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Los Alamos
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REMOVAL AND RECOVERY OF METAL IONS FROM PROCESS AND WASTE STREAMS USING POLYMER FILTRATION

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ABSTRACT

Polymer Filtration (PF) is an innovative, selective metal removal technology. Chelating, water-soluble polymers are used to selectively bind the desired metal ions and ultrafiltration is used to concentrate the polymer-metal complex producing a permeate with low levels of the targeted metal ion. When applied to the treatment of industrial metal-bearing aqueous process streams, the permeate water can often be reused within the process and the metal ions reclaimed. This technology is applicable to many types of industrial aqueous streams with widely varying chemistries. Application of PF to aqueous streams from nuclear materials processing and electroplating operations will be described.

INTRODUCTION

Separation processes are an important part of industrial operations and are often a major portion of product cost (1). The requirements that an industrial separation process must satisfy derive from a variety of sources, including meeting feed criteria for subsequent processing steps, final product quality standards, product cost constraints, safety and health regulations, and regulatory limits for waste generation. All these requirements have an effect on the overall cost of the separation process, but the last two regulatory items indicate that factors outside the traditional industrial profit "envelope" are also driving the development of new processing strategies in recent times. Many of these external requirements may be grouped under the general heading of "sustainability," which includes such areas as environmental protection, pollution prevention, recycle, and renewable sources of raw materials. Government regulations and tax policies have been and will continue to be formulated to encourage activities consistent with the perceived goals of sustainability. Improved separation technology will be a key part of new industrial processes that accomplish the goals of sustainability. This is evident because many of the components of sustainable industrial processing require separations, such as purification of new feed materials, recycle of portions of a process stream or of products after their useful lifetime, and removal of contaminants before release of materials to the marketplace or the environment. Metal separations are an important part of industrial separations and are used in a diverse set of industrial operations.

Separation processes for removal of metal ions from aqueous solution are a major industrial activity covering processes ranging from production of potable water, to leaching and recovery of metals from ores, to detoxification of process and waste waters. A variety of separation processes for metal ions have been developed for industrial needs including precipitation, liquid-liquid extraction, inorganic and polymeric adsorbents, evaporation, reverse osmosis, electrowinning, and electrodialysis. The use of adsorbents made by attaching metal-ion-specific binding groups to solid polymers is an important approach to removing metal ions from water and has received considerable attention over the past 50 years. The metal-ion binding sites in the polymers may include ion-exchange and chelating functionality or both. In fact, very similar metal-ion coordination chemistry can be deployed in different ways to effect mass transfer in several of these metal-ion separation technologies. For example, materials containing phosphonic acid functionalities can be used as precipitants, as liquid-liquid extractants, or as the key binding sites in certain inorganic and organic adsorbents. Chemical modifications of the structure attached to the metal binding site provide the means to allow separation and can also influence the binding to the metal ion. For example, the organic groups that make a phosphonic acid derivative soluble in an organic phase for liquid-liquid extraction must also solubilize the metal complex in the organic phase under process conditions and can be used to fine tune the metal binding through steric and electronic effects.

The use of water-soluble polymers to bind metal ions combined with ultrafiltration (UF) to separate the polymer and bound metal ions from the bulk aqueous phase has been developed less extensively than solid adsorbent technology, but is currently being deployed for a number commercial applications (2, 3). As noted above, the metal-binding sites in these polymers can offer very similar coordination environments for the metal ion as those used in adsorbents or liquid-liquid extractants, but the polymers are designed to remain soluble in an aqueous solution with and without bound metal ions. These water-soluble polymers can be viewed as part of a continuum of separation reagents that proceeds from small molecular reagents used as precipitants and extractants to solid adsorbents. The improvements in commercial UF technology over the last 10-15 years have made the use of water-soluble polymers with UF a more reliable and cost-effective approach for separations. Some developing applications of these water-soluble polymers for metal-ion removal and recovery will be described briefly in this paper.

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 have a sufficiently large molecular size that they can be separated and concentrated using 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. By adjusting the conditions in the retentate solution, the sequestered species are released from the receptor sites. A second UF step with a small volume of wash solution recovers the sequestered species 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 (4). 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 (5). A variety of terms and associated acronyms have been used in the literature for this technology including polymer-supported ultrafiltration (PSU) (5), liquid-phase polymer-based retention (LPR) (6), polyelectolyte-enhanced ultrafiltration (PEUF) (7), and polymer-assisted ultrafiltration (PAUF) (8). The term Polymer Filtration was adopted for this technology by PolyIonix Separation Technologies, Inc. during the course of commercialization activities (3).

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.
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 which 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.
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 solvent 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.

Plutonium Removal from Aqueous Process Streams

As noted in the introduction, regulatory limits play a crucial role in driving the requirements for separations. This is true at U.S. Department of Energy (DOE) nuclear facilities in which regulatory limits for discharge of radioactive metal ions have become markedly lower in recent years. Older technologies for treating waste streams such as carrier precipitation have become much less efficient from an overall systems engineering perspective in meeting these lower limits. Our separations team at Los Alamos has been evaluating the use of PF as a more cost-effective way of meeting the increasingly stringent regulatory requirements for removal of actinides from waste waters. Exploratory work with actinide metal ions using a variety of water-soluble metal-binding polymers was done by Bayer and Geckeler et al. (9). Bayer and Geckeler collaborated with Myasoedov, Spivakov and coworkers at the Vernadsky Institute in Moscow to continue more extensive studies with the actinides (5, 10).

We tested some of the polymers reported in the literature along with a number of other commercially available polymers and found that although some polymers did indeed concentrate americium(III) and plutonium (III)/(IV) (the major alpha-active contaminants in our waste waters), our goal of reaching DOE limits could not be readily met with these polymer systems (11). Consequently, we began designing polymers that would have higher binding constants for the actinides (particularly americium and plutonium) and would have overall better physical properties for use in the UF process.

We prepared a variety of phosphonic acid derivatives of polyethyleneimine and found compositions that gave good results for removing actinides from some Los Alamos process and waste waters (11). For example, the Los Alamos Plutonium Facility presently sends actinide activity in three liquid streams to the Radioactive Liquid Waste Treatment Facility (RLWTF):

- a caustic stream with a pH greater than 7 and alpha activity less than 4500 μCi/L,
- an acid stream with pH less than 1 and alpha activity less than 60 μCi/L,
- and an industrial waste water stream with a pH between 2 and 12 and alpha activity less than 0.5 μCi/L.

The RLWTF further processes the waste waters to meet EPA and DOE guidelines before discharge to the environment. Until very recently, this was accomplished through a series of precipitations followed by settling in large tanks. The sludge containing the radionuclides was periodically removed and cemented in drums for disposal. New processes based on UF and reverse osmosis are presently in the start-up phase at the RLWTF.

The near-term goal at the Plutonium Facility is to reduce the activity in various caustic and acid waste streams to allow them to be disposed of as industrial waste water. This will reduce the load of actinides that the RLWTF must handle and simplify operations. Polymer Filtration has been tested at a pilot-scale on a number of streams. Some of this preliminary work was discussed in reference (2). Polymer Filtration technology will likely become a part of overall waste minimization efforts at the Plutonium Facility.

The process stream where PF is closest to implementation in the Plutonium Facility is in the Pu-238 scrap recovery operations. An aqueous process will be used to recover and purify Pu-238 from various residue materials for use in radioisotope heat sources. This process precipitates plutonium(III) oxalate from nitric acid solution. The oxalate precipitate is calcined to produce the plutonium oxide that is used in the heat sources. The filtrate from the oxalate precipitate still contains a substantial amount of alpha activity that is higher than either the acid or caustic waste line disposal limits. The filtrate also contains urea and hydroxyl amine used to reduce the plutonium to the trivalent state and excess oxalic acid. Addition of sodium hydroxide to the oxalate filtrate produces a hydroxide precipitate that recovers most of the Pu-238 for recycle to the purification operations, but the caustic oxalate filtrate solutions often contain alpha activity higher than the waste line limit. We have tested PF at a small scale for treatment of the neutralized oxalate filtrate using 2 mL samples and Centricon units. These units use a centrifuge to drive the liquid through an ultrafilter and have proved very useful to obtain data for the design of PF processes (2). Table 1 lists the test results on two actual samples of neutralized oxalate filtrate, OHFLT-12A and OHFLT-12B. Ultrafiltration alone of the original filtrate or the filtrate acidified to pH 7 or 10 removed less than 60% of the activity. However, two stages of PF reduced the alpha activity levels several orders of magnitude to near those required for disposal in the industrial waste line. These tests were run with 0.5 wt/volume % of the phosphonic acid polymer acid, but siimilar results have been observed with 0.1 wt/volume % of the polymer.

Table 1. Ultrafiltration and Polymer Filtration Treatment of Neutralized Pu-238 Oxalate Filtrate Solutions

Sample	OHFLT-12A µCi/L (alpha)	OHFLT-12B µCi/L (alpha)
filtrate, pH 13	500	1200
pH 13, UF, no polymer	250	460
pH 7, UF, no polymer	280	680
pH 7, PF #1, 0.5%	48	18
pH 7, PF #2, 0.5%	0.96	0.42
pH 10, UF, no polymer	290	620
pH 10, PF #1, 0.5%	9.9	18
pH 10, PF #2, 0.5%	0.57	0.65

The polymer in the retentate solutions could be reused by releasing the Pu-238 at low pH and ultrafiltering to separate the Pu-238 solution from the polymer. The concentrated Pu-238 solution would be returned to the purification process. However, the cost of the polymer is relatively small compared to other costs of the waste treatment operation. Therefore, we are considering an option of using the polymer once and treating the retentate solution to destroy the polymer with hydrogen peroxide and ultraviolet light. This oxidized solution would then be returned to the purification operation.

Metal Recovery from Waste Streams from Metal Finishing Operations

PolyIonix Separations Technologies, Inc., has partnered with Los Alamos to commercialize PF technology for a number of industrial applications. Recycle of metal ions from rinse waters in metal finishing and printed wiring board operations are nearest to commercial use. A demonstration was performed in 1998 at the Pottstown Plating Works in Pottstown Pennsylvania under the EPA Common Sense Initiative as part of the Metal Finishing Sector's Approaching Zero Discharge (AZD) Program. The goal of the Common Sense Initiative is to demonstrate commercially available technologies in an industrial setting to improve the economics and ecology of production facilities through the recovery of valuable resources and reduction in emission of toxic substances.

The focus of the commercial demonstration of the Polymer Filtration technology at the Pottstown Plating Works facility was the removal of zinc from several zinc chloride rinse tanks. At this plating operation, a typical processing run was 250 to 370 gallons of zinc rinse water containing an average of 60 ppm zinc.

The objectives of the demonstration included:

- Operate for 2 weeks in the continuous mode, treating ~250 gpd, with no major mechanical problems, and obtain results for the AZD program
- Demonstrate recovery and reuse of permeate water from the PF process
- Demonstrate efficacy of recovery and reuse of reclaimed zinc in the plating process
- Removal of zinc to meet permit discharge limits (2.37 ppm)
- Gathering usage data concerning quantity and concentration of chemicals used in each operation
- Operate the system for 3 days to treat the higher zinc concentrations in the drag-out solution
- Perform personnel monitoring and emission testing of VOCs and zinc metal

For demonstration purposes, rinse water was transferred to a common 250 gallon holding tank, and processed at a rate of 1.0 gallon per minute. To demonstrate the effects of process variation on the system, the unit was operated in a semi-continuous mode, whereby the rinse water was introduced into a smaller tank containing the polymer solution that circulates through the UF unit at the same rate permeate was leaving the system. This mode has advantages of reduced labor and process time requirements. The water-soluble polymer used to bind the zinc has different chelating functional groups than that used to bind plutonium in the example described above. The rinse water was introduced until the entire volume of rinse solution was concentrated. Composite samples of the permeate were collected periodically.

Throughout the process, "fresh" permeate water (~1 gpm) from the PF process was returned to a rinse tank, reducing make-up water requirements by 20 percent for the total rinse operation. The pH of the remaining concentrated metal/polymer solution was then adjusted to a predetermined set point designed to separate metal from the chelating polymer. The regenerated polymer was then returned to the polymer feed tank for subsequent use in treating additional batches of rinse water.

The PF automated equipment and technology was successful in treating zinc rinse water and was easily operated. Based on the objectives set for this demonstration, the following are typical results from this application:

- PF was able to remove zinc to below permit discharge limits for various volume sizes and zinc concentrations
- The automated PF unit was operated successfully for 2 weeks with no operational problems
- The permeate water generated in the PF process was recycled back to a rinse tank, with no adverse effects to the plating process
- Zinc metal was reclaimed in concentrated form and returned to the original plating bath solution with no adverse effects on plating quality
- Air monitoring tests indicated that the PF unit operator had no detectable exposure to zinc metal or VOCs during unit operation
- The polymer was successfully regenerated for use in treating subsequent batches

- PF successfully treated the higher concentration drag-out tank and the permeate water was recycled to a rinse tank without problems
- The PF system showed a significant reduction in chemical usage, compared to chemical precipitation

Table 2 lists typical data obtained during the demonstration for the concentration of zinc in the permeate. The PF process performed very well for this application. A number of other demonstrations of PF applied to various metal finishing and printed wiring board applications are described in a recent report from Polylonix (12).

Table 2. Mean Permeate Zinc Concentrations and Rejection Coefficients for Polymer Filtration Treatment Runs of Plating Rinse Waters

Rinse Bath Zn Conc. (ppm)	Volume Treated (gallons)	Mean Permeate Conc. (ppm)	Average Rejection Coefficient (%)
89	370	0.46	99.48
55	370	0.47	99.15
49	370	0.2	99.59
66	370	0.2	99.70
66	370	0.28	99.58
40	370	0.31	99.23
60	270	0.37	99.38
43	270	0.16	99.63
71	270	0.40	99.44

In collaboration with Polylonix and other industrial partners, a number of other applications of PF for removing and recycling metal ions from industrial process and waste streams are under development [32]. Among these are the following:

1. Analytical preconcentration,
2. Nuclear power/nuclear facility waste streams,
3. Photofinishing waste streams,
4. Acid mine drainage/advanced mining techniques,
5. Treatment of ground water/drinking water,
6. Precious metals processing streams,
7. Catalyst waste streams,
8. Electronics manufacturing waste streams,
9. Cooling tower water,
10. Textile waste streams,
11. Municipal waste streams,
12. Soil remediation,
13. Surface decontamination and
14. Decontamination and decommissioning of nuclear facilities.

Pilot-scale demonstrations have been completed for a variety of other waste streams containing low concentrations of metal ions. We feel Polymer Filtration will find broad application in industry.

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REMOVAL AND RECOVERY OF METAL IONS FROM PROCESS AND WASTE STREAMS USING POLYMER FILTRATION^{TM}

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