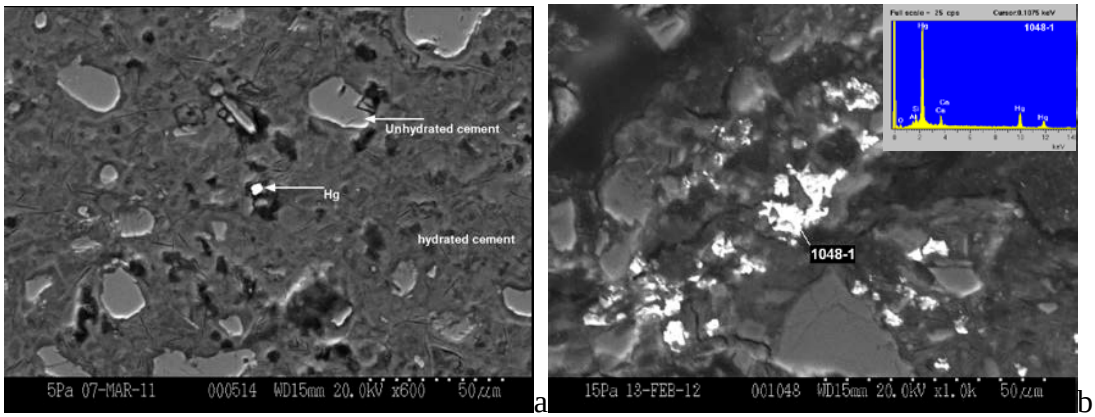


Figure 1SCRW:X-ray dot map showing grains enriched with uranium

The mercury in the SCRW originated from the precipitation of inorganic (mercuric nitrate solution) with a base (lime available from the cement hydration) to produce a mercuric oxide precipitate (Figure 2a). Mercury in the SCRW occurred as spots, as small as sub-micrometer size, with tendency to agglomerate into large (~ 50 μm) spots. It is quite possible that the reduction potential of the SCRW was enough to partially reduce the mercury oxide to metallic mercury. The mercury spots in the SCRW appear to be a combination of mercury oxide and metallic mercury (Figure 2b). The mercury spots appear to agglomerate more with time and at high curing temperature. It is likely that the proportion of metallic mercury will increase with time and at high curing temperatures. Thus the leaching will sulphuric acid alone willleavemore metallic mercury and will require removal by thermal distillation. Sub-micrometer mercury spots are likely to have poor liberation by comminution to ~10-20 μm. Large mercury spots will liberate easier than sub-micron spots.



a b

Figure 2SCRW: EDS spectra of agglomerated mercury oxide (a) and elemental mercury (b)

3.2 Comminution

A sampling scheme was developed, calibrated and validated using SCRW. The main challenges addressed are the no-mass transfer assumption between solid and liquid phases in BILMAT, versus the transition of solid into the liquid phase due to lixiviation and vice versa due to the hydration of a large proportion of cement still un-hydrated in the waste.

SCRW was confirmed to be a friable and low abrasive material with a Bond work index of 7.7 kWh/t. Dry grinding was selected for the laboratory comminution process because it facilitates the splitting of the waste and provides samples without any possible dissolution required for the leaching experiments. Process equipment includes a laboratory jaw crusher, a disc mill, an attrition mill Model 01 HD from Union Process, a 20 kg capacity rotary table sample splitter designed by TM Engineering, a micro rotary riffler Model LA 817103 from Quantachrome and a rotary cone sample divider Model Laborette 27 from Fritsch.

At pilot scale, a wet comminution process was given preference for containing more efficiently the radioactive dust. The main piece of equipment included in the pilot scale comminution process are a Gardner Denver High Pressure Water Jet (HPWJ), Model 100-20H-E, for unmolding and coarse crushing the waste, and a Union Process Attrition Mill, Model S-30, for fine grinding the waste.

In the proposed comminution flowsheet, the SCW is unmoulded and coarse crushed by HPWJ inside the grinding chamber for minimizing pulp transfer and equipment contamination. HPWJ fragmentation is done at 19 kpsi for 2 minutes. Excess water produced by the unmolding process is decanted and transferred to the leaching process where calcium ions are transformed into calcium sulphate,then removed as precipitate. A pail holder was designed, built and tested for manipulating the pail within the grinding chamber and for separating the plastic and metal.

Pilot scale testwork demonstrated that fine grinding can be done in a less sturdy grinding chamber, which can subsequently serve as a lixiviation and disposal vessel. Basket milling was found as efficient as attrition milling for fine grinding the waste down to 20 µm, with the exception of the fraction of residual pebbles (larger than 5 cm and most probably unsuitable for lixiviation), which increased from 0.5 to 2.5%. There is no indication that the residual pebbles would accumulate in the grinding media; however some concerns were expressed regarding the total mass balance of the contaminants for a

batch processing. The requirement of a mechanism for manipulating the basket, and for washing both the media and the external side of the basket are two additional difficulties with the basket mill option.

A grinding chamber was successfully designed for grinding the SCW in the absence of grinding media. This autogenous grinding mode is a simpler process and was considered as preferable, if the long term research on lixiviation confirms that a top particle size of 6 mm is suitable for the three contaminants (Hg, Cs, U) lixiviation. So far the leaching experiments indicate that the maximum particle size achieved by autogenous grinding can be reduced to ~ 4 mm. Grinding the waste in absence of grinding media requires about 2-hours at 60 RPM for batches of 60 kg of solid waste diluted at 60% pulp density. The grinding chamber must be equipped with both bottom and side deviation rods that leaves a clearance between the attrition impeller and the bottom and side of the grinding chamber to 3 mm and 11.5 mm respectively. A 3-layers stainless steel drum was identified as the minimal requirements for a less sturdy grinding chamber that can subsequently serve as an unmolding, lixiviation and disposal vessel. A sampling scheme was designed and validated for this coarser material produced in autogenous mode.

3.3 Leaching and Recovery

The technology for recovering uranium from its most common ores is well established and a vast amount of information is available in the technical literature [8,9]. By contrast, the cemented waste differs significantly from common uranium ores. The cemented radioactive waste has a unique mineralogy, a high pH, a relatively low U grade, and a high content of Ca (~35%), SiO_2 (~20%) and Hg (~1,500 ppm). The composition of the cemented radioactive waste poses significant impediments to the extraction and recovery of uranium using conventional technology. The high Ca content will interfere with both carbonate leaching and sulfuric acid leaching by forming large amounts of $CaCO_3$ and $CaSO_4$, respectively. Furthermore, the high silica content of the cemented radioactive waste may lead to the formation of colloidal silica, which is known to create severe problems in hydrometallurgical circuits [10]. Ion exchange systems have a higher tolerance to colloidal silica, but the adsorption of U on strong-base anionic in chloride media requires a high HCl concentration (>4M) and under these conditions, Fe(III) is also strongly adsorbed on the resin [11,12]. The extraction of U from sulfuric acid media using anion exchange resins has been widely applied and is well-documented[8,9]. The adsorbed uranium is usually eluted (desorbed) from the resin with dilute HCl or HNO_3 solutions and subsequently precipitated with ammonia or magnesium hydroxide.

3.3.1 Key Elements SolubilizationIn Old Wastes

In previous work [13], lower Hg recovery was obtained for the SCRW cured at 60°C. This result was attributed to the presence of more Hg^0, which does not dissolve in sulfuric acid, or to the formation of slightly soluble mercuric basic sulfate, $2HgO{\cdot}HgSO_4$ but could be due to the formation of insoluble mercury sulfide [14]. Various SCRW cured at 60°C and/or aged during 30 months were subjected to leaching using sulfuric acid and potassium iodide. A 50 g sample of SCRW crushed at 0.3 mm was mixed with 500 mL of distilled water to obtain a 10% pulp density. Potassium iodide was also added to obtain a concentration of about 1.2M. Then pure sulfuric acid was added to obtain a concentration of about 1M. Agitation using an immersed impeller during 2 hours at ambient temperature was performed. Table 2 presents the solubilisation of Cs, Hg, and U from five mentioned SCRW using sulfuric acid and potassium iodide (particle size = 0.3 mm, t = 120 min, H_2SO_4 = 1M, PD = 10%, T = 20°C, KI = 1.2M). For all the tested SCRW, solubilisation yields are above 97% for Cs and 98% for U and Hg.

Sulfuric acid and potassium iodide improves the solubilisation of Hg by a combination of oxidation, acidification and complexation and form mercury tetraiodide complex (HgI_4^{2-}, $K_f = 5.6.10^{29}$) [15].

Table 2Cs, Hg, and U solubilisation yields from five different SCRW using sulfuric acid and potassium iodide. Particle size = 0.3 mm, t = 120 min, H_2SO_4 = 1M, PD = 10%, T = 20°C, KI = 1.2M.

Batch Code	Initial Cs (ppm)	Initial Hg (ppm)	Initial U (ppm)	Cs removal yields (%)	Hg removal yields (%)	U removal yields (%)
U13	3.5	1,116	893	98.0	99.5	99.4
U28	8.5	1,973	1,150	99.1	99.6	99.3
U29	7.2	1,977	1,104	98.0	99.8	99.5
U32	6.0	1,277	850	98.7	99.7	99.3
U34	8.0	2,651	1,355	98.9	99.1	99.7

3.3.2 Separation AndRecovery Of Uranium

Ion exchange was considered the best method to separate the uranium from the impurities and to produce a purified and concentrated uranium solution suitable for yielding a uranium product. The extraction of U from sulfuric acid media using ion exchange resins has been widely applied and is well documented[8,9]. The Lewatit TP260 resin was selected to perform several ion exchange tests with sulfuric acid leachates obtained at different iodide concentrations from 1 g/L to 100 g/L. Best breakthrough was obtained with the 50 g/L KI leachate. A good uranium uptake was also obtained with the 100 g/L KI leachate, which has the highest initial U concentration. Resin capacity reached 6 mg/g and a breakthrough of 60 BV was obtained.Uranium loaded in the Lewatit TP260 chelating resin was eluted using several stripping reagents. The best uranium stripping from the resin was obtained using 1M sodium carbonate, which allows 99% of uranium recovery.Uranium is commonly precipitated from solution using MgO, NaOH, NH_4OH or H_2O_2 [8,16]. Several experiments were done to produce yellow cake from the elution solutions.Figure 3 presents an optical microscope photograph and the typical EDS spectrum of the SDU yellow cake from the U recovery in sulfuric and iodide media and precipitation using sodium hydroxide. The EDS spectrum of the yellow cake indicates it is a Na-U-O compound with a high concentration of uranium and minor impurities of Si, P, and Al.

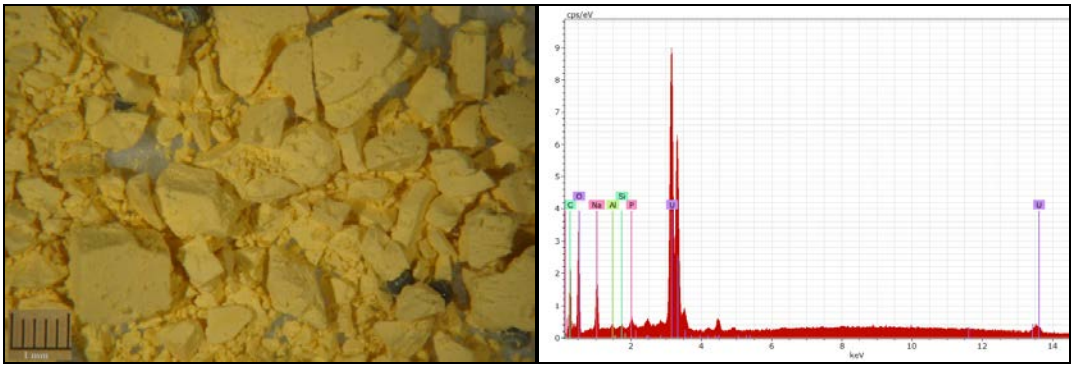


Figure 3Optical microscope photograph and EDS spectrum of the uranium precipitate (SDU) from the U recovery in sulfuric and iodide media and precipitation using sodium hydroxide.

3.3.3 Leaching Summary

Sulfuric acid leaching with KI media in optimized conditions allow key elements recovery yields of about 97% for Cs and 98% for U and Hg. This was validated with different SCRW batches, including old SCRW cured at 60°C. The large volumes of $CaSO_4$ formed in the process can be disposed in an appropriate manner as the Hg level is below the USEPA value. The Cs and Hg in the leachate are removed using potassium cobalt ferrocyanide (KCFC) and a thiol resin (Lewatit TP214 or Dowex XUS 43604), respectively. Hexacyanoferrates such as KCFC have been used industrially for the recovery of cesium from nuclear liquid wastes because of their high affinity for the Cs^+ ion. Chelating ion exchangers, such as thiol-functionalized resins, have a high affinity for mercury and the chelating ability is not vulnerable to ionic complexation of Hg^{2+} in media. The absorbents loaded with Cs and Hg can be disposed of in an appropriate manner. Then the U-bearing leachate, which also contains large amounts of Al, Fe and Ca, is contacted with a chelating resin (Lewatit TP260) that adsorbs the U, but also some base metals. The resin loaded with U is eluted with 1M Na_2CO_3 to desorb U selectively. The U-bearing eluate is treated with NaOH solution to precipitate sodium diuranate (yellow cake). The yellow cake produced in the process is a Na-U-O compound with a high concentration of uranium and minor impurities. The XRD pattern indicates the yellow cake is partially crystalline and identifies it as a sodium uranium oxide.

3.4 Microencapsulation Methods

For health and safety considerations, the first phase of experiments was done using SCW i.e.notincorporating mercury or uranium. Following this, the mixtures were validated using SRCW i.e. incorporating both Hg and U.

3.4.1 Producing And TestingTheMicro-encapsulation Mixtures

The method for producing and testing the mortars for workability (flow) and compressive strength were adapted from appropriate ASTM standard proceduresused for portland cement mortar testing [11]. The curing procedure used for most of the mortar specimens was to wrap them in a thin plastic film, then with a layer of wet tissue followed by a second layer of thin plastic film. Those were then put in a plastic bag, which was sealed and stored at room temperature (23°C) until required for testing. With this method, the specimens were prevented from drying, and no external moisture was provided to the specimens. This curing procedure was selected to reproduce what would probably be the actual conditions for the material in the field.The selected test method for assessing the leaching resistance of the mortars was the American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by Short-Term Test Procedure (ANSI/ANS-16.1), published by the American Nuclear Society [18]. Briefly, the procedure can be described as the following:

- Mortar specimens are immersed in demineralised water for different time intervals.
- At the end of each leach interval the specimen is transferred to a new container with fresh leachant (demineralised water) and sample of the leachant is taken for chemical analysis for determining the content of the species of interest
- The leachability index (L) was determined, after 7 days for the standard test or after 91 days for the extended test.

In these tests, higher values of the leachability index indicate a better resistance of the mortar to leaching.For several mixtures, the pore solution was extracted from the mortars at different ages and analyzed to determine the concentration of the elements of interest. The pore solution was extracted from a sample of approximately 250 g of mortar using a steel die following a specific procedure [19].

3.4.2 Development OfMixtures Without Mercury Or Uranium InThe SCW

A large number of mortars were made using different cementing materials-to-SCRW (CM/SCRW) and water-to-cementing materials (W/CM) ratios, and incorporating various proportions of supplementary cementing materials (SCMs) and zeolites as partial replacement for cement. The proportion of slag and fly ash ranged from 30 to 50% whereas that of the zeolites from 7 to 20%. Two percentages (7 and 10%) of silica fume were used either as single replacement for cement or in combination with 30% slag or fly ash.Fine (4.5 mm maximum size) and coarse (12.5 mm maximum size) SCW materials were also used. The effect of the SCRW composition was also examined. It was found that themaximum particle size of the crushed SCRW (12.5 mm vs 4.5 mm) did not have a significant effect on the workability or the strength of the mixtures. Also, neither the slag nor the fly ash used had a significant effect on the workability whereas the silica fume and the zeolites slightly reduced it.

The levels of compressive strength achieved by all the mortars investigated were more than adequate, in general with values exceeding 20 MPa at 7 days and 30 MPa at 28 days. Silica fume contributed to increase the strength of the mortars.Actually, the strength was surprisingly high given the range of W/CM used in the mixtures, i.e., approximately 0.9 to 1.6. The data confirmed the contribution of the un-hydrated cement present in the SCRW to the strength development of the mortars. If there is no un-hydrated cement left in pails stored in the field for several years, or only a negligible amount, then the proportions of the actual micro-encapsulation mortars may need to be adjusted accordingly.All mixtures performed well in the leach test with leachability index (L) values ranging from 6.9 to 9.1. The leaching resistance increased significantly (higher L values) when 50% slag or a combination of 30% slag and 7% silica fume were used in the mixture. The use of 10% Chabazite zeolite ($L \approx 8.5$) resulted in a good performance in the leaching test. The pore solution Cs concentration of the mixtures incorporating the Chabazite zeolite was considerably lower than that of the other mixtures tested in this part of the study indicating the ability of the zeolite to immobilize cesium ions.

3.4.3 Validation OnMortars Made With SCRW

A number of mixtures identified as potentially suitable for micro-encapsulation were validated using SCRW containing U and Hg. Mixtures with different proportions of slag, silica fume and Chabazite zeolite were made(Table 3). The CM/SCRW and W/CM of the mortars were 0.32 and 0.99, respectively. As shown in Table 3, the presence of U and Hg had no noticeable effect on the compressive strength development. Strength values of the mortars are remarkably high.

Table 3 Proportions and properties of mixtures for the leach test on mortarsincorporating U and Hg.

Mix.	Pail	Cement, %	Slag, %	Silica Fume, %	Zeolites, %	Flow, %	Compressive strength, MPa	
							28 days	91 days
UM1	U9	100	0	0	0	120	39.5	46.8
UM2	U9	63	30	7	0	108	42.5	49.5
UM3	U9	90	0	0	10	96	47.3	51.3
UM4	U9	53	30	7	10	89	43.5	56.3

UM5	U9	70	30	0	0	124	42.3	51.6
UM6	U9	93	0	7	0	106	46.7	52.4

The leaching resistance of the mortars for cesium was not affected by the presence of U and Hg in the mortars ($7.9 < L < 9.2$). Once again, the use of SCMs improved the cesium leaching resistance, and in particular the use of 10% Chabazite resulted in superior Cs leaching resistance ($8.9 < L < 9.2$). The leaching resistance for Hg was excellent for all the mixtures with L values above 10. The Hg leaching resistance was remarkably improved by the use of slag in the mortars with L values above 13. This is probably due to the presence of sulphides in the slag; sulphides are commonly used for stabilization of Hg in waste stabilization technology [20-22]. The leaching resistance for U was very high for all mixtures with L values ranging from 14.6 to 17. The pore solution analyses are in line with the results from the leach test. The concentrations of Cs were significantly lower when Chabazite zeolites were used in the mortars whereas those of Hg were considerably reduced when slag was used. Also, the concentrations of U were very low for all the mortars.This is probably due to the formation of calcium uranate resulting from the reaction between U and $Ca(OH)_2$, which is produced by the hydration of cement [23]. The solubility of calcium uranate in water is low [24].

4. Conclusion

Significant amount of research was completed on the surrogate cemented radioactive wastes. The surrogates used within the scope of study provided much more flexibility in handling the material compared to what is technically possible to be done in a hot cell on active material. Understanding the chemical and mineralogical characteristics of the surrogates was essential in developing technical solutions that can be used for a long term disposal strategy. Characterization of the radioactive waste surrogate revealed that the uranium is as calcium uranate. Mercury exists as a combination of mercury oxide, elementary mercury and with ageing, mercury sulphide is produced. This research proved that the use of sulfuric acid with salts allows the complete dissolution of U, Cs and Hg. Mercury and cesium were recovered selectively from the leach solution with removal efficiencies reaching 99%. The U recovery from sulfuric liquor using the chelating resin was 98% and high purity yellow cake was obtained by precipitation. Micro encapsulation formulations were also successfully developed for long term storage. The next step for this project will be to validate the comminution, characterization, leaching and recovery and encapsulations methods on active material.

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