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Concepts in Waste Management: Decontamination of Plutonium-Bearing Mixed Wastes with Efficient Water and Acid Recycle

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ABSTRACT

Two integrated flowsheet concepts are presented for treating high-activity plutonium-contaminated mixed wastes containing materials that generate hydrogen on storage. A specialized electrocell can be used to generate cerium(IV) to dissolve high-fired plutonium oxides and simultaneously to oxidize organic species in the wastes that are susceptible to hydrogen formation. Nitric acid and water decontamination and recycle can be achieved using resin adsorption without evaporation. Transuranic contamination may be concentrated in a precipitate suitable for incorporation into borosilicate glass or other final waste forms using Fenton's chemistry or, preferably, immobilized in a silicate matrix directly from an adsorption resin and

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converted to a final waste form. Decontaminated TRU wastes are either converted to low-level wastes or packed to meet transuranic waste packing and shipping requirements. Preliminary results from Oak Ridge National Laboratory suggest that HEPA filter wastes can be processed to achieve decontamination factors of 10^4 for highly fired Pu oxide. Studies at the Argonne National Laboratory and Florida State University suggest that nitric acid and water can be recycled with decontamination factors in excess of 10^4 without evaporation. Alternative methods for using this technology are discussed.

INTRODUCTION

Ceric acid promoted oxidation and dissolution of actinides and organic matrices [also known as mediated electrochemical oxidation (MEO)] has potential applications in the treatment and decontamination of a wide variety of solid and liquid mixed wastes. Examples of such wastes include contaminated solvents, aqueous wastes, incineration ash, contaminated HEPA filters, contaminated soils, glove box and cabinet wastes, and other mixed solids. Historical defense wastes, particularly transuranic (TRU) solid wastes, are candidates for such treatment, as well as future wastes that are generated during fuel reprocessing or refabrication operations.

Any viable process for treating HEPA filters, other solid mixed waste, contaminated solvent wastes, and the like, must deal with the chemical and mechanical handling problems associated with these wastes and must also address the general intractability of refractory Pu oxide. Nitric acid alone is largely ineffective in dissolving PuO_2 once it has been fired to temperatures above 850°C.[1] The traditional methods for dissolving plutonium, using nitric and hydrofluoric acids with reflux, suffer from the disadvantage of creating fluoride-contaminated wastes.[2] The fiberglass contents in HEPA filters, for example, are readily dissolved using hydrofluoric acid. Other techniques, such as acid digestion,[3] also yield secondary waste residues that are difficult to manage.

In contrast, cerium-based treatment provides a suitable, low-temperature oxidation technology where the resulting nitric acid and water wastes can be decontaminated and recycled using multifunctional-chelating, ion exchange resins to remove virtually all metal contaminants. Effluents from resin bed regeneration can be treated using Fenton's chemistry to precipitate metal phosphates, an inorganic waste that is suitable for incorporation into glass, or

other final waste forms. Alternatively, the metal-loaded resin bed may be converted directly to a final waste form either by calcination or incorporation into a borosilicate glass for geologic disposal.

For a treatment method to receive serious consideration as a practical technology, it must provide efficient decontamination from waste residues without generating unmanageable secondary wastes. In addition, it must not materially increase the final waste volumes or deleteriously affect glass or concrete waste forms. Decontamination using MEO requires the use of an acidic electrolyte solution that must subsequently be decontaminated so the acid can be reused. It also requires the use of washwater solutions that must be recycled. Relatively large quantities of aqueous wastes may be generated and, although they typically contain low actinide concentrations, high alpha decontamination factors are required to recycle them. The traditional recycle method, water and acid evaporation, is not practical for this application, especially when used on a small scale, but decontamination using suitable resins appears attractive. Resins may either be regenerated or converted into a final waste form without regeneration.

Variations in MEO have been widely investigated both for the oxidation of organics,[4–11] glove box wastes such as contaminated gauntlets,[12] and insoluble actinide oxides.[13–15] Earlier studies by Navratil and Thompson[14] focused on the dissolution of refractory actinide species as they exist in incinerator ash. They noted that carbonaceous residues are oxidized to CO_2 more readily than refractory PuO_2 is dissolved. Savage and Kyffin[16] offer evidence that Ce(IV) induces the oxidative breakdown of polymeric Pu(IV), which is significant if colloidal Pu exists in the waste and its recovery is desired.

More recent studies focused on the destruction of organic species. Mediated electrochemical oxidation has been studied at Lawrence Livermore National Laboratory by Chiba et al,[17,18] by Farmer[19] using Ag(II), and at Pacific Northwest Laboratories by Bray et al,[20] and by Surma et al,[21] where similar technology is referred to as catalyzed electrochemical oxidation (CEO). Elmore and Lawrence[22] and Hobbs et al[23] examined the use of both divided and undivided cells for treating alkaline high-level tank wastes.

Mediated electrochemical oxidation using Ce(IV) was also examined as an alternative nonflame technology for the destruction of organic waste by Schwinkendorf et al[24] and by Chen et al[25] as a possible technology for decontamination in DOE facilities. Twenty-three alternative technologies were considered in the former study; thirty-three were considered in the latter. Schwinkendorf et al. found Ce-based MEO preferred over Ag- or Co-based mediation. Smith et al[26] explain the differences in reported reaction rates for the three mediators, cited as a point of confusion by Schwinkendorf et al, as attributable to the greater temperature dependence of the Ce(IV) reaction rate. At

room temperature, Ce(IV) is slower than either Co(III) or Ag(II) in oxidizing standard sulfonated styrene-divinyl benzene based cation exchange resin, a common waste form at many DOE sites, but it is about four times faster at 70°C.

Schwinkendorf et al ranked Ce-based MEO only moderately high as an alternative. They found it to be limited because it is not particularly suited to aqueous wastes (e.g., containing low concentrations of organics) and it is not fully developed. However, they did not consider the possibility of aqueous pretreatment followed by Ce(IV) oxidation of the secondary waste resulting from the pretreatment step. Chen et al found it suitable for surface decontamination in pipes, primarily based on the work reported by Bray et al,[27–29] but found it limited in that three moles of Ce(IV) are required to produce one mole of Fe^{+3}, and that a suitable process is needed to recycle water and nitric acid. Whenever large amounts of Ce(IV) are required to decontaminate a waste, the efficient use of Ce(IV) clearly requires effective methods for continuous recycle and regeneration.

The ability of cerium to catalyze the oxidation of a wide range of organic species is well known. The Cerox process,[30–32] for example, uses similar chemistry to that proposed here, and is being commercialized specifically to provide a low-temperature means of oxidizing organic liquids. Examples of organic species known to be oxidized by Ce(IV) include alcohols, ketones, aldehydes, furans, dioxins, species containing chlorine, phosphorous, sulfur, and many other hetero atoms.

Fully fluorinated carbon-based polymers are not readily oxidized by Ce(IV). Polyvinylidene fluoride (Kynar) and polytetrafluoroethylene (Teflon) are resistant to attack by Ce(IV). Kynar is used in the Cerox process as a material of construction, but may not be suitable in high radiation fields due to the possible formation of HF by radiolysis. Known suitable materials of construction are titanium and glass-lined vessels. Stainless steel is not a suitable material of construction. Polypropylene may be suitable at room temperatures, but the suitability of other polymers as materials of construction[a] for this application needs further evaluation.

WASTE PRETREATMENT

Waste pretreatment is probably an essential requirement for the effective use of most, if not all, technologies for treating mixed wastes. Pretreatment is

[a]Thermal, radiation, and chemical resistance must all be considered when selecting materials of construction.

certainly helpful in the case of cerium-promoted oxidation and essential for the efficient treatment of certain mixed wastes, such as aqueous streams and solids. Figure 1 summarizes some of the pretreatment options that should be considered and may be required, based upon the waste feed that is envisioned for treatment. Even for relatively small, solid objects, sizing can be important, especially if they are decontaminated in a fixed bed as described as follows. Extensive classification and sorting of solid wastes may be avoidable, but solids handling (i.e., transfer) is unavoidable in any case. Some solid wastes may require low temperature oxidation as a pretreatment to partly liberate binding materials (e.g., HEPA filters).

Organic liquids should be largely oxidizable to CO_2 and water. High-molecular weight perfluoronated polymers are the notable exception to this rule. Halogenated solvents will frequently produce either halogenated acids or, possibly, halogen gases, so minimal pretreatment is required for their destruction using cerium oxidation. They are simply metered slowly into the oxidizer, possibly after filtration to remove excessive solids concentration, and destroyed.

Aqueous mixed wastes, however, are less amenable to cerium-promoted decontamination without pretreatment. In some cases, it may be possible to use such wastes to makeup cerium and nitric acid electrolyte solution and thus avoid further water additions, but in other cases, pretreatment and management of the secondary wastes will prove more effective.

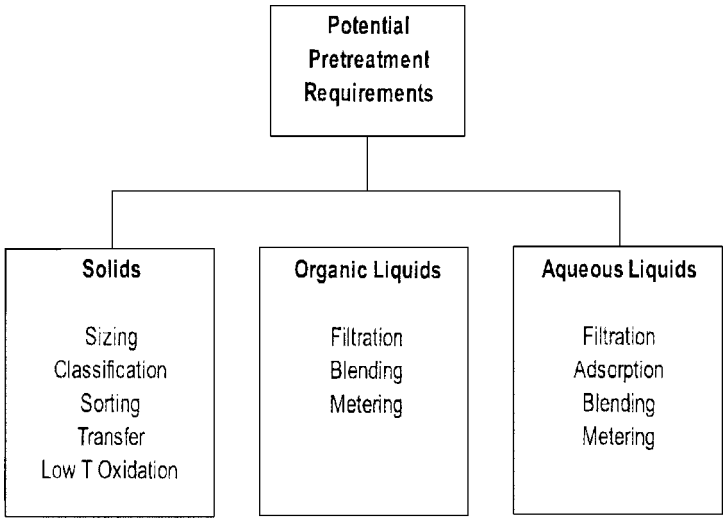

Figure 1. Pretreatment options for ceriuim-promoted decontamination.

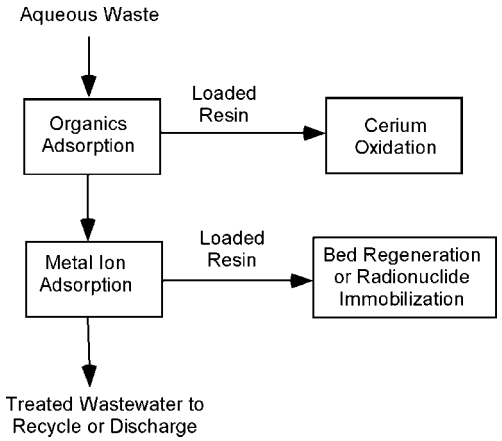

Figure 2. Conceptual pretreatment for aqueous mixed wastes to remove and separate low-molecular weight organics, which are readily oxidizable by Ce(IV), from actinides or other adsorbable radionuclides. Organics are subsequently oxidized with Ce(IV) as part of the loaded bed. Actinides are either recovered by bed regeneration or incorporated into a final waste form by calcining the bed.

For aqueous mixed wastes containing both organic and metal radionuclide contaminants, a two-step adsorption strategy (Fig. 2) may be preferred. In this case, the primary Aqueous waste is first passed through a suitable adsorbant to remove organics (e.g., activated carbon). It is then treated by passing it through a second adsorbent bed with high affinity for the metal ions to permit separation of most of the radionuclides from the organic contaminants. In the case of actinide contamination in the aqueous waste, this second step should result in removal of virtually all radioactive contamination and may permit the aqueous waste to be discharged or recycled as treated water. The loaded adsorbent from the first organics removal step may then be treated by cerium oxidation or otherwise managed.[b] The resin-loaded metal ions from the second adsorption step are either removed from the bed and

[b]The attractiveness of managing adsorbent waste by cerium oxidation depends upon the contamination levels in the primary wastes, their affinity for the adsorbent, and the quantities of resin that must be managed. This strategy would probably not be attractive in situations where relatively large quantitites of resin waste are generated. It may be more helpful if the organic concentrations are relatively low, but still problematic insofar as treatment by evaporation is concerned (e.g., if a significant potential exists to form nitrated aromatics or phosphorous-based red oils during evaporation).

converted to a final waste form or encapsulated into the bed to produce a final waste form, depending upon user preference.

ELECTROCELL DESIGN

The principal anode reaction under process conditions described here may be given by Eq. (1):

$$Ce(NO_3)_3 + HNO_3 + H_2O \rightarrow Ce(NO_3)_4 + H_3O^+ + e^- \quad (1)$$

with the formation of ceric nitrate.

Other studies[33] showed that nitrous acid is the principal species formed at the cathode at low current densities under these conditions. It may come into existence by reaction 2,

$$2\,H_3O^+ + HNO_3 + 2e^- \rightarrow HNO_2 + 3\,H_2O \quad (2)$$

where the hydronium ion is postulated to be the principal aqueous species that migrates from the anode to the cathode. As nitrous acid is formed, it can be removed from the liquid phase by an air sparge to prevent reduction of the ceric nitrate. In this case, the nitrous acid is decomposed primarily[34–38] by reaction 3,

$$3\,HNO_2(\ell) \rightarrow HNO_3(\ell) + 2\,NO(g) + H_2O(\ell) \quad (3)$$

although other side reactions are possible.

Equations 1 through 3 may be combined to give the following overall reaction for the oxidation of cerium in the electrolytic oxidizers:

$$3\,Ce(NO_3)_3 + 4\,HNO_3 \rightarrow 3\,Ce(NO_3)_4 + 2\,H_2O + NO(g) \quad (4)$$

It is postulated that Eq. (4) represents the most important net reaction in this system. Also, from Eq. (4), the principal reagent of the oxidation process is nitric acid, which is converted to nitrogen oxides and water by sparging the nitrous acid that is formed in the vicinity of the cathode. The cerium acts as a catalyst.

Highly fired Pu oxide is dissolved by reaction 5,

$$PuO_2 + 2\,Ce(NO_3)_4 \rightarrow 2\,Ce(NO_3)_3 + PuO_2(NO_3)_2 \quad (5)$$

Organic species are oxidized[31] via reactions similar to Eq. (6), using amino-dichloro-benzaldehyde as an example,

$$C_7H_5Cl_2NO + 36\,Ce(IV) + 17\,HNO_3 + 36\,e^- \rightarrow 7\,CO_2 + Cl_2 + 18\,HNO_2 + 36\,Ce(III) + 2\,H_2O \quad (6)$$

with the resulting production of carbon dioxide, chlorine, water, and nitrous acid.

EQUIPMENT CONFIGURATION

Studies at ORNL[15] suggest that the electrolytic oxidation of cerium can be carried out in a stirred tank (Fig. 3) in which the cathode is only partly shielded from the anode. However, it is not essential to separate the two electrodes by a diaphragm or membrane since Ce(IV) apparently exists in solution either as a neutral species or as nitrato-complexed

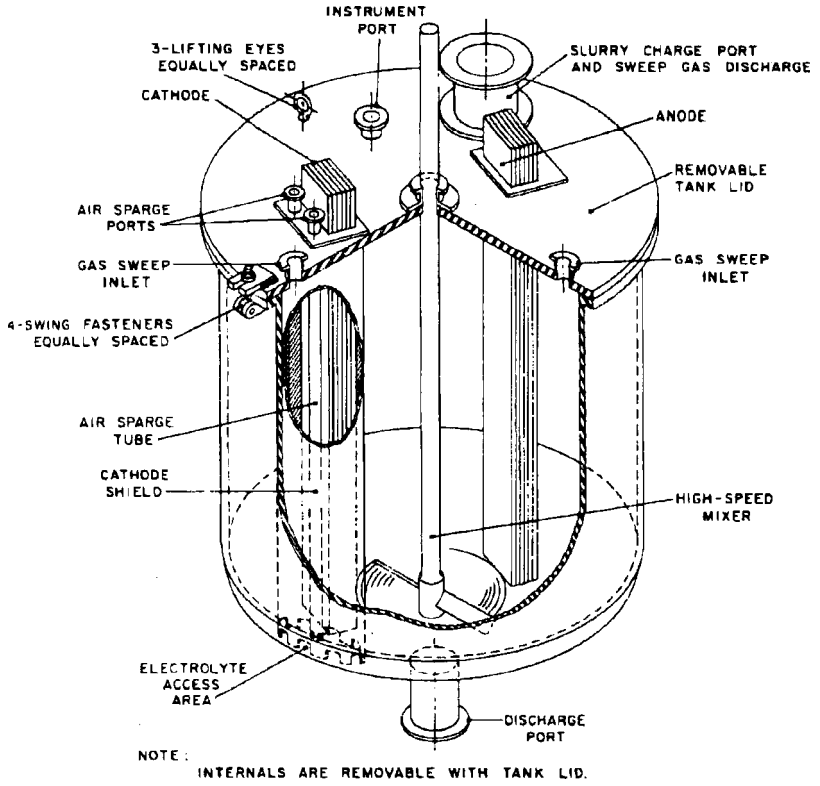

Figure 3. Stirred tank for electrolytically oxidizing and decontaminating solids. Adapted with permission from Tedder and Finney.[15]

anions[39,40] under acidic conditions. An air sparge introduced into the cathode chamber at the bottom of the cylindrical tube barrier can be used to sparge nitrous acid as it is generated near the cathode and to remove it from the solution by venting to the vessel off-gas. The cylindrical tube barrier permits electrical contact, but partly isolates the NO_2^- from the cerium species so that the oxidation efficiency of the system is not greatly reduced. Experimental studies[33] at ORNL suggest that such a system could exhibit reasonable current efficiencies, but less is known about the most effective geometric layout for such a cell, or the requirements for air sparging or other means to control nitrite concentrations.

Of equal importance, ORNL studies[33] also demonstrated that Flanders and Cambridge HEPA filter media can be decontaminated from fired Pu oxide with 99.99% Pu dissolution to achieve a decontamination factor of at least 10^4. In these tests, HEPA matrix was decontaminated by passing leachant through the waste, rather than in a stirred tank. Using a stirred tank resulted in a viscous mixture, but this problem was avoided using a fixed bed. Other independent studies[2,20] confirm the effectiveness of cerium in dissolving highly fired Pu oxides.

HEPA FILTER DECONTAMINATION

Based on this work, a conceptual process for decontaminating HEPA filters using an upflow leach process is illustrated in Fig. 4. Cerium oxidation occurs in a stirred tank with a shield cathode with air-sparging to promote NO_x removal, but oxidizing solution is recirculated between the stirred-oxidizer tank and a fixed bed containing the contaminated HEPA filters.

Using this concept, HEPA filters are decontaminated batchwise. Contaminated filters are added to the top of the bed. The system is then charged with cerium and nitric acid and oxidation is initiated. Ceric acid solution is recirculated in the bed with heating for a period of time. This solution is then drained from the system and acidic wash solution is circulated and drained. This is followed by additional water wash. The decontaminated HEPA filter plug is then discharged from the bottom of the fixed column and sent to certification and immobilization. Ceric acid solutions are reduced using dilute oxalic acid and then transferred to treatment with multifunctional-chelating, ion-exchange resin for acid and water recycle.

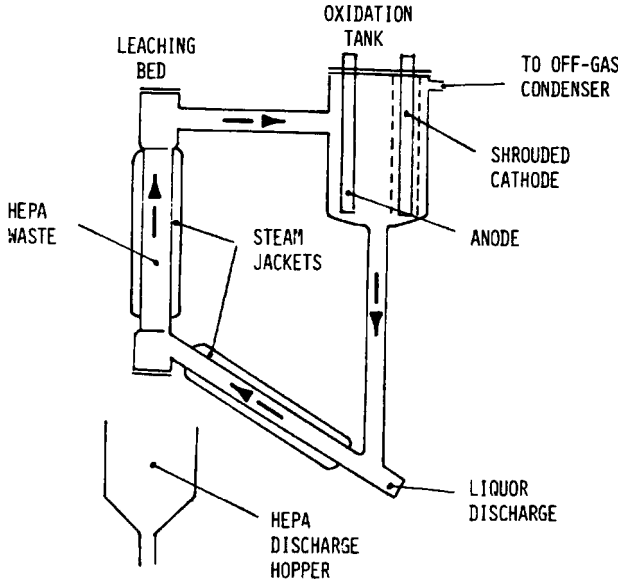

Figure 4. Conceptual process for decontaminating HEPA filters. Adapted with permission from Tedder and Finney.[15]

ALTERNATIVE CONFIGURATIONS

Other electrocell configurations may be useful. The Rocky Flats dissolver investigated by Brown et al[41] uses HF and HNO_3 acids to dissolve PuO_2. A similar electrocell configuration is depicted in Fig. 5. The coaxial layout is especially effective in recirculating small particulates by using thermal gradiants and airlift, so it effectively avoids the need for a pump. As shown in Fig. 5, the unit includes an anode and cathode electrode, but it may be possible to further simplify by eliminating the electrodes and simply using the tanks walls (e.g., inner and outer) as the cathode and anode, respectively. With this concept, the center tube becomes the cathode and the outer vessel wall is the anode. Nitrogen oxides are still liberated from the air sparge action within the central tube.

While this design seems promising, it is not clear that it will provide adequate surface area to achieve a reasonable oxidation rate within the vessel. Mass transfer may be limited not only by boundary layer diffusion to and from

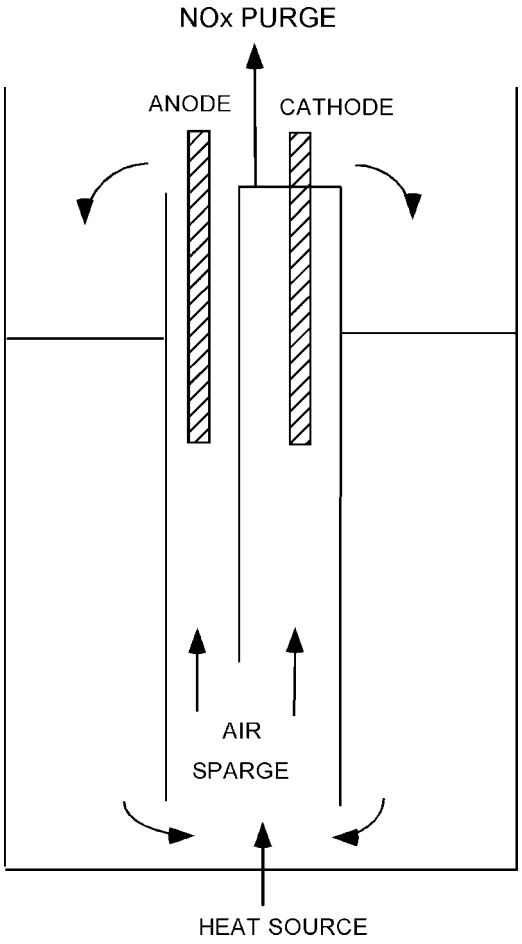

Figure 5. Coaxial electrocell concept based on Rocky Flats dissolver design.[41]

suspended particles, but also by boundary layer diffusion to and from the cell walls, where oxidation and reduction reactions will occur. One additional option to improve mass transfer at the walls is to use alternating current to prevent the buildup of oxide films on the walls, but this approach has not yet been tested.

The layout depicted in Fig. 4 for HEPA filters and small solids should be effective in hot cell applications, but it would probably be somewhat awkward

in gloveboxes due to size limitations. A more compact electrocell concept that combines the features shown in Fig. 4 is illustrated in Fig. 6. This configuration may be suitable for small quantities of shredded HEPA filter wastes or contaminated glovebox and cabinet wastes after size reduction. The primary goal is to achieve reasonable surface decontamination, thus converting these solids to low-level status.

Several novel features are appropriate for inclusion into the electrocell and decontamination cell design, and Fig. 6 illustrates some of them. This concept evolved from Fig. 3, but instead of providing separate electrodes,

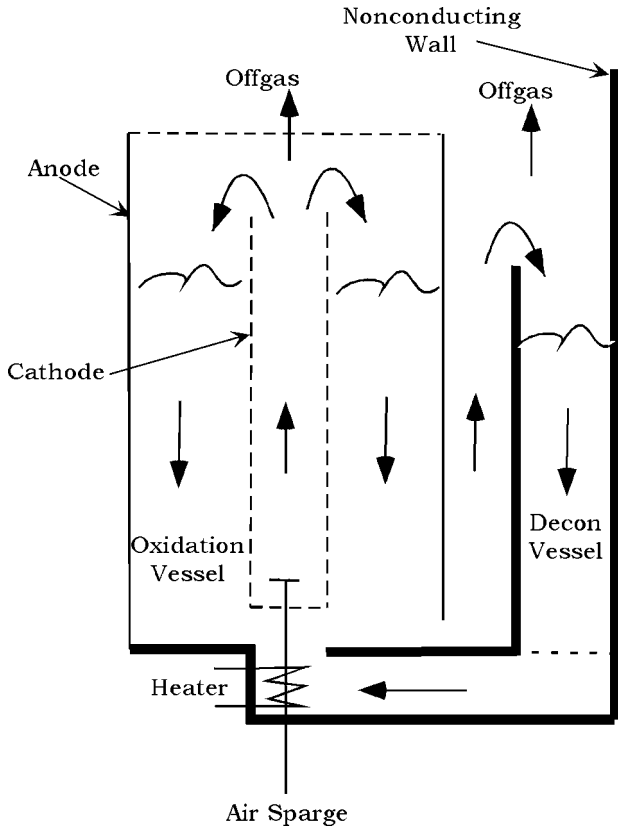

Figure 6. An integrated concept for recycling leachant and wash solution between the oxidizer and decontamination vessels. The latter vessel contains contaminated solids in a basket (not shown).

the vessel body is used either as the cathode or anode. A symmetrical layout is envisioned for the electrocell in an attempt to maintain a more uniform electrical field potential throughout the working volume. The use of an alternating current may improve overall oxidation rates.

The electrocell in Fig. 6 consists of two concentric cylinders with air sparging inside the cathode cylinder to remove NO_x. Cerium(IV)-rich electrolyte is withdrawn at the right of the electrocell, just inside the anode surface, and transferred to the decontamination vessel hydraulically. Wastes are lowered into the decontamination vessel inside a basket. Hot leachant is then recirculated between the two vessels using air sparging so as to avoid the use of a mechanical pump. At the end of a leach cycle, all electrolyte is drained into a reduction tank (see Fig. 8). Wash water is added to the electrocell and recirculated through the decontamination vessel using an air lift pump. So this design configuration is still essentially a batch operation.

Since Pu oxide is dissolved at near reflux conditions, some evaporation of water and HNO_3 will occur in the electrocell, and a scrubber column or some other technique is needed to control NO_x and the emission of volatile organic species from the cell off-gases. The column may require scrubbing[c] using dilute electrolyte solution (not shown in Fig. 6) if excessive volatile organic concentrations are formed during waste oxidation and decontamination. However, VOCs are not expected to be a significant problem unless the wastes entering the system contain high concentrations of organic species. Nitrogen oxides that dissolve in the scrubber liquids can be partly reoxidized to nitric acid in the presence of excess oxygen[34–38] before these liquids are returned to the electrolyte solution by reflux.

This design is significantly simpler than earlier concepts in several ways: (1) it eliminates the use of special anodes and cathodes; (2) it eliminates a membrane barrier separating the anolyte and catholyte; and (3) it eliminates the use of mechanical pumps with seals that may leak. These features make it particularly attractive for radiochemical applications. The use of concentric cylindrical cell walls with a central air sparge is similar in design to the well-known Rocky Flats type air-lift dissolver,[41] except that HF is not being used. Fluid can be recirculated through the decontamination cell through the differential hydrostatic head between the two cells and the pumping action of the air lift.

[c]If required, a magnet coupling pump will be used to provide diluted electrolyte to the top of the scubber. This pump design does not require seals.

ACID AND WATER RECYCLE

Virtually all decontamination operations result in significant quantities of secondary wastes. It is not uncommon, for example, for decontamination operations to generate secondary waste volumes from washing that are two or three times the volume of the originally contaminated solid wastes. While detailed material balances illustrating the decontamination of reference wastes are not presently available for these systems, the operations proposed here are nonetheless expected to be no exception to this rule. Hence, it is essential to have very efficient methods for recovering Pu from aqueous streams, the main secondary wastes generated from decontamination operations that use cerium and HNO_3.

Diphonix-Based Recycle

One approach to acid and water recycle is to treat them for actinide removal using a resin with high affinity for actinides. One possibility is to use Diphonix resin,[42–45] as produced by Eichrom Industries (Eichrome Industries, Inc., Darien, IL). This resin is capable of achieving very high distribution coefficients, in excess of 10^4 mL/g for Pu(III) and Pu(IV), and should be very effective in this application. Fig. 7 summarizes distribution coefficient data in nitric acid as reported by Horwitz et al.[42] Elution of wastewaters at pH 7 should remove virtually all metal species in solution. Distribution coefficients are still very high, particularly for the tetravalent actinides, when adsorbing under acidic conditions, say containing no more than 2-M HNO_3.

A conceptual flowsheet for using Diphonix resin to recycle nitric acid and water is shown as Fig. 8. It combines the Diphonix regeneration steps and shows additional processing with the calcium and actinide coprecipitate being sent to a waste glass. The top three boxes in Fig. 8 represent specialty equipment that are envisioned to implement this technology (also see Fig. 6). The subsequent steps in Fig. 8 can be completed using more conventional equipment. Water and acid recycle are shown as streams A, B, and C. The flowsheet, shown as Fig. 8 is applicable whenever resin bed regeneration is preferred. It has the disadvantage of requiring additional chemical processing steps and the addition of species containing iron and calcium ions, which further dilute the actinide constituents. On the other hand, resin regeneration facilitates actinide recovery and purification if desired.

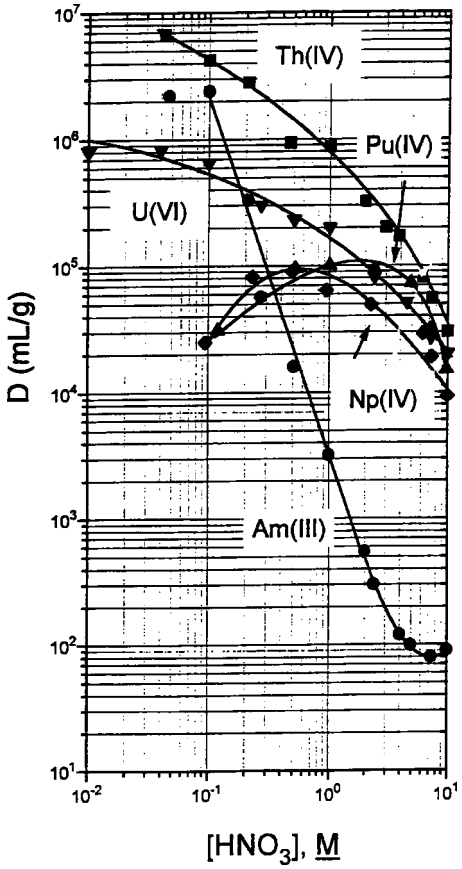

Figure 7. Uptake of various actinides by Diphonix resin in the presence of nitric acid. (Adapted with permission from Chiarizia et al.[44])

One possible recycle strategy is to operate two Diphonix beds in parallel, as shown in Fig. 8. One bed is dedicated to treating acidic electrolyte, after cerium reduction, and the second bed is used to treat wastewaters containing little or no free acid or cerium. Based on the data in Fig. 7, it should be possible to achieve very high decontamination factors from wastewater and acceptable decontamination for nitric acid so that the latter can be recycled back to the electrocell. Cerium reagent is disposed with iron and the actinide elements. Monovalent cations (e.g., Na or Cs) are not appreciably adsorbed by the resin and will be recycled with nitric acid, but may be removed using another

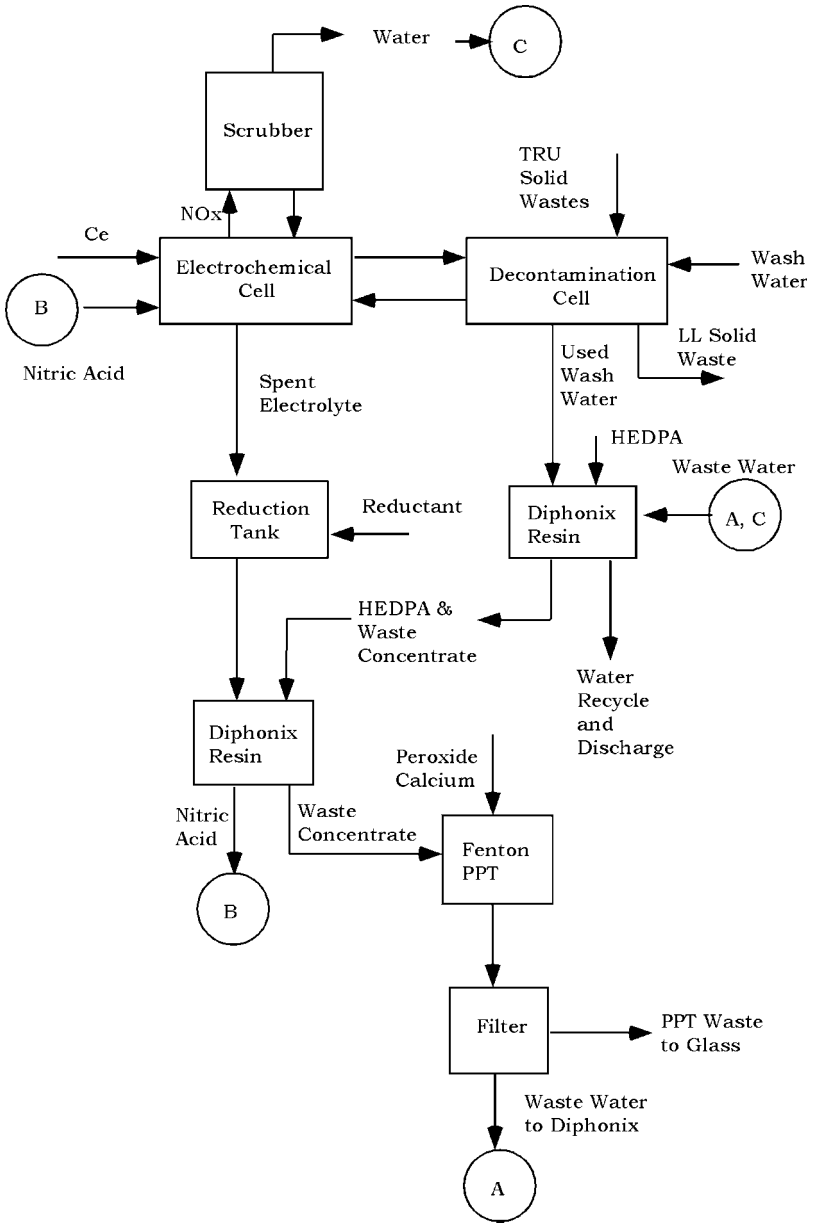

Figure 8. Conceptual flowsheet for recycling water and nitric acid using Diphonix resin.

adsorbent, if necessary. Water accumulation is a concern, but some nitric acid concentration is expected to occur as part of normal electrocell operations. In any event, excess water will need to be eventually discharged through a second resin bed.

Resin bed regeneration or management may be handled in one of several ways. One possibility is simply to load the resin with Pu and treat the resulting matrix as a final waste form. After all, Pu is well immobilized in this matrix, but hydrogen formation would probably become an issue for long-term storage since Diphonix is manufactured using an organic matrix. Alternatively, the resin may be regenerated and this is probably the preferred option when using this resin, particularly for larger-scale applications where criticality[d] may be an issue.

Because of the extremely high affinity of actinide elements for Diphonix resin, regeneration is challenging. However, Diphonix resin beds can be regenerated[44,45] (Fig. 9) using HEDPA (0.5-M 1-hydroxyethylidene-diphosphonic acid). As can be seen in Fig. 9, the distribution coefficient for Pu(IV) is approximately 0.6 mL/g in 0.5-M HEDPA. So Pu can be eluted in several bed volumes. Even if elution requires 10 bed volumes, the resulting concentration factor is in excess of 10^3, when compared to the wash solutions that are generated by the electrocell decontamination operations, so the resulting secondary waste volumes after regeneration are small. Moreover, HEDPA may be used repeatedly, first to regenerate the wash water column in Fig. 8 and, secondly, to elute the acid column also as shown in Fig. 8.

Elution from Diphonix resin with HEDPA results in a waste concentrate that may still require treatment to produce a suitable final waste form. Since iron is expected to be present due to its presence in the waste matrix, particularly when decontaminating iron-bearing solids, the addition of 30% H_2O_2 with heating to 90°C forms reactive intermediate OH radicals:

$$H_2O_2 + Fe^{2+} \rightarrow OH + OH^- + Fe^{3+} \quad (7)$$

which oxidize HEDPA via Fenton's chemistry. If necessary, excess Fe may be added. After oxidation, the addition of a calcium carrier coprecipitates actinides with $CaH(PO_4)$. The actinide, cerium, iron, and calcium precipitate mixture may then be removed by filtration and converted to a final waste form. Excess water from the precipitation step

[d]Gadolinium many be loaded onto the bed with Pu if criticality is a concern.

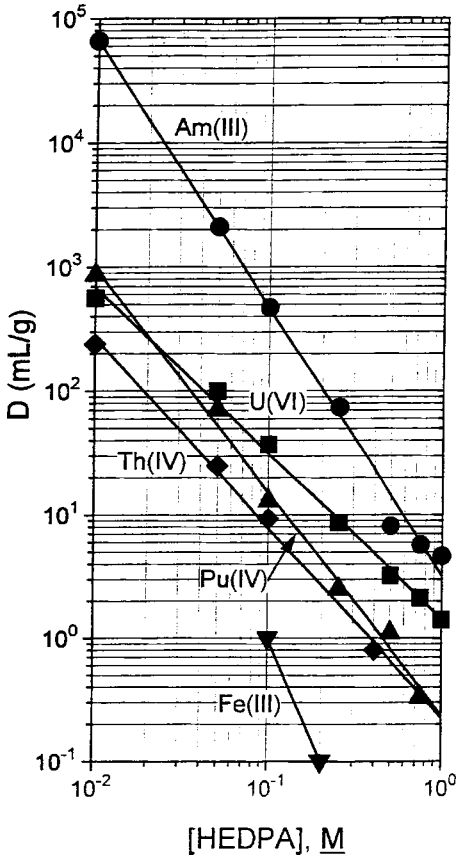

Figure 9. Uptake of selected ions by Diphonix resin in the presence of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) solutions. (Adapted with permission from Chiarizia et al.[44])

can be recycled through Diphonix resin and then either discharged or recycled back to the decontamination cell.

Diphosil-Based Recycle

The potential advantages of resin disposal without regeneration are: (1) reduced chemical processing and flowsheet simplification and (2) reduced use

of water and other chemical additives. The potential disadvantages are that disposing of the loaded resin: (1) may not be suitable[e] as a final waste form, (2) may not lend itself to incorporation into a suitable final waste form, and (3) may result in excessive costs. Regardless of whether Diphosil or Diphonix resins are used, Ce(IV) must be reduced (e.g., with oxalic acid) prior to passing cerium-bearing streams through such columns for actinide removal. Otherwise, Ce(IV) will attack the bed.

In cases where actinide recovery is not desired, Fig. 8 can be simplified if the actinides can be safely incorporated into the resin matrix as a final waste form. This option may be particularly attractive whenever the actinide concentrations in the primary wastes are very low (e.g., solids decontamination), or the quantitities of primary wastes that must be managed are small, or the working space for decontamination operations is limited. Glovebox operations may, therefore, be candidates for decontamination where acid and water are recycled, but the adsorptive resin is not regenerated.

Diphosil resin, also produced by Eichrom Industries, is a reasonable candidate for acid and water recycle in this case. This resin is a silica-grafted diphosphonic acid that is about 85 mass% inorganic material.[46] This resin has generally higher affinities for actinide elements than Diphonix, described previously. It also has reasonable capacity and kinetics and should, therefore, be equally, or more effective, than Diphonix for acid and water recycle.

Beitz and Williams[47] determined the maximum metal loading for Diphosil and, using FTIR analysis, showed that heating metal ion-loaded Diphosil in air converts its organic content primarily to CO_2 and water. Their studies further suggest that heating the loaded resin to 1000°C microencapsulates metal ions and chemically fixes them to the Diphosil residual matrix. These results suggest that after loading and heating, the resulting TRU matrix may be suitable as a final matrix. Otherwise, it should readily incorporate into a borosilicate glass insofar as most of the water and organics initially present in the resin are removed by heat treatment.

Earlier studies by Chiarizia and Horwitz[48] found that while the capacities of both Diphonix and Diphosil deteriorate with absorbed dose,

[e]Studies by Beitz and Williams[46] suggest that Diphosil can be converted into a suitable waste form by calcination. Leach tests are still needed to prove this point. We expect, however, that Diphonix would probably not yield a suitable final waste form by itself, although it may be possible to incorporate Diphonix residuals into glass. The amount of resin that can be added per unit mass of borosilicate glass may be limited by the allowable amounts of phosphorous in the glass.

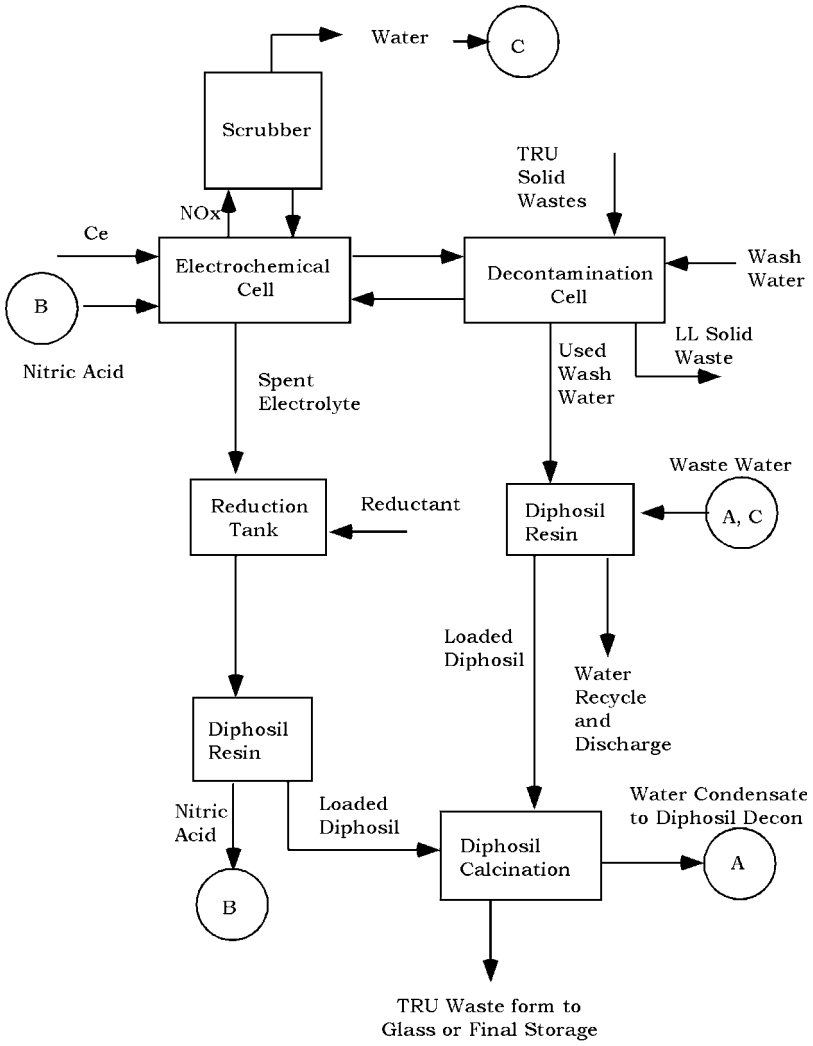

Figure 10. Conceptual flowsheet for recycling water and nitric acid using Diphosil resin. Since Diphosil is 85 mass% inorganic, it can probably be converted directly into a final TRU waste form without regeneration. Calcination encapsulates the metal ions, but may not be required if the waste is incorporated into borosilicate glass.

their affinities for actinide ions are not seriously compromised. Radiolytic degradation reduces the kinetics of metal ion uptake by Diphosil more than for Diphonix, but this deterioration should not be a problem, especially if resin regeneration and reuse is not anticipated.

The conceptual flowsheet, shown as Fig. 10, is based on the assumption that metal-loaded Diphosil can either be converted directly into a TRU waste form, or else the heat-treated resin can be dissolved into borosilicate glass. We expect that one of these two techniques will result in a final waste form that is suitable for geologic disposal. Comparison of Figs. 10 and 8 shows that Diphosil results in greater simplicity because it avoids the use of HEDPA to regenerate the resin, the use of Fenton's chemistry to oxidize diphosphonic acids, and carrier precipitation to convert actinides into a solid. Qualitatively, these differences suggest that Diphosil may be preferred from the operational standpoint, particularly if the loaded Diphosil matrix can be incorporated directly into glass without prior calcining, or can be calcined to produce a suitable final waste form for geologic disposal, as suggested by Fig. 10.

DISCUSSION

Mediated electrochemical oxidation is a potentially effective method for treating a wide variety of wastes. It is of particular interest for mixed wastes contaminated with PuO_2 because of the ability of Ce(IV) to both dissolve refractory Pu oxide and, thereby, enable waste decontamination, and its ability to oxidize many organic species and to convert them safely to carbon dioxide and water at low temperatures. This technology can provide both high decontamination of inorganic solids and the destruction of many hydrogen formers that make existing wastes unacceptable as final waste forms.

Cerium-promoted oxidation is particularly attractive for HEPA filter decontamination insofar as the fiberglass matrix can be treated without substantial degradation. In contrast, fluoride-promoted decontamination of HEPA filters results in fiberglass dissolution and increased waste volumes, particularly since the resulting fluorinated fiberglass solution must eventually be converted to a solid waste form for final disposal.

Key issues that could limit the deployment of this technology relate to its complexity, particularly the concept of using electrocells in a contaminated environment. Proposed simplifications include the use of an undivided cell and the provision of electrolyte and wastewater recirculation without a mechanical pump. Key unresolved issues relate to the rates at which cerium can be oxidized in these systems, hydraulic stability, off-gas scrubbing, overall current efficiency, effective oxidation rates, the ultimate potential for

decontaminating waste, and the ability to maintain adequate catalytic activity even with very low cerium concentrations.

Bray and Ryan[20] found that the Ce(IV) to Ce(III) ratio has a much more pronounced efect on the PuO_2 dissolution rate than the total cerium concentration. They found that with a total Ce concentration of 0.005 M and a Ce(IV) to Ce(III) ratio of 9, the Pu dissolution rate is significantly greater than with a total Ce concentration of 0.05 M and a Ce(IV) to Ce(III) ratio of 0.1. Since higher Ce concentrations increase resin loading and compete with Am, it is desireable to operate with the lowest possible Ce concentration, but still maintain adequate oxidation rates. Bray and Ryan further suggest that the Am(IV)–Am(V) couple of 1.60 volts may also catalyze dissolution. Since Pu usually contains some Am, it may be possible to operate without cerium additions at all, but this strategy needs further evaluation. In any event, lower Ce concentrations in the oxidizer result in lower resin loadings.

Pretreatment of some type is generally required to use this technology effectively. Solids will likely require some sorting and sizing. Neutral wastewaters can be treated by first decontamining them using activated carbon to remove low concentrations of organics and then by using either Diphonix or Diphosil resin to remove Pu. Organic wastes can often be oxidized directly, but may require filtration and metering.

Electrocell decontamination should be highly effective on surface contamination, such as occurs from HEPA filter operations and many glovebox operations, based on earlier studies at ORNL and elsewhere. It is not clear, however, that cerium-promoted decontamination will be effective in cases where Pu has penetrated into a matrix. In cases where the matrix is readily oxidized (e.g., paper or cloth wastes), matrix oxidation should liberate the Pu and allow its oxidation and subsequent disposal. The fact that Ce(IV) can oxidize many organics is a benefit in this case. Since it does not readily oxidize perfluorinated polymers, cerium treatment would likely be less effective for similar matrices that also suffer from Pu penetration, but this issue has not been studied and cerium oxidation may be surprisingly effective in such cases if it can penetrate the contaminated matrix without oxidizing it. Some heating (e.g., to 90°C) may be beneficial in this regard, depending upon the expansion and softening coefficients of the contaminated polymer matrix.

Several aspects remain unproven with this concept. It remains as an important task to demonstrate that the ceric acid system can be operated with reasonable overall current efficiency, even if the cell is not divided. Typically, electrochemical cells are divided by semipermeable membranes, which separate the anolyte and catholyte fluids. In principle, the ceric acid system can be operated without a membrane barrier and this feature is of particular interest for waste management operations insofar as it avoids potential

membrane fouling problems, simplifies the design, and reduces maintenance requirements.

Operating an undivided cell without a membrane can result in lower overall current efficiencies[22,23] when operating under alkaline conditions and with a plate-and-frame electrochemical cell. Nitrite ion is formed when nitric acid is reduced at the cathode. Under alkaline conditions, it exists primarily as sodium nitrite, which is relatively nonvolatile and can migrate back to the anode and be reoxidized to nitrate by reducing Ce(IV). Such reactions compete with Ce(III) for electron removal and reduce the overall current efficiency. Under acidic conditions, as proposed here, it should be possible to maintain current efficiency by air sparging to remove nitrogen oxides, rather than allowing nitrous acid to reoxidize to nitric acid.

Flowsheet improvements include a strategy for recycling nitric acid and wash water solutions without evaporation. Key unresolved issues relate to measuring the effects of reducing cerium and nitric acid concentrations in the electrolyte on the effectiveness of treating these wastes, the ability to maintain reasonably low alpha activity levels in recycled fluids, and the characteristics of TRU precipitates generated from decontamination operation.

Although cerium could be recycled, in small-scale applications, it may be more economical to discard cerium rather than recycle it. This approach simplifies flowsheet operation, but incurs the cost of additional cerium makeup. An economic analysis is required to clarify this point, but we suspect that the anticipated large reductions in TRU-waste volumes from operating this flowsheet will be more important than the cost of cerium reagent makeup. The anticipated increases in waste residuals from cerium discard are expected to be modest since cerium is a catalyst that can be electrochemically reoxidized many times.

Other key issues, in addition to clearly demonstrating the ability to adequately remove actinides prior to reuse, relate to water and acid balances for this system, and determining the effective resin bed loadings. Actinides will likely[f] be present in lower concentrations than either cerium or iron. It is expected, however, that there will be adequate concentration of the TRU elements by either Diphonix or Diphosil resin to avoid any need for further processing (e.g., isolating iron or cerium rather[g] than disposing of them as part of the TRU precipitate).

[f]Depending upon the contamination levels and iron content of the wastes.

[g]The TRU and TEVA resins, also manufactured by Eichrom Industries, could be used in conjunction with Diphonix to isolate a purer TRU fraction, free of iron and cerium, but the flowsheet is more complicated than that proposed in Fig. 8.

CONCLUSION

This concept focuses on the use of Ce(IV) and nitric acid chemistry to dissolve highly fired Pu oxide, simultaneously destroy organic species, and use Diphonix resin to recycle water and nitric acid without evaporation. Actinide elements can be concentrated and recovered as inorganic phosphates in a form suitable for immobilization in a final waste form. After decontamination, residual solids can be compacted, packaged, and, hopefully, disposed as a low-level waste. Significant reduction in the volumes of TRU waste requiring geologic disposal are expected. Diphosil is probably preferred in many glovebox operations where operating space is limited and there is a clear need to minimize the use of wet chemical processing.

A specialized electrocell can be used to generate Ce(IV) to dissolve high-fired plutonium oxides and simultaneously to oxidize organic species in the wastes that are susceptible to hydrogen formation. Nitric acid and water decontamination and recycle can be achieved using resin adsorption without evaporation. Transuranic contamination can be concentrated in a precipitate suitable for incorporation into borosilicate glass or other final waste forms using Fenton's chemistry. Decontaminated TRU wastes are either converted to low-level wastes or packed to meet transuranic waste packing and shipping requirements. Preliminary results from Oak Ridge National Laboratory suggest that HEPA filter wastes can be processed to achieve decontamination factors of 10^4 for highly fired Pu oxide. Studies at the Argonne National Laboratory and Florida State University suggest that nitric acid and water can be recycled with decontamination factors in excess of 10^4 without evaporation. Alternative methods for using this technology are discussed.

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