LA-UR- **00-4875**

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OCT 1 2 2000

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Removal of Pu-238 from aqueous process streams using a polymer filtration process

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Abstract. A glovebox facility is under construction at Los Alamos that will recover a significant quantity of the impure Pu-238 that exists in scrap and residues from past production operations. The general flowsheet consists of milling, acid dissolution, ion exchange, precipitation, calcination, oxygen isotope exchange, and waste treatment operations. As part of the waste treatment operations we are using polymer filtration to remove Pu-238 to meet facility discharge limits. Polymer filtration (PF) technology uses water-soluble polymers prepared with selective receptor sites to sequester metal ions, organic molecules, and other species from dilute aqueous solutions. The water-soluble polymers have a sufficiently large molecular size that they can be separated and concentrated using ultrafiltration (UF) methods. Water and small, unbound components of the solution pass freely through the UF membrane while the polymer concentrates in the retentate. The permeate stream is "cleaned" of the components bound to the polymer and can be used in further processing steps or discharged. The concentrated retentate solution can be treated to give a final waste form or to release the sequestered species from the receptor sites by adjusting the conditions in the retentate solution. The PF technology is part of our work to develop a safe, reliable and cost-effective scrap recovery operation with high process efficiencies, minimal waste generation, and high product purity.

INTRODUCTION

Plutonium-238 is an excellent radioisotope for providing heat and power to NASA deep space probes because of its power density, useful lifetime, minimal shielding requirements, and oxide stability. General Purpose Heat Source (GPHS) units containing ~150 g $^{238}PuO_2$ are used in Radioisotope Thermoelectric Generator (RTG) units such as those used to provide electrical power for the Cassini mission to Saturn. Smaller amounts of $^{238}PuO_2$ fuel, typically ~2.7 g, are also used in Radioisotopic Heater Units (RHU) employed recently in Cassini and on the Mars Pathfinder Rover to keep critical components warm.

A Pu-238 aqueous scrap recovery facility is under construction in the Los Alamos Plutonium Facility at Technical Area 55 (TA-55). This glovebox facility will recover a significant quantity of impure Pu-238 that exists in scrap and residues from past production operations and this material will provide heat and power sources for additional NASA missions. The feed material generally contains high-fired plutonium oxide that is first ball milled to reduce its particle size. The finely divided feed is then dissolved in refluxing nitric acid containing some hydrofluoric acid that aids the dissolution process. The dissolution solution is diluted and pretreated for ion exchange purification if needed or for direct oxalate precipitation. Addition of oxalic acid to a Pu(III) solution in 1-2 N nitric acid precipitates Pu(III) oxalate that is collected by filtration. The oxalate precipitate is calcined to produce the plutonium-238 oxide that is used in the heat sources after isotope exchange with O-16 enriched water vapor to reduce the O-18 content of the oxide. The reduced O-18 content lowers the neutron emission of the plutonium oxide product.

The filtrate from the oxalate precipitation and the effluent from the ion exchange process (when needed) still contain a significant amount of Pu-238. Adjustment of the filtrate or effluent pH to 10-13 by the addition of sodium hydroxide produces a hydroxide precipitate that contains most of the Pu-238. The precipitate is dried, stored, and then recycled to the dissolution process. The hydroxide filtrate solution often contains alpha activity that is higher than the TA-55 caustic waste line limit of 4.5 millicuries per liter. In the past, carrier precipitation with iron hydroxide was used to further reduce the alpha activity of this filtrate solution, but this process generates large volumes of ferric hydroxide sludge that are difficult to filter. We are planning to use a polymer filtration process in the scrap recovery facility to reduce the alpha activity in the hydroxide filtrates to meet the caustic waste line discard limit and, if necessary, to meet the industrial waste line limit of 0.5 microcurie per liter of total alpha activity.

POLYMER FILTRATION TECHNOLOGY

Polymer Filtration (PF) technology uses water-soluble polymers prepared with selective receptor sites to sequester metal ions, organic molecules, and other species from dilute aqueous solutions. The water-soluble polymers are designed with a large enough molecular size that they can be separated and concentrated using ultrafiltration (UF) methods. Water and small, unbound components of the solution pass freely through the UF membrane while the polymer concentrates in the retentate. The permeate stream is "cleaned" of the components bound to the polymer and can be used in further processing steps or discharged. The polymer that is concentrated in the retentate can be recycled or prepared for disposal. For recycle, the conditions in the retentate solution are adjusted to release the sequestered species from the receptor sites. A second UF step with a small volume of wash solution recovers the released ions or molecules in a concentrated form in the wash for recycle or disposal and retains the polymer for additional process cycles.

The concept of using water-soluble polymers to retain small ionic species in this way was first discussed in the late 1960s by Michaels (1968). Most of the work to date has involved chelating polymers for metal ions, but polymers with receptors for other ionic and molecular species have been developed. A good review of the area up to 1994 was published by Geckeler and Volchek (1996). A variety of terms and associated acronyms have been used in the literature for this technology including polymer-supported ultrafiltration (PSU) (Geckeler, 1996), liquid-phase polymer-based retention (LPR) (Spivakov, 1989), polyelectolyte-enhanced ultrafiltration (PEUF) (Scamehorn, 1990), and polymer-assisted ultrafiltration (PAUF) (Smith, 1995). The term Polymer Filtration was adopted for this technology by PolyIonix Separation Technologies, Inc., during the course of commercialization activities (Thompson et al., 1999).

Some advantages of PF technology include the following:
1. The reactions between the target species and the receptor sites occur in a single liquid phase. This tends to give rapid attainment of equilibrium relative to separations requiring phase changes such as liquid-liquid extraction.
2. Synthesis of the polymers is also generally a homogeneous solution process and potentially all the polymer structure can be used for binding sites. There are no requirements to use part of the polymer to maintain mechanical stability such as the crosslinking required for macroporous polymer beads.
3. A mixture of polymers can be used to target a group of components of the solution. If polymers have been developed for individual components of a mixture then it is often possible to mix the polymers and remove multiple components in the same UF step rather than requiring a stepwise removal or developing a new polymer.
4. The UF step will remove colloidal material that is larger than the size cutoff of the ultrafilter and this can be useful in some cases. For example, radionuclides can be sorbed on colloidal material in waste streams and PF can remove both dissolved species that bind to the receptor sites and the colloidal material in a single operation.
5. The scale-up of UF operations is generally routine and a wide variety of commercial systems are available.
6. The UF requires relatively low pressures, usually 10-50 psig.

The major potential drawbacks of the PF process are the fouling of the UF unit and a single stage of equilibrium binding is obtained for each UF operation. Modern UF technology has many approaches to minimizing fouling and there are a great variety of commercial designs to tailor to a particular application. If multiple stages of PF are needed to accomplish a desired separation, then staging of the PF units can be designed much like the staging of contactors in liquid-liquid extraction systems.

The properties of the water-soluble polymer are key to successful implementation of PF. The receptor sites must have the required selectivity and binding constant for the target species to yield permeate that meets the specifications of the process. The polymer before and after loading must remain soluble under the process conditions. The polymer should be completely retained by the UF membrane, but not interact with the membrane to give excessive fouling. The polymer must remain stable under the process conditions and the viscosity of the polymer solution must allow reasonable flux rates to be maintained during the concentration and regeneration phases of the process. The concentration range for the water-soluble polymer typically ranges from 0.001 weight/volume percent up to 20 weight/volume percent in the final retentate solution. Regeneration of the polymer can be accomplished by a variety of processes including competition for receptor sites by protons at lower pH, competition for the bound metal ions by ligands in the wash solution, and oxidation/reduction reactions of the metal ion to change its affinity for the receptor site.

We have prepared a variety of phosphonic acid derivatives of the water-soluble polymer polyethyleneimine (PEI) and found compositions that gave good results for removing actinides from some Los Alamos process and waste waters (Smith, 1998). Figure 1 shows a structural diagram of the PEI polymer that has been modified by the addition of methylenephosphonic acid groups. The oxygen atoms of the phosphonic acid groups bind strongly to high valent metal ions such as Pu(IV). The PEI starting material is purified using an ultrafilter with a molecular weight cutoff of 30,000 daltons. The product of the reaction to add the phosphonic acid groups to PEI is also purified with a 30,000 dalton cutoff ultrafilter. We use an ultrafiltration module with a 10,000 dalton cutoff when operating the polymer filtration process to assure complete retention of the polymer. Typically the polymer used to bind the Pu-238 has about one-half of the nitrogen atoms in the PEI functionalized with phosphonic acid groups and has been given the acronym PEIP. This was the polymer used in the qualification of the bench-scale Pu-238 aqueous recovery process to be described below.

FIGURE 1. Structural diagrams of polyethyleneimine modified with phosphonic acid chelating groups.

PEIP - high pH   PEIP - low pH
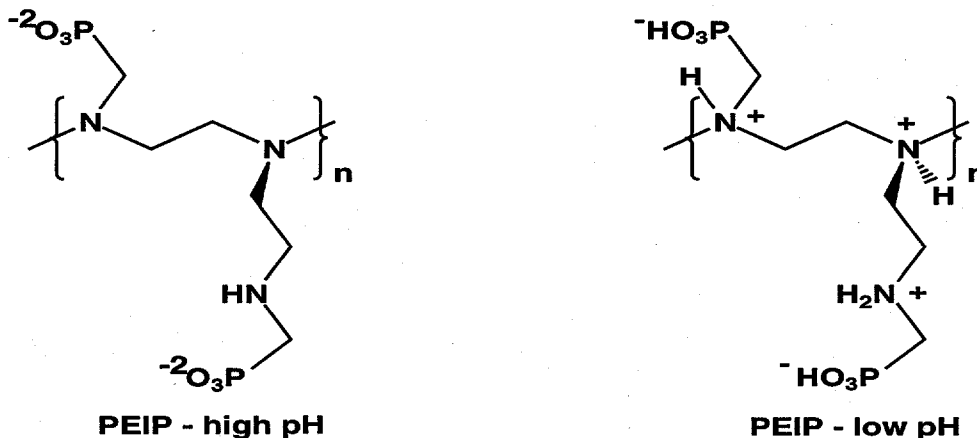
QUALIFICATION OF BENCH-SCALE SCRAP RECOVERY PROCESS

The Power Source Technologies Group of the Nuclear Materials Technology Division at Los Alamos recently completed a set of six qualification runs of the Pu-238 aqueous scrap recovery process. The purpose of these qualification runs was to demonstrate the ability of the process to produce NASA flight quality feed material with high Pu-238 recovery and generate further operational data useful for refining the full-scale scrap recovery process. Three runs each of two scrap feed types were processed: Milliwatt heat source returns and high-fired scrap Pu-238 oxide from the Los Alamos fuel reprocessing line.

Two methods were used to process the feed. Method 1 comprised dissolution, ion exchange, precipitation of Pu-238 oxalate, and calcination to the oxide. Method 2 was the same as Method 1, but without the ion exchange step. Eliminating the ion exchange step reduces the amount of aqueous effluent that must be treated. The dissolution

solution for each batch of feed material was split in each run with 25% going to Method 1 and 75% going to Method 2. The effluent solutions from Method 1 and 2 were neutralized with sodium hydroxide to pH 10-12 as described in the Introduction. The hydroxide cakes were collected on 10 micron filter pads, dried and stored. The filtrate solutions were then treated with the polymer filtration process.

Two stages of polymer filtration were used to treat the hydroxide filtrates from Method 1 and 2. A schematic of the bench scale unit is shown in Figure 2. A concentrated solution of the PEIP polymer (8.4 wt/vol%) was added to the hydroxide filtrate to give a final wt/vol% in the range of 0.1 to 0.35 g/L and the pH was adjusted to the range of 8-10 with the addition of nitric acid if necessary. As the first solution was ultrafiltered, the permeate accumulated in a second reservoir where additional concentrated polymer solution had been placed to give a second stage of polymer binding. The wt/vol% in the second reservoir was also set to be in the range of 0.1 to 0.35 g/L. These starting polymer wt/vol percentages are based on the total volume of the hydroxide filtrate solution. As the UF operation proceeds, the polymer concentrates in the retentate along with the bound metal ions. Typically, 5-10 liters of hydroxide filtrate was processed to leave about 0.2 liter of moderately viscous retentate solution in each stage with a final polymer wt/vol% of 6-12 g/L. The retentates will be cemented for disposal or treated with an oxidation process such as hydrogen peroxide/UV irradiation to destroy the organics before recycle or discharge of the water.
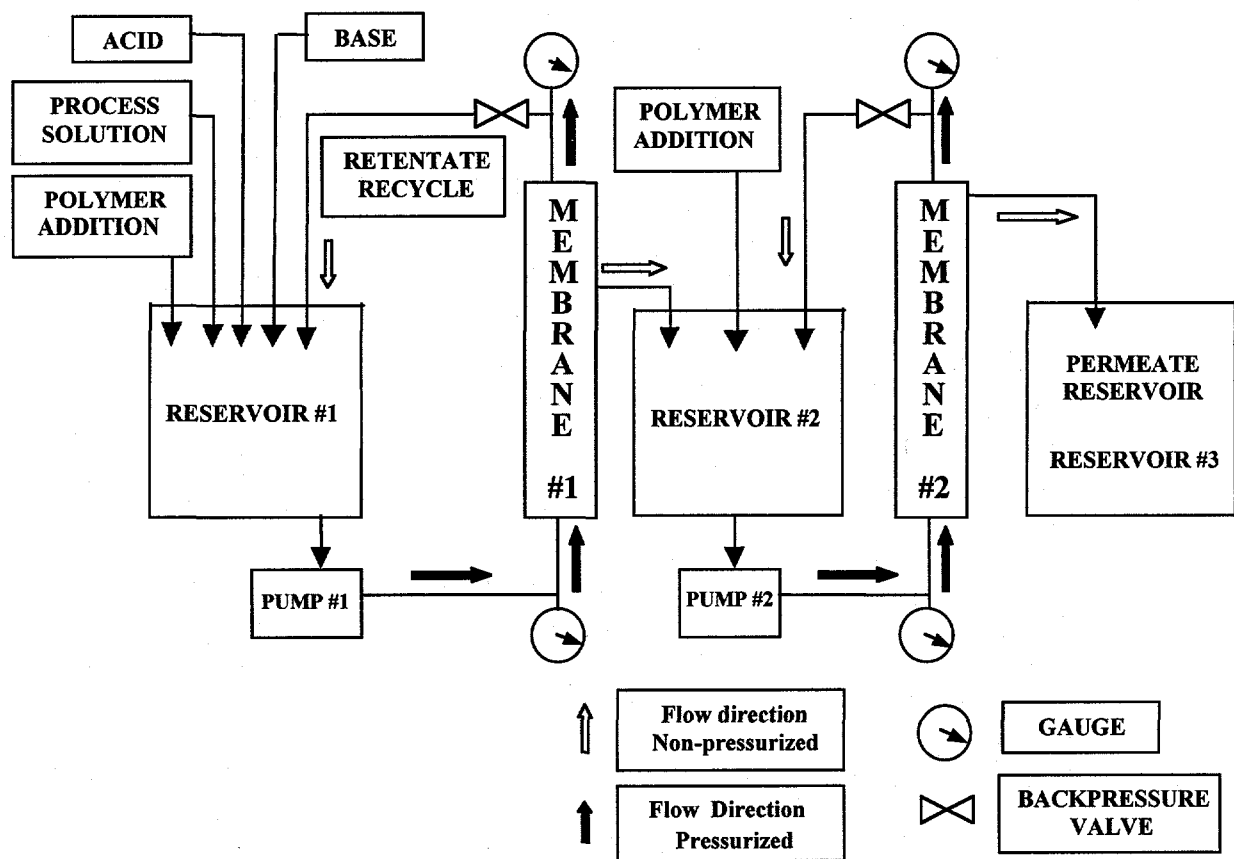

FIGURE 2. Schematic of two-stage polymer filtration unit used for qualification runs.

The UF modules are commercially available and consist of dozens of small polymer hollow fibers. The solution is pumped rapidly through the hollow fibers and the water and components of the solution small enough to pass through the tiny pores in the polymer fibers accumulate in the enclosed space outside the fibers and then flow to a reservoir connected to this space. The transmembrane pressure was maintained in the range of 15-30 psig.

The results for the removal of alpha activity from the hydroxide filtrates from Methods 1 and 2 are presented in the Table. The solutions from the polymer filtration operation met the required facility caustic waste line discard limit of 4.5 millicuries/L of total alpha activity. The UF modules operated efficiently throughout the twelve runs. The UF modules were washed with about 0.2 L of water after each PF run and the wash solution left in the reservoirs to be mixed with the next batch of solution for processing. There was no sign of a loss of flux through the UF modules between runs.

TABLE. Alpha Activity Reduction from Polymer Filtration Treatment of Hydroxide Filtrates in Qualification Runs

Run No.	Method	Initial Activity (Ci/L)	Permeate Activity (Ci/L)	Final Volume (L)	Decontamination Factor	% of Discard Limit
1	1	3.18E-01	2.81E-04	6.3	1133	6.
1	2	1.46E-01	2.13E-03	5.8	68	47
2	1	7.29E-01	1.18E-03	6.2	618	26
2	2	8.56E-02	2.14E-04	6.4	400	5
3	1	9.89E-02	7.45E-05	6.0	1328	2
3	2	8.87E-02	4.12E-03	6.8	22	92
4	1	4.86E-02	3.41E-04	8.9	143	8
4	2	1.57E-01	4.24E-03	4.9	37	94
5	1	1.26E-01	1.05E-04	8.3	1203	2
5	2	2.89E-02	1.28E-03	5.2	23	28
6	1	3.13E-02	2.43E-04	8.8	129	5
6	2	1.06E-01	1.51E-03	5.2	70	34

The permeates from Method 2 had generally higher alpha activity levels than the permeates from Method 1. This was most likely caused by the higher oxalate concentrations (2.5-4.5 times higher) in the Method 2 hydroxide filtrates. The Method 1 filtrates have a lower oxalate concentration because these solutions are diluted by the neutralized ion exchange effluent. The excess oxalate competes with the polymer for binding the plutonium that is in solution. An enhancement to the scrap recovery flowsheet that is under evaluation is addition of hydrogen peroxide and ultraviolet irradiation of the oxalate filtrates to oxidize excess oxalate, urea, and hydroxylamine. This step would improve plutonium removal in both the hydroxide precipitation and PF operations.

Another factor that could lead to a reduced alpha removal efficiency was higher U-234 concentration in the Method 2 hydroxide filtrates. The U(VI) in Method 2 may not precipitate during the neutralization of the oxalate filtrate with sodium hydroxide, but could remain in solution as anionic complexes such as $UO_2(C_2O_4)_2^{2-}$ and $UO_2(C_2O_4)_3^{4-}$. The U(VI) is expected to precipitate from the ion exchange effluent in Method 1 where there are no strong competing complexants present such as oxalate. On a molar basis, the uranium concentration can be up to a thousand times the plutonium concentration. The U(VI) in the Method 2 hydroxide filtrate could compete with plutonium for the binding sites on the PEIP polymer. The partitioning of the U-234 during the scrap recovery process will be followed in future runs because methods to recover the U-234 are under evaluation.

Overall, the present PF process met the requirements of the aqueous scrap recovery process. A larger PF unit has been assembled for installation in the full-scale scrap recovery facility. Some enhancements to the PF operation will be evaluated for the full-scale process. Several water-soluble polymers with stronger complexing ability for plutonium could be substituted for PEIP in one of more stages of the PF operation. Additional stages of polymer filtration could be added to reach the industrial waste line limit 0.5 microcuries/L of total alpha activity.

CONCLUSIONS

A polymer filtration process has been tested to remove alpha activity from the aqueous effluents from a Pu-238 scrap recovery process under development at Los Alamos. The polymer filtration process met the facility discharge requirements in a set of qualification runs of the scrap recovery process performed in the first quarter of 2000. A polymer filtration unit sized for the full-scale scrap recovery facility will be installed in 2001 and Pu-238 production is expected to begin in 2002.

ACKNOWLEDGMENTS

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