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Waste Stream Minimization and
Utilization Innovative Concepts

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# Proceedings of Waste Stream Minimization and Utilization Innovative Concepts - An Experimental Technology Exchange

## Volume 1 - Mining and Metals Remediation

Washington, D.C.
April 25-26, 1991

R. L. Watts, Project Manager
V. E. Lee, Editor

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April 1991

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Prepared for the U.S. Department of Energy
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# WASTE STREAM MINIMIZATION AND UTILIZATION INNOVATIVE CONCEPTS

## PROCEEDINGS OF WASTE STREAM MINIMIZATION AND UTILIZATION INNOVATIVE CONCEPTS - AN EXPERIMENTAL TECHNOLOGY EXCHANGE

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Richland, Washington 99352

# ABSTRACT

This two-volume proceedings summarizes the results of fifteen innovations that were funded through the U.S. Department of Energy's Innovative Concept Program. The fifteen innovations were presented at the fifth Innovative Concepts Fair, held in Washington, D.C., on April 25-26, 1991.

The concepts in this year's fair address innovations that can substantially reduce or use waste streams. Each paper describes the need for the proposed concept, the concept being proposed, and the concept's economics and market potential, key experimental results, and future development needs. The papers are divided into two volumes; Volume 1 addresses innovations for mining and metals remediation that can reduce or use waste streams, and Volume 2 addresses general industrial innovations that can reduce or use waste streams.

# SUMMARY

In 1983 the Office of Energy Utilization Research within the U.S. Department of Energy (DOE) initiated the Innovative Concepts Program (ICP). The objective of this program is to identify immature concepts having the potential for saving substantial amounts of energy and to provide seed money for a preliminary investigation of their technical feasibility. This report provides information on the fifteen waste stream minimization and utilization concepts selected for further examination during the fifth cycle of the ICP.

The approach used in this project assumes that 1) good concepts come from experienced, knowledgeable innovators; 2) innovators frequently generate more good ideas than can be used within their own organizations; and 3) ideas are frequently generated in an organization unable to realize the benefits of further development. Therefore, other industrial organizations or federal agencies may be interested in providing financial support for further development of such concepts.

This project is an experiment in a continuing program to harvest creative, novel approaches to saving energy. This year's fair sought innovative concepts and inventions that could reduce or use waste streams. This year's project is unique in that three other agencies with interests in this topic are co-sponsoring it: the U.S. Bureau of Mines, the U.S. Environmental Protection Agency, and DOE's Environmental Management Division.

Over 100 innovative proposals were received by the ICP in response to the formal call for concepts. Fifteen were selected to receive seed money and nonfinancial assistance. The highlights of each paper are presented in two volumes: Volume 1 presents the concepts focusing on reducing or using waste in mining and metals applications, and Volume 2 presents the concepts focusing on reducing or using waste in general industrial applications.

This volume, Volume 1, contains papers on the six concepts dealing with mining and metals waste use or reduction. Those papers are briefly summarized below. The abstracts contained in each paper provide more highlights of each concept.

## RADIAL FLOW EXTRACTION TO REMOVE HEAVY METALS FROM GROUNDWATER

EIChroM Industries, in conjunction with researchers at Argonne National Laboratory (ANL), has developed a novel scheme of extraction chromatography paired with radial flow chromatographic columns for the rapid and effective extraction of toxic metals from aqueous solutions. Radial flow columns, designed initially for bioprocess separations, use smaller quantities of column packing material and smaller particle sizes, allowing better separations and easier recovery for recycle.

## BIOMIMETIC MEMBRANES TO REMOVE METAL

This project is aimed at developing novel membrane systems that mimic their biological counterparts not only in function, as liquid membranes do, but also in structure. The goal is to avoid problems with stability and organic contamination of the treated stream. The focus has been on developing colloidal, capsular-geometry membranes one-tenth the diameter of a bacterial cell, or about 100 nanometer (nm). Aqueous suspensions of these vesicular membranes or vesicles are engineered to scavenge and to concentrate metal ions by selective metal carriers in the vesicle wall and by a chelator in the aqueous core.

## AC ELECTRO-COAGULATION PROCESS FOR REMOVING PARTICULATES AND METAL IONS FROM WASTEWATERS

A novel process involving alternating current (AC) and electro-coagulation (EC) has been developed to remove ultra-fine solids from an aqueous suspension. The AC/EC process can achieve liquid-liquid and solid-liquid phase separation and can be easily integrated with conventional processes and central systems to increase the recovery of solids and to purify water. Waste can be reduced by integrating this technology with various operations that generate contaminated water.

## A NOVEL ION-EXCHANGE MEDIA FOR REMOVING LEAD FROM WASTEWATER STREAMS

Zeolites are being used to develop an ion-exchange media for removing lead from wastewater streams. Zeolites, naturally occurring minerals, are framework aluminosilicates with an infinitely extending three-dimensional network of $AlO_4$ and $SiO_4$ tetrahedra linked to each other by sharing of all the oxygens. Many types of zeolites exist and can be found throughout the United States. Zeotech Corporation recently developed an ion-exchange media by agglomerating natural zeolite fines from two natural zeolites into hard, permeable pellets that have a carbon matrix.

## USE OF CHITOSAN BEADS TO REMOVE HEAVY METALS FROM WASTEWATER

A magnetically stabilized fluidized bed filled with biopolymer beads is being developed to selectively remove heavy metals from groundwater. The process uses a selective, high-capacity adsorbent, minimizes fouling, and can generate a concentrated heavy metal stream that can be processed to recover heavy metals. The adsorbent particles were produced using chitosan, a low-cost aminopolysaccharide that is a by-product of shellfish processing and has a very high affinity for nonalkali metals.

## CAULOBACTERS TO SEPARATE TOXIC HEAVY METALS FROM WASTEWATER STREAMS

Caulobacters are being engineered for sequestering toxic heavy metals such as cadmium, mercury, cobalt, or copper. These bacteria attach to surfaces via an adhesion device at the end of a stalk. The bacteria can be used to produce fixed-cell bioreactors--high surface-area filter devices through which waste streams can be passed to remove toxic metals before treatment of cellulosic fines or sludges. The appropriate segments of metallothionein genes are being inserted into the gene structure, specifying a high copy number surface protein of Caulobacter.

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# INTRODUCTION

The initiation of invention/innovation needs to be accelerated in the United States to speed up the entire process of technology transfer. During the past several years, business leaders, engineers, scientists, and lately, politicians have recognized that our industrial competitiveness has been deteriorating while our excellence in research continues. This trend has produced a growing consensus that we must improve our ability to bridge the gap between research and the marketplace in the United States. We can no longer afford the patterns of the past where innovative technology trickled out into the marketplace in a serial process that took as long as 25 years. International competitors are bringing technology into the marketplace in months instead of years. Many solutions are being proposed to accelerate technology into the marketplace. Acceleration of the latter stages of this process is already occurring.

The U.S. Department of Energy (DOE) established the Innovative Concepts Program (ICP) in the Office of Energy Utilization Research in 1983 after two years of planning. The ICP objective is to develop and demonstrate methods for identifying and encouraging the growth of immature concepts having the potential to save energy and increase productivity through innovative approaches fundamentally different from current practices. The ICP is encouraging the first steps of the invention/innovation (technology transfer) process.

Pacific Northwest Laboratory (PNL)[a] operates the ICP for DOE to provide a bridge between fundamental scientific progress and technology areas of Energy Utilization Research and to identify large energy-saving improvements to eliminate energy-intensive activities. The program is designed to accomplish these tasks by the following activities:

- identify a focus area (for example, waste stream minimization and use) for a cycle of innovation
- solicit concepts in this focus area and select a limited number for further investigation
- provide modest funding to innovators for investigating the concepts' technical and economic potential
- personally visit each inventor to provide encouragement and concrete suggestions for making the most efficient use of the limited funding
- introduce the selected concepts to potential sponsors at a fair.

This document is provided to assist potential sponsors in their search for worthwhile products or programs for reducing or using waste streams.

Innovators who originated these concepts received approximately $20K to perform a preliminary investigation of the technical and economic potential of a concept. A preliminary investigation sometimes proves that a concept should be developed further.

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(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute.

The original goal of the ICP was to have 10% of the funded concepts receive follow-on funding by other programs or organizations. This is the fifth funding cycle sponsored by the ICP. Twelve building materials concepts, 10 industrial process concepts, 10 industrial separation process concepts, and 8 building retrofit concepts were funded in four previous technology fairs: Buildings Innovative Concepts in May of 1984; Industrial Innovative Concepts in November of 1985; Industrial Separations Concepts in May of 1988; and Building Retrofit Innovative Concepts in October of 1989. In addition to more than $9 million in follow-on funding received to date, 2 companies have been started, 9 patents have been issued, 7 patents are pending, and many master theses and more than 50 journal articles have been written on these concepts. The last fair, held in 1989, has already resulted in one innovator receiving $100,000 in follow-on funding.

# 1.0 RADIAL FLOW EXTRACTION TO REMOVE HEAVY METALS FROM GROUNDWATER

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## ABSTRACT

Interest in removing toxic metal contaminants from groundwater and process waste streams has been widespread since a National Environmental Policy was developed in the early 1970s. In the past, the most effective methods of such separation for metal-bearing aqueous wastes was using an ion-exchange resin. Ion-exchangers, while effective, have no selectivity for toxic metals over the more prevalent nontoxic elements and need frequent and expensive regeneration and maintenance. More selective systems, such as supported-liquid membranes, do not possess sufficient stability to be used as a process solution.

The proposed concept involves a system that integrates several known technologies from divergent fields into a system for removing metals from solutions. This system, using resin-based solvent extraction in a radial-flow column, promises to be highly selective and cost-effective. Extraction chromatography uses the chemical specificity of extractants and the mass transfer effects of a packed bed. In extraction chromatography, an organic phase containing an extractant is adsorbed on the surface of an inert support.

Radial flow extraction systems have been designed to integrate directly into ion-exchange resin-based pump-and-treat systems for waste treatment. Because of the flow characteristics of the radial flow system, little or no additional engineering design is needed to implement the extraction chromatography solution.

Ion-exchange resins represent 40% to 70% of the operating costs of a resin-based treatment system. The remaining costs of such a system are represented by regenerants and chemical modifiers needed for ion-exchange resins to function. Implementing an extraction chromatography system, while presenting slightly higher resin costs (about 30% to 50% more than ion-exchange resins), greatly reduces the cost of regenerant materials.

By increasing the selectivity of the resins, extraction chromatography materials reduce the mean interval between regeneration and, therefore, replacement. Because of the increased selectivity of the extraction chromatography system, specific materials can also be recovered for ultimate recycle. For example, in a system that is being considered for decontaminating transuranic-bearing laboratory wastes, EIChroM's TRU•Spec material is used to concentrate and recover transuranic elements for reuse, rather than for low-level waste disposal.

Bench-scale experiments examining uranium removal from groundwater have shown that extraction chromatography materials can obtain decontamination factors greater than $1 \times 10^4$, which both exceeds standards for groundwater contamination and represents allowable disposal limits for mixed

wastes. Process-scale experimentation with 100 to 200$\mu$ resin particles have shown excellent kinetics, capacities, and breakthrough curves.

Five areas need further study as a result of the preliminary experimentation: 1) determine the actual residual amount of uranium remaining in the groundwater, 2) explore the overall purity of the recovered uranium and, by extension, the opportunity for recovering and recycling commercially important metals from contaminated groundwater, 3) process a larger volume of material ($>$10 L) through the radial flow column, 4) determine the long-term stability of the extraction chromatographic column, 5) perform multiple runs of the chromatographic columns to examine the completeness of column stripping and the possibility of performance degradation through multiple use. When stability and characterization experiments are completed, enough data will have been generated to undertake engineering design and process implementation.

## 1.1 INTRODUCTION

Many industrial processes produce large quantities of metal-bearing waste solutions. Some wastes are recycled, some are disposed of as liquids and others as precipitate sludge. In other cases, these wastes have been disposed of illegally or have otherwise entered the groundwater system and now pose remediation problems.

Existing technologies for metals abatement share one common problem: a lack of selectivity. Typically, metals are removed and recovered using ion exchange resins similar to those used in water softeners and drinking water treatment. These resins are unselective and are subject to fouling by large quantities of alkaline earth metals (Ca, Mg, etc.) in the feedstream. Small-scale water treatment systems using reverse osmosis or ultrafiltration membranes have similar problems and are extremely expensive to regenerate.

In the metals finishing industry, increased emphasis on the quality of finished products is leading to increased emphasis on the purity of plating baths and rinse waters. Tighter environmental regulations are putting pressure on improving the purity of discharge and on decreasing disposal costs of current control technologies. Therefore, any evaluation of wastewater treatment systems must consider the life-cycle cost from installation and operation through residual liability for wastes (Clark and Pechan 1988; Higgins and Desher 1988).

The most common metals used in the plating and finishing industries are copper, nickel, and chromium. Although the process chemistries available for these metals are diverse (ranging from cyanide or acid-based electroplating solutions to proprietary electroless processes), the waste streams are subject to similar treatment processes (*Metal Finishing Guidebook* 1989).

Several separation processes have been used to remove and concentrate pollutants from metals finishing. While chemical precipitation has typically been the method of choice, it produces a large amount of toxic sludge that must be further processed and disposed of. Reverse osmosis, electrodialysis, and vacuum distillation have also been used to remove and concentrate pollutants. However, all of these suffer from high costs, complexity, and nonspecificity. Process separations, such as liquid-liquid extraction, are effective but often are too large and capital-intensive for treating waste streams. Liquid membrane separations, despite moderate capital costs, are unstable and suffer from low mass transfer rates.

Recently, increasingly complex and selective ion exchange processes have been proposed for metal finishing wastes. When these processes are used with segregated waste streams, it is possible to recover valuable metals, to recycle the treated water, and to minimize the creation of the hazardous waste products. Metals can be recovered by using electrowinning or by "plating out" the concentrated regenerant, disposing of regenerant or exhausted resins to a refiner or returning the regenerant to plating baths (Wright et al. 1989; Hosea et al. 1988).

The chief drawbacks of these systems are their complexity and dependence on identifying an ion exchange resin with the required selectivity and pH operating range. By operating on segregated streams, a full plating shop will typically require at least three systems, each requiring multiple cation and anion exchange columns, carbon filtration, and extensive valving and control automation.

## 1.2 DESCRIPTION OF THE CONCEPT

Traditional methods for separating toxic metal ions from wastewater have significant technical and economic limitations. A separations technology is needed that has the positive characteristics of traditional technologies in a cost-effective and flexible system. The proposed concept involves a system that integrates several known technologies from divergent fields into a system for removing metals from solutions. This system, using resin-based solvent extraction in a radial-flow column, promises to be highly selective and cost-effective.

The column materials used in resin-based solvent extraction are prepared by the adsorption of a conventional or slightly modified solvent extraction system on a macroporous polymeric support. This process immobilizes the diluent and extractant while retaining their bulk chemical properties. In essence then, the stationary phase of this separation system is a liquid-liquid extraction system, incorporating all of the properties (distribution ratio, selectivity) of the original bulk phase system. Resin-based solvent extraction therefore possesses great specificity for individual metal ions, substantial extraction capacity, and favorable extraction rates. A resin-based solvent extraction system can therefore be produced for many liquid-liquid extraction systems.

To date, no commercially viable process has been identified using extraction chromatography in traditional axial flow columns because, to obtain process-scale separations with an axial column, the particle size of the resin must be increased by an order of magnitude above the effective range. With large particle-size resins, diffusion of ions into and out of the particles is slow, resulting in inefficient separations and requiring large volumes of stripping solutions.

The research conducted to date on the proposed concept examines the use of radial-flow chromatographic columns (designed for protein separations in biotechnology) combined with small particle size resin-based solvent extraction systems. Radial flow columns have been shown to maintain high flow rates (upwards of 2 L/min. through a 100 L column) without substantial pressure drop using conventional chromatographic packings (Saxena et al. 1989; Saxena 1989, 1987, 1986). In tests using fine mesh (20 $\mu$) high-pressure liquid chromatographic packings, substantial flow rates are maintained, without a corresponding increase in operating pressure.

To date, radial flow columns have been used exclusively in the biotechnology industry for separating high-value proteins. They combine low capital equipment costs with savings in column-packing materials. Many effective biological separations use packing materials costing more than $50 per gram. Radial flow columns reduce the volume of packing material needed, thus decreasing the costs of the purification step. In extraction chromatography, while packing materials are not prohibitively expensive, radial flow chromatography will substantially reduce costs while improving performance over traditional ion exchange, liquid-liquid, and liquid membrane systems.

The objective of the research conducted here is to determine the potential of radial flow extraction chromatography for groundwater remediation and waste minimization. We will examine an extraction chromatographic system that may be effective for both uranium extraction from groundwater and nickel removal and recycle from plating baths. Our model system will explore the use of resin-based solvent extraction incorporating Cyanex liquid extractants commercially available from American Cyanamid (1989/1990).

## 1.3 ECONOMICS AND MARKET POTENTIAL

In the following subsections, the economics and market potential of the proposed radial flow extraction system are described.

### 1.3.1 Economics of the Concept

Figure 1.1 plots the relative capital vs. operating costs of the four systems discussed in the introduction: liquid-liquid extraction, ion exchange, supported liquid membranes, and radial-flow extraction chromatography. As the figure indicates, radial flow extraction possesses the best mix of moderate capital costs and moderate operating costs. In liquid-liquid extraction, capital costs are high enough to make the process viable only for large-scale projects. Using either centrifugal contractors or large mixer-settlers, large volumes of material must be processed to break even.

Capital costs for current supported liquid membrane systems run high because of a limited supply of suitable hollow-fiber membranes and the high cost of permeable sheet membranes. Supported liquid membrane systems also require extensive tubing and plumbing. A system to process 10,000 L of contaminated groundwater hourly would occupy nearly 1000 ft$^2$. Based on experimental data from the most stable supported liquid membranes, operating costs will not be as high as for conventional liquid-liquid extraction because less solvent and strip solutions are lost.

Ion-exchange systems have the lowest capital costs of the four technologies, largely because the materials used to construct ion exchange systems are readily available. However, because the resin is expendable and the regenerant solutions are very expensive, ion-exchange systems represent significant investments in operating costs. This feature often results in the misuse or disuse of ion-exchange systems in small- and medium-size applications. After undertaking what they believe to be the low cost solution, owners bulk at the expense needed to maintain the system.

Radial flow extraction represents the best of both worlds. It possesses the operating cost advantages of supported liquid membranes with the ease of use of ion-exchange resins. This low-cost combination will allow users to purchase a reasonably priced capital system with minimal operating costs and superior performance.

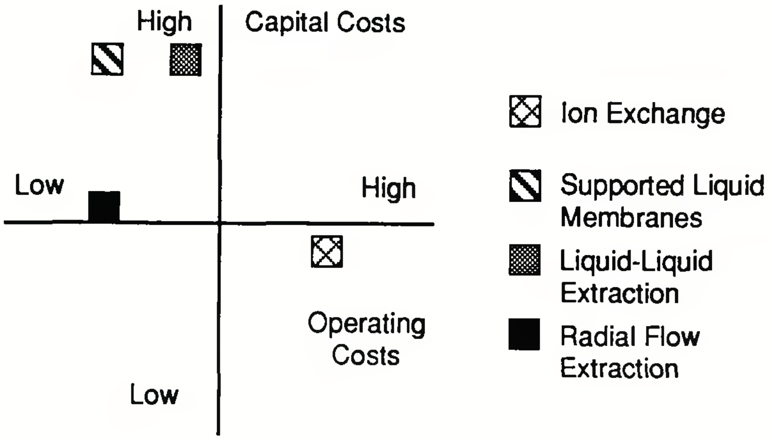

**Figure 1.1.** Relative Economics of Metals Separation Technologies

Both solvent extraction and ion exchange use little energy in the extraction phase but each requires energy for stripping and/or recovery. Liquid-liquid extraction systems have high energy costs resulting from the size of the equipment; energy costs are offset as throughput increases. The radial flow extraction system, on the other hand, requires little more energy than required to drive the pumping system (a prerequisite for any liquid system) and in most cases requires less energy to strip than ion exchange systems.

Radial flow extraction systems will also produce a strip solution of higher purity (due to selectivity) and concentration than an ion exchange system. Higher purity lowers energy consumption in the recovery stage, especially in energy-intensive electrowinning operations. In a recycle operation, radial flow extraction systems provide a purer recycle matrix, lowering energy costs during the plating operation.

### 1.3.2 Market Potential of the Concept

Radial flow extraction systems would have a significant impact on the ability of the DOE, the Environmental Protection Agency, and private industry to remediate numerous groundwater systems contaminated with metals. In the DOE, facilities such as the Hanford Site (Richland, Washington) and the Fernald Feed Materials Production facility (Ohio) have significant amounts of uranium-contaminated groundwater, measured in the tens of cubic miles. For these and other facilities, a cost-effective, rapid pump-and-treat system would be valuable. In areas contaminated with leachate from mine or mill tailing wastes, radial flow extraction could provide a highly specific extraction system for copper, lead, zinc, nickel or uranium. The system would allow effective groundwater remediation at these seriously contaminated sites.

The most significant application of radial flow extraction systems will be in minimizing and subsequently recycling metals wastes. As described above, radial flow extraction is applicable to a broad range of metals refining, processing, finishing, and plating operations. These industries account for the vast majority of metal-bearing waste solutions produced in the United States. EIChroM's radial flow extraction system could be integrated into the operations of many small- and medium-sized producers to make them significantly more efficient and productive.

Current environmental regulations in each of the above-named industries are placing a burden on the small producer, cutting into the diversity and competitiveness that has been a hallmark of these industries. The burden placed on the larger producers, however, is no less onerous, driving up prices, reducing productivity and, in extreme cases, resulting in criminal behavior.

Radial flow extraction could be of significant interest to the U.S. Defense Department's nuclear and civilian nuclear waste reduction and fuel reprocessing programs. Conventional fuel/scrap recovery operations, such as plutonium uranium extraction, need to ensure that the activity of the effluent from the process is as low as reasonably achievable. When introduced as a polishing or finishing step in solvent and wastewater recovery systems, radial flow extraction systems designed for removing transuranics (using EIChroM's TRU•Spec material) and other fission products can provide a wide measure of surety.

Radial flow columns could be used to remove transuranics, strontium, and other radionuclides from low-level mixed waste in which the organics have been removed through combustion or oxidation. The resultant ash could be disposed of as nonhazardous solid waste and the radioactive component could be concentrated for geologic disposal.

Last, extraction chromatographic materials would be useful in specific separation of metals for producing commercially valuable materials such as zirconium, rhodium, or rare earth elements.

## 1.4 KEY EXPERIMENTAL RESULTS

The following subsections discuss the parameters of the experimental design, the analytical methods used in the experiments, and the experiments' results.

### 1.4.1 Experimental Design

The parameters of the experimental design are described below.

**Synthetic Groundwater** - Synthetic groundwater (SGW) simulating the composition of contaminated groundwater found at the Hanford Site was prepared as described in Chiaizia and Horwitz (1990) and acidified to pH 2 using sulfuric acid. The composition of this acidified synthetic groundwater is summarized in Table 1.1.

**Table 1.1.** Composition of Synthetic Groundwater

| Sulfate-bisulfate | Molarity (moles/L) |
|---|---|
| Calcium | 0.012 |
| Magnesium | 0.0062 |
| Sodium | 0.017 |
| Silicon | 0.0009 |
| Chloride | 0.0016 |
| Sulfate-bisulfate | 0.017 |
| Nitrate | 0.030 |
| pH | 2.00 |
| Sum of molarities | 0.094 |

**Reagents** - The uranium extractant, Cyanex 272, was obtained from the American Cyanamid Company and used as received. Dodecane, the diluent for Cyanex 272, was obtained from Aldrich Chemical Company and used without further purification. The 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) was obtained from Albright & Wilson. Before being used, the HEDPA was purified by recrystallization from acetic acid. All other reagents were of analytical grade and were used without further purification. Deionized water from a Milli-Q2 system was used to prepare all solutions.

**Uranium** - In preliminary experiments to define conditions for subsequent column runs, a $^{233}$U tracer obtained from Argonne National Laboratory (ANL) stocks was used. Uranyl nitrate (obtained from ANL stocks), however, was used to spike the contaminated groundwater.

**Extraction Chromatographic Support** - The Cyanex-dodecane solution was supported on Amberlite XAD-7, a macroporous polyester resin (from Rohm and Haas, Philadelphia). Before being used, the resin was washed with water to remove preservatives, then with methanol to remove water and residual monomers. The resin was then dried under vacuum to constant weight.

**Resin Preparation** - A weighed quantity (typically 300 g) of the dried resin was slurried in absolute methanol, then combined with a weighed amount (typically 200 g) of an 0.8 M extractant solution in dodecane. After thorough mixing, the methanol was removed by rotary evaporation, leaving a resin loaded to ~40% weight/weight (w/w) with extractant solution.

**Distribution Ratio Measurements** - A weighed amount (~0.02 g) of the Cyanex 272 resin was transferred into a culture tube. A known volume of a $^{233}$U-spiked aqueous solution of appropriate composition was introduced, and the mixture was agitated for ~10 minutes. The sample was then centrifuged for ~5 minutes. A portion of the aqueous phase was drawn off from the top of the sample and 100λ added to 5 mL of scintillation cocktail. The activity of this aliquot was then measured by liquid scintillation counting. Appropriate blanks, consisting of unspiked aqueous phase, were also run. The distribution ratio of uranium between the resin and the aqueous phase can be calculated from the activity initially introduced and that remaining in the aqueous phase after equilibration with the resin.

**Preparation of Feed Solution** - The feed solution was prepared by diluting 80λ of a ~0.511 M solution of uranyl nitrate [$UO_2(NO_3)_2$] in 0.1 M nitric acid to 2000 mL with synthetic groundwater.

**Preparation of Strip Solution** - The column strip solution was prepared by dissolving a weighed quantity of HEDPA in a measured volume of Milli-Q water to yield a 0.1 M solution.

**Axial Column Experiments** - The axial column experiments were conducted as follows.

Two conventional axial flow columns packed with Cyanex 272/n-dodecane coated resin were arranged in tandem. Figures 1.2 and 1.3 show the column design and configuration. The tandem configuration was used to prevent uranium loss if premature breakthrough occurred on the first column. That is, the second column would sorb uranium if the first column failed in some regard. A third column, packed with uncoated XAD-7 resin, served as a filter, adsorbing any extractant or diluent leached from the Cyanex columns by the groundwater sample.

All three columns were packed in the same fashion. Briefly, a slurry of the XAD-7 or Cyanex resin in Milli-Q water was prepared and gently stirred for several minutes. Aliquots of the slurry were then transferred to the appropriate column and packed under nitrogen pressure. Addition of slurry aliquots was repeated until the desired bed height was reached. A small piece of glass wool was then placed atop the resin bed to prevent disruption of the bed during sample introduction.

The column was preconditioned with 10 mL (~10 free column volumes, fcv) of pH 2 $HNO_3$. A 1000 mL (~1000 fcv) aliquot of synthetic groundwater spiked with uranyl nitrate (feed solution) was then passed in succession through each of the two Cyanex columns and the XAD-7 column. Ten fractions, each consisting of ~100 fcv, were collected in pre-weighed bottles. Each filled bottle was then weighed to determine the actual weight (and therefore the volume) of each fraction. An aliquot of each fraction was then treated as described below to determine uranium content. A second aliquot was submitted for phosphorus analysis.

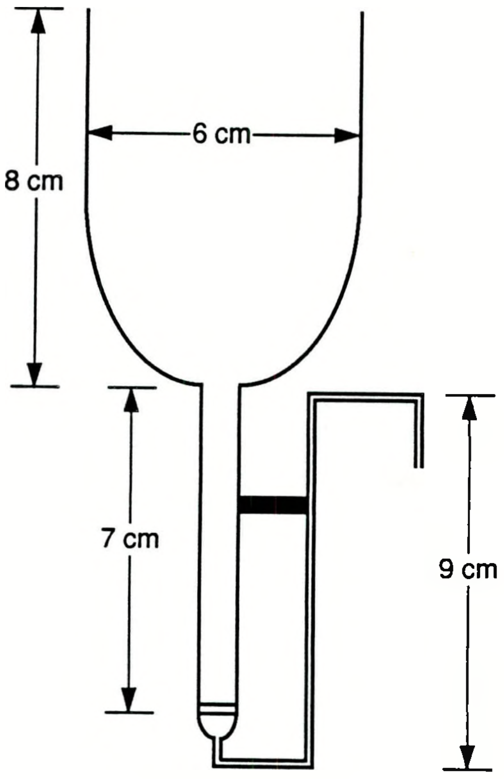

**Figure 1.2.** Design of Axial Column Used in the Experiment

After passage of the feed solution, each of the three columns was treated independently. Each of the Cyanex columns was rinsed with 10 mL (~10 fcv's) of 0.010 M $HNO_3$ and the solutions were submitted to determine phosphorus content (see below). Each of the Cyanex columns was then stripped with (~10 fcv) of 0.10 MHEDPA. Two 5 mL fractions were collected for each column and submitted to determine their uranium content (see below).

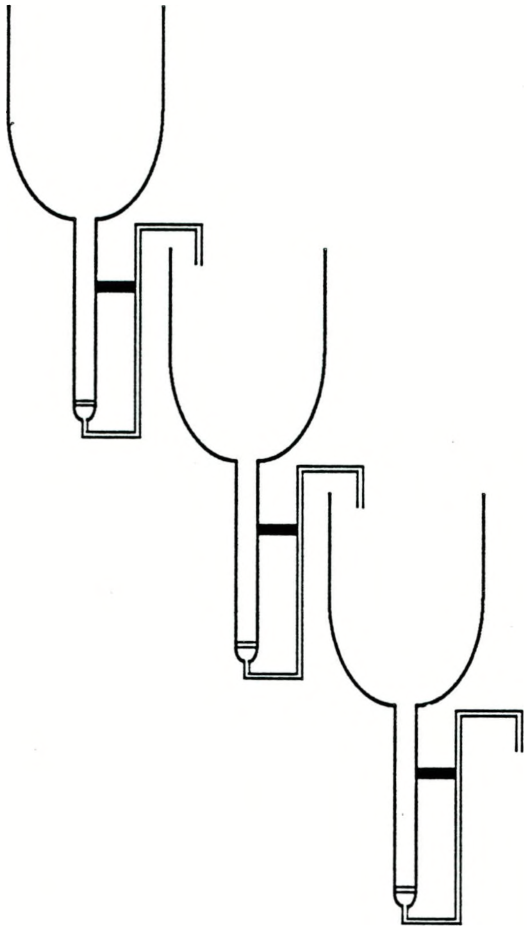

Figure 1.3. Column Configuration Used in the Axial Column Experiment

**Column Stability** - To assess column stability, each of the fractions collected from the axial column experiments was analyzed for phosphorus. (Because Cyanex 272 is a phosphorus-based extractant, loss of it from the resin during sample loading/elution would be reflected as an increase in the phosphorous content of the column effluent). In addition, after passage of 1000 fcv of feed solution through the columns, the XAD-7 filter was stripped of all sorbed organics by methanol. These methanol washings were taken to dryness under a heat lamp and the residue taken up in concentrated nitric acid. This too was taken to dryness and the process of dissolution/evaporation repeated, this time using a 1:3 volume/volume (v/v) $HNO_3$:HCl mixture. Finally, the residue was dissolved in 1 mL of concentrated nitric acid, then diluted to 25 mL with deionized water and submitted for phosphorus determination.

**Radial Flow Column Experiment** - The radial flow column experiment was conducted as follows.

Before it was packed, the radial flow column (see Figure 1.4) was backflushed with deionized water using a peristaltic pump to remove air from the column. A slurry of Cyanex resin in Milli-Q water was prepared and drawn into the column through the packing ports. When the column was completely packed, the ports were closed and the column flushed with deionized water. The column was then equilibrated with ~10 fcv of pH 2 $HNO_3$.

Approximately 500 mL of the feed solution was passed through the radial flow column. Five fractions were collected, each approximately 100 mL. As before, the exact sample volume in each case was determined by weight. Each of the five samples was then treated, as described below, to determine their uranium content.

### 1.4.2 Analytical Methods

The analytical methods used to test the concept are described below.

The uranium content of most of the fractions collected was expected to be too low to be detectable by the method used to quantitate uranium. Therefore, all samples other than the solutions resulting from the strip of the Cyanex columns were concentrated on a uranium-tetravalent actinide specific extraction chromatographic column (U/TEVA•Spec, EIChroM Industries, Inc.) before being submitted for analysis.

Specifically, each of a series of U/TEVA•Spec columns was preconditioned with 5 fcv (6.5 mL) of 2 M $HNO_3$. An aliquot (56.8 mL) of each of the fractions collected in the column runs was then acidified to 2 M in $HNO_3$ (yielding a total sample volume of 65 mL, ~50 fcv) and introduced to aU/TEVA•Spec column. Each column was then rinsed with 10 fcv(13 mL) 2 M $HNO_3$, then stripped with

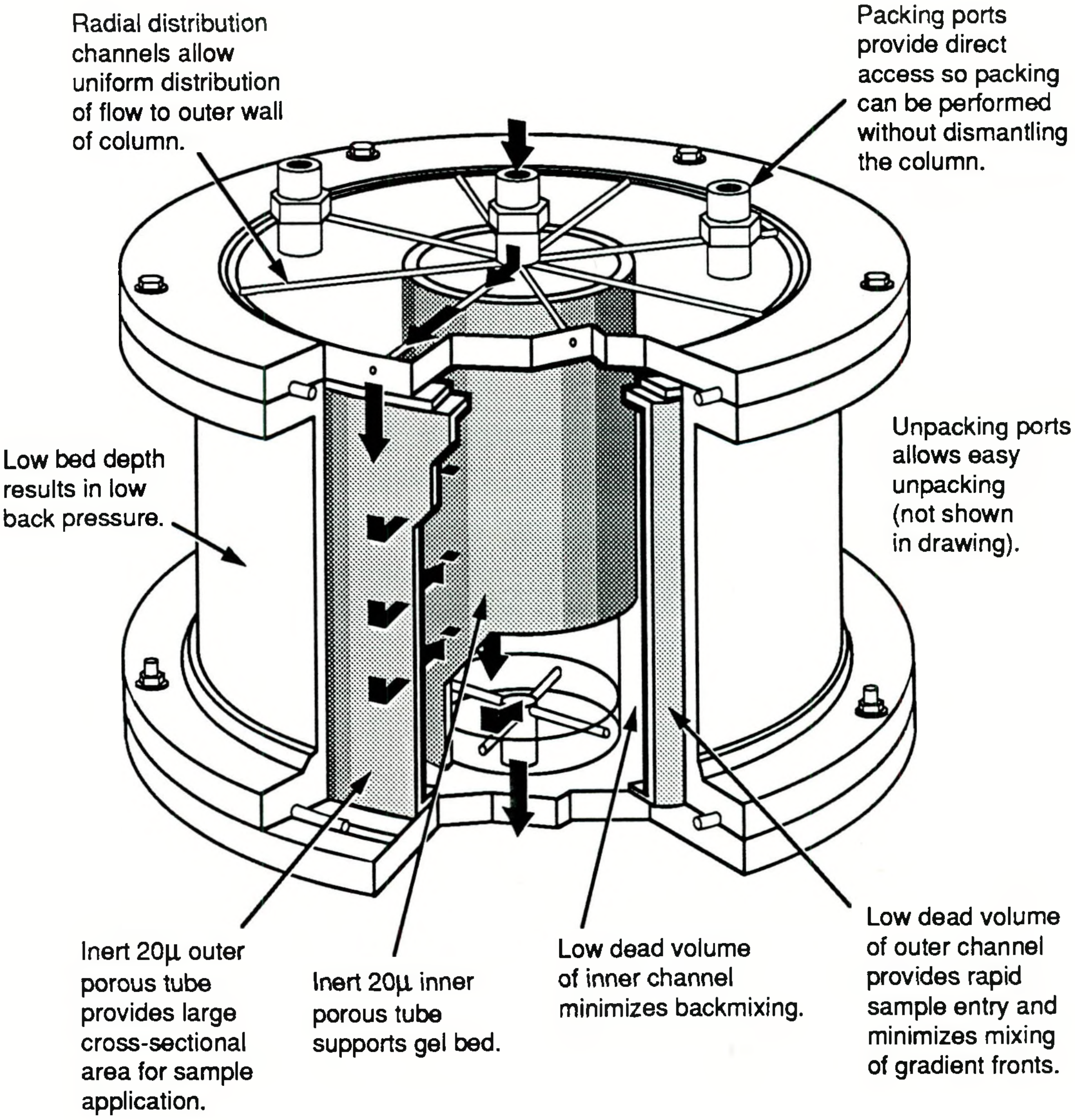

**Figure 1.4.** Configuration of the Radial Flow

5 fcv (6.5 mL) of 0.01 M HNO3. Each strip fraction was collected in a weighed scintillation vial, which was then re-weighed after sample collection to determine sample volume. The samples collected were then submitted for uranium analysis.

Uranium determinations were conducted at ANL using the method of Kinetic Phosphorescence Assay (Chem-Chek Instruments, Richland, Washington). Results were typically reproducible to within ±5%.

Phosphorous determinations were performed at ANL using inductively coupled plasma atomic emission spectroscopy. Results were typically reproducible to within ±10%.

### 1.4.3 Results and Discussion

Measuring uranium distribution ratios between Cyanex-dodecane solutions or between Cyanex-loaded XAD-7 and various aqueous phases provides a simple method for determining a suitable extractant concentration for preparing the extraction chromatographic resin. Previous work by Chiarizia and Horwitz (1990) has shown that as little as 0.05 M to 0.1 M Cyanex 272 in dodecane yields distribution ratios for uranium (VI) greater than $10^5$ from pH 2 synthetic groundwater.

However, subsequent work (Chiarizia et al. 1991) on using Cyanex as a uranium carrier in a supported liquid-membrane system for removing uranium from groundwater has shown that a gradual loss of membrane permeability occurs over time, indicating that the extractant is soluble in the aqueous phases that contact the membrane. For this reason, a high initial concentration of Cyanex in dodecane, 0.8 M, was selected for the experiments here. In this way the distribution ratio of uranium could be maintained at an acceptable level, even if some loss of extractant were to occur during sample loading.

Measuring distribution ratios also provides a way to quickly define solution conditions that are appropriate for the uptake of uranium from groundwater by an extraction chromatographic column and its subsequent elution from the column. Table 1.2 summarizes the distribution ratios measured between the Cyanex-loaded resin and various aqueous phases. These results clearly indicate that the resin is extremely effective at extracting uranium from a pH 2 aqueous phase and that uranium uptake from solutions containing higher concentrations of either sulfuric or nitric acid is also substantial. Thus, neither of these solutions would be effective for removing uranium sorbed by the resin.

**Table 1.2.** Uranium Distribution Ratios between 40% (w/w) 0.8 M Cyanex 272 in Dodecane on Amberlite XAD-7 and Several Aqueous Phases

| Aqueous Phase | Distribution Ratio |
|---|---|
| pH 2 $H_2SO_4$ | $3.1 \times 10^5$ |
| 2 M $H_2SO_4$ | 20 |
| 2 M $HNO_3$ | $3.3 \times 10^3$ |
| 6 M $HNO_3$ | $1.9 \times 10^3$ |
| 0.1 M HEDPA | <the limit of detection |

In contrast, the uptake of uranium from the 0.1 M HEDPA solution is very low, in agreement with the results of Chiarizia and Horwitz (1990). Therefore, using this solution to remove sorbed uranium from the Cyanex resin should be simple.

Because a direct relationship exists between the value of the distribution ratio of a metal ion and the volume of solution required to elute it from an extraction chromatographic column (Braun and Ghersini 1975), it should be possible to pass several thousand free column volumes of feed solution through a Cyanex - XAD-7 column before elution of uranium begins. (The capacity of each axial column is 0.1 mmol of uranium; therefore, only about 5000 fcv of the groundwater sample could be put through the column before saturation is reached.) Similarly, it should be possible to elute sorbed uranium using only a few free column volumes of 0.1 M HEDPA.

Unfortunately, because a 100 mL bed volume radial flow column has a free column volume of ~67 mL, it is difficult to conduct a benchtop test of these predictions directly. (The 1000 fcv here would correspond to 67,000 mL of solution.) For this reason, uranium retention and stripping were evaluated using a pair of small (1 mL fcv) axial columns, arranged in tandem (see Figure 1.2).

Table 1.3 summarizes the results of uranium analyses performed on a series of 100-fcv aliquots of uranium-spiked feed, following passage of the aliquots through these columns. Also shown are the uranium concentrations observed in the HEDPA solutions used to strip sorbed uranium from each of the columns following passage of the feed. As the table shows, uranium is efficiently extracted by the Cyanex columns. In fact, in each of the feed aliquots passed through the columns, the uranium concentration has been reduced from the ~5500 ppb initially present to only ~0.1 ppb, making it indistinguishable from the blank. This reduction corresponds to an overall decontamination factor for the column pair of 5.5 x $10^4$ or a decontamination factor of ~235 ppb per column. This final concentration is a factor of 100 lower than the Maximum Contaminant Limit (for uranium in groundwater) of 10 ppb (Chiarizia et al. 1991).

**Table 1.3.** Axial Column Experiment: Uranium Content of Feed and Strip Solutions

| Fraction | Volume (mL) | Uranium Concentration[(a)] (ppb) | Total Uranium (ng) |
|---|---|---|---|
| Feed-1 | 97.9 | <0.1 | <10 |
| Feed-2 | 95.79 | <0.1 | <10 |
| Feed-3 | 96.0 | <0.1 | <10 |
| Feed-4 | 96.8 | <0.1 | <10 |
| Feed-5 | 97.4 | <0.1 | <10 |
| Feed-6 | 98.1 | <0.1 | <10 |
| Feed-7 | 98.3 | <0.1 | <10 |
| Feed-8 | 97.8 | <0.1 | <10 |
| Feed-9 | 96.7 | <0.1 | <10 |
| Feed-10 | 98.7 | <0.1 | <10 |
| Strip-1-1 | 3.89 | 1.2 x $10^6$ | 4.7 x $10^6$ |
| Strip-1-2 | 5.25 | 2.12 x $10^5$ | 1.1 x $10^6$ |
| Strip-2-1 | 3.33 | 3.0 x $10^2$ | 1.0 x $10^3$ |
| Strip-2-2 | 5.33 | NA[(b)] | NA |
| Blank | | <0.1 | <10 |

---

(a) Initial uranium concentration in feed: 5.5 x $10^3$ ppb

(b) Value too low to be measured in the presence of 0.1M HEDPA.

The results shown also demonstrate that sorbed uranium can be efficiently stripped from the column with only a few free column volumes of 0.1 M HEDPA. In fact, all of the uranium retained on the first column (essentially 100% of that introduced) can be eluted with only 9 free column volumes of solution. The remaining trace of uranium sorbed by the second column can be eluted in a similar volume. Thus, essentially all of the uranium initially present in 1000 mL of synthetic groundwater can be recovered in ~12 mL of strip solution, corresponding to a concentration factor of ~80. This compares quite favorably with the value of 25, reported for a Cyanex-based SLM system for uranium removal from groundwater (Chiarizia et al. 1991).

These results only establish the *minimum* possible concentration factor for this system. That is, the volume of feed solution passed through the column here, 1000 mL (1000 fcv), is far less than the volume that could be passed through the column before uranium breakthrough will occur (as estimated from the distribution ratios or column capacity). We anticipate, in fact, that the actual concentration factor could be several times higher.

Table 1.4 summarizes the results of the column stability experiments. As indicated above, column instability (i.e., removal of the organophosphorus extractant from the support by the feed solution) should be reflected as an increase in the concentration of phosphorus in the column effluent. As the data show, after passage through the three columns, none of the feed aliquots has a phosphorus content distinguishable from the blank. This indicates either that no deterioration of the Cyanex columns is occurring or that, if it is, any extractant removed is efficiently taken up by the uncoated XAD-7 column.

To distinguish between these two possibilities, two additional experiments were conducted. First,

**Table 1.4.** Axial Column Experiment: Phosphorus Concentrations

| Fraction | Phosphorus Concentration (ppm) |
|---|---|
| Feed-1 | <0.2 |
| Feed-2 | <0.2 |
| Feed-3 | <0.2 |
| Feed-4 | <0.2 |
| Feed-5 | <0.2 |
| Feed-6 | <0.2 |
| Feed-7 | <0.2 |
| Feed-8 | <0.2 |
| Feed-9 | <0.2 |
| Feed-10 | <0.2 |
| Rinse-1 | <0.2 |
| Rinse-2 | <0.2 |
| Strip | 4.8 |
| Blank-1 | <0.2 |
| Blank-2 | <0.2 |

each of the Cyanex columns was rinsed individually with 0.01 M nitric acid and the rinses analyzed for phosphorus. In addition, the XAD-7 column was stripped of adsorbed organics using methanol and, after appropriate treatment to solubilize the eluted materials (see above), the strip solution was also analyzed for phosphorus. As shown in Table 1.4, neither of the Cyanex column rinses contains a measurable quantity of phosphorus. In addition, the amount of phosphorus recovered from the XAD-7 column corresponds to <1% of the extractant initially present on the two Cyanex columns. Taken together, these results indicate that it should be possible to pass several thousand free column volumes of feed solution through a Cyanex column before appreciable loss of extractant will occur.

Table 1.5 summarizes the results of the radial flow column experiment using the same feed conditions used for the axial column run. The values shown refer to the uranium concentrations of a series of 100-mL aliquots of feed after passage through the column. As the table shows, none of the aliquots contains a concentration of uranium greater than the blank, indicating that despite the change in column configuration, the Cyanex resin is efficiently removing the uranium present in the feed. It is worth noting that the same decontamination factor was achieved with a single radial flow column as with a pair of axial columns operating in tandem. Thus, the radial flow column is actually more efficient than the axial flow column used. The reason for its higher efficiency is unclear right now, but may indicate that wall effects are not as pronounced in radial flow columns.

**Table 1.5.** Radial Flow Experiment: Uranium Content of Feed Solutions

| Fraction | Volume (mL) | Uranium Concentration (ppb) | Total Uranium (ng) |
|---|---|---|---|
| Feed-1 | 101.6 | <0.1 | <10 |
| Feed-2 | 100.1 | <0.1 | <10 |
| Feed-3 | 101.1 | <0.1 | <10 |
| Feed-4 | 101.9 | <0.1 | <10 |
| Feed-5 | 103.5 | <0.1 | <10 |

## 1.5 FUTURE DEVELOPMENT NEEDS

Several additional areas need to be studied as the result of this preliminary investigation. Those areas, along with implementation needs, are discussed below.

### 1.5.1 Future Research Needs

We have identified five additional areas that need further study as a result of the preliminary experimentation described in this paper.

First, we will determine the actual residual amount of uranium remaining in the groundwater. As described earlier, our decontamination exceeded the limit of detection of the Kinetic Phosphorescence Assay. We have subsequently submitted samples for determination using alpha-pulse height analysis, which affords a limit of detection of ~0.02 disintegrations per minute, which corresponds to a level of ~0.3 ppb natural uranium. If this method fails to identify any uranium present, we may submit samples for inductively-coupled plasma-mass spectrometric analysis. This method has a sensitivity below 1 ppt.

We are also interested in the overall purity of the recovered uranium and, by extension, the opportunity for recovering and recycling commercially important metals from contaminated groundwater. We will analyze the chemical composition of the recovered uranium fraction by using inductively-coupled plasma-atomic absorption spectroscopy.

Because of the time constraints of this preliminary investigation, we were unable to study extended radial flow column runs (>1000 free column volumes) and therefore did not approach breakthrough conditions. We will process a larger volume of material (>10 L) through our radial flow column. We expect to achieve decontamination of large samples with the same efficacy as the smaller volumes. This experiment will give us additional information concerning the suitability of this system for process scale separations.

We have also been unable to determine the long-term stability of the extraction chromatographic column. As described above, we have shown that no extractant material was detectable in the column effluent, within the limits of our instrumental analysis ($10^{-6}$ M). We will run these process columns in a continuous fashion and will remove column material in weekly intervals for characterization. Appreciable loss of functionality will serve as evidence of degradation of the material.

Lastly, we have been unable to do multiple runs of the chromatographic columns to examine the completeness of column stripping and the possibility of performance degradation through multiple use. This problem is likely the most pressing question remaining. Multiple uses of the columns without appreciable degradation of column performance would demonstrate the utility of these materials in a process environment and would allow further research on process-scale implementation.

### 1.5.2 Implementation Needs

When stability and characterization experiments are completed, enough data will have been generated to undertake engineering design and process implementation. A groundwater remediation or pollution abatement system developed using extraction chromatographic materials is expected to be operated in a continuous fashion. To accomplish this with a radial flow chromatographic column, the system must be operated in a "swing" fashion. Swing systems typically consist of two columns and piping and valving, which allow the system to automatically switch between columns so that exhausted columns may be stripped and regenerated. Some form of an on-line monitoring system also will be needed to look for the ion of choice.

For the uranium system examined above, a laser kinetic phosphorescence spectrophotometer (Chem-Chek Instruments, Richland, Washington) can be used in a "flow injection" mode, taking discrete samples at four to ten second intervals. Such a system should allow the breakthrough of uranium from the column to be measured in real time and the swing column operation to be successful.

For other systems, numerous ion-specific real-time analytical tools have been developed from ion-selective electrodes to ChemFET-based microsensors. Again, real-time monitoring of column performance would allow for continuous processing of groundwater and wastewater streams using radial flow columns.

In conjunction with several chemical engineering process consultants, EIChroM has developed process flowsheets for using extraction chromatography for processing radioactive waste streams, dump leach liquors, and contaminated groundwater. These flowsheets and supporting information are available on request directly from EIChroM.

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# 2.0 BIOMIMETIC MEMBRANES TO REMOVE METAL

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*University of California*

## ABSTRACT

Highly toxic, metal-laden aqueous waste is generated by a number of industries, including oil refining, power, mining, nuclear, microelectronics, aerospace, and metal finishing. The impact of an effective program to minimize metal wastes could be substantial in many urban centers.

The most common methods of metal recovery--evaporation, reverse osmosis, ion exchange, electrodialysis, and electrolytic cell processes--all are less than ideal processes for one or more of the following reasons: lack of selectivity, inability to reduce metal-ion concentration to the standards of the U.S. Environmental Protection Agency (EPA), instability, and high operating cost.

This project is aimed at developing novel membrane systems that mimic their biological counterparts not only in function, as liquid membranes do, but also in structure. The goal is to avoid problems with stability and organic contamination of the treated stream. As in liquid-membrane systems, highly selective carrier compounds shuttle species across the membrane to help the biological systems achieve the separations.

This investigation has focused on developing colloidal, capsular-geometry membranes one-tenth the diameter of a bacterial cell, or about 100 nanometer (nm). Aqueous suspensions of these vesicular membranes or vesicles are engineered to scavenge and to concentrate metal ions by selective metal carriers in the vesicle wall and by a chelator in the aqueous core.

These systems for biomimetic membrane metal recovery would be competitive with existing metal-recovery processes, including increasingly popular systems based on ion-exchange resins. Our vesicular membrane media have a high metal-loading capacity and are capable of exceptional selectivity. The utility requirements for this membrane process should be minimal compared with evaporation, reverse osmosis, and electrolytic cell processes. Equipment costs should be recoverable in as little as one year, based on a preliminary comparison with ion-exchange waste treatment processes.

Vesicular biomimetic membrane systems with apparent shelf lives of several weeks have been created. Initial constructs consist of the metal carrier, A23187, in the vesicle wall with the chelating agent, nitrilotriacetic acid, in the vesicle interior. Our results suggest that $Zn^{2+}$ levels can be reduced to less than 300 ppb from a starting concentration of 1 ppm in about one minute. Bench-scale tests are planned for the metal-sorbing vesicles in a continuous process configuration using hollow-fiber micro/ultrafiltration cartridges.

## 2.1 INTRODUCTION

Processing hazardous metal-laden wastes presents a unique challenge. Unlike toxic organics, dissolved heavy-metal species cannot be converted through degradative means to nontoxic substances. Only two alternatives are possible: isolate the contaminated waste from the biosphere or selectively recover the valuable metal and recycle it to a process. Given the high strategic and economic value of many heavy metals, the latter approach, where possible, is often the most practical.

Highly toxic, metal-laden aqueous waste is generated by a number of industries, including oil refining, power, mining, nuclear, microelectronics, aerospace, and metal finishing. The impact of an effective program to minimize metal wastes could be substantial in many urban centers. For example, 94% of the hazardous waste in the San Fernando Valley consists of heavy-metal wastes, and ~95% of this metal waste is generated by metal-coating processes (Bergin and Morell 1983). Because electroplaters use many of the same toxic heavy metals in plating processes as appear in their aqueous waste streams, this industry is a logical target for a waste minimization effort. To minimize the waste, valuable metal ions must be selectively recovered from waste streams and concentrated in relatively pure form to permit resale, reuse, or recycle (for example, to plating baths).

The rising cost of disposal fees, more stringent regulations imposed by the EPA, and the value of recoverable metals have encouraged all metal waste generators to consider processes and plant designs for "zero metal discharge." To achieve that goal, technologies obviously must be developed to ensure that the only metal outlet from the plant is the final product.

The most common methods of metal recovery--evaporation, reverse osmosis, ion exchange, electrodialysis, and electrolytic cell processes--are less than ideal processes for one or more of the following reasons: lack of selectivity, inability to reduce metal-ion concentration to EPA standards, instability, and high operating cost (EPA 1987; Cushnie 1985; Snyder et al. 1983).

The most significant drawback to evaporation, reverse osmosis, and electrodialysis is their lack of selectivity. As plants approach the limit of "zero metal discharge" (total recycle), the buildup of impurities, minerals, and organics can poison the system unless highly selective separations operations are used for metal recovery. Electrolytic cell processes can be more selective, but they typically provide recoveries of just 90% to 95% and may not reduce metal-ion concentrations to emissions' standards (Cushnie 1985).

Ion exchange is increasingly becoming the popular method for removing metals from wastewater. However, ion-exchange systems have a limited pH operating range, are subject to fouling by organics used as additives in the metal-finishing industry, and require use and disposal of regenerant and wash solutions. Therefore, many metal-finishing shops still concentrate their metal-containing waste as sludges, creating a solid waste disposal problem that has become environmentally unattractive and expensive in areas with few suitable landfill sites.

Growing evidence indicates that biologically derived or biomimetic systems may exhibit the required characteristics, including cost effectiveness and selectivity, of a viable process to recover metals. A wide variety of highly efficient mechanisms has evolved to control intracellular metal concentrations such as the inducible synthesis of specific metal-complexing agents [e.g., metallothioneins (Vallee 1979) and siderophores (DeVoe and Holbein 1986)] and membrane-based metal efflux systems (Trevors et al. 1985).

Biological cell membranes have the remarkable capability to concentrate selected species several orders of magnitude by coupling a thermodynamically unfavored transport process to the flux of a second species, such as a proton, down a steep concentration gradient. The process is facilitated by selective carrier compounds that shuttle charged or large polar species across the membrane.

We are developing membrane-based biomimetic separation systems that use highly selective carriers and proton gradients or metal chelators to "pump" a particular metal species from a dilute waste stream to a metal-rich solution for eventual recycle to a process. Supported or emulsion "liquid-membrane" systems are based on an organic solvent phase harboring a lipophilic metal carrier that is trapped in the pores of a hydrophobic sheet or stabilized as a double emulsion, respectively. Our biomimetic systems are conceptually similar to those liquid-membrane systems that have been constructed and pilot tested for recovering heavy metals (Noble et al. 1989).

The best of these systems takes full advantage of the Donnan Distribution Law (see Figure 2.1). For example, by coupling divalent metal-ion transport to the opposing flux of protons down a steep

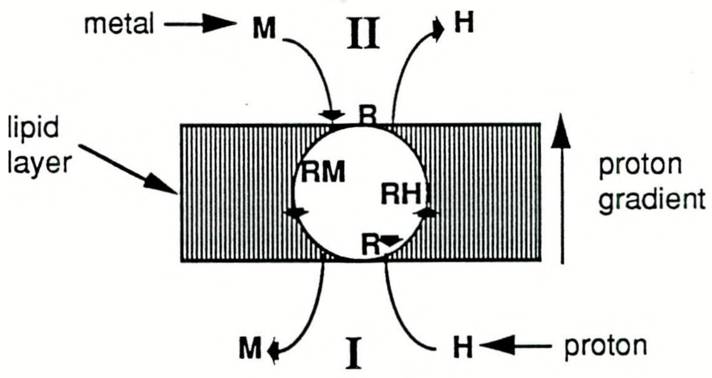

**Figure 2.1.** Metal-Ion Pump

concentration gradient, metal-ion concentration factors of 10,000-fold or more may be achieved (Lonsdale 1984).

Donnan dialysis membranes use charged carriers that must bind cations to achieve neutrality and to diffuse in the organic solvent phase of the membrane. If the initial concentration of protons on side I of the membrane is much greater than the concentration of a multivalent metal cation on side II, the flux of protons down its concentration gradient can be used to "pump" the metal cation up its concentration gradient (see Figure 2.1).

The process continues until Donnan equilibrium conditions are reached (Lonsdale 1984):

$$\frac{[H^{+}]_{I}}{[H^{+}]_{II}} = \left\{ \frac{[Me^{+z}]_{I}}{[Me^{+z}]_{II}} \right\}^{1/z} \qquad (2.1)$$

where Me is any metal ion of valence, +z. This equation suggests that given metal ions of valence, +2, and a trans-membrane pH gradient of 2 units (i.e., a 100-fold proton concentration difference), up to a 10,000-fold difference in the metal ion concentration can be achieved.

A major deficiency of currently available liquid membranes is their instability (Nobel et al. 1989; Lonsdale 1984). In some cases, continuous membrane regeneration schemes could be successful. A second problem stems from the treated water being contaminated with the organic solvent of the liquid-membrane system. After decades of research and development, only one industrial-scale liquid membrane process has been installed, a zinc recovery process in Austria (Noble et al. 1989).

## 2.2 DESCRIPTION OF THE CONCEPT

This project is aimed at developing novel membrane systems that mimic their biological counterparts not only in function, as liquid membranes do, but also in structure. The goal is to avoid problems with stability and organic contamination of the treated stream. As in liquid-membrane systems, highly selective carrier compounds shuttle species across the membrane to help the biological systems achieve the separations.

Inspired by the efficiency of biological cell membranes, we propose to use natural lipid components of bacterial membranes, including the ether lipids (de Rosa et al. 1986) of archaebacteria, or synthetic surfactants to create stable vesicular geometry membrane systems. The archaebacteria constitute a relatively recently discovered third kingdom of microorganisms, many of whom prefer extreme environmental conditions such as temperatures up to 110°C, pH values as low as 0.5 or as high as 11.5, and saturated saline (Kelly and Deming 1988).

The harsh environments preferred by these unique microbes indicate that robust biomimetic systems, based on the membranes of these bacteria, may be developed for treating industrial waste streams. In fact, the lipid membranes of some extremely thermophilic archaebacteria have been found to resist decomposition in boiling water and in eight-fold the detergent levels that normally would rupture most biological membranes (Bauer et al. 1983). Because of the extreme thinness of the lipid membranes (3 to 5 nm), much improved fluxes of metal species over liquid membranes would be expected. Because heavy metals often must be reclaimed from relatively dilute solution, biomimetic membranes capable of simultaneous, highly selective separation and concentration may be ideally suited for metal-recovery processes.

Our work focuses on developing vesicular or capsular membrane systems, which are similar in geometry to microbial cell membranes. Our vesicles are spherical capsules that are 100 nm in diameter and have walls composed of noncovalently assembled amphophilic lipid subunits. Because of the vesicles' small size, a large surface area is available for metal transport per unit mass of carrier. In fact, a typical 2% weight/volume (w/v) vesicular suspension presents a surface area for separation of approximately 6 x $10^3$ $m^2$/L. We are exploring the use of vesicular suspensions up to 10% w/v, which means the vesicles would occupy about 50% of the suspension volume.

Using vesicular biomimetic membranes for recovering metals follows two basic strategies: 1) encapsulating chelating agents in the vesicle core to give selective, high-capacity media for metal sorption, and 2) using pH gradients and selective, charged carriers to concentrate metal ions in the vesicle interior.

These two approaches differ in the method used to provide the driving force for metal uptake. In scheme (1), strong chelating agents such as ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) maintain the free metal ion concentration inside the vesicle at vanishingly low levels. In scheme (2), the vesicles can be operated as Donnan dialysis membranes, with a pH gradient serving as the driving force for metal uptake. Both schemes use 100-nm vesicles that harbor selective metal ion carriers in the vesicle shell. Figure 2.2 shows the system with the encapsulated chelating agent.

We have produced vesicles that harbor NTA at 10 millimolar concentration, and concentrations up to 1 molar are expected to be feasible. Given a 10% w/v vesicular suspension, divalent cations could be concentrated to ~0.5 molar using these media. Entrapping the chelating agents within 100-nm vesicles allows simple harvesting of the metal-laden media using micro/ultrafiltration hollow-fiber cartridges. Because the driving force for the separation is the encapsulated chelating agent and because NTA and EDTA have very high binding constants, metal ion concentrations in the surrounding solution can be driven very low. NTA-multivalent cation complexes exhibit stability constant logarithms ranging from 15.9 to 5.41 for the metal ions, which are listed below in order of affinity for NTA (Chaberek and Martell 1959):

$Fe^{3+} >> Cu^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+}, Zn^{2+} >$
$Cd^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$

Similarly, for EDTA the stability constant logarithms range from 25.1 to 8.69 for the metal-ion complexes listed below (Chaberek and Martell 1959):

$Fe^{3+} >> Cu^{2+}, Ni^{2+} > Pb^{2+} > Zn^{2+}, Cd^{2+}, Co^{2+} >>$
$Fe^{2+} > Mn^{2+} >> Ca^{2+} >> Mg^{2+}$

As a point of reference, the NTA binding constant for $Pb^{2+}$ is 6.3 x $10^{11}$ whereas it is 1.1 x $10^{18}$ for EDTA. Therefore, at equilibrium with sufficient EDTA, the concentration of lead in the chelated state is many orders of magnitude higher than that of the free ion. Obviously, this system can be used to drive metal-ion concentrations in a waste stream to vanishingly low levels, or it can be exploited for harvesting metal from very dilute solutions.

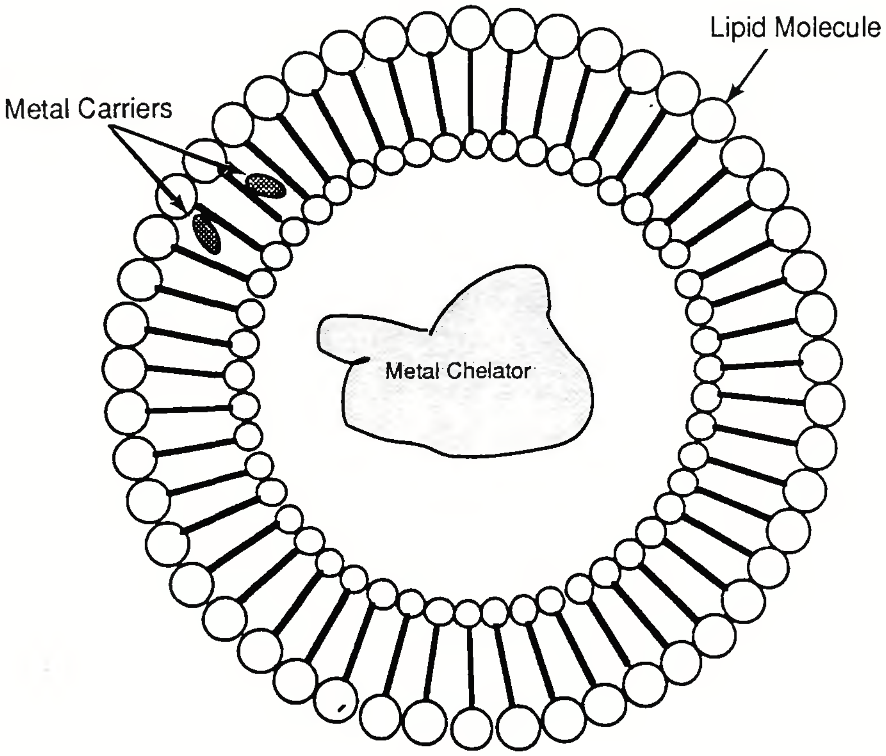

**Figure 2.2.** Metal-Sorbing Vesicle

This system's maximum selectivity is achieved when the selectivity of the metal carrier in the vesicle wall matches that of the chelator in the vesicle core. Because the chelator provides the driving force for metal uptake by depleting the free metal-ion concentration in the vesicle interior, it provides a greater driving force for ions for which it has the greatest affinity. If the metal carrier in the vesicle wall is characterized by a high affinity for the same ion(s) as the chelator, the overall metal ion selectivity of the vesicle system will be greater than that of the carrier or chelator alone. Likewise, if the selectivity profiles of the carrier and the chelator oppose one another, then the system will exhibit poorer selectivity.

Many carriers and chelating agents have been developed with various selectivity profiles that would be suitable for our system (Noble et al. 1989; Chaberek and Martell 1959). Currently, we have been working with the natural metal carrier or ionophore, A23187. The logarithms of equilibrium constants for 1:1 complexes between A23187, and various metal cations in 80% methanol in water have been reported to range from 9.77 to 4.5 for the metal ions listed below (Chapman et al. 1990):

$Cu^{2+} >> Ni^{2+} > Fe^{2+}, Co^{2+} > Zn^{2+} > Pb^{2+}, Cd^{2+} > Mn^{2+} >> Ca^{2+}, Mg^{2+}$

The data above suggest that A23187 and NTA or EDTA may work well together for the selective recovery of $Cu^{2+}$ from metal solution mixtures that do not include iron; EDTA and A23187 could perform satisfactorily for recovering nickel, if iron and copper are not present. However, the combination may perform less satisfactorily for selective lead or cadmium recovery from mixed metal solutions.

A23187 can also be used in metal-recovery schemes that do not depend on encapsulated chelating agents but use an opposing pH gradient to supply the energy to concentrate metal ions within the capsular membrane. This alternative metal-recovery strategy, scheme (2), requires the use of charged carriers that will exchange metal ions for protons. In the fully protonated or metal complexation state, the carrier system is neutral and free to traverse the hydrophobic core of the vesicle wall.

Other carriers worthy of investigation include the LIX carriers, which have proven useful for copper, nickel, and zinc recovery (Henkel Corp. 1987-88; Lonsdale 1984). Useful carriers must not only participate in proton/metal ion-exchange reactions and exhibit selectivity but also must be sufficiently lipophilic to remain immobilized in the vesicle wall. The chemistry and physical properties of the surfactants that form the vesicle wall become more important when this Donnan dialysis approach for metal recovery is taken. Vesicles composed of conventional phospholipids can maintain a pH gradient of 2 to 3 pH units, thus providing for the potential concentration of metal ions by several orders of magnitude (see 2.1, "Introduction"). However, certain LIX carriers require 1 to 2 molar sulfuric acid to strip metal ions from the carrier (Henkel Corp. 1987-88); therefore, surfactants that can withstand very low pH and much larger pH gradients may be necessary.

We have initiated a program to recover the unusual tetraether lipids from archaebacterial membranes. Certain archaebacterial species survive in environments at pH 0.5, yet their intracellular pH remains near neutral. Thus, their cell membranes, composed predominantly of tetraether lipids, can maintain pH gradients of several orders of magnitude. An example, ether lipid, which is a monoglucosylphosphoryl tetraether, is illustrated in Figure 2.3 (Bauer et al. 1983).

This surfactant is bipolar; the glycerol-based headgroups are connected to the hydrocarbon chains by ether instead of the much less stable ester linkages of conventional phospholipids. Also, the hydrocarbon chains are fully saturated and methyl branched. These features are thought to combine to make membranes composed of tetraether lipids more chemically stable and capable of holding extraordinary pH gradients. If the internal pH does not have to be maintained at very low pH values for effective metal uptake and concentration, then it may be practical to regenerate the loaded vesicles by lowering the external pH and "pumping" the metal ions out into a recovery stream.

A continuous two-step process is envisioned which uses hollow-fiber micro/ultrafiltration cartridges (see Figure 2.4). Vesicles with relatively low internal pH will be passed on the lumen side of the first-stage hollow-fiber cartridge, while a metal laden solution will flow through the shell side in countercurrent fashion. By passing the vesicles on the lumen side, they are protected from suspended solids and emulsions in the feed. Ultimately, in the envisioned process, vesicles that have sorbed metals in this first stage will pass to a second hollow-fiber cartridge, where the pH will be lower on the vesicle exterior.

The lower external pH in this second stage will release the concentrated metal species into a stream that could be treated for recovering pure

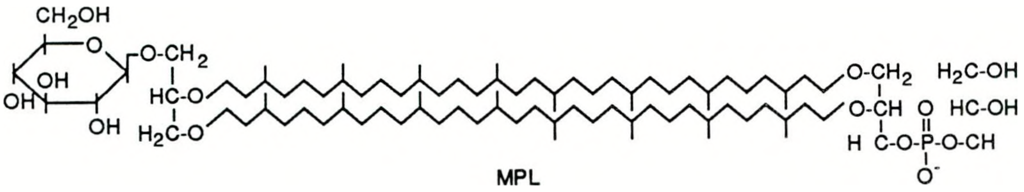

**Figure 2.3.** A Monoglucosylphosphoryl Tetraether Lipid

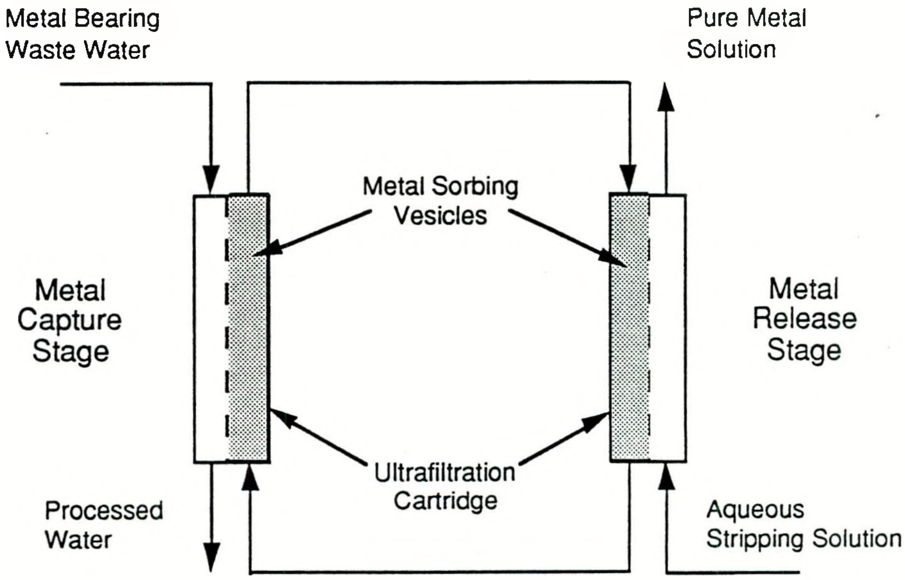

**Figure 2.4.** A Continuous Two-Step Process Using Hollow-Fiber Micro/Ultrafiltration Cartridges

metal or could be recycled to a metal-finishing process, for example. The emptied vesicles will return to the first stage to repeat the process. Two or more of these two-stage processes could be linked in series to further concentrate the metal ions.

The continuous metal-recovery scheme discussed above is most like the continuous moving bed ion-exchange system developed by CSIRO to exploit their 100-mm-particle-size magnetic resins (Bolto and Pawlowski 1987). These small particles exhibit improved metal-binding kinetics because they are small. Their size increases the fraction of binding sites exposed at the surface of the particles.

Our metal-sorbing vesicles, which are three orders of magnitude smaller than CSIRO's, push this concept further. Improved rates of metal uptake are expected, and the colloidal suspension of vesicles requires no special fluid-handling procedures. Problems in contacting waste or regenerant streams with a moving bed of small resin particles (Bolto and Pawlowski 1987) are eliminated in our hollow-fiber-based continuous recovery system, where the flow rates of the vesicle suspension, waste, and regenerant streams can be manipulated independently to optimize selective metal recovery.

## 2.3 ECONOMICS AND MARKET POTENTIAL

The traditional precipitation process to treat contaminated wastewater generates sludges that can contain highly toxic heavy metals. The EPA has explicitly defined electroplating wastewater treatment sludge as hazardous waste (EPA 1987; Cushnie 1985).

Given the diminishing number of hazardous waste landfill sites and the rising costs of disposal, increasing pressure is being placed on all aqueous metal waste generators to conserve and recycle heavy metals. Also, the EPA has placed limits of less than 1 ppm on the average concentration of heavy metal ions such as $Pb^{+2}$, $Cd^{+2}$, and $Zn^{+2}$ in effluent water from metal-finishing plants (Cushnie 1985). Therefore, the impetus for developing and commercializing new metal-recovery technologies that are highly selective and capable of reducing metal-ion concentrations into the ppb range originates from straightforward economics and from legal emissions restrictions.

The proposed biomimetic schemes should be competitive with existing metal-recovery processes, including increasingly popular systems based on ion-exchange resins. The vesicular membrane media that harbor chelating agents have a metal-loading capacity comparable to ion-exchange resins and are capable of high selectivity.

The biomimetic membrane vesicles that rely on pH gradients to concentrate metal ions have the advantage of very rapid kinetics because all the carrier binding sites are accessible at the surface of the vesicles. Also, these media can be used in continuous process configurations with a simple regeneration step for the efficient processing of large volumes of metal-laden waste. The energy requirements for this membrane process are minimal (i.e., power for fluid pumping) compared with evaporation, reverse osmosis, and electrolytic processes. Simple mineral acids solutions are used as regenerant solutions [for scheme (2)].

Estimates of capital costs for equipment and biomimetic membrane media are somewhat uncertain because no system has been constructed on even the bench-scale as of yet, and no efforts have been made to identify cost-effective materials (e.g., surfactants) for producing the metal-sorbing vesicles. However, the micro/ultrafiltration hollow-fiber cartridges will certainly be less expensive than high-pressure, reverse-osmosis cartridges; and the metal-sorbing media, if constructed with synthetic surfactants, should cost about as much as ion-exchange media. About 100 grams of surfactant will be used per liter of sorbent medium, whereas about a kilogram of resin is needed in a liter of an ion-exchange bed that gives about the same metal-sorbing capacity as the biomimetic system harboring a chelating agent.

Biomimetic membrane systems compare favorably with ion-exchange systems, which have received positive economic reports, further improving the economic outlook of biomimetic systems. For example, in 1988 dollars, an ion-exchange unit for treating 3,000 gal/day of electroplating wastewater costs about $16,000 installed (PRC 1989). The metal sludge volume was reduced 100-fold from that produced by the original precipitation/clarifier treatment system. The company saved $13,200 per year in materials purchasing and waste disposal and reduced their labor costs for operating and maintaining the system. Therefore, the payback period for the system is a little over a year. The biomimetic system may give even shorter payback times assuming that a selective system could recover reusable metallic species.

The metal-finishing and circuit board or microelectronics industries are users of the metals found in their wastewaters; therefore, these industries are logical targets for waste minimization attempts based on selective recovery and recycle of metal ions. The mining industry also generates substantial wastewater flows that contain metal ions at relatively dilute concentrations, typically less than 100 ppm (The Mining Waste Study Team 1988).

Another suitable application for our continuous metal-recovery system may be in California, where weathering and microbial action on abandoned sulfidic ore mining sites creates acid mine drainage that contains predominantly copper, cadmium, lead and zinc (The Mining Waste Study Team 1988). Other potential applications include decontaminating aqueous media contaminated with ionic radioactive species. Chelating agents such as NTA and EDTA have been used for sequestering radioactive ions and for recovering rare earth metal ions (Chaberek and Martell 1959). Vesicular membranes that harbor chelating agents may be most useful in applications requiring selectivity and the ability to reduce concentrations of target species to extremely low levels.

## 2.4 KEY EXPERIMENTAL RESULTS

We have created 100-nm-diameter vesicular membrane systems composed of the natural phospholipid surfactant--phosphatidylcholine or lecithin--with apparent shelf lives of several months. Our success stems from using equilibrium detergent dialysis rather than more traditional and harsh methods such as sonication or extrusion for vesicle formation (Szoka and Papahadjopoulos 1980).

Detergent dialysis has the added benefit of producing highly monodisperse vesicles, which we verified using light scattering. Our metal-sorbing vesicles harbor A23187 in the vesicle wall with the chelating agent, NTA, in the interior. Our current goal is to determine metal transport properties across the vesicle wall. In preliminary experiments, a vesicle suspension was loaded inside a dialysis bag in the absence of the metal to be transported. The dialysis bag has a sufficiently low-molecular-weight cutoff to prevent the escape of vesicles. The bag was then placed in a larger reservoir of an aqueous 1 ppm solution of $Zn^{2+}$.

Figure 2.5 illustrates the uptake of zinc by the vesicles along the lower curve. About 70% of the zinc in the reservoir is taken up by the vesicles during the experiment, thereby reducing the bulk metal ion concentration to about 300 ppb and concentrating it over 500-fold in the vesicle interior. The upper curve corresponds to a control experiment where the carrier is not present in the vesicle walls. Because little metal was taken up by these vesicles, the carrier clearly is critical for transferring metal ions to the chelator in the vesicle interior.

In this early work, the carrier and chelator concentrations used were low, as was the overall concentration of the vesicles in suspension. The overall kinetics of metal uptake are estimated to be able to be improved by 2 to 3 orders of magnitude by boosting the carrier concentration in the vesicle wall by a factor of 5 and the chelator and vesicle concentrations by up to a factor of 100 and 10, respectively.

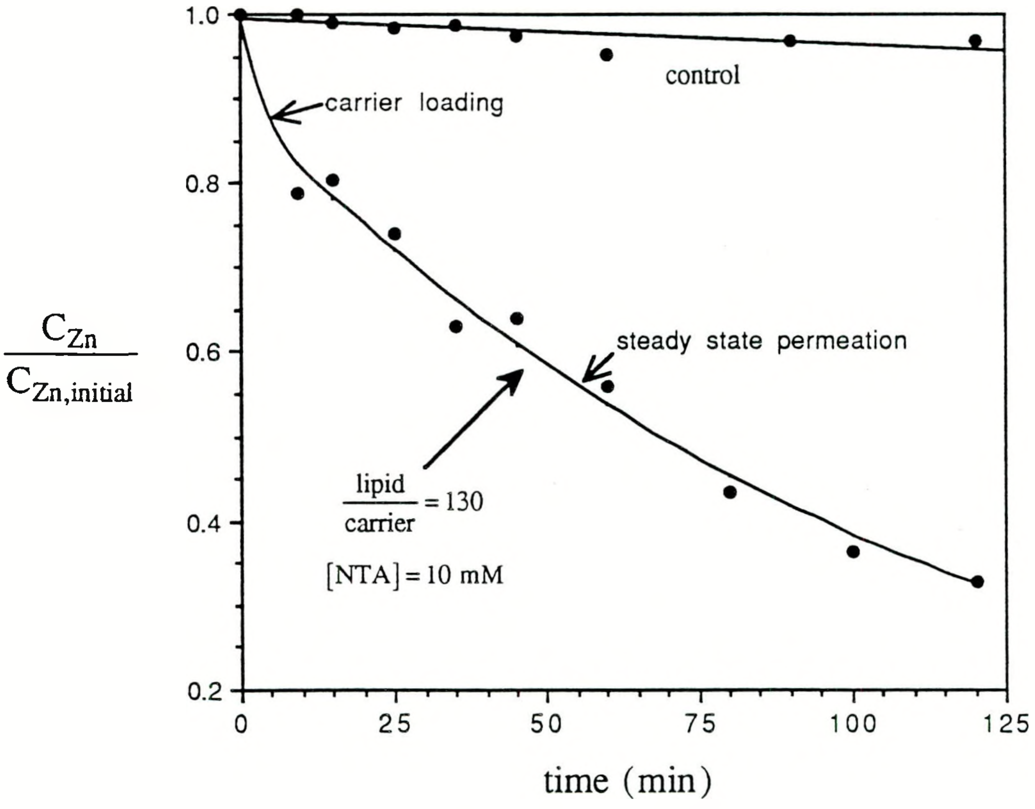

**Figure 2.5.** Uptake of Zinc by the Vesicles

Metal uptake by these vesicles occurs in two stages: 1) initial, very rapid metal complexation by the metal carrier at the vesicle surface, and 2) slower, steady-state transfer of the metal ions across the vesicle wall to the chelator in the vesicle's aqueous core.

The zinc-ion permeability through the vesicle wall was estimated at a constant $19.8 \pm 1.3 \times 10^{-10}$ cm/sec after the initial period of metal complexation by the carrier. (The experiment was not run long enough to detect saturation of the NTA.) To arrive at this estimate, we determined the permeability for the dialysis bag in the absence of vesicles and assumed zero concentration of free metal ion inside the vesicle because of the chelating agent.

This permeability is much lower than that expected for liquid-phase mass transfer through a 4-nm-thick lipid membrane, which suggests that the overall transport process is limited by the exchange of the metal ions between the A23187 metal carrier and NTA host molecules in the vesicle core. Nevertheless, extrapolating these early results to higher carrier and chelator loadings in the vesicles and higher vesicle concentrations in suspension suggests that the same experiment described above and in Figure 2.5 could be completed in one minute. Such rapid kinetics translate into higher processing rates, smaller equipment, and lower capital costs.

## 2.5 FUTURE DEVELOPMENT NEEDS

In the near future, we plan to focus our activities on determining the metal sorption kinetics and selectivity of our biomimetic vesicles for copper, cadmium, lead and zinc. These metal ions have been identified as priority metals for minimizing waste in the United States, based both on toxicity and natural resource depletion considerations (Patterson 1987).

Vesicles will be constructed with maximal carrier and chelator concentrations. Once the sorption (and desorption) kinetics of the system are known, it can be mathematically modeled to aid in designing the proposed continuous metal-recovery system. A bench-scale system will be assembled and tested, first with mock metal containing aqueous waste and second with actual process effluent. Based on bench-scale tests, the stability, treatment capacity, selectivity, and economics of the system at the commercial scale can be predicted with greater certainty.

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# 3.0 AC ELECTRO-COAGULATION PROCESS FOR REMOVING PARTICULATES AND METAL IONS FROM WASTEWATERS

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## ABSTRACT

Human health and environmental concerns dictate that industrial processes be improved or replaced and that effective control systems be developed to prevent and minimize related risks of wastewater pollutants. Wastewater treatment technologies are needed to more completely remove suspended and soluble pollutants.

As an alternative to chemical conditioning and flocculation, recent developments indicate that liquid-liquid and solid-liquid phase separation can be achieved using the alternating current electro-coagulation (AC/EC) process. The process has effectively coagulated a stable ultra-fine solid suspension using the principles of electrostriction (charge neutralization) and electro-coagulation (polymeric hydroxy species of metal ions) to facilitate rapid coagulation and to improve dewatering of stable suspension.

The AC/EC process was applied to a stable black water that was obtained from a subbituminous coal-processing plant. The water contained particles with an average size of 2 $\mu$m. The AC/EC process was successful in flocculating the particles using a slurry residence time of 20 to 60 seconds. The estimated processing cost of the process ranged from \$0.09 to \$0.36/1000 gallons, depending on the mixing proportion of the AC/EC-treated and untreated slurry.

Improving the performance of the AC/EC process is one of our main goals. Tests are being conducted on removing various metal ions from the solution, as well as improving the design of the cell, to reduce the retention time of the slurry in the cell.

## 3.1 INTRODUCTION

Our industrial society is becoming increasingly aware of the adverse impacts of inorganic and organic chemicals on the quality of water. Human health and environmental concerns dictate that industrial processes be improved or replaced and that effective control systems be developed to prevent and minimize related risks of wastewater pollutants. Wastewaters are of prime concern, and both the amount of wastewater that can be reduced and methods to remove pollutants must be reassessed. For that reason, research must continue to search for effective, efficient solutions to contamination that results from specific industrial sources and from groundwater and surface runoff.

Wastewater treatment technologies are needed to more completely remove suspended and soluble pollutants. One approach has been to adopt strategies that emphasize pollution reduction before wastewater is regenerated. One strategy involves separating fine and ultra-fine solid products that were previously wasted in waterwash operations. These solid products may be suspended, emulsified, and/or partially solubilized in aqueous media to the point of being potentially hazardous and toxic. Using conventional mechanical dewatering systems to dewater the wastewaters involves adding chemicals to increase solid agglomeration and settling.

Unfortunately, adding these chemicals increases the amount of waste generated.

Most of the ore and coal processing industries use wet processes for concentrating mineral and coal. Water, while being the workhorse of the industry, is also one of the most undesirable components in the final product. During mining and processing, excessive amounts of fine particles are generated, which are usually discarded as a stable suspension in a pond. For example, some of the hydro-metallurgical operations discard wastewaters containing various types of metal ions; removing or recovering these fine particles and metal ions from these wastewaters is costly. In addition, a vast area of prime land is required to dispose of these wastewaters, creating disposal ponds that are costly to maintain and environmentally hazardous. Coal and mineral processing industries are seeking help to resolve this problem, which would lower processing costs and protect our environment.

Several studies suggest that most solid particles suspended in aqueous media carry electrical charges on their surface (Vik et al. 1984; Jageline et al. 1979; Schwan 1962; Schwarz 1962). When the particles are larger than atomic or molecular dimensions, they tend to separate from aqueous media under gravitational force unless they are stabilized by electrical repulsion or other forces. Such forces can prevent the particles from aggregating into larger particle masses or flocs, which are more prone to settling. These surface charges may exist as an ionic double layer or as a neutralized electric depole.

Generally, the gravitational force on small particles is weaker than the other forces which can act on the particles. Collisions between particles because of Brownian motion often result in aggregates held together by Van der Waals forces, and coagulation may occur in the following ways:

- The particle's crystal lattice may contain a net charge resulting from lattice imperfections or substitutions. The net charge is balanced by compensating ions at the surface, such as zeolites, monmorillonite, and other clay minerals.

- The particle solids may contain ionizable groups.

- Specific soluble ions may be absorbed by surface complexes or compounds formed on the particle surface.

The stabilized particles in an aqueous suspension are usually removed using the flocculation technique, in which an organic polymer is added to the suspension, which attaches to the particles through a bridging mechanism. This mechanism brings particles together, forming flocs, which settle under gravitational force. Similarly, metal ions are usually removed from a solution through a neutralization process, in which alkali solution is added to precipitate the metal ion as the hydroxide precipitates.

As an alternative to chemical conditioning and flocculation, recent developments indicate that liquid-liquid and solid-liquid phase separation can be achieved using the AC/EC technique. The AC electro-coagulator has been used to flocculate and settle fine solids without using chemical aids (Parekh et al. 1990; Berry and Justice 1987). The AC/EC technique can be easily integrated with conventional processes and central systems to increase the recovery of solid products and to purify water. Waste could be reduced by integrating this technology with various operations that currently generate contaminated water.

The University of Kentucky's Center for Applied Energy Research (CAER) has been involved in research related to various aspects of coal and mineral processing waste treatment. The CAER is conducting a detailed evaluation of the applicability of the AC/EC process, which has been found to be technically feasible and cost-effective for removing fine particles and metal ions from wastewaters.

## 3.2 DESCRIPTION OF THE CONCEPT

The electro-coagulator process is based on two main colloidal chemistry principles using AC power and electrophoretic metal hydroxide coagulation:

- electrostriction, whereby the suspended particles are stripped of their charges by subjecting the particles to AC electrical field conditions in a turbulent stream
- electroflocculation, whereby minute quantities of metal hydroxides are emitted from the electrodes to help flocculate the suspended particles.

The theory of electroflocculation, or metal-ion flocculation, is well established. Iron and aluminum ions have been widely used to clarify water. Recently, Parekh (1979) and Parekh and Aplan (1988) developed a coagulation system that uses metal hydroxide and fine particles. They reported that the optimum coagulation of a metal ion/particle system occurs at the iso-electric point of the metal hydroxide precipitate. Jensen[a] suggests that optimum coagulation may not necessarily occur at the exact point of zero charge because other mechanisms, such as bridging, are also important.

The hypotheses for AC/EC operation are summarized as follows:

- Polar molecules adsorbed on the surface of small particles are neutralized by an equivalently charged diffuse layer of ions around the particle. A zero net charge results.
- Nonspherical particles have nonuniformly distributed charges (dipoles) and elongated neutralizing charge clouds surrounding them.
- These dipoles interact when the charge clouds are distorted by external forces or proximity of other charged particles.
- External forces such as electric fields can cause dipolar particles to form chains and can unbalance electrostatic forces, resulting in dramatic phase changes (coagulation).
- AC electric fields do not cause electrophoretic transport of charged particles, but do induce dipolar chain-linking and may also tend to disrupt the stability of balanced dipolar structures.

In the following subsections, the AC/EC system's design and operations are discussed.

### 3.2.1 AC/EC System Design

The design of the AC/EC system varies depending on the characteristics and quantity of waste or process streams being treated, on the treatment objectives, and on the location of the system. In the streams being treated, characteristics such as particle size, conductivity, pH, and chemical constituent concentrations dictate operating parameters of the coagulator. The quantity and flow rate of the raw solution will affect total system sizing, coagulator retention time, and mode of operation (recycle, batch, or continuous).

Treatment objectives will 1) establish the type of gravity separation system needed and the recovery criteria, 2) identify the usefulness of side stream treatment, 3) define effluent standards to be met, and 4) determine the advantages of recycling or multiple staging. Treatment objectives can include product recovery or just preconditioning before an existing process is used, or as a polishing step after treatment.

The location of the system will impact design by imposing physical size constraints and pumping

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(a) Personal communication with Professor J. Jensen, Civil Engineering Department, State University of New York at Buffalo, December 21, 1988.

requirements. In-plant industrial applications, for example, may be configured differently than a mobile onsite system used for remediating or treating ponded water.

Figure 3.1 shows a basic process flow diagram for the AC/EC process. Coagulation and flocculation occur simultaneously within the coagulator and in the product separation step. The redistribution of charges and onset of coagulation occur within the coagulator as a result of the aqueous solutions' exposure to the electric field and catalytic precipitation of aluminum from the plate electrodes. This reaction is usually completed within 30 seconds or less for most aqueous suspensions. The solution can be transferred by gravity flow to the product separation step.

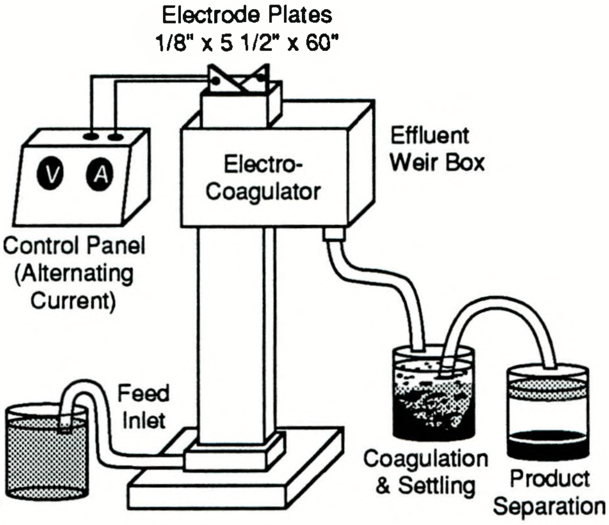

**Figure 3.1.** AC Electro-coagulator Process

Product separation can be accomplished in conventional gravity separation and decant vessels. Coagulation and flocculation continue in this step until the desired degree of phase separation is achieved. Generally, the rate of separation is faster using the AC/EC process than methods using chemical flocculants or polyelectrolytes; and for some applications, the solid phase is denser than the solids resulting from chemical treatment. A recent feasibility study demonstrated 95% to 99.5% recovery of submicron fines from a 0.6% stable suspension after 1.5 hours settling time (Parekh et al. 1990). Alternative treatment achieved only 80% removal after 1.5 hours.

In many applications, the electro-coagulator retention time may be reduced and performance improved by agitating the solution as it passes through the electric field. This turbulence can be induced by using a static aerator concept or by simply diffusing small bubbles of air or nitrogen through the solution in the space between the plates.

### 3.2.2 AC/EC Operation

The AC/EC process operates on low voltage, generally below 110 Vac. The system is designed to work at atmospheric pressure and is vented to alleviate any problems with gas accumulation. The internal geometry allows for free passage of particles less than 1/4 in. While normal operation is relatively maintenance-free, some problems can be encountered if process upsets allow heavy particulates to inadvertently enter the lines. In this case, material buildup could restrict passage and thus retard flow. No permanent damage has been experienced in these cases, and the problem has always been alleviated by reverse flushing or minor disassembly and cleanout.

While electrode deterioration was of some concern, in practice, no deterioration of consequence has been noted. Minor etching occurs on the electrode skins. As nearly as can be theorized, the AC cyclic energization retards the normal mechanisms of electrode attack that are experienced in direct current systems, and reasonable electrode life has been proven.

## 3.3 ECONOMIC AND MARKET POTENTIAL

The CAER, in conjunction with Co-Ag Technology, has conducted a survey of coal and mineral processing industries and has determined that the potential for AC/EC process is very high. Preliminary data obtained on some of the black water suspension were very impressive, and various coal companies have expressed interest in the process. Once the process is successfully tested at one plant, other plants will follow the lead.

The AC/EC process has a great potential for reducing the amount of waste being generated in the form of fine particle suspension. As mentioned earlier, this fine particle suspension is discarded in a settling pond which occupies a substantial size area. The AC/EC process will help improve productivity and maintain an ecologically safe environment.

The novel concept of the AC/EC process provides a unique economic process for effectively handling a large volume of waste steam from mineral, metal, and coal processing. The potential for applying the AC/EC process for other hazardous waste material treatment and for improving process efficiency of existing mineral and coal processing is very high. The concept provides a great opportunity for energy savings, thus reducing production costs.

Based on the flow rate and power consumption data, a preliminary economic evaluation of the AC/EC process is discussed below.

*Equipment Cost.* To treat 1800 gal/min of black water, about 9 AC/EC units, each capable of processing up to 200 gal/min, will be needed. The total equipment cost will be about $250,000. Amortizing the costs over a 15-year period of the equipment life equals a cost of $16,000/yr or $0.025/1000 gal.

*Power Cost.* Each electro-coagulator unit would consume about 50 kVA/h or 450 kVA/h for the 9 units. Assuming power cost at $0.04/kWh, the total cost would be $18.00/h, for a total power cost of $108,000/yr or $0.167/1000 gal. After the electro-coagulator has operated for a few months, the treated water is expected to have enough residual flocculating effect that a few units could be shut down; therefore, the total power cost will be decreased substantially.

*Electrode Costs.* Assuming 100% operation of the units and a changing of plates every 4 months, the total cost of the electrodes will be 9 x 3 x $3000 = $81,000/yr or $0.125/1000 gal. Again, this cost is expected to decrease because after a few months of treatment, the units will have to be operated at only 50% of the plant run time.

*Total Cost.* Assuming 100% operation of the units, the total cost will be $205,667/yr; however, at 50% operation time, the cost would be $111,167/yr or $0.17/1000 gal. Table 3.1 lists the power cost data for treating 1000 gallons of the slurry in various proportions. (For 25% AC/EC-treated slurry, the power cost will be about $0.09/1000 gal compared with the polymer cost, representing about a 75% savings.)

**Table 3.1.** Power Cost for AC Electro-coagulator-treated Slurry

| Percentage Exposed to Electro-coagulation | Dollars per 1000 Gallons |
|---|---|
| 25 | 0.09 |
| 50 | 0.18 |
| 75 | 0.27 |
| 100 | 0.36 |

Other potential benefits from retaining the propagation effect of the AC electro-coagulator-treated slurry include the following:

- longer pond life because of higher compaction of settled solids
- clearer clarified water for drain and rinse screen, resulting in improved magnetite recovery. Also, with less clay coming back into the system, a lower moisture product should result in fine coal circuit.
- cleaner screens, resulting in better classification efficiency

- less polymer consumption in the thickener (anticipated).

### 3.4 KEY EXPERIMENTAL RESULTS

As Figure 3.1 shows, the AC electro-coagulator equipment consists of two special aluminum alloy plates (5.5-in. wide x 60-in. long x 1/8-in. thick). This laboratory prototype is a single-cell setup.

The slurry enters the cell at the bottom and exits at the top. The velocity of the slurry is maintained at such a speed and agitated with air injected in the sump to provide Reynold numbers of about 10,000, thereby providing adequate turbulence and mixing. The AC power is applied to the aluminum electrodes through a variable voltage transformer. The equipment is usually operated at 100-V, 30-A, and 60-Hz frequency. However, varying frequency from 0.2 to 800 Hz with a current density of 0.08 to 6 A/in.$^2$ is recommended to identify optimum phase separation for a given system.

The CAER received two 55-gal drums of the stable suspension of black water from a subbituminous coal processing plant. After thoroughly mixing the slurry using a lightening mixture, a sample was collected to determine particle size distribution, pH, conductivity, and zeta potential. The average particle size distribution of the black-water solids was 1.8 $\mu$m. The zeta potential value of the solids was -49.9 mV, which indicates a high magnitude of negative charge and therefore a stable suspension. The pH and conductivity of the suspension were 7.37 and 2050 $\mu$Mhos, respectively. The high conductivity of the suspension is desirable for the AC electro-coagulator. The turbidity of the suspension was 3650 NTU and the percentage of solids was 0.299%.

The "as-received" slurry was treated through the laboratory-scale electro-coagulator using the conditions listed in Table 3.2. Ten liter samples of AC/EC-treated slurry were collected in cylinders that were 6 in. in diameter and 24 in. high. The settling rate of the flocculated material was monitored with time. At the end of the test, turbidity readings were taken of the supernatant.

**Table 3.2.** AC Electro-coagulator Test Conditions

| | |
|---|---|
| Flow rate of slurry | 2 to 6 L/min |
| Amperage | 10 to 25 |
| Volts | 30 to 70 |
| Frequency | 60 Hz |
| Amperage density | 0.08 to 0.20 A/in.$^2$ |
| Retention time | 20 to 60 sec |

No significant flocculation effect was shown at the 6 L/min of flow rate and 10-A (30 V) current density. Therefore, most of the tests were conducted at a flow rate of 4 and 5 L/min and 15 A and higher current density.

Figure 3.2 shows the settling rate curves of the slurry treated at various current densities at the 4 L/min flow rate; the 15- and 20-A tests had settling velocities of 20.0 cm/day and 24.8 cm/day, respectively. However, at 25 A, the settling rate was 30 cm/day. After a week's settling time, the compacted volume of settled solids for all the tests was very similar. The turbidity of the supernatant was ~15 NTU.

Figure 3.3 shows the settling rate curves at the 5 L/min flow rate. At 15 A, the settling rate of flocs was 16.4 cm/day. However, at 20 and 25 A it was 24.4 and 24.8 cm/day, respectively. Again, the clarity of the supernatant was ~15 NTU or less.

The data described above indicate that the 4-L/min flow rate provided better settling characteristics. Thus, all the tests reported hereafter were conducted at the 4-L/min flow rate.

The effect of amperage on the size of the flocs produced was examined and shows that, for a given flow rate, size of the flocs increases with increases in amperage.

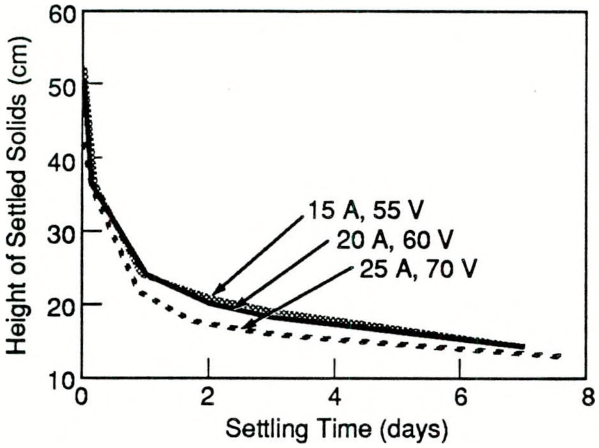

**Figure 3.2.** Settling Rate Curves of the Fine Solids Suspension at 4-L/min Flow Rate Using Various Current Densities

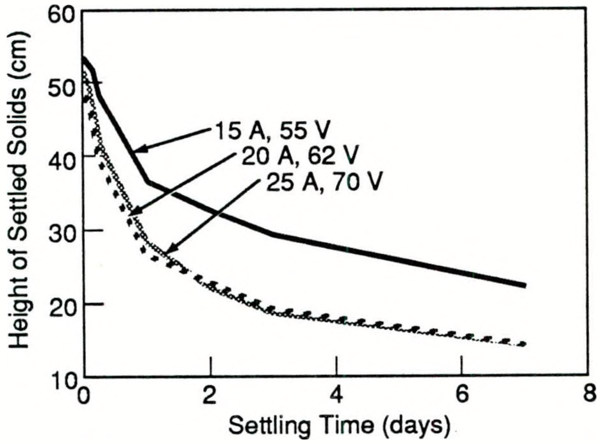

**Figure 3.3.** Settling Rate Curves of the Fine Solids Suspension at 5-L/min Flow Rate Using Various Current Densities

To study the effect of mixing the AC/EC-treated slurry with "as-received" untreated slurry, a series of tests (known as "propagation" tests) was conducted by mixing the treated and untreated slurries in various proportions, as shown in Table 3.3.

**Table 3.3.** Ratio of AC Electro-coagulator-treated and Untreated Slurries Used in the Propagation Tests

| AC Electro-Coagulator | |
|---|---|
| Treated | Untreated |
| 100% | 0 |
| 75% | 25% |
| 50% | 50% |
| 25% | 75% |
| 0% | 100% |

Figure 3.4 shows the settling rate curves for all four propagation tests. The 50% and 75% AC/EC-treated slurry had very similar settling characteristics. The 25% treated slurry, even though initially slower in settling, behaved very similarly to other slurries after 24 hours.

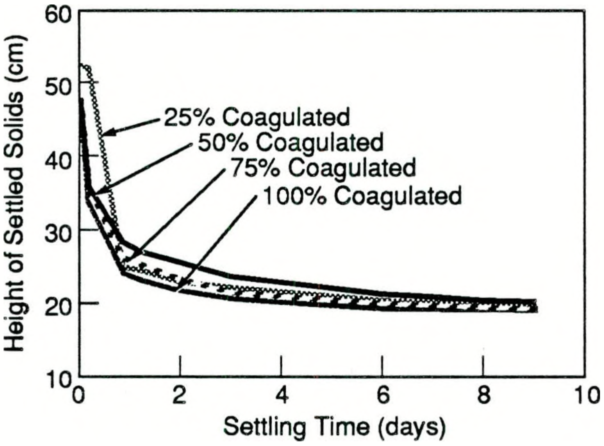

**Figure 3.4.** Settling Rate Curves for the Propagation Tests

Figure 3.5 shows the five cylinders after 2 hours of settling time. Even 25% AC/EC-treated slurry, when mixed with 75% untreated slurry, provided effective coagulation of particles. After 24 hours of settling time, all the cylinders were observed to

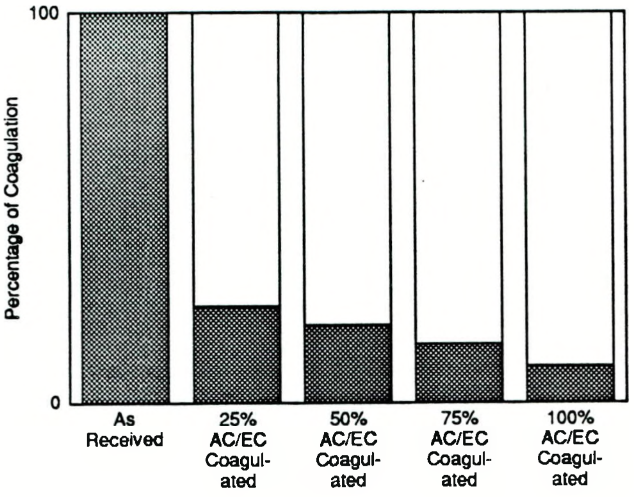

**Figure 3.5.** Propagation Test for the Black Water (dark shading indicates turbidity)

have a clear supernatant. The turbidity value of the percent solids in the settled zone was about 1.4%.

Figure 3.6 shows settling rate curves for the slurry treated with a 50-ppm AF363 polymer, manufactured by American Cyanamid in Wayne, New Jersey, and a 1:1 mixture of AC/EC-treated and untreated slurry. The AC/EC-treated slurry

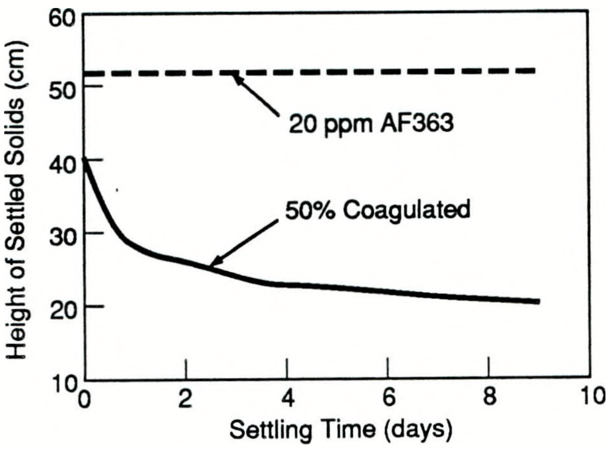

**Figure 3.6.** Settling Rate Curves Comparison of the AF363 Polymer and 50% Electro-coagulated Black-water Suspension

settled faster and gave a clear supernatant. With AF363, it was difficult to locate a clear solid-liquid interface; therefore, a straight line is shown. In this case, the turbidity of the supernatant after 8 days of settling was 2120 NTU, compared with 3650 NTU of the "as-received" slurry.

One additional test was conducted to study the effect of combining AC/EC-treated slurry with about 5 ppm of the AF363 polymer. The effect was very dramatic; big-size flocs were formed and the settling rate was much faster than the AC/EC-treated slurry alone. The supernate was clear.

## 3.5 FUTURE DEVELOPMENT NEEDS

Improving the performance of the AC/EC process is one of our main goals. Tests are being conducted on removing various metal ions from the solution, as well as improving the design of the cell, to reduce the retention time of the slurry in the cell.

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# 4.0 A NOVEL ION-EXCHANGE MEDIA FOR REMOVING LEAD FROM WASTEWATER STREAMS

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## ABSTRACT

Lead contamination in the environment has long been recognized as a serious health problem, and increasing pressure is being placed on industry to reduce lead wastes. Two bills addressing this concern are pending in Congress: the Lead Ban Act of 1990 (S-2593) and the Lead Exposure Reduction Act of 1990 (S-2367).

Current abatement and remediation procedures for process waters containing lead and other heavy metals include pH adjustment with lime or alkali hydroxides, coagulation-sedimentation, ion-exchange, and reverse osmosis. However, such procedures have drawbacks that limit their use.

In the 1960s, the U.S. Atomic Energy Commission researched the use of zeolite ion exchange of cesium from radioactive waste. Zeolites, naturally occurring minerals, are framework aluminosilicates with an infinitely extending three-dimensional network of $AlO_4$ and $SiO_4$ tetrahedra linked to each other by sharing of all the oxygens. Many types of zeolites of varying compositions exist throughout the world. The Commission's research led to the use of clinoptilolite and synthetic zeolites for removing cesium-137 from radioactive wastewaters and the sorption of radioactive wastes for long-term storage.

Zeotech Corporation recently developed an ion-exchange media by agglomerating natural zeolite fines into hard, permeable pellets that have a carbon matrix. Zeotech used the agglomerated and carbonized fines of two natural zeolite minerals: clinoptilolite from Tilden, Texas, which Zeotech calls "Zeocarb"; and chabazite from Bowie, Arizona, which Zeotech calls "Chabcarb." Zeocarb and Chabcarb demonstrate 30% to 50% greater ion-exchange capacity than their original zeolite constituents.

Chabcarb demonstrates a more rapid rate of ion diffusion than granular chabazite, and its carbon matrix may contribute additional sorption capacity by the hydrogen bonding of metal ions. Ion exchange using carbonized natural zeolite is a passive method for removing metal ions in which lead and other heavy metals are preferentially exchanged for nontoxic sodium, calcium, and potassium ions.

Leach column studies show that Zeocarb, chabazite, and Chabcarb reduce effluent lead levels from a 750 mg/L solution to less than 0.05 mg/L through many pore volumes. The column studies further demonstrate that Chabcarb can be loaded with more than 18 wt% lead.

The cost of carbonized and agglomerated zeolite pellets should be considerably less than synthetic ion-exchange resins. Accurate cost/benefit information for wastewater treatment will depend on the specific water to be treated. The most promising applications appear to be in treating wastewaters from government laboratories and processing facilities, metal-plating industries, electronics industries, smelters, foundries, and mines.

## 4.1 INTRODUCTION

The United States uses about 1.4 million tons of lead each year. Lead mining, refining, and milling are a $1.1 billion industry and employ 6,000 workers. The lead-acid battery industry contributes $3.3 billion to the U.S. economy (*Chemical Marketing Reporter* 1990).

Lead contamination in the environment has long been recognized as a serious health problem, and increasing pressure is being placed on industry to reduce lead wastes. An immediate concern is evidenced by two bills pending in Congress: the Lead Ban Act of 1990 (S-2593) and Lead Exposure Reduction Act of 1990 (S-2367).

Colorado has an estimated 15,000 abandoned metal mines and 1,300 miles of streams damaged by metals and acid drainage (Knudson 1990). The United States has an estimated 50 billion tons of mine tailings. Several of these locations have been designated Superfund sites by the U.S. Environmental Protection Agency (EPA).

Lead in drinking water is another concern. Current EPA drinking water standards for lead are 50 parts per billion (ppb), but a 20-ppb level has been proposed since 1985. The Illinois State Water Survey estimated that 53,000 water supply plants will have to improve their treatment processes to meet stringent new rules (Lin 1989).

Current abatement and remediation procedures for process waters containing lead and other heavy metals include pH adjustment with lime or alkali hydroxides, coagulation/sedimentation, ion exchange, and reverse osmosis. Lime is often used to treat waters from mining operations and contaminated areas to raise the pH and precipitate heavy metals in place. However, treating water with lime can produce metal hydroxide sludge, can resolubilize metals if the pH is lowered, and can damage aquatic organisms if the pH reaches 9 or higher or if low levels of dissolved oxygen result.

The metal-plating and metal-finishing industry generally treats acidic rinse waters with NaOH or KOH. As the pH of the solution rises above 8, the metal sludge precipitates and is disposed of in designated landfills. To meet regulatory requirements, additional treatment with ion-exchange resins or reverse osmosis is sometimes required. However, these processes have several drawbacks. Synthetic ion-exchange resins are expensive, and reverse osmosis requires considerable power to operate and is more effective for large organic molecules than uncomplexed metal ions.

To address lead abatement and remediation, in the 1960s the U.S. Atomic Energy Commission conducted research on the zeolite ion exchange of cesium from radioactive waste. Zeolites, naturally occurring minerals, are framework aluminosilicates with an infinitely extending three-dimensional network of $AlO_4$ and $SiO_4$ tetrahedra linked to each other by sharing of all the oxygens. Many types of zeolites of varying compositions can be found throughout the world. The Commission's research led to the use of clinoptilolite and synthetic zeolites for removing cesium-137 from radioactive wastewaters and the sorption of radioactive wastes for long-term storage (Mercer and Ames 1978).

By the mid-1970s the commercial potential of zeolite minerals became more widely known. Many companies acquired zeolite deposits and began researching applications. Four U.S. municipal wastewater treatment plants were constructed using zeolites to remove ammonia from tertiary effluent.

Semmens and Seyfarth (1978) found clinoptilolite to be selective for barium and lead. Their data were based on equilibration of heavy-metal solutions with zeolite washed with NaCl (conditioned) or leached with acid. Hertzenberg (1984) demonstrated that synthetic zeolite Na-A could remove heavy metals from pretreated, metal-plating wastewaters adjusted to a pH range of 8 to 10. Treating the wastewater with lime or caustic left the metal content above the EPA limits. When the wastewater was then treated with 0.25 g/L of zeolite Na-A, the levels of lead, cadmium, nickel, chromium, and copper were reduced to below the EPA effluent limits.

Blanchard et al. (1984) demonstrated that clinoptilolite may be effective for removing heavy metals, especially lead, in municipal wastewaters. Blanchard simulated removal of ammonia and heavy metals from municipal water, and a pilot plant processed 500 L/hr of water through a 65-L column of clinoptilolite. The influent concentrations were maintained at about 2.5 mg/L ammonium ions and 0.25 mg/L metal ions. Lead concentrations remained below 0.05 mg/L through 500 bed volumes.

Recently, researchers at the U.S. Bureau of Mines at the Reno Research Center compared 22 zeolites from around the United States for ion-exchange of metal ions from mine wastewaters. Clinoptilolite had the best properties for heavy-metal ion exchange (Zamzow et al. 1989). Metal ions were concentrated by a factor of 30 from the original wastewater and could be eluted with an inexpensive solution of NaCl. The researchers found that the tested zeolites had a large variability in cation composition, attrition resistance, trace mineral content, and ion-exchange capacities.

Preliminary studies at the Bunker Hill Superfund site have shown that clinoptilolite may be useful in stabilizing lead in contaminated soil so it will not leach out or be taken up by plants (Leppert 1990).

### 4.2 DESCRIPTION OF THE CONCEPT

In spite of considerable research, natural zeolites are not presently used for removing metals from waste streams because they are inferior to synthetic zeolites. Natural zeolites have low ion-exchange capacities and their chemical and physical properties vary even within a given zeolite deposit. Also, most natural zeolites contain several exchangeable cation species. They also contain trace amounts of clay, feldspar, silica, or calcite, which block channelways and reduce ion exchange well below theoretical capacity.

Cation exchange capacity (CEC) is measured by the number of channel-situated cations by unit weight that may be replaced by other ions in solution. High CEC in a zeolite mineral is favored by a low silica-to-alumina ratio (Breck 1974). CEC also is higher in monomineralic zeolites with high sodium and low amounts of other exchangeable cations. The zeolite should be hard in order to provide good resistance to attrition and should have a porous and permeable network of crystals to provide rapid diffusion of ions in solution. Natural zeolite deposits with all of these characteristics are uncommon.

Several years ago Zeotech began researching potentials uses for zeolite fines, a by-product of producing granular pet waste products and aquarium filtration media. Zeotech's process for removing lead from wastewater streams is a novel approach to enhance the CEC of inexpensive and abundant, natural zeolites. By forming pellets from natural zeolite fines, a permeable structure is created and increases ion-diffusion rates. The carbon matrix is made by agglomerating zeolite fines with lignosulfonate to form an insoluble carbon matrix around the fine zeolite particles. The carbonized natural zeolite pellets could have an immediate application at mine waste sites, metal-plating plants, lead acid-battery manufacturing sites, and contaminated industrial sites.

The zeolite's linking of the network of $AlO_4$ and $SiO_4$ tetrahedra by sharing of all the oxygens forms a molecular structure with many apertures and channelways. The net negative charge of the molecular framework is balanced by the presence of alkali and alkaline earth cations. Ca, Na, and K are loosely bonded to the crystal structure and are free to exchange with cations in solution.

Recently, Zeotech pelletized the zeolite fines in a rotating pan agglomerator with lignosulfonate solution as the pellet binder. The resulting pellets were dried and then heated in an oxygen-reducing environment until the lignosulfonate was burned off and only a carbon residue remained to bind the zeolite particles. The resulting pellets are hard, permeable, and insoluble in water.

X-ray diffraction analysis shows that the fine zeolite particles in the pellets retain their crystallinity. The surface texture of the pellets is coarse and has fissures for ingress and egress of solution for high rates of ion diffusion.

Carbonized, natural zeolite ion exchange is a passive method for removing metal ions in which lead and heavy metals are exchanged for nontoxic sodium, calcium, and potassium ions as water passes through tanks or columns. The heavy-metal, loaded carbonized zeolite could be disposed of as metal-bearing ore to a smelter or as waste to an appropriate landfill. It could also be regenerated by elution with a NaCl solution. The eluted heavy metal solution would be treated with caustic to precipitate the sludges in a holding tank. The sludge would be disposed of and more process water would be passed through the cleaned zeolite bed.

## 4.3 ECONOMICS AND MARKET POTENTIAL

Potential applications for Zeocarb and Chabcarb exist in wastewater streams that contain lead levels greater than the standards for drinking water and that have relatively low salinity. Chabcarb may be useful as an ion-exchange media in potable water systems containing lead from solder flux or from natural sources. The most promising applications appear to be in treating wastewaters from metal plating, electronic industries, smelters, foundries, and mining.

The cost of agglomerated and carbonized zeolite pellets should be considerably less than synthetic ion-exchange resins. Preliminary estimates suggest a delivered price of $0.20 to $0.35/lb depending on the type of zeolite used in the formulation. Accurate cost/benefit information for wastewater treatment will depend on the specific water to be treated.

Blanchard et al. (1984) estimated the cost of processing municipal wastewater through a clinoptilolite system to be $0.018/M$^3$ of water ($0.009/gal). Hertzenberg (1984) demonstrated that adding 0.5 g/L of synthetic zeolite Na-A could remove several metal-ion species from 1 to 2 mg/L to less than 0.3 mg/L. Zeocarb and Chabcarb may be equally as effective.

Many potential uses for Zeocarb and Chabcarb ion exchange exist where expensive treatment plants are impractical. The simplicity of flowing contaminated waters through a relatively inexpensive media and then replacing the media with a new batch will be especially beneficial for small waste sites, such as abandoned metal mines and mine tailing piles, where electricity may be unavailable. Concrete or metal tanks containing Zeocarb could be connected in series. Once a tank is saturated with 12 to 18 wt% lead or combined metals, the media could be removed and shipped to a smelter for processing or could be disposed of in an approved manner.

Ion-exchange columns of Zeocarb could be used for cleaning heavy-metal-contaminated groundwater. The cost of treatment should be less than synthetic resins and more effective than activated carbon.

## 4.4 KEY EXPERIMENTAL RESULTS

Laboratory work consisted of 1) testing ion-exchange media for selectivity at varying concentrations of lead, 2) measuring the rate of ion exchange, and 3) determining the exchange capacity. More than 1000 chemical analyses were performed using atomic absorption and inductive coupled plasma methods. The following subsections present the results of batch and column tests.

### 4.4.1 Batch-Shake Tests

Batch-shake tests were conducted to determine the selectivity that 13 ion-exchange media had for lead. Clinoptilolite, chabazite, phillipsite, attapulgite, montmorillonite, pillared clay, and granular-activated carbon were tested to determine which were most promising for continued testing. The batch-shake tests were conducted by loading a weighed amount of ion-exchange media into a known volume and concentrating metal-ion solution according to ASTM 4019 and then agitating the solution on a shaking table for 14 hours.

Clinoptilolite from Tilden, Texas (Zeobrite); agglomerated and carbonized fines of Zeobrite (Zeocarb); sodium chabazite from Bowie, Arizona;

and agglomerated and carbonized fines from the Bowie chabazite (Chabcarb) were analyzed. The purpose of the analysis was to determine chemical composition, bulk density, and surface area using nitrogen absorption. Also, standard soil sample procedures measured total CEC.

Zeobrite is composed of about 60% clinoptilolite and 40% montmorillonite and opal-CT. Calcium is the predominant, exchangeable cation; and sodium and potassium are secondary exchangeable cations. Bowie chabazite is practically monomineralic and contains sodium as the predominant exchangeable cation. Zeocarb and Chabcarb reflect the chemistry and mineralogy of their constituent zeolites and contain 3% to 4% carbon as a matrix.

Figure 4.1 is a scanning-electron micrograph of the surface of a Zeocarb granule and shows the abundant fissures and pore space for ingress and egress of metal-bearing solutions. Figure 4.2 shows the interior of the same Zeocarb granule with clinoptilolite crystals and crystal fragments cemented by amorphous carbon. Carbon coats and binds the micron-sized zeolite crystals and fragments.

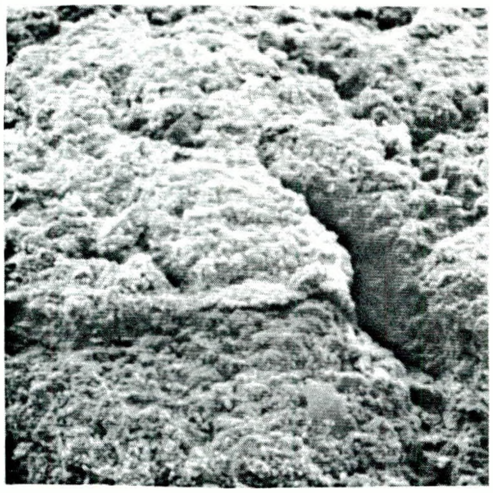

**Figure 4.1.** Scanning Electron Micrograph Showing the Rough and Fissured Exterior of a Zeocarb Granule (magnification 70 times)

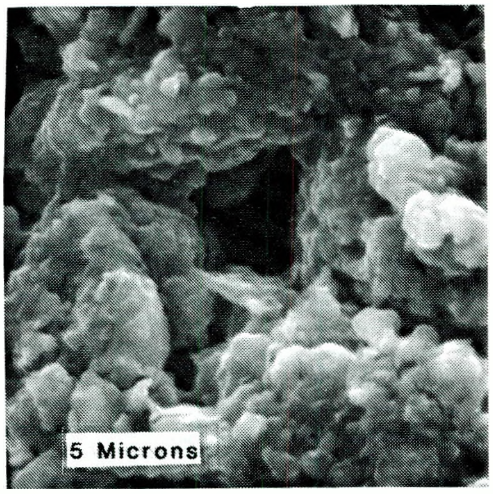

**Figure 4.2.** Scanning Electron Micrograph Showing the Interior of a Zeocarb Granule (magnification 3000 times)

Relative rates of ion exchange were tested by shaking 2.0 g of media in 100 mL solutions of 260 mg/L lead for intervals from 60 seconds up to 30 minutes. Those test results are shown in Figure 4.3 and demonstrate a very rapid rate of ion exchange for Chabcarb, probably because the agglomerated and carbonized product has better ion-diffusion rates and higher total exchange capacity. The tests showed that Zeocarb did not exchange lead as rapidly as Zeobrite; however, subsequent tests demonstrate that Zeocarb has a greater total exchange capacity. The increased exchange capacity of the pellets cannot be explained simply by the sorption onto the added carbon.

Granular-activated carbon (GAC) sorbs lead ions onto its surface by hydrogen bonding (Corapcioglu and Huang 1987), but it has limited capacity, as shown in Figure 4.3. The carbonized zeolite pellets are assumed to also sorb metal ions onto carbon in the matrix of the pellets. Initial and final solutions show good correlation of the ionic mass balance, suggesting that ion exchange is the predominant method for removing heavy-metal ions from solution. The same data further suggest that new compounds are not being formed or precipitated in the ion-exchange media.

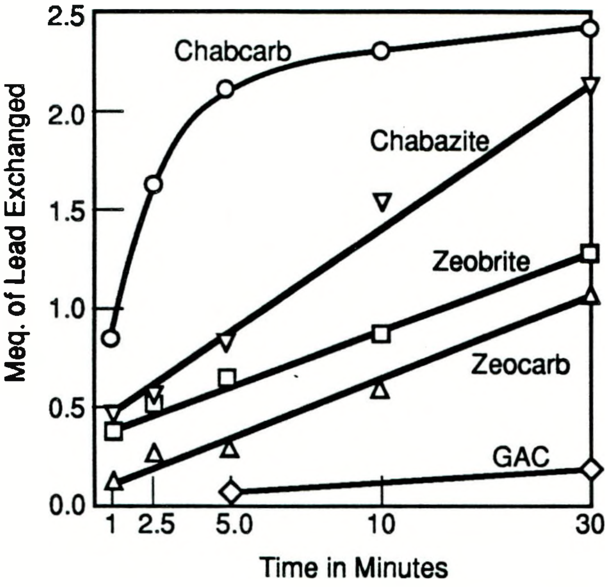

**Figure 4.3.** Rate of Ion Exchange (2.0 g of media shaken in 100 mL solutions of 260 mg/L lead)

Table 4.1 shows the cation concentrations of initial and final water in batch-shake tests with different ion-exchange media and with different initial lead concentrations. However, the efficiency of heavy-metal removal is affected by the composition of the waste stream. Many anion and cation species can be found in effluent wastewater streams from most industrial sources. Generally, anions pass through zeolite exchange media without a change in concentration. The U.S. Bureau of Mines conducted research to determine the effect of competing cations on the ion-exchange capacity of heavy metals (Zamzow et al. 1989). Their data show that each metal cation is affected at different levels of concentration of competing cations; but in general, calcium in the influent water greatly decreases the uptake of heavy-metal ions.

**Table 4.1.** Batch Ion-exchange Analyses Concentrations in mg/L
(2.0 g media in 100-mL solution shaken 14 hr, then filtered)

| | | Concentration | | | | Concentration | |
|---|---|---|---|---|---|---|---|
| Ion-Exchange Media | | Initial | Final | Ion-Exchange Media | | Initial | Final |
| Zeobrite | Pb | 83.0 | 8.7 | Zeobrite | Pb | 811.0 | 9.4 |
| | Na | <1.0 | 43.0 | | Na | <1.0 | 90.0 |
| | Ca | <1.0 | 7.5 | | Ca | <1.0 | 76.0 |
| | K | 0.6 | 7.7 | | K | 1.1 | 41.0 |
| | Mg | <0.5 | 2.0 | | Mg | <0.5 | 3.0 |
| | pH | 4.07 | 8.01 | | pH | 2.89 | 6.04 |
| Zeocarb | Pb | 83.0 | 0.86 | Zeocarb | Pb | 811.0 | 12.0 |
| | Na | <1.0 | 53.0 | | Na | <1.0 | 77.0 |
| | Ca | <1.0 | 15.0 | | Ca | <1.0 | 107.0 |
| | K | 0.6 | 4.5 | | K | 1.1 | 7.4 |
| | Mg | <0.5 | <0.5 | | Mg | <0.5 | 3.0 |
| | pH | 4.07 | 7.96 | | pH | 2.89 | 6.14 |
| Chabazite | Pb | 83.0 | 1.7 | Chabazite | Pb | 811.0 | 2.9 |
| | Na | <1.0 | 109.0 | | Na | <0.1 | 264.0 |
| | Ca | <1.0 | 1.0 | | Ca | <1.0 | 2.3 |
| | K | 0.6 | 0.9 | | K | 1.1 | 1.7 |
| | Mg | <0.5 | <0.5 | | Mg | <0.5 | 1.2 |
| | pH | 4.07 | 6.27 | | pH | 2.89 | -- |
| Chabcarb | Pb | 83.0 | 0.2 | Chabcarb | Pb | 811.0 | 1.0 |
| | Na | <0.1 | 209.0 | | Na | <1.0 | 343.0 |
| | Ca | <0.1 | 3.0 | | Ca | <1.0 | 10.0 |
| | K | 0.6 | 1.2 | | K | 1.1 | 1.8 |
| | Mg | <0.5 | 1.0 | | Mg | <0.5 | 65.0 |
| | pH | 4.07 | 7.51 | | pH | 2.89 | 6.72 |

Table 4.2 shows the batch-shake results of ion exchange of a metal-plating wastewater. The wastewater contained 130 mg/L sulphate and 80 mg/L chloride, and was spiked with 76 mg/L lead. Zeocarb removed 91% of the lead and added calcium and sodium to the final solution. Chabazite removed 99% of the lead and added sodium to the final solution. It also removed calcium and potassium from the initial solution.

**Table 4.2.** Ion Exchange of Metal Plating Wastewater (2.0 g media in 100-mL solution shaken 14 hr then filtered)

| Media | | Concentration (mg/L) Initial | Final |
|---|---|---|---|
| Zeocarb | Pb | 76.0 | 7.0 |
| | Na | 87.3 | 189.0 |
| | Ca | 39.8 | 276.0 |
| | K | 51.8 | 21.0 |
| | Mg | 7.9 | 11.0 |
| Chabazite | Pb | 76.0 | 0.9 |
| | Na | 87.3 | 397.0 |
| | Ca | 39.8 | 4.0 |
| | K | 51.8 | 4.5 |
| | Mg | 7.9 | 4.0 |

A limited amount of work was done to determine the selectivity of the ion-exchange media for cadmium. In batch-shake tests, Zeobrite, Zeocarb and chabazite removed 78%, 83%, and 99%, respectively, of 20 mg/L cadmium in 100 mL of deionized water.

### 4.4.2 Column Experiments

Column experiments were designed to provide information on the ion-exchange capacity of the zeolite media. Many filtration systems are designed using the same principles as a column experiment. Column tests simulate natural conditions and do not mechanically degrade the ion-exchange media as do batch-tests. They also allow the flow rate to be controlled and the sampling to have a greater resolution.

Ion-exchange capacity is measured by breakthrough curves; breakthrough occurs when the concentration of effluent equals the concentration of influent. A breakthrough curve is shown in Figure 4.4. The shape and position of the curve are important in evaluating the exchange characteristics of the media.

For the column experiments, ion-exchange columns were constructed with polycarbonate tubes that were 3-in. ID x 12 in. long and that were screened and stoppered at both ends. About 10 in. of media was loaded into each column. Feed solution contained in collapsible polyethylene bags was gravity-driven through the columns from the bottom up to minimize entrapped gas. Figure 4.5 shows a typical column setup. Pore volumes were calculated for each column by subtracting the volume of crystalline material loaded in the column from the total volume. Pore volumes of effluent solution were collected for analysis every 6 hours, and pH was monitored throughout the experiment. The samples were analyzed for lead and occasionally for exchanged ions.

The column tests were run in two phases. In the first phase, a 50 mg/L lead feed solution was run through three materials: Zeobrite, Zeocarb, and chabazite. Each material was tested in replicate columns. After 19 pore volumes (PV), each of the replicate columns was taken off line. After 128 PV, the Zeobrite column began to show concentrations of lead above the EPA's 0.05 mg/L maximum concentration limit for drinking water. At 200 PV, the chabazite and Zeocarb columns were still below the lead limit for drinking water. The data appear to be very promising for chabazite and Zeocarb.

In the second phase, a solution of 750 mg/L lead in deionized water at a pH of about 3.5 was run through columns of Zeobrite, Zeocarb, chabazite, and Chabcarb. The columns contained 6 in. of media in 3-in.-ID tubes. The purpose of the second phase was to accelerate breakthrough and examine ion exchange of the zeolite systems under extreme conditions. The columns were bled rapidly to produce the first pore volume. The resulting effluent contained up to 1.0 mg/L lead.

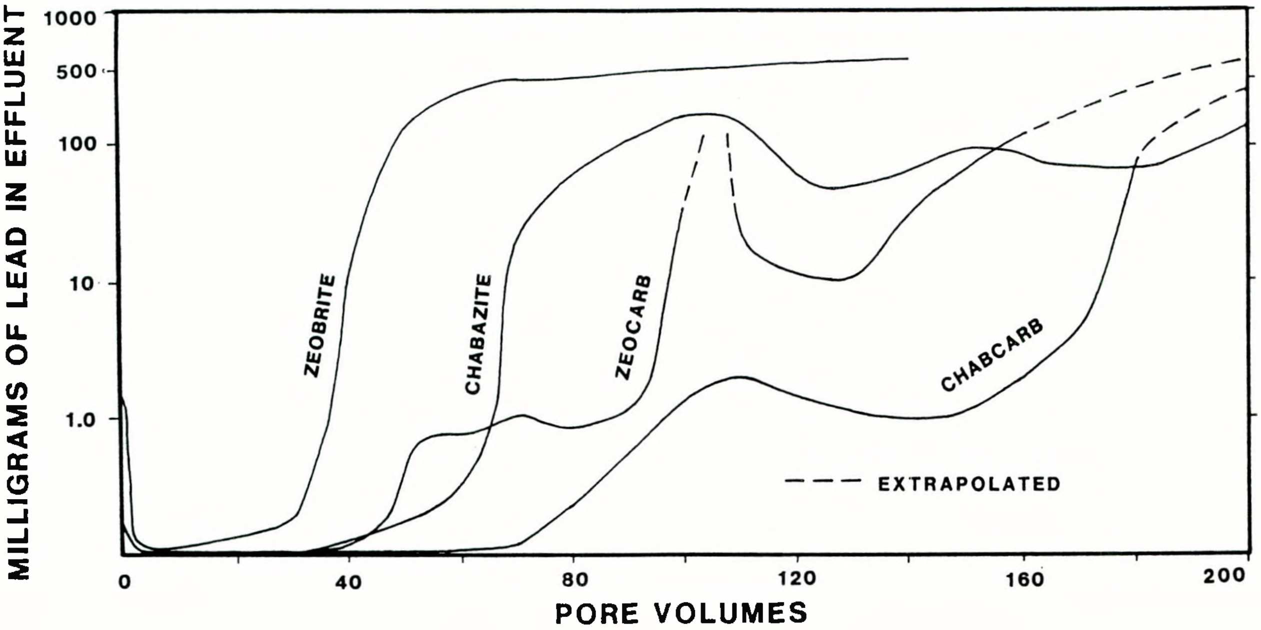

**Figure 4.4.** Breakthrough Curves for Ion-exchange Media

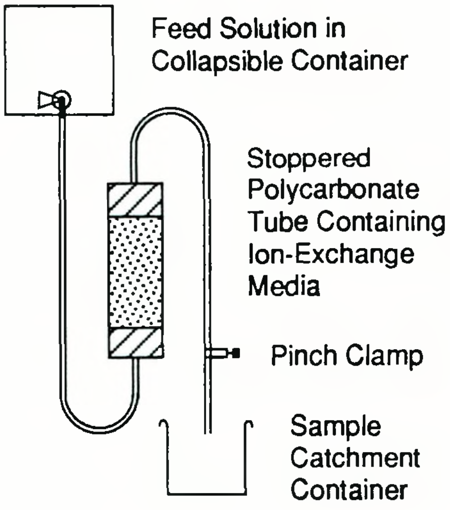

**Figure 4.5.** Design of Leach Column Apparatus

Subsequent collections of effluent demonstrated the effectiveness of all four zeolite products to remove the 750 mg/L lead influent to within EPA standards for drinking water. The media's exchange capacity for breakthrough of standards for drinking water are shown in Table 4.3. The table also shows the exchange capacity of each media extrapolated to 500 mg/L lead or 75% of breakthrough. The 75% breakthrough point was chosen because of the difficulty of extrapolating the curve as it attenuates at higher concentrations of lead in the effluent.

Breakthrough of Zeobrite occurs very rapidly between 1.0 mg/L and 100 mg/L lead, as shown in Figure 4.5. Chabazite breaks through quite rapidly between 50 and 80 PV from 1.0 mg/L to about 100 mg/L lead in the effluent. However, the normally steep breakthrough curve flattens out between 80 and 200 PV, and chabazite continues to exchange about 80% of the influent lead.

Zeocarb removes the 750 mg/L lead influent to less than 1.5 mg/L through 90 PV. A mistake in the setting of the flow rate resulted in 11 PV passing through the column in one 6-hour collection period between 100 and 111 PV. The increased flow destroyed the concentration gradient in the column and resulted in premature breakthrough, as shown by the sharp inflection in the curve for Zeocarb in Figure 4.5. After the flow was returned to the

**Table 4.3.** Ion-Exchange Column Data[(a)]

| | Zeobrite | Zeocarb | Chabazite | Chabcarb |
|---|---|---|---|---|
| Grams of media | 450 | 333 | 298 | 257 |
| Pore volume (ml) | 295 | 339 | 349 | 389 |
| Exchange capacity (meq/g) at breakthrough of 0.05 mg/L Pb | 0.07 | 0.18 | 0.30 | 0.71 |
| Exchange capacity (meq/g) measured at 160 PV | -- | 1.11 | 1.27 | 1.75 |
| Exchange capacity (meq/g) extrapolated to 75% of breakthrough | 0.47 | 1.40 | 1.60 | 2.20 |
| pH at 10 PV | 7.2 | 8.2 | 7.7 | 8.2 |
| pH at 70 PV | 3.6 | 7.0 | 4.2 | 7.1 |
| pH at 160 PV | -- | 4.9 | 4.0 | 5.9 |

---

(a) Feed solution was 750 mg/L lead at a pH of 3.5; the rate of flow was 1 PV/6 hr.

normal collection rate, the effluent lead dropped back down to less than 10 mg/L.

Chabcarb reduced effluent lead levels to within drinking water standards through 65 PV and did not break through 1.0 mg/L lead in the effluent through 95 PV. At 200 PV, Chabcarb had exchanged 1.98 meq. lead/g (20% by weight).

Zeocarb and Chabcarb may have greater exchange capacity than their original zeolite constituents as a result of hydrogen bonding of lead on carbon surfaces. The agglomerated nature of the pellets may also allow for more complete ion diffusion. Surface areas measured by BET nitrogen absorption do not appear to be any greater for agglomerated and carbonized fines than for crushed and screened granules, as shown in Table 4.1.

Zeocarb and Chabcarb buffer the influent solution to a greater extent than the regular zeolite granules, but analysis of influent and effluent solutions shows a molecular balance. The mechanism for removing lead is ion exchange rather than precipitation of lead in the media, resulting from pH change.

## 4.5 FUTURE DEVELOPMENT NEEDS

The batch and column testing to date demonstrates that the agglomerated and carbonized zeolite fines provide more ion-exchange capacity than untreated zeolites. They also demonstrate that high concentrations of lead can be reduced to levels within drinking water standards. While these findings are encouraging, considerable more research needs to be done.

Previous research has shown that heavy-metal removal by zeolites depends on the chemistry of both the influent water and the zeolite media itself.

Each wastewater stream should be analyzed to determine the number and concentration of 1) metal ions targeted for removal, 2) competing ions such as alkali and alkaline earth cations, 3) anions, and 4) pH-Eh conditions. The analytical results should indicate the feasibility of treatment for each stream. Zeolite media will not be effective for removing all species of heavy metals and will not be effective with waters of high salinity.

After the analytical screening has been done, specific process wastewaters should be tested to determine its heavy-metal content and applicability for using the concept. Then, a pilot plant should be designed and operated in accordance with the laboratory findings. Opportunities should be sought to treat heavy-metal wastewater from government laboratories and processing facilities, metal-plating wastewater, mine drainage water, and water from manufacturing. Evaluations will be necessary to determine whether it is more cost-effective to dispose of the ion-exchange media after initial use or to elute the concentrated metals and recycle the media.

The findings of this study suggest that carbonized and untreated zeolites may be useful in other waste cleanup applications. Heavy-metal sludge and smelter slag could be stabilized and solidified with zeolites to comply with recent regulations from the EPA. Zeolites could be used as a substrate in constructed wetlands for buffering acid mine drainage water and binding metals by ion exchange. Zeolites and carbonized zeolites may be useful for treating wastewater from uranium tailings and for sorption of some toxic organic compounds. Further testing will be necessary to determine if these additional applications are feasible.

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# 5.0 USE OF CHITOSAN BEADS TO REMOVE HEAVY METALS FROM WASTEWATER

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## ABSTRACT

Heavy-metal pollution of groundwater is a pervasive and extremely serious environmental problem. The cleanup costs for groundwater pollution have been very high and are likely to increase. Furthermore, the well-documented health hazards of heavy-metal contamination require that contaminated water sources be treated.

Current solutions for cleanup of heavy-metal contamination are primarily "pump and treat" processes, where the water is pumped out of an aquifer or well, treated, and returned to the aquifer or sent to municipal waste treatment. While effective, these processes generally do not permit the recycling or recovery of the potentially valuable heavy metals.

Our concept uses a fluidized bed containing magnetic biopolymer adsorbent beads that are immobilized in an externally applied magnetic field. The dilute aqueous waste stream first passes through the adsorber bed, and heavy metal ions chelate onto the biopolymer bead in concentrated form. By periodically releasing the magnetic field, the heavy-metal laden beads pass down into the desorber bed. By lowering the pH of the desorbent stream, heavy-metal ions are recovered in concentrated form, and the beads are regenerated.

We have produced the adsorbent particles using chitosan, a low-cost aminopolysaccharide that is a by-product of shellfish processing and that has a very high affinity for nonalkali metals. We have demonstrated that two methods can be used to produce magnetic adsorbent particles: incorporation of magnetite particles and in-situ generation of magnetite from iron salts. The chelation is reversible, and heavy metals can be desorbed from the bead by reducing the pH of the surrounding liquid to about 2.

## 5.1 INTRODUCTION

As a class of unit operations, separations are extremely important because they consume up to 70% of the capital costs and 80% of the energy in petroleum refining and chemical manufacturing processes. Separation processes are even more important in meeting environmental regulations, where toxic materials, often at very low concentration, must be removed from gas or liquid streams before they are released to the environment. An appropriate separation process must be chosen to remove the waste material to meet an emission standard. Not surprisingly, a National Research Council report on research needs in separations and purifications identified the removal of solutes from very dilute solutions as a high priority research need (King et al. 1987).

The U.S. Environmental Protection Agency (EPA) has designated groundwater pollution as the most serious problem resulting from over 400 Superfund hazardous waste cleanup sites. In a recent review of the escalating problem of water pollution from organic chemicals and heavy metals, Hooker (1990) estimated that 1% to 3% of all U.S. groundwater is contaminated. He presented several examples of the severity of the problem. For example, over half of New Jersey's population depends on wells for drinking water. In the last 5 years, over 2000 of their wells were closed because of groundwater pollution from waste discharges from industrial and chemical manufacturers. Also, groundwater around all 16 federal nuclear weapons production facilities is polluted with toxic and/or radioactive heavy metal wastes, and the Department of Energy estimates that cleanup costs may exceed $30 billion (Hooker 1990).

Most processes for removing heavy metals from groundwater can be classified as "pump and treat" processes, where the water is pumped out of an aquifer or well, treated, and returned to the aquifer or sent to municipal waste treatment. For example, at a cleanup project sponsored by the EPA Superfund at the site of the United Chrome plating facility in Corvallis, Oregon, approximately $7.6 million dollars has been spent in efforts to remove Cr(VI) from the groundwater.

The process used at the Corvallis site consists of several stages to reduce the hexavalent chromium to the less toxic trivalent chromium ion precipitate and to dispose of the trivalent chromium sludge.[a] At the start of the cleanup, groundwater contained 2000 ppm of Cr(VI) at a pH of 6.

In the process, groundwater is initially pumped from a well at a flow rate of 15 gallons/minute (gpm) and sent to the first stage of the process (a reactor), where the Cr(VI) is reduced to Cr(III) using sodium metabisulfite at a pH of 2.5 to maximize the reaction rate. In the next stirred tank reactor, the pH is increased to 9 to precipitate the Cr(III) as a hydroxide. Following flocculation with an anionic polymer, the solution travels to a settling tank where the supernatant water has a Cr(VI) concentration of less than 0.1 ppm and a Cr(III) concentration of 2 to 3 ppm. This purified water stream is sent to the municipal waster treatment facility. The sludge at this point only contains 0.5% to 1% solids that are 60% Cr. The sludge is aged to double the solids concentration and sent to a filter press, which produces a filter cake with 25% solids. This material is sent to a hazardous waste landfill in Washington State, and the filtrate is recycled to the first stage of the treatment process.

After about one year of operation, the Cr concentration in the contaminated well water has decreased from 2000 ppm to 200 ppm. An estimated 3 million gallons of water have been treated and 20,000 lb of Cr have been removed. Although clearly effective, the existing process is labor-intensive, requires six stages, and consumes large quantities of acid, base, and reducing agent. Also, the Cr is removed, but is not in a form that would permit the recycling or recovery of the valuable chromium metal.

Ion-exchange resins or activated carbon can also remove heavy-metal ions from dilute solution, but the adsorbent's low selectivity and cost often are limiting factors (Peters et al. 1985). Furthermore, packed beds of ion-exchange resin beads or activated carbon are prone to clogging if the aqueous waste stream contains silt or other particulates. However, using adsorbents for removing heavy-metal ions from aqueous waste streams is advantageous, if 1) the process uses an inexpensive, selective, and high-capacity adsorbent; 2) fouling of the adsorbent is minimized; 3) the adsorbent can be regenerated; and 4) the adsorbed heavy metals can be recovered as valued products while regenerating the adsorbent.

## 5.2 DESCRIPTION OF THE CONCEPT

This project will demonstrate the engineering feasibility of removing heavy-metal ions (e.g., chromium, cadmium, mercury, or strategic heavy metals) from dilute aqueous streams using porous-magnetic chitosan beads suspended in a magnetically stabilized bed. Chitosan is natural and abundant biopolymer of glucosamine, an amino sugar. Protan, Inc., (Redmond, Washington) presently manufactures chitosan from shellfish wastes, ensuring a steady supply of the adsorbent raw material. The current price of chitosan is about $7.00/lb.

The research program will define the engineering parameters necessary to design a

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[a] Personal communication (1990) with Randy Pratt, $CH_2M$ Hill, Inc., Corvallis, Oregon.

continuous-flow process for 1) selectively adsorping heavy metals onto chitosan beads from dilute aqueous waste streams without fouling, 2) desorping and recovering metals in concentrated form, and 3) regenerating and recycling the chitosan beads.

The process of the proposed concept is shown in Figure 5.1. This basic process concept is simple compared with existing "pump and treat" processes that often use reduction, precipitation, and filtration of a heavy-metal sludge, which itself is a hazardous waste and must be sent to a hazardous waste landfill.

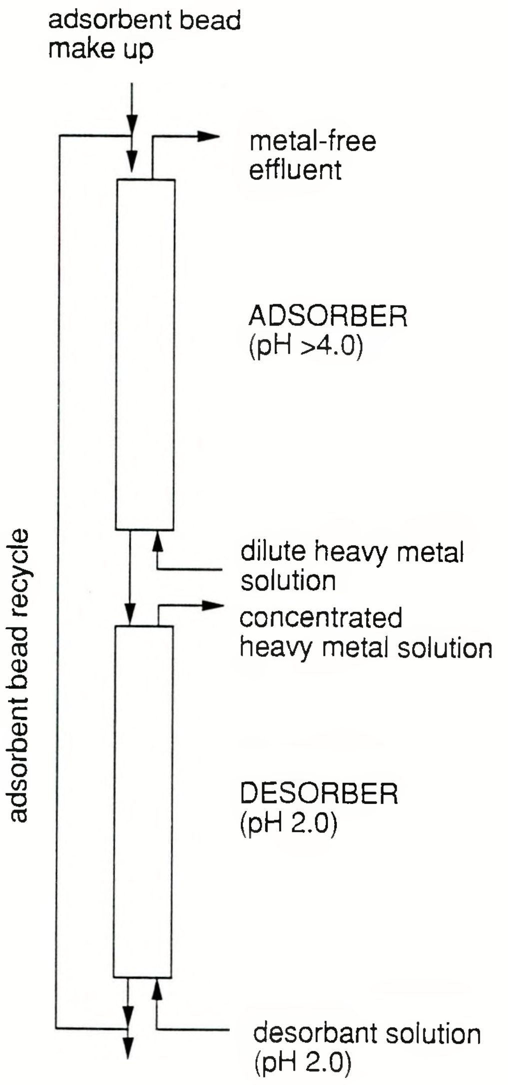


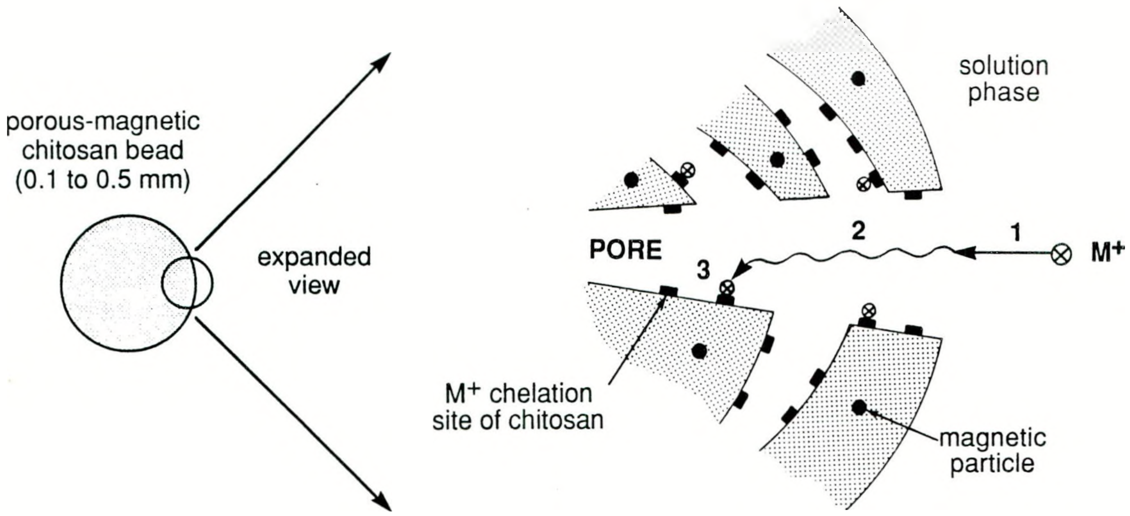
**Figure 5.1.** Adsorber/Regenerator Concept

The adsorption of heavy-metal ions by chitosan is well documented (Sandford and Hutchings 1987, pp. 363-375). The amine (-$NH_2$) groups on glucosamine units within the chitosan polymer chain serve as heavy-metal chelation sites. Alkali metals (groups I and II) do not appreciably adsorb on chitosan (Muzzarelli 1977). However, virtually all other metals, including transition metals, actinides, lanthanides, and radionuclides, can be completely adsorbed from dilute aqueous solution at pH 4.0 and greater.

Detailed adsorption isotherm data at 25°C and pH of $\geq$4.0 are reported for cadmium (Jha et al. 1988), chromium (Maruca 1982; Eiden et al. 1980), lead (Eiden et al. 1980), mercury (McKay et al. 1989), and uranium (Sakaguchi et al. 1981). Mashri et al. (1974) reported adsorption capacities on 20-mesh chitosan flakes for 15 common heavy metals, including mercury (1.1 g Hg/g-chitosan), cadmium (0.31 g Cd/g-chitosan), lead (0.82 g Pb/g-chitosan), chromium (0.024 g Cr/g-chitosan), platinum (0.88 g Pt/g-chitosan), and palladium (0.67 g Pd/g-chitosan). In general, the adsorption capacity decreased with increasing particle size (Jha et al. 1988; Maruca 1982).

In our process, chitosan is cast into beads of defined porosity and diameter (0.1 to 5 mm) (shown in Figure 5.2) . During the casting process, magnetite is added so that the chitosan beads are susceptible to a magnetic field. The chitosan is also crosslinked to render the beads insoluble at very low pH. Details on the synthesis of the porous-magnetic chitosan beads are provided in Section 5.4, "Key Experimental Results."

As shown in Figure 5.2, metal ions ($M^+$) in dilute solution diffuse into the porous matrix of the bead and then adsorb onto a chelation site (-$NH_2$ group). The porosity and size of the bead are optimized to minimize intraparticle diffusion resistances and to maximize access to chelation sites. Developmental "chitopearl" beads manufactured by Fuji Spinning, Inc. (Japan) (1990) have surface areas exceeding 100 to 150 $m^2$/g and metal-ion adsorption capacities of 0.5 meq/mL of adsorbent.



**TRANSPORT MECHANISM**

1. Convection of $M^+$ to bead surface
2. Diffusion of $M^+$ into porous bead
3. Chelation of $M^+$ onto amino groups of chitosan

**Figure 5.2.** Diffusion and Adsorption Mechanism Within a Porous-magnetic Chitosan Bead

Because chitosan is a cationic biopolymer, hydrogen ions in acidic solution displace the adsorbed metal ions at low pH (less than 2.0). Thus, the adsorbed metals can be desorbed at low pH and recovered in a highly concentrated liquid stream. The regenerated chitosan beads can then be recycled. The adsorption of cadmium at pH greater than 4 on chitosan particles (0.2 mm) and the subsequent desorption of cadmium at low pH (2.0) was recently demonstrated by Jha et al. (1988).

The suspension of porous-magnetic chitosan beads in a magnetically stabilized fluidized bed is shown in Figure 5.3. The magnetically stabilized bed is essentially a tube with Helmholtz coils spaced equally down the length of the tube. When an ac (or dc) electric current is supplied to the coils, magnetic field lines are set up parallel to the tube's long axis. Magnetic particles (e.g., the magnetite imbedded in the chitosan beads) align along the magnetic field lines. The spacing of the magnetic beads within the tube depends on the strength and distribution of the magnetic field, which is in turn a function of the applied current, coil spacing, and coil design parameters. In normal operation, the dilute aqueous waste stream is pumped into the magnetically stabilized bed. The stream flows upward and contacts the magnetically suspended beads.

The magnetically stabilized bed has three advantages over conventional packed beds or fluidized beds for contacting porous chitosan beads with aqueous waste streams. First, the spacing of the beads in the magnetically stabilized bed can be controlled independently of liquid flow rate. This control is particularly advantageous for processing silt-laden aqueous waste streams because the spacing between the beads can be increased to prevent clogging of the bed. Also, increased bead spacing can reduce pressure drop and hence reduce pumping requirements. Second, because potentially fragile chitosan beads are immobilized in the magnetic field, they are protected from shear and collision

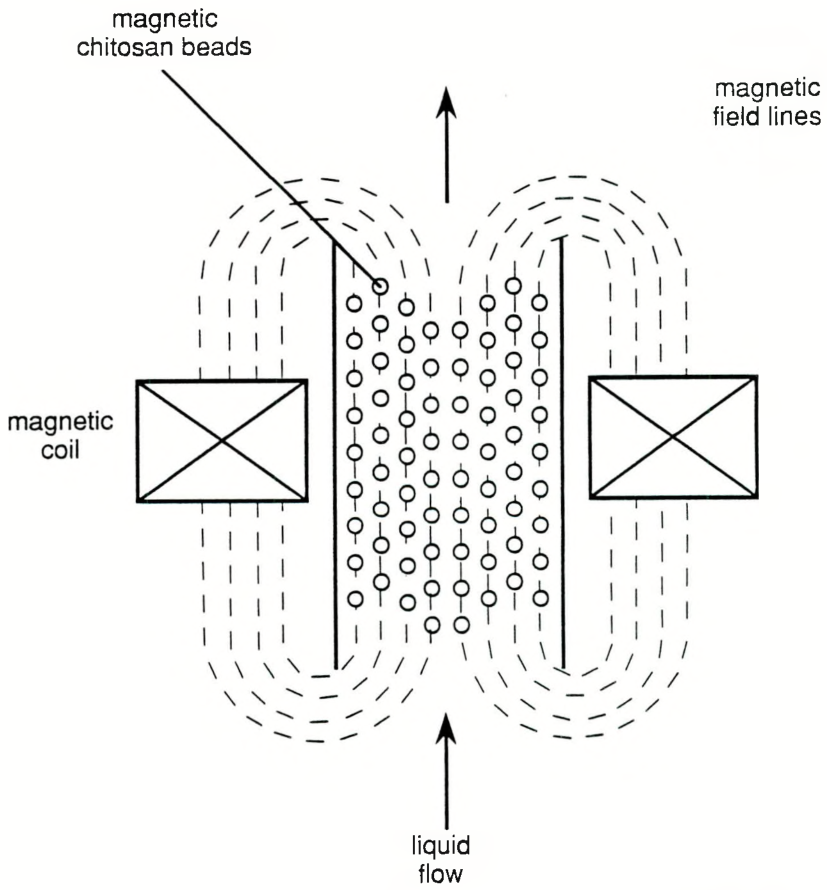


**Figure 5.3.** Porous-magnetic Chitosan Beads Suspended in a Magnetically Stabilized Bed

damage. Third, at high liquid velocities, the magnetically suspended beads resist the inertia of the fluid and remain in the bed.

By turning the magnetic field on and off periodically, the magnetic beads can move down the bed at a controlled rate. The liquid stream moves upward, countercurrent to the movement of the beads. In this mode, the beads can move down to a desorption unit to recover the adsorbed metal and regenerate the porous chitosan bead, as shown in the lower portion of Figure 5.1. Several Exxon patents (e.g., Koslow 1988) describe the industrial usefulness of this type of magnetically stabilized bed configuration for continuous-flow, countercurrent, liquid-solids contacting.

## 5.3 ECONOMICS AND MARKET POTENTIAL

Porous chitosan beads have a high ion-exchange site density comparable to many commercial ion-exchange resins, and the adsorption is reversible. Therefore, high degrees of concentration of the metal-ion species are possible, which may make recovery of the metals economically feasible. For example, for Cr(VI), when the chitosan particles are completely saturated, they will contain 4 wt% Cr. Assuming a feed concentration of 100 ppm Cr(VI), the metals ions will be concentrated by a factor of 400 in a single stage. The heavy-metal adsorption capacity is a function of the metal's atomic weight and oxidation state. The capacity for a monovalent metal ion such as silver is greater than 50 wt%. Chemical derivatization of the chitosan enables us to modify the chemical specificity of the ion-exchange reaction.

A great incentive exists to recover metals from dilute aqueous sources to reduce the U.S. dependency on imported metals. While the United States imports a large percentage of its petroleum, our dependence on foreign sources of many metals is even greater (King et al. 1987).

In 1985, the United States imported over 50% of niobium, manganese, strontium, cobalt, the platinum group, chromium, zinc, nickel, tungsten, silver, mercury, and cadmium (Anon. 1985). All of these heavy-metal ions are highly adsorbed on chitosan; and several metals, including cobalt, chromium, niobium, and titanium, are classified as "strategic materials," which are in high demand for aerospace and military applications such as jet engines. Over 90% of six strategic metals--niobium, manganese, tantalum, cobalt, chromium, and the platinum group metals--were imported.

The National Research Council (NRC) report on separation and purification (King et al. 1987) recommends four potential domestic sources of these important metals that are currently imported. Three of the four sources involve recovery and recycling from manufacturing processes, waste streams, and nuclear waste. The NRC report explicitly states that the economic exploitation of these domestic sources of metals will require that new separation processes be developed, including solid adsorbents with both high capacity and high selectivity. The purpose of the proposed concept is to develop high-capacity metal adsorbents and a process for effectively using these novel extractant materials.

Palladium and other platinum group metals are highly adsorbed on chitosan. For example, in 1990 the potential market value of nonradioactive platinum group metals that could be recovered from nuclear waste was as follows (Smith and McDuffie 1981; McDuffie 1979; Clark et al. 1973; Roberts 1972):

- rhodium-103 - An estimated 33 metric tons could be recovered at a potential value of $500 million.

- palladium - An estimated 60 metric tons could be recovered at a potential value of $900 million.

## 5.4 KEY EXPERIMENTAL RESULTS

Our research of the use of chitosan beads to remove heavy metals from wastewater has three major experimental objectives:

- to synthesize magnetic, porous chitosan beads that have been chemically modified for high metal adsorption capacity and stability in aggressive chemical environments

- to construct a magnetically stabilized fluidized bed to provide continuous contact of the chitosan beads and the aqueous waste stream

- to define the operating parameters needed to remove low-concentration heavy metals (10 to 500 ppm) in the aqueous waste stream using the chitosan beads suspended in the magnetically stabilized fluidized bed.

In our laboratory, two methods are used to cast porous-magnetic chitosan beads of defined diameter (0.1 to 5 mm) and porosity. Before solvent casting, chitosan powder is typically dissolved in 4 wt% acetic acid to a final concentration of 5 wt% chitosan.

In the first method, the chitosan solution is mixed with magnetite powder (e.g., 250 mesh, 5 wt% in solution). The viscous slurry (about 500 to 1000 centipoise) is pumped through a flared syringe needle. Beads form at the tip of the needle and then drop into a beaker of sodium hydroxide solution set inside a water bath. The solution flow rate, solution viscosity, and the inner diameter of the needle can be manipulated to control the size of the bead. During the casting process, acetic acid in the bead diffuses out of the bead at a rate proportional to the sodium hydroxide concentration and temperature. Three variables are manipulated to control the porosity of the bead: the acetic acid concentration in the chitosan solution, the sodium hydroxide concentration in the casting solution, and the casting temperature.

In the second method, ferric (III) chloride is added to the acetic acid/chitosan solution. The beads are then cast into sodium hydroxide solution as described earlier. The -OH ions in the casting solution promote the precipitation of ferric chloride to $Fe_3O_4$ (magnetite) particles within the chitosan bead. During the precipitation process, the beads change from red to speckled black. The amount of magnetite precipitated in the beads is proportional to the ferric chloride concentration in the chitosan solution and the concentration of the sodium hydroxide casting solution.

To render the chitosan insoluble at low pH and to improve adsorption capacity, our porous-magnetic chitosan beads are crosslinked with 2 wt% glutaraldehyde solution per Kurita et al. (1986), Kurita (1987, pp. 337-346), and Koyama and Taniguchi (1986). The beads are then filtered and dried in air.

Standard methods are used to determine the size, porosity, and metal-ion adsorption capacity of the beads. Target parameters for our porous-magnetic chitosan beads are as follows: size (0.1 to 5 mm), surface area (150 $m^2/g$), adsorption capacity (e.g., 1 g Hg/g-chitosan), and magnetite loading (2 to 5% by weight).

A bench-scale magnetically stabilized bed is being used in our laboratory. The apparatus is shown in Figure 5.4. The bed is 2.5 cm in diameter and 60 cm in length (300 mL working volume). Liquid flow rate into the bed ranges from 5 to 20 mL/min. Experiments are under way to determine the extent of metal-ion removal as a function of bead parameters and process parameters, including bead loading, bed void fraction, and liquid residence time.

## 5.5 FUTURE DEVELOPMENT NEEDS

As described in this paper, we have demonstrated that we can produce magnetic, microporous chitosan beads. To demonstrate the feasibility of the heavy-metal removal process, we will continue to focus on obtaining design correlations during further testing with our bench-scale (2.5 cm diameter) magnetically stabilized fluidized bed. The design correlations will be used to perform a preliminary economic analysis of the process.

We will perform batch studies to verify that the rate of the ion-exchange reaction on the surface of the adsorbent particles is very fast compared with the rate of convective mass transfer (see Figure 5.2). We will perform these studies by measuring the kinetics of metal ion removal from solution using a metal-ion selective electrode and a computer data acquisition system. Using a resistance in series model, we can estimate the order of magnitude of the surface reaction rate by using a literature correlation for the convective mass transfer in a stirred tank reactor (Cussler 1984).

The bench-scale demonstration of the magnetically stabilized fluidized bed will consist of hydrodynamic and mass transfer rate experiments. The objectives will be to demonstrate that we can operate the magnetically stabilized bed over a wide range of the Reynold's number (Re) using magnetic stabilization and to show its efficiency for removing heavy metals from dilute solutions.

To present the mass transfer data obtained in the most general way, we will correlate the mass transfer coefficient as a function of the (assuming fast ion-exchange reaction) and compare our observations with literature correlations for packed and fluidized beds (Cussler 1984; Sherwood et al. 1975). We expect that the high flow rates of aqueous solution to be treated will produce high mass transfer rates.

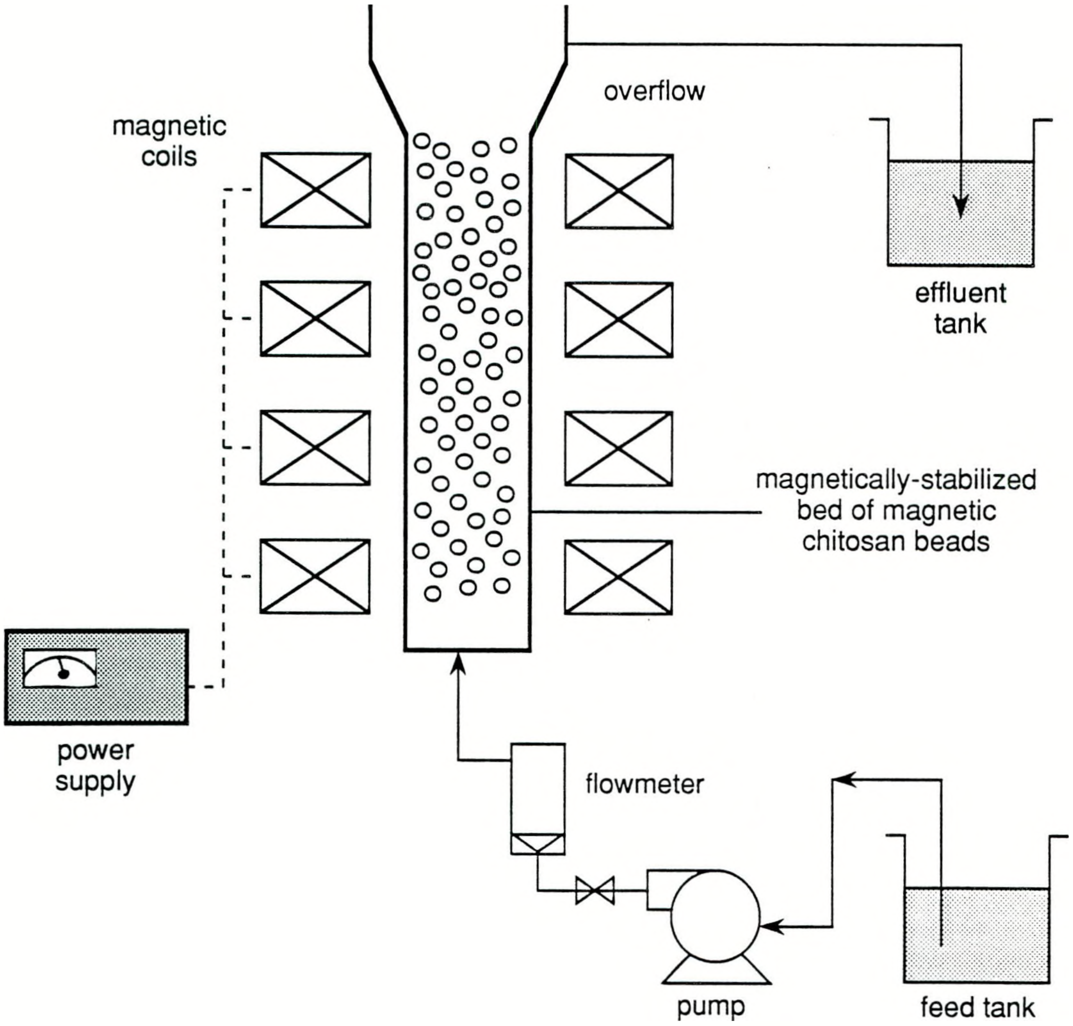


**Figure 5.4.** Bench-scale Magnetically Stabilized Bed

Following the mass transfer rate experiments, we will measure breakthrough curves for the magnetically stabilized bed containing magnetic chitosan adsorbent particles. Once the column is saturated, we will investigate regeneration of the column using lower flow rates of an aqueous pH 2 acid solution to determine the concept's applicability to concentrating and recovering metal ions.

When we obtain a correlation describing the influence of Re on the mass transfer coefficient, we can perform a preliminary economic analysis to compare our concept with existing "pump and treat" processes to determine the economic advantages of our process.

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# 6.0 USE OF CAULOBACTERS TO SEPARATE TOXIC HEAVY METALS FROM WASTEWATER STREAMS

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## ABSTRACT

Toxic metals are often a consequence of domestic, industrial, or mining activities. Although the total amount of metals released by such activities is large, concentrations are typically low, making most recovery techniques impractical. If metals could be removed before becoming associated with sludge and ash, they might have many potential uses. Conventional treatment is unable to reduce the concentration of dissolved metals to levels required for discharge of the waste stream.

We are engineering Caulobacters for sequestering toxic heavy metals such as cadmium, mercury, cobalt, or copper. These bacteria attach to surfaces via an adhesion device at the end of a stalk. The bacteria can be used to produce fixed-cell bioreactors--high surface-area filter devices through which waste streams can be passed to remove toxic metals before treatment of cellulosic fines or sludges.

Metallothionein proteins avidly bind toxic heavy metals, and various types have been cloned. We are inserting the appropriate segments of a metallothionein gene into the gene specifying a high copy number surface-exposed protein of Caulobacter and are measuring metal-binding capabilities of the surface-modified Caulobacters. We also are developing bench-scale bioreactors to assess the feasibility of this approach for sequestering heavy metals.

This approach should eventually lead to studies at a pilot plant to determine the requirements for successfully installing and maintaining selected strains of Caulobacters on a fixed-cell reactor. The overall goal of the research is to produce an efficient metal-binding biological reactor that is designed to specifically accumulate metals that are most harmful for mammalian systems. Such a reactor would allow the metals to be segregated and separately disposed of before they become municipal or industrial sludges.

## 6.1 INTRODUCTION

Heavy-metal loadings in untreated effluent from many types of industrial or municipal waste streams pose health problems (Lester et al. 1984). The following sections present an overview of the effects of heavy-metal releases, current conventional technology for treating heavy metals, and biotreatment of heavy metals.

### 6.1.1 Effects of Heavy Metal Releases

A current widespread problem with wastewater and sludge use is that the accumulation of metals is a natural consequence of the treatment regimes. Often the presence of toxic metals negates the value of pulp mill fines, sludge, incinerator ash, and municipal sludge as fertilizers, soil amendments, and inert fills. Most wastewater treatment solids are landfilled; and when heavy-metal loadings are an issue, the problem may reappear in the leachate from landfill sites.

Toxic metals are often a consequence of domestic, industrial, or mining activities. Although the total amount of metals released by such activities is large, concentrations are typically low, making most recovery techniques impractical. If metals could be removed before becoming associated with sludge and ash, they might have many potential uses.

Conventional treatment is unable to reduce the concentration of dissolved metals to levels required for discharge of the waste stream. Two situations occur frequently. First, some local jurisdictions have adopted discharge standards much more stringent than the conventional treatment processes can achieve. Second, plating wastewaters often contain compounds that interact with dissolved metals and interfere with their precipitation as metal hydroxides. Such compounds include ammonia, phosphates, tartrates, and ethylenediaminetetraacetic acid (EDTA). These compounds, called chelates, consequently find their way into the wastewater and combine with the dissolved metal ion to form a complexed ion that is relatively soluble in neutral or slightly alkaline solutions. In many cases, waste streams containing chelates cannot be treated with conventional precipitation to the level required by regulations.

Conventional treatment also can generate large volumes of sludge. Metal-finishing sludges have been classified as hazardous by many regulatory authorities, including the U.S. Environmental Protection Agency (EPA). Disposal areas for hazardous wastes often are unavailable and waste generators may be forced to transport hazardous wastes long distances, adding transportation and high disposal costs.

Another frequent problem in wastewater treatment is that metal discharge requirements are not being met, even though the level of dissolved metals in the effluent is low. In such cases, the solids separation component of the process is allowing too much suspended matter, including precipitated metals, to pass into the discharge. This condition can result from overloaded clarifiers, ineffective conditioning (coagulation or flocculation) of the clarifier feed, or poor pH control.

### 6.1.2 Current Conventional Technology for Treating Heavy Metals

Alternate technologies have been developed to reduce the costs of waste treatment or to overcome the other problems of treating many waste streams. While alternate technologies often solve the technical problems encountered with conventional treatment or may reduce equipment requirements or operating expenses, they have tradeoffs that often are site-specific and must be evaluated case by case.

Some of the alternate technologies that have been used for removing heavy metals from wastewater streams are briefly described below:[a]

- Sulfide precipitation can be a substitute for hydroxide precipitation or can be used to further reduce the dissolved metal concentration in the effluent from a hydroxide precipitation system. The technology precipitates metals as sulfides instead of hydroxides. The process achieves low levels of metal solubility in highly chelated waste streams but generates metal sulfide sludge, which may be more difficult to dispose of safely because of the sulfide's potential reactivity.

- Ion exchange, using resins that have selectivity for heavy-metal ions, can lower the metal concentration in the wastewater discharge. Heavy-metal selective resins have been used as standalone treatment systems and as a way to polish wastewater after conventional treatment. For example, ion exchange has proved to be one of the few treatment processes that can remove copper and nickel from the highly complexed wastewater of electroless plating. However, use of such resins is often limited because the presence of solids, soluble organics, and polymers of biological origin causes fouling.

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[a] Much of this information has been adapted from Cushnie (1985), Kelly et al. (1979), and Spisak (1979).

- Sodium borohydride precipitation can be substituted for hydroxide precipitation to lower effluent concentrations. Sodium borohydride is a strong reducing agent that can precipitate many heavy metals in their elemental form. This process produces a low volume of sludge, but the reagent is costly.

- Freeze crystallization has not progressed past the development stages. The process separates water from contaminates by forming water ice crystals, but is energy intensive and cannot be used with the large waste volumes encountered in most treatment situations.

- Insoluble starch xanthate (ISX) precipitation can remove heavy-metal cations from wastewaters. The ISX acts as an ion-exchange material that removes heavy-metal ions and replaces them with sodium or magnesium ions. Currently, ISX can be substituted for hydroxide precipitation or can be used to polish treated wastewater to lower the residual metal concentration. Because it is insoluble in water and its precipitation reaction rate is rapid, ISX is used either as a slurry with the stream to be treated or as a precoat on a filter.

- Sacrificial iron anodes are an alternative for the conventional sulfur compound process for capturing chromium. This technology uses an electrochemical reaction in which an electrical current is applied to consumable iron electrodes. The process can reduce chromes at neutral pH but produces ferric hydroxides, which increase the quantity of sludge.

- Ultrafiltration and microfiltration are alternatives for conventional clarification. They use a porous structure to filter particulates from a liquid phase. Previous applications were limited to effluent polishing after conventional clarification has occurred, but new design advances allow for direct filtering of flocculated wastewater. These technologies produce lower solids content of the effluent than with conventional clarification but are more expensive than clarifiers.

- Ferrous sulfate reduction is used to reduce chromate in an acid environment. The technology uses an inexpensive, abundant supply of ferrous sulfate, which is a waste product from steel pickling, but generates more sludge because of the precipitation of ferric hydroxide in the treatment's neutralization phase. Recent improvements using alkaline ferrous sulfate reduction of chromate have shown promising results. The process still has unfavorable sludge generation characteristics, but the sludges can be reduced in the same reaction vessel where neutralization occurs.

- Metal binding of particulates is a very recent technology involving the production of magnetic iron oxide particles coated with organic polymers. The process has shown promise for heavy-metal accumulation, especially for removing radioactive metals from process water generated by the nuclear power industry, where high unit cost factors often are not an important consideration.

### 6.1.3 Current Technology in the Biotreatment of Heavy Metals

Certain species of microorganisms accumulate surprisingly large quantities of important metals toxic to humans (e.g., cadmium) and metals with commercial economic value (such as using microorganisms for recovering silver from industrial waste solutions). Using microorganisms for removing, concentrating, and recovering toxic and valuable heavy metals from aqueous streams has received increased attention in the last 5 to 10 years, but was considered years earlier (Cheng et al. 1975; Neufeld and Hermann 1975; Eden 1960; Ruchloft 1949).

Although the microbial populations in waste treatment systems can remove heavy metals, these metals may poison the system, stopping biological activity and microbial growth. More recently, to avoid the toxicity problem, greater attention has been given to decoupling the propagation of the microbial sorbent from the process of contacting the sorbent with the metal-contaminated stream (Heide et al. 1975; Jilek et al. 1975). Of continuing interest are organisms specifically propagated for their metal-accumulating properties. This includes not only using microorganisms as sorbents, but also developing microbial populations that can grow in the presence of, and at the same time accumulate, heavy metals.

An important consideration in using microorganisms for treating metals is the amount of metal that the cell mass can accumulate. Those amounts vary from a few micrograms per gram to several percent of the dry cell weight. Metal accumulation has been observed to occur with extracellular products (e.g., polymers), at or within the cell membrane, and intracellularly.

Several processes can lead to metal accumulation at these sites. Biosorption is the nondirected, physical-chemical complexation reaction between dissolved metal species and charged cellular components, similar in many respects to ion exchange. The precipitation or crystallization of metals can occur at or near the cell and possibly after initial biosorptive complexation. Also, insoluble metal species can be physically entrapped in microbially produced extracellular polymers. Metabolically mediated metal uptake involves specialized cell functions such as ion transport systems, enzymes, and energy expenditure. Also, metal accumulates within microbial cells by undefined nonmetabolically mediated processes.

Many reports have addressed metals removal from aqueous streams in biological water treatment systems. Both metabolically mediated and biosorptive phenomena can occur in such systems. Most studies have concentrated on the role of extracellular polymers in removing metals (Brown and Lester 1979; Dugan and Pickrum 1972; Friedman and Dugan 1968).

Although many extracellular microbial polymers consist of neutral polysaccharides, others frequently contain compounds such as uronic acid, hexoseamines and organically-bound phosphates that can complex metal ions. Complexing metal ions by charged constituents may be likened to an ion-exchange reaction and thus can be affected by the chemical environment and the presence of other metals or ligands.

The composition and therefore the metal-binding properties of extracellular polymers differ among microbial species and can depend on the conditions in which the organisms are grown. For example, Strandberg et al. (1981) demonstrated that the uranium-complexing capacities of extracellular phosphomannans isolated from two different species of yeast were directly related to the phosphate content of the individual polymers.

Although metal accumulation by extracellular polymers is generally considered a passive phenomenon requiring no directed microbial activity, it has been suggested that bacteria produce large amounts of extracellular organic material in the presence of toxic metal ions (Jones 1967). However, during a study of the metal-binding properties of extracellular, surface-active polymers of marine bacteria, Corpe (1975) found no evidence for this.

Many studies either have demonstrated or implied that metal accumulation occurs at the cell surface or within the cell-wall matrix. The surface accumulation generally was assumed to result from complexation reactions between metal ions and the charged, receptive constituents of the cell walls. However, in only a few cases have the phenomena involved been studied in detail. The composition of cell walls of microorganisms is highly species-dependent and differs considerably among Gram-negative and Gram-positive bacteria, yeasts, filamentous fungi, and algae. Constituents in these cell walls appear to have the potential to complex metal ions. As in the formation of extracellular polymers, the wall composition is not only species dependent but, to some extent, is subject to the conditions under which the organisms are grown (McMurrough and Rose 1967).

Microorganisms encounter both essential and toxic metals in the environment and therefore require mechanisms for controlling the intracellular concentrations and the chemical states of metals. For example, highly specific, active transport systems are used for the uptake and removal of essential metal ions. Although the transport mechanism for essential elements such as sodium, potassium, and calcium has been studied extensively, much less is known about the systems for regulating the intracellular concentrations of other metals. Because of the ecological and toxicological significance of metal ions in the environment, the mechanisms by which microorganisms (and other biological systems) respond to metals are receiving increased attention.

The intracellular accumulation of many metals has been found to occur in bacteria, fungi, and algae. It has been inferred, in several instances, that metal accumulation results from the lack of specificity in a normal metal transport system and that at high concentrations, metals may act as competitive substrates in a transport system. These inferences are based on experiments measuring the competitive effects of specific metal-ion uptake (see review by Kelly et al. 1979).

Although metals such as silver, arsenic, mercury, lead, and cadmium are generally toxic, certain microorganisms show resistance. These microorganisms have been shown to be a rapid, energy-dependent efflux system for arsenate (Silver 1981). However, toxic metals may also be rendered innocuous by systems that lead to their intracellular deposition and accumulation. The specific mechanisms by which these metals are taken up by the cells are essentially unknown, but in many cases their uptake has been shown to be under genetic control and, more specifically, to be controlled by plasmid-linked genes (Silver 1981; Chakrabarty 1978, 1976).

Chakrabarty (1976) described microbial strains capable of accumulating mercury, gold, platinum, and lead. The capability for mercury accumulation was found to be transferable via a plasmid from a resistant strain to a normally sensitive strain of *Pseudomonas*. Charley and Bull (1979) established a community of three distinct species in chemostat culture that could grow in the presence of up to 0.1 mole/L silver+. Silver resistance was shown to reside in the ability of one member, *Pseudomonas maltophila*, to accumulate the metal. Circumstantial evidence was found for the existence of a plasmid specifying silver resistance in this organism.

Intracellular metal deposition occurs by nonmetabolically mediated processes as well. Heldwein et al. (1977) concluded that lead accumulated intracellularly in *S. cerevisiae* by diffusion; while in this same organism, cadmium and cobalt uptake was energy dependent. Nakajima et al. (1981) observed that uranium, copper, and cadmium accumulated intracellularly in *Chlorella regulais*. Strandberg et al. (1981) demonstrated by electron micrography the intracellular deposition of uranium by *Pseudomonas aeruginosa* and by a nondefined, mixed culture of denitrifying pseudomonads. Uranium uptake by washed, resting cells of *P. aeruginosa* was rapid and unaffected by metabolic inhibitors, interfering metal ions, or environmental conditions (e.g. temperature, pH) (Strandberg et al. 1981).

No large-scale uses of sophisticated processes based on microbiological metal separation phenomena appear to have been reported. However, a review of several cases indicates the range of possibilities.

Gale and Wixson (1979) described tailings ponds and artificial stream-meander systems using photosynthetic organisms to treat lead mining and milling effluents in Missouri's New Lead Belt. Lead mine-mill operators encountered lead, zinc, copper, and manganese problems; and one company constructed an artificial stream-meander system to encourage biological removal of metals before the stream was discharged to the receiving body. During its operation from 1972 to 1979, the system reduced the number and severity of heavy metal release episodes. Filamentous algae (e.g., *Cladophora*) were shown to have contributed significantly to heavy-metal binding. Field specimens of algae collected from the system did not release the metals when they were washed extensively with stream or tap water.

Spisak (1979) proposed a more sophisticated process for biologically removing arsenic from an aqueous effluent produced in copper refining. Pyrometallurgical smelter flue dusts are collected and treated in a hydrometallurgical process to recover valuable metals. This arsenic concentration must be reduced to 50 μg/L or less before being released to the environment. Spisak recommended an algae-based arsenic removal process. Arsenic could be assimilated in two photosynthetic reactor vessels containing 1300 kg of algae in 24,700 kg of aqueous solution. Arsenic-laden algae could be harvested from the reactors at a rate of 430 kg/day, filtered, dried, and incinerated at a temperature >300°C to vaporize the $As2O3$. The discharge liquor would contain 40 μg/L of arsenic.

## 6.2 DESCRIPTION OF THE CONCEPT

The ideal treatment process for removing heavy metals clearly does not exist, but if it did, it would have the following characteristics. The process would:

- produce a low amount of sludge relative to the metal accumulated
- be highly efficient at low concentrations of metals
- be highly effective over a wide range of concentrations and conditions, including in the presence of chelators
- not be subject to rapid failure from microbial biofouling
- be cheap to operate
- be an engineered unit process that is adaptable to various municipal and industrial situations.

We believe the strategy we propose has the potential to substantially address all these "ideals."

An especially suitable bacterium, Caulobacter, is being engineered in our laboratories for sequestrating toxic heavy metals such as cadmium, mercury, cobalt, or copper. These bacteria attach to surfaces via an adhesion device at the end of a stalk and can be used to produce fixed-cell bioreactors, which are high-surface-area filter devices through which waste streams can be passed to remove toxic metals before treatment of cellulosic fines or sludges. We are inserting the appropriate segments of metallothionein genes into the gene structure that specifies a high copy number surface protein of Caulobacter. Figure 6.1 shows the Caulobactor life cycle.

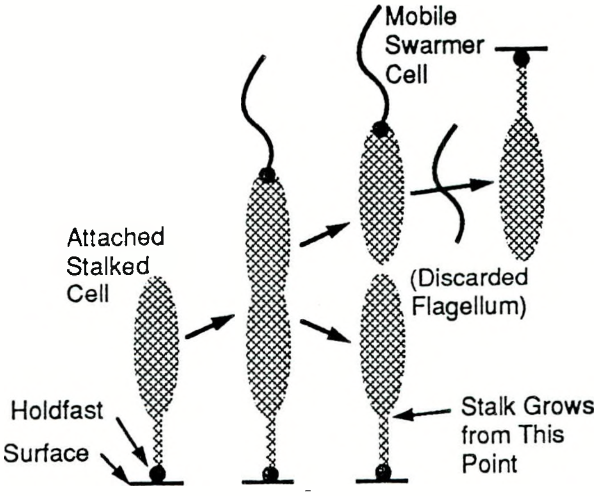

**Figure 6.1.** Caulobactor Life Cycle

Metallothionein proteins avidly bind heavy metals, and several types have been cloned. Metallothioneins are small cysteine-rich proteins induced by many higher organisms in response to exposure to heavy metals. They are expressed internally and are designed to limit exposure of other aspects of cell physiology to the toxic metals (Glanville et al. 1981).

Typically, metallothioneins are composed of about 50 to 60 amino acids. The genes from a variety of mammalian organisms, as well as yeasts, have been cloned and sequenced (Berka et al. 1988; Butt and Ecker 1987). They bind metals such as cadmium, zinc, cobalt, copper, and mercury in significant amounts--ranging from 4 to 12 moles of metal per mole of protein (Butt and Ecker 1987). Metallothioneins are the response of higher life forms to toxic metals. As such, they bind only the noxious metals.

The performance capability of the surface-modified Caulobacters is being assessed in bench-scale bioreactors and at a pilot rotating biological contactor plant to determine the requirements for successfully installing and maintaining biofilms with enhanced metal-binding capability on a fixed-cell reactor.

Caulobacter bacteria are natural inhabitants of most soil and freshwater environments and persist in most types of wastewater treatment systems or effluents (Anast and Smit 1988; Gilchrist and Smit 1991; Poindexter 1981). The bacteria alternate between a stalked cell that is attached to a surface and a motile dispersal cell that has adhesive material already expressed and is searching to find a new surface upon which to stick and convert to a stalked cell.

The bacteria attach tenaciously to nearly all types of surfaces without producing extracellular enzymes or polysaccharide "slimes" (Ong et al. 1990; Merker and Smit 1988) that are characteristic of most other surface attached bacteria (Lester et al. 1984). They have simple requirements for growth and are well-known for their ability to survive in nutritionally poor environments (Poindexter 1981).

We have extensive experience in culturing these bacteria from terrestrial and aquatic sources, including numerous wastewater treatment facilities (MacRae and Smit 1991). We have been studying selected strains for the last 13 years. The "laboratory" strains have been genetically well-characterized and we routinely accomplish virtually all bacterial genetic manipulations (Bingle and Smit 1991a; Gilchrist and Smit 1991; Barret et al. 1982; Ely and Croft 1982; Bender 1981; Ely and Johnson 1977). We therefore believe the Caulobacters are nearly ideal candidates for developing fixed-cell bioreactors, even though they have not been widely used in such a biotechnological fashion until now.

## 6.3 ECONOMICS AND MARKET POTENTIAL

In urban settings the release of metal-bearing waters to municipal systems that use conventional biological treatment compromises the disposal options of the resulting metal-bearing sludges. As a consequence, controlling the waste at the source is becoming the norm. In many cases, however, a significant gap exists between the regulatory requirements and the ability to apply engineered solutions, especially if the metals are present at low, but still hazardous, levels or when the problem is outside the industrial process facility. Effectively, this is becoming a regulatory-driven issue. Ultimately, if metals release can be controlled before they enter common waste streams, enormous savings in disposal costs of the resulting sludges are possible. In fact, the detoxification of sludges can convert them from an economic liability to a saleable resource.

We are aware of a number of waste streams where engineered Caulobacters in a contactor may be advantageous, including the following:

- leachates from landfilled ash, derived from coal- or wood-fired power generation systems and from old landfills

- effluent of the pulp and paper industry, containing low levels of cadmium and other metals and chloro-organics

- the wash stream from metal-contaminated soil that is being remediated through soil washing

- paint wastes, from manufacturers and end-users, characterized by high levels of colloidal solids, metals, and some organics

- storm sewer drainage, characterized by suspended solids, oils, and metals.

While several types of fixed-film reactors are in common use, the rotating biological contactor (RBC) is considered to be the most applicable because the surface exposures can be managed. The aerobic RBC is a fixed-film reactor in which the microbial community is allowed to develop on the surfaces provided by a built-up cylindrical rotor. The rotor rotates partly immersed in a closely-fitting trough through which the wastewater flows. The rotor serves as a simple aeration device because reaeration will occur at the air-liquid interface of the liquid film picked up by the rotor. The dissolved oxygen will then be transferred to the RBC by diffusion into the biological slime and by mixing into the liquor in the trough. The biological oxidation reactions will occur mainly within the films attached to the rotor surfaces and, to a small extent, in the liquor of the trough.

Currently, assessing the economic cost of removing toxic metals from waste streams using this approach is difficult. Many factors, including the type of waste stream, the type of toxic metal involved, the amount of metal the Caulobacters can be engineered to bind, and the feasibility of processing metal-contaminated sludges that result, are part of the economic outlook; and primary data in these areas are not yet available. However, once the molecular genetic and biochemical aspects of strain development are accomplished, RBC technology has generally been found to be an inexpensive and technically uncomplicated approach to wastewater treatment. As such, the process is likely to be easily competitive with alternative technologies.

## 6.4 KEY EXPERIMENTAL RESULTS

Caulobacters develop a protein on their surfaces that organizes into a regular hexagonally-packed structure and covers the entire cell surface. The protein is produced in large amounts; it has been estimated to be 5% of total cell protein. We have cloned and sequenced the gene for this "surface layer" protein (Fisher et al. 1988; Smit 1986; Smit and Agabian 1984). Moreover, we have several ongoing projects aimed at defining which regions of the protein are involved with excretion, attachment to the surface, and assembly as a packed geometric structure.

One major approach is a process known as "linker mutagenesis," where we have randomly inserted a short stretch of DNA that mutates the gene wherever it is inserted (Bingle and Smit 1991b). At the same time, the process creates a restriction enzyme cleavage site at the insertion point. In this way, in addition to mutating functional regions of the protein, we also create mutations that have no effect on the above processes. Such sites might be "safe" areas to insert other activities, such as metal binding. The logic is that when we have determined a safe site, we can easily insert stretches of genetic material via the restriction enzyme site created during the mutagenesis process.

The metallothionein gene is a good candidate to insert; the small size (about 50 amino acids) is an appropriately small disruption to a protein of about 1000 amino acids. We are presently working with cloned human, monkey, and Candida albicans metallothionein genes.

The surface layer protein is designed to be a densely packed monolayer attached to the surface of Caulobacter cells. This feature, combined with the high binding capacity of metallothionein for key toxic metals and the ability of Caulobacters cells to spontaneously attach to surfaces as a single layer of densely packed cells, appears to be a compelling combination for producing a metal-binding bioreactor.

Finally, Caulobacters are well adapted to persist and function in the exact environments we wish to treat. For example, they are well known for their ability to tolerate low-nutrient-level stresses, in particular, low phosphate levels (Poindexter 1981). This essential nutrient can be limiting in many leachate waste streams, especially those with high levels of iron or calcium.

Although other bacteria in the environment bind metals (as detailed above), they often do so by producing copious polysaccharide "slimes" that quickly plug filtration systems or are not surface-adherent bacteria. Typically, they do not show sufficient selectivity toward the key toxic metals, resulting in biological sludge accumulations that have relatively low amounts of bound metal per unit weight. In other words, they cannot be readily adapted to bioreactor conditions or selectively remove heavy metal ions.

## 6.5 FUTURE DEVELOPMENT NEEDS

Over the next three years, we expect to be able to make the genetic constructions, assess the metal-binding capability of the strains under ideal laboratory conditions, and then use bench-scale and pilot-scale reactors with metal-binding Caulobacters to evaluate the real potential for field use.

In situations where no practical technology addresses the metal release problem, we offer the opportunity to begin developing a key ingredient to make an engineered solution possible. We make no pretense that this approach must work or will be uncomplicated to develop. If successful, however, we believe an engineered biological contactor technology is as acceptable to the public as current wastewater treatment practices; and based on experience with RBC technology, it will be economically practicable.

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