

SA-1

The Membrane Society of Korea
November 4-5, 1994

Chemical Active Liquid Membranes in Inorganic Supports for Metal Ion Separations

Jongheop Yi
Dept. of Chemical Engineering, Seoul National University,
Seoul 151-742, Korea

Disposal of hazardous ions in the aqueous streams is a significant industrial waste problem. Waste streams from electronics, electroplating, and photographic industries contain metal ions such as copper, nickel, zinc, chromium(IV), cadmium, aluminum, silver, and gold, amongst others in various aqueous solutions such as sulfates, chlorides, fluorocarbons, and cyanides. Typical plating solutions having similar compositions are listed in Table 1. Spent process streams in catalyst manufacturing facilities also contain precious metals such as Ag, Pt, and Pd. Developing an effective recovery process of these metal ions for reuse is important.

Table 1 Compositions of Plating Solutions*

Metal	Purpose	Plating Solutions
Copper	Printed circuit boards, undercoat in decorative finishes	Plain cyanide Copper sulfate Fluoroborate
Nickel	Bright coating under thin electroplate for decorative, corrosive-and wear-resistance purpose	Chloride Fluoroborate
Chromium	Decorative, industrial finishes	Chromic acid
Gold	Engineering (switches, semiconductors), decorative	Cyanide Acid
Cadmium	Corrosion protection	Cyanide Fluoroborate

*Data from Jacobson, Kurt, and Laska, Richard, "Advanced Treatment Methods for Electroplating Wastes," Pollution Eng. Oct. 1977

The predominant method of treatment of these waste streams is the precipitation of metal ions in the form of hydroxides or carbonates [Lee et al., 1986; Chang and McCoy, 1991], which results in a sludge that is dumped at hazardous waste sites. Other recovery methods recently considered include evaporation, electrolyte metal recovery, reverse osmosis [MacNeil, 1988], ion exchange [Dejak and Nadeau, 1987], membrane separation [Weber and Bowman, 1986], and solvent extraction. A summary of these alternative recovery systems is provided elsewhere [MacNeil, 1988; Chang and McCoy, 1991].

The use of liquid ion exchange chelation molecules to selectively extract metal ions by on-site treatment of these waste streams is currently receiving substantial attention [McDonald

and Bajwa, 1977; Knocke et al., 1978; Clevenger and Novak, 1983; Brooks, 1986, 1987; Davis et al., 1987; Tavlarides et al., 1987]. This interest stems from an awareness of advances made in the development of commercial extractants for metal ion separation in the hydrometallurgical industries [Kim, 1984; Murthy et al., 1986]. Metal cations react with the organic chelating agents to form neutral complexes that are preferentially dissolved by the organic phase:



Here the overbar denotes species in the organic phase. The above equation represents a cation exchange reaction wherein hydrogen ions are exchanged for the metal cation, so the degree of extraction of metal ions depends on the pH of the aqueous phase. The forward and reverse steps represent the extraction and stripping steps, respectively. There are various commercial extractant systems in markets designed for complexing specific metal ions.

One of the important parameters for the successful extraction of metals is the acidity of the aqueous phase. For example, 2-hydroxy-5-nonylaceto-phenone oxime is used as the impregnating phase, pH can be used to control the extraction characteristics of the reagent with respect to streams with multiple metal ions. At pH 3.0, copper (+2) and iron ions are strongly extracted, while nickel and cobalt ions are not extracted by the chelation acid.

Immobilized liquid membranes have generated considerable interest for possible hydrometallurgical application [Kim, 1984] and waste treatment [Noble et al., 1989]. In this process, solutions of liquid ion exchange molecules are impregnated into the pores of a solid matrix support, typically polymeric membranes. A conceptual example is shown in Figure 1 where the forward reaction occurs on the feed side and the reverse reaction occurs on the receiving side. In the pores of the membrane, the chelated metal ion is transported to the receiving side and regenerated ion exchange molecules diffuse in the opposite direction to renew

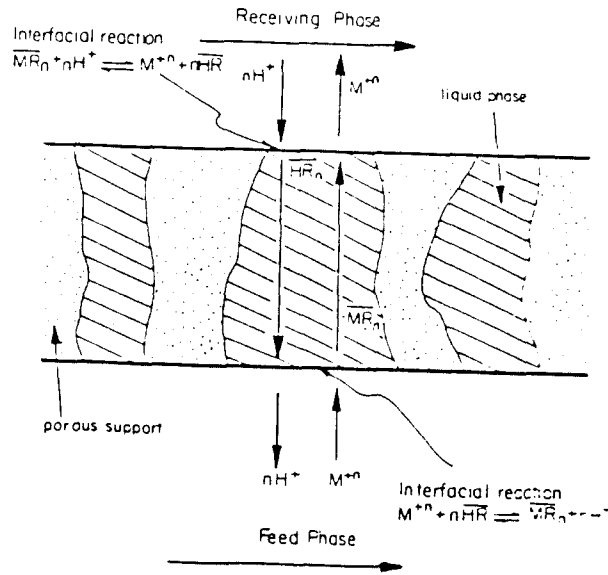


Figure 1. Coupled Transport

the process. Consequently, metal ions are transported from the feed to strip solutions by these sequential steps. Using these immobilized liquid membranes, metal ions can be selectively extracted and separated from the aqueous solutions by the proper selection of impregnating ion exchangers and operating conditions. Furthermore, the characteristics of the support membranes should be considered according to the application environment, such as operating temperature, solution acidity, and chemical reactivity, and stability of the membranes during operation.

Despite promising technical performance, few processes using supported membrane technology have been commercialized for large scale hydrometallurgical extraction [Noble and Way, 1987]. The main disadvantages exhibited by the polymeric membranes being used are their sensitivity to temperature, pH and many chemical environments [Noble, 1987] as well as plasticizer effects [Sugiura, 1990]. Loss of mechanical stability in modular operation is also a disadvantage [Teramoto and Tanimoto, 1983]. These problems suggest the use of ceramic membranes which have the potential to overcome the above difficulties for the porous matrix. They exhibit reliability and long lifetimes. Neither creep nor deformation occurs during cooling and high permeabilities can be achieved. Accordingly, ceramic membranes impregnated with suitable chelation agents show promise for selective removal of metal ions.

One of the problems for this applications is to manufacture porous membranes with tailed porosity and pore size. Porous membranes with tailed porosity are the leading candidates for new separation systems for the chemical industry, hot gas filtration, and separation media for numerous environmental cleanup technologies. In May 1993, a workshop on engineered porous materials [Schaefer, 1994] identified the following opportunities for engineered porous materials in the industrial sector: 1. High efficiency gas separation membranes, 2. Catalytic membranes for chemical processing, 3. Porous electronic substrates for high speed electronics, 4. Porous electrodes for fuel cells, 5. Separators and electrodes for batteries, 6. Materials for storing fuels, including natural gas and hydrogen, 7. Selective absorbents for environmental cleanup, and 8. Reusable particulate filters. Ceramics are most often the materials of choice for these applications. Ceramics offer high temperature stability, strength, catalytic activity, erosion resistance, and corrosion resistance. Despite these desirable properties, the potential of porous ceramics has not been realized due to well-defined technical barriers such as: 1. Brittleness, 2. Lack of pore size control, 3. Lack of continuous processing methods, 4. Absence of integrated materials and manufacturing systems, 5. Absence of models relating pore structure to mechanical properties.

In the presentation, the feasibility evaluation through copper ion extraction flux, long-term operation, and analysis of a chemically active liquid membranes in inorganic supports for the separation of copper ions from aqueous solutions, will be reported. Separately designed experiments were executed using a precise pH-static technique to obtain fluxes for comparison with experimentally determined values from batch experiments. Modeling results also will be presented for the removal process of copper ion from the aqueous solution using shell-and-tube types of membrane reactor modules. The performance of shell-and-tube type reactor module depends on the sizes and operation methods. For practical operation, the strip solution can be operated in a recycle mode while maintaining high flow rate of strip solution stream. The concept with model equations of reactor module operation reported herein could provide a basis for the design and scale-up of these units. Also, these models can serve as the basis to select more promising chelation agent systems and desirable operating conditions for high separation efficiencies.

REFERENCES

- Brooks, C.S., in Proc. of the 41st Industrial Waste Conference, May 13-15, 1986, Purdue Univ., West Lafayette, IN, Lewis Publishers, Inc., Chelsea, MI, pp. 642-651, (1986)
- Brooks, C.S., in Proc. of the 42nd Industrial Waste Conference, May 12-14, 1987, Purdue Univ., West Lafayette, IN, Ed., J.M. Bell, Lewis Publishers, Inc., Chelsea MI, pp 847-852, (1987)
- Chang, L., and McCoy, B.J., *Environmental Progress*, **10**, 110 (1991)
- Clevenger, T.E., and Novak, J.T., *Journal WPCF*, **55**(7), 984-989, (1983)
- Davis, M.L., Chang, M., Copedge, D., and Strong, M., in Proc. of the 42nd Industrial Waste Conference, May 12-14, 1987, Purdue Univ., West Lafayette, IN, Ed., J.M. Bell, Lewis Publishers, Inc., Chelsea MI, pp 803-807, (1987)
- Dejak, M., and Nadeau, T., *Haz. Waste & Haz. Mat.*, **4**, N3, 261-271, (1987)
- Kim, K., *J. Memb. Sci.*, **21**, 5-10, (1984)
- Knocke, W.R., Clevenger, T., Ghosh, M.M., and Novak, J.T., Proc. of the 33rd Industrial Waste Conference, May 9-11, 1978, Ed., J.M. bell, Purdue Univ., West Lafayette, IN, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, pp 413-426, (1978)
- Lee, C.-K., and Tavlarides, L.L., *Ind. Eng. Chem. Fund.*, **25**, 96 (1986)
- MacNeil, J.C., in *CRC Critical Reviews in Environmental Control*, Vol. **18**(2), pp. 91-131, (1988)
- McDonald, C.W. and Bajwa, R.S., *Sep. Sci. & Tec.*, **12**(4), 435-445, (1977)
- Murthy, T.K.S., Koppiker, K.S., and Gupta, C.K., in Recent Developments in Separation Science, Vol. III, pp. 1-44, (1986)
- Noble, R.D., *Sep. Sci. & Tech.*, **22**, 731 (1987)
- Noble, R.D., and Way, J.D., in Liquid Membranes, Theory and Applications, Eds., R.D. Noble and J.D. Way, ACS Symposium Series 347, Washington D.C., pp110-122 (1987)
- Noble, R.D., Koval, C.A., and Pellegrino, J.J., *Chem. Eng. Prog.*, March pp58-70 (1989)
- Schaefer, D.W., *MRS Bulletin*, April, p24, 1994
- Sugiura, M., *Sep. Sci. & Tech.*, **25**, 1189-1199 (1990)
- Tavlarides, L.L., Bae, J.H., and Lee, C.K., *Sep. Sci. and Tech.*, **22**(2&3), 581-617, (1987)
- Teramoto, M., and Tanimoto, H., *Sep. Sci. & Tech.*, **18**, 871 (1983)
- Weber, W.F., and Bowman, W., *Chem. Eng. Prog.*, P23, Nov. (1986)
- Yi, J., and Tavlarides, L.L., *AIChE J.*, **38**, 1957 (1992)
- Yi, J., Ferreira, R., and Tavlarides, L.L., *Haz. Wastes & Haz. Mat.*, **9**, 173 (1992)