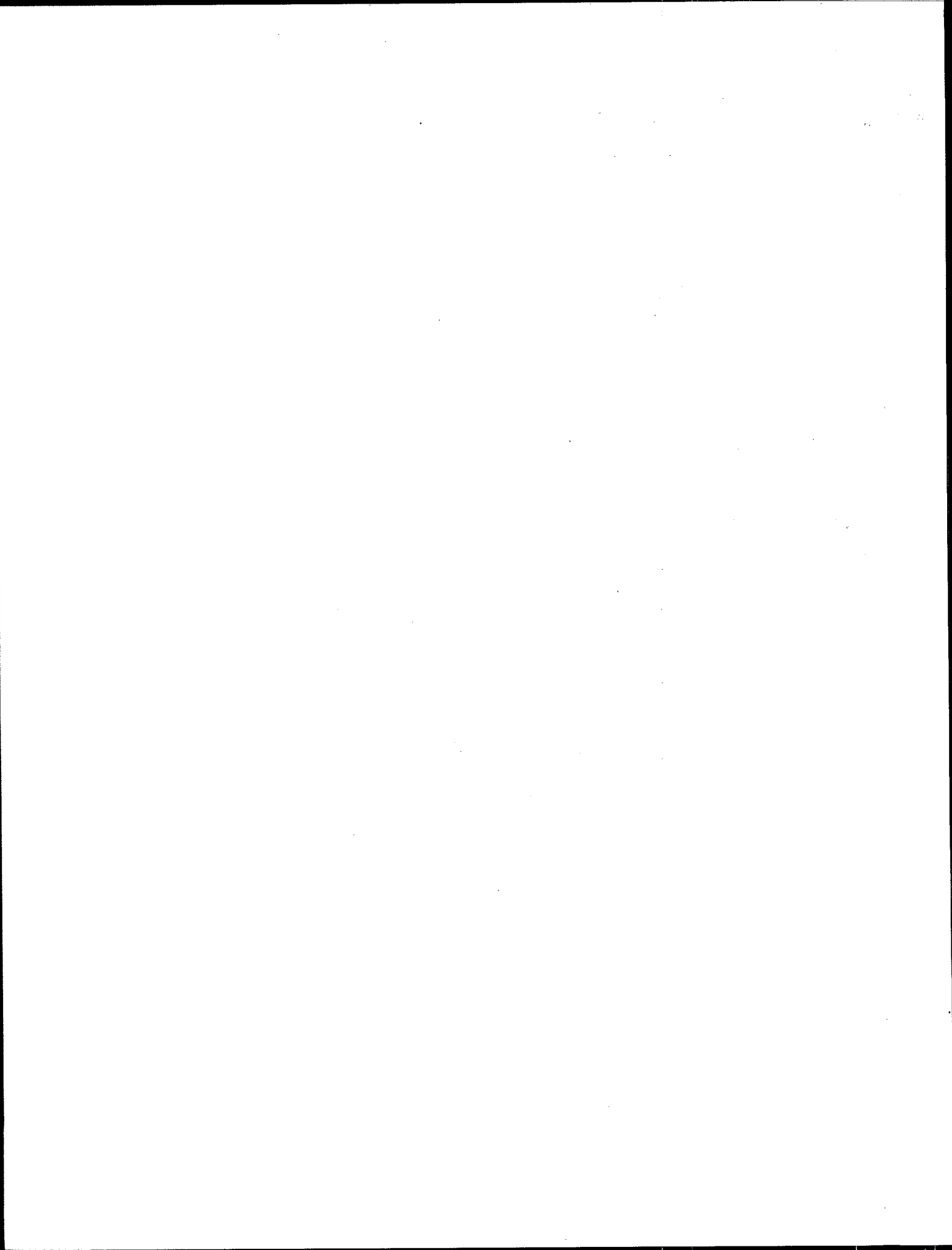




Metals Adsorption Workshop

**May 5-6, 1998
Cincinnati, Ohio**



EPA/600/R-98/127
September 1998

Metals Adsorption Workshop
May 5-6, 1998
Cincinnati, Ohio

Sustainable Technology Division
National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268



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Contents

Introduction.....	v
Metals in the Environment by Teresa Harten.....	1
South San Francisco Bay Pollutants and Programs by Alex Michailidis.....	3
Integrated Solutions for Industrial Water Management by Sam Mason.....	6
Metals in Industrial Process Wastes by Thomas Munns.....	8
Ion Exchange Resins for Metals Removal by Eric G. Isacoff.....	10
Design of Novel Polymer-Supported Reagents for Metal Ion Separations: An Overview by S. D. Alexandratos.....	12
Metals Recovery Team Research and Activities by David Szlag.....	15
Selective Adsorbents for Metal Ion Separations by Larry Tavlarides.....	18
Commercial Applications of Molecular Recognition Technology by Steve Izatt.....	21
Discussion Period 1, May 5, 1998.....	23
Molecularly Imprinted Polymers for Selective Ion Exchange by S. Muralidharan.....	24
Selective Metal Ion Complexation with Chemically Modified Calixarenes by Max Roundhill.....	26
How Chelating Resins Behave by Peter Meyers.....	29
Polymer Filtration for Selective Metals Recovery by Barbara F. Smith.....	33
High Capacity Metal Sorption by Functionalized Membranes by D. Bhattacharyya.....	35

Contents (Cont'd)

Metal-Sorbing Vesicles Immobilized in Nylon Membranes by Harold G. Monbouquette.....	38
Electrochemical/Ion Exchange Process by Robert P. Renz.....	41
Trends in Liquid-Liquid Separations of Metal Ions by Bruce A. Moyer.....	44
Design, Synthesis, and Evaluation of Highly CO₂ Soluble Chelating Agents for Carbon Dioxide Extraction by Eric Beckman.....	47
Discussion Period 3, May 6, 1998	49
Facilitated Group Discussion, Room 1705	50
Facilitated Group Discussion, Room 1706	55
Appendix: Metals Adsorption Workshop Participants	66

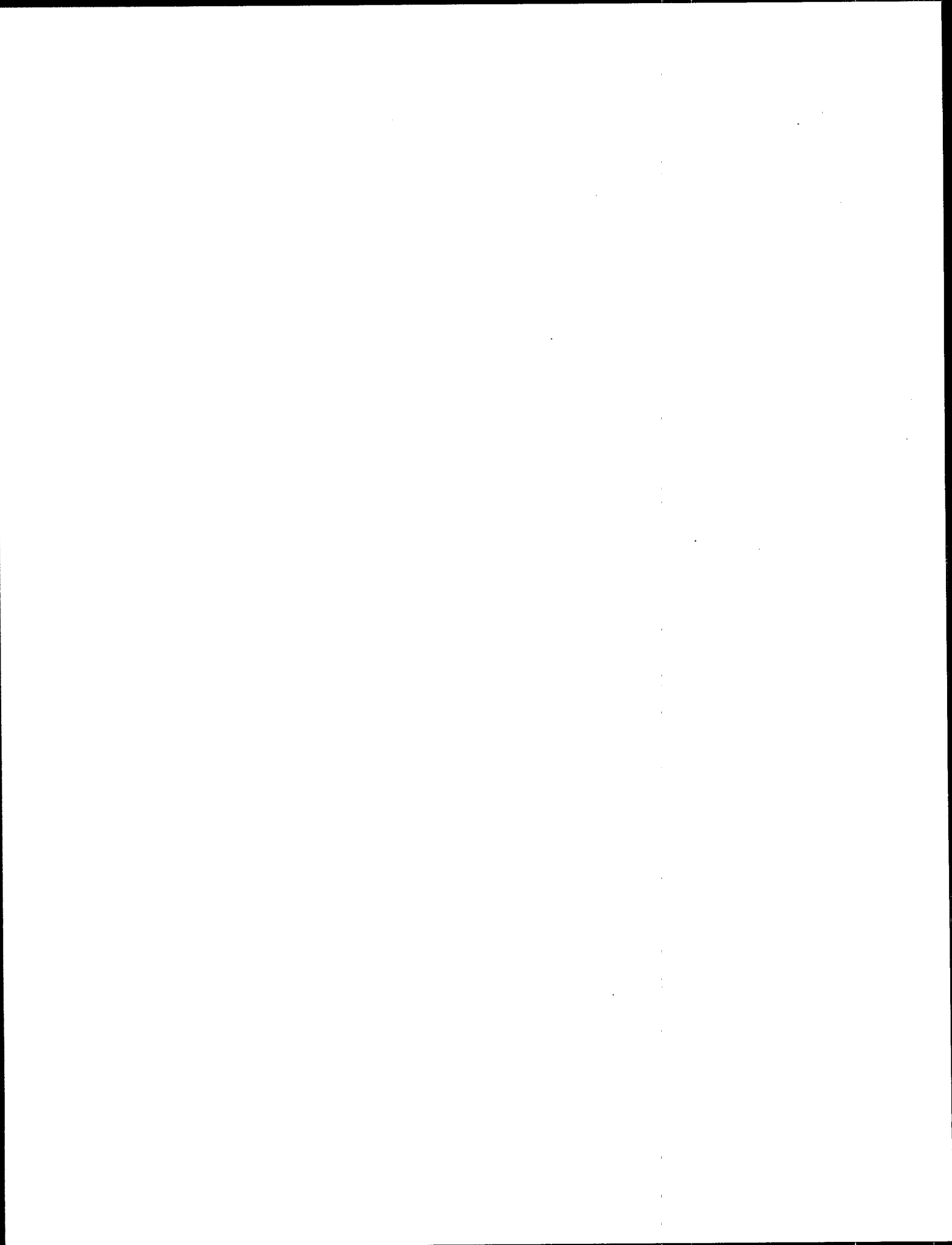
Introduction

This interactive workshop with 38 participants from industry, academia and government was held May 5-6, 1998, in Cincinnati, Ohio. Workshop co-sponsors were the USEPA's Sustainable Technology Division of the National Risk Management Research Laboratory, the Council for Chemical Research, the Department of Energy and AIChE's Research and New Technology Committee.

Ion exchange was the major adsorption mechanism discussed, including use of innovative "hybrid systems" combining ion exchange with membrane or electrochemical technology. Specific topics included derivatized membranes, electrochemical and continuous ion exchange, multiple functional groups, immobilized vesicles, new ligands, and macrocycles. Technical issues of interest were selectivity and capacity of adsorbent materials, reaction kinetics, recovery of adsorbed metals for reuse and recovery/regeneration of adsorbents.

The purpose of the workshop was to evaluate the state of the art for ion exchange and to project applicability of advanced adsorption systems to industrial needs. The participants shared information associated with industry segments and their process and waste streams which could benefit from appropriate adsorption technology. Facilitated discussion groups were utilized to identify research required to guide technology development in the future.

This document represents summary material from the presentations and discussions during the workshop. It does not constitute actual proceedings, since the presentations were informal and no written versions were required. The list of participants and contact information is included as an appendix.



Metals in the Environment

Presented on May 5, 1998 by Teresa Harten, USEPA-NRMRL

Work at EPA has begun to be prioritized using the risk assessment/risk management paradigm. A science advisory board recommended this approach to EPA in the early 1990s and continues to have input into the prioritization process. EPA's National Risk Management Research Laboratory (NRMRL) in Cincinnati, Ohio, focuses on the risk management facet of the paradigm. NRMRL researches control technologies and prevention technologies for managing the risk associated with, among other processes, metal-using industries. EPA's risk management and risk assessment laboratories interact in the area of risk characterization.

Work supported by the Risk Reduction Engineering Laboratory (now NRMRL) at the University of Tennessee resulted in the document, *Chemical Hazard Evaluation for Management Strategies: A Method for Ranking and Scoring Chemicals by Potential Human Health and Environmental Impacts*, EPA/600/R-94/177. Of the top 11 ranked chemicals selected from the Toxic Release Inventory (TRI) and the 20 most widely used pesticides, compounds containing chromium (Cr), arsenic (As), lead (Pb), copper (Cu), nickel (Ni), and cadmium (Cd) were ranked 1, 2, 3, 4, 7, and 11, respectively. The algorithm used to rank these chemicals was

$$\text{Total Hazard Value} = (\text{Human Health Effects} + \text{Environmental Effects}) \times \text{Exposure Potential}.$$

Human health effects were weighted using the acute toxicological endpoints of LC_{50} (inhalation-rodent) and LD_{50} (oral-rodent), and the chronic toxicological endpoints of carcinogenicity and other specific effects. Environmental effects were weighted using the acute toxicological endpoints LD_{50} (oral-rodent) and LC_{50} (96-hour--fish). Additionally, the chronic toxicological endpoint "no observable effect level" or NOEL (estimated from LC_{50} values) was used.

The exposure potential was determined by examining the parameters of persistence and bioaccumulation. Persistence was determined by examining the biochemical oxygen demand (BOD) half-life and the hydrolysis half-life. Bioaccumulation was determined using an aquatic bioconcentration factor (BCF), which is the ratio of the concentration of a chemical in an aquatic organism to its concentration in water.

This algorithm is similar to another one chosen by EPA's Office of Solid Waste and appears to be a credible approach to ranking chemicals for their potential human health and environmental effects. The model does have several shortcomings. These include the lack of speciation for metals, e.g., Cr^{+3} and Cr^{+6} are treated as having the same human health and environmental effects. The model also does not take into account global warming impacts or stratospheric ozone depletion and is not site specific.

Previous research on the effects of metals on human health and the environment focused on wastewater and hazardous waste. Consequently, most of the work on metals treatment in the 1970s and 1980s took place in these areas and was performed in support of regulations governing wastewater and site cleanups. EPA believes that the technologies for treatment and control in these areas are already available and has not been committing research funds into these areas recently. The area where EPA has been focusing research dollars is in pollution prevention. EPA projects, such as this workshop, have been targeting reduction of wastes, including recovery of metals.

To extend this research, EPA programs invite industry to voluntarily work with the Agency in improving regulations and developing technology. EPA's Common Sense Initiative (CSI) is one such program, started five years ago, that works with volunteering companies and nongovernmental organizations in identifying barriers to environmental improvement and suggesting ways to remove those impediments. The CSI also encourages the development of new technologies to reduce pollutant emissions. Industries involved in the CSI include automobile manufacturing, computers and electronics, iron and steel, metal finishing, petroleum refining, and printing. Significant progress in the CSI has been accomplished with the metal finishing industry by working closely with their trade organizations. In August 1997, the CSI unveiled National Performance Goals for the metal finishing industry. These goals were:

Improved Resource Utilization ("Smarter" Goals)

- 98% metals utilization
- 50% reduction in water use
- 25% reduction in energy use

Reduced Hazardous Emission ("Cleaner" Goals)

- 90% reduction in organic TRI emissions
- 50% reduction in metals emissions
- 50% reduction in hazardous sludge disposal
- reduction in sludge generation
- reduced worker and community exposure

Increased Economic Payback and Decreased Compliance Costs ("Cheaper" Goals)

- Achieve long-term economic benefits
- 50% reduction in compliance costs not directly contributing to environmental protection

Some of the technologies necessary to meet these goals may be available, but do not meet the one-year payback period, or the ease of operation requested by a majority of surveyed metal finishers. Additional research and technology development will be necessary to satisfy these concerns.

The Sustainable Technologies Division is researching these technologies as part of its mission to encourage a sustainable society with a healthy environment. Specific areas of interest within the Division include pollution prevention; life cycle assessment; clean product design; risk assessment; and materials recycling, reuse, and recovery. The Metals Adsorption Workshop is an outgrowth of this mission, and it is hoped that the assembled experts will contribute to the goal of identifying and encouraging sustainable technologies.

South San Francisco Bay Pollutants and Programs

Presented on May 5, 1998 by Alex Michailidis, City of Palo Alto, Regional Water Quality Control Plant (RWQCP)

This presentation describes pollutants of concern to the South San Francisco Bay wastewater treatment plant and the environment. It also describes some of the programs developed to reduce loading to the treatment plant and, in turn, the South Bay.

Four million people are located in a 600-square-mile watershed that drains into the South Bay. South Bay is much different from the North Bay. The North Bay receives a lot of fresh water flow from three large rivers: Sacramento, San Joaquin, and Napa. The South Bay is provided with fresh water by approximately 12 seasonal streams and by treated water from three wastewater treatment plants from the cities of Palo Alto, Sunnyvale, and San Jose/Santa Clara. Consequently, there is not much flushing of pollutants. Historical activities such as the mining boom in the mid-1800s have contributed to pollution; abandoned mines still discharge wastes to the bay. Industrial facilities question why their discharge standards continue to get tighter while pollution from historical activities is not controlled.

The RWQCP provides physical, chemical, and biological treatment of approximately 25 million gallons per day (MGD) dry weather flow. Approximately 4 MGD receives additional treatment and are reused as reclaimed water for irrigation (parks and golf courses) and dust suppression (construction sites). Much of South Bay is very shallow, not more than 5 feet deep. There is little mixing in this ecologically sensitive area. The area contains endangered species.

The treatment plant handles residential (60%), industrial (10%), and commercial (30%) wastewaters which are treated and discharged to the bay. In addition, oil and grease, detergents, and other surface water runoffs flow directly into the bay without treatment. Programs have been added to reduce pollutants in the effluent discharged to the sanitary sewer and the stormwater in order to meet the Regional Water Quality Board standards. The RWQCP has investigated treating creek water (essentially stormwater runoff) to improve water quality in the bay.

There are approximately 108 permitted facilities discharging to the RWQCP: 70 are EPA categorical dischargers, 22 are non-categorical but significant industrial users (discharge more than 25,000 GPD and pollutants of concern to the treatment plant), and 16 are non-significant dischargers. In addition, there are roughly 60 vehicle service shops (car washes, service stations, etc.) The 70 categorical dischargers consist of the following:

- 13 electrical and electronic component (semiconductor) - 40 CFR 469
- 6 electroplating - 40 CFR 413
- 20 metal finishing - 40 CFR 433
- 31 pharmaceutical (biotechnical research/manufacturing) - 40 CFR 439

Over 50% of these facilities use some form of ion exchange to reduce discharges to meet effluent limitations or to pre-treat city water for industrial use.

In the early 1990s, arsenic (As), lead (Pb), nickel (Ni), selenium (Se), silver (Ag), and tributyltin were contaminants of concern because the South Bay was identified as an impaired water body (non-attainment). Over the years, the sources of these pollutants have been identified and actions taken so that these are no longer of primary concern. The As was coming from contaminated groundwater at a Superfund site which was infiltrating into a broken sanitary sewer line. The line was repaired and As levels decreased significantly. Pb concentrations have decreased due primarily to a general awareness of the problems associated with Pb. Tributyltin was used as a cooling water additive. The city and the California Department of Pesticides placed a ban on cooling water additives containing tributyltin; significant reductions in concentrations have resulted. Cadmium (Cd) and chromium (Cr) plating operations have been changed, or they have moved operations out of town because the discharge standards were too hard to meet. The net result has been decreases in these pollutants. There is, however, still a concern with these metals. Sludge generated at the wastewater treatment plant is incinerated; emission standards for metals must be met. The incinerator ash is land applied as a soil amendment; there are also sludge disposal standards for land application which must be met.

Three success stories, dealing with silver (Ag), mercury (Hg), and copper (Cu), were discussed. Approximately 50% of the Ag was coming from small businesses such as photo shops, printers, x-ray labs, and hospitals. In early 1990, the city revised its sewer use ordinance to require photo processors to properly manage the fixer used in photo operations. There has been a significant reduction in the amount of silver found in clams in the area. Last year, the city did a source identification study for Hg and found that 46% of the Hg was coming from households. In 1998, RWQCP started a program to collect mercury-containing thermometers from households. Owners can drop the thermometers off at the treatment plant and get a coupon for a non-mercury containing thermometer. The RWQCP hopes that Hg pollution will drop in the next few years as a result of this program. Hg is a concern in the wastewater effluent discharge and in emissions from sludge incineration. The city implemented a Cu discharge reduction program. Metal finishing was identified as the primary controllable source of Cu discharges to the treatment plant. Pollution prevention measures were evaluated at platers, metal finishers, and printed circuit board manufacturers. Options with an ROI (return on investment) of 2 years or less were evaluated. Industry was offered two options: implement reasonable control measures to meet the 0.4 mg/L Cu discharge standard or RWQCP would hire a consultant to set a mass based compliance limit that could be met using any method. Reasonable control measures included minimizing dragout from plating tanks, using countercurrent rinsing, providing positive flow control devices to minimize the amount of water used, extending the bath life, pre-treating spent baths, controlling bath makeup, minimizing drag-in, and optimizing wastewater treatment. In 1992, the city received approximately 1.5 lb/day from the dozen metal finishing plants that were part of the study. By December 1997, the rate was down to 0.4 lb/day. Many of the control measures utilized are relatively inexpensive. Some facilities now have no discharge to the sanitary sewer. Only 5 % of the Cu reaching the RWQCP is currently from industrial processes. Most of the Cu coming to the plant is from the corrosion of Cu pipes. RWQCP is evaluating use of corrosion inhibitors to minimize Cu corrosion, although one inhibitor, zinc orthophosphate ($\text{Zn}_3(\text{PO}_4)_2$), resulted in higher levels of Zn at the plant. Wastewater

treatment plants account for only 15% of the Cu discharged to South Bay, while 50% comes from other unidentified sources in stormwater runoff, and 35% from automotive brake pad dust carried in stormwater runoff.

This year, the RWQCP is focusing on Hg, dioxin, diazinon, and Cu (from vehicle brake pads). Programs are being implemented now to reduce these pollutants. Concerns and areas for future studies are:

- Water quality standards are not set in stone; they are still being researched. For example, the city National Pollutant Discharge Elimination System (NPDES) permit contains discharge standards for Cu (4.9 mg/L) which may increase or decrease, depending on the outcome of current research.
- Sediment contamination is a concern. How widespread is the contamination and is sediment being re-suspended into the water column?
- Atmospheric deposition is also an issue. In a study conducted by the City of San Jose, it was estimated that over 500 lb/yr of Ni were deposited in the Bay by air emissions, equal to approximately 20% of the City of San Jose's discharge.
- Some levels of toxicity have been found in creeks, primarily from pesticides and herbicides.
- Analytical detection levels are another issue. For dioxins and PCBs, the discharge standard is below the analytical detection level; consequently, compliance can't be confirmed.

Integrated Solutions for Industrial Water Management

Presented on May 5, 1998 by Sam Mason, Kinetico Incorporated, Engineered Systems Division

Kinetico provides turnkey systems, chemical treatment and engineered systems for the separation of contaminants from various waste streams. This presentation summarizes various case studies to illustrate the sources of metal and types of streams for which their systems are applicable. Kinetico began making non-electric water softeners for the home market in 1970 followed by the manufacture of equipment for the production of deionized (DI) water. In the early 1980s, the Engineered Systems Division was started and began supplying DI water systems to plating shops. From there, Kinetico moved into water recycling/water reuse and metals scavenging waste treatment applications.

Most of Kinetico's systems provide complete management of industrial water, from purified DI water for processes to recovery of metals and reuse of water rather than discharging it to the sewer.

The first application was a pilot study of a hydrometallurgical application which used an electrolytic process to plate out cobalt. The discharge water contained 1.5 - 2 grams per liter (g/L) cobalt (Co) in a sulfate solution; trace concentrations of nickel (Ni) were also present. The Co concentration was too low to effectively leave in the Co cell, but far too high to send down the drain. Kinetico was asked to reduce Co to less than 2 milligrams per liter (mg/L) and provide a Co-containing stream of at least 10g/L to recycle back to the process. A continuous moving bed ion exchange system using metal selective iminodiacetate (IDA) resin to scavenge Co was pilot tested. A continuous moving bed system was selected rather than a fixed bed system with which most people are familiar. The continuous moving bed system consists of a countercurrent adsorption column; metal-loaded resin is intermittently transferred from the top of the column to an elution column. The tanks actually remain fixed and the resin is transported between vessels. The major advantage is that you can change the column dynamics, the flow rate and size, and the column height-to-diameter ratio to improve adsorption, which was a problem at this location due to high Co loading, and to optimize elution to get the highest concentration in the discharge stream to recycle back to the process. With the continuous bed, a nearly stoichiometric use of regenerant chemical can be achieved just by changing characteristics of the elution column.

The second case study was a fairly typical installation at a printed circuit board manufacturer in Texas. Copper (Cu)-containing rinses were segregated and sent to a Cu ion exchange scavenger. The goal was to reduce Cu to less than 0.5 mg/L. System flow was approximately 30 gallons per minute (gpm), consisting of rinse waters from Cu plating operations, etching and tank dumps, and a cation regeneration stream from a water recycling system that provides DI water to the rest of the plant. The Cu was scavenged on an IDA resin; Cu was electrolytically recovered from the acid regenerant. The spent electrowinning solution was put back through the scavenger so that all of the Cu was leaving the plant as Cu metal. The most important aspect of this system was to segregate electroless Cu and printed circuit board process streams from the acid Cu plating process streams. The electroless Cu streams contained ethylenediaminetetraacetic acid (EDTA) and weren't amenable to scavenging.

A recent installation of a Kinetico system was at a manufacturer of solar cells located in California. The facility discharged up to 150 ppm cadmium (Cd) at a 16 gpm flow rate. The Cd discharge limit was 30 ppb. A lab test was performed before the system was designed. Using a sample of rinse water supplied by the plant, a 3-stage ion exchange resin system was selected (2 columns on line at all times while the third is being regenerated). The test successfully reduced Cd concentrations below 30 ppb. Cd was electrolytically recovered from the acid regenerations and plated onto a stainless steel cathode. The system was prone to contamination from lab waste streams run to a sump that also feeds the Cd scavenger. The lab cleaner was found to contain enough EDTA to cause the discharge limit to be exceeded. Consequently, some of the drains had to be segregated.

A system is currently being designed for a groundwater remediation project at a former plating operation. The groundwater is contaminated with up to 2 mg/L hexavalent chromium (Cr^{+6}), which needs to be reduced to less than 0.1 mg/L while recovering chromic acid for reuse in chrome plating. Two ion exchange columns will be used in series, with the second one providing effluent polishing. A weak base resin will be used to remove chromate ions. A second ion exchange process will be used to get the sodium chromate regenerant solution back to chromic acid for reuse.

A system was installed at a pigment manufacturer in New Jersey which makes Cu thalocyanate blue pigments. The Cu discharge limit was less than 3 mg/L. This example was similar to the printed circuit board manufacturer. The Cu thalocyanate complex was easy to break and ion exchange worked well. One problem was that the pigment was a solid, and any lapse in the prefiltration fouled the resin with solids, causing system failure.

The last case study involved the purification of a hard chrome plating solution using cation exchange to remove metal ions from the chromic acid plating solution. This was part of a zero discharge system for a hard chrome plater in Indiana. By purifying the plating solution, a countercurrent rinse could be used. All of the rinse water could then flow back into the plating tanks to make up for evaporation. In this way, the tanks can be kept purified so that they don't need to be dumped. This is part of larger rinse water recycle system. The plating solution was diluted slightly so that the selected high-crosslink cation resin can handle the concentrations. Ni, iron (Fe), and Cr^{+3} were taken out of solution so they would not be recycled to the plating tanks.

The following statements were made in response to questions:

- Continuous feed systems are used rather than fixed bed systems when feed concentrations are greater than 1 g/L or flow rates are high, requiring a prohibitively large resin inventory. In continuous exchange systems, all resin is in service at all times. In fixed bed systems, one-half to one-third of all resin is off line at any one time. Kinetico uses the Himsley design - resin slurried off the top.
- Kinetico uses IDA in most systems. (See resin manufacturer presentation for resin selection).
- In the case where EDTA was in solution, a less selective resin would work but you would lose metal selectivity. In the future, Kinetico wants to evaluate "super" resins for breaking EDTA complexes.

Metals in Industrial Process Wastes

Presented on May 5, 1998 by Thomas Munns, National Research Council, National Materials Advisory Board

The National Research Council (NRC) is an independent, nonprofit institution and is the principal operating agency of the National Academy of Sciences, National Academy of Engineering, and Institute of Medicine. Chartered by Congress, NRC utilizes voluntary scientific and engineering resources to address issues raised by government and the public. The NRC's National Materials Advisory Board (NMAB) was started by the Department of Defense in the 1950s, and now has a variety of sponsors. NMAB addresses the entire life cycle of materials, starting with removal from the ground and finishing with recycling or disposal.

NMAB recently has convened a panel to study industrial separations in primary process industries. Sponsored by the Department of Energy (DOE) Office of Industrial Technology (OIT), the study is focusing on the identification of separation issues within "industries of the future" (i.e., aluminum, chemical, glass, forest products, steel, metal casting). The panel's mission is to review current and planned OIT research; assess current programs tasked with identifying future research and development opportunities; and suggest criteria for the identification and coordination of separations research.

When considering releases of metals and metal compounds from the primary process industries, as reported in the 1993 Toxic Release Inventory (TRI) report, the primary metals industries account for greater than 70% of all reported releases. These industries include mining, iron and steel production, nonferrous metals production, and metals finishing (including plating, surface preparation, and removal/application of organic finishes). Of the nonproduct metal-containing material generated by these industries, approximately seven times more is transferred from one medium to another than is disposed of. Recycling accounts for about 85% of the transfers. Each industry faces unique and common challenges as well as significant opportunities.

Within the mining industry, key separation issues include dilute stream recovery; capture of minor/trace components from mining waters is seldom energy efficient or cost effective. Similarly, recovery of minor/trace components from mine tailings also is seldom efficient or profitable. These recovery impediments have made legacy sites the most difficult mining issues to address.

Within the steel industry, separation opportunities exist for generated dust, sludge, slag, oil, and water. Blast furnace dust, if containing low concentrations of zinc (Zn), often is suitable for sintering (a production process that uses powders to make steel). Blast furnace sludge usually contains concentrations of Zn that prohibit recycling back into the steel production process (Zn fumes cause pitting on steel surfaces during production). This sludge, however, typically does not contain high enough concentrations of Zn to merit utilization as feed for Zn smelting operations. Sinter plant and steelmaking sludges are routinely recycled to the sinter plant as long as Zn concentrations are not too high. Blast furnace slag is sold as an aggregate product. Hot metal treatment, ladle refining, and steelmaking slags are either recycled to the production process or

disposed of if concentrations of chromium (Cr), phosphorus (P), or manganese (Mn) are too high for recycling. The presence of Cr, cadmium (Cd), and lead (Pb) in leachable forms necessitates storage of these sludges in areas where precipitation cannot reach them.

Copper production generates varying amounts of metal containing wastes, depending on the process utilized. The traditional smelting/electrorefining process (used with sulfide-bearing ores) produces slag containing Zn, copper (Cu), Pb, arsenic (As), and Cd. Electrorefining slag also contains anode and cathode scrap. Flue dust contain Cu and As. The solvent extraction electrowinning process (used with nonsulfide ores) does not produce slag or flue dust and produces less air emissions. Wastes from this process include spent leachate acid (much of which is reused) and spent electrolyte, containing small amounts of iron (Fe).

Chemical production industries, power generation operations and metal plating/finishing processes all generate aqueous streams that contain dilute concentrations of metals. Typical metals found in these wastewaters include Cd, Pb, nickel (Ni), silver (Ag), mercury (Hg), Cr, and Fe. Because these metals are usually present in small amounts, recovery can be problematic. In many cases, the goal of metals removal is to reduce contaminant concentration in the process water to levels acceptable for reuse of the water.

Of the above industrial processes, metal plating and finishing offer the best opportunities for efficient and cost-effective metals recovery. These opportunities are present in pretreatment, plating/finishing, and post-treatment phases of the process. During pretreatment operations, degreasing solutions, alkaline cleaners, desmutting solvents, and acid baths accumulate various metals. Plating baths and rinse solutions change in metals concentrations and must be treated to remove unwanted metals. Post-treatment chromating and phosphating baths also accumulate undesirable metals and must be regenerated.

There are current initiatives to find suitable replacements for heavy metals in finishing operations. One objective of this research is to investigate the substitution of Zn-Ni alloys or ion-vapor aluminum coatings for cadmium in plating operations. Another possibility is the replacement of chromic acid anodizing processes with boric-sulfuric acid anodizing operations. A third area of investigation is the replacement of chromate additives with molybdates, nitrates, borates, or phosphates.

In summary, there are a wide variety of metallic by-products and wastes produced by industrial operations. Even though most are recycled or recovered, there are significant opportunities for capturing additional quantities of metals from these sources. Some of the barriers to these opportunities are the low metals concentrations in many waste streams and the lack of economic efficiency for dilute stream separations.

Ion Exchange Resins for Metals Removal

Presented on May 5, 1998 by Eric G. Isacoff, Rohm and Haas Company

Ion exchange resins (IERs) are polymeric beads, having particle sizes ranging from 0.3 to 1.2 mm, that reversibly exchange ions in solutions. This reversibility allows IERs to be regenerated and reused, resulting in substantial cost savings over non-recyclable metals removal systems. IERs typically have one of four functionalities: strong acid cations (SAC), weak acid cations (WAC), strong base anions (SBA), and weak base anions (WBA). Another type of IER, having no functionality, is adsorbents. SAC exchange resins act as a concentrated sulfonic acid or its salt. They function well over a wide range of pH but typically require 200-300 % (stoichiometrically) of regenerant for effective regeneration. WAC exchange resins act as a carboxylic acid or its salt (e.g., acetic acid). They have significantly higher capacity and are more easily regenerated (100% stoichiometry) than SAC resins. WAC resins, however, only operate effectively at pH >6, limiting their applicability.

WBA exchange resins act as tertiary amines and have similar operating characteristics to WAC resins (i.e., higher capacity and better regeneration stoichiometry than SBA resins, but narrower effective operating pH ranges.) SBA exchange resins act as quaternary amines and have similar operating characteristics to SAC resins. Adsorbents do not have a functional group and utilize surface-to-surface interactions, such as van der Waals forces, for ion removal. The key parameters to consider for adsorbents are pore size, pore volume, surface area, and particle size.

The two main configurations of IERs are gellular and macroreticular. Gellular resins make use of micropores formed within the gel structure. This type of resin is designed for small size ions. Macroreticular resins are essentially microspheres of resin assembled in such a way as to produce mesopores and macropores between the resin spheres. They work well with large size ions.

When selecting resins, it is important to consider the following factors:

- Charge of the solute (to optimize ionic function)
- Operating temperature range (to optimize resin stability--styrene DVB resins have good thermal stability)
- pH of the solution (SAC and SBA operate in wider pH ranges than do WAC and WBA)
- Salt background (to minimize competition for ion exchange sites)
- Molecular size (small ions are efficiently exchanged using gel resins; large ions are efficiently exchanged using macroreticular resins, which are more rugged than gels)
- Solid particles (significant amounts may necessitate prefiltration prior to ion exchange)
- Target ion concentration (higher concentrations result in shorter cycles between regeneration)

- Aqueous or solvent based solute (solvent based solutes may result in resin swelling)

Chelating resins are one type of macroreticular resin commonly in use. Two types of chelating resins are aminophosphonic, which work well for most multivalent ions in concentrated as well as dilute solutions, and iminodiacetic (IDA), which are often used at lower pHs than aminophosphonic resins. WAC resins can be produced with thiol functional groups, making them especially selective for mercury (Hg), cadmium (Cd), and silver (Ag). Complexing resins can be produced with N-methyl glucamine function groups, making them selective for borate ions commonly found in irrigation waters and ceramic plant wastewater effluents.

Two primary uses of IERs are in the rejuvenation of process liquors used in operations such as chromium plating, steel pickling, and galvanizing, and in the recovery of chromate from cooling water. For chromium plating bath solutions SAC macroreticular resins work well. Besides having good capacity, these resins are less prone to attack by strong acids. Regeneration is performed using HCl or H₂SO₄ at 10 - 15 % acid concentrations. Spent pickle liquors can be treated using gellular SBA resins to remove iron (Fe⁺³) and zinc (Zn⁺²). These resins can be regenerated using 2 - 7 bed volumes of water. Galvanizing solutions can be rejuvenated using a chelating IER, such as IDA resins, to remove Fe ions. Regeneration is performed using 25% H₂SO₄. Chromate recovery from cooling waters can be accomplished using WBA resins. Regeneration and acid conditioning are performed using NaOH and H₂SO₄. If two columns are used in series, chromium (Cr⁺⁶) concentrations less than 50 ppb can be maintained prior to breakthrough.

Another common use of IERs is in the treatment of electroplating rinse waters, including chrome plating rinse waters, rinse waters from cyanide baths, and mixed rinse waters. In each case IERs are configured in series for maximum treatment. For chrome plating rinse waters, a series of SAC followed by WBA is recommended. If chromic acid is to be recovered, a second SAC resin would be employed after the WBA. For rinse waters from cyanide baths and mixed rinse waters, a series of SAC, WBA, and SBA is recommended. The SBA is included in order to remove weak acids that WBA won't capture.

A third common use of IERs is in the treatment of metal-containing waste effluents. Each resin type selectively favors certain metal ions, with WAC and IDA removing the widest variety of metals.

The following statements were made in response to questions:

- In the studies performed, copper (Cu) did not precipitate, even at pH 7.
- The thiol resins may be regenerated after removing Hg, but the decision to regenerate depends on the system in use.

Design of Novel Polymer-Supported Reagents for Metal Ion Separations: An Overview

Presented on May 5, 1998 by S. D. Alexandratos, University of Tennessee

Metal ion separation chemistry serves many purposes. These include separation of targeted metal ions from multi-component solutions, removal of toxic metal ions from process streams, environmental remediation, and precious/strategic metal ion recovery from low grade ores. Selectivity in metal ion recovery is the key to the next generation of reagents. There are many interesting developments in the design of selective polymer-supported ligands. Although there are many types of off-the-shelf resins, there are many more possibilities currently being researched. An overview of these selective ligands is presented below. It is important to remember when discussing the selectivity of ligands that the conditions under which the selectivity was observed must be defined. All of the ligands discussed below are attached to crosslinked polymer beads.

Amines--Polystyrene can be modified by adding polyethyleneimine ligands, which are selective for iron (Fe^{+3}), or copper (Cu^{+2}) in the absence of Fe^{+3} . Acrylate polymers can be modified by immobilizing amine dyes (e.g., alkali blue 6B), which sets up a selectivity series of lead (Pb^{+2})>zinc (Zn^{+2})>cadmium (Cd^{+2})> Cu^{+2} at pH 7. Nitrilon fibers (93% acrylonitrile) can be modified by attaching ethylenediamine ligands. These ligands capture gold (Au^{+3}), platinum (Pt^{+4}), palladium (Pd^{+4}), iridium (Ir^{+4}), ruthenium (Ru^{+3}), and rhodium (Rh^{+3}) quantitatively from solutions containing these metals in concentrations of 16 - 80 nanograms per milliliter (ng/mL) at pH 3, even in the presence of 100-1,000-fold excesses of other metals. The heterocyclic amine histamine can be immobilized on acrylate polymers with epoxide groups and enhance Cu^{+2} selectivity. Similarly, pyridinone can be immobilized onto acrylamide resin to chelate Fe^{+3} from poisoned blood plasma, and substituted piperazine can be attached to polystyrene to increase Au^{+3} and Pd^{+2} selectivity from 0.1 molar hydrochloric acid (0.1 M HCl) solutions. Other heterocyclic amines can be immobilized onto polymer beads in order to increase selectivity of target metals.

Amidoximes--Amidoximes can be immobilized onto starch/acrylonitrile copolymer. This ligand follows the selectivity series mercury (Hg^{+2})> Cu^{+2} > Pb^{+2} > Zn^{+2} >nickel (Ni^{+2})>chromium (Cr^{+3}) at pH 5.

Hydroxamic Acid--Hydroxamic acid can be immobilized onto polystyrene, increasing Cu^{+2} capacity from pH 6 solutions. Modified ligands of hydroxamic acid produce a selectivity series, Cu^{+2} > Zn^{+2} > Ni^{+2} >cobalt (Co^{+2})> Pb^{+2} = Fe^{+2} at pH 3.5 - 5.

Thiols--Thiol ligands can be immobilized onto polyethyleneimine resin, increasing adsorption of arsenate from water. The addition of a dithiozone ligand onto a pyridine ring enhances selective separation of Hg^{+2} from pH 3 solutions also containing Cd^{+2} and Zn^{+2} . The thiosemicarbazide ligand can be immobilized onto polystyrene facilitating the reduction of Au^{+3} and osmium (Os^{+4}) to metal, while not complexing Ir^{+3} at pH 0.

Macrocycles--Macrocyclic Schiff bases are copper selective. Crown ethers can be immobilized onto silica gel establishing, in many cases, pH dependent selectivity. Phenolics (condensation polymers) produce high Cr^{+6} selectivity in the presence of high sulfate (SO_4^{-2})/chloride (Cl^-) concentrations at pHs common to cooling tower blowdown. Calixarenes can be immobilized onto polystyrene, increasing Fe^{+3} selectivity over Cu^{+2} , Ni^{+2} , and Co^{+2} in pH 5 solutions.

Phosphorus-Based Ligands--Most of the speaker's current research is being performed in this area. Phosphonium salts can be immobilized onto polystyrene to separate Au^{+3} and Pt^{+4} as chloride anions from Cu^{+2} and Fe^{+3} in 0.1M HCl. Phosphine sulfide ligands can be attached to polystyrene to separate Pd^{+2} from pH 2 solutions also containing 10-fold excesses of Cu^{+2} , Ni^{+2} , and Pb^{+2} .

One goal of current research is to superimpose an ion-selective reaction onto the relatively non-selective ion exchange process, producing reactive ion exchange. A reduction reaction in which Hg^{+2} is reduced to Hg^0 , occurs in solution when the phosphinic acid ligand is attached to polystyrene beads. A coordination reaction can be facilitated in the presence of a phosphonate monoester and a phosphonate diester ligand, raising the distribution coefficient (D) for Ag^+ five fold over the Ds for the monoester and diester separately. A precipitation reaction can be superimposed on the ion exchange process through inter-ligand cooperation.

Intra-ligand cooperation also can be effected in resins such as Diphonix[®], where two phosphonate groups are attached to the same carbon, and they cooperate in complexing the metal ions. The complexation kinetics are enhanced by the proximity of a sulfonate ligand, which acts as an access ligand. This ligand allows ions to enter the matrix very rapidly where only certain ions are complexed. Ketophosphonate ligands immobilized onto polystyrene beads in such a way that carbonyl/phosphoryl groups can interact, produce higher metal ion affinities. The positions of the groups relative to each other greatly affects the affinities.

Bifunctional resins combine metal ion selectivity and rapid complexation kinetics. Previous research showed that increased crosslinking in phosphonated divinylbenzene (DVB) gel and macroreticular resins decreased the amount of complexation occurring in 30 minutes in both 0.1 normal (0.1N) and 1N HNO_3 solutions. The limiting mechanism for these chelating resins is thought to be that the ions cannot fit into the matrix. When the sulfonic acid ligand is added, the amount of complexation remains very high (94 - 100 %), even at 20% crosslinking. This same trend can be seen in phosphonic acid gels.

The bifunctional approach also can be used to separate cesium (Cs^+) and strontium (Sr^{+2}) from alkaline solutions. Styrene-based polyphenolic resins with phosphonic acid ligands combine the Sr^{+2} selectivity of Diphonix[®] with the high Cs^+ selectivity of phenol/formaldehyde condensation polymers. Two additional areas of current research are the preparation of polymers capable of intra-ligand cooperation via ion exchange and coordination, and the development of bifunctional anion exchange resins for the selective removal of pertechnetate ions.

In summary, the following points should be emphasized:

- New ligands continue to be immobilized onto polymer beads, which remain an important type of ion exchange support
- Post-functionalization is an effective technique for introducing ion-selective ligands
- Nitrogen- and phosphorus-bearing ligands continue to be explored
- Bifunctional resins are an important means of combining ionic selectivity with rapid rates of complexation

The following statements were made in response to questions:

- Regeneration of these new ligands has not been studied extensively to date.
- Liquid-liquid ion exchange has been explored for some of the ligands presented; sorption of these liquids into polymer beads works well and the resulting solvent impregnated resins are being studied by a number of groups.

Metals Recovery Team Research and Activities

Presented on May 5, 1998 by David Szlag, USEPA-NRMRL

The initial focus of EPA's Metals Recovery Team was to investigate low-cost, single-use adsorbents for soil washing applications. During this research, EPA looked at many natural biopolymers, such as lignin. It found that if lignin was carboxylated, a very selective ion exchange material resulted. This material was found to be selective for lead (Pb) and copper (Cu). However, many biopolymers do not occur in a very usable form; they are either fibrous or fine powders. They also tend to leach organics into the aqueous stream. EPA overcame those problems by immobilizing the polymer into a polyurethane matrix (even with this modification, a small amount of biopolymer will leak into the solution).

During this research, EPA found that selectivity and regenerability are more important factors than adsorbent cost for soil washing applications. In parallel with this project, EPA worked with NASA, which was developing a polyacrylic-based ion exchange material that is now being commercialized by Summerfield Products. This material became the basis for EPA's research in foams and films and some additional selective ion exchange materials. By incorporating a graphitic material, a foam or film can be made conductive. The idea is to develop hybrid systems, specifically, electrochemical ion exchange systems. In addition to this work, EPA is performing bench-scale research on macrocycles and hydroxamic acids.

EPA's current focus is primarily on metal finishing, specifically electrolytic nickel (i.e., Watts plating and bright nickel baths). EPA is attempting to develop a closed-loop process. It is focusing on the recycling of three streams: 1) process water (including cost considerations associated with metals recovery, makeup water, and sewerage charges), 2) metals and chemicals (major emphasis), and 3) baths (investigating whether some of the resins can be used on a static rinse or be applied directly to the plating bath). Because the ion exchange materials being evaluated are selective for Pb and Cu, they are useful for polishing rinse waters from copper plating and printed wire board manufacturing. They could also be applied to the semiconductor industry and remediation of mining sites.

The objectives for the study being presented today were to achieve selective separation and recovery of metals, specifically Cu and Pb, and to demonstrate a different type of continuous ion exchange than was previously discussed (see the Kenetico presentation). The potential application of interest was lead remediation in soils. EPA's initial focus was low-cost materials. Foams were considered because virtually any chemistry can be incorporated; a resin can be powdered (or used in the form received) and encapsulated in the polyurethane resin, or the functional group can be directly reacted into the polyurethane matrix.

Soil washing applications are the "acid test" for resins. Concentrations of Pb can range from 20 to several hundred ppm. There typically are high total dissolved solids, and other metals -- transition metals, calcium (Ca), and manganese (Mn) -- usually are present in background concentrations. In an acetic acid soil wash application with initial lead concentrations of 25 ppm, EPA found almost

immediate breakthrough with the IRC 718 resin. EPA wanted to strip metals out of the soil wash liquor and send the liquid back to the process to achieve a closed-loop system. With the NASA Ion Exchange Material (IEM) resin, which is based on a polyacrylic acid, very good performance was achieved.

Unexpectedly, the weak acid divinylbenzene-type ion exchange materials (based on acrylic or methacrylic acid) were not particularly selective for transition metals. Imminodiacetic acid (IDA) resins are, however, selective for the transition metals.

For some applications of ion exchange, beads or particles may not be the best configuration. The advantage of a foam is the ability to utilize different unit designs. Continuous moving beds (i.e., an endless belt) can be used, or floating particles (similar to duck weed floating on a pond) can be utilized. EPA wants to make hybrid systems, incorporating the electrowinning directly into this type of system. EPA ended up with the NASA IEM and a similar IEM resin developed by Southwest Research Institute (SWRI). The SWRI resin was also put into a polyurethane matrix.

The resins were screened with a solution containing equimolar concentrations of Cu, Ni, and Pb. The IRC-718 resin adsorbed all three metals more or less equally. The NASA polyacrylic acid (PAA) resin (a flexible gel resin) resulted in higher uptake of Pb and Cu as opposed to Ni which was much lower. The kinetics of Cu and Pb adsorption were about the same for both resins. The IEM resin then was incorporated into the polyurethane foam. On a PAA weight basis (i.e., grams sorbed per gram of PAA), the capacity remained the same.

The continuous ion exchange concept for these resins involves immobilizing the resin on a moving belt that passes through an adsorption stage, a regeneration phase (mineral acid), and an electrowinning stage (simple sheet electrodes). Ultimately the goal is to make the belt conductive to incorporate electrowinning or generate the hydrogen ions electrochemically. Finally, there is a rinse or conditioning stage during which it may be necessary to neutralize any acid or put the resin on the belt back into the sodium or calcium form. This system is simple to operate (one motor to drive the belt) and easy to understand mechanically. For these bench-scale tests, the system was run in batch mode (300 ml capacity); the adsorption stage is charged and then the belt is allowed to run and pull all of the metals out of solution. An exponential decrease in the metal concentrations should occur. In reality, the system would be run as a CSTI with an added adsorption stage. EPA was using the same volume of regenerant in all three stages of the continuous ion exchange process. It would be better to minimize the amount of acid that was used to get the metal concentrations higher; the use of equal volumes merely facilitated showing the data. It is also possible to vary the linear velocity of the belt and the depth of the tanks.

Results

- Adsorption stage -- very rapid and almost complete removal of Pb and Cu; after these are removed, the nickel (Ni) begins to be removed.
- Regeneration stage -- used 0.2 M HCl as the regenerant; achieved rapid desorption of Pb and Cu but removed only about half of the Pb and Cu mass off of the belt (and a smaller amount of Ni).
- Conditioning stage -- to put resin back into sodium form and to neutralize acid with NaOH;

dragout is the major limitation; not a problem with films, can use an air knife to remove all dragout. With foams, you need to wring it out very well.

These results show the feasibility of this approach. More work needs to be done; mechanical details need to be worked out and applied to real systems.

EPA's future research plans:

- Integrate the electrolytic recovery
- Set up as a true flow-through system
- Experiment with making the belt conductive and regenerate it electrochemically
- Take advantage of uptake kinetics using PAA resin or other chemistry
- Work with polyaspartic acid which is highly selective for Pb; also hydroxamic acids and polyhydroxamic acids which are selective for iron under some conditions

Additional statements concerning this presentation are covered in the summary of Discussion Period 1 which took place on May 5, 1998.

Selective Adsorbents for Metal Ion Separations

Presented on May 5, 1998 by Larry Tavlarides, Department of Chemical Engineering and Materials Science, Syracuse University

Dr. Tavlarides and his co-workers, Dr. Deorkar and Mr. Lee, are working to develop novel adsorption technologies for the removal and/or recycling of metals. Their objectives are as follows:

1 - Synthesize selective, inorganic chemically active adsorbents (ICAAs) that are:

- applicable to multiple metal ion streams
- selective, efficient, and versatile
- cost-effective

2 - Evaluate the following characteristics of ICAAs:

- distribution coefficients
- adsorption isotherms
- capacities

3 - Perform bench-scale testing of ICAA's to support the following:

- determination of long-term stability
- development and evaluation of models for performance and control
- cost analyses

In order to prepare ICAAs, one must immobilize the extractants or functional groups (which adsorb the metals using ligand bonding or ion exchange) onto a substrate. The researchers at Syracuse University use silica gel as their starting material, and prepare ICAAs using one of several two-step methods:

Step 1 - Surface modification of the substrate—accomplished using one of two techniques:

- hydrophobization (making the surface hydrophobic by adding monolayer coverage of functional groups, with chain length comparable to pore size and volume)
- titanium coating

Step 2 - Immobilization—accomplished using one of three techniques:

- solvent deposition: substrate + silylating agent + extractant = ICAA (A)
- covalent bonding: substrate + silane coupling agent + functional group = ICAA (B)
This can also be shown as: support + coupling agent + ligand derivative = ICAA
- physical adsorption

If solvent deposition is used, the organic ligands are attached to the ceramic support (silica gel) by Van der Waals forces. Numerous commercial ICAA chelating agents are prepared using solvent deposition onto silica gel.

If covalent bonding is used to attach the ligand to the ceramic support (silica gel), the attachment method can be selected from two alternative, two-step methods. In Method A an appropriate

reactive group is attached to the coupling agent. A ligand is then attached to the reactive group. The coupling agent is attached to the silica. One can modify the ligand by adding different donor groups. In Method B, an appropriate ligand or ligand derivative is attached to the coupling agent. The ligand coupling agent derivative is then immobilized. The ligand attachment scheme selected (Method A or Method B) depends on the following:

- reactive groups, reaction conditions, chemical stability of coupling agent, and ligand
- molecular size, viscosity, and reactivity of reactants
- desire to achieve ligand with specific donor atoms and preferred geometry
- desire to achieve high ligand density on the support surface

Dr. Tavlarides presented five examples to demonstrate the use and behavior of ICAAs. The first example included pH isotherms of cobalt (Co) adsorption on seven ICAAs, comparing the results of seven different ways of attaching the donor atom to the support. The percent extraction of Co^{+2} adsorption relative to final pH varied considerably between the seven ICAAs. A breakthrough curve (concentration divided by initial concentration, plotted against bed volume) was prepared for one of the seven ICAAs--one that demonstrated particularly good extraction of Co^{+2} .

The second example presented data regarding the use of an ICAA for copper (Cu) electrolyte purification. The ICAA used is a low pH antimony (Sb) and bismuth (Bi) adsorbent that has no Cu or iron (Fe) affinity and adsorbs at electrolyte conditions. This ICAA should be useful for electrowinning to produce Cu. The data demonstrated the ability of this ICAA to remove Sb^{+3} from acidic solutions and from a synthesized solution of copper electrolyte. The data also demonstrated good recovery of Sb^{+3} from a saturated ICAA-polypropylene glycol (PPG) bed (to regenerate the bed).

The third example presented data for the removal of cadmium (Cd) from a zinc (Zn) electrolyte solution. This removal was accomplished using a thio-based ICAA with an affinity for Cd and lead (Pb) over Zn. The data demonstrated that, at a pH of 4, this ICAA would extract nearly 100% of the Cd, about 75 percent of the Pb, and only about 30 percent of the Zn from a solution. Numerous other thio-based ICAAs have also been developed.

The fourth example was the application of ICAAs for acid mine waste treatment. This example included a schematic of a hypothetical, integrated process with four ICAA beds to treat waste from the Berkeley Pit. This waste has a low pH (less than or equal to 3) and a high sulfate concentration (7,600 ppm). The hypothetical process uses selective adsorbents for a multi-step adsorption process that allows recovery and reuse of metals. Four adsorbents are used to separate Fe^{+2} , Fe^{+3} , Cu, Zn, Cd, and Pb. The first ICAA bed removes Fe^{+3} , the second ICAA bed removes Cu^{+2} , the third ICAA bed removes Fe^{+2} , and the fourth ICAA bed removes Zn, Cd, and Pb.

The fifth example was the application of ICAAs for treatment of Cu cyanide waste. Because cyanide is used in electroplating, metal finishing, and gold mining, most cyanide wastes contain valuable metals as cyanide complexes. For the waste used in this example, researchers plotted the prevalence of three Cu cyanide complexes versus pH. At a pH of 4, the monovalent species was almost exclusively present. As the pH increased from 4 to 8, the monovalent species was replaced by the

divalent species. As the pH increased further from 8 to 9, the divalent species began to be replaced by the trivalent species. This example demonstrates the need to understand the chemistry of the solution being treated by an ICAA, because the species being absorbed controls the number of sites consumed per molecule (a monovalent molecule only consumes one site; whereas a divalent molecule consumes two sites). This information can be used to design the ICAA and the operation of the treatment system (in this example, the pH was maintained below 8 to avoid the formation of the trivalent species). An equation was developed to model the equilibrium adsorption of Cu cyanide from these solutions based on bench-scale adsorption tests that reached equilibrium in 30 seconds or less. A second model was developed to predict adsorption in a packed column. The second model assumes no rate-limiting steps, as well as plug flow, constant superficial velocity, and no axial dispersion. The model equations were solved to predict a breakthrough curve for Cu cyanide on a specific ICAA at an influent pH of 4.1. The predicted breakthrough curve closely matched actual experimental results.

Future work at Syracuse University is targeting other significant separation problems, such as toxic and RCRA metals, radioactive separations, hydrometallurgical separations, and ultrapure separations for microelectronics applications. Researchers at Syracuse University also plan to investigate novel synthesis methods, such as sol-gel processing for organic-ceramic polymers and self-assembly processing for unique structures.

Commercial Applications of Molecular Recognition Technology

Presented on May 5, 1998 by Steve Izatt, IBC Advanced Technologies, Inc.

IBC puts unique chemistry (called a molecular recognition system) into existing systems to remove ions or other molecules from solutions in the most cost-effective manner. Selectivity is key in all cases because it relates directly to economics. IBC utilizes various complex ligands. The ligands are dissolved in solvents or attached to solid particles (silicates or polymeric substances), columns, or membranes. Use of these types of systems is common in industry; IBC takes advantage of the widespread acceptance of these systems by incorporating its chemistry into well-established systems.

A comparison was provided of the molecular recognition technology (MRT) to ion exchange or other types of exchange technologies. Market needs dictate that the MRT be able to achieve log K values of greater than 10^5 between ions of interest and ligands; this is what is needed to be selective. There is a coincidental requirement that the system be able to elute the ions off of the column. The holding capacity for ions of interest is very high with the MRT (as high as or higher than ion exchange systems). The advantage of this system is that a smaller equipment footprint is required, in one case as little as 10% the size of a comparable ion exchange system. In addition, there are associated decreases in capital cost, elution water volume, downstream treatment costs for elution water and operator time requirements. These factors make the additional cost of the resin inconsequential. The MRT operates efficiently with target ion concentrations in the parts per million (ppm) or parts per billion (ppb) ranges, even in the presence of high concentrations (0.1 to 100 grams per liter [g/L]) of other species. The MRT is effective in difficult matrices such as strong acids and the presence of other complexing agents. There are other issues that are bigger than cost. Industry is generally seeking a zero discharge technology; this is driven by environmental reasons and, to a larger degree, by product quality concerns.

The MRT uses polymer or ceramic support bases. Rapid release of ions in a concentrated form (20 to 40 g/L) is important because the economics dictate that the effluent has to either be recycled back to the system or sold as a relatively high purity material. It is important that the selected eluent is compatible with the process that is being treated. MRT ligands can be chemically bonded to various stable solid supports so that the ligands don't leak into the solution.

A test was performed on water samples from the Berkeley Pit site. Metals were sequentially removed as metal sulfates. Recoveries were greater than 99% for copper (Cu), iron (Fe), aluminum (Al), zinc (Zn), and manganese (Mn). The resultant metal purity met standards for recycle to metal refiners. An economic analysis showed a positive cash return due to the ability to recover these metals.

Another application cited was the removal of lead from fly ash. The fly ash was dissolved in

hydrochloric acid and sodium chloride. A high-purity lead hydroxide (93.1% by weight) was recovered and sold (the ability to sell the recovered metal depends on the market).

Smelters produce large volumes of concentrated sulfuric acid (H_2SO_4) contaminated with mercury (Hg) and other metals. This contaminated acid must be sold at low prices due to metals contamination. The MRT can remove the Hg (typically 0.3 to 3 ppm); the Hg is eluted with thiourea. Part of the thiourea is recycled and the remainder is treated with sodium hydroxide (NaOH); the resultant byproduct may or may not be further treated before it is sold (depending on the market available). A Hg-polishing system can also be applied when the Hg concentration is 0.3 to 5 ppm. The H_2SO_4 is treated to less than 0.1 ppm of Hg; in this case, the SuperLig® is used once (not regenerated) and sent to disposal when fully loaded.

The last example was of the removal of halides from a refinery. The high selectivity and use of an efficient eluent result in a calcium halide effluent that can be sold to aluminum smelters.

A table was presented listing 25 elements (or groups of elements) as typical separations of industrial interest. The associated matrix and types of industrial applications were listed for each element. It was pointed out that similar ions in solution can overwhelm ion exchange systems; this is why selectivity is critical. The selectivity of the MRT system is very beneficial to the economics of the overall system as compared to other, less-selective ion exchange systems.

Discussion Period 1, May 5, 1998

Discussion of Dave Szlag's Presentation

A concern was raised about the size of a scaled-up version of the belt ion exchange system, with an estimate of 780 square feet necessary to treat a 1,000 gallon tank. The size of the belt is dependent on the application and operating parameters. For instance, maintaining a target copper (Cu) concentration in a static rinse tank would not require capacity to treat highly contaminated water. Also, the support and ion exchange materials have improved since belts were used in the 1960s. Two improvements to the prototype system would be to incorporate electrowinning directly into the system and to use multiple regeneration baths where each one is specific for a target metal. The film used on the belt can be attached to a fiberglass backing, making a strong system. A belt system is being set up for the city of Bethlehem's water treatment plant.

Molecularly Imprinted Polymers For Selective Ion Exchange

Presented on May 5, 1998, by S. Muralidharan, University of Arizona

The University of Arizona, Department of Chemistry, Strategic Metals Recovery Research Facility (SMRRF) is performing research in conjunction with EPA. The focus of that research is the recovery and remediation of nickel (Ni) from plating baths. The research objective was to achieve higher selectivities in metal ion separations. Nickel plating solutions contain chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), and other contaminants, often at concentrations in excess of 100 parts per million (ppm). The spent plating solutions contain nickel (Ni^{+2}) in concentrations between 0.16 and 1.3 molar (M) and other complexing ions (e.g., citrate and chloride). The problem is to selectively remove the low-level contaminants (to less than 10 ppm) yet not remove the Ni so that the solution can be reused.

The university is working with a number of organized molecular assemblies (OMAs), particularly micelles and dendrimers and their chelating analogs. In micelles, the ligand is distributed into a pseudo-phase. Chelating micelles consist of a ligand that is attached to a surfactant, so that when the micelle is formed the ligand is a physical part of the micelle and on the surface of the micelle; this improves the kinetics. Dendrimers are highly organized three-dimensional polymers; ligands are attached to dendrimers in both solid-liquid and liquid-liquid systems.

The area discussed in this presentation was imprinted polymers. The fundamental principle is to pre-organize the ligands in a configuration that is favorable for a specific metal -- molecular imprinting. Metal ion imprinted polymers (MIIPs) can be derivatized from polymeric particles with a ligand imprinted with a metal ion. Alternatively, MIIPs can be formed by seed polymerization with a metal-ligand complex as a monomer; the imprinted ligand groups reside predominantly on the surface of the polymeric particles. Seed polymerization is capable of yielding highly uniform polymeric particles. Pore size, particle size, and surface area can be controlled. The presence of ligands on the surface avoids many of the diffusion and mass transfer problems.

Three groups are doing work in this area: SMRRF, Johns Hopkins Applied Physics Lab (G. M. Murray), and Kyushu University (M. Takagi and M. Goto). As discussed earlier, the SMRRF group is doing derivitization and imprinting of polymeric particles and seed polymerization with oil/water emulsions.

The Johns Hopkins group is using conventional polymerization with vinylbenzoic acid and 5-vinylsalicylaldehyde monomers and divinylbenzene cross-linker. Imprinting is achieved by complexing monomers with metal ions prior to polymerization. After polymerization, the polymers are ground and sieved, and metal ions are removed with hydrogen ions (H^+) from acids or ethylenediaminetetraacetic acid (EDTA). An imprint of the metal ion remains after the metal is removed. The disadvantage is that these are bulk polymers and have the typical mass transfer and diffusion problems. However, highly selective polymers have been developed for lead (Pb^{+2}), and other metals, using this approach. They have also deposited these polymers on optical fibers (optrodes) and made electrochemical sensors (ion selective electrodes).

The Kyushu University group is using emulsion polymerization involving a water/oil emulsion in the presence of a metal ion. Carboxylic and organophosphoric acids with double bonds are used as monomers and divinylbenzene is used as a cross-linker. Metal ions are removed by acid or EDTA treatment. A solid material that must be ground and sieved results from this process. Using each of the monomers, they have been able to make highly selective polymers for zinc (Zn^{+2}). Selectivity can be improved by a factor of a thousand as compared to non-imprinted polymers.

The idea of imprinting (a "lock and key" approach) for metals has been demonstrated to be as valid for metals as it is for biological molecules (the historical area for this lock and key approach). The ligand systems that SMRRF is looking at are acylpyrazolones and acylisoxazolones. These ligands have been selected because the electroplating baths of concern are very acidic; a low pK value is desirable so that the complexation of metal ions from a highly acidic medium can be achieved. The pK values for acylpyrazolones and acylisoxazolones are 4 and 1.5, respectively. The other advantages are that you can vary the substituents and the corresponding properties to achieve the desired selectivities. An example of a synthesis of 1-phenyl-3-methyl-4-undecenoyl-5-pyrazolone (HPMUDP) was provided.

The general seed polymerization method was described. Seed polystyrene particles ($1.5\mu\text{m}$) are formed from styrene, sodium chloride (NaCl), $\text{K}_2\text{S}_2\text{O}_8$, and water at 70°C ; more than 95% of the particles are monodispersed. In the presence of an organic solvent (toluene), the particles are swelled using sonication. The particles are further swelled in an oil/water emulsion using a surfactant. The ligand previously synthesized with the double bond at the end is added. The ligand group is aligned on the outer surface of the oil/water emulsion with the hydrophobic end on the inside. This mixture is heated to 75°C for 24 hours in the presence of a radical initiator (benzoyl peroxide) and then added into methanol. After the metal is removed, a polymer with the ligand groups predominantly on the surface of the particles which is selective for that metal ion results. The resulting imprinted polymer will be tested by comparing its performance to that of a non-imprinted polymer with the same chemical composition.

Polymer characterization is obtained by:

- using a scanning electron microscope to examine morphology and particle size
- developing a N_2 sorption isotherm to determine specific surface area
- utilizing Hg intrusion porosimetry to determine pore size distribution
- measuring metal loading as a function of pH
- using HPLC to determine the selectivities of imprinted and non-imprinted polymers
- evaluate the stability of polymers as a function of pH, temperature, and repeated use

Polystyrene was derivatized with acylpyrazolone and used to separate Mn^{+2} and Fe^{+2} from each other. This non-imprinted polymer was compared to an imprinted polymer (imprinted with Fe). There is a good selectivity between Fe and Mn. The experiment was performed using a polymer imprinted with Mn; the selectivity was better than for the non-imprinted polymer, but not as good as for the Fe-imprinted polymer.

SMRRF has demonstrated that either the derivitization or the seed polymerization method is a viable approach for creating selective MIIPs; additional work needs to be done.

Selective Metal Ion Complexation with Chemically Modified Calixarenes

Presented on May 5, 1998 by Max Roundhill, Texas Tech University

Calixarenes are a class of ligands that have been produced since the 1920s. Even though this is not a new area, there are new developments. Calixarenes are made from phenol and formaldehyde, similar to bakelite. They are produced from fairly inexpensive starting materials, but cost is a problem. There are many different conformers of calixarenes.

Calixarenes are three-dimensional hosts -- they have a conical form with an upper rim and a lower rim. Calixarenes can be made with different ring sizes, and they can have different cavity sizes in the upper and lower rims. This allows one rim to pick up one kind of metal and the other rim to pick up another type of metal. Alternatively, one rim could be used to bind the calixarene onto polymers or other types of materials.

Ring sizes that are currently being researched typically contain four, six, or eight carbons. Most of the tests at Texas Tech use four-carbon rings because they are especially easy to synthesize and result in fairly good yields. The heavy metal chemistry of calixarenes is not very well developed, so tests are being performed to determine whether they can be used as ligands for heavy metal applications. The main factors that determine the applicability of calixarenes are stability, selectivity, cost, and complexation.

Stability

Calixarenes are quite robust in their resistance to air, acids, and bases. During production, they are typically refluxed for 12 to 18 hours at about 170°F in a 1 to 2 molar sodium hydroxide (NaOH) or potassium hydroxide (KOH) solution. If calixarenes are refluxed overnight in concentrated sulfuric acid (H₂SO₄), the ring structures stay intact and the calixarenes become sulfonated (and therefore quite water-soluble). This demonstrates that calixarenes are robust at high temperatures and extreme pHs (from about -2 to about 16), even when exposed to air.

Selectivity

Producing calixarenes with different ring sizes and functional groups can result in quite good selectivity. Producing calixarenes using sodium hydroxide yields a certain ring size; potassium hydroxide and cesium hydroxide (CsOH) result in larger ring sizes. The literature documents syntheses that produce different ring sizes with good yields.

Researchers comparing the applications of calixarene esters and ketones have concluded:

- Tetramers (calixarenes with four carbons) show good selectivity for the extraction of sodium (Na), regardless of whether the substituent on the calixarene is an ester or a ketone.
- Tetraketones are generally more effective extractants for lithium (Li), rubidium (Rb), and cesium (Cs) than are tetraesters.

- Larger calixarenes are used to bind the larger cations. Hexamer ketones and esters show a preference for the larger cations. These compounds have a good affinity for potassium (K); they bind Na only poorly, and they do not bind Li. Their maximum preference is for Rb and Cs, but there is little selectivity between these two metals.
- Octamers show low levels of phase transfer effectiveness for Group I cations. They favor the larger cations, but their selectivity among these cations is poor.

Calixarenes are conformationally very flexible, some even at ambient temperature. They will flip between various conformers, so they can open out, the metal can come in, and then they will reform around that metal. This allows the calixarenes to almost engineer themselves around a metal. The calix[6]arenes are conformationally mobile at 0°C; the calix[4]arenes at 40 or 45°C.

Texas Tech has also performed research into the production of calixarenes with good selectivity for heavy metals. They have targeted two groups: precious metals such as gold (Au), palladium (Pd), platinum (Pt), and silver (Ag); and toxic metals which are an environmental problem, such as lead (Pb), cadmium (Cd), and mercury (Hg). They are focusing on the heavy metals.

Researchers at Texas Tech have synthesized numerous calixarene derivatives using the bromo derivative. Some of the sulfur derivatives (which have functional groups such as thioether, carbamoyl, and thiol) provide good extraction for heavy metals. The research is focusing on stable derivatives that provide good, reversible, and selective extraction capabilities. To generate quick, comparable data for the different derivatives, extractions are performed using aqueous metals solution and a chloroform solution of the calixarene. The two solutions are shaken together for 60 seconds, and the percentage of metal extracted is reported. Two thiocarbamoyls resulted in good extractions of Hg^{+2} (over 80%), Ag^{+1} (60 to 74%), Pd^{+2} (100 percent), and Au^{+3} (97 to 100 %). Two thioethers resulted in good extractions of Ag^{+1} (65 to 97%), Pd^{+2} (63 to 70%), and Au^{+3} (99 to 100%). The percentages of Pb and Cd extracted are much lower (below 12%), and the lighter metals, such as iron (Fe), nickel (Ni), cobalt (Co), and manganese (Mn), are not extracted.

To avoid the need for the chloroform solvent, researchers have added longer alkyl chains to the calixarenes so they can be dissolved in octane solutions.

Texas Tech also investigated the ability of calixarene amides and amines to extract anions, such as chromate, dichromate, and selenate. Extraction tests (using a 60-second contact time, as before) showed some extraction and selectivity. Several calixarene amides demonstrated anion extractions of up to about 40% under certain conditions. The calixarene amine tests demonstrated up to 87% extraction of selenate and up to about 90% extraction of chromate. After further investigation, researchers developed a reversible extraction for chromate by putting amine functions on just two of the four positions on a calix[4]arene. In an acidic environment, this calixarene derivative extracted chromate from an aqueous solution, and the reaction was reversed by making the environment basic.

Attachment to Supports

Researchers at Texas Tech have also investigated methods for attaching calixarene to supports. One method is to make a calixarene with a single carbon-carbon double bond on one of the positions, and co-polymerize it onto methacrylate. Another method is to cross-link calixarene with polyethyleneimine, which is a commercially available polymer, available in an aqueous solution.

Related Topics

Texas Tech is currently investigating the similarity between the calixarene framework and some lignin structures. The goal of this research is to determine whether it is possible to computationally predict (based on the molecular mechanics of the cavities) which ligands will bind which metals. If calixarene can be linked into a 3-dimensional lignin structure, or if a lignin monomer can be added to calixarene as a functional group and then polymerized, this may solve some potential leaching problems.

The following statements were made in response to questions:

- Functional groups on calixarenes were attached to the oxygens. The ketone functional groups were assembled onto the calixarene, rather than being formed by oxidizing the phenol to the ketone.

How Chelating Resins Behave

Presented on May 5, 1998 by Peter Meyers, ResinTech, Inc.

The word *chela* is defined as "the pincer-like claw of a crab, lobster, or scorpion," but it can also be used to describe the parts of chelant groups that "grab" onto ions. Ligand is the chemical term for an electron pair donor (Lewis base) when it forms a bond with a metal cation that is a Lewis acid. Chelating resins are ion exchange resins that have ligands that can bond with metal cations. The ligands may be in addition to or in place of conventional ion exchange sites.

Ion Exchange Selectivity

Ion exchange selectivity refers to the equilibrium constant for the metal ions between the solid resin phase and the mobile liquid phase. So-called "selectivity constants" for ion exchange resins are not true constants, as they vary with the dynamic conditions of the process. The variable that has the most significant effect on the selectivity is pH. Although we use ion exchange selectivity as a working tool to predict the behavior of chelating resins, we must understand that the solution variables have a profound effect on the observed selectivity. The following text includes the basis for selectivity, followed by a more practical description of how chelating resins are used.

The following criteria determine the selectivity of a chelating resin for a given metal:

- 1) Ionic Charge (Valence) Most chelating resins prefer di-valent ions to mono-valent or tri-valent ions, because the chelant group has two "chela."
- 2) Hydrated Ionic Radius When the hydrated ion closely fits into the space between the "chela," the resin is very selective for that particular ion.
- 3) Ligand Bonding Nitrogen or oxygen can possess an exposed electron pair, making them Lewis bases. Metals that are Lewis acids form ligands with Lewis bases.

Relative selectivities for different ions can be determined for a given chelant. The equilibrium constant, which describes the relationship of the ionic concentrations of two different ions in the resin and in the water, can be calculated based on the concentrations and relative selectivities of the two ions.

Descriptions of Various Chelants

There are three types of chelating resins that are commercially available and in general use: iminodiacetate chelants, aminophosphonic chelants, and polyamine chelants. There are also other chelants that are less commonly used, and there are other selective resins available that are not true chelants.

An iminodiacetate chelant, such as SIR-300, has a functional group that consists of two carboxylic acid groups attached to a nitrogen (N) atom, which is bonded to the resin's polymer structure. At a pH below approximately 2, the N is stabilized by the presence of hydrogen (H) ions, and the resin has no capacity whatsoever for any other cations. As a result, the resin can be regenerated using a solution with a pH of less than 2. Between pH 2 and approximately 4.5, half of the diacetate group is destabilized, and the resin reaches peak efficiency. Above pH 4.5, the other half of the diacetate

is destabilized, and the resin becomes more selective for monovalent ions. Above a pH of approximately 9, almost all the exchange groups are destabilized. The resin's selectivity for monovalent ions increases to the point where the removal of divalent metal cations is not preferred. Iminodiacetate chelants are useful for removing divalent transition metals (Group IV), such as copper (Cu), nickel (Ni), cadmium (Cd), and zinc (Zn), from slightly acidic solutions. They can function in the presence of high total dissolved solids (TDS) and a significant calcium (Ca) concentration (greater than 1000 ppm).

An aminophosphonic chelant, such as SIR-500, is quite similar in structure to an iminodiacetate chelant, except that the carboxylic groups are replaced by phosphonate groups. The differences between these two types of chelants are rather subtle, and in many applications they can be interchanged without any observable difference in performance. Two differences are 1) aminophosphonic chelants have higher selectivity for alkaline metals, such as Ca, than do iminodiacetate chelants; and 2) aminophosphonic resins remain more selective at elevated pH (because the phosphonate groups do not destabilize). Aminophosphonic chelants can effectively remove divalent Group IV (transition) metals, in the absence of Ca and other Group 2A metals, from solutions that are slightly acidic to significantly basic. Aminophosphonic chelants are often used, at temperatures between 140 and 160°F, to remove Ca and other Group 2A metals from saturated brine with a basic pH (optimum pH is approximately 11).

Picolylamine chelants are significantly different from the iminodiacetate and aminophosphonic chelants. The only picolylamine chelant being manufactured is Dow 4196, and it is significantly more expensive than most chelants. A picolylamine chelant is a weakly basic anion resin. It works solely by its strong chelating properties, as it has no ion exchange capacity for metals. It can operate with a pH as low as about 1, and loses its selectivity above a pH of about 8. It is unaffected by sodium (Na), and has a low selectivity for Ca and other Group 2A metals. The picolylamine resin has been successfully used to treat acid plating baths. Due to its high cost, it is seldom used to treat rinse waters.

Thiol and thiuronium functional resins, such as SIR-200 and SIR-400, depend on the sulfur atom built into the functional group of the resin. Regeneration of these resins is difficult at best and more likely impossible. If a waste contains non-target metals that form insoluble sulfide precipitants, these metals must be removed prior to the use of sulfur-based chelants, or they will saturate the resin and cause it to become exhausted prematurely. Sulfur-based chelants have had limited use in removing mercury (Hg) and precious metals.

Natural zeolites, such as clinoptilolites, SIR-600, and manganese greensand, have properties that make them selective for certain classes of metals. For example, clinoptilolite is exceptionally selective for cesium (Cs), and it is also used to remove ammonia from water (provided the water does not contain high levels of Na). Some zeolites, such as manganese greensand, are used as redox media for the removal of iron (Fe) and manganese (Mn). Zeolites are generally stable in oxidizing environments and at moderate pH, but dissolve at very high or low pH.

Conventional ion exchange resins, such as strong cation resins, weak cation resins, chelating cation resins, and mixed bed resins, can be useful for recycling and recovering individual rinse waters,

provided their TDS concentrations are not too high. Strong cation resins and mixed bed resins should not be used if TDS concentrations are greater than 500 to 1,000 ppm. Weak cation resins (Na form) can be used for TDS concentrations up to 10,000 ppm; however, they are not selective between alkaline metals (such as Ca) and transition metals (such as Cu), and cannot be used if the pH is less than 4.

Operational Considerations

Due to the relatively bulky exchange groups of chelating resins and the stability of the chelant bonds, a chelating resin's rate of exchange is limited. Chelating resins cannot operate at high flow rates without a very significant loss of capacity and increase of metal leakage. The optimum flow rate is about 1.0 gallon per minute per cubic foot (gpm/ft³). Flow rates higher than 2.0 gpm/ft³ cause a chelating resin's performance to suffer and will probably lead to disappointing results. Deep beds work better than shallow beds. A bed depth of 4 to 6 feet is ideal; a depth of 2 feet is marginal. Surface flow rates should not exceed about 12 gpm/ft², and pressure loss across the bed should not exceed 20 pounds per square inch (psi). All chelating resins are stable to at least 140°F and, in general, capacity increases with increasing temperature.

Chelating resins are sensitive to certain inlet contaminants. Inlet chlorine should be less than 0.1 ppm, because all organic ion exchangers are sensitive to oxidation (oxidizing chemicals other than chlorine are also problematic). Suspended solids can foul chelating resins, since the resins normally have extremely long run lengths. Turbidity should be kept as low as possible (1 ppm is too high). Polar and non-polar solvents do not harm chelating resins; however, some solvents can complex with metals and prevent them from being removed by the resin. Polymers and other long-chain molecules (particularly if they are only partially water-soluble) will coat the resin beads and prevent the exchange of ions.

The following statements were made in response to questions:

- In response to a question about applications to electroless copper and nickel rinsewaters, Mr. Meyers stated that electroless nickel rinsewater can be effectively treated by a weak base, strong cation, strong base series. The small amount of metal that is present will be trapped on the cation resin, and the rinsewater can be returned to the system. This is not a popular application, though, because there are less expensive methods for recycling plating solutions. Most platers either put the bath in a drum and send it back to the recycler, or do a chemical precipitation and reconstitution. "I've had commercial experience for several years and we've regenerated electroless copper bath very successfully. We're working right now on nickel solutions, also. What we found was that not only taking out the species was what makes the bath go south on you. You're entrapping what I call tramp oils that come in off of metal products, you're leaching out of FR4 epoxy boards, you're leaching out of other materials, so you have to address the other transient materials that are coming in there, also."
- In any bath or rinsewater, it is never possible to remove all the contaminants. At some point, some contaminant will build up and cause problems. It is, however, possible to extend the life of a bath or rinsewater for a long period of time. Carbon beds are strongly recommended, because metal plating applications always involve some drag-in of oils and

greases on the surfaces of those metals, despite precleaning stages. It may be feasible to use membranes instead of carbon beds, but many platers are reluctant to use membranes because they had bad experiences with membranes about 15 years ago.

- In response to a question regarding the selection of ion exchangers when chelating agents are present, Mr. Meyers stated that it is probably possible to use an ion exchanger with a class of selective anion resins. He agreed that chelating agents are problematic, and mentioned that ammonia can be removed using one of the natural zeolites (assuming the sodium concentration isn't too high).
- In response to a question regarding the effects of solvents, Mr. Meyers stated that the solvents do not hurt the resin, even at 50 to 60% solvent concentrations. The resins swell, but they are not chemically or physically altered. Resins can even be used to purify dry cleaning solvents, such as ethylene glycol. The design of the system must take the swelling into account, as well as changes in selectivity. The best way to evaluate the selectivity is through bench-scale testing.

Polymer Filtration for Selective Metals Recovery

Presented on May 6, 1998 by Barbara F. Smith, Los Alamos National Laboratory

Current research at Los Alamos National Laboratory includes the development of hybrid processes for metals removal that make use of polymeric binding followed by ultrafiltration. These investigations are utilizing more than 30 different water-soluble metal-binding polymers with several different types of ligands, chosen to achieve the required selectivity and binding constants for the metals of interest. The approach results in concentration factors of 20 to several thousand when metal ions are present in concentrations $\leq 1,000$ ppm.

Polymer FiltrationTM combines two operations into one hybrid process. In the first step, pH adjustments are made and water-soluble polymers are added to the metals-bearing solution. The concentration of the polymer in solution during bench scale tests typically is in the range of 0.01 to 2% weight to volume (% wt/v). During mixing, the metal(s) of interest bind to the polymer. The solution then is filtered through a properly sized ultrafiltration membrane (often in the range of 10-200 Angstrom (Å) pore size). The polymer-metals complex is retained while the water and smaller unbound ions pass through the membrane. The filtration typically takes place under pressures of 10-35 pounds per square inch gauge (psig). The resulting retentate contains the selected metals in a greatly reduced volume of solution. The polymer can then be regenerated by lowering the pH of the retentate and flushing the metals using water. The metals also could be selectively stripped using different regeneration conditions. These concentrated metals may then be recovered from the water and recycled.

Two primary conditions affect the ability to use Polymer FiltrationTM effectively. First, the rejection coefficient (a measure of the equilibrium or stability constant for the polymer-metals complex) must be high enough to scavenge the metals of interest down to target levels, but not so high that the polymer-metal complex cannot be economically broken during regeneration. The end use or discharge requirements for the filtered water must be considered, as must the volume equivalents and characteristics of the regeneration water. Second, the polymers must be sized correctly in relation to the ultrafiltration membrane to ensure that no detectable concentrations of polymers can penetrate the membrane.

There are numerous advantages to the Polymer FiltrationTM process.

- Metal-ion binding takes place in a homogeneous solution.
- High metal-ion capacities and metal-ion selectivity are possible.
- Suites of polymers can be blended to bind multiple metal ions.
- There are no requirements for the mechanical stability of the polymers.

- No hazardous organic solvents are used.
- There is no formation of sludge, and colloids do not interfere with the process.
- Energy requirements are low .
- Working pressures and temperatures are typically 25 psig and room temperature.
- Systems are directly scalable from bench-top to process scale and can be used in a variety of configurations.
- Systems require small footprints (i.e., require little floor space) and can be mobile.
- Treated water easily meets metals discharge limits.
- The process is effective in removing Resource Conservation and Recovery Act (RCRA) and precious metals, actinides, cations, anions, and metals from photofinishing, electroplating, textile, and process cooling operations. Polymer Filtration™ potentially could be used for soil remediation (e.g., soil washing) and surface decontamination (as in decontamination of waste debris).

One potential environmental application is the treatment of metal-contaminated water from the Berkeley Pit mine in Butte, Montana. The water accumulating in Berkeley Pit contains elevated levels of numerous metals, including iron (Fe), aluminum (Al), manganese (Mn), cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), and arsenic (As), as well as high levels of sulfate (SO₄). Although not of economic value in their present concentration, the total mass of certain metals present in the water is economically significant. Bench-scale tests have shown pH adjustment followed by Polymer Filtration™ to be effective in reducing metals concentration in the treated water. The further treatment of permeate prior to discharge and the recovery of the target metals still need to be developed.

The following statements were made in response to questions:

- Polymer fragmentation has not been observed using the current mixing methods.
- Process monitoring is very important when determining the concentration of polymer to add (typically between 0.1 and 1.0 % wt/v). Above 10 %, performance may vary.
- The process will work under high salt conditions
- Polymer loss due to irreversible adsorption to the ultrafiltration membrane has not been observed.

Additional statements concerning Polymer Filtration are covered in the summary of Discussion Period 2 which took place on May 6, 1998.

High Capacity Metal Sorption by Functionalized Membranes

Presented on May 6, 1998 by D. Bhattacharyya, University of Kentucky

Co-Authors: J. Hestekin, S. Ritchie, S. Sikdar, and L. Bachas

There are various membrane-based treatment schemes for metal-containing wastes. These approaches include precipitation followed by microfiltration, chelation (using surfactants or polymers) followed by ultrafiltration, nanofiltration, and reverse osmosis. The current research centers on the use of functionalized microfiltration membranes at low pressures (e.g., 5 pounds per square inch [psi]) to produce high quality permeates. In addition to metals recovery, recycled high quality water is an important resource returned for reuse.

Standard microfiltration uses low pressure (e.g., 5 - 10 psi) to remove particles or bacteria from solutions. The typical pore size ranges from 0.1 - 0.5 microns (μ) and allows ions and some polymers to pass. If a polymeric functional group with recognition properties is covalently attached to the membrane pore surfaces, selected metal ions can be captured. (The idea of using polypeptide originated from studies in which enzymes were imbedded in membranes to effect selective biocatalysis.) If the metal is to be recovered, the membrane can be regenerated or ashed; if the metal is to be disposed, the membrane can be encapsulated and managed as waste.

In Japan, hollow fiber polyethylene microfilters are being modified by irradiation with cobalt (^{60}Co) and functionalized by the attachment of iminodiacetic acid (IDA). The resulting IDA density is approximately 2.0 mole/kg of fiber. The functionalized membranes are more selective for copper (Cu) than Co and can be used to separate the two metals. The market for these membranes is in the production of ultrapure water with concurrent metals separation (removal of metals in the range of 1 ppb - 20 ppb.) At these concentrations, large volumes of water can be filtered before the membranes must be regenerated or replaced.

The functional groups used in the current research are the polymerized amino acids poly-L-glutamic acid (PLGA) and poly-L-aspartic acid (PLAA). These compounds can be synthesized or purchased commercially. The compounds' end amine group can be attached to epoxide or aldehyde groups on the membrane. When attached in this way, the poly-amino acids form an α -helix. The poly-amino acids have a repeat unit measuring approximately 0.15 nanometer (nm) and a helix diameter of approximately 1.4 nm. At pH 2 - 4, the compounds are present almost entirely in the helical configuration. The percentage in this configuration drops with increasing pH and disappears by pH 6. If metals such as cadmium (Cd^{+2}) and zinc (Zn^{+2}) are present however, the helical structure is preserved to pH 6. This phenomenon opens the possibility for selective regeneration of the functionalized membranes. If the compounds are used with ultrafiltration, the pore size of the membrane can be changed by changing the pH conditions to which the poly-amino acids are subjected. The change in pore size results from the differential extension of the α -helix at different pH values, which, in turn, compresses the membrane stack.

There are several mechanisms responsible for the removal of metals when using functionalized membranes. When PLGA or PLAA is attached to the membrane, a very strong negative charge

field is produced. This field is produced by the presence of one carboxylic acid group for each repeat unit. The surface area of the membrane is reduced by the presence of the poly-amino acid, but the electronegative carboxylic acid groups "dangle" in the membrane pores and more than offset this reduction. The metal ions enter the field and are trapped. If the pH is lowered, the α -helix forms, compressing the space between membranes and lowering flux rates. In addition to the electric field capture mechanism, chelation and ion exchange also occur.

The current research uses two types of microfiltration membranes. Polymeric membranes with pore sizes ranging from 0.2 - 0.6 μ , surface areas of 9 -35 m²/g, and thicknesses of 100 - 900 μ are one type. Examples are cellulose acetate, cellulose acetate with polyolefin backing, modified polyether sulfone, and pure cellulose. Composite silica membranes with pore sizes ranging from 0.1 - 0.45 μ , surface areas of 80 m²/g, and thicknesses of 200 - 500 μ are the second type. Two examples are polyethylene-silica and polyvinylchloride-silica. Both contain approximately 80% silica particles with diameters of about 20 nm.

Functionalization of the cellulose acetate membrane is performed by a series of steps that hydrolyze the acetate groups and attach the poly-amino acid groups. Functionalization of the silica membranes is performed by formation of epoxide groups to which the poly-amino acid groups are attached. The microfilter pores then have polymeric chains within them.

Results from the testing of functionalized membranes are impressive. As would be expected, PLGA-derivatized membranes adsorb considerably more lead (Pb) than membranes derivatized with the monomers. Higher functionalization of membranes with PLGA correlates positively with higher metals adsorption. Adsorption capacities for various PLGA-functionalized membranes included 1.5 gram of Pb adsorbed per gram of membrane (g/g) for cellulose acetate composite membranes and 1.4 g Cd/g for cellulose membranes. With adsorption capacities in this range, it is possible to treat 55 gallons of water containing 40 mg/L Pb⁺² to concentrations less than 1 mg/L and dispose of 0.02 ft³ of membrane containing 8.2 g Pb.

When regenerating the membranes, virtually all of the adsorbed Cd is released when a pH 3 solution containing 20% sodium nitrate (NaNO₃) is used. Only 16.5% of the adsorbed Pb is released under these conditions, suggesting the possibility for selective regeneration of metals. Approximately 56% of the Pb is released when 0.1 normal nitric acid (0.1 N HNO₃) is added to the regeneration solution.

Major conclusions of the current research:

- Heavy metal sorption with poly-amino acid functionalized membranes is considerably higher than conventional ion exchange.
- Use of poly-amino acids provides single point attachment on membrane material.
- The metal ion transfer mechanism is convective flow (at 5 -10 psi), as opposed to ion exchange, where diffusive forces are the transfer mechanism.

- Metal sorption capacities >1 g/g of membrane material have been achieved.
- High sorption capacity has also been demonstrated with poly-arginine (amine functionality) for dichromate Cr^{+6} anions.
- Selective sorption of heavy metals (Pb, nickel [Ni]) over calcium (Ca) has been demonstrated.
- A minimum of 400-fold volume reduction (Pb-containing aqueous waste) through membrane encapsulation has been established.
- A wide range of inexpensive microfiltration membranes can be used.
- PLGA (even with molecular weights up to 6,000) functionalized pure cellulose membranes can be made with extremely high numbers of aldehyde groups, allowing metal sorption capacities for Cd as high as 1.4 g/g of membrane.

Additional statements concerning functionalized membranes are covered in the summary of Discussion Period 2 which took place on May 6, 1998.

Metal-Sorbing Vesicles Immobilized in Nylon Membranes

Presented on May 6, 1998 by Harold G. Monbouquette, University of California, Los Angeles

Metal-sorbing vesicles (MSVs) represent a fundamentally different approach to selective metal ion extraction from most other approaches. MSV research builds on previous studies where membranes were used as adsorbents in protein separation. The current research indicates that polymerized MSVs that have been immobilized in porous membranes can be used for continuous metal ion extraction at high throughput and low pressure drops. Regeneration at low pH also may be possible, but further research is required.

MSVs are lipid bilayers composed of two-tailed surfactants that self-assemble into three dimensional, hollow, spherically shaped "capsules" measuring about 100 nanometers (nm) in diameter with a wall thickness of approximately 4 nm. If they are assembled in the presence of a water soluble chelating agent (e.g., nitrilotriacetic acid) the agent can be captured inside the vesicle. The vesicles can then be used to remove metals from aqueous solutions. Since the lipid bilayer is essentially impermeable to ions, selectivity is achieved by choosing appropriate lipophilic metal ion carriers that dissolve in the lipid bilayer and transport the metal ions inside to the chelating agent. The system resembles a cell membrane.

The vesicles will rapidly take up selected ions. In order to study the uptake, a solution containing approximately 0.1% MSVs is used; higher concentrations make the process too rapid to study. Selectivity can be designed into the system using off-the-shelf ion carriers and chelaters. In an experiment where triazole combined with two molecules of Kemps triacid was the ion carrier, lead (Pb) was removed at a much faster rate than cadmium (Cd) at pH 7. Pb was removed slower at pH 5.5, and Cd was not removed at all at this pH. Depending on the carrier employed, initial permeabilities for the vesicles are two to three orders of magnitude greater for Pb than for Cd. Concentration factors (CFs) for Pb range from 740 at pH 5.5 to 1200 at pH 7. CFs for Cd range from non-detected (indicating no permeation) at pH 5.5 to 610 at pH 7. The selectivity cannot be explained by equilibrium binding factors and kinetic factors may be the controlling actions.

The MSVs can be polymerized to increase stability and allow stacking. The vesicles can then be immobilized in porous nylon membranes. The primary amine on the surface of the polymerized MSVs allows the coupling of biotin to the vesicles, with the distance between the two determined by the number and types of "spacers" used to connect the vesicle to the biotin molecule. Two of the organic spacers used in current research are LC, which has a 12 carbon chain, and PEG, which has a 250 carbon chain. Biotin has a strong affinity for avidin (a protein found in egg whites), producing a strong, noncovalent linkage. Avidin can be attached to a preactivated commercially obtained nylon membrane (e.g., Loprodyne). The membrane then can be passed through a suspension of MSVs that have been biotinylated, allowing the avidin-biotin linkage to hook the MSVs to the membrane.

Looking at Cd breakthrough curves for a single MSV-supporting membrane and a flow rate of 20 mL/hr (equivalent to about 200 bed volumes/ hr), breakthrough occurred after a volume equivalent to approximately 90 bed volumes. A sharp breakthrough curve typical of membrane adsorbers was observed (diffusive mass-transfer resistance is eliminated with membranes, since the adsorbing sites are on the surface of the pores.) When three membranes are stacked, breakthrough volume is extended to over 300 bed volumes. Stacking membranes also improves performance at higher flow rates (e.g., 700 bed volumes/hr.) With a feed concentration of 1 ppm Cd, pre-breakthrough concentrations of treated water are less than 10 ppb.

Multiple layers of MSVs can be stacked by introducing additional avidin, which then links with biotin on introduced MSVs. When using the short spacer, multiple layers increase breakthrough volume but flatten the breakthrough curve. One explanation is that mass transfer resistance is occurring due to the multiple MSV layers. If the longer spacer is used, the shape of the breakthrough curve is much sharper and performance is greatly improved. The shape of the breakthrough curve for the multiple layers remains constant, but increases in efficiency are less with each additional layer.

Regeneration of MSVs is an area for additional research. Metals are removed from the MSVs when the pH is lowered but the concentration in the flush stream is relatively low (3.5 ppm). At pH <3 the phospholipids begin to hydrolyze, reducing the capacity of the system.

In summary, the observed treatment capacity of a 200 microns (μ) thick membrane is approximately 0.5 mg/g, which is sufficient for the treatment of 60 L of 1 ppm Cd per m^2 of membrane. Multiple membranes may be stacked and still permit high flow rates (a stack of 100 still allows 700 bed volumes/hr.) When multiple layers of short spacer vesicles are used, performance is controlled by the Damkohler number; when long spacers are used, performance may be controlled by the Peclet number. Regeneration at low pH (e.g., pH 1) disrupts phospholipids. The process may be improved by using different compounds that are more resistant to pH changes.

The following statements were made in response to questions:

- The MSVs form in equilibrium with the two-tailed surfactants in solution, although the solubilities of the surfactants are extremely low. Polymerized MSVs are different from micelles and are very stable in solution.

Additional statements concerning MSVs are covered in the summary of Discussion Period 2 which took place on May 6, 1998.

Discussion Period 2, May 6, 1998

With Polymer Filtration™, the loss of polymer during extraction applications (e.g., soil washing) is somewhat dependent upon the polymer employed. In bench-scale experiments, recovery rates of 98-99% have been achieved. The costs of the polymers are similar to ion exchange resins. With the Berkeley Pit research, the first step was to precipitate the Fe and Al using NH_4OH and a water soluble polymer (to aid in the precipitation.) The test was performed at pH 4.8 and flocculation occurred rapidly. In an actual application, settling or filtering would be used to remove the floc. The supernatant would then be treated by Polymer Filtration™.

With functionalized membranes, biodegradation of the polypeptides is a possibility (as with other organic compounds.) Current research shows the systems can be regenerated for many cycles. Longer time frames may yield different results. The cost of the components of the functionalized membranes is approximately \$3.00/ft², and the system cost compares with the cost of microfiltration. Research on incorporating electrical properties has not been performed in conjunction with this research.

The material used in functionalized membranes may be similar to 3M materials, which are polymer meshes with incorporated particles that can be used as a membrane. The 3M materials have been used with 10 μ particles containing Cd-binding ligands producing removals of 1 g/g at a high flux through the membrane. The 3M Empore cartridges are thought to have a radial flow and not be a dead-end filter. The composition of the filter is Teflon. The support polyethylene-silica composite membranes used by the University of Kentucky investigators are commonly used as battery separators and are made by extrusion process.

With MSVs it is possible to increase the steepness of the breakthrough curves either by stacking the membranes or decreasing the flow velocity. With larger membrane areas, the possibility of weak points is increased. Since avidin is a tetramer, it is possible to attach up to four biotin molecules (and consequently four MSVs) to each avidin.

Electrochemical / Ion Exchange Process

Presented on May 6, 1998 by Robert P. Renz, Faraday Technology, Inc.

The ElectrochangeTM and ElectrocleanTM processes are two of the approaches to metals removal currently offered by Faraday Technology, Inc. These processes are fundamentally different from the conventional approaches commonly in use. Currently, precipitation is the most common type of treatment for metal bearing industrial process waters. Precipitated sludge typically is landfilled, while the effluent water is discharged to publicly owned treatment works or lakes, rivers, and streams. In 1992, approximately 227,00 metric tons of metal compounds were released into the environment. Metal containing sludge transportation and disposal costs were \$168 and \$73 per metric ton, respectively. Additional costs may be incurred due to cleanup liability issues. Other metal recovery methods include electrowinning, which can remove metals only to concentrations around 50 ppm; ion exchange, which can remove metals to <1 ppm but produces a secondary waste stream during regeneration; evaporation, which is difficult with dilute solutions; and freeze crystallization, which is another water removal technology that has limitations when used with dilute solutions.

The ElectrochangeTM in-process recycling system combines the principles of electrochemical ion recycling and chemical ion recycling. The process eliminates the aforementioned cost and performance limitations of electrowinning and ion-exchange approaches to metals recovery. The ElectrochangeTM system consists of an Integrated Ion Exchange (IIX) cathode and an IIX anode. The IIX cathode consists of cation exchange resin intermixed with graphite particles. When electric current is present, metal cations are drawn to the cathode and exchanged for hydrogen in the resin. Additionally, metals are plated onto the graphite particles. The IIX anode is composed of anion exchange resin. When electric current is present, anions are drawn to the anode and are exchanged for hydroxyl groups. The H⁺ and OH⁻ molecules combine to form high purity water, which may be used for rinsing during regeneration.

In the regeneration process, the charges of the cathode and anode are reversed, releasing the ions that were held by electrical charge. Reactions at the cathode produce H⁺, which regenerates the cation resin. The anode is regenerated during the production of OH⁻ ions. The released metals are collected in rinsewater (that could have been generated during the treatment phase) in a more concentrated form that can be recycled to the plating operations.

A comparison of conventional ion-exchange, conventional electrowinning, and ElectrochangeTM highlights several advantages of the ElectrochangeTM system. The ElectrochangeTM system requires only one cell, instead of the two required by ion exchange systems. The treatment eluant is recycled to the rinse operation, unlike electrowinning where the treatment eluant is not neutral and, therefore, not recycled. Regeneration of the ElectrochangeTM system is accomplished using water, instead of strong acids or alkali required for regeneration of ion-exchange and electrowinning systems. The regenerant eluant can be recycled back to the plating operation, an advantage over ion-exchange and electrowinning.

As currently built, the Electrochange™ system can be envisioned as a vertically rectangular box that has inlets at the bottom and outlets at the top. The inside is composed of a number of vertical rectangular "frames" that are assembled into the box next to each other. One end frame contains anion exchange resin mounted on a DSA electrode. A Nafion membrane separates this frame and the next, which contains a mixture of cation resin and graphite. (The Nafion membrane permits only cations to pass, excluding water and anions.) Another Nafion Membrane separates this frame from the other end frame, which contains more anion exchange resin. A cover is placed over the end frames and electrical connections are attached. The complete system includes the assembled treatment cell, a rectifier, control panel, and containers for receiving treated water.

In laboratory experiments, rinse water containing approximately 24 ppm of copper (Cu) at pH 2 was treated using three different frame thicknesses, 11.5, 22.3, and 45 mm. At a flow rate of 0.2 L/min, the 11.5 mm thickness frame reduced Cu concentrations to 0.1 ppm and removed 932 mg of Cu during a single pass. At a flow rate of 2.4 L/min, this frame reduced Cu concentrations to 4 ppm, while removing a total of 7,992 mg Cu. Optimum mass removal appears to have occurred at a flow rate between 0.8 and 2.4 L/min. As might be expected, the thicker frames, which contain more resin and graphite, yielded overall lower concentrations of Cu (and sulfate [SO₄]). The experiment also showed that pulsed current produced a consistently lower concentration of Cu in the treated water when compared to direct current.

Regeneration, using the same length of time as treatment, showed fairly consistent results when regeneration conditions were similar. The concentration of Cu in the treated water after regeneration ranged from 4 - 6 ppm, while SO₄ concentrations on similar runs remained below 50 ppm. The mass removed also was consistent for similar runs.

The projected capital cost for the Electrochange™ system over a six-year period ranges from \$98,690 for a 4,000 L/day system to \$266,991 for a 36,000 L/day system. Annual projected savings, due to water recycling, lack of sludge generation, and metal recovery, is estimated at \$47,999.

The Electroclean™ particulate/colloid removal system is a complementary system designed to remove particulate matter instead of ionic contaminants. The system works by electric-field assisted adsorption of particulate contaminants onto Fe(OH)_x. The current application under study is the removal of mercury amalgam (dissolved and particulate) from dental wastewater. Within the system, the anode donates Fe²⁺ ions to the wastewater, while the cathode forms OH⁻ ions. The resulting Fe(OH)₂ combines with the Hg and the complex is removed from the water.

The envisioned commercial system will treat approximately 20 gallons/day of dental wastewater, containing up to 100 ppm of Hg, to concentrations <50 ppb. (The current system is capable of achieving Hg concentrations <2 ppb while removing a wide range of particulate matter without changing system parameters.) The estimated cost of this system is approximately \$7,000. A larger system, designed for automotive waste streams, would treat approximately 30,000 gallons/day and cost \$120,000.

The following statements were made in response to questions:

- The $\text{Fe}(\text{OH})_2$ and associated Hg from the Electroclean™ system will probably be collected and sent off site for Hg recycling or disposal.
- The Electroclean™ system is different from electrocoagulation in that a modulated current is used.

Additional statements concerning the Faraday Technology presentation are covered in the summary of Discussion Period 3, which took place on May 6, 1998.

Trends in Liquid-Liquid Separations of Metal Ions

Presented on May 6, 1998 by Bruce A. Moyer, Oak Ridge National Laboratory

The purpose of this presentation was to provide an overview of liquid-liquid separations (LLS) and, by way of illustration, discuss current LLS research at Oak Ridge National Laboratory (ORNL). The prospects for future innovation and utilization of LLS are greater than ever. Over the next 20 years, four trends will develop. LLS will be subjected to research and market pressures and respond by changing. The theory and tools for LLS will become more effective. New extractants will continue to be developed, and LLS technology (in particular liquid-liquid contacting mechanisms) will continue to diversify.

LLS involves two processes, coordination and partitioning. In coordination, the metal and solvent react to form a complex. Partitioning in LLS is the chemical process by which metal ions and their complexes become distributed between the aqueous and organic phases. While coordination is a fairly well understood process, partitioning is not. Several models have been proposed over the last 100 years to explain partitioning. New techniques currently being applied include quantum mechanics and molecular dynamics.

LLS has many advantages. It can be highly selective in metal ion removal, with the ligands binding the ions in a three-dimensional configuration that is difficult to achieve with many other metal removal technologies. Similarly, the stability and recyclability of LLS solutions makes them advantageous over some solid sorbents. The fast kinetics of LLS result in high throughput capacities. The reversible equilibria of LLS produce good recovery of separated metals. In many applications, they require less pretreatment of the feed prior to the separation step. Downstream processing requirements also may be less in some instances. Such advantages often result in reduced waste generation compared to alternative ion exchange technology, even though LLS methods employ organic solvents.

The equipment used in industrial applications of LLS is relatively simple to design, fabricate, and operate. Also, LLS can be scaled to recover a full range of metal ions, from atoms to kilotons. Finally, the technology has a proven track record in the analytical, nuclear, and hydrometallurgical fields.

Balancing these advantages are several shortcomings of LLS. While the economics of some applications (such as hydrometallurgy) may be favorable for removal of low ppm metal concentrations, the technology typically is used for solutions with higher concentrations (greater than 100 ppm) of metal ions and electrolytes. Solvent loss to the aqueous phase is a concern, sometimes necessitating the use of solvent recovery techniques after LLS. Solvent loss also is the primary cost criterion. Additionally, LLS suffers from the negative connotations associated with "solvent using" technologies.

One of the LLS trends previously identified is that the technology will be subjected to research and

market pressures and will respond by changing in ways that create new opportunities. The changes will be driven by several factors. Economics will be a major influence. Basic research will develop new extractants and ways of contacting the two phases. Alternative technologies will compete with LLS, as mineral resources decline and metal recovery becomes more cost effective. The need for more precise analytical devices will drive further innovation, as will the shift in Department of Energy funding to site cleanup activities. Tightening environmental rules and good stewardship practices will make their mark on LLS trends also. In response to these pressures, LLS technology will need to improve in ways such as employing alternative LL techniques, moving into related solid-liquid extraction systems, and promoting better public relations.

A second identified trend is that the theories and tools used in LLS will become more effective. Historically, LLS has progressed toward more sophisticated extractants and techniques. Up until the 1940s, LLS used neat solvents, which often precluded the use of the technology for metal salt extraction. In the 1940s chemists began using chelating extractants, opening up the possibility of metal removal. In the 1970s, hydrometallurgical extractants became commercially available. During this time, crown ethers were developed as extraction chemicals. Subsequent to this era, lariat ethers and calixarenes were developed to augment the available extraction approaches.

While extraction chemicals were evolving, techniques for contacting liquids also changed. Separation funnel technologies lead to continuous-contacting devices such as the Craig extractor, pulse columns, mixer-settlers, centrifugal contactors, and centrifugal partition chromatography (CPC). Extraction chromatography is a recent adaptation of LLS in which the solvent is sorbed onto porous solids, allowing a chromatographic approach with stationary solvent. Related membrane technologies included bulk liquid membranes, supported liquid membranes, emulsion membranes, and membrane-assisted solvent extraction. The membrane-assisted solvent extraction techniques are sometimes referred to as dispersionless solvent extraction, because they allow separation to occur without dispersion and accompanying solvent entrainment.

A third trend over the next 20 years will be that LL extraction technology will continue to diversify. Areas where this diversification will be seen include solvent extraction, supercritical extraction, extraction chromatography, liquid membranes, liquid membrane electrodes, LL electrochemistry, and the use of lipophilic ligand vesicles. This diversification will lead to improvements in each of these areas. For example, diversification of solvent extraction technology will produce improvements to solvent chemistry, including better ligand selectivity, faster kinetics, lower cost, less volatility, and faster coalescence. Diversification in this technology also will drive the design of more effective processes (i.e., ones that reduce secondary waste, have greater internal recycling, and more precise process controls) and the development of better contactors that produce faster mass transfer, reduced entrainment, and increased energy efficiency. Since many of the recently employed solvents are relatively expensive, diversification will lead to the development of better solvent recovery methodology. Finally, these improvements in solvent extraction technology will require additional fundamental research to determine the environmental and toxicological fate of new solvents and to provide deeper insight into LLS chemistry and improved research tools.

A fourth identified trend in LLS is that, despite concerns expressed by some authorities, new extractants will continue to be developed and utilized. This development will be driven by several

factors. Scientific curiosity will produce hundreds of new candidate extractants each year. New, demanding applications and environmental needs will place a premium on performance. Also, the current technology isn't perfect. Finally, extractant design and development will become more economical. Use of newly developed extractants, even if the chemical is expensive, may be justified if overall process costs are cheaper, or if the extractant performs a specific extraction that is currently not possible (i.e., a niche application.)

As an illustration of the use of LLS, ORNL has developed the SRTALK process for removal of pertechnetate from wastes at Oak Ridge, Tennessee and Hanford, Washington. The process uses a crown ether to effectively extract sodium pertechnetate. The pertechnetate ion can then be stripped using water. While the capital costs of the process are greater than for a representative ion exchange column system, operating costs are significantly cheaper. The process is made possible by new, advanced contactors. The rapid cycling of the solvent keeps solvent volumes low during the process. Also, the high cost of the solvent requires solvent recovery. Up- and down-stream benefits of this application include the lack of generated spent resin or stripping wastes, the ability to treat variable waste streams, and the generation of a relatively "pure" pertechnetate residue that can then be vitrified.

The following statements were made in response to questions.

- The problem with the use of highly selective, expensive extractants in solvent impregnated ion exchange resin is that only a portion of the extractant is actually being used at any one time. New contacting approaches have made LLS the preferred technology in these cases. This is especially true when the metals concentrations are in the range of 1-50 g/L, where the amount of waste generated is greater than for LLS.

Additional statements concerning this presentation are covered in the summary of Discussion Period 3, which took place on May 6, 1998.

Design, Synthesis, and Evaluation of Highly CO₂ Soluble Chelating Agents for Carbon Dioxide Extraction

Presented on May 6, 1998 by Eric Beckman, University of Pittsburgh

The use of liquid carbon dioxide (CO₂) as an extraction solvent has many advantages. These include low toxicity, non-flammability, wide availability, low cost, minimal governing regulations, and relatively low critical pressure (72.8 atmospheres) and temperature (31.1 °C). Conversely, CO₂ has several disadvantages, including high vapor pressure in liquid form (925 pounds per square inch (psi) at 25 °C), which increases equipment costs, and poor solvent properties. The University of Pittsburgh is investigating reasonable application targets for liquid CO₂ extraction. Liquid-liquid extraction from water is an excellent application, because it doesn't contaminate the water with organic solvents. Gaseous hydrogenation of organic liquids is another advantageous application that greatly reduces safety concerns during the process.

Ideally, it is better to recover solutes from liquid CO₂ without reducing the pressure to the boiling point. This approach is preferable due to the relatively high cost of repressurizing the gas. In addition, CO₂-philic compounds can be used to lower the absolute pressure required in a process, thus reducing capital costs. These compounds are relatively expensive, making recycling of them economically advantageous.

An example of the use of these concepts is the decaffeination of tea and coffee. Liquid CO₂ is used to strip caffeine from the product. Using liquid-liquid extraction with water, the caffeine is then transferred to the water while the CO₂ remains in liquid form. The caffeine then is removed from the water using reverse osmosis.

When used for metals extraction, liquid CO₂ is a poor extractant. In order to reduce this problem, CO₂-philic compounds are introduced. These compounds typically contain a conventional chelating head group and a CO₂-philic tail. CO₂-philic tails can be made from fluoroalkyls, fluoroethers, and silicones. The reason these and certain other compounds are CO₂-philic is unclear. The chelating head groups are chosen to target the metal(s) of interest.

When performing liquid-liquid extractions, it is important to stay above the cloud point -- the point at which the temperature and pressure cause phase splitting of the liquid CO₂. This facilitates even distribution of the chelating compound, which will be miscible in all proportions. Increasing the length of the CO₂-philic tail makes the compound miscible at lower pressures. Lower operating pressures must be weighed against the increased cost of compounds with longer tails. Silicones are the least expensive CO₂-philic compounds but require the highest operating pressures. Fluoroethers are the most expensive compounds but require the lowest pressures.

There are two ways to obtain selectivity in liquid CO₂ extractions. The choice of chelating agent head group provides selectivity for certain metals over others. Also the pressure at which the extraction is performed favors capture of certain metals. It, therefore, is possible to use a general chelant and still obtain good selectivity by varying the operating pressure.

In laboratory experiments, the University of Pittsburgh looked at removal of lead (Pb), mercury (Hg), and arsenic (As) from laboratory sand. Initial Hg levels were about 2,000 ppm. Approximately 1.5 moles of chelant were added for each mole of metal. Good Hg extraction was observed for all chelating head groups used. Poor extraction was observed for Pb. It appeared that interactions between the head group and tail caused the poor removal. By adding alkyl spacers between the head and tail, improved removal was achieved.

A problem when using liquid CO₂ and water is that the CO₂ dissolves in the water, lowering the pH to approximately 2.8. This lower pH hampers extraction efficiencies. A review of extraction literature showed that the compound APDC (ammonium pyroldine dithiocarbamate) is very effective in removing a wide range of metals from solutions with pHs as low as 0.5. A piperazine-based compound was utilized as a functional analog to APDC, resulting in good removal of copper (Cu), nickel (Ni), and cadmium (Cd), down to pHs approaching 1. Chromium (Cr) and zinc (Zn) were not removed as effectively.

Although most of the University of Pittsburgh's liquid CO₂ extraction research has focused on environmental remediation, precious metals refining appears to be an industry in which this technology can make great contributions. Instead of traditional solvent extraction methodologies, liquid CO₂ containing a CO₂-soluble ligand (typical ligands for this application are tertiary amines) would be contacted countercurrent to the metal-bearing acid. The metal ions would bind to the ligand until displaced by hydrogen (H₂) in the recovery step. H₂ is a preferred reducing agent for liquid CO₂ extractions because the extraction system is single phase and the required concentrations of H₂ do not exceed lower explosive limits.

In summary, the following points should be emphasized:

- The strategy of generating CO₂-soluble chelating agents is fairly general.
- Almost any chelating head group can be functionalized to work in liquid CO₂.
- The use of CO₂ allows for creative approaches to recovering metals from the extraction solution.

The following statements were made in response to questions:

- Liquid CO₂ extraction can be designed and operated as a continuous process, particularly when metals are being extracted from aqueous streams and then back extracted into water.
- Research to date has not produced the undesirable metal carbonyls during metal recovery when H₂ is used, possibly due to the lower temperatures at which the regeneration takes place.

Discussion Period 3, May 6, 1998

Discussion of the Faratech Presentation

With the Electrochange system, operation can continue until the anionic resin is exhausted. Since metals are being plated onto the cation resin/graphite mixture, this step does not limit operation time. The process is different from electrowinning due to the presence of the resin, and the ability to remove metals to lower concentrations (below 1 ppm).

During regeneration, the present unit uses approximately 10 gallons of rinsewater. Since water is the only regenerant, a final rinse of the resin to remove regeneration chemicals is not required. Both the anionic and cationic resins are regenerated at the same time and may either be managed separately, or combined and returned to the plating operation. The key to optimizing the system is to size the anionic and cationic portions of the unit so both become exhausted at about the same time. The unit also should be sized to accommodate peak concentrations and flows.

During regeneration, hydrogen (H_2) and oxygen (O_2) gases are evolving from the anionic and cationic frames of the unit. At the present time, these gases are not captured. A suggestion was made to make the polymer electroactive and switchable. By reversing the current during regeneration anions and cations would be replaced without the generation of gases. This approach also would make the process more energy efficient. For example, Oak Ridge National Laboratory is looking at anion exchange chemistry and, in particular, crown ether complexes that act as lipophilic cations. They also are looking at coating cathodes and anodes with a ferrocene polymers (with an ion exchange membrane in between). At the anode, anion exchange could be started, creating ferrocenium cations which extract an anion from the aqueous phase. At the cathode the ferrocenium cations will be stripped. Gases will not be generated at either the anode or cathode and energy use will be reduced.

Faratech has tried to recover some of the energy in previous plating projects. By modulating the current, hydrogen was readsorbed before it could escape.

Even though gases are generated at the anode and cathode, there is no evidence that gas bubbles interfere (e.g., block) the ion exchange process.

Question related to the reluctance of industry to try new technologies (directed to Bruce Moyer).

A reluctance to use new, expensive compounds may, in part, be due to the additional engineering necessary for their use. The key may be to find individuals who are enthusiastic about the chemistry and the engineering involved in implementing the new technology.

Facilitated Group Discussion, Room 1705

Wednesday, May 6, 1998, Jack Watson, AIChE, Moderator

Objective

The stated objective of the discussion was to use the information shared during the Workshop presentations and whole-group discussions to construct a vision for metals adsorption over the next 20 years and set goals for the next 5, 10, and 20 years that will help achieve the vision. Recommending EPA's role in helping achieve the vision was another objective of discussion.

Problem Identification

The approach used was to first identify the elements and compounds of concern, as well as their primary sources. Table 1 lists this information.

Table 1. Elements/Compounds of Environmental Concern and Their Sources.

Element/Compound	Primary Sources
Ammonia (NH_4^+)	Sanitary wastes, Scale inhibitors
Arsenic (As) and its oxides	Mining, Sediments, Solid wastes
Barium (Ba)	Natural gas wells and pipelines
Boron (B)	Agricultural operations
Calcium (Ca) salts	Treatment of metal-bearing production and waste streams
Chromium (Cr)	Leather tanning, Plating, Sediments, Solid wastes
Cobalt (Co)	Nuclear materials production and usage sites
Copper (Cu)	Electronics industry, Consumer products, Water supply systems, Sediments, Solid wastes
Iron (Fe)	Consumer products, Pipes
Mercury (Hg)	Ground water, Combustion sources, Sediments, Solid wastes
Lead (Pb) and ^{210}Pb	Sediments, Solid wastes, Consumer products, Natural gas wells and pipelines

Element/Compound	Primary Sources
Molybdate (MoO_4^-)	Cooling water
Nickel (Ni)	Electronics industry, Waste water, Petroleum refinery vacuum residuals
Palladium (Pd)	Automobile catalytic converters
Phosphate (PO_4^{3-})	Agricultural runoff
Rhodium (Rh)	Automobile catalytic converters
Selenium (Se)	Petroleum wastes
Silver (Ag)	Photoprocessing, Mining
Sodium (Na) salts	Treatment of metal-bearing production and waste streams
Technetium	Nuclear materials production and usage sites
Tin (Sn)	Coatings, Preservatives
Vanadium (V)	Natural gas wells and pipelines, Petroleum refinery vacuum residuals
Zinc (Zn)	Furnace dust

Quantitative Goals

Vision 2020 set goals of 30% reduction in wastes and 30% reduction in energy costs for a large number of industries by the year 2020. The Department of Energy (DOE) and Council for Chemical Research (CCR) are interested in assisting in the achievement of these goals from an energy and manufacturing perspective, respectively. EPA also is interested in the achievement of these goals from those perspectives, but also from the perspective of the environmental benefits associated with them.

It was difficult for the discussion group to agree upon any quantitative goals for metals reduction or technology development. The consensus was that environmental goals will be set by the regulating agencies, that quality goals will be set by the manufacturers. (It was acknowledged that overlap will exist between these two sets of goals.) Technologies will then be developed to meet these goals, because manufacturers will purchase effective systems.

Approaches, such as identifying two or three candidate technologies to research in the next five years, developing the technologies in the following five years, and then allowing market forces to drive implementation during the succeeding ten years has several serious problems. It was felt that the time frames for research and development were too long (18 months was suggested as a realistic

time frame that would be supported by manufacturing companies.) Also, changes to regulations during the longer time frames could adversely affect deployment of the technology (i.e., changes to discharge limits could make newly developed technologies unnecessary or inadequate.)

Opportunities for Reaching Goals

Computer-aided design for the development of functional groups. The current applications are primarily found in the development of biological materials. This approach can be used for a wide variety of compounds, including cations, anions, and chelating groups. Computer-aided design offers opportunities for lower-cost screening of potentially useful materials. This tool could positively affect the metals adsorption field within five years. Academia, government, and industry all could assist in this opportunity.

Development of complete treatment processes that separate metals and organics. The idea is to close the loop and have a complete process that can be understood and demonstrated by the user. The information included on the system would include an economic analysis, extensive and clear engineering, and marketing. The system would be highly specific and generate minimal waste. A 5 - 10 year time frame for development of this opportunity is realistic. Academia, government, and industry all could assist in this opportunity.

Process control and zero discharge. Benefits include reduced exposure to workers, with increased use of remote sensors. Zero discharge needs to include discharge of regenerant solutions, salts, etc. The opportunity lies in creating a complete cycle where a company uses another company's wastes to make their product. This approach is particularly difficult to implement on a small scale. A 10 - 20 year time frame for implementation was estimated. Academia, government, and industry all could assist in this opportunity.

Remediation. Opportunities exist for the cleanup of impacted environmental areas using currently available adsorption technologies. The use of bifunctional chelants and innovative concepts, such as foams, can be used to remediate particular aspects of contaminated sites. DOE has a model for the partial cleanup of sites. Economic forces then can drive the partial remediation. These ideas could be implemented within a 5 - 20 year time frame. Academia, government, and industry all could assist in this opportunity.

Information management. The World Wide Web offers great opportunities for information sharing. Professional societies also offer conduits. A searchable, interactive database would help technology developers and users share information. This type of database would facilitate the spinning-off of technologies, where a technological solution to a problem in one field could be identified and tried in another application. A directory similar to the Thomas Register for metals adsorption would be beneficial. A government "seal of approval" for new technologies also may be helpful, although government endorsement should not be implied. These opportunities could be implemented within 5 years. Government could take the lead on these areas.

Education. If industry is better educated/trained in the types of technologies available today, they may be more receptive to innovative ideas. Engineers may not be buying new technologies because

they do not understand the separation mechanics and associated chemistry. Additionally, industry has become skeptical about new ideas due to misrepresentation and failed technologies in the past. The risk factors for small companies to try innovative technologies are large. One solution to get companies to try new ideas is to discount the purchase price for the first units. A 10 year time frame may be realistic for this opportunity. Academia and industry could take the lead on this area.

Recycling/segregation for recycling of wastes by small companies. Due to economies of scale, large companies seem to be recycling well. Small companies, however, appear to be disposing instead of recycling. In particular, dilute waste streams could be recycled/utilized by other companies. This opportunity could be implemented in 5 years. (No lead was identified.)

Technology improvements

Off the shelf continuous ion exchange. The development of turn-key continuous ion exchange systems would help small and medium businesses access the technology without all of the engineering design typically associated with purchase and installation. Given the diversity and specificity of applications, however, turn-key systems may never be profitable and therefore not be available. If commercially viable, a 5 year time frame may be sufficient to implement this opportunity. (No lead was identified.)

Highly selective separation media. Opportunities exist for the development of media with the ability for high rates of removal of specific components within a mixture. The approach would allow recovery of high purity material. A time frame of 5 - 10 years should be sufficient. (No lead was identified.)

Improved ion exchange kinetics. Development of this opportunity would reduce capital cost. A 5 - 10 year time frame was suggested as adequate for development. (No lead was identified.)

Membrane contactors for liquid-liquid extraction. Development of this opportunity may take 5 - 20 years. (No lead was identified.)

Solid-state ligands. These ligands could be electrically controlled with multifunctional groups. Using redox reactions and improved kinetics these ligands would be versatile and an important addition to separation technologies. A time frame of 10 years may be appropriate. (No lead was identified.)

Improved synthesis chemistry. There are opportunities for better materials and better pathways/methods for synthesis of these materials.

Obstacles to Reaching Goals

One impediment to commercialization of technologies developed in academia is a lack of knowledge on whether a technology is marketable and, therefore, merits further research and development. There needs to be an organization where chemists and engineers can link up to examine the commercialization potential of a new or improved technology. These "centers of commercialization"

also could bring together technology developers and potential users to discuss changes that would improve the technology. Additionally, the centers could help arrange start-up funds. Small Business Innovative Research (SBIR) grants are one option, but increased competition for these funds have made it difficult to obtain financial resources through this mechanism. Additionally, the cost and difficulty in applying for grants and the costs of administering them are very burdensome to smaller organizations.

Examples of this type of center are the Alfred University/Corning Glass business incubator in New York and the Ben Franklin Institute in Pennsylvania. Concerns with these two organizations were expressed, including nonresponsiveness to innovative ideas and preferential treatment of large companies with new product ideas. A similar approach that funds small-to-medium size company research would be beneficial in advancing innovative metals adsorption technologies.

A lack of an ombudsman to help coordinate technology development is another obstacle.

A system to allow incremental remediation has not been developed. There is no mechanism for treatment of part of the problem. Also, Records of Decision (RODs) lock in older technologies.

Low fines and legal delays hinder adoption of new technologies.

The Role of EPA

There were numerous concerns with the mechanisms by which EPA develops and licenses technologies. The concerns included the agency competing with small businesses on research and development of innovative technologies. Cooperative research and development agreements (CRADAs) are out of reach for small businesses. The consensus was that EPA should not compete with or provide a competitive advantage to selected companies.

EPA should be doing the following activities:

- Looking at metals originating from consumer wastes.
- Addressing orphan sites, such as abandoned mines.
- Developing processes for municipal waste plants and have "street enforcement" of low level regulations for consumers.
- Develop regulations that are applied to everyone regardless of specific circumstances.
- Work closer with industry on identifying priorities while avoiding political considerations.
- Explore technologies (internally and externally) to determine what minimum discharge levels are achievable.
- Take on "high-risk" research with payback periods greater than 20 years.

Facilitated Group Discussion, Room 1706

Wednesday, May 6, 1998, S. D. Alexandratos, University of Tennessee,
Moderator

Objective

A facilitated discussion group met to discuss metals separation issues. Emphasis was placed on identifying areas for future research, as well as goals, milestones, and measures for assessing progress. Participants were asked to focus on priority metals, due to their toxicity or prevalence in effluents and emissions, and on Vision 2020's goal to reduce process related wastes and energy usage by 30%. Participants were informed that the topics discussed during the facilitated discussions may be used by the research community to guide separations research efforts. The EPA firmly stated that this information would not be used to develop Requests for Proposals (RFPs) or serve as the basis for unsolicited proposals. Discussions were organized under the following topics: 1) research areas; 2) research needs; 3) how to achieve research needs; and 4) milestones 5/10/20 years.

Research Areas

Participants identified four general research areas during the facilitated discussion: Resource Conservation and Recovery Act (RCRA) metals; the semiconductor industry; the primary metals industry; and the electroplating industry. Although not discussed in detail, participants noted that Superfund site wastes and mine drainage (Berkeley Pit) could also serve as potential research areas.

RCRA Metals. The discussion of priority metals was quickly narrowed to RCRA metals. Although a number of traditional technologies are currently available to reduce RCRA metal concentrations below current regulatory limits, new technologies with higher selectivities for RCRA metals may be needed if regulatory limits drop and for companies having difficulties meeting the current limits. Although some RCRA metals [i.e., copper (Cu), mercury (Hg), and lead (Pb)] are being phased out of use by the DOE and other organizations, participants agreed that additional separation and recovery research is needed to deal with trace and non-process specific impurities.

Arsenic (As) was discussed in detail during the facilitated discussion. It was targeted because it is a drinking water issue in the United States and developing countries and also is present as a trace contaminant in lead smelting, zinc smelting, and the oil industry. Although some participants identified a general need for As removal technologies, particularly low-cost technologies for developing countries, others countered that there were a number of effective traditional technologies currently available (e.g., ion exchange, ferric hydroxide precipitation, and aluminum coagulation). As an extension of this topic, oxyanion separation (arsenate, chromate, selenate, etc.) was identified as a potential research area because the resins used to remove these compounds often have low capacities and have selectivity problems in the presence of high sulfate concentrations.

Semiconductor Industry. The semiconductor industry was identified as an industry that would benefit from the development of new metals separation technologies. The semiconductor industry is one of the most profitable and least regulated industries in the United States. In addition to providing technologies for generating ultrapure water for processing, metal separating companies may be able to supply "value added processes" to the semiconductor industry. Although not a current effluent or recovery issue, copper discharge/recovery may become an issue as the industry develops the ability to do copper plating in 0.25 micron trenches. If this technology is successfully developed, metals separations vendors may be able to "break into" this industry as copper plating replaces aluminum plating.

Participants noted that metal separation technology vendors may have some difficulties convincing the semiconductor industry to adopt their technologies. Many semiconductor manufacturers are reluctant to use recovered water in the front end of a ultrapure water train (although this is being done to a limited extent in Europe). The use of new and or add-on technologies is also hampered by a general reluctance to adopt technologies not in use by their competitors. (Note: Overall, the different semiconductor manufacturers use basically the same technologies.)

Technology vendors will also need to provide detailed data to semiconductor manufacturers demonstrating that their technology/product does not interfere with production. This data will have to meet exacting precision requirements.

Primary Metals Industry. The primary metals industry was identified as a potential research area because of its size (it is much larger than the electroplating industry) and because this industry typically disperses a large amount of Toxic Release Inventory (TRI) metals to the environment. Cobalt (Co) and nickel (Ni) were identified as two commonly released metals. Since both of these metals are considered "valuable" (cobalt because of its cost and need to be imported; nickel because of its cost, which is \$3 to \$6 per pound), the primary metals industry may be amenable to using new or existing separations technologies to recover these metals for resale or reuse. Workshop participants cautioned, however, that it may be difficult to persuade this industry to use metals recovery technologies for the following reasons:

- Difficulties forming effective in-house partnerships between facility production personnel and facility environmental personnel
- Manufacturing space requirements for the metals recovery equipment
- An industry-wide move away from diversification and a move to mainstream production issues/processes
- Acid waste has not been specified as a major environmental concern and there are no regulations driving the use of metals separation technologies
- Many "traditional" cost-effective acid recovery technologies are already available (vacuum evaporation, electrodialysis, etc)

Metals separation technologies which improve the effectiveness and efficiency of anodizers and picklers and are capable of handling high impurity loadings may be needed.

Electroplating Industry. The electroplating industry was also identified as an industry which would benefit from the development and use of industry-specific metals separation technologies. Although ion exchange technologies are being used by some platers, many small platers still rely on low current density dummyming or chemical alternatives. Premature bath disposal (i.e., after only 3 rinses) and difficulties removing metal ions in the presence of chelators are common industry problems.

(Note: Many participants believed that use of metals separation technologies would increase if the chemical companies responsible for providing plating chemicals/solutions supported their use. In general, these companies have a large impact on the electroplating industry. The chemical companies also need to be convinced that recycling/recovering plating solutions for end users is to their benefit and can result in cost savings to their users over disposal.)

Research Needs

A variety of generic, general, and media and technology specific research needs were proposed during the facilitated discussion. These research needs are listed, with supporting text, in the following subsections.

Generic Research Needs. In response to the request to identify metals separation research needs, participants proposed the following:

- identify methods for defining selectivity (e.g., ranges and needs)
- increase research into selective material development
- define what selectivities are needed
- develop systems to improve kinetics (i.e., techniques that minimize internal mass transfer systems, whether monomeric or polymeric)

In response to Vision 2020's goal of 30 % reduction of process wastes, one participant proposed the following "programmatic" research approach:

- focus on industries which currently use separating media/technologies
- identify their waste production/recovery problems and research needs
- focus the majority of the research on ion exchange because it is used most often
- cut wastes at these locations (by 30 %) rather than going into new industries which you are not even sure want to use new technologies

General Research Needs. General research areas are discussed in the sections below.

General Resin Research. Ion exchange is the most frequently used metals separation technology; however, the following customer concerns need to be addressed:

- reduce the amount of regenerates used
- reduce the amount of rinse water used to treat the ion exchange resins
- improve equipment and resin efficiency, including replacement of dated equipment which cannot be retrofitted, oversized equipment that takes up valuable manufacturing space, and ion exchange resins with low capacities or poor selectivities

In response to these and other concerns, Workshop participants proposed that research be performed to develop resins with the following general characteristics:

- higher transfer rates
- better selectivities
- higher capacities

According to participants, higher transfer rates should result in smaller equipment and, thus, reduced costs. Improved selectivities would also improve resin efficiency and reduce the amount of regenerates used. Capacity improvements should result in smaller resin inventories, the use of less regenerate, and, ultimately, reductions in equipment size and technology costs. (Note: Although not a true "research need," system designs can also be modified to minimize the amount of resin used to handle a required throughput.)

Hybrid Applications. Participants also identified the need to research hybrid applications of ion exchange and other commercially available technologies. In many cases, existing ion exchange technologies can be combined with other commercially available technologies to improve resin efficiency (e.g., the capacity of an ion exchange resin can be improved by adding a modulated electric field.)

Modification of Existing Resins. Resin efficiency may also be improved by modifying an existing resin to change its kinetics and overall performance. For example, participants noted that you could potentially take a Rohm & Haas resin (IRC 718) and attach a sulfonate group to improve kinetics (e.g., generate sharper breakthrough curves) and selectivity.

Future Resins with Broader Applications. When asked to come up with a description of a future resin which can be broadly applied, participants proposed the development of a "scavenging resin" to support current manufacturing technologies (which frequently emphasize end of pipe treatment over pollution prevention). This resin would need to:

- possess a 20 to 50% greater capacity than present resins
- exhibit the ability to overwhelm chelants
- demonstrate improved selectivity for target metals over the alkali/alkaline earth metals
- regenerate efficiently
- cost the same or less than present day resins

Ideally, this material would be identified as a separation media rather than a resin.

Media/Technology Specific Research Needs.

Metals Separation for Separating Electrolytic Copper from EDTA and Formaldehyde. Research is needed to develop metals separation technologies which can separate electrolytic Cu from ethylenediaminetetraacetic acid (EDTA) and formaldehyde. This research is needed so that U.S. plating companies can compete with foreign platers who are still using electrolytic Cu processes. Although many larger electroplaters in the U.S. have replaced electrolytic Cu technologies with direct plating processes because of EDTA and formaldehyde pollution issues, many foreign competitors with less stringent pollution regulations are still using electrolytic Cu processes. Because electrolytic copper vertical plating is generally superior to direct horizontal plating, companies in Japan and Europe are able to produce better quality plating than their counterparts in the U.S. As PWBs get more sophisticated (3 millimeter holes, fine features, etc.), the U.S. may need to return to electrolytic Cu plating to compete.

Premature Bath Disposal Research. In addition to addressing the more obvious reasons for early bath disposal, such as the rapid buildup of aluminum ions (Al^{+3}) concentrations during the plating of electrolytic Ni onto Al substrates, future research needs to address the less obvious causes for early bath disposal (e.g., elevated sulfate, Al, and orthophosphate concentrations.) These contaminants are not necessarily detrimental to processing/production and may be in fact be added as part of the production process (e.g., orthophosphate development during electrolytic Ni bath processes). Research into this area should focus on selective anion and cation exchange (including organics), not just metals.

Resins with Selectivities for Metals Over Chelators. Many ion exchange resins do not work effectively in the presence of chelators and often compete unsuccessfully with chelators to separate metals from solutions. Since this is a key issue for electroplaters, the future development of resins with selectivities for metals over chelators (e.g, iron specific resins or resins which work in the presence of EDTA) was identified as an important research need.

Arsenic, Arsenate, and Oxyanions. Typically, resins used to remove arsenates and other oxyanions (chromate, selenate, etc.) have low capacities and have selectivity problems in the presence of high sulfate concentrations. New resins need to be developed which are selective for arsenate and other oxyanions over sulfate.

Although there are a number of traditional technologies (e.g., current Al coagulation processes), which can be used to reduce As concentrations to 10 ppb, new technologies with a higher selectivity for As may also be needed if the regulatory limit drops from 50 ppb to below 5 ppb. Technologies/resins are also needed for those companies who are having problems meeting the current regulatory limit using available technologies.

How to Achieve Research Needs?

A variety of generic, EPA-specific, and general approaches were proposed during the facilitated discussion to achieve the metals separation research needs. These research needs are listed, with supporting text, in the following subsections.

Generic Approaches to Achieving Research Needs.

True Basic Research vs. Directed Research. Participants proposed encouraging a mixed approach to metals separation research, in which true basic research was balanced by utilizing directed research goals developed in response to market and industry needs. Although some participants were concerned that too much direction would stifle creativity, other believed that real-world goals help to focus research.

Motivating Technology Use--Regulations vs. Cost. Some participants believed that new regulations addressing metals in the environment would foster the development and use of new metals separation technologies. They noted that many companies will only use a new metals separation technology if the technology was economically feasible and satisfied a regulatory compliance need. They questioned why manufactures would use technologies which reduce concentrations to part per trillion (ppt) levels if these levels were not a regulatory requirement.

Future EPA regulations may not be solely based on best demonstrated available technologies (BDATs). If the Agency directs its focus towards determining the risk associated with specific metals and identifying technologies that can treat to below the risk levels, participants agreed it is unlikely that new regulatory limits would be adopted which would result in new metals separation processes being adopted by industry.

In response to these issues, participants stated that the best way to get industry to use metals separation technologies is to demonstrate an economic as well as an environmental benefit. They noted that most large companies will consider using a new technology if payback is less than 2 years. In most cases, however, the larger companies are in compliance using presently available technologies. They also noted that even if you could demonstrate a payback of less than 1 to 1 ½ years, many smaller companies will still not use new technologies.

Technology Validation. Although many manufacturers are interested in new metals separation technologies, they are unwilling to be the first to use a technology and to serve as a test site for a technology (too much risk). Many of the participants thought that technology utilization would improve if independent technology evaluations could be performed to validate technology

performance. They suggested that the EPA continue to support existing programs for technology validations (CTC and ETV) and develop additional independent verification testing partnerships with other federal organizations (e.g., DOE). The following suggestions were offered:

- set up small test beds where you can have long term beta testing of new technologies and hybrid technologies
- dedicate test sites for sustained testing which can support a variety of industries
- test the technologies under a number of different environmental circumstances
- publish and distribute the test results to the public

Participants with experience in existing technology verification programs offered the following cautions:

- the organizing group (DOE) or third party test site (CTC) currently selects/prioritizes technologies for testing
- existing validation testing programs are relatively expensive and the testing process is slow

They also noted that with internal corporate research and development (R&D) and government funding on the decline, funding for technology validation testing may be difficult to obtain. This claim was countered by participants who believe that funding is always available for technologies with a real market. They noted that academia receives a large amount of corporate R&D funding. Participants also noted that ATB funded millions of dollars in research this year, although most of the awards required small business involvement. Additionally, some communities are in the process of developing partnerships (among academia, research facilities, new technology vendors/developers, etc.) to encourage new economic development and that these communities may have funding available for technology validation testing within the next couple of years.

Employing a Systematic Approach to Develop Systems with High Capacity and Selectivity. Participants noted that a systematic approach is needed to develop systems with high capacity and selectivity. As part of this approach, research needs to identify what selectivities are needed, e.g., Pb vs calcium (Ca), Pb vs Cu, or toxic/valuable materials versus innocuous background metals, such as sodium (Na), Ca, and magnesium (Mg), and predict performance characteristics before development, e.g., for complexation of metals from chelants. They then need to review various system designs and select an appropriate support media. Capacity and regenerability can be improved by modifying the system design and selecting a different support media (e.g., membranes typically regenerate easily and can handle higher concentration factors than other platforms.)

Support Media Issues. System kinetics can be impacted by the type of support media used. Although the intrinsic kinetics of most binding agents are fast, the kinetics of a polymer bond can be slow. For example, the kinetics of a binding agent bound to a microporous particle is usually slow. If the binding agent is attached to the pore surface of a macro porous membrane, however, the kinetics will not be limited by the support system (although capacity

may be impacted). Ultimately, the issue is not kinetics, but the elimination of internal mass transfer resistance. This can be readily accomplished by employing membrane, liquid/liquid extraction, and other approaches.

System Design Issues. In order to design a cost effective metals separation system, fluid mechanics, separating media quantities, and the quantity and nature (chemical and physical) of the influents and effluents need to be considered. Participants noted that "orders of magnitude" levels of improvement can be achieved by choosing an appropriate system design (e.g., the selection of a membrane systems with a bed volume per hour flow rate in the 100s rather than selecting a fixed bed system with flow rate of 30 bed volumes per hour.)

EPA-Specific Approaches to Meeting Research Needs.

General Program Approach--EPA In-house Research: Historically, EPA researched basic processes, new technologies, and generic technology issues (such as the ability of a technology to reduce contaminant concentrations to less than 1 ppb). This research was then used by private industry to develop new technologies directed at specific markets (i.e., new products). Although the EPA research role has changed somewhat (a lot of research is done under grant programs), participants encouraged the EPA to continue supporting "early research" efforts. The following research efforts/goals were also identified:

- to encourage research which promotes a better general understanding of how to reduce metals to ppb levels
- to support research which can be used to help specific industries reduce concentrations to specific levels

EPA-Identified Metals Separation Needs. In order to help communities and, to a lesser extent, corporations select the appropriate technologies for testing, participants suggest that the EPA identify future metals separation technology needs. This will help communities and business direct their research funding.

EPA-Generated Guidance on Ligand Use Platforms. Although fundamental chemistry determines ligand use and performance, some participants believed that metals separation research would benefit from the generation of ligand use platform guidance by the EPA. This would help prevent researchers from investigating inappropriate platform applications (e.g., it could help prevent a researcher from developing a ligand for ion exchange resins when vesicles are more appropriate). The guidance could help divide separate metals separation technologies into application classes based on the following:

- loading requirements
- volume throughput
- solution severity -- e.g., high pH, low pH, high chlorine (Cl)
- selectivity, including trace and accidental compound removal

This information could also be used to develop three or four classes of separation problems. Additionally, the guide could be used to help identify where material is being wasted because a technology does not exist to recover the material, to develop technology maps for particular systems, and to develop/identify research needs and milestones.

EPA Generated Guidance on Ligand Design. Participants noted that EPA-developed guidance to help in ligand design would be beneficial. This guidance could be used to help ligand developers:

- write computer code to design the correct ligand around a given metal ion
- determine context in which to apply the ligand
- configure ligands to address important and practical mass transfer and support issues

Milestones: 5/10/20 years

Most participants agreed that in order to define milestones, Vision 2020 goals (e.g., 30% reduction of process wastes) need to be better defined. In particular, the following questions need to be answered:

- What portion of the 30% target is metals?
- What process wastes are specifically targeted by this goal?
- What impact do regional/geographic considerations have on this goal? For example, trivalent Cr sludge can be landfilled in Ohio but not in Florida. Therefore should it be targeted for reduction only in Florida and not in Ohio?

Although these questions could not be completely resolved during the facilitated discussion, the following milestones were proposed.

General Milestones. The following "general" milestones were proposed:

- eliminate/reduce the offsite transfer of objectionable metal bearing waste (e.g., Cr, Pb, and Ag) by 30%
- reduce the amount of regenerates used by 30%
- reduce the amount of process waste produced by 30%
- improve efficiency by 30%, by reducing capital costs and the cost per pound of metals removed
- employ complete in-house recycling of metals and zero discharge where substitutes have not been employed

Specific Milestones. The following "specific" milestones were proposed.

Chromium. Some participants proposed that Cr^{+6} use during plating operations should be reduced by 60 to 65%. Although acceptable substitutes are available, these substitutes are not always appropriate.

Cadmium, Mercury, and Lead. Participants proposed that cadmium (Cd), Hg, and Pb use during plating operations should be reduced by 100%. This milestone concurs with both EPA and DOD current/proposed policy. These metals were targeted because of their toxicity and because products plated with these materials often end up in the environment. Participants noted that because these metals will always be present in some area of manufacturing, either as a residual or a process waste, adsorption/separations research should continue to target these metals even though they may not be main components of the production process in the future.

Metals Finishing Industry Goals. In response the questions regarding how much of the 30% waste reduction identified in Vision 2020 addresses metals, a participants proposed targeting the metal finishing industry's goals of 98% utilization of metals and 50% waste reduction on a facility basis. These goals were proposed by the metal finishing industry, in part because industry members believe that the resulting increases in metals utilization will result in higher profits.

EPA Strategic Partnerships. The development of strategic partnerships between EPA and other organizations (e.g., academia, entrepreneurs, and new technology vendors) is needed to encourage new technologies and concepts. As part of this effort, EPA would help prioritize metals problems and research needs, as well as encourage/promote the collection of performance and cost data.

Federal Definition of High Risk Metals Issues. Participants concurred that regional considerations should be replaced with federally defined high risk metals issues within 5 years. Specific pollution prevention and control/treatment goals should be attached to these high risk issues. Conflicting federal policies focused on eliminating metals use as opposed to preventing releases through control/in-plant recycling need to be resolved. Federal agencies need to concur that the overall goal is to eliminate risk by achieving zero discharge, whether through recycling or process replacement.

Rules and guidelines also need to be developed within 5 years to help industry respond to priority issues (constituents and problems). These guidelines need to clarify when replacement of a process chemical (e.g., chromic acid during plating) is more appropriate than in-plant recycling with zero discharge. This guidance also needs to identify appropriate pollution prevention efforts for specific materials and clarify when a material becomes a pollution issue (e.g., when it is first produced, when it enters the plant, when it leaves the plant, etc.).

Other Comments

Participants also had the follow recommendations:

- EPA should educate the public about metals separation technologies, specifically the cost savings associated with using metals separation technologies

- EPA should promote interdisciplinary cooperation within different researchers doing separation
- EPA should determine what the real market is for separated metals and evaluate whether there is enough value to generate interest/research

Participants also thought that the following may be helpful in encouraging metals separation technology use:

- tax incentives to encourage business to use new technologies (although some participants believed that "good technologies" do not need incentives to encourage technology use; the technology saves money and that is why it used
- federal patent protection so that U.S. companies can compete in international markets and develop technologies in cooperation with researchers from other countries
- technical liaisons assigned to specific SBR technology projects

Appendix: Metals Adsorption Workshop Participants

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