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A NEW MATERIAL FOR REMOVING HEAVY METALS FROM WATER

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ABSTRACT

The NASA Lewis Research Center developed and is patenting a new high capacity ion exchange material (IEM) that removes toxic metals from contaminated water in laboratory tests. The IEM can be made into many forms, such as thin films, coatings, pellets, and fibers. As a result, it can be adapted to many applications to purify contaminated water wherever it is found, be it in waste water treatment systems, lakes, ponds, industrial plants, or in homes. Laboratory tests have been conducted on aqueous solutions containing only one of the following metal cations: lead, copper, mercury, cadmium, silver, chromium (III), nickel, zinc, and yttrium. Tests were also conducted with: (1) calcium present to determine its effects on the uptake of cadmium and copper, and (2) uranium and lanthanides which are stand-ins for other radioactive elements, (3) drinking water for the removal of copper and lead, and (3) others compositions. The Results revealed that the IEM removes all these cations, even in the presence of the calcium. Of particular interest are the results of the tests with the drinking water: the lead concentration was reduced from 142 ppb down to 2.8 ppb (well below the accepted EPA standard).

BACKGROUND

Many industries, such as the electroplating and mining companies, produce large amounts of waste water that contains hazardous amounts of mercury, lead, cadmium, silver, copper, and zinc ions. They are required by law to reduce the concentrations of these toxic metals in their waste water before it is discharged into sewers, lakes and streams. A number of companies we have contacted have told us that existing technology appears to be too expensive or inadequate for meeting the new lower limits. Also pressure is developing for eliminating the disposal of the wastes in land fills. For these reasons, industries and some government agencies are looking for new technology with which to clean the water.

The IEM is a spinoff from research done on space batteries. During the research, it was discovered, quite by accident, that it had an affinity for heavy metal ions, **even when calcium ions are present**. This is an important feature because many commercial ion exchange materials cannot remove heavy metals when the calcium is present. The calcium saturates the resins, thereby blocking the adsorption of heavy metal ions. This is not the case for this new IEM. Those commercially available ion exchange resins that do pick up the metal cations when calcium is present are very expensive. As a result, it was realized that this new IEM may have direct application to cost effective purification of contaminated water.

Once this potential became apparent, the NASA Lewis Research Center started a program in fall of 1991 to determine if the IEM was indeed an advance over existing technologies and if the IEM could be spun off as a new commercially viable product. The Cleveland Area Manufacturing Program (CAMP) helped by pointing out that the local electroplating industry was seeking new technology with which to remove heavy metal cations from their waste rinse water. The Northeastern Ohio Regional Sewer District also helped by explaining the nature and magnitude of the heavy metal disposal and cleanup problems facing the electroplaters and other

industries. Opinions were sought from waste water treatment experts, in particular an expert at the Cleveland State University. He called the IEM "an exciting new material". With this information, it was decided to proceed with a modest program to first characterize the key heavy metal adsorption rates, quantity adsorbed per unit weight, and other important physical properties such as the mechanical strength, tear resistance, resistance to degradation by chemical attack from a variety of aqueous solutions, etc. Simultaneously, the Lewis Technology Transfer Office began to search for the potential applications for the IEM and to determine the status of the existing technology being used to remove the heavy metals from waste and potable water.

THE ION EXCHANGE MATERIAL - IEM FILM PREPARATION

The IEM is composed of a crosslinked copolymer of polyvinyl alcohol and polyacrylic acid (Patent Pending). The IEM is made, in sheet form, by casting an aqueous solution of the two polymers on a flat surface to the desired thickness and allowing the water to evaporate. The water soluble sheet is crosslinked at elevated temperature in an aqueous solution containing a salting-out agent, the crosslinking agent and an acid catalyst. The resulting water insoluble film, in the acid form, is then converted to the desired salt form which is usually the calcium form.

LABORATORY TESTS AND EXPERIMENTS

The following adsorption characterization tests have been completed on:

- (1) Single ion aqueous solutions contaminated with one of the following ions: lead, copper, mercury, cadmium, silver, chromium(III), nickel, zinc, yttrium, and mercury.
- (2) Hard water solutions containing cadmium or copper to determine the effects of the hard water on the adsorption.
- (3) An electroplater's rinse water containing primarily zinc, some other heavy metal ions, and some unknown contaminants, e.g. brighteners and chelating agents.
- (4) Solutions of uranium and lanthanides, which are stand-ins for other radioactive elements.
- (5) Drinking water containing copper and lead at levels exceeding those recommended in the new drinking water standards. These tests were conducted in a flow system. The lead laden water was passed through an annulus whose inner surface was coated with the IEM. The calcium content of the water was approximately 40 ppm.
- (6) Copper and lanthanides to determine if superior spectroscopic chemical analysis methods could be developed.

TEST RESULTS

This report contains some of the significant results from the tests conducted to date. They are described below and supported by tabular and graphical illustrations. A study of those results show that the adsorption rates and the mass adsorbed per gram of the IEM vary with the pH of the solutions and on the initial concentrations. The most noteworthy findings are:

- (1) The adsorption of an ion is not affected by the presence of other ions (including calcium) in the mixture so long as there is sufficient ion exchange material in the solution to absorb all ions. For example, it is seen in Figure 1 that the rate and amount of copper adsorbed is the same whether it is in a mixture containing other ions (listed in Table 2) or it is the only ion in a solution.

- (2) The amount of an element adsorbed varies with the pH of the solution. This is shown in Figure 2 for cadmium, mercury, copper and zinc. For most metals the lower pH limit for effective uptake of metal is governed by the acid exchange constant for the film, and the upper pH limit is governed by the affinity of the particular metal to form insoluble or anionic hydroxy species. Using the zinc curve, for example, the lower limit is at approximately pH=5, and the upper limit is approximately pH=7.
- (3) Acid and base titrations of the IEM indicate the capacity for metal uptake to be in the range of 3.5 to 5.0 milliequivalents/gram, depending on the form of the IEM film. These uptakes are comparable to commercial high capacity ion exchangers. In Table 1 are the calculated maximum uptakes of various metals based on the titration capacity. For comparison, the experimentally determined IEM saturation for zinc occurred at 170 grams zinc per kilogram IEM in a system containing a limited amount of IEM and excessive amounts of zinc ions.
- (4) Table 2 gives the IEM recoveries from an actual electroplaters waste solution which contained all of the ions listed in the table plus others not measured.
- (5) The final concentration of most of the elements tested are below the EPA discharge limits for those ions.
- (6) Table 3 indicates the ability of the IEM to recover uranium and other elements used to model the behavior of various radioactive elements.
- (7) The results presented in Table 4 indicate that the IEM, when used in a flowing system, removes copper and lead in drinking water from an order of magnitude above the recommended concentration levels down to levels an order of magnitude below the recommended value.
- (8) A simple colorimetric test was developed for use in the field or in homes to determine the concentration of copper in water. This test is done by simple eye comparison similar to a color chart. More sophisticated methods of spectroscopic analysis have also been developed based on the superior optical properties of the IEM film.

Other tests have shown that the ion exchange polymer is:

- * Easy to use and inexpensive to make.
- * Strong, flexible, and cannot be easily torn.
- * Chemically stable in storage, in aqueous solutions, and in acidic or basic solution.
- * Although no toxicity tests have been performed, it is anticipated that this IEM is safe and non-toxic to handle.

DISPOSAL

Another important feature of the material is that the adsorbed metals can be easily reclaimed by either a destructive or a non-destructive process. With the destructive process, the spent IEM is burned, thereby producing carbon dioxide, water vapor, and oxides of the adsorbed metals which can be recycled. With the non-destructive process, the heavy metals are removed from the IEM and reclaimed by an acid stripping process. The IEM is then reusable and the metal concentrate can be recycled.

The acid stripping procedure uses nominal concentrations of simple mineral acids to strip the IEM of metals within 5 to 10 minutes. Tests with zinc and other heavy metals indicate that the recovery of metal is in the range of 95-100% (see footnote Table 3). The film is then reconverted to the appropriate salt form for reuse as discussed above in the Film Preparation discussion.

PROJECT STATUS

- (1) Some of the characterization tests, which were conducted on the thin film form of the IEM, are complete.
- (2) The patent covering this IEM has been filed.
- (3) A test has been started at a local electroplating firm to determine the effectiveness of the IEM in a zinc plating process. The test will determine how well the waste zinc ion is removed from the first wash bath which also contains brighteners, carriers, etc. associated with the plating process.
- (4) Work has started to develop the methods for making the IEM into fine pellets for use in packed columns and to measure their adsorption properties.

CONCLUDING REMARKS

It is the mission of the NASA Lewis Research Center's Technology Utilization Office (TUO) to spin-off technology developed inside NASA to U.S. industry. When a new NASA technology is developed, usually for an aerospace application, the TUO tries to determine where in the U.S. market the new technology might be used and whether there is a market potential for it. We learned through many contacts with industries and government agencies who are addressing the problems of heavy metal removal from waste water, that there is a need for new technology because the existing technology is either too expensive or not suitable. Based on the responses we received from these contacts, we concluded that the IEM appears to be a promising technology that could contribute to improving the environment. Our contacts told us that the IEM appears to have some unique characteristics that are not available in ion exchange resins on the market today and that it should be developed to the point where it can be made available commercially.

The IEM is still in the development stage. Much work remains to be done to fully characterize the adsorption characteristics of the film and pellet forms. At present, only the film form has been well characterized in the laboratory. Tests of the film in an industrial setting has started. A number of such tests are planned in selected applications. The method for making pellets is under development. Once pellets are available laboratory characterization tests and industrial tests will also be performed. However, if any companies are interested in licensing the IEM technology at this stage, they are invited to do so.

Table 1 - CALCULATED ION EXCHANGE UPTAKE OF INDIVIDUAL METALS.

METAL ION	gms metal/kg IEM
Zinc	168
Cadmium	289
Lead	533
Chromium(III)	89
Copper	163
Mercury	516
Nickel	151

Table 2 - ADSORPTION PROPERTIES OF THE IEM IN AN ELECTROPLATERS WASTE MIXTURE¹

METAL	pH = 5		pH = 7	
	INITIAL CONCENTRATION (ppm)	PERCENT RECOVERY	INITIAL CONCENTRATION (ppm)	PERCENT RECOVERY
Zinc	8.38	97.6	8.38	96.4
Cadmium	0.88	> 97.7 ²	0.88	> 97.7 ²
Nickel	1.11	82.0	1.11	82.0
Copper ³	0.11	> 90.9 ²	0.07	85.7
Manganese	0.22	95.4	0.22	> 99.6 ²

¹ The mixture contained ions of all of the metals listed in this table. The following elements are initial concentrations measured at pH 7 which were not followed during the course of this experiment: Silver, 0.01 ppm; Sodium, 1415 ppm; Cobalt, 0.01 ppm; Magnesium, 0.9 ppm; Lead, <0.03 ppm; Chromium (III), 0.03 ppm, Iron, 0.02 ppm.

² Final concentration at or below limit of instrument detection.

³ Northeast Ohio Regional Sewer District determination.

Table 3. Uranyl and lanthanide ion uptake by the IEM from water.

METAL	INITIAL CONCENTRATION (ppm)	PERCENT REMOVED	pH
U (VI)*	15.2	68	6.3
	15.2	78	6.6
	1.0**	80	6.6
Ce (III)	14.2	99.6	7.0
Eu (III)	15.6	96.4	6.9
Gd (III)	13.4	99.9	7.0
Tb (III)	16.6	86.7	7.0

* UO_2^{2+} + dimers, etc.

** 96% U(VI) recovered by acid stripping of film.

Table 4. Removal of lead and copper from spiked tap water.

<p>Batch Testing Technique for Lead</p> <p>Test Conditions: Sample Size: 1 liter with 0.4 grams of IEM film Sample continuously stirred Initial Lead Concentration: 56 ppb Equilibration time: 2.5 hrs.</p> <p>Results: Final lead concentration: 1.5 ppb</p>
<p>Dynamic Testing Process for Lead and Copper</p> <p>Test Conditions: Flow inside an annulus (length 3 ft.) IEM film wrapped around inner surface of annulus Residence time: 3 hrs.</p> <p>a) Lead tests Initial Lead Concentration: 142 ppb</p> <p>Results: Final lead concentration: 2.8 ppb</p> <p>b) Copper tests Initial copper concentration: 15 ppm</p> <p>Results: Final copper concentration: 0.004 ppm</p>

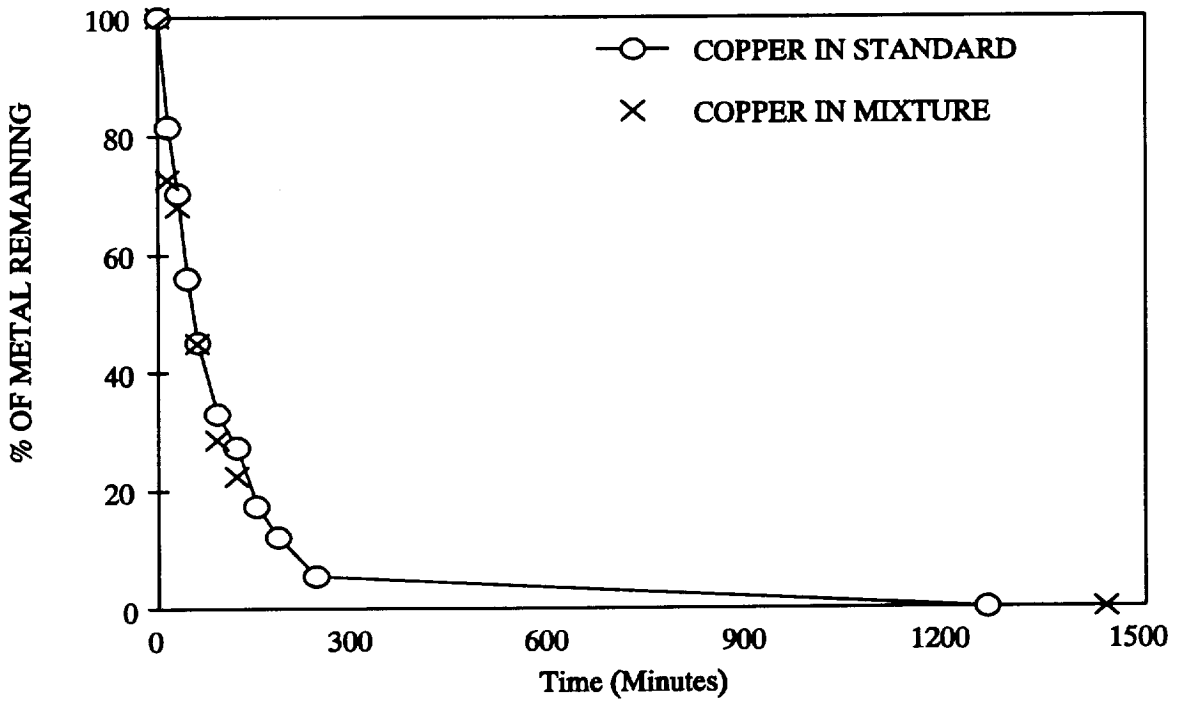


Figure 1. The adsorption rate characteristics of the New Ion Exchange Material for copper alone in a standard solution and in a solution of the rinse water from a copper electroplating process.

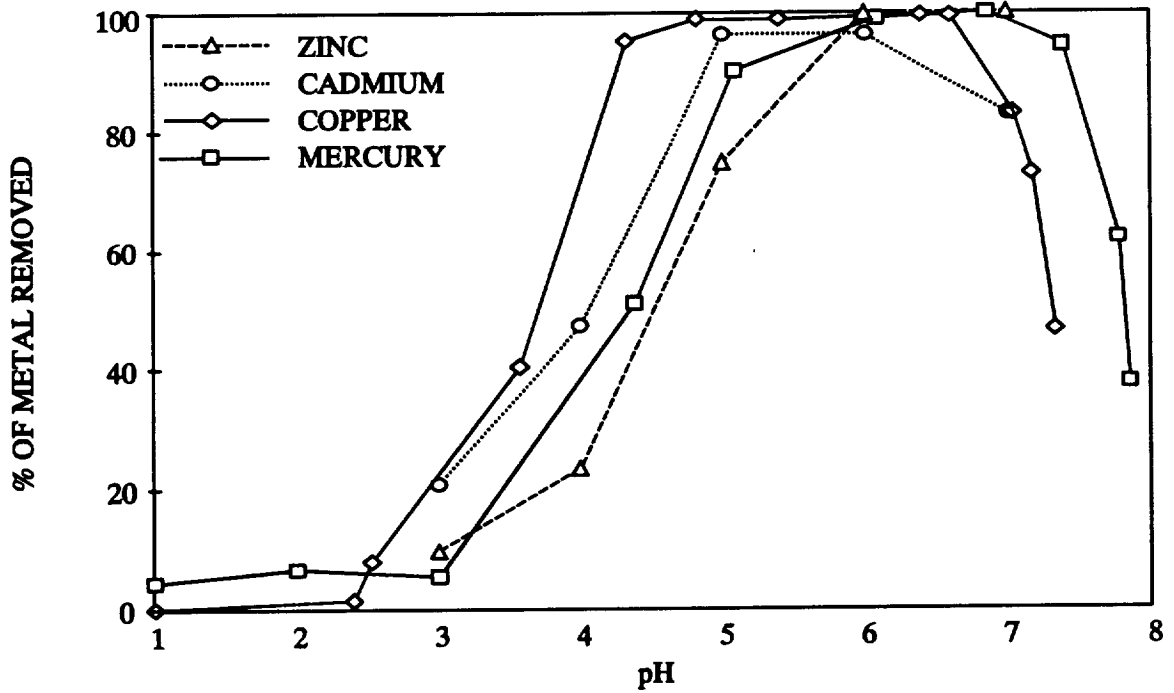


Figure 2. Metal Adsorption by the New Ion Exchange Material as a function of the solution pH.