LA-UR- 96-3312

CONF-9610184--1

THE REMOVAL OF PRECIOUS METALS BY CONDUCTIVE POLYMER FILTRATION

Michael E. Cournoyer,
CMR Organic Analysis Team Leader,
Chemical Science and Technology Division,
Los Alamos National Laboratory,
Los Alamos, NM 87545

Abstract:

The growing demand for platinum-group metals (PGM) within the DOE complex and in industry, the need for modern and clean processes, and the increasing volume of low-grade material for secondary PGM recovery has a direct impact on the industrial practice of recovering and refining precious metals. There is a tremendous need for advanced metal ion recovery and waste minimization techniques, since the currently used method of precipitation-dissolution is inadequate. Los Alamos has an integrated program in ligand-design and separations chemistry which has developed and evaluated a series of water-soluble metal-binding polymers for recovering actinides and toxic metals from variety of process streams. A natural extension of this work is to fabricate these metal-selective polymers into membrane based separation units, i.e., hollow-fiber membranes. In the present investigation, the material for a novel hollow-fiber membrane (CP1) is characterized and its selectivity for PGM reported. Energy and waste savings and economic competitiveness are also described.

DISCLAIMER

The Removal of Precious Metals by Conductive Polymer Filtration

Background and Rationale

The need for new advanced metal separations technologies is evident not only within the DOE complex but also within other governmental agencies such as DOD and EPA as well as with private industries. This need is driven by a variety of reasons ranging from environmental remediation, regulatory restrictions, economics, resource conservation, and/or waste minimization. Over the past fourteen years, Los Alamos National Laboratory has had an active inter-divisional program in ligand-design and synthesis and the development of new separations technologies for metal ions. Solvent extraction, chelating resins, ion-exchange, electrodialysis, electrowinning, and polymer filtration are among some of the technologies being developed and evaluated for a wide range of metal recovery applications.

The best available technology for treating precious metal process streams concentrates the precious metal by evaporation, after which it is shipped to a metal reclaimer. Operating costs are high due to the large energy use. What is needed are energy efficient, point-source reduction technologies that meet current and future discharge limits. The solution to this problem is found in the technical transfer activities of the national laboratories, where processes developed for removing radioactive metals from aqueous waste streams are being modified to the remove heavy metals from industrial waste streams.

Silver Removal: The first target area is industrial processes which have silver as effluent. Silver is used today in a variety of industrial applications, from the manufacturing of photographic materials to the manufacture of cutlery and coins. Many silver-bearing secondary materials that are generated from industrial processes contain enough silver to retain an intrinsic value. Extensive reclamation processes are employed to regain this value and reuse the material in manufacturing. Over 26 million troy ounces of silver annually are recovered from secondary materials in the United States.

Currently, over 60% of the silver used for industrial purposes in the United States is used in the manufacture of photographic materials. Electrical and electronic product manufacturing accounts for almost 20%; sterling ware, electroplated ware, and jewelry manufacturing accounts for over 12%; and brazing alloys and solders manufacturing accounts for over 5%. These uses combine to make up over ninety percent of the United States industrial consumption of silver.

Each of these silver operations generate silver-bearing waste. These wastes are either treated on-site with silver recovery techniques, typically electrolytic, metallic replacement, ion exchange, chemical precipitation or combinations of these. The treated waste is then combined with other processing waste water and sent to a publicly-owned treatment works (POTW) for further treatment. The unrecovered silver remains primarily in process streams which are sent to POTW's for additional treatment. Silver is not typically recovered from waste water treatment sludges at POTW's because of relatively low concentrations in the sludge material. In areas where sewer discharge limits prohibit the discharge of silver-bearing waste waters, the spent solutions are collected and transported to an off-site location for subsequent treatment and reclamation. At facilities where no silver recovery is employed prior to transportation, those materials would be characterized and transported as a hazardous waste.

Proposed new technology: LANL is developing a conductive Polymer Filtration (**CPF**) is a membrane-based technology where ultrafiltration is merged with specially designed metal-binding polymers. The metal-binding groups make up the backbone of the ultrafiltration membrane. These ligands selectively attach to precious metals and reject metals such as iron, neodymium, and copper. Once the membrane becomes saturated with the metal, the metal ions can be removed by some chemical process, possibly lowering the pH and allowing for both the removal and concentration of the metals from the rinse waters.

Advanced materials fabricated as hollow fiber membranes: A conductive polymer being developed at LANL is CP1. CP1 is emerging as one of the more promising new materials for metal-ion separations and can be manufactured into various products for the separation, concentration and recovery of metals ions in aqueous and nonaqueous solutions. CP1 manufactured in the form of a hollow fiber membrane is used to selectively bind target metals. Separations can be accomplished by filtration.

Experimental

CP1 Evaluation: We have developed standard methods for evaluating the polymer s metal capacity and metal-binding profiles for a suite of metals. Preliminary polymer evaluation involves contacting a solution containing seven transition metals (Ag, Au, Pt, Cu, Fe, and Nd) with excess polymer at various pHs. The solutions are shaken for 60 minutes followed by filtration through a 0.45 micron filter, and filtrates are analyzed for metals by ICP-AE. This process give a metal retention vs. pH profile for each polymer.

Controls: Prior to performing any of the filtration experiments, solubility profiles in the absence of CP1 were generated for each of the metals slated to be tested. This was accomplished by taking a 250 ppm solution of the metal ion of interest, adjusting the pH from 2.0 to 12.0, diluting the sample such that a 50 ppm solution of the metal ion was formed, shaking the control sample for 1 hour followed by filtering with a 0.45 um filter syringe. The filtrates were then analyzed for the given metal by ICP-AE.

Metals: Retention studies were performed using CP1 as the metal-binding polymer. The general procedure involved additioning of an excess (0.1%) CP1 to an aqueous solution of 50 ppm of the metal being tested. The solution was adjusted to the desired pH for silver, neodymium, iron, europium, and copper using either 1.0 M nitric acid or 1.0 M NaOH. The solution was adjusted to the desired pH for gold and platinum using either 1.0 M hydrochloric acid or 1.0 M NaOH.

Recovery of Silver (I) from an actual X-Ray imaging fixer solution: A photographic fixer solution containing 722 ppm silver was mixed with an excess (3%) of CP1. The solution was adjusted to a pH of 8.2. The solution was stirred for 30 minutes and filtered through a 0.5 filter. This experiment was repeated at a pH of 12.0.

Metal Analysis: Metal analytical results were obtained through the use of a Varian Liberty 220 sequential ICP-OES system arranged and operated according to manufacture s recommended procedures. Data from the spectrometer was collected by a GRIFF MFP+ MS-DOS based data acquisition station. Three replicates were performed for each sample and the mean concentration reported. The detection limit for these metal ions using this analytical technique is 0.01 ppm (ug/mL).

Results and Discussion

Retention Studies: The results for the retention of silver, gold, and platinum by CP1 are shown in Figure 1. The CP1 has good retention for silver and gold throughout a pH range of 2 to 12. Platinum is retained by CP1 at pH 5 and above. Below pH 5, the polymer begins to release the metal, and by pH 3, most of the platinum is free in solution. The results for the retention of copper, neodymium, europium, and iron are shown in Figure 2. Throughout a pH range of 2 to 12, retention of these metals by CP1 is negligible relative to the controls. These results clearly show that CP1 is selective for precious metals over other heavy metals and lathanides.

Table 1. Composition of a Common Fixer & Replenisher Working Solution

Working Solution =		10 Liters	pH =	4.0	
Rinse Volume =		31 Liters	Temp =	25	
Dilution Factor =		3			
INPUTS					
COMPONENTS	MWT	g/L	mol/L	ppt	
H2O	18.01	850	47.20	4	NH4
NH4S2O3	148.20	30	0.20	22	S2
NaS2	87.20	30	0.34	16	Na
NaOAc	82.03	30	0.37	2	Al
Al(SO4)3	342.15	30	0.09	25	SO4
Na Citrate	214.11	30	0.14	27	CIT
TOTAL		1000	48.34	96	
RINSE WATER COMPONENTS	MWT	mg/L	mmol/L	ppm	
Ag	107.87	722	6.69	722	Ag
NH4S2O3	148.20	9701	65.46	7142	S2
NaS2	87.20	9701	111.25	5279	Na
NaOAc	82.03	9701	118.26	765	Al
Al(SO4)3	342.15	9701	28.35	900	SO4
Na Citrate	214.11	9701	45.31	8659	CIT
TOTAL		49226	375.31	23467	

Evaluation of CP1 for photographic effluent applications: the composition of a common fixer & replenisher working solution is shown in Table 1. As one can see, removing the silver metal ions in the presence of large concentrations of organics and aluminum represents a real challenge. CP1 was effective in removing and concentrating silver, as shown in Table 2. At a pH of 12, the silver concentration was 1 ppm, well below the EPA discharge limit of 5 ppm. The filtrate generated from the 200 ml processed contained 1 ppm silver (removal efficiency of 99.9%).

Table 2. Silver Removal from X-Ray Fixer.

SAMPLE 1 3% CP1	Ag(I) ppm ICP	% Removal
Initial	722	
pH = 8.6	9	98.8%
pH = 12.0	1	99.9%

Energy Savings: Energy is saved in at least three places; (1) the energy involved in transporting the hazardous waste to a licensed disposal site, (2) the energy required to produce the precious metals that are discarded, and (3) the energy required to replace the waste water that is discarded.

Waste Savings: The CPF system is an on-site recycling process. Recycling precious metals in the mining, photoprocessing, and electroplating plating operations reduces the amount of waste water that must be treated, the sludge that must be disposed of in a hazardous landfill, and the amount of precious metal that enters the environment. In addition, the waste water in certain processes and the metal-binding membrane are also recyclable.

Economic Competitiveness: As discussed above, the **CPF** process has been shown to remove silver from photographic effluent. If the **CPF** process can be proven to have general application to all silver containing waste streams, it could easily be implemented in all operations where these types of wastes are currently produced. Since different silver operations have different reagents, it will be necessary to test the system on several of the different commercial waste streams to assure that the new technology has broad application to these market segments. Success at this stage will allow ready commercialization of this technology.

Conclusion

The technology evaluated for the recovery of plating metal ions from rinse waters involves the process of Conductive Polymer Filtration (CPF), which combines the use of metal-binding polymers and ultrafiltration. Metal ions in dilute rinse water solutions, typically less than 1000 ppm in precious metal ion concentration, are retained by the polymers, while the unbound species freely pass through the ultrafiltration membrane. This selectivity allows for the concentration of the precious metals by retention and the ultrafiltered permeate water meets EPA discharge limits for the RCRA (silver) metals.

Acknowledgments

The author would like to acknowledge the Department of Energy, Office of Waste Management, Waste Minimization Program for support of this development effort. I would also like to thank Dr. Pete Stark for the ICP analyses and Steve Trujillo and Reanna Aguino for carrying out the pH retention studies.

References

1. Randol Mining Directory 1993/94; World Silver Survey 1994; Waste Management Practices o Industrial Silver Users; Thomas Register of American Manufacturers.

2. Cross, Lisa "Film, Chemical Disposal: a Top Eco-Priority," *Graphic Arts Monthly*, Vol. **65**(1) Pg. 58, Jan. 1993.

3. Barbara F. Smith, Thomas W. Robison, Michael E. Cournoyer, Kennard Wilson, Nancy N. Sauer, Man T. Lu, Earl C. Groshart, and Mary C. Nelson, "Polymer Filtration: A New Technology for Selective Metals Recovery, International Technical Conference Proceedings from SURFIN 95, June 26-29, pp. 607-616.

4. Branch, D.A. "Silver Recovery Methods for Photoprocessing Solutions," *Journal of Imaging Technology*, Vol. **14** (6), Pg. 160, December 1988; LePerle, Robert L. "The Removal of Metals from Photographic Effluent by Sodium Sulfide Precipitation," *SMPTE Journal*, Vol. **85**, Pg. 206, April 1976.

5. Quinones, P.R. "In-Situ Precipitation as the Regeneration Step in Ion Exchange for Silver Recovery," *SMPTE Journal*, Vol. **93**, Pg. 800, 1984.

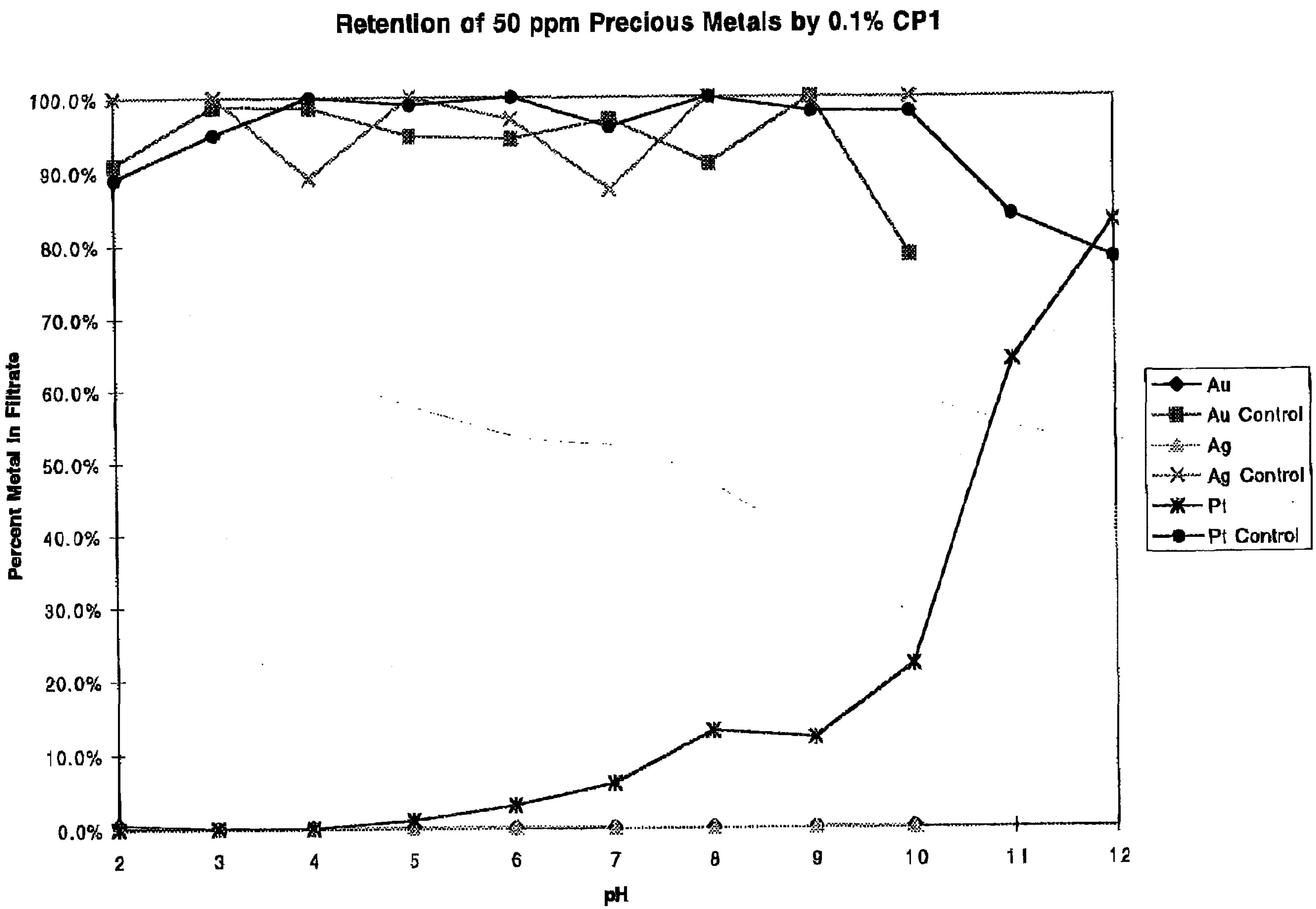
Retention of 50 ppm Precious Metals by 0.1% CP1
Percent Metal in Filtrate
100.0%
90.0%
80.0%
70.0%
60.0%
50.0%
40.0%
30.0%
20.0%
10.0%
0.0%
2
3
4
5
6
7
8
9
10
11
12
pH
Au
Au Control
Ag
Ag Control
Pt
Pt Control

Figure 1

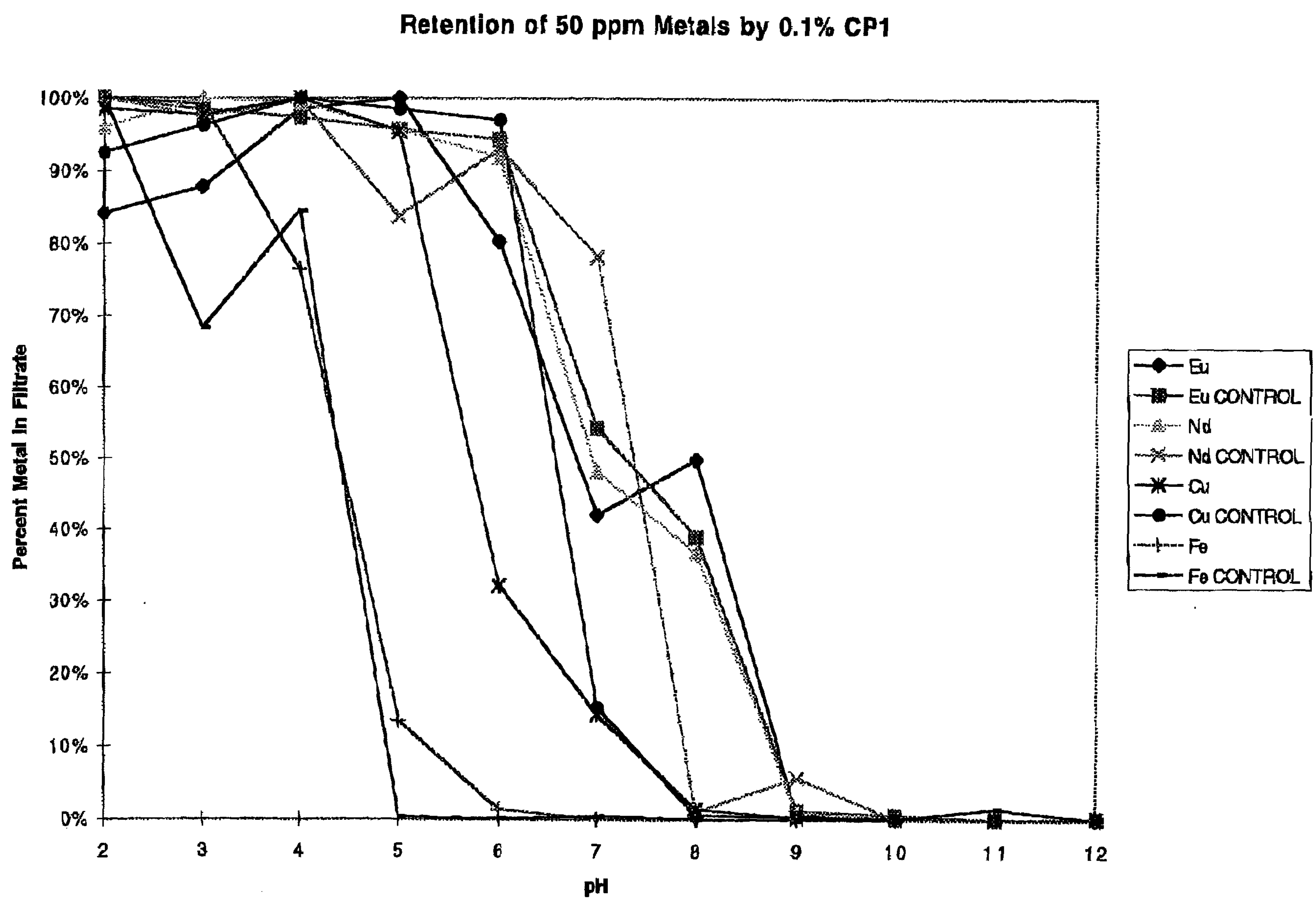
Retention of 50 ppm Metals by 0.1% CP1
Percent Metal in Filtrate
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
2
3
4
5
6
7
8
9
10
11
12
pH
Eu
Eu CONTROL
Nd
Nd CONTROL
Cu
Cu CONTROL
Fe
Fe CONTROL

FIGURE 2