

Use of a NASA-Developed Ion Exchange Material for Removal of Zinc from Electroplating Baths

O. Manuel Uy, Mike J. Ginther, John T. Folkerts, and Kenneth W. Street, Jr.

A new NASA-developed ion exchange material significantly reduces toxic metal effluent from rinse baths of electroplating facilities. The ion exchange material, originally developed as a battery separator for space applications, is a polymer made from polyacrylic acid and polyvinyl alcohol and converted to a calcium or sodium form. It exhibits a very high intake of metal ions such as zinc, cadmium, and copper, even in the presence of hard-water constituents. In this study, the adsorption efficiency for zinc was measured with a portable ion exchange system placed at the discharge end of a zinc plating line. The results show a significant reduction in the amount of zinc discharged into the sewer system.

INTRODUCTION

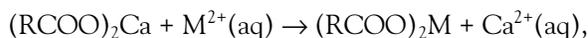
Chemists at the NASA Lewis Research Center recently developed and patented a new high-capacity ion exchange material (IEM)¹ that removes toxic metals from contaminated water. This polymeric IEM was originally developed to physically separate the anodic and cathodic components of an electrolyte while acting as an ionic conductor. The chemists, quite accidentally, found that the IEM removes zinc, cadmium, copper, and other metals from aqueous solutions (see Table 1), even in the presence of hard-water constituents such as calcium.²

An ion exchange material is a solid that exchanges one ion for another ion. The process of ion exchange involves the exchange of atoms but with conservation of charge. In other words, if the ion exchanger is loaded with sodium—a singly charged ion—and the ion to be removed is lead—a doubly charged ion—then two sodium ions must be released to accommodate the uptake of the lead ion into the resin. The ion exchange process is typically performed by packing particles (1 to 2 mm

in diameter) into a column with a screen at both ends to retain the particles; then, the solution to be cleaned is forced to flow through the column.

The NASA-developed IEM is prepared from two common raw materials, polyacrylic acid and polyvinyl alcohol, and can be manufactured in both a calcium and sodium form. Both calcium and sodium are considered by the Environmental Protection Agency (EPA) to be acceptable for discharge into the sewer system. The calcium form of the IEM is mechanically more stable; hence, it is the preferred exchange form.

To be suitable for various applications, the IEM can be manufactured as a film, powder, filament, or beads. The chemical reaction is very simple for the calcium form of the IEM:



where M represents various metals and R represents any alkyl group.

Table 1. Calculated IEM uptake of various metals (5.14 moles of charge are neutralized per kilogram of resin).

Metal ion	Uptake (g metal/kg IEM)
Zinc	168
Cadmium	289
Lead	533
Chromium(III)	89
Copper	163
Mercury	516
Nickel	151

The ion exchange process is dependent on the pH of the solution. Figure 1 shows that the operational pH of the IEM for zinc lies between 6.0 and 7.0. At a pH below 6.0, the hydrogen ion effectively competes with the metal; above a pH of 7.0, the hydroxide ion reacts with the zinc cation to form insoluble zinc hydroxide or anionic zinc hydroxide complexes.

Recently, APL researchers used the IEM to remove zinc from rinse baths at A-1 Plating Company in Baltimore, Maryland, as a means of reducing the amount of sludge produced in the electroplating process. The rinse line had a pH range of 6.3 to 7.3, making it ideal for zinc recovery by the IEM.

BACKGROUND

Approximately 13,000 electroplating operations in the United States generate about 1 million tons of sludge per year via wastewater treatment. The precipitation process by which the wastewater is treated before disposal in industrial sewers is becoming inadequate as environmental laws become more stringent. In the near future, the final treatment of waste streams will require ion exchange, or similar technologies, to

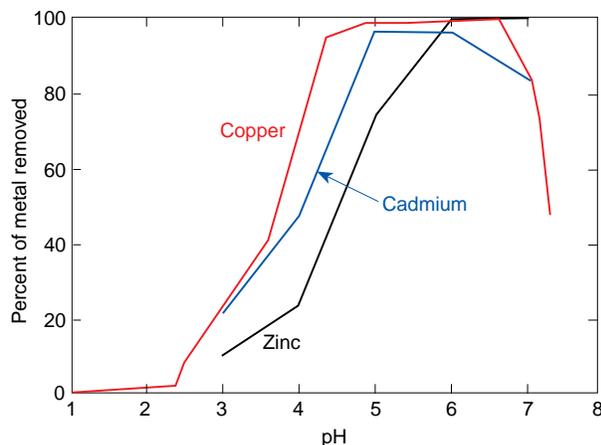


Figure 1. Metal absorption by the NASA-developed ion exchange material (IEM) as a function of the solution pH.

lower the levels of toxic metals discharged into sewer systems. It is easier to treat the wastewater at each plating line source rather than at the merged waste streams, where the treatment would require removal of both cations (e.g., zinc, lead) and anions (e.g., chromate from chromating operations) in combination with brighteners, carriers, and chelating agents. Another benefit of treating each line separately is that less processing is required in the sludge generating system.

INITIAL RESULTS

Initially, we tested the IEM for its uptake of zinc at the NASA Lewis Research Center. Figure 2 compares the uptake of zinc by sodium- and calcium-charged IEM films and shows that the concentration of zinc decreases over time for solutions treated with these films. At the beginning of the ion exchange process for the calcium-charged film, however, some singly-charged ions, i.e., CaOH^+ or CaOAc^+ , take up only one site on the resin (a solution counter ion neutralizes their other charge), whereas Ca^{2+} takes up two sites. Hence, at the start of the ion exchange, the apparent metal uptake is greater than the capacity of the resin based on stoichiometric considerations. At equilibrium, however, stoichiometry prevails and the theoretical amount of uptake is observed. Note that these tests were performed in a beaker with the IEM film present and being stirred with a magnetic stirrer, hence the variability of the time scale during the initial reaction.

The IEM was also tested at the NASA Lewis Research Center for potential interference by other constituents of electroplating operations such as carriers and brighteners. A zinc test solution, with a nominal concentration of 100 ppm of zinc, was prepared at the operational pH, and a piece of ion exchange film was added. Samples were removed from the solution at specified times and analyzed for zinc content. This experiment was repeated with the manufacturer-recommended amounts of brightener, carrier, and both

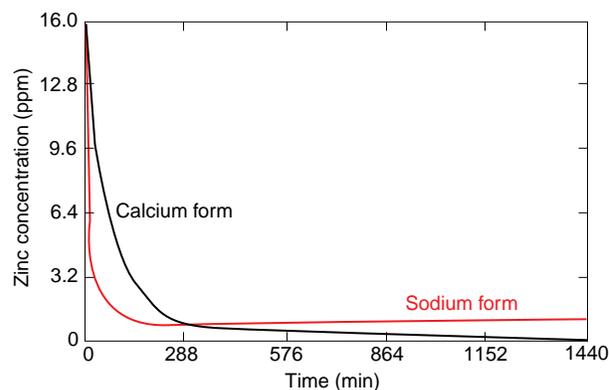


Figure 2. Zinc concentration vs. time for solutions treated with calcium- and sodium-charged ion exchange films ($6.0 < \text{pH} < 7.0$).

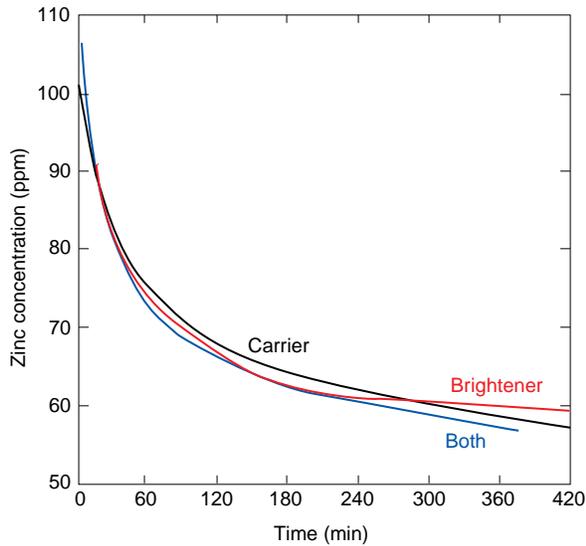


Figure 3. Zinc concentration vs. time for IEM-treated solutions containing the manufacturer-recommended amounts of carrier, brightener, or both carrier and brightener.

brightener and carrier. Figure 3 shows the zinc concentration versus time for IEM-treated solutions containing the recommended amounts of carrier, brightener, and both. These curves overlap the control curve (not shown) within experimental error, confirming that the carriers and brighteners do not adversely affect the uptake of zinc by the IEM.

Periodically, plating baths become depleted of zinc because of the various rinses and the plating operation itself. The baths are easily replenished with zinc by adding a concentrated zinc solution at the appropriate pH that contains current-carrying ions such as sodium or ammonium chloride. These solutions can be prepared with zinc chloride that is quantitatively recovered from the IEM with an acidic solution (Fig. 4). Thus, the acidic solution used to strip zinc from the IEM, when properly neutralized, serves as a regeneration solution for the zinc plating bath.

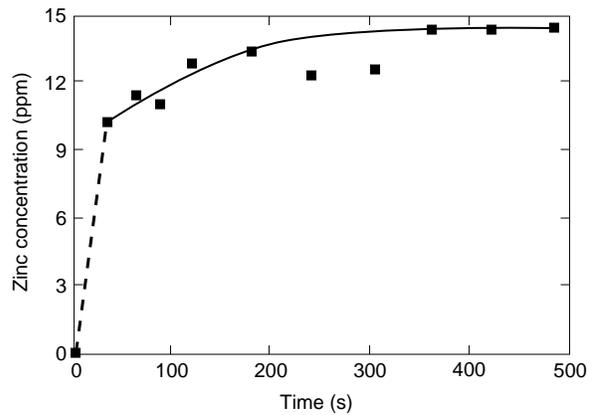


Figure 4. Recovery of zinc from the IEM with an acidic solution. The dashed line indicates an interpolation from the initial time to the earliest time to perform an analysis.

IN-PLANT RESULTS

The zinc rinse line evaluated at A-1 Plating Company was part of a potassium chloride/zinc chloride plating process (Fig. 5). We evaluated the calcium-charged IEM, in bead form, along with a commercial ion exchange resin for the recovery of zinc. Beads were chosen because of their ease of handling, durability, and ability to be used in existing ion exchange systems. The system consists of a particulate filter, a carbon cartridge, an ion exchange cartridge, and a final organic removal cartridge (Fig. 6).

First, we inserted the commercial resin cartridge, containing approximately 1460 g of resin, into the system and tested it. Because of the pressure head available, the flow rate was limited to about 0.10–0.50 L/min. Water samples from the rinse tank, before and after treatment, were quantitatively analyzed by an inductively coupled plasma mass spectrometer. Figure 7 shows the efficiency of zinc removal from the rinse tank for about 40 h of continuous operation.

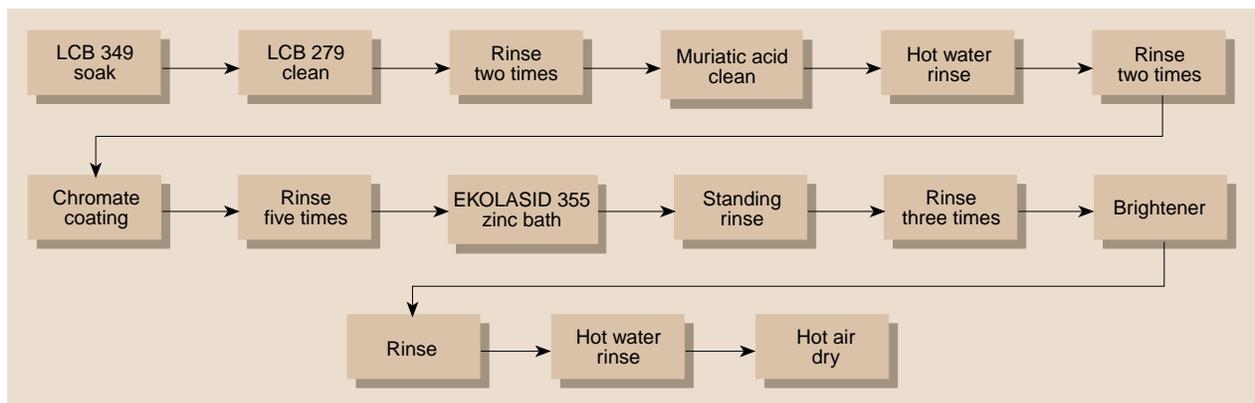


Figure 5. Process flow for the zinc plating line at A-1 Plating Company.

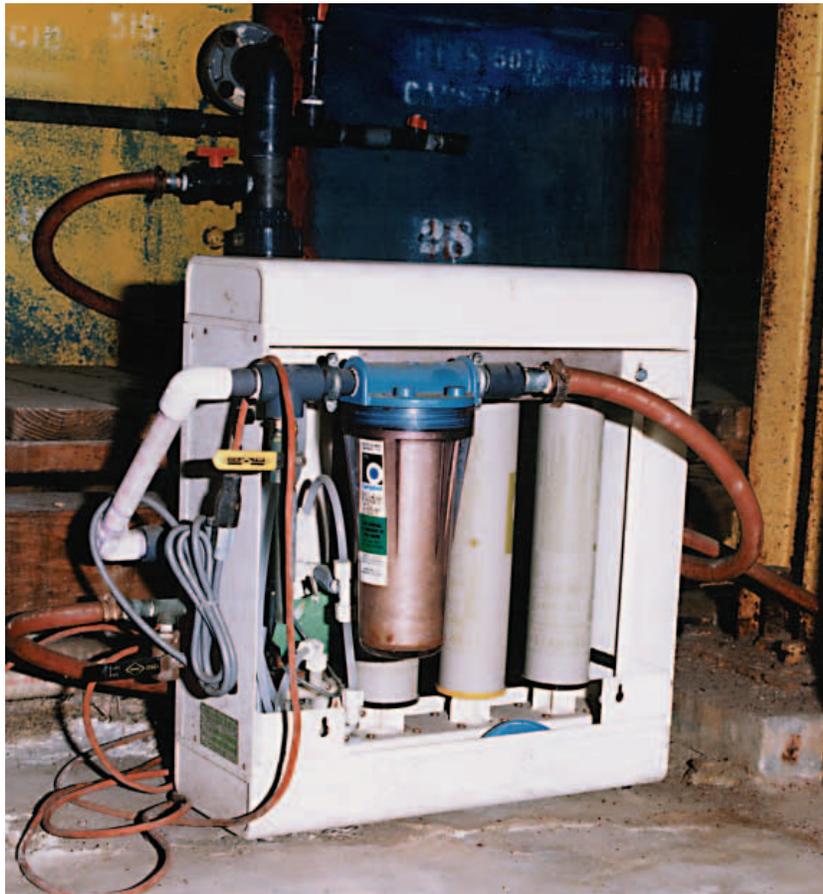


Figure 6. Ion filtration system at A-1 Plating Company installed between the final rinse tank and the discharge line connected to the sewer line. The system consists of a particulate filter, a carbon cartridge, an ion exchange cartridge, and an organic removal cartridge.

After the commercial resin test was completed, the IEM cartridge, containing approximately 250 g of polymeric material in bead form, was inserted into the system. Figure 8 shows the efficiency of zinc removal from the rinse tank for about 154 h of operation.

The discharge limit for zinc at A-1 Plating Company is 5 ppm, as set by Baltimore City to meet EPA require-

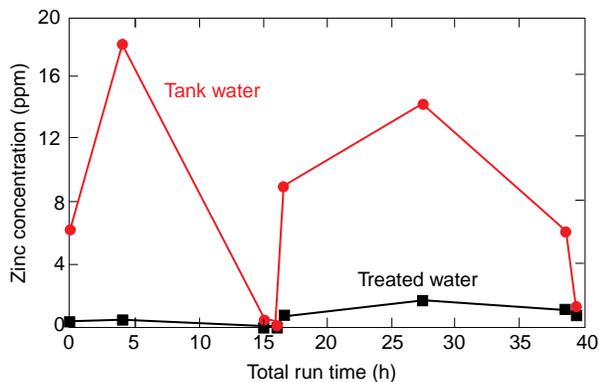


Figure 7. Zinc concentration vs. time for water samples from a rinse tank at A-1 Plating Company. The treated water flowed through a commercial resin cartridge at a flow rate of 400–450 mL/min.

ments. These tests showed that both the IEM and the commercial resin allowed A-1 Plating Company to meet EPA requirements. Testing of both the IEM and the commercial resin is continuing.

ADVANTAGES OF THE IEM OVER COMMERCIAL RESINS

The IEM is a typical weak-acid-type ion exchanger. As such, it has a modest chelating ability for metals having an affinity for acetate-type chelators. The major advantage of the IEM is that it has very good selectivity for toxic and heavy metals in comparison with calcium. Commercial resins used when calcium exclusion is required include the iminodiacetate-type resins, which are moderately expensive because of the need to incorporate a specific chelator into the starting polymer. The IEM, however, can be manufactured from two of the cheapest polymeric feedstocks commercially available. Several licenses and trade agreements are being pursued to manufacture the IEM in large quantities.

A further advantage of the IEM is that it can be readily manufactured in various forms such as films, beads, powders, and filaments. Although it is difficult to compare manufacturing costs because the IEM has not yet been manufactured on a large scale, the estimated cost is \$140–\$280 per cubic foot. Current commercially available resins are

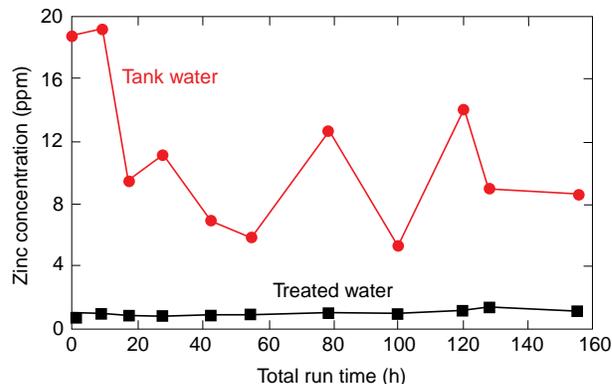


Figure 8. Zinc concentration vs. time for water samples from a rinse tank at A-1 Plating Company. The treated water flowed through an IEM cartridge at a flow rate of 400–450 mL/min.

\$200–\$1800 per cubic foot. Moreover, the higher ion exchange capacity of the IEM² should make it a lower-cost alternative on the basis of effectiveness, which we hope to prove in the near future.

CONCLUSIONS AND FUTURE PLANS

We have shown that the NASA-developed IEM removes zinc from a commercial electroplating rinse tank. We are now investigating the IEM for treating wastewater created by Tomahawk cruise missile and Trident missile launches. Further study is planned to demonstrate the use of the IEM in removing other metals such as cadmium, mercury, and lead, and to increase the size of the system to treat all of the rinses

after the zinc plating bath. A more extensive cost analysis will be conducted after a commercial IEM manufacturing process is established.

REFERENCES

- ¹ Philipp, W. H., Jr., and Street, K. W., Jr., *Ion Exchange Polymers and Method for Making*, U.S. Patent 5,371,110 (6 Dec 1994).
- ² Philipp, W. H., Jr., and Street, K. W., Jr., *Toxic Metals Removal from Water—Update 1: A New Material for Removing Lead, Mercury, Cadmium, Copper, Zinc, and Other Metals from Aqueous Solutions*, NASA Technical Focus (Nov 1993).

ACKNOWLEDGMENTS: We would like to acknowledge the support of APL's Independent Research and Development (IR&D) Committee headed by Vince Pisacane and the IR&D Environmental Thrust Area Panel headed by Hal Heaton. We would also like to thank Judy Zhuang of APL's Materials Laboratory for performing the quantitative analyses, and John Naumann, Jr., President of A-1 Plating Company, for allowing us to conduct this study at his electroplating facility.

THE AUTHORS



O. MANUEL UY is the Section Supervisor of the Materials Laboratory in the Technical Services Department. He received his Ph.D. in physical chemistry from Case-Western Reserve University and did postdoctoral work at Rice University and the Free University of Brussels. He joined APL in 1981 and was appointed to the Principal Professional Staff in 1985. He has been engaged in research in space environmental effects, contamination of optical systems, advanced materials, mass spectrometry, and thermodynamics. Presently, Dr. Uy is the Principal Investigator for the Contamination Experiments of the Midcourse Space Experiment and heads a Navy project on the removal of hazardous metals from wastewaters. He is a member of the American Chemical Society, Sigma Xi, SPIE—the International Society of Optical Engineering, the American Institute of Aeronautics and Astronautics, and the American Electroplaters Society. He has published more than 100 papers. His e-mail address is Manny.Uy@jhuapl.edu.



MIKE J. GINTHER is APL's Safety Manager, working in the Environmental/Health/Safety Program Office of the Administrative Services Department. He received his B.S. and M.S. degrees in safety sciences from Indiana University of Pennsylvania. His experience includes the recognition, evaluation, and control of occupational exposures; development and presentation of safety programs; hazardous waste management; and consultation on technical issues for environmental projects. His e-mail address is Mike.Ginther@jhuapl.edu.



JOHN T. FOLKERTS received a B.S. degree in chemistry from Towson State University and an M.S. degree in engineering administration from George Washington University. Before coming to APL, he worked at AAI Corporation, where he was responsible for the operation of a large ion exchange waste treatment facility for a printed circuit board operation. Mr. Folkerts joined APL in 1990 and is a member of the Senior Professional Staff in the Technical Services Department. His primary responsibility is the manufacture of high-reliability printed wiring boards for various applications, including satellites. In addition, he works in the Materials Laboratory performing metal analysis and wastewater studies. His e-mail address is John.Folkerts@jhuapl.edu.



KENNETH W. STREET, JR. received a B.A. degree from the University of Connecticut in 1970, an M.S. degree from Cleveland State University in 1973, and a Ph.D. from Wayne State University in 1977; all of his degrees are in chemistry with a specialization in chemical analysis. From 1977 to 1979, Dr. Street was a postdoctoral fellow at the University of Cincinnati. After that appointment, he held assistant professorships at Loyola University of Chicago and Kent State University. Dr. Street came to the Office of Environmental Programs at the NASA Lewis Research Center in Cleveland in 1991. His research interests are in spectroscopy and chromatography applied to the solution of biological, pharmaceutical, and environmental problems and materials characterization. He is the co-inventor of the ion exchange material described in this article and has co-authored more than 100 technical publications and presentations. His e-mail address is Kenneth.W.Street@lerc.nasa.gov.