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Polymer Filtration Systems for Dilute Metal Ion Recovery

Barbara F. Smith, Thomas W. Robison, Gordon D. Jarvinen
Los Alamos National Laboratory
Los Alamos, New Mexico

Introduction

In electroplating-depositing a protective coating of metal on a object- the item to be plated is first passed through an electroplating bath of metal ions and then washed in a series of rinsing baths. Traditionally, when the process is complete, the electroplating metals that remain in the rinse water are precipitated, collected, and buried as toxic sludge. The sludge is both a waste of valuable material and a potential environmental hazard: by 2010 U. S. electroplating shops will be generating at least 50,000 tons of sludge a year. Over the last 30-40 years, thousands of tons of electroplating metals have been buried as toxic sludge because the technology to recover them from dilute rinsing baths has been cumbersome or prohibitively expensive. Elsewhere in the world, environmental concerns have lead Germany to ban the use of toxic electroplating metals such as cadmium, and in some countries the metal rinse is directly discharged into rivers and oceans.

Scientists at Los Alamos National Laboratory have developed a metal recovery system that meets the global treatment demands for all kinds of industrial and metal-processing streams. The Polymer Filtration (PF) System—a process that is easily operated and robust—offers metal-finishing businesses a convenient and inexpensive way to recover and recycle metal ions in-house, thus reducing materials costs, waste removal costs, and industrial liability. As a valuable economic and environmental asset, the PF System has been named a winner of a 1995 R&D 100 Award. These awards are presented annually by *R&D Magazine* to the one hundred most significant technical innovations of the year. The Technology was initially tested at Boeing in Seattle, Washington in concert with the Boeing Space and Defense Group. The PF System was licensed by PolyIonix, Separation Technologies, Inc. of Dayton, NJ and they have made the technology commercially available. In the process PolyIonix has performed numeerour beta tests at actual electroplating and other facilities.

Characteristics and Advantages of PF Systems

The PF System is based on the use of water-soluble metal-binding polymers and on advanced ultrafiltration membranes. Customers for this technology will receive new soluble polymers, especially formulated for their waste stream, and the complete PF processing unit: a reaction reservoir, pumps, plumbing, controls, and the advanced ultrafiltration membranes, all in a skid mounted frame.

Metal-bearing waste water is treated in the reaction reservoir, where the polymer binds with the metal ions under balanced acid/base conditions. The reservoir fluid is then

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pumped through the ultrafiltration system—a cartridge packed with ultrafiltration membranes shaped in hollow fibers. As the fluid travels inside the fiber, water and other small molecules—simple salts such as calcium and sodium, for example—pass through the porous membrane walls of the fibers and are discharged through the outlet as permeate. The polymer-bound metal, which is too large to pass through the pores, is both purified and concentrated inside the hollow fibers and is returned to the fluid reservoir for further waste water treatment. In this manner 500 gallons of rinse water can be treated and the metal ion concentrated to approximately 1 gallon in 2 hours (5 gallons per minute flux rate). The PF System discharges water that easily meets or even improves on EPA discharge limits. Regeneration of the polymer is easily and rapidly accomplished by adjusting the concentrate to acid conditions and then stripping the metals-ions from the polymer (about 15 minute cycle time) using a diafiltration process. The metal ions are conveniently recovered in a solution concentrated enough for direct reuse in the original electroplating bath. The Polymer Filtration System built to test nickel and zinc removal from electroplating rinse baths at Boeing is shown below in Figure 1.

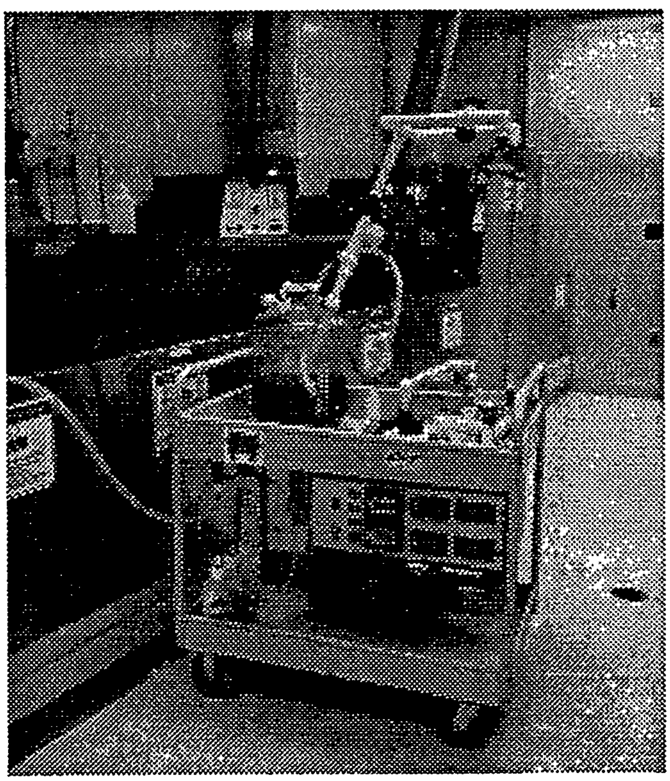

Figure 1. The Polymer Filtration System, developed to recover zinc and nickel from electroplating rinses, can be applied to a variety of other metal-bearing process streams. Two key components of this mobile unit are (1) a water-soluble, metal-binding polymer, which is added to the units 5 gallon fluid reservoir on the left side of the cart and (2) the two cylindrical ultrafiltration cartridges on the right side of the cart. Controls for monitoring the recovery process can be seen underneath the cart's top shelf.

Comparison of Polymer Filtration System with Other Commonly Used Separation Technologies:

PF is a technology for the concentration, removal, and recovery of metal-ions from dilute aqueous solutions. In general, we have applied this technology to feed concentrations of ≤1000 ppm metal. Though higher metal-ion concentrations can be treated, the concentration factors become small. Other processes for metal removal/recovery from dilute solutions can include Precipitation (PPT), biphasic Liquid-Liquid EXtraction (LLEX), Ion eXchange (IX), Chelating Ion eXchange (CIX), Reverse Osmosis (RO), Evaporation (EV), filtration (carbon, sand, etc.), ElectroDeposition (ED), and ElectroRecovery (ER). Aqueous chelating ion exchange is the technology most closely aligned with PF Systems because the metal-ion binding chemistry is similar and the chelators can have high metal-ion selectivity. LLEX can also employ very selective chelators, but uses two immiscible liquid phases rather than a solid and liquid phase as in CIX.

Binding kinetics are very rapid with PF because of the homogeneity of the system. With CIX phase transfer between the aqueous solution and the solid resin must occur. This process can be relatively slow in both the metal uptake and release. For example, 90% loading can be attained in PF within seconds, while it may require hours to attain the same level of loading with some resins. This difference makes the kinetics of PF in the range of 10^4 times faster than CIX. Thus, in CIX, column flow rates and column material amounts have to be optimized to allow for slower metal binding and release, and the amount of regeneration solution required to recover the metal-ions can be large. PF can significantly reduce processing times and process volumes relative to CIX.

A useful aspect of PF is its ability to recover metal-ion concentrate in a small volume and potentially recycle it directly to the original process all in a single unit. This ability can translate into smaller equipment and fewer polymer requirements for PF technology.

A water-soluble chelating polymer can have metal-ion loading capacities considerably greater than that of similar chelating ion exchange resins because of the greater density of binding sites. For example, Amberlite IRC-718 has a loading capacity of approximately 0.025 g Ni/gram of dry resin, while a water-soluble analogue called Poly-Met™-Z has about 0.25 g of Ni/gram of dry polymer.

Metal-binding groups can be built into the water-soluble polymer structure to select specific metal-ions and reject benign impurities such as calcium, potassium, and other salts. Unlike LLEX, no organic solvents are required. In addition, cooperative effects between ligands on soluble polyelectrolytes can give higher binding affinity than the monomer ligands. For example, polyacrylic acid has a 10^4 greater binding constant than the monomer ligand, glutaric acid. PF systems can potentially take advantage of such cooperative effects to obtain higher metal binding relative to monomeric extractants.

The PF system can have advantages over other conventional metal recovery processes depending on the application. By contrast with RO, PF is carried out at low pressure (commonly 25 psi). PF is a relatively low energy process compared to EV and will not damage heat-sensitive solutes. RO and EV, as compared to PF, are unselective processes for solutes, concentrating all waste stream salts and materials, including metal-ions that may be impurities. PPT is often unspecific, generates large amounts of secondary waste, and is limited by solubility products. PF functions well, perhaps even better, at low metal-ion concentration, whereas some technologies like PPT have limited applicability. ED can recover metal-ions selectively as pure solids, but not as ions in solution. This process does not allow for efficient recycling in some applications. ED/ER tends to be inefficient at low metal-ion concentrations. The choice of a particular technology is dictated by the required end result and the total system cost. For dilute solution and waste polishing requirements, PF is a cost-effective option.

A very useful aspect of PF is the possibility of developing formulations (mixtures) of polymers with different chelators to recover suites of metal-ions and of separating the concentrated metal-ions from each other with different stripping chemistry. The polymers can also lend themselves to having multiple ligand groups on one polymer. We have over 30 different polymers under development with a variety of functionalities and many polymeric structures are already reported in the literature.

The combination of concentration and diafiltration ultrafiltration processes provides an effective method for the recovery, concentration, and purification of metal-ions in solution. Permeate streams 'free' (in a regulatory sense) of hazardous metal-ions will result. A number of industries successfully use simple ultrafiltration processes for various applications, including water purification, waste treatment, pharmaceuticals, and the food and beverage industries. Consequently, ultrafiltration is an accepted technology in Industry.

Cost Comparison:

Though it is difficult to do a direct cost comparison for every process stream, as different streams present different selectivity issues, we can make some comparisons on a defined process. We have often considered chelating ion exchange as the technology that is most comparable or most closely aligned with Polymer Filtration. If we were to treat 500 gallons of rinse water containing 100 ppm nickel and 50 ppm of zinc (0.624 pounds total metal) in 8 hours or less to give less than 1 ppm of metal in the final stream the following comparison could be made between a chelating exchange resin column system and the PF System:

Though these comparisons are on polymer/resin costs alone, they translate into faster process times which are smaller foot print units or lower capital costs. Because the recovered metal ion solution is more concentrated the metals can easily be reused in the original process without further treatment (e.g., evaporation). The resin system requires an offline regeneration system or it would require double the amount of resin in two columns. This allows processing to occur in one column while regeneration occurs in the other column. This doubles the cost for resin and increases the capital costs.

Parameters	PF System (soluble chelating polymer)	Chelating Ion Exchange* (chelating resin)	Comments
Relative Capacity of Binding Agent -	4.3	1.0	The PF polymer can load 3-8 times as much metal as resin.
Amount of Binding Agent Needed	1.9 kg	23.3 Kg	The amount of resin is a company quote
Cost of Binding Agent per kg	$164**	$210	The cost is a company quote. The polymer and resin is resuable
Total Cost of Reagent needed	$310	$4,893	
Regeneration Time of Binding Agent	Time: 15-30 min.	Time 2-4 hrs.	Regeneration is within the PF System
Regeneration Volume	3-5 gal	10-15 gal	Resin System requires separate regeneration unit

* The actual company and brand name has been omitted.

** Polymer is not sold separately from the PF System, thus this is just for comparison purposes.

Applications

The PF System is a quantum step forward for all dilute metal recovery and recycling, not just electroplating. The PF System can be made available to any size electroplating business, and testing is in progress to apply similar concepts to other metal-containing processes. The future applications are many, including recovery of metals from photo-finishing solutions, electronic solutions, mining industry, precious metals industry, and general wastewater treatment including nuclear waste waters to give a few examples. A picture of a commercial unit is shown in Figure 2.

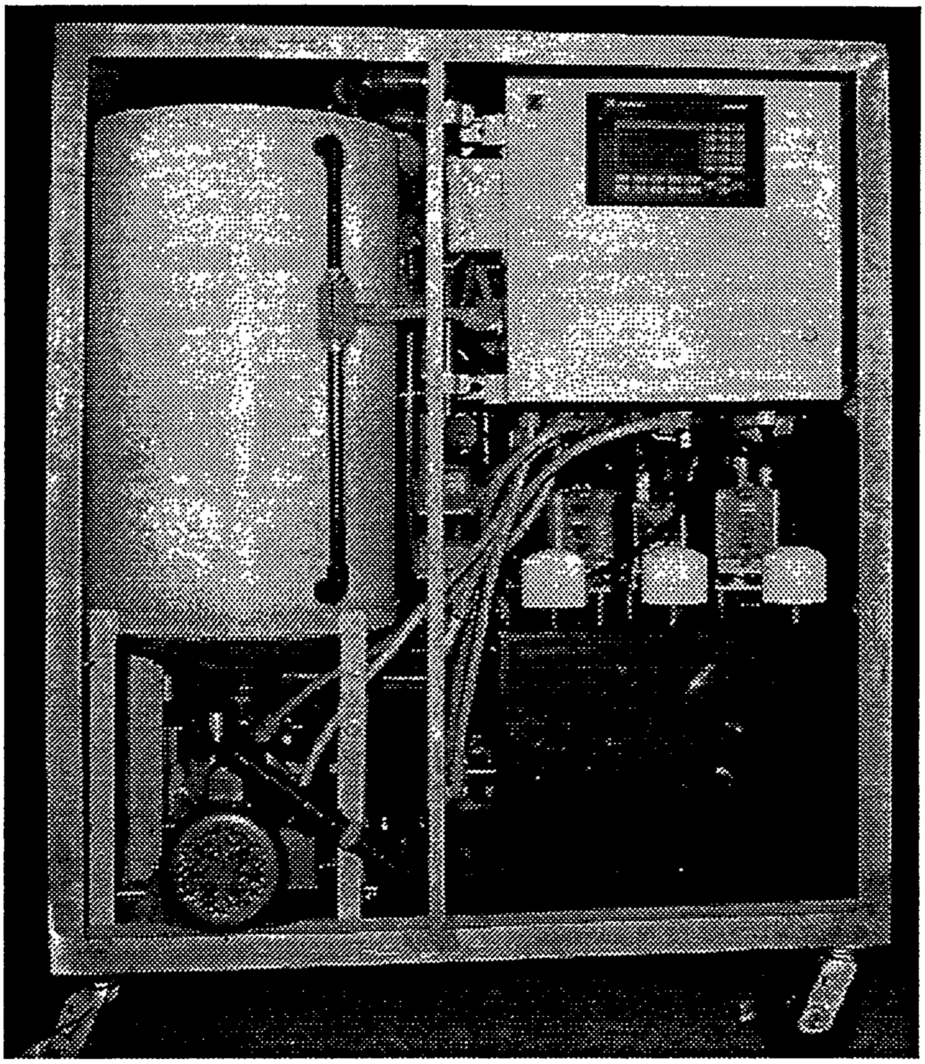

Figure 2. Picture of a commercial Polymer Filtration System with complete PLC-controlled automation of all Polymer Filtration functions.

Contacts

For further information contact Karl Kraus, of PolyIonix - Separation Technologies, Inc., 2351 US Route 130, PO Box 1004, Dayton, New Jersey 08810-1004; 888-249-4469, FAX 732-274-3144

Los Alamos National Laboratory
Civilian and Industrial Technology Program Office
PO Box 1663
Los Alamos, New Mexico 87544

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