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Enhanced Selective Leaching of Chromium from Radioactive Sludges

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Abstract: An enhanced selective oxidative alkaline leaching (ESOAL) process has been developed for the removal of chromium from high level waste (HLW) tank sludges. Because of the adverse effect of excess chromium on the vitrification process, chromium removal becomes a critical factor in the pretreatment of underground storage tanks (USTs) containing nuclear waste. The ESOAL process described here uses a unique approach based on the innovative combination of an effective oxidant and sonochemical oxidation, achieving efficiencies and removal rates substantially better than either of the processes used independently. Results are shown here for the ESOAL treatment of a tank sludge simulant (Hanford tank S-101). The effects of different variables (e.g., time, ultrasound power, temperature, sodium hydroxide concentration, and the use of an oxidant) on the amount of sludge dissolved are presented.

Keywords: Enhanced selective leaching, chromium removal, radioactive sludges

INTRODUCTION

The Department of Energy (DOE) is faced with the formidable task of developing techniques for the safe and cost effective remediation of 1×10^8 gallons of radioactive waste stored in more than 300 underground storage tanks (USTs) at Hanford, Savannah River, Oak Ridge, and Idaho (1). Pretreatment is an essential component of the remediation process, and will separate the tank waste into low level waste (LLW) and high level waste (HLW)

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fractions which will then be vitrified and stored. The cost associated with both the vitrification process and storage of the resulting glass can be substantially reduced by decreasing the volume of the HLW fraction, and minimizing the presence of non-radioactive components, especially those that adversely impact the vitrification process.

Chromium minerals (mainly Cr(III) species) present in the UST sludges produce insoluble phases in the HLW waste melter. A relatively small amount of chromium in the sludge can limit the amount of waste that can be incorporated into the glass and, therefore, has a relatively large impact on the total volume of HLW glass produced. Previous studies indicate that removal of chromium (due to dissolution as a soluble Cr(III) species) is poor during the baseline caustic leaching pretreatment (2–4). Therefore, an effective and selective oxidative alkaline leaching during the sludge pretreatment is necessary to reduce the amount of Cr(III) present in the HLW fraction (e.g., by oxidizing Cr(III) to Cr(VI), which becomes soluble in alkaline solutions).

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In the past, permanganate and ozone have been used as chemical agents for chromium oxidation/dissolution with a certain degree of effectiveness (5). The use of other chemicals such as oxygen, hydrogen peroxide, and persulfate has been also proposed. However, processes using those chemicals suffer from one or more drawbacks:

(i) low efficiency for Cr removal,
(ii) slow kinetics,
(iii) lack of selectivity,
(iv) addition of mass to the solid waste,
(v) dissolution of TRU elements,
(vi) adverse effects in the vitrification process,
(vii) incompatibility with other process streams,
(viii) safety,
(ix) cost,
(x) corrosion damage to the tanks, and
(xi) the use of complicated systems.

Any oxidant selected for Cr removal (including in the ESOAL process) has to avoid or minimize most of these problems.

In this work, the use of an enhanced selective oxidative alkaline leaching (ESOAL) process for chromium removal from HLW tank sludge simulants is presented. The enhancement is provided by a sonication process, which has been recognized to have great potential for use in a wide variety of industrial processes (6). When a liquid-solid interface is subject to ultrasonic irradiation, transient cavitation occurs with major changes in the nature of the bubble collapse. No longer does a spherical implosion of the cavity occur, but instead there is a markedly asymmetric collapse that generates a jet of liquid directed at the surface (7). The jet velocities have been measured

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greater than 100 m/s. The impingement of this jet can create a localized erosion, surface pitting, and ultrasonic cleaning. A second contribution to erosion created by cavitation involves the impact of shock waves generated by cavitational collapse (8). The magnitude of the shock waves is thought to be as high as 10^4 atmospheres, which will easily produce plastic deformation of metals (9).

Enhanced chemical reactivity of solid surfaces is associated with the following processes. The cavitational erosion generates highly reactive surfaces, causes short-lived high temperatures and pressures at the surface, produces surface defects and deformations, forms fines and increases the surface area of friable solid supports, and ejects material into solution. Finally, the local turbulent flow associated with acoustic streaming improves mass transport between the liquid phase and the surface, thus increasing observed reaction rates. In general, all of these effects are likely to be occurring simultaneously. Examples of the application of ultrasonic irradiation to (non radioactive) sludge treatment include the physical deterioration of sludge flocs (10) or microorganisms (11), and the extraction of chemicals bound to solids (12–14). To our knowledge, this work presents the first application of sonication for the dissolution of chromium and other elements from tank sludges.

Mass transport is especially critical for oxidation processes. The use of ultrasound enhances the oxidation process by increasing the surface area, raising the temperature, and aiding the mass transport of reactants. Some advantages of the ESOAL process are:

(i) The efficiency for chromium removal from the sludge is substantially better than any of the processes used independently.
(ii) The amount of oxidant required to achieve a high chromium removal rate from the sludge is substantially reduced compared to oxidation processes not combined with ultrasound.
(iii) The required sodium hydroxide concentration (traditionally used in caustic leaching for the removal of chromium from sludges) can be kept to a low level without impacting the effectiveness of the process.
(iv) A high co-dissolution rate of the non-radioactive species, such as aluminum, silicon, and phosphorus, can be also achieved, considerably reducing the sludge mass.
(v) Minimal mass is added to the sludge due to oxidation byproducts.

The use of an ESOAL process to treat tank sludges will have a direct impact on the vitrification process because:

(i) chromium minerals are effectively removed from the sludge;
(ii) the total mass of sludge to be vitrified is substantially reduced by the dissolution of non-radioactive elements; and

(iii) radioactive elements (e.g. TRUs, strontium-90) are concentrated in the sludge because they are not removed during the ESOAL treatment.

EXPERIMENTAL SECTION

Preparation of Sludge Simulant

The studies of chromium removal by the ESOAL process were conducted with a simulated Hanford tank (S-101) sludge. Little information is available on the actual mineral phases present in the tank waste, so the waste was formulated to give elemental compositions similar to the real tank waste. Elements were expected to be primarily present as insoluble hydroxides, with minor amounts of phosphates, sulfates, and silicates. The total chromium content in the sludge in tank S-101 is 10.5 mg/g.

Table 1 lists the salts used in preparation of the S-101 sludge simulant. Some of the aluminum was added as Boehmite because this compound had previously been identified in actual S-101 sludge. The compounds were added to deionized water and the volume made up to approximately 3.5 liters. 50% sodium hydroxide solution was then added until a pH of approximately 9 was reached. The mixture was heated at 100°C for 48 hours, centrifuged, washed with 0.01 M sodium nitrate that had been adjusted to pH 9 with sodium hydroxide solution. The wet sludge simulant was stored in a plastic bottle until used.

Table 1. Compounds used in the synthesis of an S-101 sludge simulant

Element	Conc. in dry actual sludge (mg/g)	Source	Amount added (g)	Conc. in wet[a] simulant (mg/g)
Al	343	$Al(NO_3)_3 \cdot 9H_2O$	951	53.8
		Boehmite, AlOOH	152	
Ca	2.17	$Ca(NO_3)_2 \cdot 4H_2O$	5.12	0.558
Cr	10.5	$Cr(NO_3)_3 \cdot 9H_2O$	32.3	1.92
Fe	5.51	$Fe(NO_3)_3 \cdot 9H_2O$	15.9	1.03
Mn	6.90	$Mn(NO_3)_2$[b]	18.0	1.12
Na	15.2	$NaNO_3$	22.5	N/M[c]
P	0.763	$Na_3PO_4 \cdot 12H_2O$	1.22	0.133

[a] Dry/wet ratio is 3 : 1.

[b] Account for the 50% aqueous solution of which density is ca. 1.54 g/mL.

[c] Not measured.

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Analysis

The sludge sample was analyzed using X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), and elemental analysis. The water content was also determined.

XRD

Samples of the sludge were dried at 100°C overnight, ground to a fine powder and analyzed with a Scintag PAD V diffractometer, using Cu K_α radiation, at a scan rate of 1°/min at 40 kV and 30 mA. The X-ray patterns produced little information on the species present in the sludge simulant. The only identifiable sharp reflections were attributed to sodium nitrate (used in the wash) and the Boehmite that was initially added. A few other peaks were apparent, but they were weak and broad and thus not attributable to any well-defined chemical compounds. This was not unexpected because the primary species present in the sludge were expected to be metal hydroxides exhibiting low crystallinity.

TGA

The dried sludge was analyzed using TGA. Approximately 20 mg of dried sludges were heated to 1000°C at a ramp rate of 10°C/minute, under a nitrogen atmosphere, and the mass losses plotted. The weight decreased gradually until a constant weight was obtained at around 700°C. The weight loss is due to the loss of waters of crystallization (generally below 200°C) followed by the condensation of hydroxyl groups, releasing water. A typical reaction that would be expected to occur is shown below, using iron hydroxide as an example.

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O_{(g)} \uparrow \qquad (1)$$

Other reactions likely to occur include the condensation of phosphate groups to form pyrophosphate, and the decomposition of residual nitrate in the sludge.

Elemental Analysis

A sample of the sludge (1 g) was dissolved in 50 mL of 6 M nitric acid and gently heated. A few milliliters of 48% hydrofluoric acid were also added to ensure complete dissolution. The solution was then made up to 100 mL and analyzed using Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES) (for aluminum and phosphorus) or Atomic Absorption Spectrometry (AAS) (for chromium, iron, manganese, and calcium). Three separate samples of the sludge were analyzed. Variation between

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individual analyses was generally within 5% indicating good homogeneity of the sludge simulants. The sodium content of the sludge was not analyzed.

Water Content

The water content of the sludge simulant was determined in triplicate by heating a known mass of sludge at 105°C until a constant weight was obtained. The mean water content of the sludge was 67.7%.

Sample Preparation

Wet sludge simulant (1 g) was placed in a 50 mL centrifuge tube and 30 mL of 1, 2, 3, or 5 M sodium hydroxide solution added. The mixture was then subject to a treatment procedure for between 30 minutes and 2 hr and filtered through a 0.2 μm syringe filter. The aqueous phase was then acidified with nitric acid and analyzed by ICP/AES or AAS. The percentage dissolution of the sludge components was calculated from the analytical results.

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Sample Treatment

Several procedures were used to treat the sludge simulant samples:

(i) Sonication. An ultrasound processor (VC130 from Sonics & Materials, Inc., Newtown, CT) with a frequency of 20 kHz was used. Sonication was used in the absence and presence of oxidants. Three ultrasound power levels were used and maintained through the experiments: 1/4 power (6W), 1/2 power (13-16W) and full power (26-34W). During the experiments, the power output tended to decrease with time, particularly at high powers. The use of full power for 2 hr period was discontinued because it tended to cause a rapid deterioration of the ultrasonic probe (especially at high sodium hydroxide concentration), and also caused the ultrasound equipment to overheat and shut off.

(ii) Shaking at room temperature, no ultrasound. To evaluate the effect of mixing on the chromium dissolution, samples were placed on a shaker (New Brunswick Scientific Co., Inc., Edison, NJ) at 200 rpm for 30 minutes to 2 hr.

(iii) Stirring at 80°C, no ultrasound. To evaluate the effect of mixing and heating on the chromium dissolution, samples were stirred at 80°C for 30 minutes to 2 hr. Samples were placed in a water bath on a magnetic stirrer.

Three oxidants were tested on the sludge simulants: ferrate (FeO_4^{2-}), permanganate (MnO_4^-), and oxygen (O_2). Ferrate was produced electrochemically from an iron wire immersed in 10 M NaOH. The highest ferrate concentration obtained by this method is about 70 mM. A ferrate stock solution was prepared and stored in a freezer (at −15°C) to prevent self-decomposition. The ferrate concentration was determined by means of UV/VIS spectroscopy (UV-2101, Shimadzu Scientific Instruments, Inc., Columbia, MD) at 505 nm. Permanganate was prepared by dissolving potassium permanganate (Aldrich Chemical Co.) in 5 M sodium hydroxide. Oxygen (99.6%) from a compressed gas cylinder (Brazos Valley Welding Supplies, Bryan, TX) was bubbled through the solution containing the sludge at a rate of 10 mL/min during the sonication experiment.

RESULTS AND DISCUSSION

Chromium Dissolution in the Absence of an Oxidant

The effects of sonication time (0.5, 1, and 2 hours) and power (1/4, 1/2, and full), and sodium hydroxide concentration were explored on the chromium removal by applying ultrasound to 1 g of the sludge sample in 30 mL of various sodium hydroxide solutions (1, 2, 3, and 5 M). Chromium oxidation/dissolution was indicated by the appearance of a yellowish color in solution due to the formation of chromate (Cr(VI)) species in the sodium hydroxide solution. Quantitative analysis of the solution was done by the AAS or ICP/AES. Figure 1 shows the removal percentages of chromium from the sludge under various conditions.

When full power sonication was used, most of the dissolution occurred in the first hour. At 2 hr, where maximum dissolution was achieved, there was not much difference between full and half power with respect to the amount of chromium dissolved. At 1/4 power, no significant dissolution of chromium occurred.

An effect of the sodium hydroxide concentration in the chromium dissolution could be observed at short sonication times (0.5 hour) at full power, and after 1 hr of sonication at half power. Improved dissolution was obtained in more concentrated NaOH solutions. At 1 hour at full power, and 2 hours at half and full power, the sodium hydroxide concentration did not have a significant influence on the total amount of chromium dissolved.

To differentiate the ultrasound process from a vigorous agitation, a sludge mixture in 1, 2, 3, and 5 M NaOH was shaken at room temperature for 0.5, 1, and 2 hours without sonication. In another experiment, a sludge mixture in 1, 2, 3, and 5 M NaOH was immersed in a hot bath (80°C) under constant stirring for 0.5, 1, and 2 hr without sonication (during sonication, the temperature was typically raised to 80°C). Figure 2 shows the chromium removal under these two conditions compared to the removal obtained using sonication

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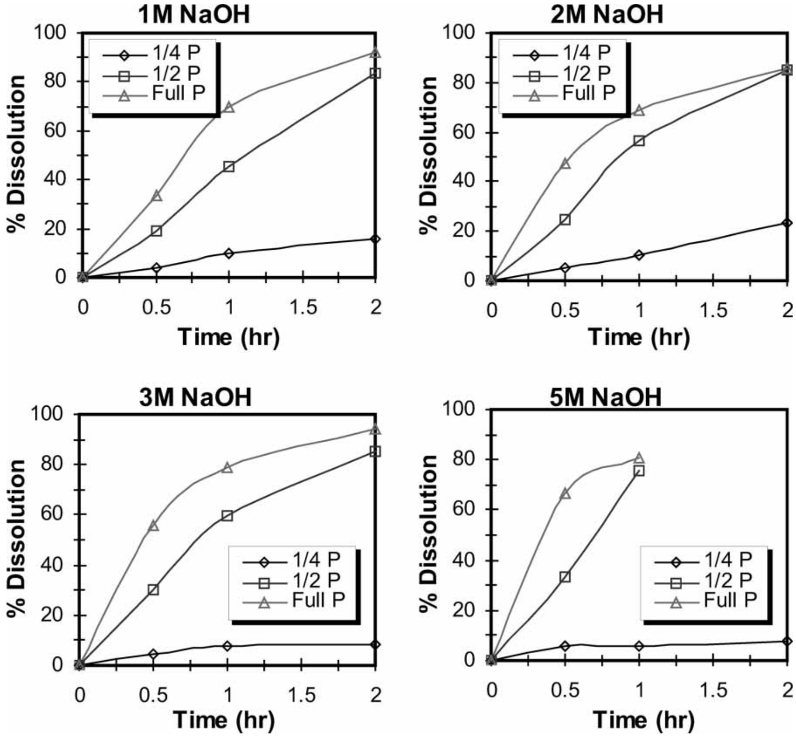

Figure 1. Cr removal from an S-101 sludge simulant as a function of time in four different NaOH concentrations (1, 2, 3, and 5 M) using three different ultrasonic powers (1/4, 1/2 and full).

at full power. At any time, chromium removal by sonication was much better than by stirring at 80°C, which was better than agitation at room temperature. It is understood that the ultrasonic process brings at least two effects—raising the solution temperature and increasing the surface area of the sludge by disrupting the solid particles. Because neither stirring nor high temperatures by themselves or in combination could achieve the Cr dissolution obtained by sonication, and because the presence of Cr(VI) in solution was observed when sonication was used, we can conclude that sonication caused the oxidation of Cr(III) to Cr(VI).

The oxidation process was investigated by applying ultrasound to dissolved Cr(III) (from $Cr(NO_3)_3$) in 2 M NaOH for 30 minutes. This eliminated possible interactions between Cr(III) and other sludge components. The presence of Cr(VI) in solution, from the oxidation of Cr(III), was determined by means of the UV/V is spectroscopy at 372 nm. As shown in Fig. 3, ultrasonic treatment oxidized only 10% of Cr(III) present in the solution. Other compounds known to be present in the sludge were then

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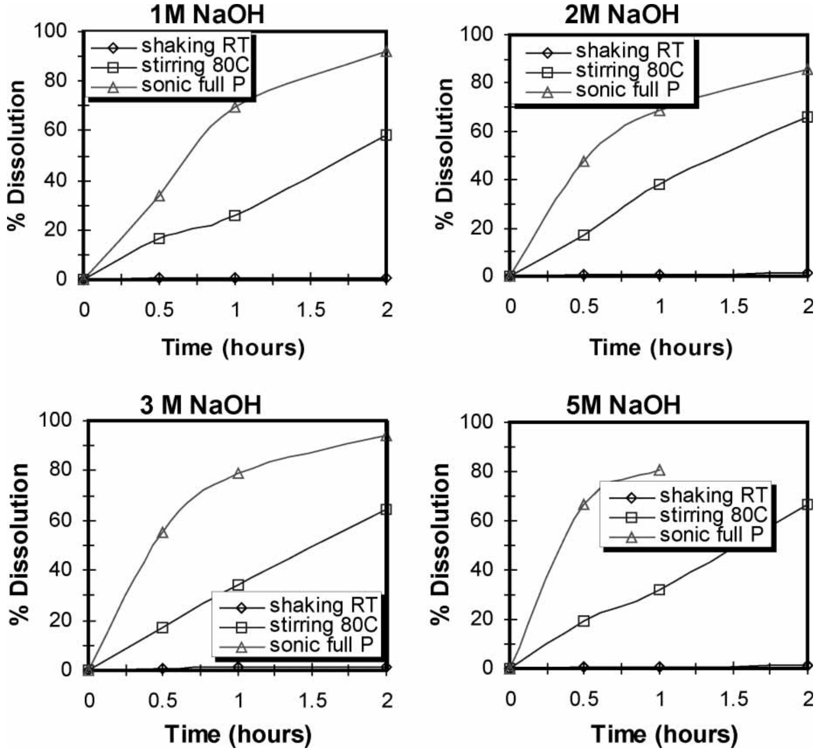

Figure 2. Cr removal from an S-101 sludge simulant under three conditions: ultrasound at full power, stirring at 80°C, and shaken at room temperature.

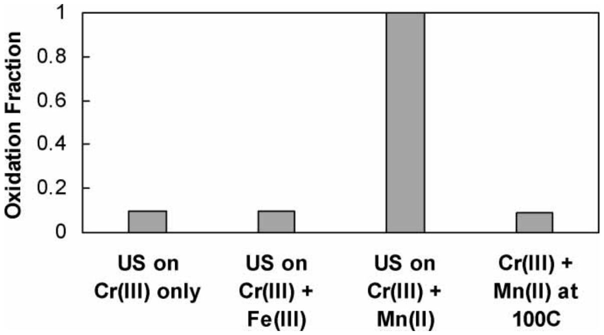

Figure 3. Oxidation of Cr(III) (from $Cr(OH)_3$) to CrO_4^{2-} in 20 mL of 2 M NaOH under ultrasonic (US) irradiation for 30 minutes in the presence and absence of Fe(III) and Mn(II) and under no US in the presence of Mn(II) at 100°C.

added. In the presence of dissolved Fe(III) (added as $Fe(NO_3)_3$), no improvement was observed. However, sonication of a sodium hydroxide solution containing Cr(III) and Mn(II) (added as $Mn(NO_3)_2$) completely oxidized all Cr(III) to Cr(VI) within 30 minutes. On the other hand, heating the NaOH solution containing dissolved Cr(III) and Mn(II) to 100°C for 30 minutes, only oxidized 10% of Cr(III) to Cr(VI). Therefore, Mn(II) appears to significantly aid Cr oxidation by ultrasound. Accordingly, Cr(III) in the sludge simulant (which contained Mn(II)) was oxidized and removed by the ultrasonic irradiation due to the catalytic oxidation by Mn(II).

To optimize chromium removal by the ultrasound process, it is important to know how much sludge could be treated with a fixed volume of sodium hydroxide. Different amounts of sludge simulant (1–5 g) in 30 mL of 1, 2, and 3 M sodium hydroxide were treated for 1 hour by either the ultrasound process or the hot bath/stirring process. As shown in Fig. 4, chromium removal with the ultrasound at 1/2 power was always better than either the hot bath or the ultrasound at 1/4 power. Chromium removal was better at higher NaOH solutions when either ultrasound at 1/2 power or the hot bath/stirring was used (cf., Table 2 and Fig. 1). Treatment with the ultrasound at 1/4 power dissolved less than 10% of the Cr(III) in all cases, with better total dissolution with a small sludge mass. At 3M NaOH, the chromium removal efficiency was about the same for 1 to 4 g using the ultrasound at 1/2 power. Similar result was obtained with the 1 M and 2 M NaOH for sludge masses between 1 and 3 g. Using the hot bath, 1 to 3 g could be treated with a similar efficiency at any NaOH concentration.

This experiment shows that, with the same experimental conditions, the best Cr removal (as an absolute value) was achieved using 3M NaOH to treat 4 g of sludge. This would give an idea of how much mass of sludge can be effectively treated per batch of sodium hydroxide.

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Cr Dissolution in the Presence of Oxidant & Ultrasound

Figure 5 shows the effect of ferrate concentration on the removal of chromium from 1 g of the S-101 sludge simulant after 30 min of sonication at half power. At any sodium hydroxide concentration, chromium removal increased with increasing ferrate concentration, except at 1 M, where chromium removal reached a plateau at 3 mM ferrate. At 10 mM ferrate, 5 M NaOH solution, chromium removal was about 2.25 times the value obtained in the absence of ferrate. Similar removal efficiencies can be reached with ultrasound with no oxidant if longer treatment times are allowed (cf., Fig. 1).

Figure 6 shows the effect of permanganate concentration on the chromium removal from the S-101 sludge simulant after 30 minutes of ultrasonic treatment at half power. At all sodium hydroxide concentrations, chromium removal was significantly improved by the addition of the oxidant. For permanganate concentrations higher than 2 mM, the chromium

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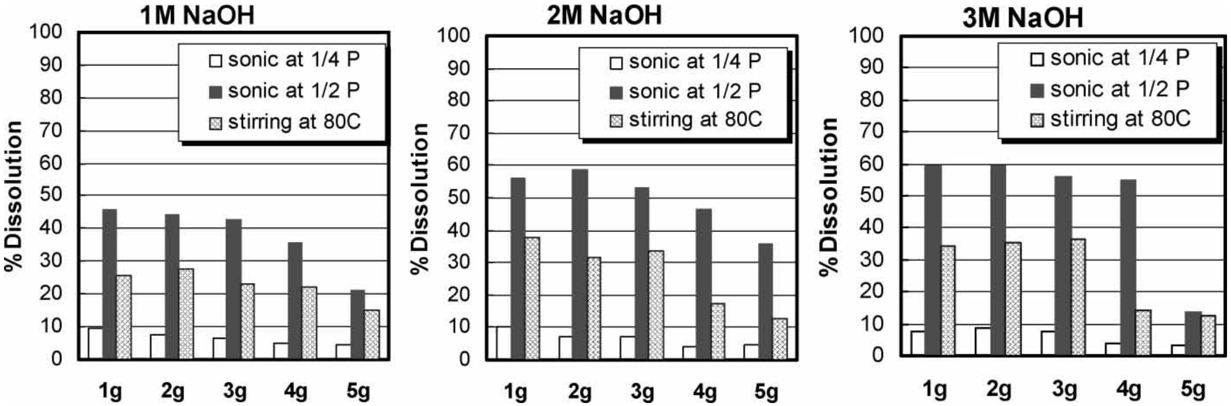

Figure 4. Cr removal from an S-101 sludge simulant as a function of the sludge mass after 1 hr of treatment. Different NaOH concentrations were used, as indicated in each figure.

Table 2. Percentage removal of Fe, Mn, Ca, Al, and P from 1 g S-101 sludge simulant under ultrasonic irradiation

Time, hours	[NaOH], M	Power level[a]	Temperature, °C	Amount removed, %				
				Fe	Mn	Ca	Al	P
0.5	1	1/4	58	<1	1	6	9	18
0.5	1	1/2	81	<2	1	4	21	30
0.5	1	full	90	5	<2	4	35	49
0.5	2	1/4	57	<1	2	6	10	19
0.5	2	1/2	79	2	2	5	18	27
0.5	2	full	91	10	3	14	42	60
0.5	3	1/4	59	<2	4	12	10	19
0.5	3	1/2	80	7	5	12	24	30
0.5	3	full	91	18	<2	18	48	61
0.5	5	1/4	57	4	10	25	9	17
0.5	5	1/2	86	16	13	20	30	39
0.5	5	full	92	35	5	30	62	65
1	1	1/4	64	<1	1	4	13	25
1	1	1/2	79	3	1	4	35	46
1	1	full	87	9	<2	14	61	69
1	2	1/4	63	1	4	4	13	27
1	2	1/2	81	10	8	2	44	53
1	2	full	89	19	<2	20	61	70
1	3	1/4	66	<5	23	33	12	18
1	3	1/2	81	16	4	24	43	45
1	3	full	88	33	<2	17	79	80
1	5	1/4	68	7	37	19	16	30
1	5	1/2	86	29	20		70	62
1	5	full	90	42	3	18	92	77
2	1	1/4	67	<2	1	11	18	42
2	1	1/2	84	6	1	9	68	98
2	1	full	89	12	1	9	81	115[b]
2	2	1/4	68	2	3	7	23	51
2	2	1/2	83	14	1	11	67	94
2	2	full	82	21	1	9	77	95
2	3	1/4	63	4	19	9	17	35
2	3	1/2	82	26	2	7	68	68
2	3	full	88	36	2	13	84	77
2	5	1/4	67	23	54	26	23	33

[a] Measured power outputs were 6 W for 1/4 power level, 13–16 W for 1/2 power level, and 26–34 W for a full power level.

[b] (The dissolution of phosphorus in excess of 100% is an artifact caused by a combination of sludge non-homogeneity and analytical errors).

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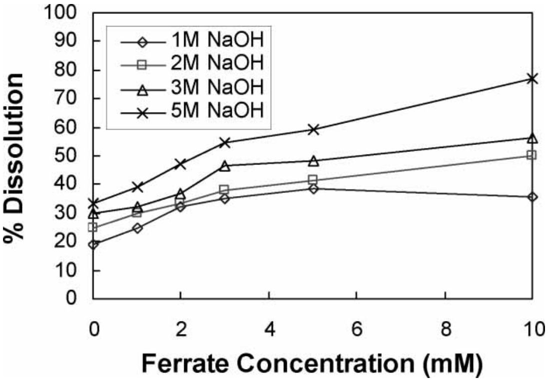

Figure 5. Effect of ferrate concentration on the removal of Cr from an S-101 sludge simulant. Ultrasound was used at 1/2 power. Treatment was carried out during 30 min.

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removal reached a plateau at all sodium hydroxide concentrations. The maximum chromium removal was from 2.25 to 4.5 times the level obtained in the absence of permanganate. Sodium hydroxide concentration had little effect on the efficiency of chromium dissolution. Similar removal efficiencies can be reached with ultrasound with no oxidant if longer treatment times are allowed (cf., Fig. 1). As a comparison, chromium removal in the presence of permanganate was better than in the presence of ferrate.

In the past, treatment with $KMnO_4$ has been found to be effective in the removal of chromium from SY-102 sludge (15). However it added an insoluble residue, MnO_2, to the sludge. This not only has the obvious disadvantage of increasing the mass of the sludge, but also, Mn(IV) may be

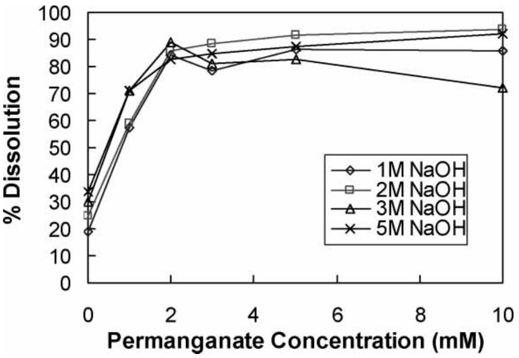

Figure 6. Effect of permanganate concentration on the removal of Cr from an S-101 sludge simulant. Ultrasound was used at 1/2 power. Treatment was carried out during 30 min.

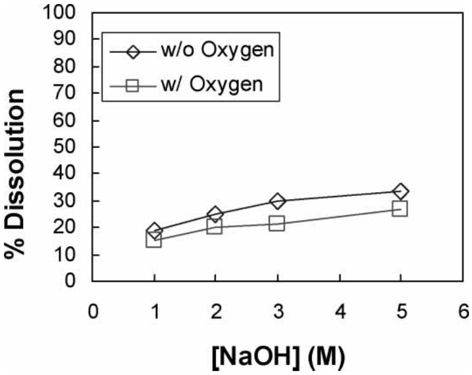

Figure 7. Effect of the presence of oxygen on the removal of Cr from an S-101 sludge simulant. Ultrasound was used at 1/2 power. Treatment was carried out during 30 min.

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incompatible for the glass formulation of the HLW fraction (16). In that sense, ferrate is more benign.

Figure 7 shows the effect of oxygen on the chromium removal from the S-101 sludge simulant after 30 minutes of sonic treatment at half power. At all sodium hydroxide concentrations, there is no significant enhancement in Cr dissolution due to the presence of oxygen. Although oxygen has an advantage over ferrate and permanganate (in the sense that the product of oxygen reduction is water and does not add mass to the sludge), its oxidation power is negligible.

Dissolution of Other Elements from the S-101 Sludge Simulant Using Ultrasound

Elemental analysis by ICP and AAS provided information on the dissolution of other components from the sludge during the ultrasound treatment. Table 2 lists the percentage removal of iron, manganese, calcium, aluminum, and phosphorus. S-101 sludge simulant (1 g) was treated using different NaOH concentrations (1, 2, 3, and 5 M), ultrasound power (1/4, 1/2, and full), and time (0.5, 1, and 2 hours). Some trends can be observed:

- Iron dissolution increased with ultrasound power, treatment time, and sodium hydroxide concentration. Up to 42% removal was achieved.
- Manganese dissolution increased with sodium hydroxide concentration. However, it seems to decrease with the increase of ultrasound power. There is not a clear correlation with treatment time. Up to 54% removal was achieved.

- There is not a clear dependence of calcium dissolution on the time, sodium hydroxide concentration or ultrasound power. Up to 33% removal was achieved.
- Aluminum dissolution increased with ultrasound power and treatment time. Aluminum dissolution above 80% was achieved with 1 and 2 hours of treatment time at full sonic power.
- Phosphorus dissolution increased with ultrasound power and treatment time. Phosphorus removal close to 100% was achieved at 1/2 and full power at 2 hours.
- The best mass reduction from the sludge was 80% at a full power in 1M NaOH for 2 hours of treatment. These results show that the ultrasound process not only removes Cr, but significantly reduces the sludge mass, by removing other non-radioactive species.

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Dissolution of Other Elements from the S-101 Sludge Simulant Using Stirring and/or a Hot Bath

Sludge samples (1 g) treated in either a hot bath (80°C) under constant stirring or shaken at room temperature (RT) were analyzed for the dissolution of iron, manganese, calcium, aluminum, and phosphorus. Samples were treated at different NaOH concentrations (1, 2, 3, and 5 M) for 0.5, 1, and 2 hours without sonication. Table 3 shows the removal of iron, manganese, calcium, aluminum, and phosphorus. Observed trends include:

- No significant dissolution of iron, manganese, and aluminum occurred at RT/shaken conditions.
- For both processes, calcium dissolution increased with an increase in the NaOH concentration (except RT/shaken treatment at 2 hr, 3 and 5 M NaOH). At all NaOH concentrations, treatment time did not have a significant effect on calcium dissolution, in most cases. Up to 13% was removed by the RT/shaken treatment, while the high temperature process removed up to 18%.
- Phosphorus dissolution was significant at the RT/shaken treatment, between 5 and 16%. After 0.5 hour of treatment, phosphorus dissolution seemed to increase with the NaOH concentration. At 1 and 2 hours of treatment, phosphorus dissolution was not significantly affected by the NaOH concentration. At all NaOH concentrations, phosphorus dissolution increased with treatment time.
- Iron dissolution was significant at the hot bath/stirring treatment, between 3 and 38%. For any given treatment time, iron dissolution increased with the NaOH concentration. For all NaOH concentrations, iron dissolution increased with treatment time.
- Manganese dissolution was significant at the hot bath/stirring treatment, up to 28%. For any given treatment time, manganese dissolution increased

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Table 3. Percentage removal of Fe, Mn, Ca, Al, and P from 1 g S-101 sludge simulant stirred in a hot bath (80°C) or shaken at room temperature

Process	Time, hours	[NaOH], M	Amount removed, %				
			Fe	Mn	Ca	Al	P
Shaken at room temperature	0.5	1	<1	<1	5	0	6
	0.5	2	<1	0	5	0	5
	0.5	3	<2	1	9	0	9
	0.5	5	<2	2	13	1	10
	1	1	<1	0	6	1	9
	1	2	<1	1	5	1	10
	1	3	<2	1	9	1	10
	1	5	<2	2	12	1	11
	2	1	<2	0	5	1	12
	2	2	<2	1	6	1	16
	2	3	<2	0	2	1	16
	2	5	<2	1	4	2	15
Stirred at 80°C	0.5	1	<3	<2	4	21	36
	0.5	2	3	3	14	20	37
	0.5	3	4	4	13	20	37
	0.5	5	11	20	18	25	37
	1	1	<3	<2	3	28	41
	1	2	8	2	6	35	51
	1	3	8	4	7	33	47
	1	5	20	28	9	40	50
	2	1	7	<2	6	49	62
	2	2	17	<2	11	55	87
	2	3	22	2	13	58	70
	2	5	38	10	13	66	70

with the NaOH concentration, especially at 5 M. Manganese dissolution was insignificant at 1 M NaOH.

- Aluminum dissolution was significant at the hot bath/stirring treatment, between 21 and 66%. For any given treatment time, NaOH concentration did not have a significant effect in aluminum dissolution. For any given NaOH concentration, aluminum dissolution increased with treatment time. These trends coincide with previous findings (17, 18).
- Phosphorus dissolution was significant at the hot bath/stirring treatment, between 35 and 87%. For any given NaOH concentration, phosphorus dissolution increased with treatment time.
- At any time and NaOH concentration, dissolution of iron, manganese, calcium, aluminum, and phosphorus was better in the hot bath/stirring treatment than at the RT/shaken treatment.
- The best mass reduction for the hot bath/stirring treatment was 67% (1 M NaOH, 2 hours of treatment), and for the RT/shaken treatment was 66% (1 M NaOH, 2 hours of treatment).

A comparison with the ultrasound treatment (cf., Table 2) shows that:

- At any time, iron, aluminum, and phosphorus dissolution was better in: ultrasound full power $>$ ultrasound 1/2 power $\geq$ hot bath/stirring treatment $\geq$ ultrasound 1/4 power $\gg$ shaken at RT.
- There is no definitive trend for manganese dissolution when the ultrasound and the hot bath/stirring treatment are compared. Removal at the RT/shaken treatment was minimal.
- Calcium dissolution in the ultrasound processes was similar to or better than the hot bath/stirring treatment and the RT/shaken treatment.
- Sludge mass reduction with the ultrasound process was higher than with the hot bath/stirring treatment or with the RT/shaken treatment.

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CONCLUSIONS

These experiments have clearly demonstrated that it is possible to dissolve substantial amounts of the components from the S-101 sludge simulant using ultrasound alone, without the addition of oxidants. Time, ultrasound power, temperature and sodium hydroxide concentration have all been shown to affect the amount of sludge dissolved. These studies indicate that it is viable to dissolve Cr(III) in low sodium hydroxide concentrations. This has the added benefit that lower amounts of Low Level Waste (LLW) will be produced because of the reduced amount of NaOH. The presence of Mn(II) compounds in the sludge aids the oxidation of Cr(III) from the sludge by the ultrasound process. The use of ferrate and permanganate combined with ultrasound enhanced the Cr removal from the sludge. Permanganate was more effective than ferrate. Oxygen had no effect on the removal of Cr from the sludge.

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