United States
Environmental Protection
Agency

Office of
Research and Development
Cincinnati, OH 45268

EPA 540/R-94/522a
February 1995

EPA

SITE Technology Capsule

Dynaphore, Inc., Forager™ Sponge Technology

Introduction

In 1980, the U.S. Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund, committed to protecting human health and the environment from uncontrolled hazardous wastes sites. CERCLA was amended by the Superfund Amendments and Reauthorization Act (SARA) in 1986 - amendments that emphasize the achievement of long-term effectiveness and permanence of remedies at Superfund sites. SARA mandates implementing permanent solutions and using alternative treatment technologies or resource recovery technologies, to the maximum extent possible, to clean up hazardous waste sites.

State and federal agencies, as well as private parties, are now exploring a growing number of innovative technologies for treating hazardous wastes. The sites on the National Priorities List total over 1,700 and comprise a broad spectrum of physical, chemical, and environmental conditions requiring varying types of remediation. The U.S. Environmental Protection Agency (EPA) has focused on policy, technical, and informational issues related to exploring and applying new remediation technologies applicable to Superfund sites. One such initiative is EPA's Superfund Innovative Technology Evaluation (SITE) program, which was established to accelerate development, demonstration, and use of innovative technologies for site cleanups. EPA SITE Technology Capsules summarize the latest information available on selected innovative treatment and site remediation technologies and related issues. These capsules are designed to help EPA remedial project managers, EPA on-scene coordinators, contractors, and other site cleanup managers understand the types of data and site characteristics needed to effectively evaluate a technology's applicability for cleaning up Superfund sites.

This capsule provides information on the Dynaphore, Inc. Forager™ Sponge technology, a technology developed to remove heavy metal contaminants from groundwater, surface waters, and process waters. The Forager™ Sponge process was evaluated under EPA's SITE program in April 1994, at the NL Industries, Inc. Superfund Site in Pedricktown, NJ. The site was originally a secondary lead smelting facility. The groundwater at the facility is contaminated with heavy metals, including lead, cadmium, and chromium in excess of NJ groundwater standards. Information in the Capsule emphasizes specific site characteristics and results of the SITE field demonstration at the NL Industries, Inc. site. This capsule presents the following information:

- Abstract
- Technology Description
- Technology Applicability
- Technology Limitations
- Process Residuals
- Site Requirements
- Performance Data
- Technology Status
- Source of Further Information

Abstract

The Forager™ Sponge is a volume reduction technology in which heavy metal contaminants from an aqueous medium are selectively concentrated into a smaller volume for facilitated disposal. The technology treats contaminated groundwater, surface waters, and process waters by absorbing dissolved ionic species onto a sponge matrix. The sponge matrix can be directly disposed, or regenerated with chemical solutions. The Sponge can remove toxic heavy metals from waters in the presence of high concentrations of innocuous, naturally occurring dissolved inorganic species.

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TECHNOLOGY EVALUATION

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The Forager™ Sponge technology was demonstrated under the SITE Program at the NL Industries, Inc. Superfund site in Pedricktown, NJ. The mobile pump and treat system treated groundwater contaminated with heavy metals. The demonstration focused on the system's ability to remove lead, cadmium, chromium, and copper from the contaminated groundwater over a continuous 72-hr test. The results from the demonstration indicated that cadmium was reduced by 90%, copper reduced by 97%, lead reduced by 97%, and chromium reduced by 32%. The removal of heavy metals proceeded in the presence of significantly higher concentrations of innocuous cations such as calcium, magnesium, sodium, potassium, and aluminum.

The Forager™ Sponge technology was easy to operate and exhibited no operational problems over the course of the demonstration. The system is trailer-mounted, easily transportable, and can be operational within a day upon arrival at a site. The spent Sponge can be compacted into a small volume for easy disposal.

The Forager™ Sponge technology was evaluated based on the seven criteria used for decision making as part of the Superfund Feasibility Study (FS) process. Results of the evaluation are summarized in Table 1.

Technology Description

The Forager™ Sponge is an open-celled cellulose sponge which contains a water-insoluble polyamide chelating polymer for the selective removal of heavy metals. The polymer is intimately bonded to the cellulose so as to minimize physical separation from the supporting matrix. The functional groups in the polymer (i.e., amine groups in the polymer backbone and pendent carboxyl groups) provide selective affinity for heavy metals in both cationic and anionic states, preferentially forming coordination complexes with transition-group heavy metals (groups IB through VIIIB of the Periodic Table). The order of affinity of the polymer for metals is influenced by solution parameters such as pH, temperature, and total ionic content. The following affinity sequence for several representative ions is generally expected by Dynaphore:

$Cd^{++} > Cu^{++} > Fe^{+++} > Au^{+++} > Mn^{++} > Zn^{++} > Ni^{++} > Co^{++} > Pb^{++} > Au(CN)_2^- > SeO_4^{-2} > AsO_4^{-3} > Hg^{++} > CrO_4^{-2} > UO_4^{-2} > Ag^+ > Al^{+++} > K^+ > Ca^{++} > Mg^{++} >> Na^+$

The high selectivity for heavy metals, and the low selectivity for alkali and alkaline earth metals (Na^+, K^+, Mg^{++}, and Ca^{++}), is especially useful for the treatment of contaminated natural waters which may contain high concentrations of these innocuous chemical species. These monovalent and divalent cations do not interfere with or compete with absorption of heavy metals, therefore allowing for maximum removal of heavy metals from contaminated waters.

The Sponge is highly porous which promotes high rates of absorption of ions. Absorbed ions can be eluted from the Sponge by techniques typically employed for regeneration of ion exchange resins. Following elution, the Sponge is ready for the next absorption cycle. The useful life of the media depends on the operating environment and the elution techniques used. Where regeneration is not desirable or economical, the Sponge can be compacted to an extremely small volume to facilitate

Table 1. *FS Criteria Evaluation for the Forager™ Sponge Technology*

FS Criteria						
Overall Protection of Human Health and the Environment	*Compliance with federal ARARs*	*Long-Term Effectiveness and Permanence*	*Reduction of Toxicity, Mobility, or Volume Through Treatment*	*Short-Term Effectiveness*	*Implementability*	*Cost*
Protects human health and the environment by removing contaminants from groundwater or surface water.	*Requires compliance with RCRA treatment, storage, and disposal regulations and pertinent radioactive and mixed waste regulations.*	*Permanently removes contamination from the affected matrix.*	*Volume reduction technology which transfers contaminants from aqueous media to a smaller volume.*	*Presents minimal risk to workers and the community.*	*Easily implementable and transportable.*	*$340/1,000 gal with regenerate ion.*
Minimizes or eliminates the further spread of contaminants within the aquifer.	*Well construction activities may require permits.*	*Residuals from the process must be disposed of in an appropriate manner.*	*Ability to compact Sponges to small volumes may be advantageous for radioactive or mixed waste.*		*Requires minimal site preparation and utilities (water & electricity).*	*$238/1,000 gal with Sponges regenerated twice providing for 3 useful cycles.*
	Disposal of treated waters may require compliance with Clean Water Act and Safe Drinking Water Act.					

**Actual cost of a remedial technology is site-specific and is dependent on factors such as the cleanup level, contaminant concentrations and types, waste characteristics, and volume necessary for treatment.*

disposal. The metal-saturated Sponge can also be incinerated with careful attention given to the handling of resultant vapors.

The Sponge can be used in columns, fishnet-type enclosures, or rotating drums. For this demonstration, the Sponge was utilized in a series of four columns. Each column was comprised of a 1.7 ft^3, pressurized acrylic tube containing about 24,000 half-in. Sponge cubes contained within a fishnet bag. The columns were mounted on a mobile trailer unit.

Technology Applicability

The Forager™ Sponge is capable of removing dissolved heavy metals from a wide variety of aqueous media including groundwater, surface waters, landfill leachate and industrial effluents. The chemistry employed for metal removal is selective, allowing for the treatment of toxic heavy metals in the presence of high concentrations of innocuous cations, such as Ca^{++}, Mg^{++}, Na^{+}, and K^{+}. The selective affinity of the polymer is similar to commercially available selective chelating resins. However, the Sponge's unique supporting cellulosic matrix may provide the technology with distinct advantages under certain processing conditions.

The Forager™ Sponge could be potentially incorporated into varied treatment configurations. The technology can be utilized in a conventional pump-and-treat remedial process, as was performed during the SITE Demonstration. The Sponge can be utilized as the primary or secondary removal mechanism, dependent on the type and concentration of contaminants, as well as the properties of the influent wastestream. For example, the Sponge may be used as a polishing step in conjunction with a technology that can remove high concentrations of metals to moderate levels (e.g., chemical precipitation). According to the developer, the Forager™ Sponge technology can also be used in applications requiring in-situ treatment. In these applications, the Sponge can be placed into tubular fishnet containers and emplaced within wells or trenches to intercept groundwater flow. The Sponge can be used to treat surface waters by placing the Sponge in a fishnet configuration across channels or within other surface water bodies.

In addition, to potential different treatment applications, the Sponge's unique matrix provides advantages in terms of disposal and operating conditions. The metal-laden Sponge can also be compacted into small disposal volumes, which could aid in lowering disposal costs, and is beneficial where a minimum volume of residual waste is needed due to the properties of the contaminants being absorbed. For example, this may be advantageous in the treatment of radiologically contaminated waters, where the need to minimize residual waste is a critical disposal issue.

The high porosity of the Sponge enables a low pressure system to be used. For this demonstration, the four column unit operated under an inlet pressure as low as 4.4 psig. Although not demonstrated, if sufficient head were provided, the system could have operated by gravity flow.

Technology Limitations

The technology is considered a volume reduction technology since the contaminants are removed from the waste stream and concentrated into a smaller volume which can be more easily handled and disposed. The reduced volume, either sponge or acid regenerant solution, must be immobilized by other means on-site or off-site.

According to the developer, the scope of contaminants suitable for treatment using the Dynaphore Inc. Forager™ Sponge Technology is limited to heavy metals. The technology's affinity and absorption capacity for given metals can vary and is dependent on a number of waste characteristics including pH, concentration and types of cations and anions present, and the presence of complexing agents.

The technology usefulness may be limited by its overall absorption capacity for the heavy metals of concern. If frequent changeout or regeneration of the columns is required, it could make this technology cost prohibitive. In these applications, pretreatment may be necessary in order to reduce the concentration of specific contaminants to technically and/or economically optimal levels.

Process Residuals

The residuals generated from the Sponge technology consist of either solid sponge material or liquid (acid) regenerant solution. These residuals will be concentrated with heavy metals, and depending on contaminant levels, may be subject to RCRA regulations as a hazardous waste. These waste materials can be easily stored in appropriate 55-gal drums for off-site transport and disposal. For the demonstration, four Sponges were hand compacted into one 55-gal drum. Further compaction is possible utilizing a waste compactor. Following completion of the demonstration, the developer sent four fishnet bags of virgin Sponges to a waste compacting firm to determine maximum compaction achievable. Tests performed revealed compaction ratios of 4:1 and 10:1 utilizing compaction forces of 20,000 lb and 85,000 lb, respectively.

Treated wastewater can be discharged to a Publicly Owned Treatment Work (POTW), into surface waters, or reinjected through underground injection wells, if appropriate discharge limitations are met and the proper permits are obtained. For this demonstration, the treated effluent was suitable for off-site treatment at a local POTW.

Site Requirements

The Forager™ Sponge treatment unit is mounted on a flat bed trailer and is easily transportable. The four-column trailer unit, measuring approximately 50 ft^2, is equipped with a water heater, wastewater pump, flow

meter and totalizer. Once on site, the treatment system can be operational within a day, if all necessary facilities, utilities, and supplies are available. On-site assembly and maintenance requirements are minimal.

Utilities required for the trailer unit are limited to water and electricity. Electricity requirements are dependent upon the need to pump the wastewater, if gravity feed is not feasible, and the need to heat the wastewater to improve absorption of metals. The water can be pumped with the 12-V pump equipped on the trailer. This pump can also run off a car battery, which was done for the demonstration. The water heater requires a 220-V electrical outlet. Water will be required occasionally for regeneration of the Sponges, cleanup and decontamination.

Support facilities include an area for untreated and treated groundwater storage tanks (if used), a chemical storage area for regenerant chemicals (i.e, acids) and any other process chemicals, and a waste drum storage area for spent Sponges, regenerant solutions, and other wastes requiring disposal. These areas must be constructed to control run-on and run-off. Additionally, an enclosed building or shed may be necessary to protect equipment and personnel from weather extremes. During the demonstration, the treatment unit was housed in a tent. Mobile office trailer(s) may also be needed on site.

Support equipment for the Forager™ Sponge Technology may include a drill rig for well installation, containers for waste storage, a forklift for moving waste drums, and a waste compactor for compaction of Sponges. In addition to an influent equalization tank, a treated storage tank may be needed if the water can not be directly discharged to a POTW or stream, or reinjected into the ground.

Performance Data

The Forager™ Sponge Technology was evaluated for its ability to remove heavy metals from groundwater. Lead, cadmium, and chromium are contaminants of concern at the NL site, and are therefore the critical parameters for this study. In addition, copper was also considered a critical parameter because of the high removal efficiency observed in predemonstration treatability tests.

The developer claimed that the technology would achieve at least a 90% reduction of lead and copper, an 80% reduction in cadmium, and a 50% reduction of chromium (as trivalent chrome) in the groundwater.

In addition to the primary objective, other secondary (non-critical) objectives included:

- determine removal efficiencies for other heavy metals present in txhe groundwater;
- determine removal efficiencies for critical parameters across the four columns;
- evaluate the absorption capacity and regenerative capabilities of the Sponge for the critical parameters;
- gather information to estimate operating costs, (e.g., utility and labor requirements, waste disposal costs, treatment capacity, etc.).

The technology was evaluated over a continuous 72-hr operational period, resulting in a total treatment volume of approximately 4,300 gal. Groundwater was pumped from the influent storage tank through the four-column system at a treatment flow rate of 1 gpm or 0.08 bed volumes/min. The influent temperature was raised approximately 15° C to increase reaction rates (i.e.,improve absorption of the critical metals). The treated effluent was initially discharged to a 250 gal portable tank from which it was subsequently pumped to a 20,000 gal effluent storage tank. The stored effluent was transported off-site for treatment at a local POTW. A flow schematic of the system is shown in Figure 1.

According to the developer, replacement or regeneration of the columns was not necessary, since none of the columns were anticipated to become saturated (i.e., no further absorption capacity available for the critical metals). Four columns were reportedly needed to provide sufficient path length to meet the demonstration goals.

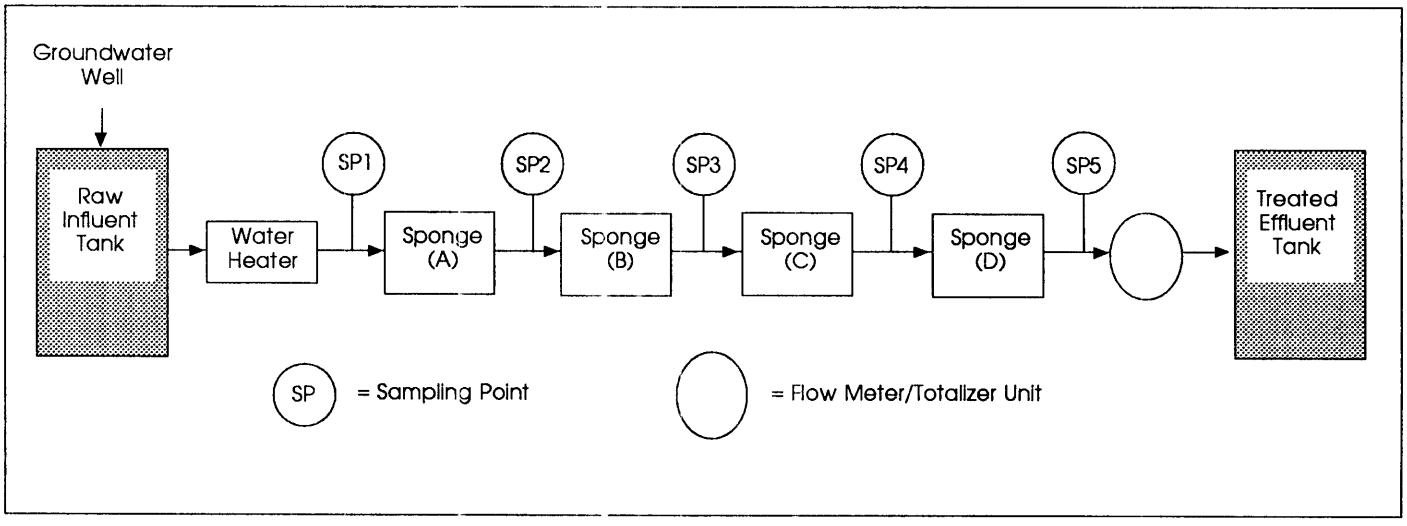

Figure 1. *Process flow diagram for the Dynaphore, Inc., Forager™ Sponge demonstration.*

Although concentrations of some of the critical metals exceeded cleanup goals for the site, the groundwater was spiked with solutions of lead, copper, and cadmium to assure effective evaluation (quantification) of the developer's claim.

Grab samples for analysis of critical parameters were collected from the raw influent, final effluent, and intermediate column effluent points (see Figure 1). In addition, equal volume 24-hr composite samples were collected for total metals, chemical oxygen demand, total suspended solids, total dissolved solids, sulfate, and gross alpha and gross beta radioactivity. Process measurements for flow rate, total volume, pressure, pH, and temperature were also monitored at these locations. Since the developer reported that replacement or regeneration of the columns was not necessary, side tests on laboratory scale columns treating standard metal salt solutions were performed to aid in evaluating the absorption capacity and regenerative capabilities of the Sponge.

Analytical results of critical parameters for the raw influent and final effluent are presented in Table 2 and depicted in Figure 2. These data show that treatment claims for cadmium, copper, and lead were achieved. The developer, however did not achieve treatment claims for chromium. The treatment claim was based on comparing the mean concentration of the raw influent to the mean concentration of the final effluent.

As shown in Figure 2, effective removal of chromium (based on the 50% claim) was achieved within the first 10 hr of operation until performance markedly decreased. The decrease in removal efficiency could be the result of the Sponge's higher affinity for the other critical metals. Although the cadmium claim was met based on the overall effluent average, final effluent cadmium concentrations were below desired performance levels (107 ug/L) at approximately the 61st hr of operation. This is due to the lower than anticipated absorption capacity for cadmium which resulted in saturation of the first two columns within the test period.

The technology had the greatest efficiency for copper. One column was sufficient to meet the developer's 90% removal claim for approximately 53 hr of the 72-hr test. Copper concentrations for columns 2, 3, and 4, were at or near detection limits throughout the demonstration test. With regard to lead, three columns were sufficient to meet the developer's 90% claim for approximately 61 hr of the demonstration test.

Although claims for cadmium and lead were met, some of the columns became saturated with these metals during the demonstration. Specifically, the first column became saturated with both cadmium and lead, while the second column became saturated with only cadmium. Saturation is defined when the effluent concentration of a given metal is approximately equal to or greater than the influent concentration. The first column was saturated with both cadmium and lead at approximately the 49th hr. Approximately 10 hr later, cadmium saturated the second column. None of the columns were saturated with copper during the demonstration test. Based on a non-linear extrapolation of the data, the first column would have become saturated with copper after approximately 4 days of continuous operation.

Based on data from the 72-hr demonstration, the actual absorption capacity for the critical metals was significantly lower (approximately 10 to 100 times lower) than the developer's predemonstration estimates. These estimates were based on absorption capacity tests on standard metal salt solutions rather than the groundwater. The developer theorizes that anion species such as sulfate and phosphate may have interfered with the effective removal of these metals. These results show the need to conduct treatability tests on each wastestream proposed for treatment to determine the true absorption capacity of the system prior to implementing the technology.

Effective removal of cadmium, copper, and lead was achieved in the presence of a groundwater pH ranging from 3.1-3.8, a sulfate concentration of approximately 20,000 mg/L, a TDS concentration of approximately 23,000 mg/L, and disproportionately higher concentrations of other cations such as magnesium (72 mg/L), potassium (82 mg/L), aluminum (149 mg/L), calcium (224 mg/L), and sodium (6,000 mg/L).The technology's low affinity for these cations was supported by the near zero removal rates of these ions. Table 3 presents a summary of data for the non-critical heavy metals.

In addition to the regeneration of the small test columns, the developer conducted regeneration tests in his laboratory on Sponge cubes taken from the demonstration columns. Both tests showed that regeneration is feasible for lead, copper, and cadmium. Regeneration of chromium was evaluated only for the small test columns and showed only partial regeneration.

The cost to treat heavy metal contaminated groundwater over a one year period with the Dynaphore, Inc. Forager™ Sponge Technology is estimated at $340/1,000 gal, assuming the Sponges are not regenerated and are replaced upon saturation and $238/1,000 gal, assuming the Sponges are regenerated twice providing for three

Table 2. *Treatment Performance for Critical Metals*

Parameter	*90% Confidence Interval for Avg. Influent Conc. (ug/L*	*90% Confidence Interval for Avg. Effluent Conc. (ug/L*	*90% Confidence Interval for Percent Removal (%)*	*Developer's Treatment Claim (%)*
Cadmium	*537 ± 11*	*56 ± 13*	*90 ± 2.7*	*80*
Chromium	*426 ± 31*	*290 ± 30*	*32 ±5.8*	*50*
Copper	*917 ± 14*	*25 ± 0*	*97 ± .04*	*90*
Lead	*578 ± 12*	*18 ± 3*	*97 ± .59*	*90*

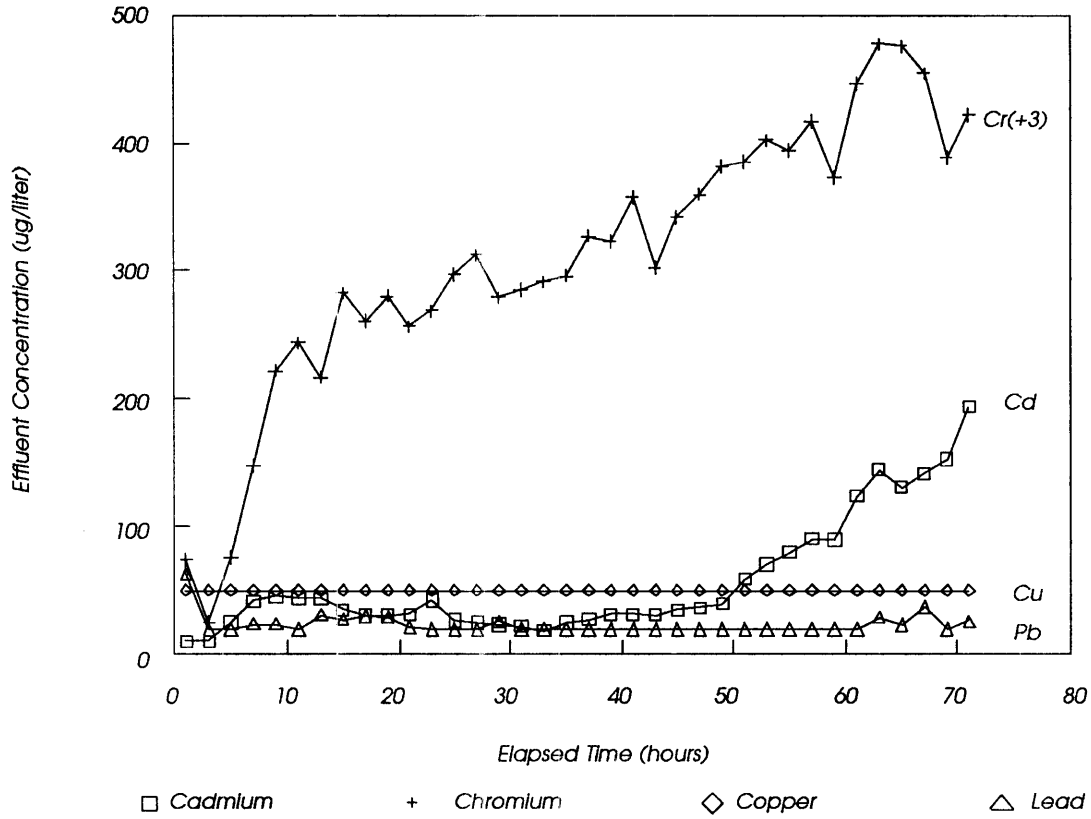

Figure 2. *Final effluent - critical metals.*

Table 3. *Data Summary for Non-Critical Heavy Metals*

Parameter	Avg. Influent Conc. (ug/L)	Avg. Effluent Conc. (ug/L)	Avg. Total % Removal
Aluminum	149,000	152,000	-2
Arsenic	47.7	44.4	7
Barium	50.2	46.3	8
Beryllium	15.9	13.9	13
Calcium	224,000	248,000	-11
Cobalt	176	146	17
Iron	199,000	199,000	0
Lithium	460	473	-3
Magnesium	71,700	72,300	-1
Manganese	5870	5880	-1
Mercury	0.39	0.21	46
Nickel	378	107	72
Phosphorus	1520	557	63
Potassium	82,300	83,700	-2
Sodium	6,030,000	6,130,000	-2
Strontium	557	562	-1
Vanadium	1310	53.2	96
Zinc	1300	1190	9

useful treatment cycles. This cost estimate assumes groundwater characteristics are similar to the demonstration groundwater and cadmium, lead, and copper are treated to demonstration performance claims utilizing a four-column, pump-and-treat unit similar to the demonstration unit. The system would operate 24 hr a day, 7 days a week at a flow rate of 1 gpm resulting in a total treatment volume of approximatley 525,000 gal.

A significant portion of the cost is attributable to the frequent replacement or regeneration of the Sponges due to the limited absorption capacity for cadmium in this groundwater. The developer believes that a modification of the polymer may improve its overall absorption capacity for the critical metals which would greatly aid in lowering treatment costs. Additionally, further cost reduction may be achieved through the use of larger scale units which could handle higher flow rates (see below) and the use of an industrial compactor to compact Sponges to lower disposal costs.

Technology Status

To date, this SITE demonstration represents the first full-scale use of this technology. The trailer mounted-unit was built exclusively for this SITE Demonstration. This unit can be modified to include additional columns of the same size. Additionally, a larger scale unit can also be constructed. This unit uses larger columns and would be just as effective as the smaller system, but could operate at approximately double the flow rate.

Dynaphore, Inc. has formed a liaison with a known environmental remediation firm, Adtechs Corporation of Herndon, VA, to provide the necessary expertise in performing full-scale remediations at contaminated waste sites.

Potential in-situ applications, as previously discussed, may be promising. However, insufficient data is currently available which demonstrates the viability of this treatment option. The effectiveness and cost of in-situ applications have not been evaluated in this study nor has the developer commercially utilized the technology in these applications. EPA is, however, planning to conduct a second demonstration which will evaluate the technology in an in-situ scenario.

Disclaimer

While the technology conclusions presented in this report may not change, the data has not been reviewed by the Quality Assurance/Quality Control Office.

Source of Further Information

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