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PLUTONIUM AND AMERICIUM SEPARATION USING ORGANOPHOSPHORUS EXTRACTANT ABSORBED ONTO FERROMAGNETIC PARTICLES

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INTRODUCTION

Nuclear fuel reprocessing and nuclear weapons production have generated high-level waste (HLW) containing low concentrations of long-lived radioisotopes, most importantly the transuranic (TRU) elements. Separating out the TRU elements can alleviate the burden of disposing of large volumes of TRU wastes. The TRUEX solvent extraction process has been demonstrated to separate TRU elements from radioactive liquid waste. This process uses organophosphorous compounds such as tributyl phosphate (TBP) and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO).¹⁻⁴ This low concentration of extracted TRU elements can be processed into a final waste form that is based on a glass matrix and deposited into a deep geological repository, while the bulk of the nuclear waste can be disposed of in a near-surface, (more economical) low-level waste (LLW) facility. Thus, TRU separation processes are necessary and can achieve high cost savings. One waste site at Hanford is the residence of millions of gallons of tank waste from the plutonium finishing plant (PFP).

Magnetically-assisted chemical separation (MACS) processes use magnetic particles prepared with an extractant-specific, organic complexant-containing solvent. The organic complexes are selective extractants for feed waste components like Cs, Sr, or TRU elements. The particles are prepared by coating iron or another ferromagnetic material with either an organic polymer or ion-exchange resin. The ion-exchange resin is attached to the particle by an adhesive or by direct bonding. Organic solvents can be adsorbed onto the polymeric surface by contacting the particles with the solvent in a volatile diluent that is subsequently removed by evaporation. These coatings selectively separate the contaminants onto the particles due to their chemical nature. Once loaded, the particles can be recovered from the tank using a magnet.

Once particle recovery is achieved, the contaminants can either (1) be left on the loaded particles and added to the glass feed slurry or (2) be stripped into a small volume of solution to regenerate the extracting particles. For example, the selective extractant coating can be washed from the particles with hexane or alcohol, which acts to dilute and thus diminish the extraction power of CMPO and TBP for TRU complexation. It is then stripped of activity by dilute acid. The organic solution can then be evaporated to regenerate the particles. The greatest benefits of the technology are the simple separation of radionuclides from various waste streams using a compact, cost-effective process that does not produce additional large waste streams. This process is applicable to many DOE liquid TRU wastes.

The actual process development studies in this paper are: (1) particle morphology and effects on sorption of organophosphorous extractants, (2) optimizing separation capabilities

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of the magnetic particles, (3) temperature effects on extraction, (4) stripping of particles for regeneration, and (5) acid degradation effects on particles.

PROCESS DESCRIPTION

Figure 1. Concept Diagram of MACS Process

The MACS process is still in the developmental stage. Figure 1 shows a diagram of the MACS concept. In this concept the dissolved sludge or aqueous stream is added to a treatment tank, which can also be used for the stripping stage. Magnetic particles coated with extractants are added to the treatment tank to separate the TRU and/or other contaminants from the dissolved sludge or liquid waste. To maintain particle suspension, the tank contents can be mixed by mechanical stirring, magnetic fluidization, or other methods. After extraction, the particles are magnetically separated by one of three methods: (1) placing a magnetic field around the treatment tank, (2) pumping the solution through a magnetic filter (e.g., commercially available magnetic units), or (3) introducing a magnet into the tank. The waste solution, now decontaminated, is withdrawn and can be sent to grout. The TRU-loaded particles are either sent to a vitrification process or left in the tank for stripping with a smaller volume of liquid (compared to the original feed volume). The TRU contaminants are separated from the magnetic particles and sent to a vitrification process (e.g., glass melter) while the particles are recycled for further extraction.

The MACS process has the advantages of (1) less complex equipment, compared with solvent extraction and ion exchange and (2) simplicity that will facilitate scale-up. One of the Hanford tank wastes that the MACS process can successfully treat is the acid-dissolved waste from their neutralized PFP. The Hanford Site currently has many tanks filled with PFP wastes, each tank containing approximately one million gallons.⁵

A variety of applications of superparamagnetic (ferromagnetic) particles has increased their use for detection and monitoring in assay developments and analysis. Immunological analysis, chemiluminescence⁶, and immunomagnetic separation of food bacteria⁷ and genes⁸ are areas where superparamagnetic particles have found wide applications. Magnetic particles are available from several commercial suppliers. These particles come in a variety of sizes and magnetic properties with different functionalized and nonfunctionalized polymeric coatings. On the basis of our own experience, the literature, and discussions with the suppliers' technical experts, we have chosen the materials best suited for our application.

EXPERIMENTAL

Reagents

All the reagents used to prepare the simulant waste were ACS reagent grade. The reagent-grade TBP was obtained from Aldrich Chemical Company used without further purification, but the CMPO was recrystallized for purity⁹. All radioactive tracers were obtained from the Chemical Technology Division at ANL. The superparamagnetic or magnetic particles were manufactured from either CORTEX, BioMag, or Bang companies, and pretreated with filtered deionized water to eliminate any preservatives.

Preparation of PFP Simulant

Table 1 shows the composition and ion concentrations of the PFP simulant waste prepared.

Table 1. PFP Simulant Waste

Component	Molarity
H ⁺	1.50E+00
Be ²⁺	7.00E-05
Na ⁺	4.00E-02
Mg ²⁺	6.00E-02
Al ³⁺	4.30E-01
K ⁺	3.00E-03
Ca ²⁺	6.00E-02
Cr ³⁺	4.00E-04
Mn ²⁺	3.00E-03
Fe ³⁺	3.00E-02
Ni ²⁺	8.00E-02
Cu ²⁺	3.00E-04
Zn ²⁺	6.00E-04
Pb ²⁺	5.00E-04
F ⁻	9.00E-02
SO ₄ ²⁻	1.00E-02
NO ₃ ⁻	3.05E+00

Microscopy and Electron Dispersive Spectroscopy (EDS)

The MACS particle samples were prepared for electron microscopy: dried, embedded in epoxy, and sliced into 500- to 1000-Å-thick sections with an ultramicrotome. Samples were then examined in a JEOL 2000FXII Transmission Electron Microscope (TEM) at 200 kV. Samples that were suitable for electron dispersive spectroscopic (EDS) analyses and experiments were performed in tandem using a NORAN ultrathin window system in the horizontal port of the JEOL 2000. The morphology studies included resin effects on the particles and particle morphology.

Coating Procedure

All particles in this study exhibit superparamagnetic properties because of magnetite incorporated in their structure. The particles range from 0.1 to 25 μm and exhibit a wide variety of shapes. The commercially purchased particles have a polymeric coatings. The polymeric coating that demonstrated the most promise for CMPO/TBP adsorption was charcoal in a cross-linked N, N-methylene bis-acrylamide. The particles were washed with

0.02- μ m-filtered deionized water several times to eliminate preservatives and additives, dried, and weighed. Then, 0.02- μ m-filtered hexane or ethanol was used to disperse the particles and act as a volatile solvent for the coating. A dissolved CMPO/TBP mixture ($> 0.6 \text{ M}$ CMPO) was added to the particles, which were dispersed by an ultrasonic bath, dried in a rotoevaporator at 80-100°C, and heat-treated in an oven at 100-150°C until a constant weight was obtained.

Extraction Process

Particle suspensions of $\sim 1 \text{ wt } \%$ or less were contacted with nitric acid or simulant solutions containing ^{241}Am or ^{238}Pu . This low particle-mass-to-solution ratio was chosen to allow this process to compete with more traditional separation techniques, such as solvent extraction and ion exchange. The suspensions were placed for a few minutes in a sonic cleaning bath to enhance the dispersion. Then they were moved to a temperature bath at 25°C for thermal equilibration, and vortexed to further disperse the solid suspension. These two steps were repeated twice. Then the suspensions were centrifuged and placed in a rare-earth permanent magnetic rack to induce physical separation of the particles from the solution. An aliquot of the solution was taken for alpha-beta counting with a Packard 2200CA TRI-CARB liquid scintillation analyzer (^{238}Pu) or gamma counting (^{241}Am) on a Packard (Minaxi γ Autogamma 5000 Series) 3-in. (7.62-cm) NaI crystal detector. Mass balance calculations were used to determine partition coefficients (K_d). All nitric acid solutions were titrated using the Metrohm 670 Autotitrator with a glass electrode containing 3 M KCl.

Stripping Measurements

The radionuclide-loaded magnetic particles were dried in preparation for stripping experiments. Fresh stripping agent was added and contacted, following a procedure similar to that used in the extraction experiments. The volume of stripping agent was no more than 1/100 that of the aqueous phase volume used for extraction experiments.

Nitric Acid Dissolution

Even though the magnetite is often coated by a polymer, the high solubility of magnetite in nitric acid required us to study a series of experiments to determine the dissolution from the coated particles. Six prepared particle samples were weighed, and each mixed with 5 mL of a nitric acid solution (0.02 - 8 M). These samples were mixed following the extraction procedure and allowed to settle for 336 hours (2 weeks). They were magnetically separated, and 1-mL samples of the aqueous aliquots were analyzed for iron using atomic emission spectroscopy (AES). An aqueous phase sample without any particles present was analyzed as the background.

RESULTS AND DISCUSSION

Morphology Studies and Magnetite Distribution Experimentation

The capacity of the particles to absorb the organophosphorous extractants and maintain physical integrity under chemical (acid) and physical (gamma irradiation)¹⁰ conditions was examined using TEM. The combination of the TEM results, K_d values, gamma irradiation, and magnetic measurements was used to select a suitable particle type for MACS applications. The K_d measurements are determined by Eq (1).

$$K_d = \left(\frac{C_i - C_f}{C_f} \right) \times \frac{V}{M} \quad (1)$$

where

V = contact volume of TRU solution in mL

m = mass of particles in grams

C_i = initial stock solution counts before contact

C_f = final solution counts after contact

Commercially available coated superparamagnetic particles were chosen that were judged as best for the MACS process. An important criteria for selecting a particle is a heavy radionuclide loading ability. This requirement was not an original application for which the particles were developed. For a biochemical assay applications, maximizing absorption is unnecessary. Loading capacity is obviously an important concern for the task of recovering a particular component of the nuclear waste stream.

Another important consideration for applications of the MACS particles is the absorption or binding strengths exhibited between (1) the magnetite core and the polymeric coating and (2) the polymeric coating and the absorbed organophosphorous extractants. Loss of interfacial integrity in either case under HLW tank conditions is undesirable. The chemical durability of the magnetite core is also required for separation. The pretreated waste streams can be either a harsh acid or base environment, and dissolution of the magnetite would behave in a similar manner to physical separation of the magnetite and polymer. In this report, we intend to show the durability of the particles in an acidic environment using the K_d values and information obtained by TEM and other experiments.

Resin Effects, and Inner-Outer Polymeric Sphere Magnetite Distribution

In the first stage of this work, TEM sample preparation techniques were examined to determine whether samples could be produced without chemical interaction with the embedding resin used to mount them for ultramicrotomy and to provide a baseline view of samples before complexation or exposure to radiation. Five samples were selected (Table 2) four of which were examined by TEM. Sample 3, the charcoal coated sample, was not used for microtomy because particles were quite large (up to 25 µm).

Table 2. Particle Type Selected for TEM Studies

Sample	Description	Size, µm	Manufacturer
1	DVB ^a /acrylic acid (58%) bound to magnetite core (35%)	0.68	Bang
2	Magnetite particles bound to polyacrolein core	1-10	Cortex
3	Charcoal-coated magnetite particles	1-25	Cortex
4	Magnetite particles embedded in s/DVB ^b	12	Bang
5	Acrulamide-based magnetite particles with charcoal-dextran coating	12	BioMag

^aDVB = divinylbenzene.

^bS = styrene.

Each sample (1, 2, 4, & 5) was embedded in Medcast, Araldite, and LR White embedding resins. All particles sectioned well, and there was no significant difference between particles embedded in the different epoxy resins. However, magnetite crystallites were observed to be bound to the surface of particles in sample 2 and appeared to loosen from LR White epoxy prior to curing. The samples in TEM micrographs in Figure 2 were embedded in Medcast or Araldite.

Sample 1, divinylbenzene-magnetite particles, is pictured in Figure 2a. The magnetite cores are rather large (0.2 µm) and irregularly shaped. The polymer appears to be randomly bound to the surface of the core. The divinylbenzene polymer demonstrated low sorption of the organophosphorous extractants, with K_d ≤ 100 for Am in 2 M nitric acid.

Sample 2, polyacrolein-magnetite particles, is pictured in Figure 2b. The magnetite particles are extremely small (<1 nm) where the magnetite is attached to the outer surface of the polymer rather than being located in the core. Two deleterious effects are likely. First, the magnetite particles obstruct access of the organophosphorous solution to the absorbent polymer core. The effective surface area of the particle is dramatically reduced and absorption is limited by how quickly the solution can percolate or diffuse through the narrow

spaces between the magnetite particles. Secondly, an exposure to radiation that is likely to embrittle the polymer may result in loss of the very small magnetite particles attached to the surface. The nonporous polyacrolein polymer demonstrated insignificant sorption of the organophosphorous extractants, with $K_d \leq 10$ for Am in 2 M nitric acid.

Sample 4, styrene/divinylbenzene-magnetite particles, is pictured in Figure 2c. The particles are uniform in shape, with magnetite particles embedded as clumps within the absorptive polymer. Most of the surface is available for absorption. The styrene/divinylbenzene polymer showed low sorption of the organophosphorous extractants, with $K_d \leq 100$ for Am in 2 M nitric acid.

Sample 5, acrylamide-based magnetite particles, is shown in Figure 2d. The particles here are randomly shaped, and the distribution of magnetite particles is also irregular. Some particles appear to be a mass of magnetite, while others have very little magnetite attached. It is possible that a significant number of particles would not be magnetically separable because few magnetite particles are present. The charcoal/dextran polymer showed low sorption of the organophosphorous extractants, with $K_d \geq 100$ for Am in 2 M nitric acid, but the polymer combination of charcoal in a cross-linked N, N-methylene bis-acrylamide gave $K_d \geq 4000$ for similar tracer solution. This high partition coefficient was attributed to the chemical affinity of the polymer and the large surface area of the particles.

Figure 2a. TEM Micrographs. Sample 1, which is comprised of large, irregular-shaped magnetite particles (0.2 μm) with polymer randomly bonded to surface core. **2b.** Brightfield Image of sample 2 (polyacrolein) embedded in Araldite. Magnetite particles are small (<10 nm) and attached to the outer surface of the particles. **2c.** Mag-encapsulated particles. The magnetite particles are small (~10 nm) and are embedded as agglomerates within the polymer. **2d.** Dextran-coated particles are shown here. Polymer particles are randomly shaped, with a non-uniform polymer coating. In most cases, it does not appear that the magnetite and polymer are tightly bound.

With the aide of TEM, the physical features of the particles were determined allowing for the selection of the charcoal in a cross-linked N, N-methylene bis-acrylamide particle type for the MACS process.

Nitric Acid Dependence

The nitric acid dependency of the MACS process is important for applying of this process to waste streams having a wide range of acidities. Dissolution of solid or sludge waste is usually achieved by acid hydrolysis. The chemical stability of the TRU under acidic condition is well-documented.¹¹⁻¹²

The partition coefficients for various coatings were monitored using ^{241}Am and ^{238}Pu tracers. Samples were tested in 0.001, 0.01, 0.1, 2, 5 and 8 M nitric acid with CMPO concentrations of 1.0 M. The results are presented in Figure 3.

Figure 3 shows that the two curves have similar shapes. The K_d values for Am and Pu increase slowly with HNO_3 concentration, reaching peaks at 2 M and 5 M HNO_3 , respectively. These results suggest that the process can be applied in a batch mode for a wide range of high nitric acid concentrations without a large loss in extraction capabilities.

Figure 3. K_d vs. Nitric Acid Concentration for ^{241}Am and ^{238}Pu for 1.0 M CMPO/TBP Coatings on Magnetic Particles at 25°C

The volume of solvent absorbed on the surface of the particle can be estimated using the solvent coverage fraction, which allows the K_d value to be transformed into the more traditional distribution ratio (Figure 4). The ratio of gram-of-extractant to gram-of-particles can be determined from the coating process and the density of the particles.

The volume occupied by the extractant and particles was previously reported.¹³ The density of particles is assumed to be in the range of 2.5-2.7 g/cm^3 (mainly due to Fe_3O_4). The value of f (conversion factor), which can vary from 25 to 60, is defined as the fraction of the gram of particles per mL of extractant. The Am and Pu distribution ratios are higher than traditional solvent extraction values and those found for CMPO absorbed onto silica particles.¹⁴

Figure 4. Distribution Ratios Converted from Particle K_d Values for Am and Pu Using 1.0 M CMPO/TBP Particles at 25°C vs. Nitrate Ion Activity.

Although the precise chemical equilibrium is not determined, the K_d values obtained are much larger than D values obtained in a solvent extraction process. Increases in K_d may be a result of a synergistic effect between CMPO/TBP and the polymer on the particle in the absence of a diluent, (such as normal paraffinic hydrocarbons (NPH) or trichloro-ethylene (TCE)). Although CMPO/TBP systems have been extensively investigated, the current studies without a standard diluent are unique. Further studies are necessary to determine the precise driving mechanism that aids in the extraction. The MACS process shows promise in using more efficiently the standard organophosphorous extractants such as CMPO and TBP for TRU separation applications.

Nitric Acid Dissolution

Magnetite is soluble in nitric acid, but the polymeric coating can partially protect it. Dissolution of the magnetite would inhibit particle recovery and hinder application of the MACS process. A series of experiments were performed to determine the extent of dissolution of the magnetite from the particles as a function of nitric acid concentration.

The hydrolysis of magnetite increased with acid concentration, as evidenced by ICP analysis of dissolved iron. The dissolution occurs linearly (Figure 5) throughout the nitric acid range, including the expected MACS process ranges of 2-4 M HNO_3 . The presence of exposed magnetite, which allows for its dissolution, is evident in TEM micrographs, where a significant amount of magnetite particles are in the outer sphere of the polymeric material for irregularly shaped particles. The information provided by these experiments is limited to dissolved iron, not magnetite remaining on the particles.

Figure 5. Dissolved Iron in Supernatant vs. Nitric Acid Concentration

Figure 5 shows a steady increase in the amount of dissolved iron in the supernatant with increasing nitric acid concentration. In shorter contact times (minutes), the effect is expected to be smaller, but it remains a major concern for process recycling.

Temperature Dependence

Due to the possible application of the MACS process to wastes that have been stored in tanks for decades, the true operation temperature may vary between 20-50°C. The MACS process must evaluate the temperature dependence within such a temperature range.

The extraction of americium was monitored as a function of temperature for 1 M CMPO/TBP coating. Three temperatures were used for the experiments (10°, 25°, and 50°C). Figure 6 illustrates the general trend.

Figure 6. The K_d Values for 1 M CMPC vs. Nitric Acid for 10°, 25°, and 50°C

All three K_d -vs.-nitric acid curves (10°, 25°, 50°C) have the same general shape. In many solvent extraction systems,¹⁵ the distribution ratios of the metals decrease with increasing temperature, especially between 0-60°C. The MACS particles show negligible temperature dependency between 10-50°C for the extraction of americium.

PFP Simulant Waste Stream

The K_d values for Pu(IV) in PFP simulant were on the order of 20,000. However, Am showed very low values of K_d , 100. Figure 8 shows the results for various saturated particles of CMPO/TBP. The K_d values show little dependence on CMPO concentration for both Am and Pu (Figure 7). The solution chemistry of Pu and Am favors complexation with fluoride. These fluoride complexes have very low extractability with CMPO; however, results from this study show that Pu is highly extractable even in the presence of fluoride. The decrease in the K_d for Am is probably due to some effects other than fluoride competition for the actinide. High iron concentration present in the simulant solution may interfere with Am extraction. The Am separation was then predicted for the addition of oxalic acid solution using the Generic TRUEX Model (GTM) to complex the free iron.¹⁻⁴ This model allows the determination of TRUEX solvent extraction chemistry based on a thermodynamically correct mechanism.

Figure 7. Am and Pu Separation Using PFP Simulant Solution at 25°C with 1.5 M CMPO/TBP Coated Particles

Using the PFP waste stream components and the GTM speciation with oxalic acid addition, the concentration of free iron was calculated to be 0.001 M for a 0.28 M oxalic acid solution. This addition resulted in an increase of the K_d at room temperature from 100 to 3500 for 1.5 M CMPO particles.

Stripping Measurements

Because the K_d values obtained using magnetic particles are quite large, an efficient recovery stage is required. The usual stripping process for nitrate waste streams involves using dilute nitric acid for Am and an aqueous phase complexant or reducing agent for Pu. However, because the MACS process results in large K_d values (partly due to the high concentration of CMPO), dilute nitric acid would be inefficient for stripping Am. A three-step stripping process is necessary. In the first step, complexants (CMPO and TBP) and the TRU elements are stripped from the particles using a hydrocarbon or an alcohol. In the second step, the TRU are stripped from the organic phase, which is now a dilute CMPO solution, using an appropriate aqueous phase. Finally, the volatile hydrocarbon or alcohol (e. g., octanol) is evaporated leaving the CMPO/TBP residual on the particle surface.

Table 3 gives the stripping K_d values for plutonium. Some of the K_d values not reported gave negative values and were attributed to an error in the mass balance assumptions (e.g., carry over of phases, conservation of particle mass). The values were derived from the mass balance equation:

$$g_p[\text{cpm} / \text{g}]^{\text{original}} = g_p[\text{cpm} / \text{g}]^{\text{final}} + (\text{mL})[\text{cpm} / \text{mL}]^{\text{final}} \quad (2)$$

assuming that there is negligible loss in particle mass before and after stripping.

The results are promising, but work is needed to develop a stripping step that can obtain a stripping stage K_d value of 1/1000 for an efficient recovery process. This value is calculated as follows:

$$K_d^{\text{strip}} = \frac{\left[\left(\frac{g_p}{V} \right) K_d^{\text{ext}} C_{\text{final}}^{\text{ext}} - C_{\text{final}}^{\text{strip}} \right]}{\left(\frac{g_p}{V} \right) C_{\text{final}}^{\text{strip}}} \quad (3)$$

where, g_p is the mass of the particles in grams, V is the volume of waste solution in mL, and $C_{\text{final}}^{\text{strip}}$ and $C_{\text{final}}^{\text{ext}}$ are the final concentrations after stripping and extraction, respectively, and K_d^{ext} is the extraction partition coefficient.

Table 3. Stripping K_d for ^{238}Pu in PFP Simulant

Sample	Stripping Solvent	K_d Loading	K_d Stripping	O/A ratio	Volume Reduction
1.2 M CMPO	ethanol	1850	0.73	0.01	400
1.0 M CMPO	butyl alcohol	3323	4.75	0.008	100
1.0 M CMPO	ethanol	1553	0.65	0.008	100

We were able to easily reduce the volume by a factor of 400 from the original feed solution. Since the volume of solvent on the particles is small, having organic phase/aqueous phase ratios (O/A) of 0.01 or smaller suggest that higher volume reductions are attainable. For a one batch operation, the stripping stage recovers greater than 99% of the Pu and up to 92% of the Am, for an overall recovery of greater than 95% of TRU.

SUMMARY

The MACS process is a promising efficient separation technology that uses organophosphorous extractants absorbed on superparamagnetic particles. The large K_d values obtained for plutonium and americium illustrate the efficiency of separation using the CMPO/TBP on superparamagnetic particles, which surpasses traditional liquid/liquid

extraction processes for similar waste streams. The studies of plutonium and americium extraction as a function of nitric acid concentration suggested that the extraction CMPO/TBP species are different from those modeled by the GTM for the TRUEX process. They indicate that further studies are needed to model the data and determine a precise mechanism. Stripping the particles using alcohols instead of a stripping agent and hydrocarbons has been successful with large volume reduction. The most efficient stripping process for such high TRU K_d values is a three-stage process. Activities are underway to optimize these stages. Magnetite dissolution in acid seems to be a limitation on the recyclable batch process. We are investigating the possibility of designing particles with a smaller fraction of exposed magnetite to minimize the solid/liquid interface. On the other hand, for applications of MACS on basic solutions containing TRU, exposure of the magnetite can lead to an added sorption mechanism.¹⁵ At this point, we have succeeded in stripping at least 95% of the TRU from the particles in batch testing.

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Separation Science and Technology Section

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OUTLINE

- OBJECTIVE
- CONCEPTUAL DESIGN
- PARTICLE PREPARATION
- TARGET WASTE STREAM
- TRU PARTICLE DEVELOPMENT
- Cs PARTICLE DEVELOPMENT
- SUMMARY

BACKGROUND

The MACS Process

- Tailored for applications where processes are already developed.

solvent extraction
ion exchange

Anticipated benefits

reduction of cost
timely implementation

Advantages over existing technologies

inherent simplicity
compactness
low maintenance

The in-situ MACS process can be used

in any tank
remote operation

OBJECTIVE

The MACS Process

- Combines selective and efficient separation
 - chemical sorption
 - magnetic recovery of beads
- Sorbant-coated magnetic beads
 - radionuclides
 - heavy metals
- In simple stirred tanks without complex equipment
 - solvent extraction
 - chromatography
- After contact, separation of the solid sorbant from the tank by a magnet
- After removal, the contaminants can either be
 - left on the loaded beads for disposal
 - stripped, to regenerate, and recycle beads

OBJECTIVE

- To be successful for decontamination of I, MACS particles must
 - have very high affinity for I, ($D, K_d > 1000$)
 - have very high selectivity for I, ($\alpha > 10^5$)
 - recoverability of beads from solution ($> 99.9\%$)
 - ability to be stripped and recycled ($K_d > 1/1000$), or ability to be disposed

MACS

(Conceptual Process)

- CMPO

Octyl(phenyl)-N,N-
diisobutylcarbamoylmethylphosphine
oxide

Tributyl Phosphate (TBP)

PARTICLE SELECTION

MAGNETITE PARTICLE

charcoal/cross-linked N, N-methylene
bis-acrylamide

- COATING
- octyl(phenyl)-N, N
diisobutylcarbamoymethylphosphine oxide
(CMPO)

tributyl phosphate (TBP)

EQUATION

$$K_d = \left(\frac{C_{ORIGINAL} - C_{FINAL}}{C_{FINAL}} \right) \times \left(\frac{mL}{g} \right)$$

OTHER ACTIVITIES

sorption kinetics

- loading effects

gamma irradiation effects on
magnetite

alpha irradiation

- laboratory demonstration

NITRIC ACID DEPENDENCY

TRU SIMULANT WASTE STREAMS

- Plutonium Finishing Plant (PFP)
- Cs and Sr Hanford tank supernatant
- Dissolved single shell Tank (SST) combined sludge
- Idaho Chemical Processing Plant (ICPP)

COMBINED SST WASTE STREAM

Composition of the Simulated Dissolved Sludge from all the
Hanford SSTs

Component	Conc. (mol/L) ^a
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Fe	1.72E-01
Na	7.08E-02
Ca	4.91E-02
Mn	4.29E-02
Cr	3.77E-02
Bi	1.79E-02
Zr	1.30E-02
Eu	9.67E-03
Sr	6.53E-03
Ag	5.61E-03
Ba	5.32E-03
Zn	2.46E-03
Mg	1.58E-03
Co	7.21E-04
Cd	5.94E-04
Pb	5.21E-04

^aDetermined by Inductively
Coupled Plasma analysis.

PFP WASTE STREAM

PFP Waste Simulant Composition

Component	Component Charge	Conc. (mol/L)
H	1	1.5E 00
Be	0	7.0E-05
Na	1	4.0E-02
Mg	2	6.0E-02
Al	3	4.3E-01
K	1	3.0E-03
Ca	2	6.0E-02
Cr	3	4.0E-04
Mn	2	3.0E-03
Fe	3	3.0E-02
Ni	2	8.0E-02
Cu	2	3.0E-04
Zn	2	6.0E-04
Pb	2	5.0E-04
F	-1	9.0E-02
SO4	-2	1.0E-02
NO3	-1	3.05E 00

TRU SEPARATION OF PFP WASTE

TRU-C8 SUPERNATANT

SIMULANT TABLE

[CMPO] M	SIMULANT	ISOTOPE	K_d
1.2	TRU-Cs	^{241}Am	7000
1.2	TRU-Cs	^{238}Pu	20,000
1.2	PFP	^{241}Am	150
1.2	PFP	^{238}Pu	18,000
1.2	SST	^{238}Pu	3000

SORPTION KINETICS

changed concentration and vortex time

50% equilibrium occurs in less than 10 sec

process not limited by interparticle diffusion

STRIPPING PARTITION MEASUREMENTS

three-phase stripping

stripping K_d between 0.01-0.1 for TRU

volume reduction of 400

Radiation Studies of TRUEX Solvent

Little change in extraction efficiency for doses < 3 Mrad

Degradation of TBP greater than that of CMPO

G - value (radiation chemical yield) for the degradation
of CMPO = 0.76 molecules per 100 eV

Dose Approximation

Dose to magnetic particles is due to α -decay of TRU

TRU Activity (PFP Waste)

Am-241, Pu isotopes

Specific Activity = 2.6×10^{12} dph/L

Only 1/2 of α -decays deposit energy in particles

Energy deposited by ionization

$$\left. \frac{dT}{ds} \right|_{\text{ion}} = \frac{4\pi z^2 e^4}{m_o V^2} N Z \left\{ \ln \frac{2m_o V^2}{kZ} + \beta^4 \right\}$$

Assume: $Z = 10$, $A = 20$, $\rho = 2.5$, $s = 8 \mu\text{m}$

Dose to magnetic particles

Dose rate = 3000 rad/hr

0.5 hr per contact cycle

10 cycle dose = 1.5×10^4 rad

100 cycle dose = 1.5×10^5 rad

GAMMA IRRADIATION MEASUREMENTS

Electron Micrographs of Magnetic Particles

Irregular shaped charcoal-polymer particles with random distribution of magnetite

Damage evident for low dose

Density and size of aggregations increase as dose increases

Polymer begins to crystalize for doses in Mrad range

Electron Dispersion Spectroscopy (EDS) used to determine distribution of elements on particles

1.36 M CMPO/TBP

1.4 μm coating thickness

PFP simulant irradiation solution

1.3×10^5 rad (100 cycles)

Separation Science and Technology Section

Chemical Technology Division, Argonne National Laboratory

1.36 M CMPO/TBP

1.4 μm coating thickness

PFP simulant irradiation solution

3.1×10^6 rad (2000 cycles)

Separation Science and Technology Section

Chemical Technology Division, Argonne National Laboratory

1.3×10^4 rad (10 cycles)

PFP simulant irradiation solution

1.4 μ m coating thickness

1.36 M CMPO/TBP

100mm

Charcoal-polymer particles with magnetite

No irradiation

Separation Science and Technology Section

Chemical Technology Division, Argonne National Laboratory

GAMMA IRRADIATION EFFECTS ON MAGNETITE

LOADING EFFECTS

0.42% weight particles

PARTICLE DISSOLUTION

Cs REMOVAL FROM TANK SUPERNATANT

- K_d for silico-titanate ~620 for simulant
- reduction of K_d with gamma irradiation
- loading capacity is limited after 100 cycles of use
- Economical analysis of comparison of MagSep with ion exchange for Cs separation from tank supernatant

SUMMARY

$K_d(\text{Am}) > 3500$ and $K_d(\text{Pu}) > 10,000$

- larger partition values than solvent extraction processes
- magnetic portion of the particle is stable to irradiation but polymer portion suffers irradiation damage at medium and high gamma doses
- K_d decreases as a function of irradiation doses
- stripping is possible with volume reduction
- Cs removal will require further study of economic compared with ion-exchange
- Sr studies are just underway at NIU

FUTURE STUDIES

- Other candidate waste streams
- Cs low-level groundwaters
- ICPP waste streams
- ORNL/TETL waste streams
- Sr removal
- Other solvent extraction process
- Hg, Cd, transition metal, noble metal
- synergistic systems
- homogenous catalysis- organometallic complexes

DATE

FILMED

10/19/94

END