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**CHEMICAL PRETREATMENT OF NUCLEAR
WASTES FOR DISPOSAL**

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MICROBIOLOGICAL TREATMENT OF RADIOACTIVE WASTES

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INTRODUCTION

A major national concern is the remediation of contaminated materials, soils, and water as well as disposal of wastes containing radionuclides and toxic metals safely and economically. Large volumes of wastes containing toxic metals and radionuclides are generated by nuclear- and/or fossil-fueled power plants, the metal fabrication industries, and by facilities producing nuclear weapons. New innovative treatment and remediation technologies are needed because the problem is pervasive. Options for microbiological treatment include stabilization, or the removal and recovery of the contaminants. Stabilization means that the radionuclides and toxic metals are converted chemically or biologically to an insoluble form which is stable in the environment. For decontamination, both metal and radionuclide must be removed and recovered from the contaminated site, so that the site is restored. Stabilizing and reducing the mass of the radionuclides and toxic metals contained in such wastes would facilitate their disposal.

The ability of microorganisms which are ubiquitous throughout nature to bring about transformation of organic and inorganic compounds in radioactive wastes has been recognized¹. Unlike organic contaminants, metals cannot be destroyed, but must be either removed or converted to a stable form. Radionuclides and toxic metals in wastes may be present initially in soluble form or, after disposal, may be converted to a soluble form by chemical or microbiological processes. The key microbiological reactions include (i) oxidation/reduction; (ii) change in pH and Eh which affects the valence state and solubility of the metal; (iii) production of sequestering agents; and (iv) bioaccumulation. All of these processes can mobilize or stabilize metals in the environment. The types of radionuclides and toxic metals commonly found in wastes include uranium, thorium, plutonium, cadmium, cesium, chromium, cobalt, copper, lead, manganese, nickel, strontium, and zinc. They are present in various forms such as elemental, oxide, ionic, inorganic complex, and organic complex. Biotransformation of the various forms of the metal depends upon the type of microbes present, the

presence of suitable electron donors and acceptors, and environmental factors such as pH, temperature, and moisture.

Basic studies at Brookhaven National Laboratory (BNL) dealing with the mechanisms of microbiological transformations of radionuclides and toxic metals have resulted in the development of two novel processes for treating radioactive wastes. One process uses anaerobic bacteria to stabilize the radionuclides and toxic metals in the waste with a concurrent reduction in volume due to the dissolution and removal of nontoxic elements in the waste. In the second process, the toxic metals are removed from the waste by citric acid extraction and the metals and radionuclides in the extract are recovered by biodegradation followed by photodegradation.

EXPERIMENTAL

Waste Sample

A sludge sample was collected from the West End Treatment Facility, at the U.S. Department of Energy, Oak Ridge Y-12 Plant, Oak Ridge, TN. The sludge was generated from a uranium process waste stream after biodenitrification of nitric acid uranium waste. Several million gallons of the sludge is in storage awaiting disposal. Table 1 gives the chemical characteristics of the sludge sample. It contains a small amount of organic carbon and nitrogen, but is high in sulfate concentration and ash content. Sulfate in the sludge resulted from adding sulfuric acid and ferric sulfate during waste treatment. The sludge contains varying levels of major elements, such as aluminum, calcium, iron, magnesium, potassium, and sodium; and toxic metals of arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium, uranium, and zinc. The concentrations of calcium, nickel, and uranium in the sludge are high.

The mineralogical association of cadmium, chromium, copper, manganese, nickel, lead, uranium, and zinc in the sludge was determined by a selective extraction procedure^{2,3}. It involved the determination of water soluble, exchangeable, carbonate, iron-manganese oxide, organic, inert, and residual fractions. For example, uranium was associated with the exchangeable (400 mg), carbonate (1600 mg), iron oxide (216 mg), organic (516 mg), and inert (80 mg/g dry wt) fractions (Figure 1). Nearly half the total uranium in the sludge was associated with the carbonate fraction.

Stabilization and Volume Reduction by Anaerobic Bacterial Treatment

The sludge was treated with anaerobic bacteria to release a large fraction of the waste solids into solution. The radionuclides and toxic metals were converted to a more concentrated and stable form. At the same time, the volume and mass were reduced. In this process, the unique metabolic capabilities of dual-action anaerobic bacteria were exploited to solubilize and precipitate radionuclides^{3,4}. The non-hazardous materials in the solid phase such as calcium, potassium, sodium, magnesium, and iron were solubilized and easily removed from the waste, thus reducing its volume. The re-mobilized radionuclides and toxic metals were stabilized by precipitation and redistributed with stable mineralogical fractions of the waste (Figure 2).

Five grams of sludge in 160 ml acid washed sterile serum bottles with and without nutrients were incubated anaerobically in the presence of N₂ atmosphere. One hundred millimeters of deionized water or deionized water containing glucose and NH₄Cl were pre-reduced by boiling for 15 minutes while purging with N₂ (99.99% purity), and then added to the sludge sample; the serum bottles were sealed with butyl

Table 1. Characterization of Oak Ridge site sludge sample.

Constituents	Concentration
Physical, %	
moisture	56.7 $\pm$ 0.4*
ash	65.3 $\pm$ 0.00
Chemical, % dry weight	
carbon	1.35 $\pm$ 0.00
nitrogen	0.12 $\pm$ 0.00
sulfate sulfur	2.57 $\pm$ 0.05
Major metals, % dry weight	
aluminum	5.21 $\pm$ 0.02
calcium	24.1 $\pm$ 1.2
iron	0.50 $\pm$ 0.01
magnesium	1.30 $\pm$ 0.09
potassium	0.05 $\pm$ 0.00
sodium	1.87 $\pm$ 0.04
Toxic metals, μ g/g dry weight	
arsenic	1.3 $\pm$ 0.0
cadmium	93.5 $\pm$ 0.3
chromium	396 $\pm$ 9
cobalt	38.7 $\pm$ 10.5
copper	371 $\pm$ 1
lead	267 $\pm$ 18
manganese	244 $\pm$ 4
mercury	10.6 $\pm$ 1.1
nickel	1260 $\pm$ 5
selenium	< 1.0
uranium	2700 $\pm$ 200
zinc	1000 $\pm$ 30

* $\pm$ 1 Standard error of the mean.

rubber stoppers. The samples were inoculated with the *Clostridium* sp. ATCC #55102. The treatments consisted of (i) sludge sample plus deionized water (unamended); (ii) sludge sample plus deionized water containing 0.5% glucose and 0.015% NH_4Cl (amended); and (iii) control (autoclaved) sludge sample with deionized water. All samples were incubated at 24°C, in triplicate, except the control samples, which were incubated in duplicate. Periodically, unamended, amended, and the control samples were analyzed for the production of total gas, CO_2 , H_2 , and CH_4 . An aliquot of the samples was removed for pH determination and then filtered through a 0.22 μm Millex filter. A portion of the filtered aliquot was analyzed for anions by ion chromatography using a conductivity detector; for organic acids by HPLC, using a UV detector at 210 nm; and for alcohols and glucose by HPLC, using a refractive index detector. Another portion of the aliquot was acidified with HNO_3 , and analyzed for uranium and metals.

Table 2. Anaerobic microbial activity in sludge.

Treatment	pH	Gas Produced (ml)	CO ₂	H ₂	CH ₄
			-----	mmoles -----	-----
Control (Unamended)	8.89 ± 0.03	0.74 ± 0.15	0.965 ± 0.090	0.002 ± 0.000	0.001 ± 0.000
Treated (Amended)	6.40 ± 0.0	52.4 ± 4.6	5.74 ± 0.75	0.771 ± 0.16	0.006 ± 0.000

Notes: Samples were analyzed after 35 days incubation.

Error bar represent ± 1SEM.

Organic by-products detected: ethanol, formic, acetic, propionic, butyric, isobutyric, valeric, isocaproic, lactic, and pyruvic acids.

Table 3. Dissolution of metals from sludge by anaerobic microbial activity.

Treatment	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	U	Zn
	-----	-----	-----	-----	-----	-----	-----	μgdw ⁻¹ -----	-----	-----	-----	-----	-----	-----	-----
Control (Unamended)	<25	180±19 (0.07)	<1	ND	<2	<1	<5	345±66	240±2 (2)	<1	5240±0	17.6±0.6 (1)	<2	<5	1.24±0.24 (0.12)
Treated (Unamended)	<25	49000±5300 (20)	<1	2.53±0.47	<2	<1	966±8 (19)	419±23	5400±60 (42)	19.9±0.7 (8)	5540±2	69.9±1.4 (5)	<2	<5	10.8±3 (1)

Notes: () = % of total metal.

< values reported for each element are below the detection limit; values reported in parenthesis are % of total metal.

Error bars represent 1 ± SEM.

Table 2 shows the results of anaerobic microbial activity in the sludge. The unamended samples showed neither significant microbial activity nor production of organic acid metabolic products. However, the amended samples showed an increase in total gas, CO_2 , H_2 , CH_4 , and organic acids; its pH was lowered by about 2.5 units. This change was due to the production of organic acid metabolites from glucose fermentation. The organic acids consisted of acetic, butyric, propionic, formic, pyruvic, lactic, isobutyric, valeric, and isocaproic acids. A significant amount of gas was produced due to glucose fermentation by anaerobic bacteria, as well as the dissolution of CaCO_3 in the sludge by the organic acids. A decrease in sulfate concentration was observed only in amended samples, but the formation of sulfides (blackening of waste) was not evident.

Dissolution and Precipitation of Metals. The dissolution due to metals by anaerobic bacterial activity are shown in Table 3. The unamended sludge showed little dissolution of calcium (0.07%), magnesium (2%), nickel (1%), and zinc (0.1%). In the amended samples, increased concentrations of calcium (20%), iron (19%) magnesium (42%), manganese (8%), and lesser amounts of nickel (5%) and zinc (1%) were found in solution, but aluminum, cadmium, chromium, copper, lead, and uranium were not detected in solution. Analysis of the remaining solids showed enrichment of aluminum, cadmium, chromium, copper, nickel, lead, uranium, and zinc (Figure 3). These metals were concentrated in the solids after anaerobic microbial activity.

Mineralogical Association of Metals Before and After Microbial Action. The mineralogical associations of the toxic metals in sludge showed changes after microbial action (Figure 4). Cadmium associated with the carbonate fraction decreased, while the oxide, organic, and inert fractions showed an increase after microbial action. Chromium was present in the carbonate, oxide, organic, and inert fractions and all the fractions showed an increase in concentration of chromium after treatment with anaerobic bacteria. Copper was associated with the organic fraction and a small amount with the oxide and inert fractions. After microbial activity, the concentrations of copper in the organic and inert fractions increased. Most of the manganese was associated with the carbonate fraction. Enrichment of Mn in the carbonate and oxide fractions were observed after microbial activity. The bulk of the nickel was associated with the carbonate and oxide fractions and a small fraction with the organic and inert phase. Microbial activity caused an increase in concentration of nickel in the oxide, organic, and inert fractions, and a decrease in concentration in the soluble and the carbonate fractions. Lead was predominantly associated with the carbonate and the oxide fractions, with only a small amount present in the organic fraction. The concentration of lead in all three fractions increased as a result of microbial activity. Zinc was present in association with the carbonate, oxide, organic, and inert fractions. After microbial activity the concentration of zinc increased in the oxide, organic, and inert fractions and decreased in the carbonate fraction. Uranium was predominantly associated with the carbonate fraction and to a lesser extent with the oxide, organic, and inert fractions. The concentration of uranium associated with the carbonate, oxide, and inert fractions increased after microbial activity. Figures 5 and 6 show the theoretical vs. observed uranium in solution on the basis of dissolution of calcium and the association of uranium with the carbonate fraction. However, uranium was not detected in solution.

Weight Loss. Substantial amounts of calcium, iron, potassium, magnesium, manganese, and sodium were solubilized from the waste, resulting in a reduction in mass; the net reduction due to the anaerobic bacterial in these batch cultures was

Figure 1. Mineralogical association of uranium in sludge. Uranium was predominantly associated with the carbonate fraction.

Figure 2. Stabilization and volume reduction of uranium waste. Sludge treated with Clostridium sp. showed stabilization and enrichment of uranium and toxic metals.

~ 15%. An additional reduction in waste volume can be achieved by optimizing the process using a continuous culture treatment system to solubilize and remove the bulk of non-toxic waste components, particularly calcium, potassium, iron, magnesium, and manganese.

This biotreatment process can be applied to wastes generated from defense, energy, and industrial wastes containing radioactive elements and toxic metals. The microbial treatment of such mixed wastes chemically converts the radionuclides and metals to a more stable form. Reducing the mass of the wastes means that more material can be stored or disposed of, can be handled easier, and can be transported or chemically treated more easily. Changing the radionuclides and toxic metals to a more stable form allows the material to be, chemically processed more readily or disposed of in shallow or deep geological formation where the material is less susceptible to chemical change or transport. Microbial treatment results in a waste that is less susceptible to environmental factors and can be disposed of more economically.

Removal and Recovery of Radionuclides and Toxic Metals

An alternative treatment method for radionuclide or toxic metal-contaminated materials, soils, sediments, and wastes involves extracting the metals and radionuclides with citric acid as citrate complexes^{5,6}. The extract then is treated with *Pseudomonas fluorescens* ATCC No. 55241 to recover the toxic metals. The supernatant containing

Figure 3. Enrichment of metals in sludge after anaerobic microbial treatment. [Enrichment factor is the mean concentration in the sludge divided by that after microbial activity. A ratio of 1 indicates no action a ratio > 1 shows enrichment, and < 1 shows removal from the sludge.]

Figure 4. Mineralogical association of uranium and toxic metals in sludge before (□) and after (■) microbiological activity. Error bars represent $1 \pm \text{SEM}$.

Figure 5. Dissolution of calcium from amended sludge. A substantial amount of calcium was solubilized due to indirect action of the anaerobic bacteria; there was no dissolution in the control and unamended samples.

Figure 6. Theoretical and observed concentration of uranium in solution. Uranium associated with the carbonate fraction was released due to dissolution of calcium, and subsequently reduced to a lower oxidation state due to direct enzymatic action of the bacteria.

the uranium-citrate complex is subjected to photolysis to degrade the complex and recover the uranium in a concentrated polymeric form (Figure 7).

Citric acid, a naturally occurring organic complexing agent, forms different types of complexes with the transition metals and actinides, and may involve the formation of bidentate, tridentate, binuclear, or polynuclear complex species (Figure 8). Citric acid is used to extract metals such as barium, chromium, nickel, zinc, and radionuclides, such as cobalt, strontium, thorium, and uranium from solid wastes by generating water-soluble, metal-citrate complexes. The extract containing the radionuclide/metal complex then is subjected to microbiological degradation, followed by photochemical degradation under aerobic conditions. Several metal citrate complexes are biodegraded, and the metals are recovered in a concentrated form with the bacterial biomass. Uranium forms a binuclear complex with citric acid and is not biodegraded. The supernatant containing this complex is separated and upon exposure to light, rapidly degrades forming an insoluble, stable polymeric form of uranium. Uranium is recovered as a precipitate ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) in a concentrated form for recycling or for disposal. This treatment process, unlike others which use alkaline or acidic reagents, does not create additional hazardous wastes for disposal, and causes little damage to the soil which can then be returned to normal use.

Figure 7. Citric acid treatment process. Flow chart showing the extraction and recovery of uranium and toxic metals from waste by biodegradation/photodegradation processes.

Previous large-scale methods devised to deal with the problems of contaminated materials and soils used corrosive reagents, such as hot sulfuric or hydrochloric acids, and oxidizing agents, such as sodium hypochlorite, to extract the metals. However, these methods also cause irreparable damage to the soil and generate secondary waste streams which create further problems of hazardous waste disposal.

Many chelating agents used in decontamination undergo little degradation by microorganisms^{1,7}. Biodegradation of these metal chelates should cause the precipitation of released ions as water-insoluble hydroxides, oxides, or salts, thereby retarding the migration of metals. Recently, we reported that the type of complex formed between the metal and citric acid plays an important role in determining its biodegradability^{8,9}. The presence of the free hydroxyl group of citric acid is the key determinant in effecting biodegradation of the metal complex. For example, Ca, Fe(III), and Ni formed mononuclear bidentate complexes and were readily biodegraded, whereas, Cd, Cu, Fe(II), and Pb formed mononuclear tridentate complexes, and U formed a binuclear complex involving the hydroxyl group of the citric acid, and were not biodegraded. The lack of degradation of the latter complexes was not due to their toxicity, but was probably limited by the transport and/or metabolism of the complex by the bacteria¹⁰.

Citric acid has been used to decontaminate components of nuclear reactors, but the methods of metal recovery involve ion-exchange, porous DC electrodes, or burning the organics. Citric acid was used to extract plutonium from contaminated soils to determine plutonium uptake by plants¹¹. Several metal citrate complexes are readily biodegraded by microorganisms, with recovery of the metal species with the biomass. Uranyl citrate is recalcitrant to biodegradation but upon exposure to visible light undergoes photochemical degradation resulting in the formation of an insoluble, stable polymeric form of uranium identified as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ¹²⁻¹⁴.

Figure 8. Types of complexes formed between citric acid and metals.

to 6.5 with NaOH, and then the extract (100 ml) was inoculated with 4 ml of an 18-hour old culture of *Pseudomonas fluorescens* ATCC 55241. The samples were incubated for 118 hours on a shaker at 24°C. The bacterial inoculum was grown in medium containing citric acid, 2 g; NH₄Cl, 1 g; KH₂PO₄, 1 g; K₂HPO₄, 1 g; NaCl, 4 g; MgSO₄, 0.2 g; distilled water, 1000 ml; and pH 6.5. All samples were prepared under low light to minimize any photochemical reactions. Periodically, 5 ml aliquots were removed, filtered through a 0.22 µm filter, and analyzed for (i) pH; (ii) citric acid biodegradation by HPLC using UV detector; and (iii) soluble uranium. At the end of incubation, the supernatant and the solids consisting of bacterial biomass and the precipitated metals were separated by centrifugation. The dry weight was determined, and the solids were digested in a mixture of hot nitric and perchloric acids. The supernatant liquid and the digested solids were analyzed for uranium and other metals by ICP-MS. The bacteria degraded citric acid at a rate of 0.5-0.7 mM per hour (Figure 10); there was little change in concentration of uranium suggesting that the uranium citrate complex was not biodegraded. Cobalt, nickel, zinc, and zirconium were present along with the biomass, indicating that their citrate complexes were readily biodegraded.

Photodegradation of Uranium Citrate Extract. After adjusting the pH to 3.5 with HCL the supernate from the biodegradation treatment primarily containing uranium citrate complex was exposed to high output fluorescent growth lights to degrade the complex and recover uranium (Figure 11). Periodically, samples were withdrawn, filtered through a 0.22 µm filter, and analyzed for uranium, citric acid, and photodegradation products. At the end of the experiment (after 157 hours of exposure to light), the solutions were filtered and analyzed for citric acid degradation products and metals. The uranium precipitated out of solution as a polymer soon after it was exposed to light. After 50 hours, ~ 85% of the uranium was removed from solution.

Figure 9. Extraction of uranium from sludge with citric acid.

Table 4. Extraction efficiency of metals from sludge by citric acid.

Metal	Total Metals in Sludge ($\mu\text{g.gdw}^{-1}$)	% Metal Extracted
Ag	41 $\pm$ 30	2.4
Al	30500 $\pm$ 500	58.7
Au	1800 $\pm$ 500	<1
Ba	427 $\pm$ 25	24.4
Be	5.21 $\pm$ 0.45	60.1
Cd	66 $\pm$ 6	9.1
Co	0.7 $\pm$ 0.3	74.8
Cr	342 $\pm$ 10	74.6
Cu	329 $\pm$ 18	1.2
Ga	28.8 $\pm$ 0.6	25.7
Mg	7510 $\pm$ 100	89.2
Mn	234 $\pm$ 3	82.9
Ni	1120 $\pm$ 10	80.0
Pb	224 $\pm$ 27	<1
Pd	5.51 $\pm$ 0.70	49.0
Sb	5.67 $\pm$ 0.05	68.8
Sn	17.6 $\pm$ 0.4	93.1
Sr	125 $\pm$ 5	59.2
Th	3.08 $\pm$ 0.10	94.2
Ti	922 $\pm$ 95	28.4
U	2410 $\pm$ 100	86.8
V	121 $\pm$ 7	4.1
Zn	839 $\pm$ 7	59.6
Zr	209 $\pm$ 4	84.2

Extraction of Radionuclides and Metals. Ten grams of sludge containing uranium and several toxic metals (Table 1) obtained from the Oak Ridge Y-12 Plant, were extracted with 100 ml of 0.40 M citric acid, for five hours in the dark. The citric acid extract and the solids were separated and analyzed for metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Figure 9 shows the extraction efficiency of uranium by various concentrations of citric acid. Table 4 shows extraction efficiency of various metals from sludge by citric acid. In this sample, metals of aluminum, beryllium, cobalt, chromium, manganese, nickel, antimony, tin, zinc, and zirconium were extracted with >50% efficiency by citric acid treatment. The radionuclides, uranium and thorium, were extracted with 87% and 94% efficiency, respectively. Silver, copper, lead, and vanadium were not extracted, probably due to the nature of their association with stable mineral phases⁴. For example, copper was predominantly associated with the organic fraction and a small amount with the iron oxide and inert fractions and was not extracted by citric acid (Figure 4).

Biodegradation of Metal Citrate Extract. Citric-acid sludge extract was amended with nutrients consisting of 0.1% NH_4Cl , K_2HPO_4 , and KH_2PO_4 . The pH was adjusted

5. Effects of biodegradation followed by photodegradation in the treatment of citric acid sludge extract.

Metal	Before Treatment (μM)	% Removal		Total
		After Bio-Treatment	After Photo-Degradation	
Al	7410	92	1	93
Ba	12.0	92	< 1	92
Be	3.22	> 99	< 1	> 99
Co	0.87	71	6	77
Cr	60.8	< 1	25	25
Ga	0.89	73	16	89
Mn	37.2	98	< 1	98
Ni	192	64	1	65
Pd	0.31	64	30	94
Sb	0.36	2	14	16
Sn	1.71	> 99	< 1	> 99
Sr	10.2	98	1	99
Th	0.11	96	3	> 99
Ti	80.2	96	< 1	96
U	94.8	9	78	87
Zn	86.1	90	5	95
Zr	61.7	97	2	99

Table 5 shows the efficiency of removal of various metals from the citric acid sludge extract subjected first to biodegradation, then to photodegradation.

Characterization of Uranium Precipitate. The uranium precipitate was identified as $(\text{UO}_3 \cdot 2\text{H}_2\text{O})$ by X-ray Photoelectron Spectroscopy (XPS) and by X-ray Absorption Near-Edge Spectroscopy (XANES) at the National Synchrotron Light Source (NSLS)¹⁴. The uranium precipitate was quite insoluble at the near neutral pH and soluble in acidic pH (<3.5).

Weight Loss. The solids remaining after extraction with citric acid were washed with deionized water, and dried in an oven overnight at 105°C to determine the weight loss due to citric acid extraction. The extraction of metals from the waste resulted in significant reduction (47%) in weight.

These results show that (i) uranium was extracted from the mixed waste with >85% efficiency using 0.4 M citric acid; (ii) other metals such as chromium, cobalt, manganese, nickel, strontium, thorium, zinc, and zirconium were also extracted from the waste; (iii) the uncomplexed excess citric acid and several metal citrate complexes (Co, Ni, Zn and, Zn) with the exception of binuclear uranium citrate complex, were readily biodegraded by *Pseudomonas fluorescens*, and the metals were recovered with the bacterial biomass; and (iv) the uranium citrate complex was photodegraded, allowing the uranium to form a polymer which was recovered as a concentrated solid.

Figure 11. Photodegradation of uranium citrate complex in sludge extract after

Figure 10. Biodegradation of citric acid sludge extract.

SUMMARY

Two microbiological processes are described for treating wastes, soils, and materials containing radionuclides and toxic metals. In one process, anaerobic microbes are used to concentrate, contain, and stabilize the toxic metals and radionuclides in the waste with concurrent reduction in volume. In the second process, the radionuclides and toxic metals are removed from the waste or contaminated material and recovered in a concentrated form for recycling or for disposal.

Stabilization and Volume Reduction by Anaerobic Bacterial Treatment. Stabilization of toxic metals and radionuclides in wastes is accomplished by exploiting the unique metabolic capabilities of the anaerobic bacterium, *Clostridium* sp. Mixed wastes, sludges, and contaminated soils or sediments are treated with the anaerobic bacteria. In this novel approach, the radionuclides and toxic metals are solubilized by the bacteria directly by enzymatic reductive dissolution or indirectly due to the production of organic acid metabolites. The radionuclides and toxic metals released into solution then are immobilized in the waste matrix by (i) enzymatic/chemical reductive precipitation processes; (ii) redistributed with stable mineral phases in the waste due to readsorption with the reactive surfaces; and (iii) biosorbed by the biomass. The re-mobilized radionuclides and toxic metals are thus stabilized by bacterial action. The iron, calcium, and other non-hazardous materials in the soluble phase are easily removed from waste so reducing its volume. The remaining solids, which contain the hazardous components in a concentrated, stable form, then can be disposed of safely in the subterranean environment. The reduced volume of the waste also results in considerable savings in disposal costs.

Removal and Recovery of Uranium and Toxic Metals from Waste. Removal and recovery of toxic metals and uranium in waste is accomplished aerobically using citric acid, aerobic microorganisms, and photochemical action. Uranium and toxic metals are removed from wastes or contaminated materials or soils by extracting with the complexing agent citric acid. The citric acid extract is subjected to microbiological degradation to recover the toxic metals, followed by photochemical degradation of the uranium citrate complex which is not biodegraded. The toxic metals and uranium are recovered in a concentrated form for recycling or for disposal. This process has significant potential for commercialization because (i) it can be applied to a variety of materials and waste forms; (ii) mixed waste is separated into radioactive and hazardous waste; (iii) uranium is separated from the toxic metals and recovered for recycling or disposal; (iv) it does not generate secondary waste streams; (v) it causes little damage to soil; and (vi) environmentally and economically important metals are removed in a concentrated form. The use of combined chemical, photochemical, and microbiological treatment processes of contaminated materials will be more efficient than present methods and result in considerable savings in clean-up and disposal costs.

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6/15/94

END