United States
Environmental Protection
Agency

EPA/540/S5-90/005
August 1990

EPA

SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

# Emerging Technology Summary

# Removal and Recovery of Metal Ions from Groundwater

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

**The AlgaSORB® process is based on the natural, very strong affinity of biological materials, such as the cell walls of plants and microorganisms, for heavy metal ions. Biological materials, primarily algae, have been immobilized in a polymer to produce a "biological" ion exchange resin called AlgaSORB®. The material has a remarkable affinity for heavy metal ions and is capable of concentrating these ions by a factor of many thousandfold. Additionally, the bound metals can be stripped and recovered from the algal material in a manner similar to conventional resins.**

**This new technology has been demonstrated to be an effective method for removing toxic metals from groundwaters. Metal concentrations can be reduced to low parts per billion (ppb) levels.**

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

**Onsite, 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 Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the SITE Emerging Technology program that is documented in two separate reports (see ordering information at back).***

## Introduction

In response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), the U.S. Environmental Protection Agency's (EPA), Office of Research and Development (ORD) and Office of Solid Waste and Emergency Response (OSWER) have established a

formal program to accelerate the development, demonstration, and use of new or innovative technologies as alternatives to current containment systems for hazardous wastes. This program is called Superfund Innovative Technology Evaluation, or SITE.

The SITE Program is part of EPA's research into cleanup methods for hazardous waste sites throughout the nation. Through cooperative agreements with developers, alternative or innovative technologies are refined at the bench-scale and pilot-scale level and then demonstrated at actual sites. EPA collects and evaluates extensive performance data on each technology to use in remediation decisionmaking for hazardous waste sites.

This report documents the results of laboratory and pilot-scale field tests 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.

Groundwater contamination is found at over 70% of the sites currently on the National Priority List. Groundwaters have been contaminated with either toxic organic molecules or heavy metal ions, or both. The most common means of addressing contaminated groundwater is extraction and treatment. Although 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 to remove dilute concentrations of heavy metals from groundwaters.

The AlgaSORB® process is based upon the natural affinity of algae cell walls for heavy metal ions. The sorption medium, AlgaSORB®, is composed of a nonliving algal bio-mass immobilized in a silica polymer. AlgaSORB® is a hard material that can be packed into columns which, when pressurized, exhibit good flow characteristics. This technology functions well for removing heavy metal ions from groundwaters that contain high levels of dissolved solids, or organic contaminants, or both.

The immobilized algal process was tested at bench-scale and pilot-scale on a groundwater contaminated with mercury at levels near 1 ppm and with a total dissolved solid content of over 11,000 ppm. The objective was to treat the waters with AlgaSORB® so that discharge limits of 10 ppb could be achieved.

## Procedure

In the initial bench-scale tests, mercury-contaminated groundwaters passed through small glass columns (1.5 cm i.d. x 20 cm) containing 25.0 mL of sorbent. An automatic fraction collector collected effluents from the column, and EPA Method 245.1, cold vapor atomic absorption, determined the mercury concentration. Once the sorbents became saturated or leaked mercury at levels above 10 ppb, the column was stripped of mercury with 5 to 10 bed volumes of 1.0 M sodium thiosulfate. After water rinsing, the column was ready for reuse.

Groundwaters collected October 4, 1989, containing 1550 µg/L mercury, were passed through two columns (1 0 cm i d. x 37 cm) coupled in series, at a rate of six bed-volumes per minute. Ten bed volume fractions were collected and analyzed for mercury. Data shown in Table 1 are mercury concentrations in effluents from the second column

**Table 1. Test of AlgaSORB®-624 and AlgaSORB®-640 on Mercury-Contaminated Groundwaters**

| Bed Volumes of Effluent | Effluent Hg (µg/L) |
|---|---|
| 0-12 | 0.3 |
| 12-24 | 0.2 |
| 24-36 | 0.2 |
| 48-60 | 0.3 |
| 60-72 | 0.5 |
| 84-96 | 0.7 |
| 108-112 | 0.8 |
| 132-144 | 0.9 |
| 168-180 | 0.8 |
| 192-204 | 0.9 |
| 252-264 | 0.6 |
| 288-300 | 0 6 |
| 312-324 | 2.0 |
| 324-336 | 1.9 |

Onsite, pilot-scale demonstrations were conducted with the use of a small portable water treatment system manufactured by Bio-Recovery Systems for these studies. This portable unit is designed so that columns ranging in size from 1 to 4 in. in diameter can be placed on the unit. For the pilot testing, 1- diameter columns were used. Fr laboratory experiments, it was predict that 1 in. diameter columns wou become saturated with mercury in 3 tc weeks at flow rates of 10 bed volum per hour.

One column was filled wi AlgaSORB®-624 and another was fill with AlgaSORB®-640. Each column hac volume of 0.4 L. The two columns we run in series so that groundwater. with pH adjustment, was directed first throu the AlgaSORB®-624 column, and th through the AlgaSORB®-640 column, al flow rate of 6 bed volumes per hou Effluent samples were collected from sample port between the two columns well as from effluent emanating from tl second column. Effluent samples we split into three portions. One portion w sent to Woodward-Clyde Consultants f immediate mercury analysis (within 12 24 hrs. of collection) Another portion w acid-preserved and sent to EE Technology for mercury analysis; tl third portion was preserved and sent Bio-Recovery Systems for analysi Results are reported in Table 2.

Onsite pilot-scale testing wa conducted from November 6 t December 1, 1989. The site was availab for testing only from 7:00 AM-3:30 P each day. At the end of a treatment da the system was simply shut down ar then restarted the next day. Flow rate through the system was 10 bed volume per hour.

## Results and Discussion

Groundwater samples, collected a various times during 1989, were acidifie to pH 2 with nitric acid in the field befor being sent to the laboratory. Once th samples were received at Bio-Recover Systems, the solutions were neutralize to the original pH with dilute sodiur hydroxide. Laboratory and field studie were complicated by the fact that, over 10-mo. period, mercury concentration changed by an order of magnitude.

Different species of algae can b immobilized to produce differer AlgaSORB® resins. Since differer bioploymers comprise the cell walls c different algae, some species of alga behave differently from others wit respect to metal ion binding. Thus different AlgaSORB®s containing differer algal species were tested for mercur removal from the groundwaters. Becaus both mercury concentration and chemica

speciation appeared to change over the sampling period (January through October 1989), removal performance was inconsistent when a single immobilized alga was used on these waters collected at different times.

After examining several different AlgaSORB® preparations, two different AlgaSORB® resins were used for final testing. Although these two resins could have been blended into a single column, they were placed in two columns, connected in series, from which effluents samples could be taken from each column for mercury analysis. Table 1 shows results of these experiments.

Data in Table 1 show that the two columns arranged in series effectively removed mercury to below 1 ppb through passage of 250 bed volumes of mercury-contaminated waters that contained 1550 ppb mercury.

Two columns (2.54 cm i.d. x 81 cm) were separately filled with AlgaSORB®-624 and AlgaSORB®-640. The columns each had a bed volume of 400 mL and were connected in series. Mercury-contaminated waters were pumped through the two columns and two bed-volume fractions (800 mL) were collected, split, and sent to EER Technologies, Woodward-Clyde and Bio-Recovery Systems for analysis. Results of onsite pilot testing are shown in Table 2. With the exception of the first fraction collected, the data in Table 2 show that over 500 bed volumes of mercury-contaminated waters were treated before mercury in effluents approached the 10 ppb discharge limit

## Conclusions and Recommendation

Onsite, pilot scale testing on AlgaSORB® showed effective mercury recovery from contaminated groundwaters. Initial laboratory experiments however, illustrated 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 the chemical species of mercury varied as well. Combining two different AlgaSORB® preparations effected mercury removal to levels below 10 µg/L.

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

**Table 2. Onsite 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 |



☆U. S. GOVERNMENT PRINTING OFFICE: 1990/748-012/20078

*The EPA Project Officer,* ***Naomi P. Barkley****, is with the Risk Reduction Engineering Laboratory, Cincinnati, OH 45268 (see below).*
*The complete SITE Emerging Technologies report consists of two volumes:*
*Volume I "Removal and Recovery of Metal Ions from Groundwater," (Order No. PB 90-252 594 ; Cost: $17.00 , subject change)*
*Volume II "Removal and Recovery of Metal Ions from Groundwater: Appendices," (Order No. PB 90-252 602; Cost: $23.00, subject to change).*
*Both volumes of this report will be available only from:*
*National Technical Information Service*
*5285 Port Royal Road*
*Springfield, VA 22161*
*Telephone: 703-487-4650*
*The EPA Project Officer can be contacted at:*
*Risk Reduction Engineering Laboratory*
*U.S. Environmental Protection Agency*
*Cincinnati, OH 45268*

United States
Environmental Protection
Agency

Risk Reduction Engineering
Laboratory
Cincinnati OH 45268

Official Business
Penalty for Private Use $300

EPA/540/S5-90/005