Uranium, Cesium, and Mercury Leaching and Recovery from Cemented Radioactive Wastes in Sulfuric Acid and Iodide Media

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Abstract: The Canadian Nuclear Laboratories (CNL) is developing a long-term management strategy for its existing inventory of solid radioactive cemented wastes, which contain uranium, mercury, fission products, and a number of minor elements. The composition of the cemented radioactive waste poses significant impediments to the extraction and recovery of uranium using conventional technology. The goal of this research was to develop an innovative method for uranium, mercury and cesium recovery from surrogate radioactive cemented waste (SRCW). Leaching using sulfuric acid and saline media significantly improves the solubilization of the key elements from the SRCW. Increasing the NaCl concentration from 0.5 to 4 M increases the mercury solubilization from 82% to 96%. The sodium chloride forms a soluble mercury complex when mercury is present as HgO or metallic mercury but not with HgS that is found in 60 °C cured SRCW. Several leaching experiments were done using a sulfuric acid solution with KI to leach SRCW cured at 60 °C and/or aged for 30 months. Solubilization yields are above 97% for Cs and 98% for U and Hg. Leaching using sulfuric acid and KI improves the solubilization of Hg by oxidation of Hg^0, as well as HgS, and form a mercury tetraiodide complex. Hg and Cs were selectively removed from the leachate prior to uranium recovery. It was found that U recovery from sulfuric leachate in iodide media using the resin Lewatit TP260 is very efficient. Considering these results, a process including effluent recirculation was applied. Improvements of solubilization due to the recycling of chemical reagents were observed during effluent recirculation.

Keywords: uranium; radioactive wastes; sulfuric leaching; iodide media; cesium; mercury; ion exchange

1. Introduction

Canadian Nuclear Laboratories (CNL) is developing a long-term management strategy for an inventory of cemented radioactive waste, which contains uranium, mercury, fission products, and a number of minor elements. An earlier study indicated that extracting the uranium would be advantageous for decreasing the radioactivity of the waste and, consequently, reducing the hazards and cost of long-term management [1]. Two recent literature reviews indicated that the cemented waste would be amenable to conventional stabilization procedures, although the effective immobilization of Hg and Cs may be challenging because of their relatively high water mobility and

weak chemical interaction with the cement matrix [2,3]. Consequently, there are safety and economic incentives for the extraction of uranium, mercury and cesium before subjecting the cemented waste to a stabilization process.

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 [4,5]. Uranium is normally leached from its ores with sulfuric acid, separated from impurities using solvent extraction or ion exchange, and precipitated with magnesium hydroxide or ammonium hydroxide to yield a commercial product, known as **"yellow cake"**. By contrast, the cemented waste differs significantly from common uranium ores, mostly hosted in quartz or granite with typically more than 40% silica. The cemented radioactive waste has a unique mineralogy, a high pH, a relatively low U content, and a high content of Ca (~35%), SiO_2 (~20%) and Hg (~1500 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 [6].

Prior work of this research was focused on the optimization and validation of a process for U, Hg and Cs leaching from SRCW (Surrogate Radioactive Cemented Waste) developed by Riveros *et al.* [7]. In previous work [7,8], lixiviants selected using information found in the technical literature were tested to solubilize efficiently both uranium and mercury. Sulfuric acid and carbonate salts were tested because they are used industrially to leach U from common ores [4,5,9]. Hydrochloric acid is used to dissolve cement/concrete for analytical purposes [10]. Nitric acid was tested because it has been used to leach U and other fission products from radioactive waste [11]. Ammonium nitrate was tested because ammoniacal solutions have been used to leach Hg from fly ash and other matrices [12–15]. Caustic dissolution tests for the recovery of U from radioactive waste have also been performed [16,17]. Kitts and Perona tested dilute aqua regia for the treatment of Stainless Steel-Uranium Fuels [18]. Lime has been used for the dissolution of vitrified wastes in a high-pH calcium-rich solution [19]. A mix of carbonates (Na_2CO_3/NH_4HCO_3) was also tested at room temperature and at 80 °C relating to studies on the removal of uranium from uranium-contaminated soils [9,20]. Sodium hydroxide was also tested at high temperature (80 °C) to mimic a process developed for the solubilization of arsenic from polluted soils [21]. In previous work [8], best results were obtained using a sulfuric acid leaching in saline media as it has been applied successfully for the chemical leaching of antimony and other metals from small arms shooting range soil [22]. However, we observed lower Hg recovery yield for the U13 SRCW (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, $2HgO \cdot HgSO_4$ [23]. However, it could also be due to the formation of insoluble mercury sulfide, or the reduction of Hg^{2+} in $Hg(NO_3)_2$ to elemental Hg^0, or the conversion to HgS in the alkaline conditions of the cement matrix.

The goal of this study was to develop an innovative method for uranium, mercury and cesium recovery from the SRCW. A chemical leach process using sulfuric acid and potassium iodide was developed and optimized for metals solubilization from the wastes. Ion exchange was applied to separate selectively the cesium and the mercury. Uranium was recovered using a chelating resin and precipitated as yellow cake using sodium hydroxide. Considering the improved metal recovery, the process was modified to include effluent recirculation to improve both the U solubilization and recovery. A process overview including a flow sheet and an economic analysis is also presented.

2. Experimental Section

2.1. SRCW Preparation

All the experiments were done with various surrogate radioactive cemented wastes (SRCW) prepared at CanmetMINING. The procedure involves mixing a synthetic solution with either General Use (GU) or High Early Strength (HE) cements manufactured by Lafarge Canada Inc. (Mississauga, ON, Canada), in a manner that mimics the process done at CNL, as described by Fiset *et al.* [24]. All added contaminants species in the synthetic solution are soluble salts in the nitric acid medium, which is representative of the CNL procedure. Table 1 gives the composition of the solution used for preparing the SRCW. Table 2 gives the experimental conditions used to prepare various SRCW batches and their compositions.

Table 1. Chemical composition of the solution used for preparation of the surrogate radioactive cemented waste (SRCW). Final pH is about 1.63 and redox potential is about 467 mV.

Element	Concentration	Added as
Aluminum	26,371 ppm	$Al(NO_3)_3 \cdot 9H_2O$
Uranium	4760 ppm	$UO_2(NO_3)_3 \cdot 6H_2O$
Mercury	6622 ppm	$Hg(NO_3)_2 \cdot H_2O$
Rubidium	6.44 ppm	$RbNO_3$
Cesium	29.1 ppm	$CsNO_3$
Strontium	25.9 ppm	$Sr(NO_3)_2$
Barium	31.4 ppm	$Ba(NO_3)_2$
Ruthenium	30.5 ppm	1.5% $RuNO(NO_3)_3$ solution
Lanthanum	20.0 ppm	$La(NO_3)_2 \cdot 6H_2O$
Cerium	54.5 ppm	$Ce(NO_3)_3 \cdot 6H_2O$
Praseodymium	14.3 ppm	$Pr(NO_3)_3 \cdot 6H_2O$
Neodymium	41.0 ppm	$Nd(NO_3)_3 \cdot 6H_2O$
Samarium	5.11 ppm	$Sm(NO_3)_3 \cdot 6H_2O$
Europium	0.75 ppm	$Eu(NO_3)_3 \cdot 6H_2O$
Gadolinium	0.23 ppm	$Gd(NO_3)_3 \cdot 6H_2O$
Yttrium	11.3 ppm	$Y(NO_3)_3 \cdot 6H_2O$
Iron	55.9 ppm	$Fe(NO_3)_3 \cdot 9H_2O$
Nickel	10.3 ppm	$Ni(NO_3)_2 \cdot 6H_2O$
Chromium	17.0 ppm	$Cr(NO_3)_3 \cdot 9H_2O$
Nitric acid	0.36 M	HNO_3 (16M)

Table 2. Main experimental parameters used to prepare cemented wastes batches and partial composition.

Batch Code	Cement Type	S/C Ratio*	Aging Time	Aging Temperature	Cs (ppm)	Hg (ppm)	U (ppm)
U5	GU	0.29	7 days	Ambient	7.9	1598	1182
U8	GU	0.39	18 months	Ambient	8.6	1785	1177
U10	GU	0.29	18 months	Ambient	8.2	1462	959
U13	GU	0.29	18 months	60 °C	3.5	1116	893
U18	GU	0.39	18 months	Ambient	5.8	1093	759
U20	HE	0.39	18 months	Ambient	8.1	1644	1243
U22	HE	0.29	18 months	Ambient	7.3	1415	1,018
U24	HE	0.21	18 months	Ambient	6.0	1121	785
U28	GU	0.39	30 months	60 °C	8.5	1973	1150
U29	GU	0.29	30 months	Ambient	7.2	1977	1104
U32	GU	0.29	30 months	60 °C	6.0	1277	850
U34	HE	0.39	30 months	Ambient	8.0	2651	1355

* Solution/Cement Ratio.

The SRCW batches were allowed to age and subsequently removed from the pails with an air hammer. The whole pail content (~20 kg) was fragmented in a laboratory jaw crusher (Retsch, model BB200, Haan, Germany) to about 2 mm and then split into 12 fractions of about 1.7 kg each, using

a large capacity (20 kg) rotary splitter (GENEQ, model SEO4OJ-001, Montreal, QC, Canada). One of the 12 fractions was further ground in a disc mill (Retsch, model DM200) to less than 300 µm and split into ten fractions of about 170 g, using a medium capacity rotary splitter (Fritsch Rotary Cone Sample Divider, Model Laborette 27, Montreal, QC, Canada), before being re-sampled at 50 g using the quartering sampling technique.

2.2. Leaching Experiments

The screening leaching tests were done by mixing 50 g of SRCW with a known volume of a selected lixiviant in a 1-L glass Erlenmeyer flask, which was agitated in a temperature-controlled orbital shaker (Labnet, Model 211DS, Cole-Palmer, Edison, NJ, USA). The optimization and validation leaching tests were performed in a 2-L beaker. Leaching steps were done by mixing 50 g of the cemented sample (SRCW) 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 then filtered onto Whatman No. 4 cellulose paper (porosity = 20–25 µm). The residue and filter were then dried at room temperature. The process effluents were generated during leaching, rinsing and leachate treatment steps. These effluents can be recycled using a counter-current recirculation. In five treatment loops, leaching and rinsing effluents were reused from a loop (X) to the next loop (X + 1) to improve the process efficiency and metal recovery.

2.3. Key Elements Recovery

Experiments were undertaken with various ion exchange resins to assess the potential of selective recovery of key elements. Experiments were conducted in batch and continuous column modes. One gram of resin as mixed with 100 mL of leachate using a 500 mL Erlenmeyer flasks and shaken at 200 revolutions per minute (rpm) (Orbital shaker, Lab-line Environ-Shaker, model 3528, Cole-Plamer, Vernon Hills, IL, USA) for 24 h to ensure that chemical equilibrium was attained. It was followed by liquid–solid separation by filtration using Whatman 934AH filters (Cole-Plamer). Cesium, mercury, and uranium were removed selectively using potassium cobalt hexacyanoferrate (KCFC, Santa Cruz Biotech., Dallas, TX, USA), resin Lewatit TP214 (Lanxess, Köln, Germany), and resin Lewatit TP260 (Lanxess), respectively. Lewatit TP 214 is a macroporous chelating resin with thiourea groups having a high affinity for mercury. Lewatit TP260 is macroporous cation exchange resin with chelating amino methyl phosphonic acid groups having a high affinity for uranium (UO_2^{2+}). The column experiments were conducted using an Omnifit column (Diba Inc., Sigma-Aldrich, St. Louis, MO, USA) with a bed volume of 12 mL. Leachate was passed through the resin using a peristaltic pump (Masterflex, Cole-Palmer, Montreal, QC, Canada) at a flow rate of 3 BV/h. An automatic fraction collector (Eldex Laboratories, Napa, CA, USA) was used to take samples of the column effluent. Uranium was then eluted from the resin with 1 M Na_2CO_3 (ACS, Sigma-Aldrich) or 1 M NH_4NO_3 (ACS, Sigma-Aldrich) or 6 M NaOH (ACS, ACP Chemicals, St-Leonard, QC, Canada), or 2 M HNO_3 solutions (ACS, Fisher Sci., Ottawa, ON, Canada) and subsequently precipitated using sodium hydroxide or hydrogen peroxide (30%) (ACS, Sigma-Aldrich) or ammonium hydroxide (28%) (ACS, ACP Chemicals) or magnesium hydroxide solutions (ACS, ACP Chemicals).

2.4. Analytical

The liquid samples from leaching and recovery test were analyzed by ICP-MS (Thermo-Fisher Scientific, X-Series II, Waltham, MA, USA), after appropriate dilution with HCl to stabilize the Hg(II). The solid initial and final samples were digested in HCl before being analyzed by ICP-MS. The mineralogical characterization of the SRCW test samples and leach residues was done using a combination of X-ray Diffraction (XRD) (Rigaku, model D/Max, Allison Park, PA, USA), Scanning Electron Microscopy (SEM) (JEOL, model JSM 820, St-Hubert, Laval, QC, Canada) and

Variable-Pressure Scanning Electron Microscopy (VP-SEM) (Hitachi, model S-3200N, Mississauga, ON, Canada), both with Energy Dispersive X-Ray Analyzer (EDS).

3. Results and Discussion

3.1. Mercury Oxidation in Old Wastes

In previous work [8], lixiviants selected using information found in the technical literature were tested to solubilize both uranium and mercury. Best results were obtained using a sulfuric acid leaching in saline media as it has been applied successfully for the chemical leaching of antimony and other metals from small arms shooting range soil [22]. However, lower Hg recovery was obtained for the U13 SRCW (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 also be due to the formation of insoluble mercury sulfide [23]. Figure 1 presents BSE (Back Scattered Electron) electron image of U13 SRCW and EDS spectra. The Hg spots in the SRCW appear to be a combination of mercury oxide and metallic mercury. The EDS spectra also indicate the presence of S.
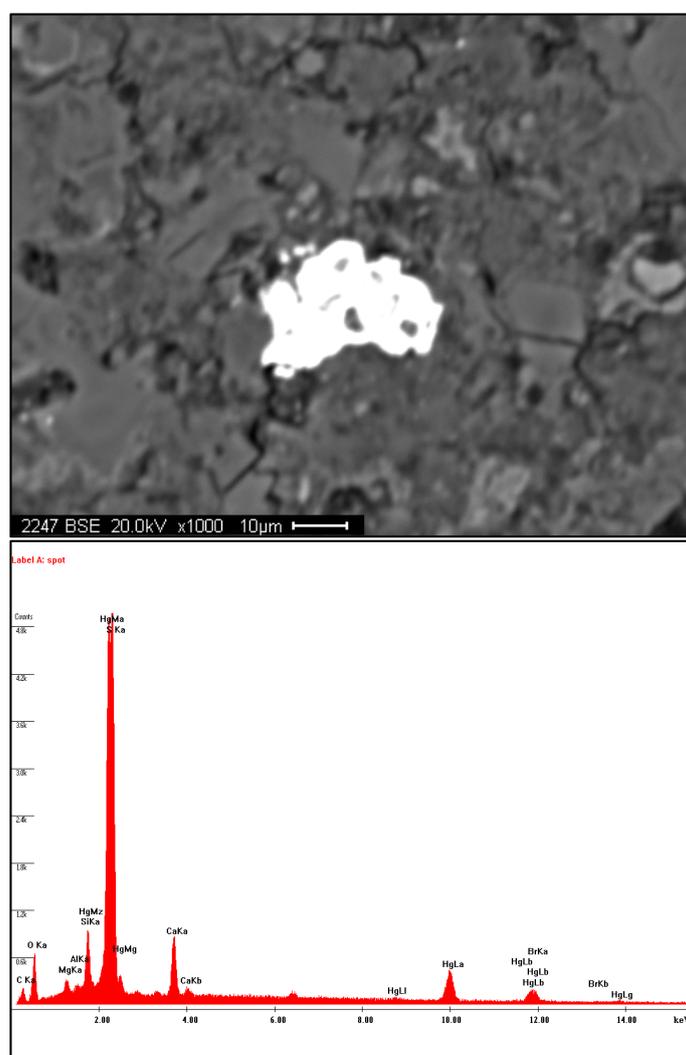

Figure 1. BSE electron image of U13 SRCW and EDS spectra.

Several SRCW were cured at 60 °C and several were aged for 30 months. These wastes were subjected to characterization in order to investigate the influence of aging time and curing temperature on uranium and mercury speciation. In general, the layers of Ca-uranate become thicker after 30 months of ageing time at 60 °C. The layers are large (several mm long by ~100 μm thick). The concentration of uranium in the layers of Ca-uranate is variable. Presence of thick Ca-uranate layer should improve U leachability. Results show that part of the mercury occurs as mercury oxide but part of this mercury oxide has been reduced to metallic mercury and some has agglomerated. The agglomeration of the metallic mercury is similar to the observed after 18 months. Some evidence was found that after 30 months of aging, one small portion of the metallic mercury is reacting with S-containing species from cement and forming mercury sulfide. Mercury sulfide formed when pails were cured at 60 °C. Hg leaching may be more difficult for older pails as HgS is extremely insoluble (pK = 52). In order to investigate the influence of aging time and curing temperature on mercury leaching, experiments were done using the 30 months SRCW (U29) containing 7.2 ppm of Cs, 1977 ppm of Hg and 1104 ppm of U. These tests were done by adding a mercury oxidant at different concentrations (between 0.5 and 4 M). Figure 2 shows the solubilization yields from the U29 SRCW after the processing in sulfuric media using the optimized conditions with sodium chloride (ACS, ACP Chemicals), sodium sulfide (ACS, Sigma-Aldrich), potassium permanganate (ACS, ACP Chemicals) and hydrogen peroxide (ACS, Sigma-Aldrich) (t = 2 h, T = 20 °C, $[H_2SO_4]$ = 1 M, $[NaCl]$ or $[Na_2S]$ or $[KMnO_4]$ or $[H_2O_2]$ = 0.5–4 M, L/R = 1/2).

Figure 2 shows that the addition of oxidants does not increase the solubilization of mercury. Sodium sulfide, potassium permanganate and hydrogen peroxide are not strong enough to oxidize metallic mercury Hg^0 or mercury sulfide HgS. The use of sodium chloride seems to be the best technique to increase the solubilization of mercury from aged SRCW. However, the addition of sodium chloride was not efficient enough to solubilize mercury from U13 SRCW cured at 60 °C. The sodium chloride allows to complex the mercury as $HgCl_4^{2-}$ ($HgCl_4^{2-}$, Kf = 5.10^{15}) when mercury is present as mercury oxide HgO or metallic mercury Hg^0 in 30 months aged SRCW like U29, whereas the oxidation of insoluble mercury sulfide HgS (pK = 52) formed in 60 °C cured SRCW like U13 did not occur.
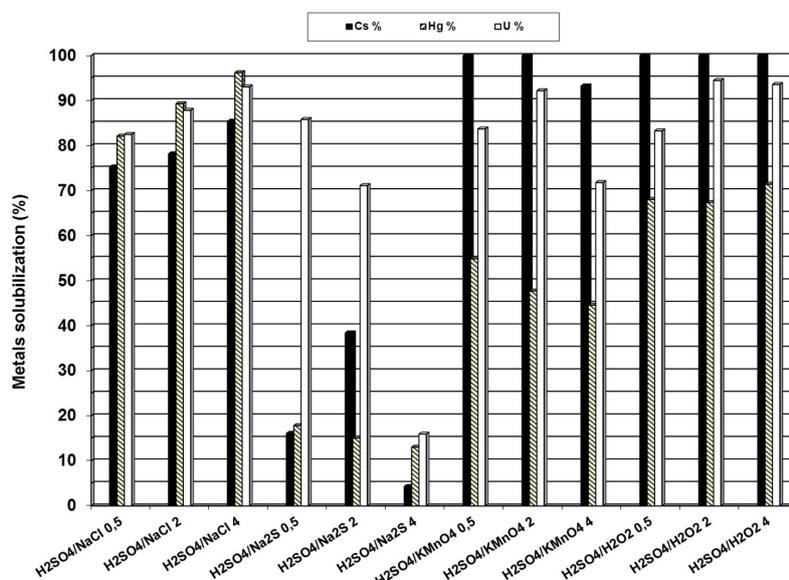

Figure 2. Percentage of key elements, Cs, Hg and U, dissolved from U29 SRCW in sulfuric acid (pH = 2) using the optimized conditions with sodium chloride, sodium bisulfide, potassium permanganate and hydrogen peroxide (Particle size = 0.3 mm, t = 2 h, T = 20 °C, $[H_2SO_4]$ = 1 M, $[NaCl]$ or $[Na_2S]$ or $[KMnO_4]$ or $[H_2O_2]$ = 0.5–4M, L/R = 1/2).

3.2. Use of Potassium Iodide as Mercury Oxidant

Sodium chloride formed mercury complex ($HgCl_4^{2-}$, Kf = 5.10^{15}) when mercury is present as mercury oxide HgO or metallic mercury Hg^0 in 30 months aged SRCW but not with mercury sulfide HgS (pK = 52) formed in 60 °C cured SRCW. In order to oxidize HgO, as well as HgS, tests were performed using iodide halogen salt as strong oxidant to form Hg complex (HgI_4^{2-}, Kf = 2.10^{30}). As background, it can be mentioned that a patented process was developed for soil remediation by removing mercury using a treatment with an oxidant, such as iodide, and a complexing or solubilizing agent, such as potassium iodide [25]. In addition, Klasson and Koran studied the removal of Hg from solids using a potassium iodide/iodine leaching process [26]. Various SRCW cured at 60 °C and/or aged for 30 months were subjected to leaching using sulfuric acid (ACS, ACP Chemicals) and potassium iodide (ACS, Ficsher Sci., Ottawa, ON, Canada). These SRCW were U13 (18 months at 60 °C), U28 (30 months at 60 °C), U29 (30 months at ambient temperature), U32 (30 months at 60 °C), and U34 (30 months ambient temperature). A 50 g sample of SRCW crushed at 0.3 mm was mixed with 500 mL of distilled water to obtain a 10% pulp density. Potassium iodide was then added to obtain a concentration of about 1.2 M. Then concentrated sulfuric acid was added to obtain a concentration of about 1 M. Agitation using an immersed impeller during 2 h at ambient temperature was performed. Figure 3 presents the solubilization of Cs, Hg, and U from five mentioned SRCW using sulfuric acid and potassium iodide (particle size = 0.3 mm, t = 120 min, H_2SO_4 = 1 M, PD = 10%, T = 20 °C, KI = 1.2 M). Initial concentration of Cs, Hg, and U in each SRCW are given in Table 2.
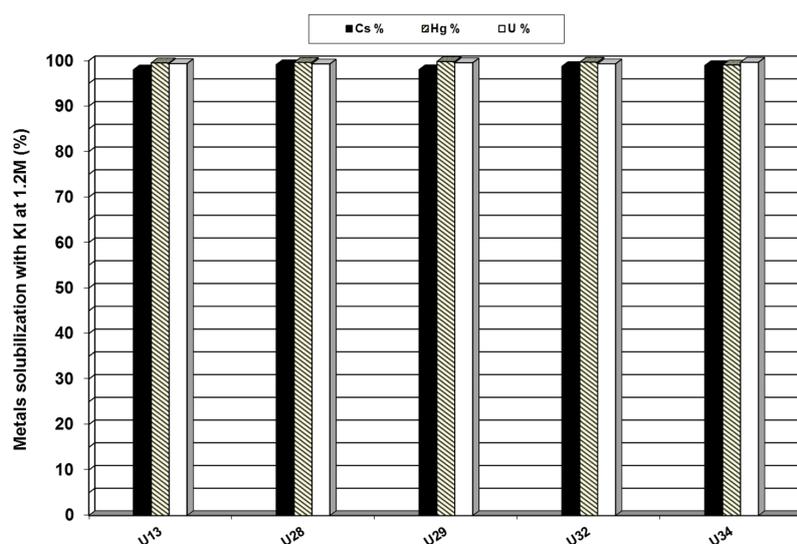

Figure 3. Cs, Hg, and U solubilization yields from five different cemented wastes using sulfuric acid and potassium iodide: U13 (18 months at 60 °C), U28 (30 months at 60 °C), U29 (30 months at ambient temperature), U32 (30 months at 60 °C), and U34 (30 months ambient temperature). Particle size = 0.3 mm, t = 120 min, H_2SO_4 = 1 M, PD = 10%, T = 20 °C, KI = 1.2 M.

For all tested SRCW batches, solubilization yields are above 97% for Cs and 98% for U and Hg. Sulfuric acid and potassium iodide improves the solubilization of mercury by oxidation of all the mercury species and form mercury tetraiodide complex (HgI_4^{2-}, Kf = 2.10^{30}).

3.3. Leaching Optimization in Iodide Media

Further optimization tests were done to evaluate the influence of potassium iodide concentration and SRCW particle size on the solubilization efficiencies. The optimization experiments were done in a 2-L beaker by mixing 50 g of U29 SRCW with 500 mL of solution for a pulp density of 10% v/w.

Leaching of U29 cemented waste was performed using different concentration of KI from 0.01 to 1.2 M. Another set of experiments were done using a particle size from 0.3 to 6 mm. Figures 4 and 5 present the influence of the iodide concentration and the cement particle size, respectively, on Cs, Hg, and U solubilization.
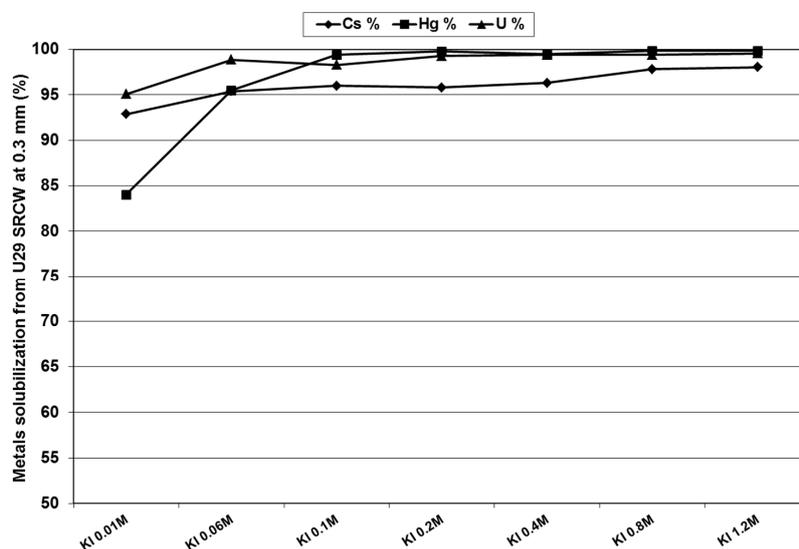

Figure 4. Cs, Hg, and U solubilization yields from U29 cemented waste using sulfuric acid and various concentrations of potassium iodide. Initial concentrations are about 7.2 ppm for Cs, 1977 ppm for Hg, and 1104 ppm for U. Particle size = 0.3 mm, t = 120 min, H_2SO_4 = 1 M, PD = 10%, T = 20 °C.
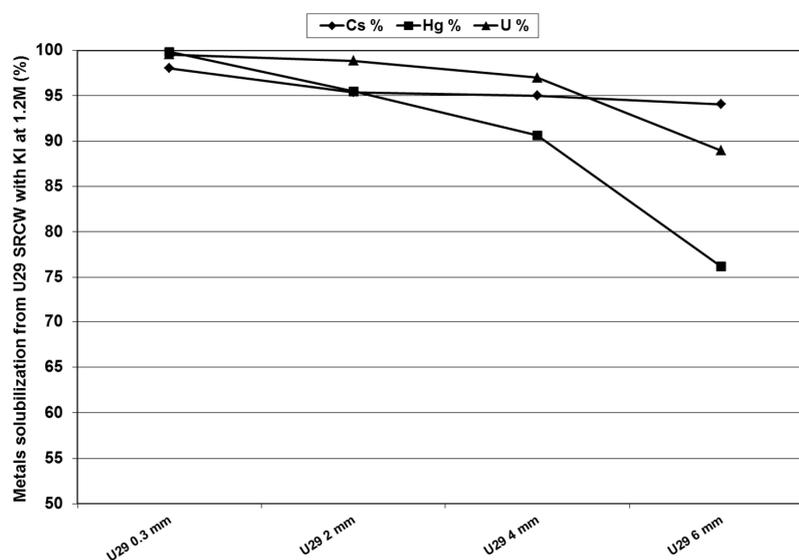
Figure 5. Cs, Hg, and U solubilization yields from U29 cemented waste using sulfuric acid and potassium iodide. Initial concentrations are about 7.2 ppm for Cs, 1977 ppm for Hg, and 1104 ppm for U. t = 120 min, H_2SO_4 = 1 M, PD = 10%, T = 20 °C, KI = 1.2 M.

Figure 4 shows no decrease of solubilization yields for potassium iodide concentration from 1.2 to 0.2 M. At 0.1 M and lower concentration of KI, the process efficiency decreases slightly especially for mercury. This result indicates the importance of potassium iodide to oxidize the mercury species in the SRCW. Potassium iodide is effective even at low concentrations of 0.1 M, whereas a high concentration of sodium chloride of 4 M is needed to achieve good mercury solubilization. Figure 5 shows that the particle size of the cemented waste has an important influence on the

solubilization efficiency. The increase of the particle size decreases the solubilization efficiency. Mercury solubilization decreases form 99% to 95% and then to 90% when particle size increases from 0.3 to 2 mm and then to 4 mm. These results are explained by the mineralogy of the cemented waste. Uranium phases were found mainly as long layers (400 μm) and some small grains. Mercury phases were found as grains below 20 μm and the small grains that tend to agglomerate with longer aging times and higher aging temperatures. Moreover, the proportion of metallic mercury and mercury sulfide appears to increase with aging times and aging temperatures. Figure 6 presents BSE electron image of U34 SRCW with presence of Hg (brighter) with HgS (middle grey) and EDS spectra.
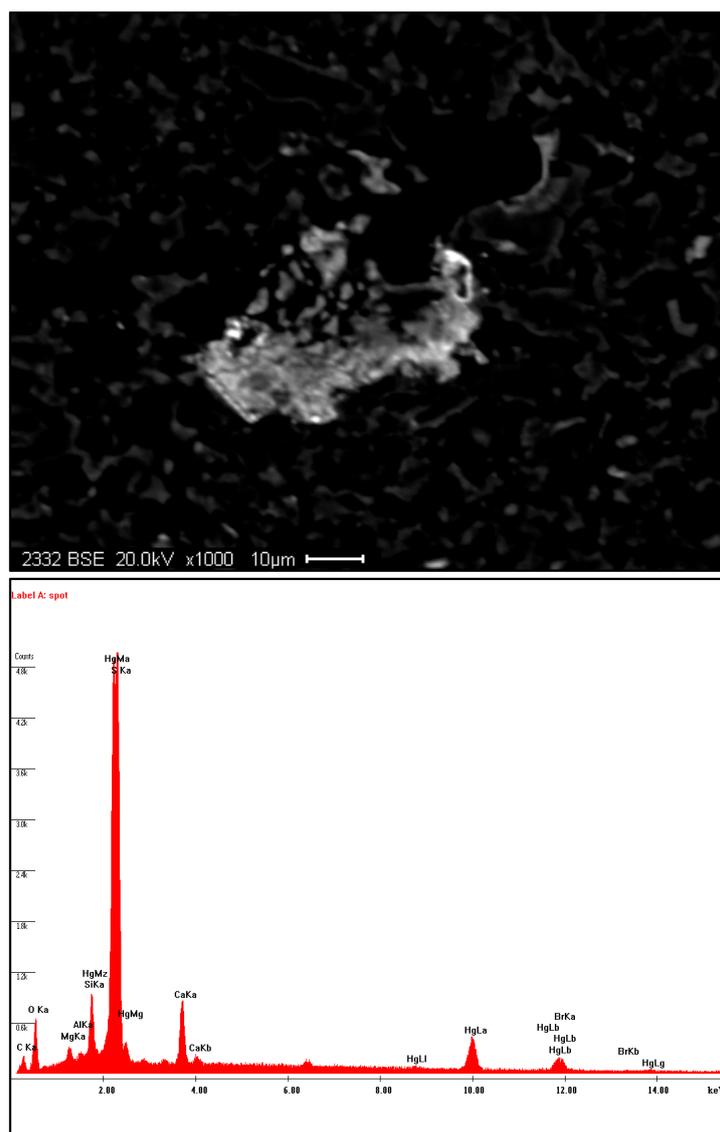
Figure 6. BSE electron image of U34 SRCW and EDS spectra.

3.4. Separation and Recovery 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 (yellow cake). Ion exchange resins can be broadly classified as cation exchangers, anion exchangers, and chelating exchangers. Chelating resins are specific exchangers developed to obtain high selectivity of at least one particular counter-ion species. In the case of chelating resins, counter ions are bound to resin by coordinate covalent bond or by its combination with electrostatic interactions.

Typical functional groups of chelating resins are iminodiacetic acid, aminophosphonic, thiourea, and bis-picolylamine. The presence of salt in uranium sulfuric leachate is a major problem for nuclear and mining industries. Several investigations were done to improve the selectivity of resins for uranium especially in sodium chloride media. In case of uranium recovery from sulfuric acid leachate containing potassium iodide, no studies exist in the literature. Zhang *et al.* have investigated the recovery of gold from iodine-iodide solutions using an anion exchange resin [27]. The gold iodide complex can be effectively loaded on the resin provided the resin is not heavily loaded with triiodide. The Cs and Hg in the leachate are removed using potassium cobalt ferrocyanide (KCFC, Santa Cruz Biotech.) and a thiol resin (Lewatit TP214, Lanxess, or Dowex XUS 43604, Dow Chemicals, Midland, MI, USA), respectively. 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 that adsorbs the U, but also some base metals. Lewatit TP260 (Lanxess) is a weakly acidic, macroporous cation exchange resin with chelating amino methyl phosphonic acid groups for the selective removal of transition heavy metals and a high affinity for uranyl ions (UO_2^{2+}). Uranium loaded in the Lewatit TP260 chelating resin was eluted using several stripping reagent. The best U stripping from the resin was obtained using 1 M sodium carbonate (ACS, Sigma-Aldrich), which allows 99% U recovery. Thus, separation of the Cs, Hg and U from the leachate can be done in an efficient manner. It is considered that the efficiency of the processes will be improved when effluent recirculation is used.

3.5. Reuse of Washing Solutions for Subsequent Leaching

Counter-current leaching is a common method used to reduce the reagent consumption and to increase the solubilization of contaminants [28–30]. The process effluents are generated by a leaching step, a rinsing step or a leachate treatment step. These effluents can be recycled using a counter-current recirculation. In five treatment loops, leaching and rinsing effluents were reused from a loop (X) to the next loop ($X + 1$) to improve the productivity of the process. The U29 SRCW was subjected to several leaching using sulfuric acid and potassium iodide. The leaching steps were carried out using washing solution instead of water. After the leaching steps, washing steps were done using water. The reuse of washing solution allows reducing the process costs and the volume of liquid waste produced. Five 150 g sample of SRCW crushed at 2 mm were mixed with 1500 mL of washing solution to obtain a 10% pulp density. Potassium iodide was also added to obtain a concentration of about 0.06 M. According to solubilization efficiencies obtained in Figures 4 and 5 particle size of 2 mm and KI concentration of 0.06 M were used in order to have a better evaluation of effluent recirculation on process efficiency. Metals solubilization reached 99% in the optimal condition (particle size of 0.3 mm and KI concentration of 0.6 M).

Then, concentrated sulfuric acid was added to obtain a concentration of about 1 M. Agitation using an immersed impeller during 2 h at ambient temperature was performed. After a filtration step, the leaching solution were treated to remove cesium and mercury, and then to recover the uranium. The treated-leaching solution is recycled and reused for the washing steps. Figure 7 presents the solubilization of Cs, Hg, and U from SRCW using sulfuric acid and potassium iodide (particle size = 2 mm, t = 120 min, H_2SO_4 = 1 M, PD = 10%, T = 20 °C, KI = 0.06 M). Initial concentration of Cs, Hg, and U of U29 SRCW are given in Table 2.

According to Figure 7, solubilization efficiencies increase for each element during the five recirculation experiments. Improvement of solubilization is due to the recycling of chemical reagents which concentration increase during counter-current recirculation. These results show that the washing solution can be reused in this process without affecting the leaching performance. The leaching solution can also be reused for washing steps after the recovery of metals by the separation step.
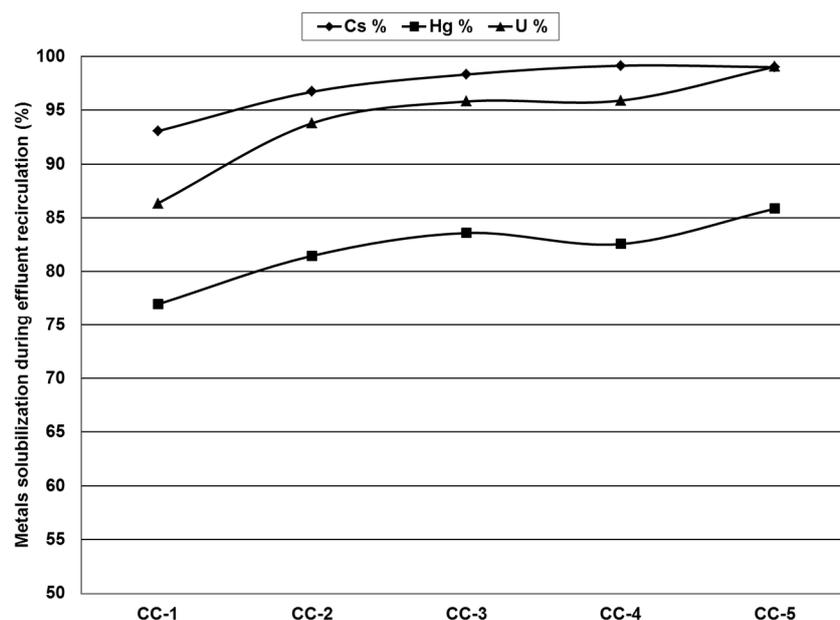
Figure 7. Cs, Hg, and U solubilization from SRCW using sulfuric acid and potassium iodide in effluent recirculation (particle size = 2 mm, t = 120 min, H_2SO_4 = 1 M, PD = 10%, T = 20 °C, KI = 0.06 M).

3.6. Process Overview, Flow Sheet and Economic Analysis

In this process, the SRCW can be leached efficiently at 2 mm particle size with effluent recirculation, which would allow simplification of the grinding step (without grinding media). In the next step, potassium iodide and concentrated H_2SO_4 are added to the slurry until the pH is about 2. This slurry is then filtered to yield a leachate, which contains most of the uranium and a residue consisting mostly of $CaSO_4$ and minor amounts of SiO_2. The residue is not re-pulped as it has a low Hg content and can be disposed in an appropriate manner. 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. 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 acid consumption is about 1 kg of concentrated H_2SO_4 per kg of SRCW. Sulfuric leaching and 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 SRCW batches, including old SRCW 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 (United States Environmental Protection Agency) value for mercury hazardous wastes classification (260 ppm). The yellow cake produced in the process is a Na-U-O compound with a high concentration of uranium and minor impurities of Si, P, and Al. The XRD pattern indicates the yellow cake is partially crystalline and identifies it as mainly a sodium uranium oxide.

A simplified flow sheet for the above-described process for Cs, Hg and U recovery is shown in Figure 8. An economic analysis was estimated for a plant with an annual capacity of 60,000 t, an operating efficiency of 90% and operating 300 days/year at 0.6 t/day. The cost estimation was assessed based on the following unit prices: 125 US$/t of H_2SO_4 (solution at 93% w/w), 2500 US$/t of KI, 25 US$/kg of ion exchange resin, 22.5 US$/h as average labor cost, 0.06 US$ per kWh of electricity, and process water (tap water) unitary price of 0.5 US$/m^3. The economic analysis show a process cost of about 100,000 US$/t for the key elements leaching and recovery, and the radioactive waste stabilization. This cost is about 90% lower than actual cost for the treatment of such radioactive

wastes. However, this cost may be much lower since the produced gypsum has a mercury level below the USEPA value for mercury hazardous wastes classification (260 ppm).
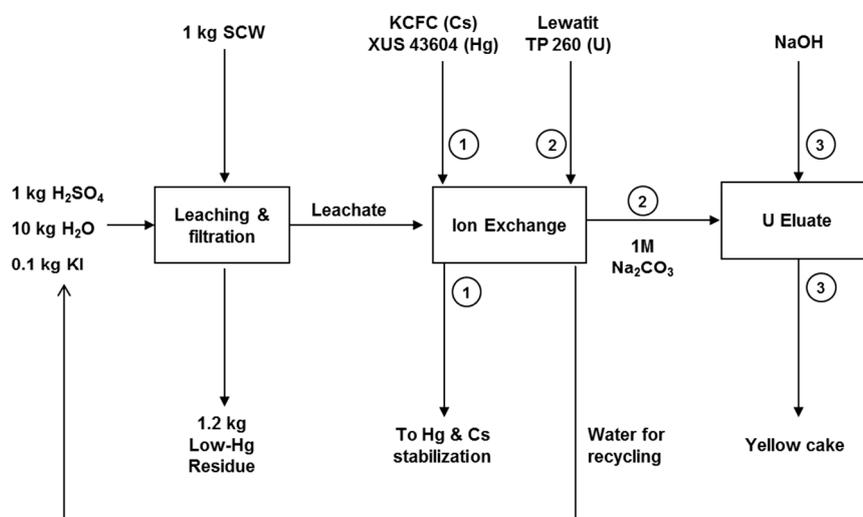
Figure 8. Simplified process flow sheet.

4. Conclusions

Several SRCW were cured at 60 °C and several were aged for 30 months. Under these aging conditions, one small portion of the metallic mercury reacts with S-containing species and forms mercury sulfide. Samples of these batches of SRCW were subjected to chemical leaching using sulfuric acid and KI. Recovery yields were above 97% for Cs and 98% for U and Hg. Sulfuric acid and KI improved the dissolution of Hg. No change in recovery yields was observed for KI concentrations from 1.2 to 0.2 M. Hg solubilization decreased from 99% to 95% and then to 90% when particle size increased from 0.3 to 2 mm and then to 4 mm. Cesium was removed from the leachate using potassium cobalt hexaferrocyanide (KCFC). Mercury was selectively removed from the leachate using a thiol ion exchange resin (Lewatit TP214 or Dowex XUS 43604). U recovery from potassium iodide leachate using the resin Lewatit TP260 was efficient and U uptake appeared to be improved by the presence of higher iodide concentration. Considering these results and the effect of potassium iodide on Cs, Hg, and U solubilization, the process was successfully applied with effluent recirculation to improve both the U solubilization and recovery efficiencies. Improved species recovery was observed with recycling of chemical reagents during counter-current recirculation. A pilot plant study is recommended to verify the efficiency of the process and to provide a better understanding of the operational requirements. This will allow better assessment of economic and environmental benefit related aspects of the process application.

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