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Emerging Technologies:

Bio-Recovery Systems Removal and Recovery of Metal Ions from Groundwater

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Risk Reduction Engineering Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

DISCLAIMER

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FOREWORD

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. As the enforcer of national environmental laws, the EPA strives to balance human activities and the ability of natural systems to support and nurture life. A key part of the EPA's effort is its research into our environmental problems to find new and innovative solutions.

The Risk Reduction Engineering Laboratory (RREL) is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

Now in its fourth year, the Superfund Innovative Technology Evaluation (SITE) Program is part of EPA's research into cleanup methods for hazardous waste sites around the nation. Through cooperative agreements with developers, alternative or innovative technologies are refined at the bench-and pilot-scale level and then demonstrated at actual sites. EPA collects and evaluates extensive performance data on each technology to use in remediation decision-making for hazardous waste sites.

This report documents the results of laboratory and pilot-scale field testing of dead, immobilized algal cells in a silica gel polymer to remove heavy metal ions from mercury-contaminated groundwaters. It is the first in a series of reports sponsored by the SITE Emerging Technologies Program.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

A series of laboratory tests and an on-site pilot scale demonstration of Bio-Recovery Systems' AlgaSORB® technology for the removal and recovery of mercury-contaminated groundwaters were conducted under the SITE program.

Optimum conditions were determined for mercury binding to AlgaSORB®. Conditions under which mercury could be stripped from AlgaSORB® were also developed.

On-site, pilot scale demonstrations with a portable waste treatment system incorporating columns containing two different AlgaSORB® preparations confirmed laboratory tests. Over 500 bed volumes of mercury-contaminated groundwater could be successfully treated before regeneration of the system was required. Mercury was removed to levels below the discharge limit of 10 μg/L.

This report was submitted in fulfillment of Cooperative Agreement Number CR 815318010 by Bio-Recovery Systems, Inc. under the partial sponsorship of the U.S. Environmental Protection Agency. This report covers a period from October, 1988 to January 31, 1990, and work was completed as of January 31, 1990.

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Participating in the development of this report for Bio-Recovery Systems, Inc. were Dr. Dennis W. Darnall and Michael Hosea. Special recognition is given to Sandy Svec, Dr. Maria Alvarez, Rafael Tamez and David Marrs for laboratory and on-site pilot testing and coordination of analysis.

I. EXECUTIVE SUMMARY

During 1989 laboratory and on-site pilot scale testing of Bio-Recovery Systems' AlgaSORB® technology for the removal and recovery of mercury from contaminated groundwaters were conducted. AlgaSORB®, a non-living, immobilized algal bio-mass, was packed into columns through which the mercury-contaminated groundwaters were pumped. Mercury concentrations in influent and effluent were measured to determine the effectiveness of mercury removal. Once the columns showed unacceptable mercury leakage (10 µg/L), the columns were stripped of mercury and reused.

Several different AlgaSORB® preparations containing different algal species were tested for effectiveness in mercury removal.

Summary Results

AlgaSORB® testing was complicated by the fact that over the sampling period mercury concentrations in the groundwaters varied by over an order of magnitude from 150 µg/L to 1550 µg/L.

In addition it was found that one variety of AlgaSORB® showed varied mercury-binding capability with waters collected at various times. This suggested a variation in mercury speciation over the sampling period. Because of these variations, final on-site pilot scale testing was done with a blend of two AlgaSORB® preparations. One preparation had a rather high mercury capacity but also exhibited a rather high leakage of mercury and the second preparation had a lower mercury binding capacity but exhibited low leakage of mercury.

On-site, pilot scale testing was conducted November 7 to December 1, 1989. A portable water treatment system that contained columns of the two different AlgaSORB® preparations was tested over the three week period. Waters were pumped through the AlgaSORB® resins at a flow rate of 6 bed volumes per hour. Over 500 bed volumes of mercury contaminated waters were passed through the resins before effluent mercury concentration exceeded discharge levels of 10 µg/L. These results suggest that a full-scale treatment system would be effective for mercury removal from groundwaters. Costs associated with such a treatment system should be typical of those associated with commercial ion exchange systems for treatment of industrial waste waters. In contrast to commercial ion exchange resins, however, AlgaSORB® functions well with waters which have a high total dissolved solid content and which contain organic compounds.

II. INTRODUCTION

The Superfund Amendments and Reauthorization Act of 1986 (SARA) directed the Environmental Protection Agency (EPA) to establish an "Alternative or Innovative Treatment Technology Research and Demonstration Program." In response, the EPA's Office of Solid Waste and Emergency Response and the Office of Research and Development established a formal program called the Superfund Innovative Technology Evaluation (SITE) Program, to accelerate the development and use of innovative cleanup technologies at hazardous waste sites across the country.

The SITE Program is comprised of the following five component programs:

- Demonstration Program
- Emerging Technologies Program
- Measurement and Monitoring Technologies Development Program
- Innovative Technologies Program
- Technology Transfer Program

This report is the first in a series of reports sponsored by the SITE Emerging Technologies Program. Before a technology can be accepted into the Emerging Technology Program, sufficient data must be available to validate its basic concepts. The technology is then subjected to a combination of bench- and pilot-scale testing in an attempt to apply the concept under controlled conditions.

Bench- and pilot-scale testing of the Bio-Recovery Systems, Inc. AlgaSORB® technology has been performed under the SITE Emerging Technology Program. The AlgaSORB® technology is designed to remove heavy metals from aqueous solution. The process is based upon the natural affinity of algae cell walls for heavy metal ions. The sorption medium, AlgaSORB®, is composed of a non-living algal bio-mass which is immobilized in a silica polymer. AlgaSORB® is a hard material which can be packed into columns which, when pressurized, exhibit good flow characteristics. This technology is useful for removing heavy metal ions from groundwaters that contain high levels of dissolved solids.

Groundwater contamination is found at over 70 percent of the sites currently on the National Priority List (1). Groundwaters have been contaminated with either, or both, toxic organic molecules and heavy metal ions. The most common means of addressing contaminated groundwater is extraction and treatment. While biological *in situ* treatment of groundwaters contaminated with organics may be possible, there is no effective method for *in situ* treatment of groundwaters contaminated with heavy metals. AlgaSORB® was developed for removal of dilute concentrations of heavy metals from groundwaters.

III. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions:

On-site, pilot scale testing of AlgaSORB® showed effective mercury recovery from contaminated groundwaters. However, initial laboratory experiments showed the dangers in making conclusions from a single groundwater sample. These studies showed that not only did mercury concentration vary over the sampling period, but also the data suggested that the chemical species of mercury varied over the sampling period as well. In the end it was found possible to combine two different AlgaSORB® preparations to effect mercury removal from groundwaters to levels below 10 µg/L.

B. Recommendations:

Work done at the site described herein indicates that a full treatment system for mercury recovery can be installed. However, because the chemistry of other groundwater sites will undoubtedly differ from the one tested here, laboratory treatability testing will be required before the technology can be applied at other mercury-contaminated groundwater sites.

IV. BACKGROUND INFORMATION

A. AlgaSORB® Description and Previous Work

1. Introduction

The use of microorganisms in the treatment of hazardous wastes containing both inorganic and organic pollutants is becoming more and more common. There have been two approaches to the use of microorganisms in waste treatment. One involves the use of living organisms and the other involves the use of non-viable biomass derived from microorganisms. While the use of living organisms is often successful in the treatment of toxic organic contaminants, living organisms have not been found to be useful in the treatment of solutions containing heavy metal ions. This is because once the metal ion concentration becomes too high or sufficient metal ions are adsorbed by the microorganism, metabolism is disrupted causing the organism to die. This disadvantage is not encountered if non-living organisms or biological materials derived from microorganisms are used to adsorb metal ions from solution. Instead the biomass is treated as another reagent, a surrogate ion exchange resin. The binding, or biosorption, of metal ions by the biomass results from coordination of the metal ions to various functional groups in or on the cell. These chelating groups, contributed by the cell biopolymers, include carboxyl, imidazole, sulfhydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide and hydroxyl moieties (2).

Various algal species and cell preparations have quite different affinities for different metal ions (3-4). The different and unusual metal binding properties exhibited by different algae species are explained by the fact that various genera of algae have different cell wall compositions. Thus, certain algal species may be much more effective and selective than others for removing particular metal ions from aqueous solution (5).

The reaction of heavy metal ions with a non-living algal cell forms complexes which are composed of the algal cell and the metal ions. The result of this reaction, i.e., the formation of the alga-metal ion complex is basically why metal ions are toxic to living organisms and explains how the toxic effect of metal ions is amplified in the food chain. The metal ions are adsorbed to the cell even at concentrations in the mg/L-μg/L range. The bound metal ions, when accumulated over time, eventually interfere with metabolism by disruption of enzyme reactions and kill the organism. If microorganisms on which metal ions have been sorbed are used as a food source by larger organisms, the metal ions find their way into the food chain which can eventually result in toxic effects for humans.

While the interaction of metal ions with microorganisms has been known for many years, it is only recently that advantage has been taken of the high affinity of microorganism cell walls to remove and recover metal ions from industrial wastewater or contaminated groundwaters. Methods to reverse the reaction of metal ion sorption have been developed so

that when metal ions are recovered from dilute solutions they can be stripped off the cell walls in a highly concentrated form. The cells can then be reused to capture more metal ions from dilute solutions. Conditions can also be adjusted so that only one or two types of metal ions are adsorbed from a solution containing several metal ions, or a variety of metal ions can be sorbed from solution and then they can be selectively stripped from the algal cell one metal at a time (2,6).

Bio-Recovery Systems, Inc. has developed a proprietary, algal based material, AlgaSORB®, which can be used on a commercial basis to remove and recover heavy metal ions from point-source industrial wastewater, contaminated groundwaters or mining process streams. AlgaSORB® functions very much like a commercial ion exchange resin. It can be packed into columns through which waters containing heavy metal ions are flushed. The heavy metal ions are adsorbed to AlgaSORB® and metal-free water exits the column for reuse or discharge. Once the AlgaSORB® is saturated with metal ions, the metals can be stripped from the AlgaSORB® which is then ready for reuse. In comparison to ion exchange resins, however, AlgaSORB® has some distinct advantages which make it superior to ion exchange resins for certain applications (see below). In other instances ion exchange resins perform better than AlgaSORB®. AlgaSORB® has a remarkable affinity for heavy metal ions; in some cases the metal-binding capacity is as much as 10 percent of the dry weight of the cells. The algae matrix is capable of concentrating heavy metal ions by a factor of many thousand-fold.

When unadulterated algal cells are packed into columns, the cells tend to aggregate and to form cohesive clumps through which it is difficult to force water even under high pressures. However, when the cells are immobilized into a polymeric matrix, this difficulty is alleviated.

The algae are killed in the immobilization process indicating that sorption does not require a living organism, and hence the algal matrix can be exposed, with little or no ill effects, to solution conditions which would normally kill living cells. The pores of the polymer are large enough to allow free diffusion of ions to the algal cells, since similar quantities of metal ions are bound by free and immobilized cells. The immobilization process serves two purposes: (I) It protects the alga cells from decomposition by other microorganisms, (AlgaSORB® immersed in aqueous solution for over two years has shown no decrease in metal binding efficiency) and (2) it produces a hard material which can be packed into chromatographic columns, pressurized and exhibits excellent flow characteristics.

In addition to the immobilized algal matrix's usefulness for the removal of the "traditional" heavy metals from solution, it also is useful for near quantitative removal and recovery of very low concentrations (in the parts per billion range) of precious metals such as gold, silver, platinum and palladium (7).

AlgaSORB® functions as a "biological" ion exchange resin and like other ion-exchange resins, can be recycled. Metal ions have been sorbed and stripped over many cycles with no noticeable loss in efficiency. In contrast to current ion exchange technology, however, a real advantage of the algal matrix is that the components of hard water (Ca^{+2} and Mg^{+2}) or monovalent cations (Na^{+} and K^{+}) do not significantly interfere with the binding of toxic, heavy metal ions. In fact calcium or magnesium ion concentrations as high as 10,000 mg/L have little or no effect on AlgaSORB® sorption of copper at concentrations as low as 6.5 mg/L. The binding of Ca^{+2} and Mg^{+2} to ion-exchange resins (even chelating ion exchange resins which are relatively selective for transition metal ions) often limits ion exchange

usefulness since calcium and magnesium ions are frequently present in high concentrations and compete with heavy metal ion binding. This means that frequent regeneration of ion-exchange resins is necessary in order to effectively remove heavy metal ions from solutions.

AlgaSORB® is also effective for heavy metal removal from waters containing organic residues. Organics often foul synthetic ion exchange resins which limits their utility in many wastewater treatment applications, including groundwater treatments. AlgaSORB®, on the other hand, functions well in waters containing organic molecules.

2. Waste Streams for which the AlgaSORB® and Other Ion Exchange Technology is Applicable

A major source of heavy metal wastes from industrial sources comes from the electroplating, metal finishing and printed circuit board manufacturing industries. Wastewaters from these industries primarily come from rinsing operations. The rinsewaters will typically contain rather low concentrations (on the order of 100 parts per million) of heavy metal ions. Certain of these waste streams are particularly amenable to treatment with AlgaSORB® or ion exchange resins. The metals can be recovered and then either recycled back into the process or recovered for use by other industries. In addition AlgaSORB® may be useful for polishing waste streams previously treated by other methods, but which still have metal ions present at concentrations above compliance levels.

Contaminated groundwaters and surface leachates often contain heavy metals in the low parts per million or even part per billion range. The AlgaSORB® technology is well suited for removing and recovering heavy metal ions from these waters, which will often contain high concentrations of dissolved materials which are non-toxic. Often these types of waters will contain high concentrations of sodium, potassium, calcium, magnesium, chloride or sulfate which are innocuous and for which no treatment is needed. AlgaSORB® is capable of preferentially removing heavy metals which are found in these streams. Toxic heavy metal ions which can be recovered with the algal biomass include copper, nickel, uranium, lead, mercury, cadmium, zinc, arsenic and silver among others.

AlgaSORB® has a higher affinity for precious metal ions than any other heavy metal ions tested (5-6). Thus another area in which the AlgaSORB® technology is useful is in the recovery of gold, silver or platinum group metals from mining process streams, wastewaters resulting from mining operations, and industrial point source wastewater.

B. The Use of AlgaSORB® and Ion Exchange to Effect Heavy Metal Waste Minimization: Comparison to Conventional Waste Treatment

The conventional method for treating wastewaters in electroplating or printed circuit board manufacturing plants has been to commingle all metal-containing wastewaters which are then sent to a central location for treatment. Treatment methods vary depending upon what metals are present in the stream, but the most common treatment is precipitation of the metals as hydroxides. If metal cyanide complexes are present, cyanide is usually oxidized prior to metal precipitation. Likewise, if hexavalent chromium is present, it is usually reduced to trivalent chromium prior to precipitation. The metal hydroxide precipitates are then dewatered and most commonly sent to a hazardous waste landfill. Since August 8, 1988, these metal-containing sludges can no longer be sent to a hazardous waste landfill unless they are stabilized so that the toxic metal ions cannot be leached from the sludge. A variety of agents such as Portland cement, fly ash or other pozzolanic materials

can be used to stabilize the sludge, but whatever the stabilization method, the disposal costs have increased dramatically since August 1988. In addition both state and federal regulatory agencies are moving toward the future complete ban of land disposal of metal hydroxide sludges in any form.

In addition to high sludge disposal cost, another disadvantage of the conventional treatment system is the difficulty in many instances of reaching effluent metal concentrations low enough to meet discharge standards. This is because hard-to-treat waters are often commingled with easy-to-treat waters thereby making all the wastewater hard-to-treat. For example, in printed circuit board manufacturing operations there are typically three different types of copper-bearing wastewaters which must be treated: copper sulfate from acid copper baths, ammoniacal copper from alkaline etchers and chelated (usually EDTA, quadrol or tartrate) copper from electroless copper baths. Copper sulfate responds very well to hydroxide precipitation, but the ammonia complex of copper and the EDTA chelate of copper are very difficult to treat with conventional hydroxide precipitation. Thus expensive chemicals such as sodium borohydride or dithiocarbamates are added to the entire wastewater stream in order to treat the ammoniacal and chelated copper which usually make up only a small proportion of the total waste streams.

When the conventional hydroxide precipitation of metals is used, usually sodium hydroxide or lime along with other reducing agents or flocculating agents are added to produce the metal hydroxide sludge. Once the sludge is removed from the wastewater the water is generally discharged to a sewer. There is no opportunity for reuse or even partial reuse of the water because the effluent water has too many dissolved salts to be effective as a rinsewater. The cost of deionizing this water is generally much higher than the cost of deionizing fresh tap water and hence water reuse is generally not a viable economic option.

Generators of toxic metal sludges are held liable, without proof of fault, for cleaning costs and natural resource damage at hazardous waste disposal sites at which the generator's waste is disposed. Therefore if the owners of a hazardous waste dump happen to mismanage the site so that toxics are allowed into the environment, it is the generator who is ultimately responsible for clean-up. Thus any process by which sludge can be minimized or eliminated will reduce liability for the generator.

Bio-Recovery Systems' technology has been incorporated into an effective recovery-recycle approach to wastewater treatment for the electroplating, metal finishing and electronics industries. The concept is illustrated in Figure 1 for a treatment system that allows for recovery of metals and recycling of process waters. In this scheme rinsewaters derived from each individual plating bath are segregated and passed through columns containing AlgaSORB® or specialty ion exchange resins. Metal ions are removed from the rinsewaters which can then be discharged directly or returned to the rinse tanks for partial water reuse. Because salts tend to build-up in the rinsewaters, deionization of the treatment effluent may be needed if it is to be reused in critical rinses. Otherwise a bleed-off of water to the sewer is adequate to keep salt-build up at acceptable levels. Such an approach can often decrease water usage by 50 to 90 percent.

Once the columns of ion exchange resins or AlgaSORB® are saturated with metals, the metal ions can be stripped from the columns. The concentration of the stripped metals is approximately 10 g/L. In certain instances these stripped metal ions can be added back to the plating bath. In instances where this is not acceptable, the metal can be recovered through electrowinning or metalwinning. Alternatively the metal ions can be further

concentrated by evaporation and sent to one of a number of companies which are now established to recycle such materials. Whichever approach is taken, however, the elimination of sludge production results in lower operational costs due to decrease in chemical costs, decrease in water usage, elimination of sludge disposal costs and minimization of future liability.

RECYCLE-RECOVERY SYSTEM

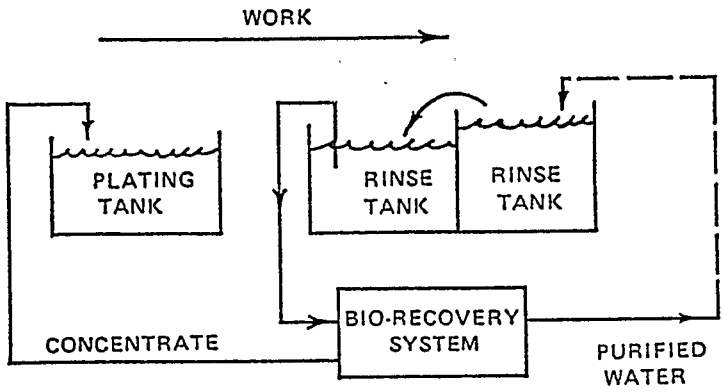

Figure 1. Recycle-Recovery System. Segregated rinsewaters from a plating process are directed through a recovery system where metal ions are recovered, and the rinsewaters are directed back to the rinse tanks. The concentrated recovered metals are sent back to the plating process tank where possible.

C. State of Development

Bio-Recovery Systems is currently manufacturing and installing wastewater treatment systems for use in recovering heavy metals from industrial point sources in the electroplating and printed circuit board manufacturing industries. Figure 2 shows one such system which has been designed for a printed circuit board manufacturer. The heart of the system is comprised of columns (B) which contain the metal-adsorbing materials. Rinsewaters which contain only a single type of plating or etching chemistry are segregated and plumbed to individual columns. When the columns become saturated with metal ions, a specific metal ion sensor signals the controller (A) to begin a regeneration cycle to strip the metals from the materials in the column and to send the stripped metal ions to one of the holding tanks (D). Once regeneration is complete, the controller automatically returns the regenerated column back into service. The stripped metals are then recovered as the metallic elements in the metalwinning unit (E).

The system shown in Figure 2 is capable of treating 30 L/min (8 gal/min), however larger flow rates (up to hundreds of gallons per minute) are accommodated by simply adding either more metal-adsorbing columns or by using larger diameter columns.

The system shown in Figure 2 was designed for a printed circuit board manufacturer, but the same type of system is also employed for metal finishing and electroplating facilities.

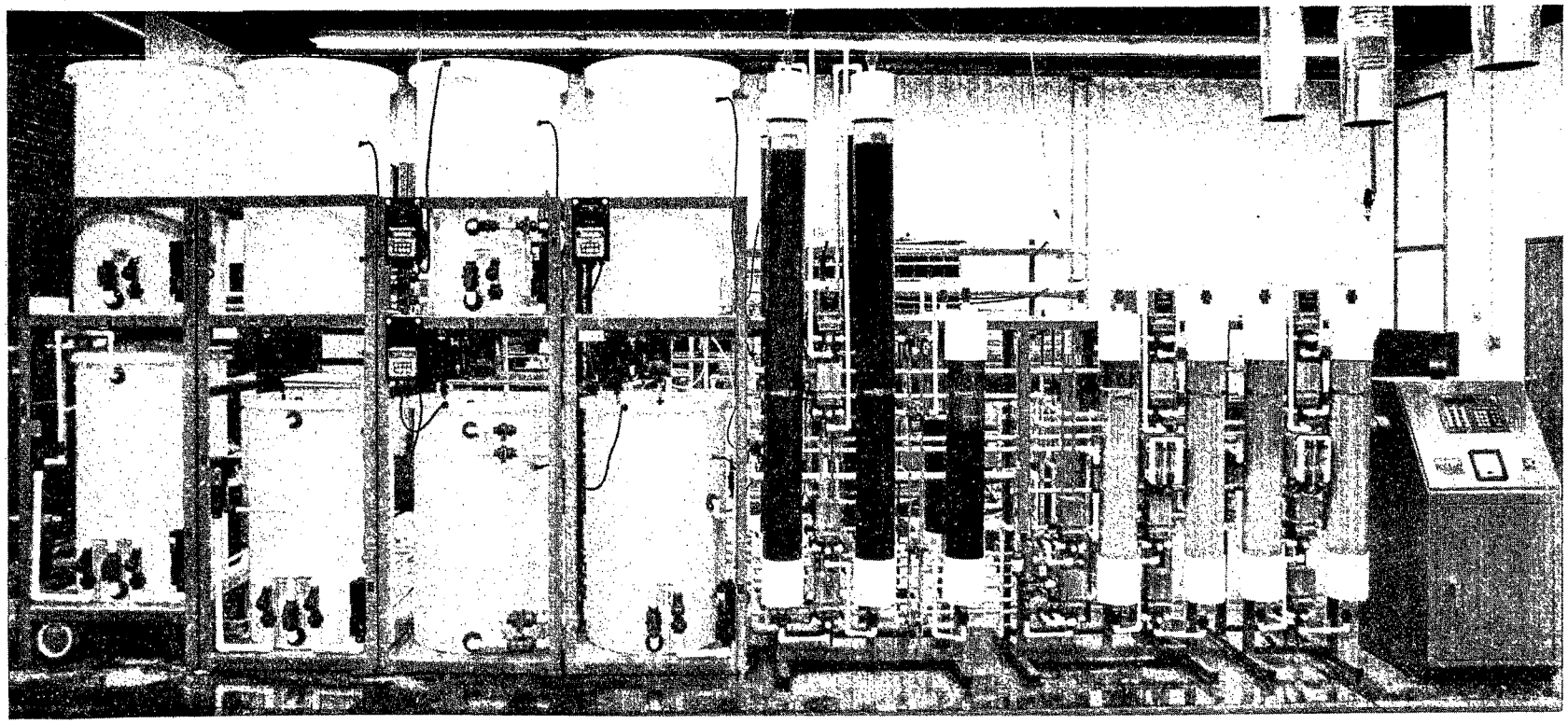

Figure 2. An Automatic Recycle-Recovery Wastewater Treatment System. A. controller. B. metal adsorbing modules. C. deionized water system. D. holding tanks for pH adjustment, regenerant chemicals. E. metalwinning module.

Different chemistries are encountered in metal finishing rinsewaters, but the approach to treatment of these waters is basically the same as that encountered in a printed circuit board manufacturer's facility, i.e., wastewaters are segregated for treatment so that maximum reuse of metals and water can occur.

D. Application of AlgaSORB® to Metal-Contaminated Groundwaters and Wastewaters

In 1986 and 1987 Bio-Recovery Systems was awarded Small Business Innovative Research (SBIR) contracts from the United States Environmental Protection Agency (EPA) to research and develop the AlgaSORB® technology for commercial applications. Results from these contracts, some of which are summarized below, show the efficiency of AlgaSORB® for heavy metal removal from a variety of sources. These successful laboratory tests led to Bio-Recovery's participation in the SITE program, through submission of a pre-proposal to the Emerging Technology Program.

1. Removal of Cadmium from Waters at a Superfund Site

Officials from EPA Region II arranged to supply samples from a well at a Superfund site in New Jersey, the Waldick Aerospace Devices site. These waters were contaminated with cadmium at a level of 0.13 mg/L. The waters at a pH of 6.0-7.1 also contained, among other organics, 0.66 mg/L of a halogenated hydrocarbon, tetrachloroethylene.

A column containing AlgaSORB® (0.7 cm i.d. x 13 cm high) was prepared, and the Waldick Aerospace waters were passed through the column. Five mL fractions of water exiting the column were collected until 500 mL (100 bed volumes) of Waldick waters were passed through the column at a flow rate of one-sixth of a bed volume per minute (total bed volume was 5.0 mL). Each fraction of effluent was analyzed for cadmium using graphite furnace atomic absorption spectrometry. All effluent fractions showed that cadmium concentration was near or below 0.001 mg/L after the passage of the 100 bed volumes of the cadmium-containing solution. Because the experiment was stopped after the passage of 100 bed volumes through the column, it is not possible to state explicitly what volume of solution could be treated before cadmium breakthrough would occur. However, experience has shown that if a test material is capable of treating at least 100 bed volumes of metal-bearing water, use of that material is economically feasible. The essential point is that AlgaSORB® removed cadmium well below those levels which are allowed in drinking water. The current drinking water levels for cadmium stand at 0.005 mg/L.

After 100 bed volumes of the cadmium-containing solution had passed through the AlgaSORB®-containing column, cadmium was stripped from the column by passing 0.15M H_2SO_4 through the column. Analysis of the column effluents showed that nearly 90 percent of the cadmium was stripped from the column with the passage of two bed volumes of sulfuric acid through the column. Most of the remainder of the cadmium appeared in the next two bed volumes. Mass balance calculations showed that, within experimental error, all of the bound-cadmium was stripped from the column.

2. Removal of Copper from Contaminated Groundwaters Containing Halogenated Hydrocarbons

Bio-Recovery Systems obtained groundwaters which had been contaminated with copper, tetrachloroethylene and dichloroethylene by a printed circuit board manufacturer. These waters contained a total dissolved solid content (TDS) of nearly 2000 ppm and had a

total calcium and magnesium content of approximately 300 ppm. Past experience had shown that ion exchange resins were not effective in treating these waters for copper removal because of i) the high mineral content and ii) the propensity of the resins to become clogged with the organics in these waters. However, experiments showed that 400 bed volumes of the copper containing waters could be passed through a column (0.7 cm i.d. x 13 cm high) containing AlgaSORB® without effluents from the column containing more than 0.01 ppm of copper. The experiments were stopped at 400 bed volumes, so undoubtedly larger volumes of waters could have been treated before unacceptable levels of copper appeared in the effluents.

After 400 bed volumes had been passed through the AlgaSORB® column, the bound copper was, within experimental error, completely stripped from the column by passing 0.5M H_2SO_4 through the column. Again, as with the previously described cadmium stripping, the copper was almost completely stripped within the first few bed volumes of eluent.

3. Removal of Mercury from Contaminated Groundwaters

Bio-Recovery was provided with water samples from a mercury-contaminated groundwater site. The site had been contaminated with mercury years ago as a result of a process used to manufacture chlorine from seawater. The groundwaters contained 2-3 ppm of mercury (both inorganic and organic mercury), had a total dissolved solid content of 7,200 mg/L and contained over 900 mg/L of calcium and magnesium. Passage of these mercury-containing waters through an AlgaSORB® column (0.7 cm i.d. x 13 cm high) resulted in effluents which contained mercury at levels below 0.006 mg/L as determined by analysis using cold vapor generation and atomic absorption spectrometry. The customer requires effluents of below 0.01 mg/L for discharge.

These experiments show, as had earlier experiments, that AlgaSORB® is effective in removing both inorganic and organic mercury from aqueous solutions even in the presence of very high concentrations of calcium, magnesium and other dissolved salts.

4. Selective Removal of Lead from Wastewaters

The printed circuit board industry frequently plates a tin-lead alloy onto printed circuit boards as a base for solder connections. The tin-lead alloy is plated from a solder bath which often contains tin and lead fluoborates. Since tin discharge is not currently federally regulated, the major problem in treating rinsewaters derived from tin-lead solder baths is lead removal. One particular AlgaSORB® preparation is especially amenable for this application since it strongly binds lead and allows the majority of the tin to pass through.

A sample of a tin-lead plating bath was obtained from a printed circuit board manufacturer. The bath composition included lead fluoborate, stannous fluoborate, boric acid and peptone. The bath rinsewaters commonly contain 10-60 mg/L of lead and about twice as much tin.

A column containing AlgaSORB® (3.3 mL total bed volume) was prepared and the tin-lead containing waters (27.4 mg/L of lead; 49 mg/L of tin) which had first been adjusted to pH 5.0 were passed through the column at a flow rate of one-third of a bed volume per minute. Two-bed volume fractions of the effluent were collected, and each of these fractions was analyzed for tin and lead by atomic absorption techniques. All effluent fractions showed

lead concentrations at or below the detection limit of 0.1 mg/L for the first 300 bed volumes, after which lead began to appear in the effluents. Influent tin-lead passage was stopped after passage of 325 bed volumes through the column after which the column was stripped of lead by elution with 0.5M nitric acid (8).

All fractions eluted through the AlgaSORB® column were also analyzed for tin. Because tin is more weakly bound than lead, tin began to exit the column after passage of only 33 bed volumes of influent. Thus the AlgaSORB® column showed marked preference for lead over tin. When the column was stripped of lead (after 325 bed volumes) the small amount of tin bound on the column was also fully recovered in the nitric acid stripping solution (8).

V. DESCRIPTION OF SITE CONTAINING MERCURY-CONTAMINATED GROUNDWATERS

A number of years ago an industrial process using mercury resulted in soil contamination with elemental mercury. The mercury subsequently percolated through the soils and contaminated groundwater. At some point the mercury was oxidized to the bivalent oxidation state and was found at various concentrations in the groundwaters depending upon the monitoring site. Currently, the groundwaters are extracted from an upper perched groundwater table via a drainage gallery. A facility has been constructed to treat extracted groundwaters by the use of precipitation with dithiocarbamates, followed by polishing with activated carbon and a specialty ion exchange resin. The water is pumped from the gallery at mercury concentrations of 0.1-3.0 ppm and is currently treated to allowable discharge limits of 10 ppb mercury.

Wells monitoring the groundwater during the late 1980's showed seasonal variations in the mercury concentrations. It appears that mercury levels decrease in the dry seasons compared to the rainy season. Chemical speciation of the mercury in the groundwaters was not rigorously determined, but speciation studies on soils overlying the groundwater indicated the predominant species was oxidized inorganic mercury. The composition of other elements in the groundwater seems to change with the seasons as well, but an average composition is given in Table 1. Variations in mercury content over a four year monitoring period in waters from two wells, about 150 feet from one another, are shown in Table 2.

TABLE 1. AVERAGE COMPOSITION OF MERCURY-CONTAINING GROUNDWATERS

Constituent	Concentrations (mg/L)
Chloride	5,800
Sodium	2,900
Calcium	460
Magnesium	440
Total Dissolved Solids	11,000
pH	8.0

Several hypotheses concerning mercury speciation in the groundwaters were considered by other contractors in the mid-1980's. Based upon available groundwater chemistry data and the presence of high chloride ion concentrations, it was considered likely that the predominant dissolved inorganic forms of mercury included chloride complexes. They were thought to vary from $HgCl^{+}$ through $HgCl_4^{-2}$. Uncomplexed ionic mercury could be either divalent or monovalent.

TABLE 2. SEASONAL VARIATION OF MERCURY CONCENTRATION IN MONITORING WELLS

Month/Yr	Well 1 (mg/L)	Well 2 (mg/L)
Oct/1	9.60	0.370
Nov/1	3.35	0.293
Dec/1	0.29	0.426
Jan/2	5.50	0.230
Mar/2	3.80	0.390
Apr/2	10.00	0.200
May/2	4.20	0.300
Sep/2	7.70	0.370
Dec/2	6.10	0.510
Feb/3	6.20	0.500
Sep/3	8.50	0.240
Dec/3	2.70	0.140
Apr/4	4.00	-
May/4	4.00	0.260
Jun/4	4.40	0.170
Aug/4	5.80	0.180
Sep/4	7.70	0.086
Oct/4	13.00	0.240

Furthermore, with many different anions present in the water, inorganic mercury could be present in a variety of complexed forms.

It was also established in the mid-1980's that the groundwaters contained significant quantities of organic compounds. It is therefore possible that some of the mercury in the groundwater could also be in the form of organo-mercury complexes. Less than one percent of the mercury present in soils at the site was found to be organo-mercury. However for an aggregate of several ppm in the recovered groundwater, even less than one percent organo-mercury could be important considering the maximum allowable discharge concentration was 10 ppb mercury. This was one of the reasons that activated carbon was selected as a part of the treatment system. Rather than spend a great deal of time in determining mercury speciation in the groundwaters, it was decided to approach the problem on a direct, empirical basis. This led to the current waste treatment process involving precipitation, carbon adsorption and ion exchange.

VI. LABORATORY TESTING

A. Experimental Procedures

Mercury analyses were performed using the EPA Method 245.1 of cold vapor atomic absorption spectroscopy (9) with the exception that sodium borohydride was used as a reductant rather than stannous sulfate, upon the recommendation of the instrument manufacturer, Perkin Elmer. The validity of this modification in EPA Method 245.1 was substantiated by experiments described in Section VIII.

A Perkin Elmer Model 3030B AAS instrument was calibrated daily for mercury, and a calibration verification record was maintained using data collected by the analysis of EPA certified check standards. Preparation of standards for mercury analysis was performed in accordance with the specifications in Methods for the Chemical Analysis of Water and Wastes (9). Spiked samples were analyzed with each batch of samples to determine if matrix interference existed, and frequent blanks were run to ensure there was no mercury carry over during analysis.

Mercury concentrations in groundwaters, column effluents and regenerating solutions were determined by linear regression calibration curves generated from four point standard calibration analysis (9).

Samples collected in the field pilot studies were split and sent to Woodward-Clyde Consultants, EER Technologies and Bio-Recovery Systems for mercury analysis.

Laboratory tests on the efficiency of mercury adsorption on AlgaSORB® were conducted using small glass columns (1.5 cm i.d. x 20 cm) which contained 25.0 mL of sorbent. Mercury-containing groundwaters were pumped through the column at flow rates which varied from 6-20 bed volumes per hour. Effluents from the columns were collected using a fraction collector and mercury content was determined. Once the columns became saturated or leaked mercury above discharge limits (10 ppb), the column was stripped with 10 bed volumes of a selected stripping reagent followed by 10 bed volumes of deionized water. Analyses of stripping effluents were performed to verify stripping.

More complete experimental procedures and data analyses are found in Section VIII. Quality Assurance.

B. Results

1. Water Analysis

Samples of groundwater were collected at various times during 1989. With one exception all samples were acidified to pH 2 with nitric acid in the field prior to transport for laboratory studies. Once the samples were received at Bio-Recovery Systems, the solutions were neutralized to the original or desired pH with dilute sodium hydroxide. Laboratory and field studies were complicated by the fact that over a 10 month period, mercury concentrations changed by an order of magnitude. Table 3 shows mercury concentration variation over the sampling period. While variations in mercury speciation were not determined, laboratory studies with AlgaSORB® implied that the mercury speciation varied over the sampling period. (See below).

TABLE 3. MERCURY CONCENTRATIONS IN GROUNDWATERS

Sample Number	Original pH	Mercury Concentration (µg/L)	Date Collected
103-13089	8.5	150	01-30-89
176-42089	8.0	435	04-20-89
177-42089-1	8.0	144	04-20-89
177-42089-2	8.0	215	04-20-89
265-070589	7.9	1120	07-05-89
343-090189	7.8	620	08-31-89
368-100489	7.9	1550	10-04-89
369-100489	7.9	1550	10-04-89

Variations in mercury content of samples 176-42089, 177-42089-1 and 177-42089-2 are due to the method of preservation. Two five-gallon water samples were collected on April 20, 1989. One sample, 177-42089-1, was not acidified in the field and was transported unpreserved to Bio-Recovery where 5 L was removed for testing. The remainder of sample 177-42089-1 was then acidified to pH 2, stored for use, and designated as sample 177-42089-2. Sample 176-42089 was acidified in the field and was transported to Bio-Recovery Systems for testing. It is clear that some mercury was lost (perhaps due to container-wall adsorption) from sample 177-42089-1. Upon acidification of the sample a slight increase in the mercury concentration was observed.

The waters shown in Table 3 were used for subsequent laboratory tests with AlgaSORB®. Water samples were adjusted to various pH values and reanalyzed for mercury just prior to AlgaSORB® testing. Thus mercury concentrations shown in subsequent tables may vary slightly from those shown in Table 3.

2. AlgaSORB® Tests

Acidified groundwater samples collected on January 30, 1989 (Sample 103-13089) were adjusted to pH 6 and were pumped through an AlgaSORB®-602 column at a flow rate of 10 bed volumes per hour. Table 4 shows mercury contents in the effluents were well below the 10 ppb discharge limit through the passage of over 200 bed volumes of sample. Table 4 also shows results

TABLE 4. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-602*

Bed Volume of Effluent	Hg (µg/L)	Spiked Hg (µg/L)	Recovery (%)	Error (%)
1-4	0.6			
5-8	0.8	0		
5-8†	7.8†	10.0	70	30
9-12	0.5			
13-16	0.5			
21-24	0.8			
105-108	2.1			
121-124	2.7			
141-144	2.0	0		
141-144†	7.7	10.0	57	43
161-164	4.4			
181-184	4.6			
185-188	1.7			
201-204	3.5			
221-225	11.7			
241-244	30.0			
256-260	16.7			

* Influent mercury concentration was 150 µg/L at pH 6.0. Water sample 103-13089

† QA samples

for matrix spikes. Once 260 bed volumes of groundwater were passed through the column, attempts were made to strip the column with 3.0 M sodium chloride. Table 5 shows results of stripping experiments. While some mercury was stripped with sodium chloride, mass balance calculations showed that only 30 percent of the loaded mercury was recovered in stripping. Based upon this poor recovery, sodium chloride was deemed to be inappropriate as a stripping agent.

TABLE 5. ANALYSIS OF STRIPPING EFFLUENTS FROM COLUMN LOADED IN TABLE 4*

Bed Volumes of Effluent	Hg (µg/L)
1-4	1290
5-8	515
9-12	208
13-16	1.8
17-20	0.8

* Stripping solution was 3.0 M NaCl.

A second column of AlgaSORB®-602 was prepared and groundwater sample 103-13089 which was adjusted to pH 5 was loaded onto the column at a flow rate of 10 bed volumes per hour. Table 6 shows results of mercury analysis of effluent fractions.

TABLE 6. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-602*

Bed Volumes of Effluent	Hg (µg/L)	Spiked Hg (µg/L)	Recovery (%)	Error (%)
1-4	0.50			
17-20	0.80			
37-40	0.65	0		
37-40†	10.7†	10.0	100	0
57-60	4.0			
73-76	2.2			
77-80	5.6			
93-96	2.3			
113-116	3.0			
133-136	2.5	0		
133-136†	9.9†	10.0	74	26
149-152	6.5			

* Influent mercury concentration was 150 µg/L at pH 5.0. Water sample 103-13089.
† QA samples

Good mercury retention by the AlgaSORB® was observed through the passage of 152 bed volumes of groundwater. Similar mercury binding performance was observed at pH 6 (Table 4) and at pH 5.0 (Table 6).

Sample 177-42089-1 (unpreserved at pH 8.0) was adjusted to pH 5.0 and was loaded onto an AlgaSORB®-602 column at a flow rate of 10 bed volumes per hour. A total of 168 bed volumes of effluent was collected and analyzed for mercury. Table 7 shows results of these analyses. After passage of 168 bed volumes, mercury concentration in the effluent was 27 ppb, which is a much higher leakage rate than observed with the same adsorbent on sample 103-13089. (Table 6 shows effluents had mercury contents below 7 ppb after passage of 152 bed volumes of sample 103-13089.)

Sample 176-42089 (acid preserved) was loaded onto another AlgaSORB®-602 column at a flow rate of six bed volumes per hour and at pH 5.0. Seventy six bed volumes of effluent were collected, and then the column was stripped of mercury by the passage of 10 bed volumes of 1.0 M sodium thiosulfate followed by 10 bed volumes of distilled water. Once the first loading and stripping cycle was completed, it was repeated twice more.

TABLE 7. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-602*

Bed Volumes of Effluent	Hg (µg/L)	Spiked Hg (µg/L)	Recovery (%)	Error (%)
1-4	42			
17-20	2.0			
33-36	3.8	0		
33-36†	14.6†	10	108	8
69-72	8.3			
117-120	12.8			
165-168	26.8			

* Influent mercury concentration was 144 µg/L at pH 5. Water sample 177-42089.
† QA sample

Table 8 shows results of mercury analysis on effluents from the three loading cycles. Again high leakage of mercury was observed with this water sample. Table 9 shows results of the three stripping cycles. Mass balance calculations showed that 84, 88 and 76 percent of bound mercury was stripped in stripping cycles 1, 2, and 3, respectively.

TABLE 8. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-602*

Cycle	Bed Volumes of Effluent	Hg (µg/L)	Spiked Hg (µg/L)	Recovery (%)	Error (%)
1	1-4	27			
	21-24	22	0		
	21-24†	31†	10	88	12
	37-40	68			
	57-60	88			
	73-76	124			
2	1-4	23			
	21-24	14	0		
	21-24†	23.5†	10	95	5
	41-44	37			
	57-60	44			
	73-76	53			
3	1-4	8.8			
	21-24	11			
	37-40	11.8	0		
	37-40†	28†	10	163	63
	53-56	40			
	73-76	68			

* Influent mercury concentration was 400 µg/L at pH 5. Water sample 176-42089.
† QA sample

TABLE 9. ANALYSIS OF STRIPPING EFFLUENTS FROM COLUMN LOADED IN TABLE 8

Cycle	Bed Volumes of Effluent	Hg (µg/L)
1	1-4	5380
	5-8	352
	9-12	171
	13-16	13
	17-20	2.6
2	1-4	5300
	5-8	625
	9-12	352
	13-16	141
	17-20	60
3	1-4	4730
	5-8	640
	9-12	278
	13-16	15
	17-20	10

A different lot of AlgaSORB®-602 was prepared and again tested on groundwater sample 176-42089. The water was loaded at pH 5 onto a 25 mL column containing AlgaSORB®-602 and after passage of 76 bed volumes the column was stripped with 10 bed volumes of 1.0 M sodium thiosulfate and 10 bed volumes of deionized water. After the first loading-stripping cycle a second loading-stripping cycle was done. Data for loading is shown in Table 10 and for stripping in Table 11. Table 10 again shows high rates of mercury leakage. Stripping of bound mercury was effective, however, with mass balance calculations showing that 99 and 92 percent of bound mercury were stripped in cycles 1 and 2, respectively.

TABLE 10. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-602*

Cycle	Bed Volumes Of Effluent	Hg(µg/L)	Spiked Hg(µg/L)	Recovery (%)	Error (%)
1	1-4	9.9			
	17-26	10.1			
	37-40	6.8	0		
	37-40†	21.8†	10	150	50
	53-56	14.6			
	73-76	31.0			
2	1-4	77.5			
	5-8	1.4			
	17-20	3.1			
	21-24	2.1	0		
	21-24†	14.9†	10	128	28
	37-40	7.2	0		
	37-40†	14.2†	10	70	30
	47-44	8.6			
	57-60	7.6			
	61-64	10.0			
	69-72	7.6			
	73-76	11.5			

* Influent mercury concentration was 400 µg/L for Cycle 1 and 200 µg/L for Cycle 2 and for both cycles the pH was 5.0. Water sample 176-42089.

† QA samples

TABLE 11. ANALYSIS OF STRIPPING EFFLUENTS FROM COLUMN LOADED IN TABLE 10

Cycle	Bed Volumes of Effluent	Hg (µg/L)
1	1 - 4	6250
	5 - 8	1020
	9 - 12	230
	13 - 16	16.4
	17 - 20	5.3
2	1 - 4	2900
	5 - 8	365
	9 - 12	198
	13 - 16	16.6
	17 - 20	8.8

AlgaSORB®-602 clearly showed different mercury binding characteristics on water sample 103-13089 (Table 4 and 6) as compared to sample 176-42-89 (Table 7, 8, 10). Unacceptable mercury leakage was observed with the 176-42089 samples as compared to the 103-13089. This suggests that the mercury speciation may have changed during the time period between sample collections.

Different algae have different mercury binding characteristics due to different biopolymers present in the cell walls. Thus a different AlgaSORB®, AlgaSORB®-601, was synthesized containing a different algal species and was tested on the 176-42089 waters. Waters at pH 5.0 were loaded into an AlgaSORB®-601 column at a flow rate of 10 bed volumes per hour. Mercury was stripped with thiosulfate as described earlier. Data for four loading and stripping cycles on AlgaSORB®-601 are shown in Tables 12 and 13. AlgaSORB®-601 was more effective in binding mercury than was AlgaSORB®-602. Table 12 shows that mercury leakage was below 10 ppb during all four loading cycles through the passage of over 100 bed volumes of sample 176-42089.

TABLE 12. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-601*

Cycle	Bed Volumes of Effluent	Hg (µg/L)	Spike Hg (µg/L)	Recovery (%)	Error (%)
1	1-4	0.5			
	21-24	1.5			
	37-40	1.8	0		
	37-40†	11.5†	10.0	98	2
	73-76	5.1			
	77-80	2.1			
	89-92	4.5			
	97-100	5.5			
	121-124	10.8			
	137-140	15.2			
	153-156	21.0			
2	1-4	2.2			
	17-20	3.1			
	37-40	2.7	0		
	37-40†	10.0†	9.0	82	18
	17-20	3.1			
	68-72	8.9			
	73-76	3.8			
	85-88	5.9			
	101-104	9.8			
	117-120	16.5			
	132-135	31.2			
3	1-4	0.7			
	21-24	1.4	0		
	21-24†	10.2†	10.0	88	12
	37-40	3.3			
	57-60	5.1			
	67-70	5.7			
	71-74	2.2	0		
	71-74†	10.3	10.0	81	19
	91-94	3.9			
	97-100	4.7			
	107-110	4.8			
	117-120	6.3			
	121-124	2.2	0		
	121-124†	12.1†	10.0	00	1
	127-130	4.4			
	131-134	4.5			
4	1-4	1.1			
	49-52	5.3			
	67-70	7.1			
	71-76	2.1			
	97-100	3.6			
	109-112	5.2			
	129-132	7.2			
	137-142	7.3			

* Influent mercury concentrations were 506, 502, 255 and 283 µg/L for Cycles 1, 2, 3, 4, respectively. All influents were at pH 5.0. Water samples 176-42089 for Cycles 1 and 2; 177-42089 for Cycles 3 and 4

† QA sample.

TABLE 13. ANALYSIS OF STRIPPING EFFLUENTS FROM COLUMN LOADED IN TABLE 12

Cycle	Bed Volumes of Effluent	Hg (mg/L)
1	1-4	15,700
	5-8	620
	9-12	235
	13-16	4
	17-20	0.6
2	1-4	14,100
	5-8	1,500
	9-12	34
	13-16	7.8
	17-20	4.2
3	1-4	5,450
	5-8	770
	9-12	390
	13-16	4.2
	17-20	3.0
4	1-4	4,100
	5-8	830
	9-12	425
	13-16	3.8
	17-20	1.6

Mass balance calculations showed 84, 92, 75 and 59 percent of the bound mercury was stripped from the columns during stripping Cycles 1, 2, 3 and 4, respectively (Table 13).

Yet a third alga was immobilized to produce AlgaSORB®-603. This adsorbent was tested in the same manner as AlgaSORB®-602 (Tables 4, 6) and AlgaSORB®-601 (Table 12) on groundwater collected 4-20-89 as well as on a new groundwater sample collected 7-5-89 (Sample 265-070589). All water samples were loaded onto an AlgaSORB®-603 column at pH 5 and at flow rates of 10 bed volumes per hour. After loading, the columns were stripped with thiosulfate as described earlier. Data for three loading and stripping cycles are shown in Tables 14 and 15. AlgaSORB®-603 was more effective for mercury removal than either AlgaSORB®-601 or AlgaSORB®-602 for Sample 176(177)-42089. Mass balance calculations showed that 95, 86 and 99 percent of bound mercury was recovered in stripping cycles 1, 2 and 3, respectively (Table 15).

TABLE 14. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-603*

Cycle	Bed Volumes of Effluent	Hg (µg/L)	Spike Hg (µg/L)	Recovery (%)	Error (%)
1	1-4	2.8			
	17-20	2.1			
	37-40	1.4	0		
	37-40†	10.8†	10.0	94	6
	57-60	3.5			
	73-76	4.5			
	77-80	3.5			
	93-96	2.2	0		
	93-96†	12.4†	10.0	102	2
	113-116	8.0			
	133-136	11.7			
	149-152	16.6			
	153-156	6.2			
	157-160	8.1			
	161-164	8.0			
	169-172	9.9			
	177-180	11.1			
2	1-4	0.5			
	21-24	0.9			
	37-40	1.0	0		
	37-40†	8.7†	10.0	77	23
	57-60	4.1			
	73-76	6.1			
	77-80	8.9			
	89-92	5.9			
	97-100	6.1			
	117-120	8.9			
	137-140	10.6			
	149-152	14.3			
3	1-4	6.6			
	21-24	1.6			
	61-64	3.9			
	89-93	8.8			
	100-103	10.5			
	104-108	4.0	0		
	104-108†	13.2†	10.0	92	8
	113-116	14.2			
	121-124	16.8			
	129-132	24.6			
	137-140	34.0			

* Influent mercury concentration for Cycle 1 was 268 µg/L and was Sample 177-42089. Influent mercury concentration for Cycles 2 and 3 were 1160 and 910 µg/L, respectively and was Sample 265-070589. All Cycle influents were at pH 5.0

† QA samples

TABLE 15. ANALYSIS OF STRIPPING EFFLUENTS FROM COLUMN LOADED IN TABLE 14

Cycle	Bed Volumes of Effluent	Hg (µg/L)
1	1-4	10,800
	5-8	540
	9-12	192
	13-16	4.4
	17-20	3.8
2	1-4	31,000
	5-8	1,250
	9-12	3,200
	13-16	2.0
	17-20	0.8
3	1-4	28,200
	5-8	2,290
	9-12	1,250
	13-16	7.0
	17-20	0.6

AlgaSORB®-602 was also tested on water Samples 265-070589. Results of that testing, under conditions as used for other sample testing, are shown in Table 16.

TABLE 16. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-602*

Bed Volumes of Effluent	Hg µg/L)	Spike Hg (µg/L)	Recovery (%)	Error (%)
1-41.3				
21-24	3.4			
41-44	0.8	0		
41-44†	8.1†	10.0	73	27
57-60	27.0			
69-72	72.5			

* Influent mercury concentration was 940 µg/L at pH 5.0. Water sample 265-070589.
† QA sample

The mercury concentration in water at the site had increased to nearly 1 mg/L by the time sample 265-070589 was taken and AlgaSORB®-602 showed unacceptable leakage rates.

New water samples were collected on 9-1-89. Since AlgaSORB®-603 appeared to be the best formulation for waters collected on 4-20-89 and 7-5-89, it was tested on water sample 343-090189. Data are shown in Table 17. Conditions of pH and flow rates were those described earlier. It is clear from Table 17, that very high unacceptable mercury leakage occurred.

AlgaSORB®-603 had proved to be effective in mercury recovery from samples 177-42089 and 265-070589 which contained 268 ppb and 1160 ppb, respectively, of mercury (Table 14). Table 17 shows that at mercury levels of 620 ppb in sample 343-090189, poor mercury recovery was observed with AlgaSORB®-603. These data again suggested that mercury speciation was changing in waters taken from the site which would account for the variation in mercury binding for different water samples.

Because of the inconsistency of performance of various AlgaSORB® preparations with different water samples, a different approach was taken.

TABLE 17. ANALYSIS OF EFFLUENTS FROM A COLUMN PACKED WITH AlgaSORB®-603*

Bed Volumes of Effluent	Hg (µg/L)
1	2.6
7	36.0
13	37.0
19	42.0

* Influent mercury concentration was 620 µg/L at pH 5.0. Water Sample 343-090189.

Work performed previous to this study indicated that two other AlgaSORB® preparations, AlgaSORB®-624 and AlgaSORB®-640, may be effective for mercury removal even if mercury concentration and/or mercury speciation changed in solutions. AlgaSORB®-624 had shown high mercury binding capacities but also rather high mercury leakage on the order of 20-40 ppb. AlgaSORB®-640, on the other hand, showed rather low mercury binding capacities, but at the same time, produced effluents which contained mercury in the low ppb range. Thus two columns, one containing AlgaSORB®-624 and the other containing AlgaSORB®-640 were prepared and connected in series. Groundwater Sample 343-090189 was adjusted to pH 7.9, the native pH, and was first passed through the AlgaSORB®-624 column and then through the AlgaSORB®-640 column. Data for these experiments are shown in Table 18. Table 19 shows repeat experiments of Table 18 using water sample 369-100489, collected on October 4, 1989.

TABLE 18. ANALYSIS OF EFFLUENTS FROM TWO COLUMNS IN SERIES PACKED WITH AlgaSORB®-624 and AlgaSORB®-640*

Bed Volumes of Final Effluent	Hg (µg/L)
12	0.0
34	0.0
43	0.6
60	1.8
80	3.3
104	3.4
113	2.9
121	3.9
130	4.4
140	3.2
159	7.5
170	4.0
180	3.5
190	0.1
200	0.1
210	0.1
230	2.3

* Influent waters were sample 343-090189 (mercury concentration 620 µg/L) for the first 90 bed volumes. Sample 368-100489 (mercury concentration of 1550 µg/L) provided influent for bed volumes 91-230.

TABLE 19. ANALYSIS OF EFFLUENTS FROM
TWO COLUMNS IN SERIES PACKED WITH AlgaSORB®-624 AND AlgaSORB®-640*

Bed Volumes of Final Effluent	Hg (µg/L)
12	0.3
24	0.2
36	0.3
48	0.3
60	0.3
72	0.5
84	0.5
96	0.7
108	0.7
120	0.8
132	0.8
144	0.9
156	0.9
168	1.0
180	0.8
192	0.8
204	0.9
228	0.9
264	0.6
276	1.2
300	2.1
324	2.0
333	1.9

* Influent waters were Sample 369-100489 (mercury concentration 1550 µg/L) at pH 7.9.

VII. ON-SITE, PILOT SCALE DEMONSTRATION

On-site, pilot scale demonstrations were conducted using AlgaSORB®-624 and AlgaSORB®-640 as adsorbents. A small portable water treatment system manufactured by Bio-Recovery Systems was used for these studies (Figure 3). This portable unit is designed so that columns ranging in size from 1-4 inches in diameter can be placed on the unit. For the pilot testing one inch diameter columns were used. Based upon laboratory experiments it was predicted that one-inch diameter columns would become saturated with mercury in 3-4 weeks at flow rates of 10 bed volumes per hour.

One column was filled with AlgaSORB®-624 and the second column was filled with AlgaSORB®-640. Each column had a volume of 0.4 L. The two columns were run in series so that groundwater, with no pH adjustment, was directed first through the AlgaSORB®-624 column and then through the AlgaSORB®-640 column. Effluent samples were collected from a sample port between the two columns as well as from effluent emanating from the second column. Effluent samples were split into three portions. One portion was sent to Woodward-Clyde Consultants for immediate mercury analysis (within 12-24 hours of collection). Another portion was acid-preserved and sent to EER Technology for mercury analysis, while the third portion was preserved and sent to Bio-Recovery Systems for analysis.

On-site pilot scale testing was conducted from November 6 to December 1, 1989. The site was available for testing only from 7:00AM-3:30PM each day. At the end of a treatment day, the system was simply shut down and then restarted the next day. Flow rates through the system were 10 bed volumes per hour.

By the time the on-site testing had begun in November, the mercury concentrations in the groundwaters had changed from about 1500 ppb (in October) to 780 ppb on November 7. During the three week on-site test period the mercury concentration continued to vary. Table 20 shows mercury concentration variations during the on-site test period. Mercury was found to vary from as low as 330 ppb to as high as 1000 ppb.

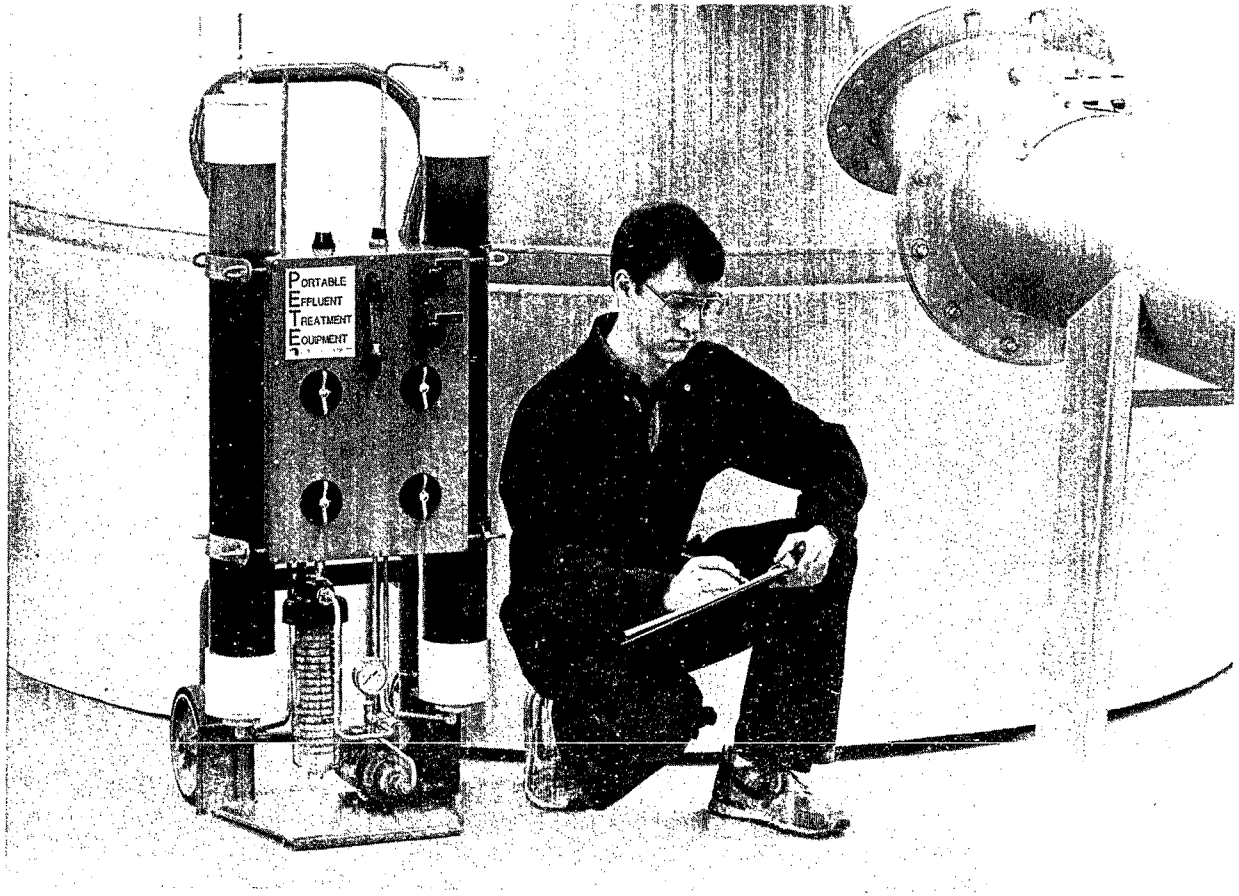

Figure 3. Portable Waste Treatment System Used for On-Site Testing

TABLE 20. VARIATION IN MERCURY CONTENT
OF GROUNDWATERS DURING ON-SITE PILOT SCALE TESTING

Date	Mercury* Concentration (µg/L)
11/07/89	780
11/08/89	500
11/09/89	332
11/10/89	490
11/14/89	810
11/15/89	700
11/16/89	730
11/17/89	690
11/20/89	850
11/21/89	970
11/27/89	1000
11/28/89	1000
11/29/89	730
11/30/89	590

* Each day during on-site testing, a water sample was analyzed for mercury content before any water was pumped through the columns.

Results of mercury analyses on effluents from the complete test system, i.e., from the effluent from the second column are shown in Table 21. Table 21 shows analytical data for only a portion of all collected samples. Full data with matrix spikes and QC/QA data are found in Appendices A and B.

TABLE 21. ON-SITE PILOT TESTING FOR MERCURY REMOVAL FROM GROUNDWATERS*

Bed Volumes of Effluent	Mercury Concentration (µg/L) Bio-Recovery Analysis	Woodward-Clyde Analysis	EER Technologies Analysis
7-8	9.5	14.2	11
85-86	5.3	8.0	<10
163-64	2.1	3.6	<10
229-230	1.4	1.4	<10
289-290	1.8	2.6	<10
313-314	1.9	2.4	<10
343-344	5.5	9.3	10.0
379-380	2.0	3.1	<10
415-416	1.8	3.2	<10
449-450	4.9	7.8	10.0
467-468	4.0	7.2	<10
503-504	5.8	9.6	<10
533-534	7.7	10.0	<10
587-588	10.5	13.0	15

* A portable water treatment system was equipped with two columns connected in series. The first column was filled with AlgaSORB®-624 and the second was filled with AlgaSORB®-640. Groundwaters were pumped through the system at a flow rate of 6 bed volumes per hour. Effluent samples were collected and sent to Woodward- Clyde Consultant, EPA (EER Technologies Corporation) and Bio-Recovery systems for analysis.

With the exception of the first fraction collected, Table 21 shows that well over 500 bed volumes of mercury-contaminated groundwaters were treated before mercury concentrations in the effluents approached the 10 ppb discharge limit.

During on-site testing, samples were collected from the sample port between the two columns and were sent to Woodward-Clyde for mercury analysis. These samples represent water treated only by AlgaSORB®-624 prior to entering the AlgaSORB®-640 column. Data from these analyses are shown in Table 22. These data show rather constant leakage of mercury from the first column in the range of 20-100 ppb over the testing period. The data in Table 20, 21, and 22 confirm laboratory experiments which showed AlgaSORB®-624 was capable of removing the majority of the mercury and AlgaSORB®-640 was capable of polishing effluents from AlgaSORB®-624 to permitted discharge levels.

TABLE 22. ANALYSIS OF EFFLUENTS FROM THE AlgaSORB®-624 COLUMN ON THE PORTABLE TREATMENT SYSTEM

Bed Volumes of Effluent	Mercury Concentration* (µg/L)
1-261	Not Determined
262	28
281	40
316	33
333	38
352	33
382	26
413	90
429	120
446	38
470	46
495	53
518	54
542	68
561	61
585	107

* Analysis by Woodward-Clyde Consultants.

VIII. QUALITY ASSURANCE

The objective of this program was to demonstrate effective mercury removal and recovery from groundwaters. The critical data needed to support this objective were measurements of mercury concentrations in water prior to treatment and after treatment. A quality assurance project plan was developed for these measurements and was approved in December, 1988.

A. Verification of Modification of EPA Method 245.1 for Mercury Analysis

Since the manufacturer of the cold vapor apparatus used in this study recommended the use of sodium borohydride instead of stannous sulfate or stannous chloride as a reducing agent, initial experiments were designed to verify the validity of using sodium borohydride as a reductant.

Two standard stock solutions containing mercury at a concentration of 1000 ppm were purchased, one from VWR and the other from J. T. Baker. The VWR standard was used solely by the analyst while the J.T. Baker standard sample was used solely by the QA chemist for spikes.

In initial tests a 100 ppb serial dilution of the VWR mercury standard was prepared by the project supervisor. This 100 ppb sample was used by the analyst to calibrate the atomic absorption spectrometer and by the QA chemist to prepare spiked samples to check calibration. These experiments were designed to verify that techniques employed by the analyst and QA chemist were comparable. Results are shown in Table 23.

TABLE 23. MERCURY ANALYSIS OF STANDARDS USING SODIUM BOROHYDRIDE AS A REDUCTANT

Sample	Actual Mercury Concentration (µg/L)	Analyzed Mercury Concentration (µg/L)	Percent Error
1	6.0	6.0	0.0
2	6.0	6.0	0.0
3	12.0	11.3	6
4	12.0	10.6	11
5	18.0	15.4	14
6	18.0	16.1	11

A second series of experiments were designed whereby the project supervisor prepared a 100 ppb mercury-containing sample from the VWR stock for the analyst and a

100 ppb mercury-containing sample from the J.T. Baker stock for the QA chemist. The analyst used his 100 ppb sample to calibrate the instrument and the QA chemist used her sample for spikes to check calibration. Results of these experiments are shown in Table 24.

TABLE 24. MERCURY ANALYSIS OF STANDARDS USING SODIUM BOROHYDRIDE AS A REDUCTANT

Sample	Actual Mercury Concentration (µg/L)	Analyzed Mercury Concentration (µg/L	Percent Error
1	6.0	5.7	5
2	6.0	5.6	7
3	11.0	10.7	3
4	11.0	9.5	14
5	16.0	15.3	4
6	16.0	15.8	1
7	6.0	5.1	15
8	6.0	5.3	12
9	12.0	10.0	17
10	12.0	11.3	6
11	18.0	16.7	7
12	18.0	16.7	7

B. Analysis of EPA-Provided Standard

The EPA Environmental Monitoring Systems Laboratory in Cincinnati sent Bio-Recovery Systems a standard Water Pollution Quality Control Sample for testing. The sample contained 15 different metal ions including mercury which was present both in inorganic and organic forms. The ampule containing the standards was opened by snapping the top at the break area on the neck, and 10.0 mL of the concentrate was transferred to a 1.0 L volumetric flask, brought to volume and analyzed. Actual concentrations of metals in the sample are shown in Table 25. Actual mercury content in the EPA sample was 5.0 µg/L. Results from Bio-Recovery analysis of the sample are shown in Table 26. According to EPA, analyzed mercury values must fall within the range of 3.85-6.25 µg/L in order to be within the 95 percent confidence interval. Table 26 shows that 8 of the 11 analytical determinations for mercury were within the 95 percent confidence level.

TABLE 25. EPA-PROVIDED SAMPLE INFORMATION

U.S. Environmental Protection Agency

Environmental Monitoring Systems Laboratory - Cincinnati

WATER POLLUTION QUALITY CONTROL SAMPLE

TRUE VALUES FOR TRACE METALS - I

The true values (T.V.) given below represent the actual weighing and all subsequent dilutions as given in the sample preparation instructions. The mean (X), standard deviation (S) and 95% confidence interval (X ±2S) are calculated from regression equations generated from date from previous Performance Evaluation Studies. Table 25 represents the statistics when the sample preparation instructions are followed.

STATISTICS USING SAMPLE PREPARATION INSTRUCTION
(All values expressed as µg/L)

Parameter	T.V.	X	S	95% Confidence Interval
Al	500	506.0	39.4	427 - 585
As	100	99.2	9.60	80.0 - 118
Be	100	99.4	5.37	88.7 - 110
Cd	25	24.4	1.64	21.2 - 27.7
Co	100	99.5	6.31	86.8 - 112
Cr	100	99.8	7.68	84.4 - 115
Cu	100	99.1	4.83	89.4 - 109
Fe	100	100.2	8.78	82.7 - 118
Hg	5.0	5.05	0.60	3.85 - 6.25
Mn	100	98.8	5.21	88.4 - 109
Ni	100	100.4	6.20	88.0 - 113
Pb	100	100.1	7.50	85.1 - 115
Se	25	22.8	2.73	17.4 - 28.3
V	250	250.9	15.5	220 - 282
Zn	100	99.8	5.44	89.0 - 111

TABLE 26. MERCURY ANALYSIS OF EPA WATER POLLUTION QUALITY CONTROL SAMPLE*

Trial Number	Analyzed Mercury Concentration (µg/L)	Within 95 percent Confidence Interval
1	6.4	No - 2.4%>6.25
2	6.9	No - 10.4%>6.25
3	6.1	Yes
4	6.7	No - 7.2%>6.25
5	5.4	Yes
6	5.3	Yes
7	5.2	Yes
8	5.1	Yes
9	5.2	Yes
10	4.6	Yes
11	4.8	Yes

* The actual mercury contraction in the sample was 5.0 µg/L. The accepted range at 95 percent confidence level is 3.85-6.25 µg/L.

C. Mercury Spikes

During the course of testing various AlgaSORB® preparations for efficiency of mercury binding, the analyst was given samples of groundwater effluents from AlgaSORB® columns which had been spiked by the QA chemist with amounts of mercury unknown to the analyst. Section VI shows tables including the amount of spiked mercury as well as the percent error and the percent recovery of the mercury spikes. However Table 27. summarizes all mercury spikes. From a total of 36 spiked samples, analysis of 26 samples

TABLE 27. ERROR AND RECOVERY ANALYSIS OF MERCURY SPIKES

Spike (µg/L)	Percent Error	Percent Recovery
10	32	68
10	43	57
10	3	97
10	0.5	100.5
10	26	74
10	27	127
10	67	167
10	213	313
10	23	123
10	40	140
10	12	84
10	5	95
10	63	163
10	50	150
10	28	128
10	30	70
10	3	97
10	19	81
10	12	88
10	19	81
10	1	99
10	42	142
10	15	115
10	215	315
10	19	81
10	0.5	100.5
10	8	108
10	6	94
10	2	102
10	23	77
10	8	92
10	7	93
10	130	230
10	147	247
10	27	73
10	10	110

were within the allowable 35 percent error range giving a 73% accuracy level on spike recovery.

D. Mercury Analysis in the Presence of Thiosulfate.

During the course of stripping the bound mercury from the AlgaSORB® columns using 1.0 M sodium thiosulfate, an analytical problem was encountered. The presence of thiosulfate appeared to interfere with mercury analysis (Table 28.)

TABLE 28. EFFECT OF THIOSULFATE ON MERCURY ANALYSIS*

Actual Mercury (µg/L)	Analyzed Mercury (µg/L)	Percent Error
0	1	-
1000	356	64
2000	528	74

* All mercury standard samples contained 1.0 M $Na_2S_2O_3$

Further investigation revealed that acid digestion of samples containing high concentrations of thiosulfate produced the interference. Thus attempts were made to alleviate the interference by oxidizing the thiosulfate with hydrogen peroxide at different pHs prior to acid digestion. Results of these experiments, shown in Table 29 indicated peroxide oxidation did not alleviate the problem.

TABLE 29. ANALYSIS OF MERCURY-THIOSULFATE SAMPLES OXIDIZED WITH HYDROGEN PEROXIDE*

Oxidation pH	Ratio of Peroxide to Thiosulfate (Molar)	Actual Mercury (µg/L)	Analyzed Mercury (µg/L)	Percent Error
2	1.0	1000	270	73
5	1.0	1000	155	85
8	1.0	1000	210	79
2	2.0	1000	240	76
5	2.0	1000	130	87
8	2.0	1000	105	90
2	5.0	1000	290	71
5	5.0	1000	150	85
8	5.0	1000	160	84
2	10.0	1000	105	90
5	10.0	1000	105	90

* All mercury standard samples were in presence of 1.0 M $Na_2S_2O_3$

The analytical interference problem was finally overcome by eliminating the acid digestion as prescribed in EPA Method 245.1. Table 30 shows results of these analyses.

TABLE 30. MERCURY ANALYSES OF THIOSULFATE CONTAINING SOLUTIONS WITHOUT ACID DIGESTION*

Actual Mercury (µg/L)	Analyzed Mercury (µg/L)	Percent Error
10	8.2	18
20	16.2	19
1000	1070	7
1000	1070	7
1000	1020	2
500	540	8
500	540	8
500	510	2
10	9.3	7
5	4.5	10
1000	1010	1
1000	1030	3
1000	1060	6
500	560	12
500	520	4
500	530	6

* All mercury standard samples contained 1.0 M $Na_2S_2O_3$

Table 30 clearly shows that elimination of the acid digestion step also eliminated the interference in the mercury analysis. Thus all AlgaSORB® column eluents resulting from stripping with thiosulfate were analyzed without the acid digestion step.

E. Analysis of Samples Resulting from On-Site Testing.

During on-site pilot scale testing of AlgaSORB® for mercury recovery from groundwaters, Effluents from AlgaSORB®-containing columns were collected, preserved, split and sent to EER Technologies (Cincinnati), Woodward-Clyde Consultants (Oakland) and Bio-Recovery Systems for mercury analysis. Results from Bio-Recovery Systems analysis and QC data have been reported earlier in Section VII. Sample numbers, and bed volumes of column effluent and influent to which sample numbers correspond are listed in Table 31. Appendices A and B show mercury analysis and QC data for Woodward-Clyde and EER Technologies, respectively.

TABLE 31. IDENTIFICATION OF SAMPLES SENT TO WOODWARD-CLYDE CONSULTANTS AND EER TECHNOLOGIES FOR MERCURY ANALYSIS

Sample Number	Description*	Hg (µg/L)	Sample Number	Description*	Hg (µg/L)
436-110789	Influent	780	473-111389	Blank	0.5
437-110789	Blank	0.4	474-111389	Influent	490
438-110789	1-2 BV	0.5	475-111389	133-134 BV	13.0
439-110789	7-8 BV	14.2	476-111389	139-140 BV	3.3
440-110789	13-14 BV	2.6	477-111389	145-146 BV	2.8
441-110789	19-20 BV	2.4	478-111389	151-152 BV	3.1
442-110789	25-26 BV	2.2	479-111389	157-158 BV	3.0
443-110789	31-32 BV	3.7	480-111389	163-164 BV	3.6
444-110889	37-38 BV	4.1	481-111389	169-170 BV	3.0
445-110889	43-44 BV	7.1	482-111389	175-176 BV	3.1
446-110889	49-50 BV	7.1	487-111489	Blank	ND
447-110889	55-56 BV	7.6	488-111489	Influent	810
448-110889	61-62 BV	7.3	489-111489	181-182 BV	2.5
449-110889	67-68 BV	8.1	490-111489	187-188 BV	2.7
450-110889	73-74 BV	8.0	491-111489	193-194 BV	4.8
451-110889	79-80 BV	8.1	492-111489	199-200 BV	2.5
452-110889	Blank	ND	493-111489	205-206 BV	2.2
453-110889	Influent	500	494-111489	211.212 BV	2.7
457-110989	85-86 BV	8.0	495-111589	217-218 BV	4.1
458-110989	90-92 BV	8.4	496-111589	223-224 BV	2.3
459-110989	97-98 BV	10.4	497-111589	229-230 BV	1.4
460-110989	103-104 BV	10.7	498-111589	235-236 BV	2.1
461-110989	109-110 BV	10.4	499-111589	241-242 BV	2.3
462-110989	115-116 BV	10.4	500-111589	247-248 BV	2.7
463-110989	121-122 BV	10.9	501-111589	Blank	ND
464-110989	127-128 BV	10.5	502-111589	Influent	700
465-110989	Blank	ND	503-111689	253-254 BV	4.3
466-110989	Influent	332	504-111689	259-260 BV	2.6

* BV, unless otherwise indicated, designates bed volumes of effluent from the second column collected into a single fraction.

TABLE 31. - continued

Sample Number	Description*	Hg (µg/L)
505-111689	265-266 BV	2.6
506-111689	271-272 BV	2.7
507-111689	277-278 BV	2.6
508-111689	283-284 BV	2.9
509-111689	289-290 BV	2.6
510-111689	Blank	ND
511-111689	Influent	730
512-111689	Lead Col Effluent @ 262 BV	28
513-111689	Lead Col Effluent @ 281 BV	40
514-111789	295-296 BV	4.0
515-111789	301-302 BV	2.4
516-111789	307-308 BV	2.4
517-111789	313-314 BV	2.4
518-111789	319-320 BV	2.5
519-111789	325-326 BV	2.3
520-111789	331-332 BV	2.4
521-111789	337-338 BV	2.8
522-111789	Blank	ND
526-111789	Influent	690
524-111789	Lead Col Effluent @ 316 BV	33
525-111789	Lead Col Effluent @ 333 BV	38
526-112089	Influent	850
527-112089	343-344 BV	9.3
528-112089	349-350 BV	4.1
529-112089	355-356 BV	0.3
530-112089	361-362 BV	0.5
531-112089	367-368 BV	0.8
532-112089	373-374 BV	2.6
533-112089	379-380 BV	3.1
534-112089	385-386 BV	4.1
535-112089	Lead Col Effluent @ 352 BV	33
536-112089	Lead Col Effluent @ 382 BV	26
537-112089	Blank	3.0
538-112189	Influent	970
539-112189	Blank	1.3
540-112189	391-392 BV	4.3
541-112189	397-398 BV	3.4
542-112189	403-404 BV	6.3
543-112189	409-410 BV	4.6
544-112189	415-416 BV	3.2
545-112189	421-422 BV	2.9
546-112189	427-428 BV	2.7
547-112189	431-432 BV	2.5
548-112189	Lead Col Effluent @ 413 BV	90
549-112189	Lead Col Effluent @ 429 BV	120

* BV, unless otherwise indicated, designates bed volumes of effluent from the second column collected into a single fraction.

TABLE 31. - continued

Sample Number	Description*	Hg (µg/L)
550-112789	Influent	1,000
551-112789	Blank	0.1
552-112789	437-438 BV	12.2
553-112789	443-444 BV	8.0
554-112789	449-450 BV	7.1
555-112789	Lead Col Effluent @ 446 BV	38
556-112889	Influent	1,000
557-112889	Blank	1.0
558-112889	455-456 BV	10.5
559-112889	461-462 BV	7.7
560-112889	467-468 BV	7.2
561-112889	473-474 BV	6.9
562-112889	479-480 BV	7.2
563-112889	485-486 BV	7.5
564-112889	491-492 BV	7.5
565-112889	497-498 BV	7.7
566-112889	Lead Col Effluent @ 470 BV	46
567-112889	Lead Col Effluent @ 495 BV	53
588-112989	Influent	730
589-112989	Blank	.08
590-112989	503-504 BV	9.6
591-112989	509-510 BV	10.1
592-112989	515-516 BV	9.7
593-112989	521-522 BV	9.9
594-112989	527-528 BV	10.3
595-112989	533-534 BV	10.7
596-112989	539-540 BV	10.7
597-112989	545-546 BV	10.6
598-112989	Lead Col Effluent @ 518 BV	54
599-112989	Lead Col Effluent @ 542 BV	68
600-113089	Influent	590
601-113089	Blank	.08
602-113089	551-552 BV	13.9
603-113089	557-558 BV	12.1
604-113089	563-564 BV	12.8
605-113089	569-570 BV	13.2
606-113089	575-576 BV	13.2
607-113089	581-582 BV	13.2
608-113089	587-588 BV	13.0
609-113089	Lead Col Effluent @ 561 BV	61.0
610-113089	Lead Col Effluent @ 585 BV	107.0

* BV, unless otherwise indicated, designates bed volumes of effluent from the second column collected into a single fraction.

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