DEVELOPMENT OF HUMASORB™ --A COAL DERIVED HUMIC ACID FOR REMOVAL OF METALS AND ORGANIC CONTAMINANTS FROM GROUNDWATER

Final Technical Report for the Period March 1995 through March 2000

Work Performed Under Contract: DE-AR21-95MC32114

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Submitted to:

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National Energy Technology
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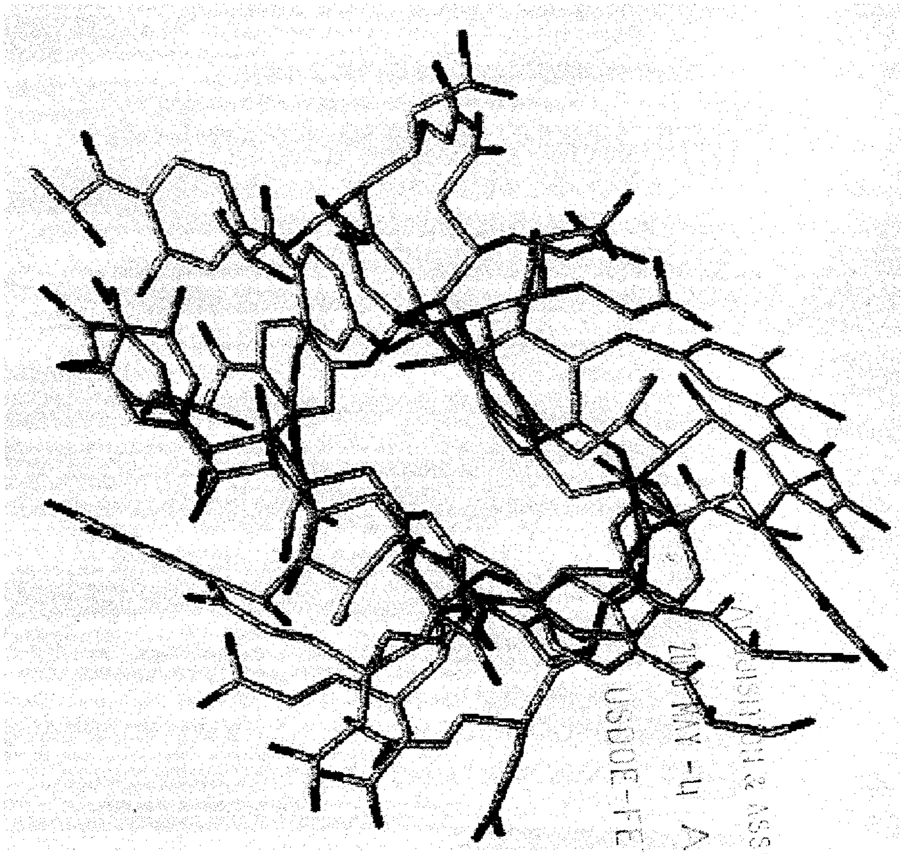

Cross section of a humic acid polymer (TNB Model)

ARCTECH Project No.: 9500

May 2000

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HUMASORB™ --A COAL DERIVED HUMIC ACID ADSORBER FOR REMOVAL OF METALS, ORGANIC CONTAMINANTS AND RADIONUCLIDES

ARCTECH, Inc. 14100 Park Meadow Drive # 210, Chantilly, VA 20151
U.S. Department of Energy Contract No. DE-AR21-95-MC32114
Period of Performance: March 1995-March 2000
DOE COTR: Mr. David Schwartz (Tel: 412-386-6714)
ARCTECH Principal Investigator: H.G. Sanjay (Tel. 703-222-0280)

EXECUTIVE SUMMARY

This report encompasses the research work on the evaluation and applicability of HUMASORB™, a coal derived humic acid adsorbent for removal of multiple contaminants from groundwater. The project was performed under the Industry Programs of the U.S. Department of Energy. This report presents the performance attributes of HUMASORB™ for removal of different contaminants and the economic analysis for HUMASORB™ use in remediation of complex waste streams. In addition a summary of treatability tests, conducted outside the scope of this contract, for a number of governmental and industrial applications are included in the appendix as additional data to support the broad applicability of HUMASORB™. A patent on this novel adsorber was issued recently on May 25, 1999 (US Patent # 5,906,960).

The number of hazardous waste sites requiring treatment for soil and groundwater remediation under current federal and state regulations is estimated to be about 217,000 sites in the United States. The sites include those that fall under the National Priorities List (NPL, Superfund), Resource Conservation and Recovery Act (RCRA) Corrective Action, Department of Defense (DOD) and Department of Energy (DOE) installations. The soil and groundwater at these sites are contaminated with various toxic metals (about 50-70% of the sites) and with organic contaminants (40-70% of the sites). In addition, radioactive contamination is found at 90% of the DOE installations. The DOE estimates that more than 5,700 groundwater plumes have contaminated over 600 billion gallons of water and 50 million cubic meters of soil throughout the DOE complex. Mixed waste containing multiple hazardous and radioactive contaminants is a problem at a number of installations. The types of contaminants present at the sites include:

- Toxic metals such as lead, chromium, arsenic, cadmium, zinc, barium, nickel, copper, beryllium, mercury and others
- Organic chemicals such as benzene, toluene, xylenes, chlorinated hydrocarbons such as trichloroethylene, (TCE), perchloroethylene (PCE), energetic chemicals such as nitroesters and others
- Radioactive contaminants such as uranium, plutonium, thorium, cesium, strontium, tritium and others.

The remediation of contaminated surface and groundwater is typically attempted with treatments such as precipitation, ion exchange, membrane separation and activated carbon adsorption. The method used most frequently to treat groundwater is the conventional pump-and-treat technology. The groundwater is pumped to the surface and treated using various technologies. At sites having mixed contaminants, two different processes are required to remediate a site, an approach that results in complex and costly processing steps. A typical approach is to remove organics using activated carbon followed by ion exchange to remove metals. However, this method is not very effective in meeting the desired cleanup criteria for sites with various types of contaminants, especially when the aquifers are contaminated with non-aqueous phase liquids (NAPLs). Pump-and-treat methods are expected to last 30-70 years at a number of sites that contain NAPLs, thus increasing the treatment costs.

HUMASORB™ is the generic name used for the technology which is the concept of utilizing humic acid derived products for the mitigation of contaminants from mixed waste streams. In Phase I of this project, liquid humic acid product (HUMASORB-L™) and purified humic acid (HUMASORB-S™) were evaluated for contaminant removal from simulated waste streams. In Phase II, water-insoluble humic acid (HUMASORB-CS™) was prepared using proprietary methods designed to improve the solubility and handling properties. The goal of this project was to develop HUMASORB-CS™ with improved solubility characteristics and to remove metals, radionuclides and organic contaminants from aqueous waste streams in a single processing step.

Humic acid is a complex aromatic macromolecule with various linkages between the aromatic groups. It is a highly functionalized carbon-rich biopolymer with functional groups such as carboxylic, phenolic, enolic and carbonyl structures of various types. Humic acid has been extensively studied and various molecular models have been proposed to explain it's unique properties. A recent article discussed the modeling of humic acid structures based on a proposed new humic acid building block (Sein, L.T. et al., ES&T, Vol.33 No.4, 1999). The first hypothetical structure for humic acid proposed in 1972 and a new proposed building block are shown in Figure 1.

Metals are bound to the carbon skeleton of humic substances primarily through carboxylic and phenolic oxygen, but heteroatoms such as nitrogen, and sulfur also have a positive effect on metal binding. The mechanisms for adsorption of organic compounds by humic acid include hydrophobic bonding, hydrogen bonding, ion exchange, ligand exchange. In addition, humic acid can influence oxidation-reduction of metal species and also stabilize the reduced cationic form by chelation/ion-exchange. This mechanism is responsible for the reduction of chromium (VI) and hexavalent actinides such as plutonium by humic acid.

The results from Phase I demonstrated the ability of HUMASORB-L™ and HUMASORB-S™ to remove various contaminants from waste streams. HUMASORB™ was shown to be effective for removal of multiple contaminants in a single step. The mechanism for metal removal is believed to be complex, and involves a combination of ion-exchange and chelation/complexation. The mechanism for organic removal is believed to be primarily by physical adsorption. The isotherms for adsorption of some of the contaminants (such as copper, nickel, cerium and uranium) were represented well by either Freundlich or Langmuir isotherm models.

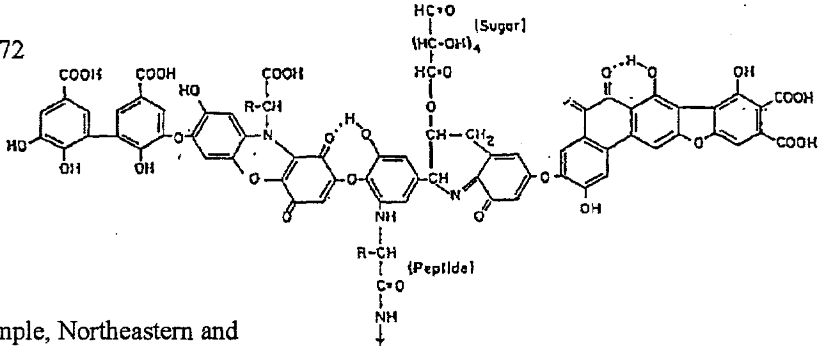
In Phase II, HUMASORB-CS™ was prepared using proprietary methods to improve the solubility and handling properties. Humic acid extracted from coal as a liquid (HUMASORB-L™) was converted to a solid adsorbent/ion-exchange material by cross-linking and immobilization to produce HUMASORB-CS™ that is insoluble in water.

HUMASORB-CS™ was evaluated in batch and column tests for removal of different types of contaminants. The contaminants evaluated include metals, radionuclide surrogates and organic compounds. The results demonstrate the improved solubility characteristics of HUMASORB-CS™ compared to HUMASORB-S™. The contaminant removal ability was either retained or enhanced with HUMASORB-CS™. Column test results were used to develop breakthrough curves for different types of contaminants including metals, radionuclide surrogates, oxy-anions and organics. The column performance was used to estimate parameters such as contaminant removal capacity at breakthrough and at saturation. In addition, the ability to regenerate and re-use HUMASORB-CS™ was evaluated. The test results demonstrate that HUMASORB-

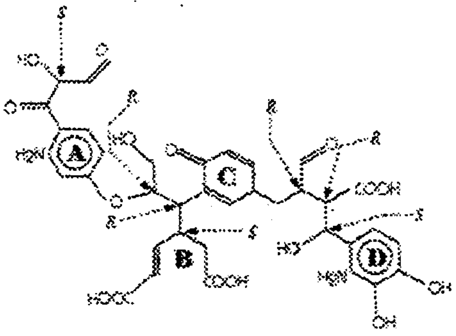
CS™ can be used for removal of multiple types of contaminants (metals, radionuclides and organics) in a single-step process.

Figure 1. Proposed Structures of Humic Acid

A. Stevenson, 1972



B. TNB, 1998 (Temple, Northeastern and Birmingham)



Empirical Formula: $C_{36}H_{30}O_{15}N_2xH_2O$
x=0-15

HUMASORB-CS™ is stable when it is stored at various temperatures for extended periods of time. It was also stable in the presence of various anions and in the presence of microorganisms. The stability tests also showed that HUMASORB-CS™ was not only stable, but also retained the ability to remove contaminants from waste streams.

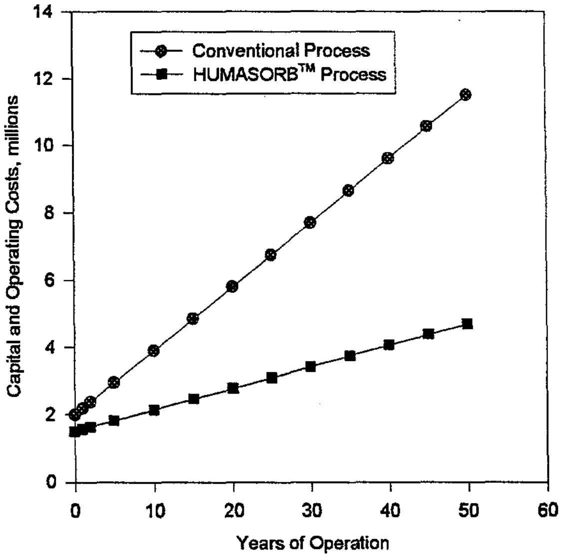
The cation-exchange capacity (CEC) for HUMASORB-CS™ is comparable to that or higher than commercial ion-exchange resins. The CEC for lead is more than 5 meq/g and that for copper is approximately 4.0 meq/g and for most metals and radionuclides evaluated in this project, the capacity if between 1.2-5.0 meq/g. In comparison, the capacity for ion-exchange resins ranges between 1-2 meq/g. In addition, HUMASORB™ has high distribution coefficient for removal of various metals and radionuclides surrogates. The distribution coefficient for uranium is greater than 100,000ml/g (at pH=5.1), lead is 3500 ml/g (at pH=2.2) and for cerium (plutonium surrogate) 5600 ml/g (at pH=2.5).

The tests with chlorinated organic compounds show that HUMASORB-CS™, due to it's inherent reductive properties, is not only adsorbing the chlorinated organic contaminants, but potentially reducing them to innocuous components, while simultaneously removing a variety of other organic and inorganic contaminants of concern in the environment. The potential for improvement in chlorinated organic removal by HUMASORB-CS™ was evaluated by incorporating Zero-Valent Iron (ZVI) into the matrix. The test results show that the TCE and PCE removal was improved with the incorporation of the zero-valent iron into the HUMASORB-CS™ matrix from about 60 % (H-CS) to about 90 % (2.5%ZVI+H-CS) and to about 93 % (7.5%ZVI+H-CS) when the contact time was 12 hours. At 24 hours contact time, however, the TCE and PCE removal was the same for all the three materials. The results indicate that the effectiveness of HUMASORB-CS™ is comparable to ZVI, if adequate contact time is provided.

HUMASORB-CS™ was evaluated for contaminant removal under simulated barrier conditions at pressures of 10 psig and 100 psig. These conditions were used to simulate barrier installation depths of approximately 10 feet and 100 feet. In these tests, simulated wastewater containing copper, cerium (plutonium surrogate), chromium (VI), trichloroethylene (TCE) and perchloroethylene (PCE) were passed through HUMASORB-CS™ bed under simulated barrier conditions. The tests continued for more than two years without breakthrough of all the contaminants. The HUMASORB-CS™ columns were only partially saturated with some contaminants at the time of this report. The results indicate that HUMASORB-CS™ is effective in removing contaminants (metals, organics and radionuclides surrogate) in a single treatment step when it is used in a permeable barrier system.

An economic analysis was performed to compare the costs for treatment of waste streams using HUMASORB™ technology and conventional treatment. The results of the economic analysis show that the use of HUMASORB™ technology for surface water treatment can result in savings of more than 50% in life-cycle costs compared to a conventional treatment system, assuming a 10-year life-cycle. The use of a HUMASORB™ permeable reactive barrier system can result in savings of more than 60% in life-cycle costs compared to a conventional pump-and-treat system. The comparison of life-cycle costs using HUMASORB™ treatment system and the conventional approach used to treat contaminated water is shown in Figures 2 & 3. In addition, an economic analysis for the production of HUMASORB-CS™ was conducted using a conceptual plant producing 150 tons per day. The analysis indicated that HUMASORB-CS™ could be produced at a cost of less than $ 1/lb in a commercial plant.

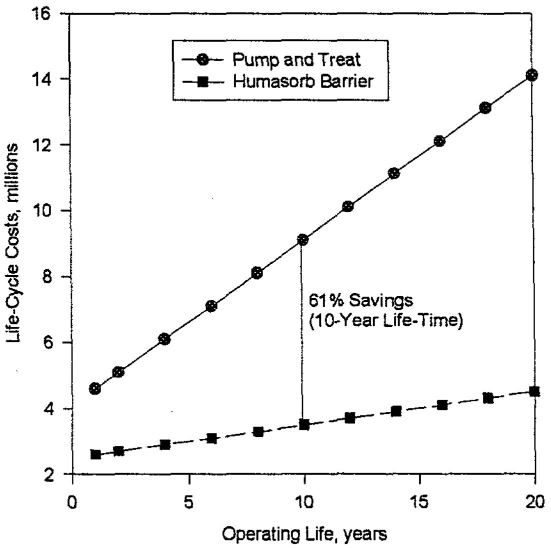
Figure 2. Life-Cycle Costs of HUMASORB™ Treatment System Compared to Conventional Approach for Surface Treatment



Conventional Process: Electrochemical treatment, filtration and clarification. Costs based on EPA Report 542-R-99-006
HUMASORB™ Process: Estimated Costs for water contaminated with multiple metals and organic compounds

HUMASORB-CS™ has also been evaluated in treatability and demonstration tests using actual waste streams from a number of government and industrial sites. These projects were conducted under separately funded contracts. HUMASORB™ has been evaluated using contaminated water from DOE sites including Savannah River Site, Idaho National Engineering and Environmental Laboratory (INEEL) and Rocky Flats. In addition, HUMASORB-CS™ has been successfully evaluated using contaminated water from industrial sites including Berkeley Pit in Montana, and Iron Mountain Site in California. A HUMASORB™ based mobile treatment system was successfully used recently to treat waste brines for removal of arsenic, mercury and lead. This project was implemented at the chemical agent disposal facility of the United States Army at Johnston Island in the Pacific. The results from these tests validate the results from the tests conducted with simulated waste streams during HUMASORB™ development. Efforts are underway at present to deploy treatment systems based on HUMASORB™ technology at various DOE sites.

Figure 3. Life-Cycle Costs of HUMASORB™ In-Situ Permeable Barrier System Compared to Conventional Approach for Groundwater Treatment



The results from this project and the treatability/demonstration tests using contaminated water from DOE and industrial sites clearly establish that HUMASORB™ is a cost-effective material for cleanup of complex waste streams. A demonstration and deployment of a process based on HUMASORB-CS™ is justified and recommended.

1.0 INTRODUCTION

Heavy metal and organic contamination of surface and groundwater systems is a major environmental concern. The contamination is primarily due to the improper disposal of industrial wastes. The presence of toxic heavy metal ions, volatile organic compounds (VOCs) and pesticides in water is of great concern and could affect the safety of drinking water. Decontamination of surface and groundwater can be achieved using a broad spectrum of treatment options such as acid precipitation, ion-exchange, microbial digestion, membrane separation, and activated carbon adsorption. The state of-the-art technologies for treatment of contaminated water, however, can remediate only one class of contaminants at a time, i.e., either organics (activated carbon) or heavy metals (ion exchange). The groundwater contamination at Department of Energy (DOE) sites is often due to the presence of both organics, heavy metals and radionuclides. Remediation, therefore, typically requires the use of two different stepwise processes. To overcome the costly sequential treatment of contaminated streams, a novel material having the capacity to remove both organics and metals in a one step process is being developed as part of this project.

1.1 Purpose

The objective of this project is to evaluate HUMASORB-CS™, a lignite derived adsorbent, to remove heavy metal and organic contaminants from groundwater and surface water streams in a one step process. As part of this project, HUMASORB-CS™ was characterized and evaluated for its ion-exchange and adsorption capabilities.

1.2 Background

Mixed waste contaminant plumes exist throughout DOE industrial complexes creating complex water remediation problems. DOE surveyed the magnitude of the problem, and in 1992 published a facility-wide survey that identified and quantified the chemical contaminants found at ninety-one (91) waste sites. Contaminants found at DOE sites are summarized in Table 1.1 and detailed in Table 1.2.

Groundwater contaminants most frequently reported are metals and chlorinated hydrocarbons (Table 1.1). The next most reported contaminants are radionuclides, oxo-anions, fuel hydrocarbons, and ketones.

The more detailed Table 1.2 information clearly shows that concentrations for most contaminants range from below regulatory guidelines to those that exceed the risk-based guidelines by several orders of magnitude.

These contaminants are not often found as a single groundwater contaminant. Rather, they exist as complex mixtures that present difficult remediation problems. The 1992 survey, for example, reports mixtures of chlorinated hydrocarbons and metals as the primary contaminants at DOE facilities.

Table 1.1. Most Frequently Reported Contaminants in DOE Facility Groundwater

Metals:
Lead, chromium, arsenic, and zinc

Chlorinated hydrocarbons:
Trichloroethylene (TCE); 1,1,1-trichloroethane (TCA);
1,2-dichloroethylene (DCE); tetrachloroethylene (PCE);
1,1-dichloroethane (DCA) and chloroform

Radionuclides:
Tritium, uranium, and strontium

Oxo-anions:
Chromium(VI)

Fuel hydrocarbons:
Toluene, xylene, benzene, and ethyl benzene

Ketones:
Acetone, methyl ethyl ketone, and methyl isobutyl ketone

Table 1.2. Concentration Ranges and Regulation Guidelines for Groundwater Contaminants at DOE Facilities

CLASS	CONTAMINANT	GROUNDWATER CONCENTRATION RANGE (1)	CONCENTRATION RANGE GUIDELINES
		µg/L unless otherwise noted	
METALS	**Lead**	0.56 to 120,000	0(3); 50(4); 5(5)
	Chromium	0.42 to 9,010	100(3); 50(4); 100(5)
	Arsenic	0.3 to 32,100	5(4)
	Zinc	1 to 697,000	5,000(6)
	Copper	1 to 3,300	1,300(3); 1,300(5)
	Mercury	0.08 to 216,900	2(3); 2(4); 2(5)
	Cadmium	0.005 to 7,600	5(3); 10(4); 5(5)
RADIO-NUCLIDES	**Tritium**	3.3(7) to 20.9 billion pCi/L	20,000 (8); 2,000,000(9) pCi/L
	Uranium	0.001 to 11.7 million (10) 0.02 to 22,700 (7) pCi/L	500 to 600(9) pCi/L
	Strontium	0.05 to 231,000 (7) pCi/L	8(8) to 1,000(9) pCi/L
	Plutonium	0.0009 to 12.8 (7) pCi/L	300(9) to 400(9) pCi/L
	Cesium	0.0027 to 1.830 (7) pCi/L	200(8) to 3,000(9) pCi/L
OXO-ANIONS	**Nitrate**	2.6 to 100 million	10,000 (3,4,5)
	Chromium	0.42 to 9,010	100(3); 50(4); 100(5)
ORGANICS	***Chlorinated Hydrocarbons***		
	Trichloroethylene	0.2 to 870,000	5(4)
	1,1,1-Trichloroethane	0.2 to 16,600	200(4)
	1,2-Dichloroethylene	0.7 to 50,000	70(cis)(3,5): 100(trans)(3,5)
	Tetrachloroethylene	0.18 to 272,000	0(3): 5(5)
	1,1-Dichloroethane	0.3 to 7,800	--
	Chloroform	0.3 to 2,070	--
	Dichloromethane	0.29 to 2.4 million	0(3): 5(5)
	Fuel Hydrocarbons		
	Benzene	0.1 to 46,000	5(4)
	Toluene	0.19 to 26,000	2,000(3): 2,000(5)
	Xylenes	1 to 14,000	10,000(3): 10,000(5)
	Ethylbenzene	1.5 to 540	700(3): 700(5)
	Ketones		
	Acetone	3 to 24,500	--
	Methyl ethyl ketone	4 to 1,500	--
	Phthalates		
	Bis-2-ethylhexylphthalate	2 to 1,050	0(3): 5(4)

(1) Micrograms per liter (µg/L) and micrograms per kilogram (µg/kg) unless otherwise indicated.
(2) Concentration data synthesized from references listed in appendix A.
(3) Proposed U.S. EPA Maximum Contaminant Level Goals (MCLG, µg/L) in drinking water.
(4) Existing U.S. EPA Maximum Contaminant Level (MCL, µg/L) in drinking water.
(5) Proposed U.S. EPA MCL (µg/L) in drinking water.
(6) Nonenforceable U.S. EPA secondary level standard (µg/L) based on taste, odor, or appearance guidelines.
(7) Picocuries per liter (pCi/L)
(8) National Interum Drinking Water Regulations, Table IV-2A (EPA 1976). Derived Guidelines (pCi/L) based on 4 millirem annual dose to target organ.
(9) DOE-derived concentration guides (pCi/L) based on effective dose limit not to exceed 100 millirem/year. Derived from DOE Order 5480.1A. (Jaquish and Bry
(10) Micrograms per liter (µg/L).

Source: "Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Subsurface Science Research". Office of Energy Research, U.S. Department of Energy, DOE-0547T, April 1992., pg. 28.

According to subsequent analyses,[2] the most problematic contaminants of concern with respect to groundwater contaminants include "...Sr-90, Cr, chelated Co-60, U, Tc-99, and chlorinated hydrocarbons." Plumes that contain cadmium, chromium, lead, or nickel are reported at the following DOE locations: Pantex SWMU #133; Pinella shallow water aquifer; INEL TRA 05 injection well; and Richland 1100 Area isolated Units #1[3]. At the Portsmouth Gaseous Diffusion Plant, the groundwater plume under the X-701B sites is over 0.5 miles long and contains high levels of TCE and Tc-99.[4] At Sandia's CWl, "..chromium contamination has been detected to a depth of 75 feet."[5].

Contaminant plumes in the Hanford 100 Areas contain tritium, nitrates, chromium, strontium-90, Tc 99, U, Hg, PCB, and TCE.[6] The water table is 30 to 70 feet below the surface, and this water discharges contaminants into the adjacent Columbia River.

Clean-up of groundwater contaminated with organics, radionuclides, and/or metals requires comprehensive treatment approaches. Typically, these approaches employ sequential treatment, i.e, activated carbon adsorption followed by ion-exchange. For comparison purposes, current and evolving water cleanup technologies are discussed in the following section of this report.

1.2.1 Competing Cleanup Technologies

Activated Carbon. Activated carbon removes organics by physically adsorbing the organic compounds onto the highly porous carbon surface. Powdered and granular activated carbon is used in these applications. The organic removal capacity of the carbon depends on its available surface area. Contaminated water may be introduced at the top (fixed bed) or at the bottom (expanded bed) of the holding vessel. It requires regeneration to minimize the cost of carbon replacement. The cost of activated carbon is $ 1.0-1.5 per pound. Activated carbon adsorption cannot remove metal ions and is seldom used as a stand alone technology in treating groundwater. For example, in a recent field test of activated carbon at Rocky Flats[4], DOE concluded that the use of this material for capturing radionuclides and chlorinated solvents may be difficult and pointless.

Ion-Exchange Resins. Resin systems depend on chemical reactions in which ions contained in the water are exchanged with ions in the resin. Resins are insoluble granular materials that have acid (H+) or basic (OH-) radicals exposed on parts of their surface. In wastewater, metal ions, which are typically positive, are exchanged for the H+ ion on the resin. This mechanism allows the metal ions to be removed from the water. The metal ions, bound to the resin as a salt, are then separated in the resin regeneration process. Likewise, the OH- ion in the resin may be exchanged for organic bases, such as phenols. This mechanism allows the ion exchange resin to remove certain negatively charged organic ions from wastewaters.

There are four major types of ion exchange resins[8]: strong acid, weak acid, strong base, and weak base. Strong acid resins are effective in removing heavy metals, and are typically employed in treating waste water. Weak acid resins are mainly used in special chemical processes to isolate alkaloids and antibiotics. Strong base resins will remove all mineral acids. Weak base resins will selectively remove strong mineral acids (hydrochloric, sulfuric, and nitric) and allow weak mineral acids (carbonic and silica) to pass through. No single ion-exchange resin is suited to all metal and radionuclide removal tasks. The ion-exchange resin must therefore be selected based on the specific ions contained in the wastewater. The cost of most resins is $ 3.0 per pound and can go as high as $ 150 per pound for some highly selective resins.

1.2.2 Comparison of Waste water Cleanup Technologies

A comparison of the HUMASORB-CS™ technology with seven other remediation technologies is displayed in Figure 1.1. As shown in this figure, only HUMASORB-CS™ has the potential to treat mixed waste contaminants of the type found at DOE sites in a single-step process. The other state-of-the-art technologies displayed in this table can remediate only one class of contaminant in one pass, i.e., either organics (activated carbon), or heavy metals (ion exchange). This requires the use of two different stepwise processes to remediate highly contaminated waters.

Groundwater contaminants at most DOE sites exist as complex mixtures that may contain metals, chlorinated hydrocarbons, radionuclides, oxo-anions, fuel hydrocarbons, and/or ketones. HUMASORB-CS™, tested in this contract, is the only material that is applicable to all the three classes: metals, radionuclides, and organics, of concern to DOE. The HUMASORB-CS™ technology is based on humic acid, the dark "humus" found in soil. It is the end product derived from plant breakdown by microbial action. Humus enriches the soil, allowing fertilizer chemicals and micronutrients to reach their maximum potential in promoting plant growth. A review of the characteristics and properties of humic acid is presented in the following section.

Figure 1.1. HUMASORB™ is a Low-Cost Water Remediation Technology that is Applicable to Metals, Radionuclides, and Organics

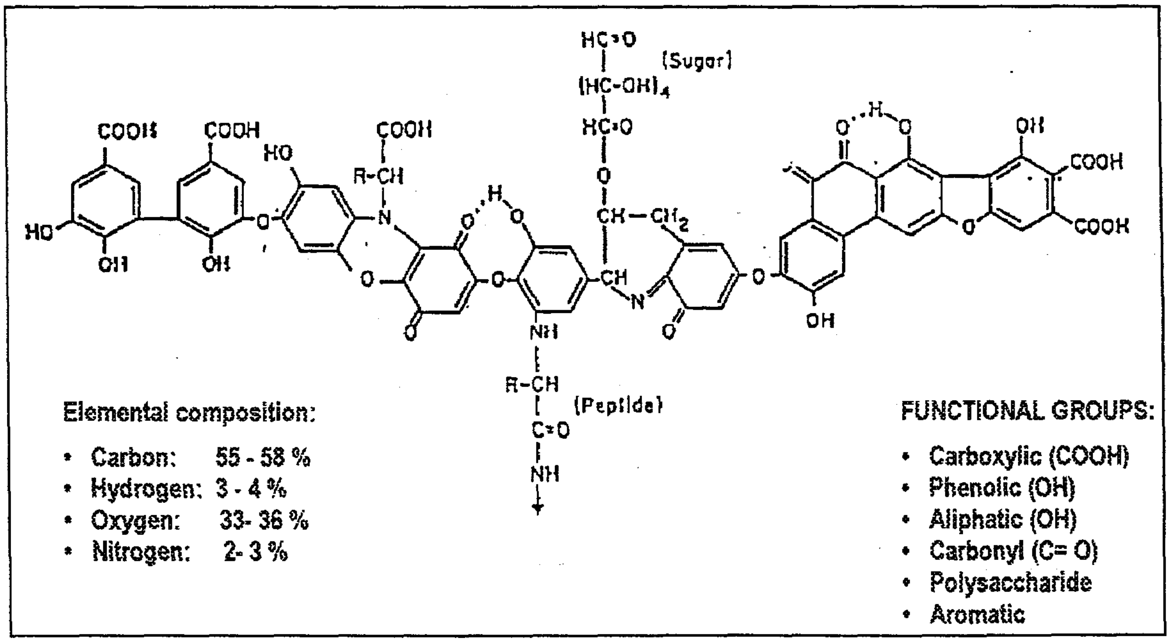
WATER REMEDIATION TECHNOLOGY	REMOVES METALS	REMOVES RADIONUCLIDES	REMOVES OXO-ANIONS	REMOVES ORGANICS	RELATIVE COSTS
HUMASORB-L™	YES	YES	YES	YES	LOW
HUMASORB-CS™	YES	YES	YES	LOW	LOW
CATION-EXCHANGE	YES	YES	NO	NO	MED-HIGH
CHEMICAL PRECIPITATION	YES	YES	NO	NO	MED
POLYMER FILTRATION	YES	YES	NO	NO	MED
MODIFIED ZEOLITE	YES	NO	NO	YES	HIGH
ANION-EXCHANGE RESIN	NO	NO	YES	NO	MED-HIGH
AMBERSORB™	NO	NO	NO	YES	HIGH
ACTIVATED CARBON	NO	NO	NO	YES	LOW

2.0 HUMIC ACID--AN OVERVIEW OF PROPERTIES

HUMASORB™ is an adsorbent having the unique properties of humic acid, a naturally occurring organic material. A major source of humic acid is coal, the most abundant and predominant product of plant residue coalification. All ranks of coal contain humic acid but lignite represents the most easily available and concentrated form of humic acid. Humic acid concentration in lignites varies from 30-90% depending on location.

Humic acid is dark brown to black in color and is considered a complex aromatic macromolecule with various linkages between the aromatic moities. The different moieties involved in linkages include amino acids, amino sugars, peptides, aliphatic acids and other aliphatic compounds. The various functional groups in humic acid include: carboxylic, phenolic, aliphatic, enolic and carbonyl structures of various types. Humic acid is therefore an association of molecules forming aggregates of elongated bundles of fibers at low pHs and open flexible structures perforated by voids at high pHs[9]. The voids can trap and adsorb both organic and inorganic particles if the charges are complementary. The structure of humic acid proposed by Stevenson[9] is shown in Figure 2.1.

Figure 2.1. Proposed Hypothetical Structure of Humic Acid



Elemental composition:

- Carbon: 55 - 58 %
- Hydrogen: 3 - 4 %
- Oxygen: 33- 36 %
- Nitrogen: 2- 3 %

FUNCTIONAL GROUPS:

- Carboxylic (COOH)
- Phenolic (OH)
- Aliphatic (OH)
- Carbonyl (C= O)
- Polysaccharide
- Aromatic

2.1 Ability to Chelate Metals

Metals are bound to the carbon skeleton of humic substances through heteroatoms such as nitrogen, oxygen or sulfur. The most common metal binding occurs via carboxylic and phenolic oxygen, but nitrogen and sulfur also have a positive effect on metal binding. The cation exchange capacity (CEC) of humic acid derived from leonardite is 200-500 meq/100 grams, whereas the CEC of leonardite is only 50 meq/100 grams.

Musani et al.[10] studied the chelation of radionuclides such as ^{65}Zn, ^{109}Cd, and ^{210}Pb by humic acid isolated from marine sediments. The chelation of metals by humic acid was observed to be significant. The binding mechanism was found to be different depending on the physical state of the humic acid. Binding was stronger with precipitated humic acid than with dissolved humic acid. The chelation effect was stronger for the metals in the absence of calcium and magnesium. The order of binding was determined to be Pb>Zn>Cd.

Pahlman and Khalafalia[11] used humic acid to remove heavy metals from process waste streams. The efficiency of heavy metal removal by humic acids derived from lignite, a sub-bituminous coal, and peat was evaluated. The effect of pH on metal removal was determined. Humic acid was found to be very effective in removing toxic metal ions. The pH range of 6.5 to 9.5 was determined to be the optimal range for complete removal of heavy metal ions by humic acids derived from lignite and subbituminous coal. The efficiency of heavy metal removal by humic acid was higher compared to the conventional lime treatment even at lower concentrations of metals. Humic acids also are very effective in the removal of the most toxic metals such as cadmium, mercury and lead. The removal of these toxic metals by lime is incomplete, particularly at near neutral pH.

2.2 Ability to Reduce Toxic Oxo-anions

The reduction of different metal species, such as mercury, vanadium, iron and plutonium by humic acid has been reported by a number of investigators[12-16]. Humic acid can act as a reducing agent and influence the oxidation-reduction of metal species. An unchelatable toxic oxo-anion such as chromium (VI), present as dichromate ($Cr_2O_7^{-2}$), is reduced to relatively non-toxic chromium (III). The reduced chromium is then stabilized through chelation by humic acid.

2.3 Ability to Adsorb Organics

The adsorption of organic chemicals onto humic substances, such as humic acid, has been studied extensively. The reported investigations on adsorption of organic compounds by humic acid include studies on:

- non-ionic organics such as benzene, halogen substituted benzene, and chlorinated hydrocarbons such as 1,1,1-trichloroethane (TCA),
- nitrogen compounds such as urea and anilines,
- polychlorinated biphenyls (PCBs),
- fumigants, such as telone, and insecticides such as DDT,
- herbicides, such as paraquat, diquat, triazines, and
- organophosphorous compounds such as parathion.

It is believed that humic acid combines with herbicides by electrostatic bonding, hydrogen bonding and ligand exchange. In addition, the high concentrations of stable free-radicals in humic acid are capable of binding herbicides that can ionize or protonate to the cation form. The mechanisms that have been postulated for the adsorption of organic compounds include [17]:

- Van der Waals attractions
- hydrophobic bonding
- hydrogen bonding
- charge transfer
- ion-exchange
- ligand exchange.

The adsorption of benzene, halogen substituted benzenes, and chlorinated hydrocarbons such as TCA, and similar non-ionic organic compounds on soil containing different amounts of soil organic matter has been reported by Chiou [18]. The adsorption on soil organic matter of various non-ionic organic compounds from water was attributed primarily to solute partitioning into the organic adsorbent. The partitioning theory was supported by experimental observations of linear adsorption isotherms up to concentrations approaching saturation. In addition, the absence of competitive effects between solutes supports the partition approach. The presumed partition was also analyzed in relation to the equilibrium properties of organic compounds in solvent-water mixtures [18].

Humic acid has been shown to adsorb considerable amounts of nitrogen compounds such as urea and anilines. The stable free radicals in humic acid are believed to play a significant role in urea-humic acid interaction[19]. In addition, it has been postulated that urea forms an addition complex with humic acid through the carboxyl and phenolic hydroxyl group[20]. It has been further determined that the complex formed is very stable and that the decomposition of urea is inhibited in the presence of humic acid. The adsorption of aniline on soil organic matter is directly related to the concentration of the humic acid. The adsorption of aniline on humic acid has been shown to follow both the Freundlich and Langmuir remodels[20].

Haque and Schmedding reported the adsorption of PCBs from aqueous streams by humic acid[21]. The adsorption on humic acid increased with the increase in the number of chlorine atoms in the PCB. Adsorption isotherms of PCBs on humic acid followed the Freundlich equation and the constant K (measure of adsorptive capacity) increased from di- to hexa-chloro PCB. The high K value on humic acid was attributed to a combination of high surface area and the number of functional groups present in humic acid.

The brief discussion in this section and the review of the literature clearly indicates the unique properties of humic acid to chelate metals and adsorb organics. The humic acid complex, however, will dissolve in water above pH 2 and in the presence of ions such as sodium and potassium. One aim of this project is to develop a humic acid polymer that will be insoluble in water under the conditions encountered during remediation of contaminated streams. Contaminant removal using HUMASORB™ adsorbents has established its versatility and applicability for complex contaminated systems as discussed in this report.

The following sections of the report provide an overview of the total project, rationale and approach behind conducting the project in two phases and the methodology as well as the results obtained. Section three provides an overview and section four describes the methodology and results of phase I. The methodology and results of phase II are discussed in section five. The performance improvement and the evaluation of HUMASORB-CS™ under simulated barrier conditions are described in sections six and seven respectively. The economic analysis is discussed in section eight and a feasibility analysis for potential application of HUMASORB™ in the DOE complex is presented in section nine. The conclusions and recommendations as a result of the project activities are presented in section ten. The summary of other related projects on the application and demonstration of HUMASORB™ technology, that were conducted outside the scope of this contract, are presented in the appendix.

3.0 PROJECT OVERVIEW

The approach used in this project is to evaluate adsorbents that are based on the unique properties of humic acid. The humic acid based adsorbents evaluated in this project include:

- liquid humic acid termed HUMASORB-L™
- purified humic acid termed HUMASORB-S™
- solid adsorbent termed HUMASORB-CS™ with lower water solubility

The starting material for the development of HUMASORB-CS™, is a liquid humic acid product manufactured by ARCTECH, Inc. The intent of this project is to develop HUMASORB-CS™ for the removal of heavy metal and organic contaminants from groundwater and surface waters found at typical DOE and industrial sites in one processing step. The development of HUMASORB-CS™ was completed in two phases. The tasks in Phase I included isolation, purification, and evaluation of humic acid. The characterization of HUMASORB-L™ and HUMASORB-S™ for contaminant removal would provide baseline data to compare with HUMASORB-CS™. The overall goal of the project was to evaluate HUMASORB-CS™ for the contaminant removal characteristics that are inherent in HUMASORB-L™ and HUMASORB-S™. In addition, the tasks in Phase I included preparation and preliminary characterization of HUMASORB-CS™. Under the Phase II activities, HUMASORB-CS™ was successfully cross-linked and immobilized, characterized for removal of contaminants, it's application tested at different DOE sites and an economic analysis accomplished on the basis of the bench scale column tests.

The Tasks in Phase I included:

- isolation and purification of humic acid (termed HUMASORB-S™)
- characterization of contaminant removal by HUMASORB-L™ and HUMASORB-S™)
- cross-linking humic acid to form HUMASORB-CS™
- evaluation of HUMASORB-CS™ for contaminant removal

The tasks in Phase II included:

- preparation of HUMASORB-CS™ to improve handling properties and lower solubility
- evaluation of immobilized HUMASORB-CS™ in batch and column studies
- stability studies on HUMASORB-CS™
- HUMASORB-CS™ performance improvement and enhance cost-effectiveness
- Evaluation of HUMASORB-CS™ under simulated barrier conditions
- conceptual process design and economic analysis

4.0 PHASE I: METHODOLOGY AND RESULTS

In Phase I of this project, liquid humic acid product (HUMASORB-L™) was evaluated for contaminant removal from simulated waste streams at various pH ranges, and purified humic acid (HUMASORB-S™) capacity was evaluated for metal and organic removal and different adsorption models were used to fit the data.

4.1 Methodology: Isolation and Purification of Humic Acid

Humic acid was isolated and purified from HUMASORB-L™ by acidification using concentrated hydrochloric acid (HCl) to lower the pH (below 2). The precipitated solid was purified by repeated washing with distilled water and acidification. A pressure filter (60 psig) was used to separate the precipitated humic acid from the other humic substances dissolved in water. The amount of humic acid recovered ranged from 11.79 % to 14.79 % of HUMASORB-L™ by weight. Approximately 300 grams of humic acid was isolated and purified to conduct the various experimental tasks in the project. The purified humic acid is termed HUMASORB-S™.

4.2 Metal Sorption

4.2.1 HUMASORB-L™ Tests

HUMASORB-L™ is a liquid humic acid product as indicated in Section 3. Humic acid precipitates below pH 2 and dissolves as the pH is increased. Most of the metals are soluble in water at low pH and precipitate as the pH is increased. The objective in the tests was to evaluate if the humic acid present in HUMASORB-L™ would adsorb the metals at various pHs.

4.2.1.1 Methodology

The effect of pH on the sorption of metals by HUMASORB-L™ was evaluated in polypropylene centrifuge bottles, by contacting HUMASORB-L™ with spiked water solutions containing known concentrations of metals. The spiked solution was prepared by dissolving the metal salts in water. The pH of the mixture was adjusted with sodium hydroxide (NaOH, 1 N) or concentrated hydrochloric acid (HCl, 1 N). The centrifuge bottles were shaken at 300 rpm and 25°C for one hour. Initial experiments conducted with a contact time of one hour and 24 hours did not show any significant difference in metal removal. The contact time used for most of the HUMASORB-L™ tests was one hour. The bottles were then centrifuged at 2000 rpm for 30 minutes to separate the solid and liquid phases. In a second set of tests, after the contact time, alum (10% solution) was added to the centrifuge bottles to coagulate humic acid, before centrifugation. The supernatants were then analyzed for the target metal. Controls containing only the spiked water and alum solution were also analyzed.

4.2.1.2 Results & Discussion

The effect of pH on uranium removal using HUMASORB-L™ is shown in Figure 4.1. Clearly, the results indicate that humic acid is very effective in removing uranium from water under acidic conditions. Uranium is soluble in water under acidic conditions and increasing the pH to 4 using NaOH resulted in only 6 % removal of uranium. Uranium was completely removed from the solution at pHs greater than 6. The addition of NaOH increases the pH and removes uranium by precipitation. In the presence of HUMASORB-L™ at pH 4, uranium was removed from solution and was bound to precipitated humic acid. As the pH was increased in the presence of HUMASORB-L™, the removal of uranium from the water decreased. The observed decrease in uranium removal at higher pH in the presence of HUMASORB-L™ can be expected if uranium is bound to humic acid. The comparison of uranium recovery both in the absence and presence of HUMASORB-L™ indicates that uranium is bound to humic acid over the pH range 2-12 and remains in solution under basic conditions (where it is insoluble as shown by the data with NaOH) in the presence of humic acid. The addition of a coagulant such as alum did not have a significant effect at higher pH. However, at near neutral pH (6-8), the addition of alum increased the amount of uranium recovery from water compared to uranium removal with HUMASORB-L™. The effect of pH on the removal of different metals using HUMASORB-L™ is shown in Figure 4.2

4.2.2 HUMASORB-S™ Tests

HUMASORB-S™ is purified humic acid derived from HUMASORB-L™ by precipitation using hydrochloric acid. The objective in these tests was to evaluate the capacity of

HUMASORB-S™ to remove metals from simulated waste streams and to determine if the metal removal could be represented by different adsorption models.

Figure 4.1. HUMASORB-L™ Binds Uranium over a Wide pH Range

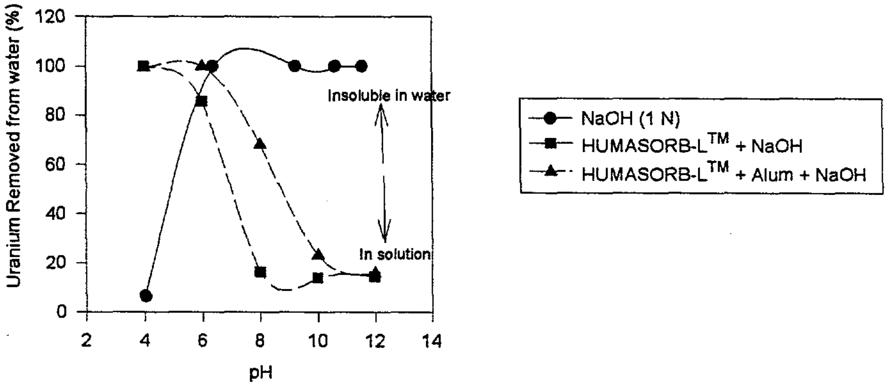
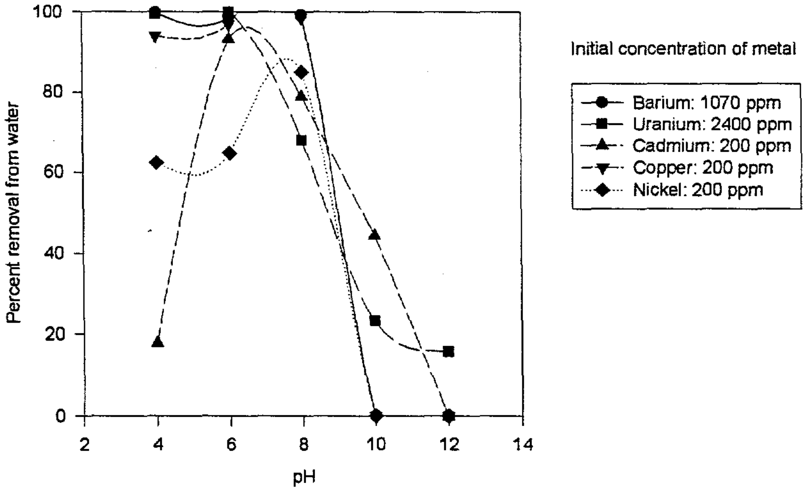


Figure 4.2. HUMASORB-L™ Binds Various Metals Over a Wide pH Range



4.2.2.1 Methodology

Metal Removal: The adsorption capacity of HUMASORB-S™ was evaluated by developing metal sorption isotherms. Spiked water solution, prepared by dissolving metal salts in water, was contacted with different amounts of HUMASORB-S™ in centrifuge bottles. The pH was not adjusted in these tests to avoid any competition for binding sites by metals such as sodium (in sodium hydroxide) or calcium (in calcium hydroxide) used to adjust the pH. The centrifuge bottles were shaken at 300 rpm and 25°C for two hours to allow sufficient contact time between the solid and liquid phases. After the two hour contact time, the bottles were centrifuged at 2000 rpm for 30 minutes to separate the solid and liquid phases.

Reduction of Oxo-anions: The ability of HUMASORB-S™ to reduce toxic metals such as chromium (VI), present as oxo-anions (for example $Cr_2O_7^{-2}$), to less toxic Cr (III), was evaluated. In this test, a simulated waste stream containing chromium (VI) was contacted with HUMASORB-S ™in centrifuge bottles. The pH in these tests was between 2.5 to 3.0. The centrifuge bottles were shaken at 300 rpm and 25 °C for different contact times ranging from one to 16 hours. After the reaction time, the bottles were centrifuged at 2000 rpm for 30 minutes. The liquid phase was then analyzed for both Cr (VI) and Cr (III) by HACH™ method using UV spectroscopy.

4.2.2.2 Results & Discussion

The effect of HUMASORB-S™ loading on the removal of metals from simulated waste streams was evaluated for a number of metals. HUMASORB-S™ has a high affinity for lead and cerium, as shown in Figure 4.3.

The isotherms generated from the adsorbent loading tests was represented well by Freundlich and/or Langmuir models. The mechanism for contaminant removal is believed to be a combination of ion-exchange and chelation/complexation.

According to Freundlich equation,

$$x/m = KC^{1/n}$$

where:

x/m = amount of metal adsorbed per unit weight of humic acid
C = concentration of the target metal in solution after reaction
K = constant, related to adsorbability of the contaminant (represents capacity at concentration of 1 ppm)
$1/n$ = constant, indicating sensitivity to concentration

A plot of the equilibrium concentration (C) versus the amount of metal adsorbed (x/m) on log-log coordinates will be a straight line if the Freundlich model represents the isotherm. The slope of the line is equal to 1/n and the intercept is equal to K.

According to Langmuir adsorption model,

$$\frac{x}{m} = \frac{K_{lan} \times (bC)}{1 + bc}$$

where:

K_{lan} = amount of solute adsorbed per unit weight of adsorbent to form a monolayer coverage (representing saturation capacity)

b = constant

The Langmuir equation can be linearized as,

$$\frac{m}{x} = \frac{1}{K_{lan}} + \frac{1}{K_{lan} \times b}(\frac{1}{C})$$

A plot of the reciprocal equilibrium concentration (1/C) versus the reciprocal of amount of metal adsorbed per unit weight of adsorbent (m/x) will be a straight line if the adsorption can be described by the Langmuir isotherm. The intercept of such a plot can be used to estimate the constant K_{lan} and the slope used to estimate the constant b.

The sorption of copper and nickel by HUMASORB-S™ was represented well by both the Freundlich and Langmuir models (Figures 4.4 and 4.5). The Langmuir model for nickel gave negative values for the constants while the sorption of cadmium and lead did not follow either the Freundlich or the Langmuir model, indicating a complex mechanism for sorption. The sorption of the radionuclide surrogate cerium was represented well by the Langmuir isotherm (Figure 4.6). In addition, the sorption of uranium by HUMASORB-L™ was represented by both Freundlich and Langmuir models (Figure 4.7). The capacity parameters estimated from the adsorption models are tabulated in Table 4.1.

Figure 4.3. HUMASORB-S™ is Effective for Metal Removal

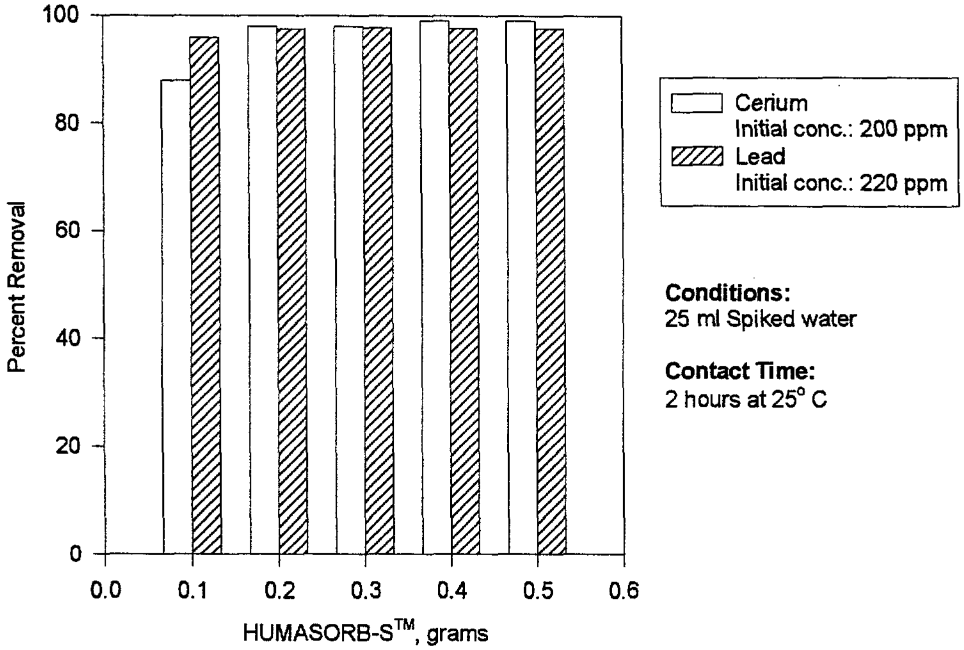
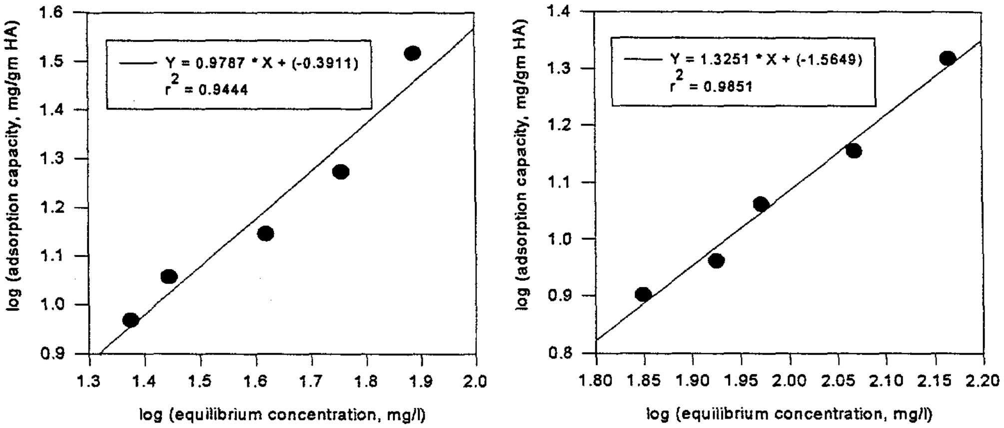


Table 4.1. Freundlich and Langmuir Model Parameters

Contaminant	Freundlich	Langmuir
Copper	K = 0.4064 mg/gm n = 1.0218	K = 142.91 mg/gm b = 0.0029 l/mg
Nickel	K = 0.0300 mg/gm n = 0.7500	Negative values
Cerium	-	K = 89.29 mg/gm
Uranium	K = 100.91 mg/gm	K = 526 mg/gm
PCE	K = 0.07691 mg/gm n = 0.6697	Negative values

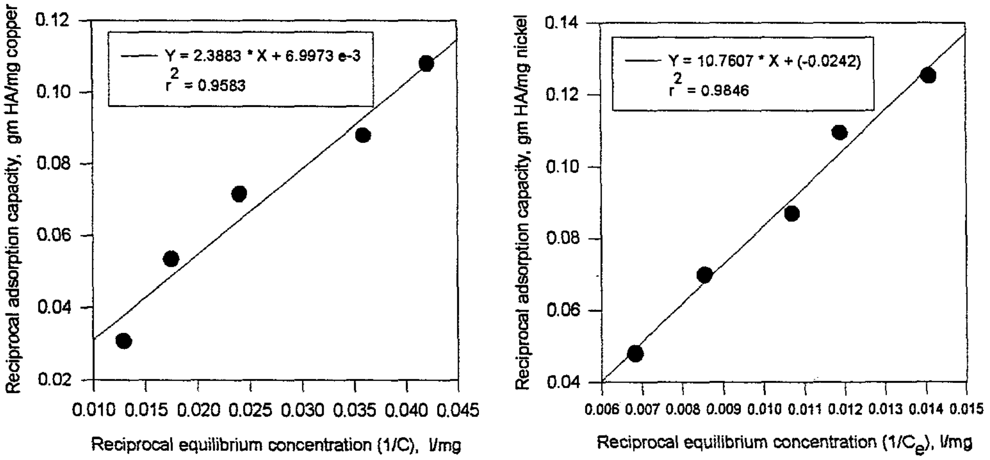
Figure 4.4. Copper and Nickel Sorption on HUMASORB-S™ Followed Freundlich Model



(A) Copper

(B) Nickel

Figure 4.5. Copper and Nickel Sorption on HUMASORB-S™ Followed Langmuir Model



(A) Copper

(B) Nickel

Figure 4.6. Cerium Sorption on HUMASORB-S™ Followed Langmuir Model

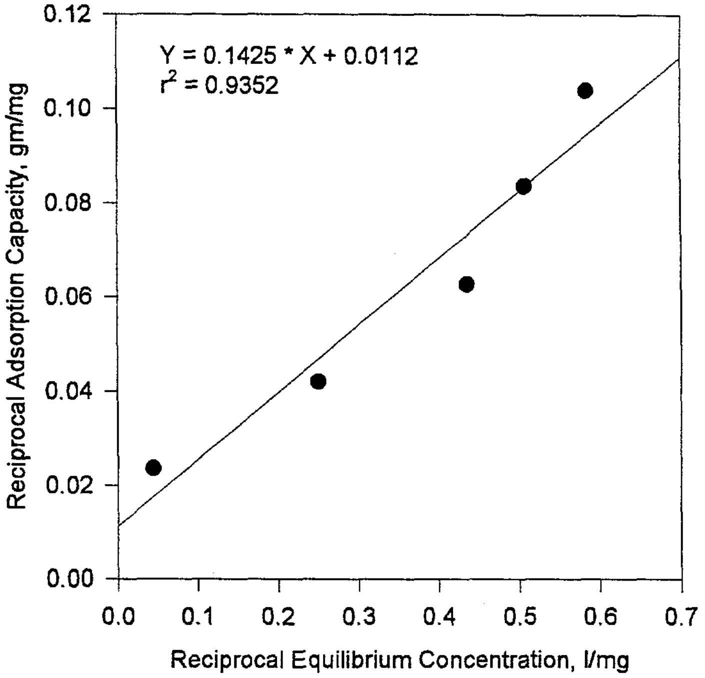
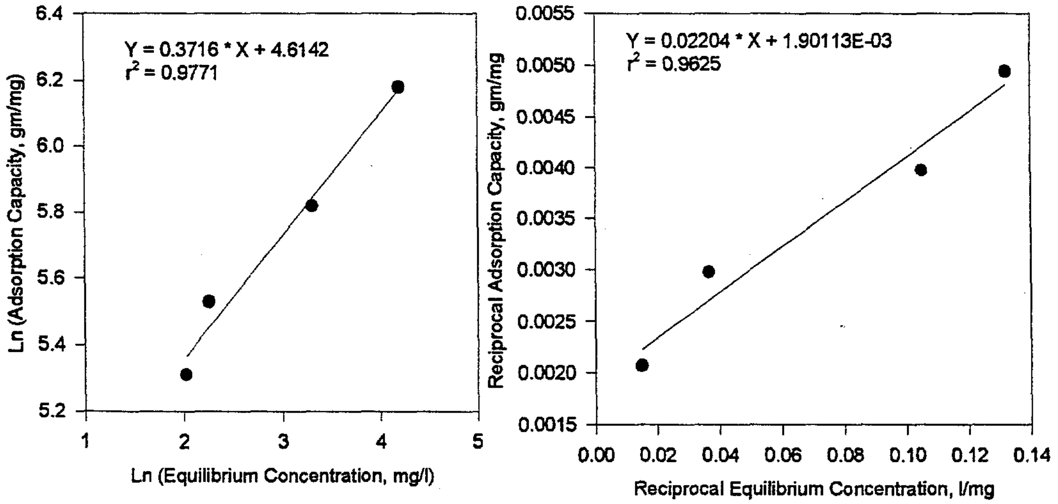


Figure 4.7. Uranium Sorption on HUMASORB-L™ Followed Freundlich and Langmuir Models



Batch tests were conducted with HUMASORB-S™ to evaluate its effectiveness for the removal of various metals from simulated waste streams. The tests were conducted using

100 ppm of metal (As, Cd, Ce, Cs, Cr, Cu, Pb, Hg, Ni, Sr, U, Zn) in the waste stream. Experiments were conducted with only one metal in solution. In addition, a simulated waste stream containing all 12 metals at 100 ppm each was also contacted with HUMASORB-S™. The simulated waste solution (25 mL) and HUMASORB-S™ (approximately one gram) were shaken at 300 rpm and 25°C for two hours. After the two hour contact time, the mixture was centrifuged to separate the solid and liquid phases. The liquid phase was analyzed for the metals using ICP or AA spectroscopy. The pH was between 2-2.5 in all these batch tests.

The results from the batch tests are presented in terms of percent removal of metals. The removal of individual metals (shown in Figure 4.8) indicates high removal of a number of metals. The removal was greater than 60% for at least six of the metals under the very low pH (2-2.5) conditions used in the study. Metal removal from the simulated waste stream containing multiple metals (shown in Figure 4.9) was similar to that observed in tests using individual metals. Cesium removal was higher in the test with multiple metals compared to the removal when only cesium was present.

The effect of HUMASORB-S™ loading and contact time was evaluated using a simulated waste stream containing copper, chromium and lead. The contact times used were two hours and 24 hours. The results indicate a relatively higher affinity for lead and copper removal compared to that for chromium (Figure 4.10). Increasing the contact time did not have any significant effect on the removal of lead and copper. However, the removal of chromium increased with longer contact time and chromium removal was relatively lower compared to lead and copper for a given adsorbent loading. This indicates that the removal of chromium could be the rate limiting step under the conditions of this study.

The metal sorption data was also analyzed using the method developed by Scatchard (22). The presence of more than one inflection point on a plot based on Scatchard analysis usually indicates the presence of more than one type of binding site. The Scatchard plot for the sorption of different metals by HUMASORB-S™ is shown in Figure 4.11.

Figure 4.8. Removal of Individual Metals from Simulated Waste Stream Using HUMASORB-S™

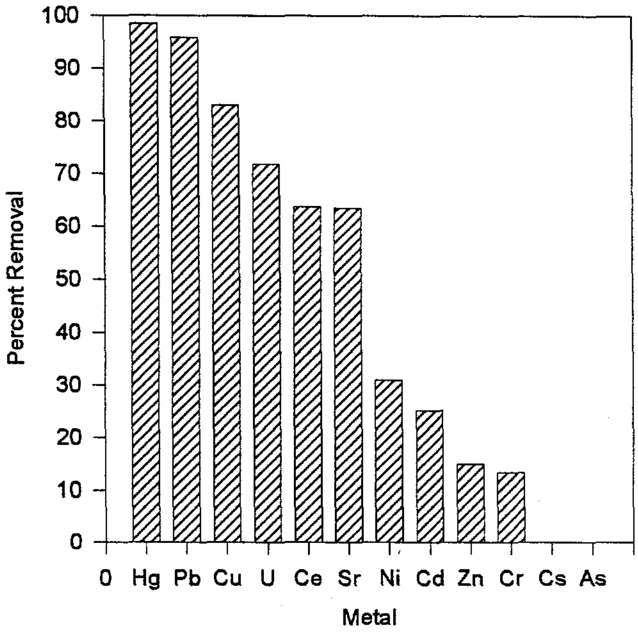
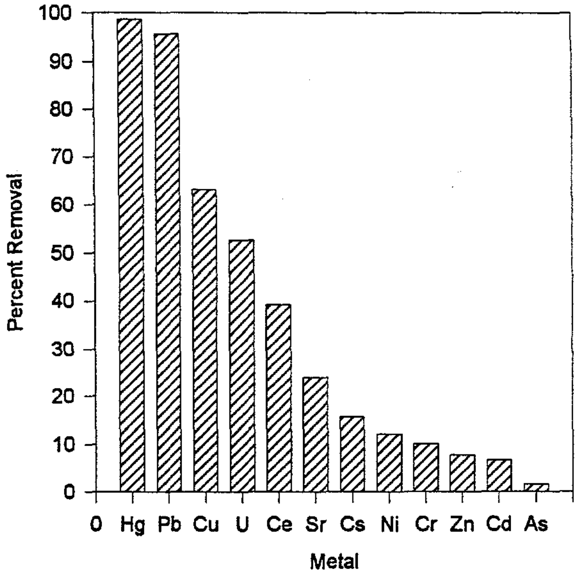


Figure 4.9. Removal of Multiple Metals from Simulated Waste Stream Using HUMASORB-S™



The plot clearly indicates the presence of more than one type of binding site for copper and nickel sorption. The plot was, however, linear for cadmium indicating that only one type of binding site was active for cadmium sorption.

Reduction of oxo-anions: The ability of HUMASORB-S™ to remove chromium (VI) from a simulated stream containing 60 ppm Cr (VI) was investigated. The concentrations of both Cr (III) and Cr (VI) in the system were followed during the 16-hour batch tests. The results, shown in Figure 4.12, indicate that the concentration of Cr (VI) decreases during the reaction and Cr (III) remains constant at 2-3 ppm. This indicates that Cr (VI) is reduced to Cr (III) which is then immediately removed from the liquid phase by HUMASORB-S™. The mechanism of Cr (III) removal is most likely a combination of ion-exchange and complexation.

Figure 4.10. Metal Removal from Simulated Waste Streams Containing Multiple Contaminants Using HUMASORB-S™

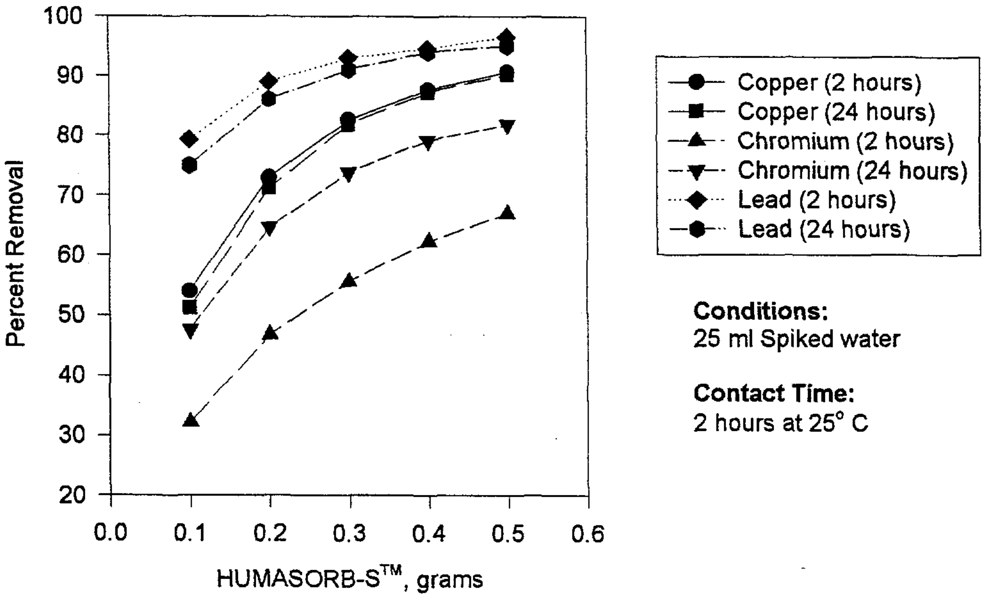
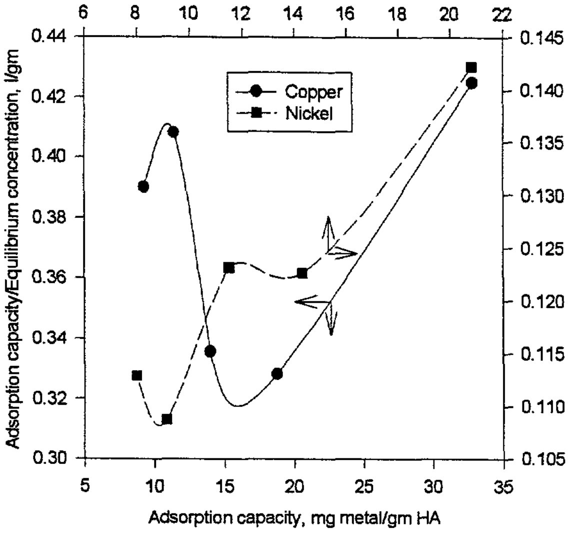
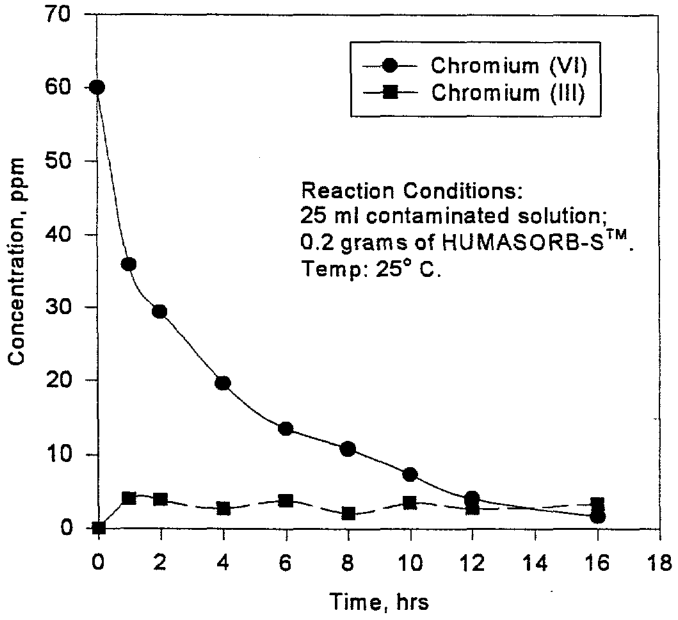


Figure 4.11. HUMASORB-S™ has more than One Binding Site Based on Scatchard Analysis



Non-linearity indicates the presence of more than one type of binding site

Figure 4.12. HUMASORB-S™ Reduced Chromium (VI) to Chromium (III) and Removed Chromium (III) from a simulated waste sream



4.3 Organic Adsorption

4.3.1 Methodology

Isotherms for adsorption of chlorinated and petroleum hydrocarbons were developed using HUMASORB-S™. The chlorinated hydrocarbons used were trichloroethylene (TCE) and tetrachloroethylene (PCE); benzene was the representative petroleum hydrocarbon used in this study.

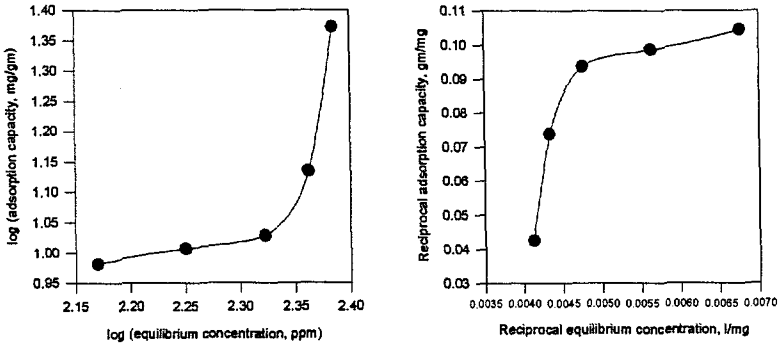
Isotherms were developed by contacting spiked water samples with different amounts of HUMASORB-S™ in a 20-ml serum vial. HUMASORB-S™ was ground to less than 350 mesh to increase the surface area for use in the experiments. The spiked water solution and HUMASORB-S™ were contacted in the crimp-sealed vials at 300 rpm and 25°C for the desired time (24 hrs for most of the tests with organic contaminants). The vials were centrifuged at 2000 rpm for 30 minutes after the contact time to separate the liquid and solid phases. The liquid phase was analyzed by using purge and trap GC-MS.

4.3.2 Results and Discussion

Freundlich and Langmuir adsorption plots were used to represent the data obtained for organic adsorption. The data for TCE adsorption was not represented by either model (Figure 4.13). The isotherms show two distinctive phases with adsorption capacity increasing only slightly with concentrations up to 210 ppm and increasing rapidly above 210 ppm. The shape of the isotherm indicates the possibility of multi-layer adsorption, with adsorption capacity increasing rapidly at higher concentration.

The adsorption of PCE on HUMASORB-S™ was represented well by both Freundlich and Langmuir models as shown in Figure 4.14. However, the Langmuir model gave slightly negative values for the constants. The Freundlich and Langmuir model parameters determined from various contaminant isotherms are shown in Table 4.1.

Figure 4.13. TCE Adsorption on HUMASORB-S™

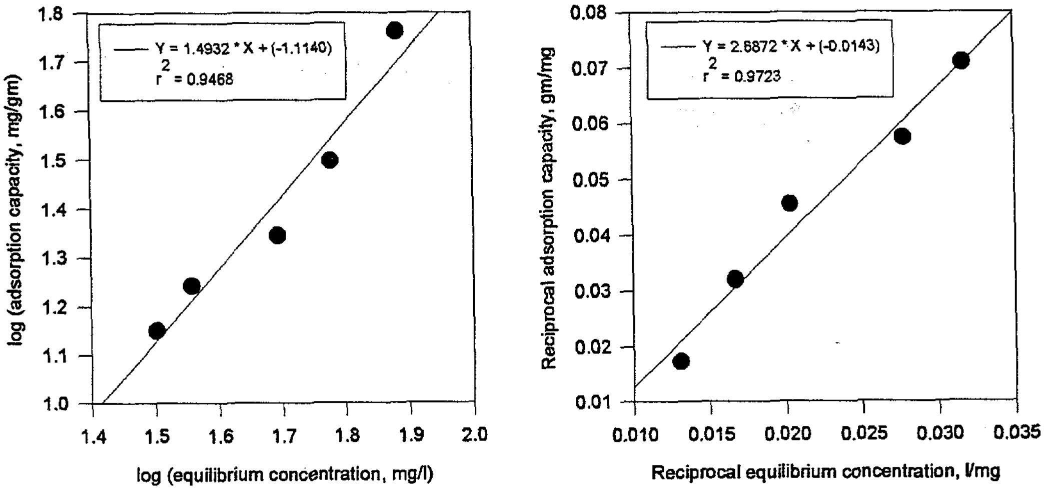


(A) Freundlich

(B) Langmuir

Benzene adsorption on HUMASORB-S™ was represented very well by both the models at the relatively higher equilibrium concentrations obtained in this study. The removal of PCE from spiked water was higher compared to the removal of both TCE and benzene under the conditions used for the development of the adsorption isotherms. However, the removal of both TCE and benzene increased significantly with the increase in the amount of HUMASORB-S™.

Figure 4.14. PCE Adsorption on HUMASORB-S™



(A) Freundlich

(B) Langmuir

4.4 Summary

The results presented in this section clearly demonstrate the ability of HUMASORB-L™ and HUMASORB-S™ to remove various contaminants from waste streams. Based on the results obtained in this study and the analysis of isotherms, HUMASORB™ has been shown to be effective for removal of multiple contaminants in a single step. The mechanism for metal removal is believed to be complex, and involves a combination of ion-exchange and chelation/complexation. HUMASORB™ removes organics from waste streams, primarily by physical adsorption. The isotherms for adsorption of some of the contaminants (such as copper, nickel, cerium and uranium) were represented well by either Freundlich or Langmuir isotherm models.

5.0 PHASE II: METHODOLOGY AND RESULTS

In Phase II, HUMASORB-CS™ was prepared using proprietary methods designed to improve the solubility and handling properties. HUMASORB-CS™ was evaluated in batch and column tests for removal of different types of contaminants. The contaminants evaluated include metals, radionuclide surrogates and organic compounds. The column performance was used to estimate parameters such as contaminant removal capacity at breakthrough and at saturation. In addition, the ability to regenerate and re-use HUMASORB-CS™ was evaluated.

5.1 Preparation of HUMASORB-CS™

HUMASORB-S™ is insoluble in water at lower pH, but will dissolve at higher pH in the presence of monovalent metal ions such as sodium and potassium. A cross-linked humic acid polymer, HUMASORB-CS™ was produced to overcome this limitation and lower the solubility at higher pH values. HUMASORB-CS™ was produced by cross-linking and immobilization of HUMASORB-S™ or HUMASORB-L™ using proprietary methods.

5.1.1 Solubility of HUMASORB-CS™

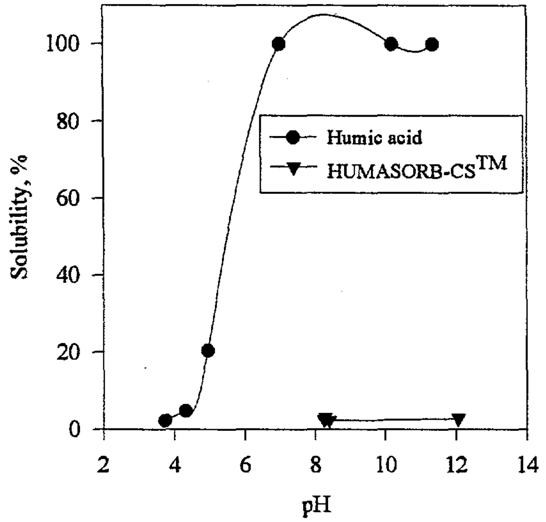
The solubility of the cross-linked product was determined at various pHs and compared with humic acid. In these tests, HUMASORB-CS™ (0.5 grams) was mixed with water and the pH was adjusted to the various pHs by using either sodium hydroxide or hydrochloric acid. The mixture was then placed on a shaker at 300 rpm and 25°C for two hours. After the contact time, the mixture was centrifuged to separate the liquid and solid phases. The liquid phase pH was measured and analyzed for humic acid to determine solubility. The results shown in Figure 5.1 indicate that the solubility of HUMASORB-CS™, as determined under the conditions of this study, is significantly lower compared to that of humic acid. The pH used in Figure 5.1 is that of the liquid phase measured after the contact time. It was observed that in HUMASORB-CS™ tests, the pH increased to 8 at the end of the experiment for tests where the pH was initially adjusted to 4 and 6.

The different functional groups present in HUMASORB™ before and after cross-linking were estimated using ^{13}C-NMR. The analysis indicates that all the functional groups believed to be responsible for contaminant removal are retained after cross-linking.

5.2 Batch Tests

HUMASORB-CS™ is prepared from HUMASORB-L™ or HUMASORB-S™ by proprietary methods. The objective in the batch tests was to evaluate the contaminant removal capacity of HUMASORB-CS™ and compare with the removal by HUMASORB-S™. The objective was to develop a product with improved solubility characteristics and similar contaminant properties.

Figure 5.1. HUMASORB-CS™ Solubility over a Wide pH Range



5.2.1 Methodology

The removal of contaminants by HUMASORB-CS™ was evaluated by contacting with simulated waste streams. Simulated waste streams, prepared by dissolving metal salts in water, were contacted with different amounts of HUMASORB-CS™ in centrifuge bottles. The pH was not adjusted in these tests to avoid any competition for binding sites by metals such as sodium (in sodium hydroxide) or calcium (in calcium hydroxide) used to adjust the pH. The centrifuge bottles were shaken at 300 rpm and 25°C for two hours to allow sufficient contact time between the solid and liquid phases. After the two hour contact time, the bottles were centrifuged at 2000 rpm for 30 minutes to separate the solid and liquid phases. The liquid phase was analyzed for the metals using ICP or AA spectroscopy.

Batch tests were also conducted with HUMASORB-CS™ at pH 2-2.5 to evaluate its effectiveness for the removal of various metals from simulated waste streams and to compare with HUMASORB-S™. The tests were conducted using 100 ppm of metal (As, Cd, Ce, Cs, Cr, Cu, Pb, Hg, Ni, Sr, U, Zn) in the waste stream. Experiments were conducted with only one metal in solution. In addition, a simulated waste stream containing all 12 metals at 100 ppm each was also contacted with HUMASORB-CS™. The simulated waste solution (25 mL) and HUMASORB-CS™ (one gram) were shaken at 300 rpm and 25°C for two hours. After the two hour contact time, the mixture was centrifuged to separate the solid and liquid phases. The liquid phase was analyzed for the metals using ICP or AA spectroscopy.

5.2.2 Results and Discussion

The ability to remove different contaminants was evaluated and compared with removal by HUMASORB-L/S™. The results from simulated streams containing single contaminants such as chromium (Figure 5.2) and strontium (Figure 5.3), and streams containing multiple contaminants such as copper, chromium and lead (Figure 5.4) indicate that the contaminant removal properties of humic acid are retained in HUMASORB-CS™ and in a few cases even enhanced. In addition, the results with a stream containing multiple contaminants indicate that chromium removal is the rate limiting step and removal requires a greater contact interval than the other metals evaluated. This is similar to the performance of HUMASORB-S™.

The results from the batch tests are presented in terms of percent removal of metals (Figures 5.5 and 5.6). A comparison of results from tests with waste streams containing only a single metal using the two forms of HUMASORB™ (Figures 4.8 and 5.5) clearly shows that metal removal is higher for most metals with HUMASORB-CS™. However, with a waste stream containing multiple metals (Figures 4.9 and 5.6), HUMASORB-S™ is more effective for a few of the metals (copper, lead and mercury). The overall total removal expressed as milliequivalents (meq) of metal removed was similar for both HUMASORB-S™ and HUMASORB-CS™ (approx. 0.25 meq) under the conditions (pH 2-2.5) of this study. It is clear from the batch tests that the proprietary methods used to produce HUMASORB-CS™ improve the solubility characteristics while retaining the ability of HUMASORB-L™ and HUMASORB-S™ to remove contaminants.

Figure 5.2. Chromium (III) Removal is Enhanced by HUMASORB-CS™

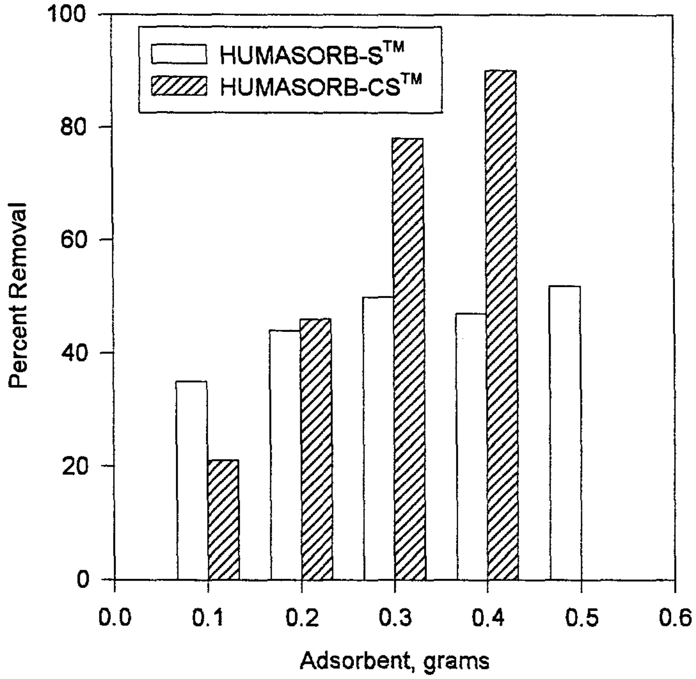


Figure 5.3. Strontium Removal by HUMASORB-CS™ and HUMASORB-S™

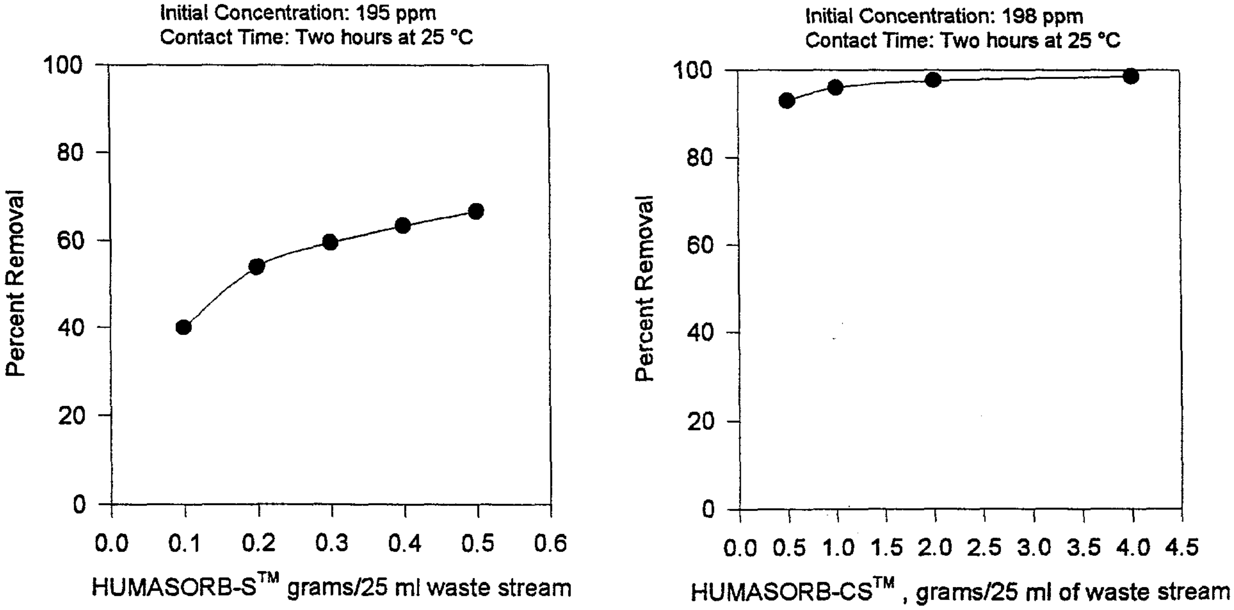


Figure 5.4. Multiple Toxic Metals are removed from Spiked Water by HUMASORB-CS™

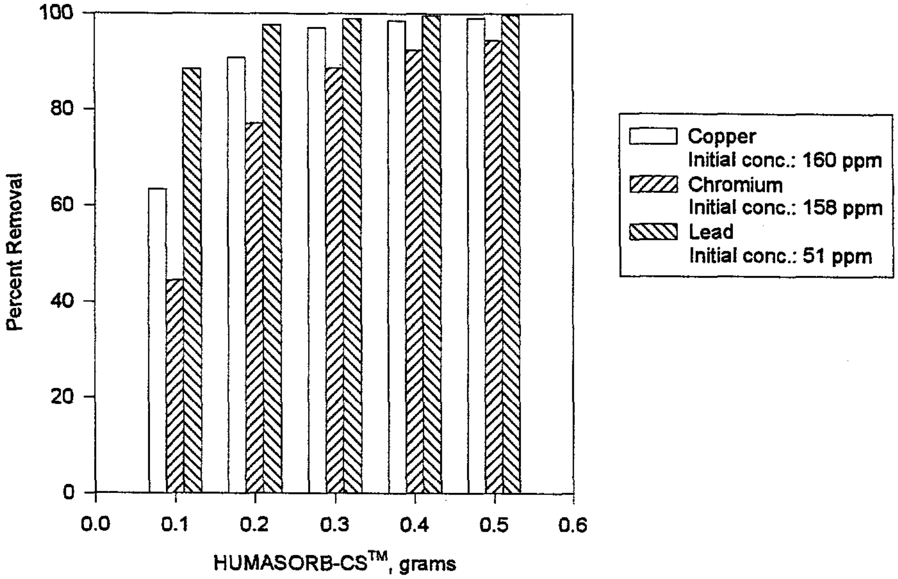


Figure 5.5. Removal of Individual Metals from Simulated Wasste Stream Using HUMASORB-CS™

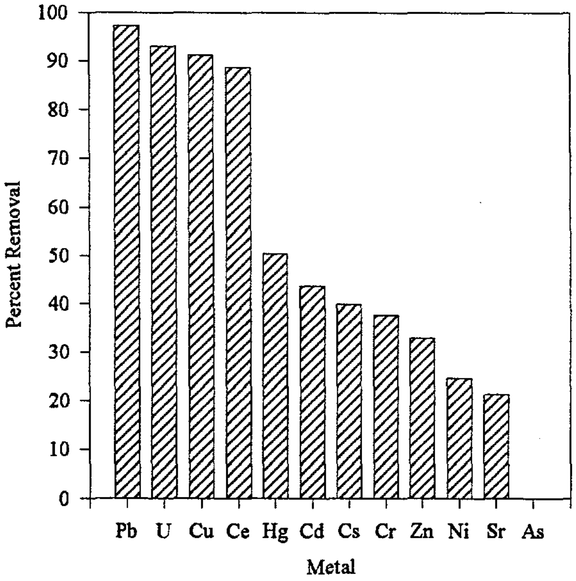
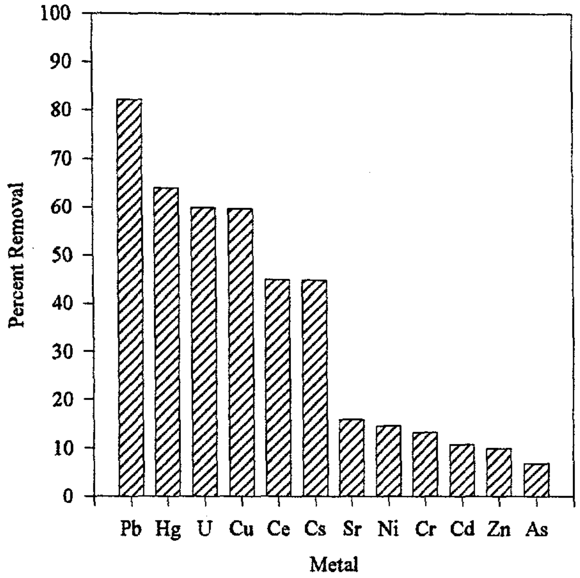


Figure 5.6. Removal of Multiple Metals from Simulated Mixed Waste Stream Using HUMASORB-CS™



HUMASORB-CS™ was evaluated in batch mode for removal of contaminants such as lead and chromium in the presence of high concentrations of background metals such as calcium. In these tests, simulated waste streams were prepared by spiking water with approximately 10,000 ppm calcium and nearly 200 ppm of either lead or chromium (III). The simulated waste streams (25 mL) were then contacted with HUMASORB-CS™ (0.5 grams) at 300 rpm and 25°C for two hours. The solid and liquid phases were separated after the contact time and analyzed for calcium and either lead or chromium (III). The results from these tests shown in Table 5.1 clearly show the effectiveness of HUMASORB-CS™ for toxic metal removal even in the presence of high background concentrations of metals such as calcium. The increase in calcium concentration is due to the presence of calcium in the HUMASORB-CS™ matrix.

HUMASORB-CS™ was also used in batch mode with a simulated mixed waste stream containing three inorganic contaminants and two chlorinated organic contaminants. The results shown in Table 5.2 clearly show that HUMASORB-CS™ is very effective in removing multiple contaminants in a single-step process.

TABLE 5.1. Metal Removal by HUMASORB-CS™ in the Presence of High Background Concentration of Calcium

CONTAMINANT	SIMULATED WASTE Concentration, ppm		
	Waste stream containing chromium and calcium Initial pH: 3.56 Final pH: 5.18		
	Initial	Final	Removal %
Chromium (III)	196	28.5	85.5
Calcium	11,280	13,527	-
	Waste stream containing lead and calcium Initial pH: 5.70 Final pH: 7.58		
Lead	169	4.78	97.2
Calcium	9,670	11,110	-

TABLE 5.2. HUMASORB-CS™ is Effective for Mixed Waste Remediation

CONTAMINANT	SIMULATED WASTE Concentration, ppm		
	Initial	Final	Removal %
Chromium (III)	88	< 0.5	> 99
Copper	98	< 0.5	> 99
Lead	18	< 0.5	> 97
Trichloroethylene (TCE)	140	1	>99
Perchloroethylene (PCE)	26	N.D.	>99

N.D.= Not Detected.

5.2.3 Distribution Coefficients

The results from experiments conducted as part of this project were used to determine the distribution coefficients. The coefficient K_d is defined as

$$K_d = C_s / C_l$$

where, C_s is the concentration of the contaminant in the solid phase and C_l is the concentration in the liquid phase.

The distribution coefficients for various contaminants are listed in Tables 5.3 and 5.4. The distribution coefficients were determined from batch isotherm studies in which different amounts of the adsorbent were contacted with simulated waste streams. The table indicates that HUMASORB-S™ has a very high affinity for uranium, and is also very effective in removing different metals from simulated waste streams.

The data presented in Tables 5.3 and 5.4 indicate that HUMASORB-CS™ has higher distribution coefficients than HUMASORB-S™. These higher distribution coefficients at comparatively lower equilibrium concentration indicate that metal removal from contaminated water is enhanced by HUMASORB-CS™. Higher distribution coefficients with HUMASORB-CS™ for different metals are also evident in batch adsorption studies with contaminated streams containing multiple metals as shown in Table 5.4.

Table 5.3. HUMASORB-CS™ Enhances Strontium and Chromium Distribution Coefficients

CONTAMINANT	EQUILIBRIUM CONCENTRATION IN THE LIQUID PHASE, ppm	DISTRIBUTION COEFFICIENT*, K_d, ml/gm	pH
WITH HUMASORB-S™			
Uranium	0.01	> 100,000	5.1
Lead	5	3500	2.25
Cerium	1.7	5600	2.5
Strontium	65.3	99	2.2
Chromium	138	54	3.2
WITH HUMASORB-CS™			
Strontium	2.87	430	5.1
Chromium	22.65	566	3.2

*: As determined from batch isotherm studies with only one contaminant present in the system.

Table 5.4. HUMASORB-CS™ Enhances Copper, Chromium, and Lead Distribution Coefficients

CONTAMINANT	EQUILIBRIUM CONCENTRATION IN THE LIQUID PHASE, ppm	DISTRIBUTION COEFFICIENT*, K_d, ml/gm	pH
WITH HUMASORB-S™			
Copper	6.8	666	2.2
Chromium	14	260	2.2
Lead	2	450	2.2
WITH HUMASORB-CS™			
Copper	< 0.5	11,870	4.0
Chromium	< 0.5	8514	4.0
Lead	< 0.5	1700	4.0

*: As determined from batch isotherm studies with three inorganic and two organic contaminants present in the system.

5.3 Column Tests

The tests in the preceeding sections were conducted in batch mode. Most of the adsorption/ion-exchange operations involve continuous processes with the media packed in columns. The objective in these tests was to evaluate HUMASORB-CS™ in bench scale columns. The goal was to develop preliminary data leading to design of pilot and commercial scale applications.

5.3.1 Methodology

Column tests were conducted using glass columns having an internal diameter of 22 mm and an approximate bed height of 20 cm. The columns were packed with 80% sand and 20% HUMASORB-CS™ on a weight basis. Sand was used to lower channeling effects and to allow the use of relatively larger columns. The sand and HUMASORB-CS™ were uniformly mixed and wet-packed into the column. The packed column was visually inspected for uniform distribution of HUMASORB-CS™.

Simulated waste streams were passed through the columns in downflow mode via gravity flow. The flow rate was adjusted using a valve at the column outlet. A constant liquid head was maintained above the bed by using an inverted flask containing the liquid to be passed through the column. This setup eliminated the need for pumps and flow meters while maintaining a relatively constant flow through the column. The flow rate for each test was monitored by measuring the volume of the collected sample against the time used to collect the sample. Column tests were conducted with simulated waste streams at relatively similar rates defined as Empty Bed Contact Time (EBCT). EBCT is the time required for the fluid to pass through the volume occupied by the adsorbent bed. The Empty Bed Contact Time (EBCT) and the bed volumes used in these tests are based on the volume occupied by dry HUMASORB-CS™ in the column. The amount of HUMASORB-CS™ in the column and the bulk density (~ 1gram/mL) was used to estimate the volume to calculate EBCT.

5.3.2 Results and Discussion

The results from the column tests were used to develop breakthrough curves. In the breakthrough curves, the ratio of the column output to column input concentration is plotted against number of bed volumes passed through the column. The column was assumed to be saturated when the output concentration was nearly 95% of the input concentration. The breakthrough point was assumed when the output concentration was between 2-5% of the input concentration. The flow rates (and thus EBCT) selected were designed to allow for relatively quick breakthrough and saturation of the column for logistics reasons. The number of bed volumes passed at breakthrough and saturation were used to estimate the breakthrough and saturation capacity of HUMASORB-CS™.

The breakthrough curve for removal of lead from a simulated waste stream containing lead and perchloroethylene (PCE) is shown in Figure 5.7. In this experiment, approximately 2700 bed volumes of contaminated water (lead: 20 ppm) was passed through the column. The contact time based on HUMASORB-CS™ in the column was less than four minutes. As shown in the figure, there was no breakthrough of the contaminant after 2700 bed volumes. To obtain breakthrough of lead and to estimate the breakthrough and saturation capacity, the same column was used again with the input concentration of lead increased to 200 ppm. Lead breakthrough was observed after additional 500-600 bed volumes were passed through the column. The column was approximately 70% saturated at the end of the test at which point 3600 bed volumes had passed though the column. The breakthrough curves for copper and chromium are shown in Figures 5.8 and 5.9. In these tests, the input concentration was 200 ppm. The contact time in these tests was similar to the test with lead. The breakthrough curves from the column tests indicate that HUMASORB-CS™ has higher capacity for lead than for copper and chromium. The higher capacity for lead is also indicated in column tests with a simulated waste stream containing multiple contaminants. The breakthrough curve shown in Figure 5.10 shows a relatively quick breakthrough of chromium followed by copper and lead. The higher capacity for lead and copper removal compared to chromium in the column tests is similar to that observed in batch tests (Figure 5.4).

Figure 5.7. Column Breakthrough Curve for Lead

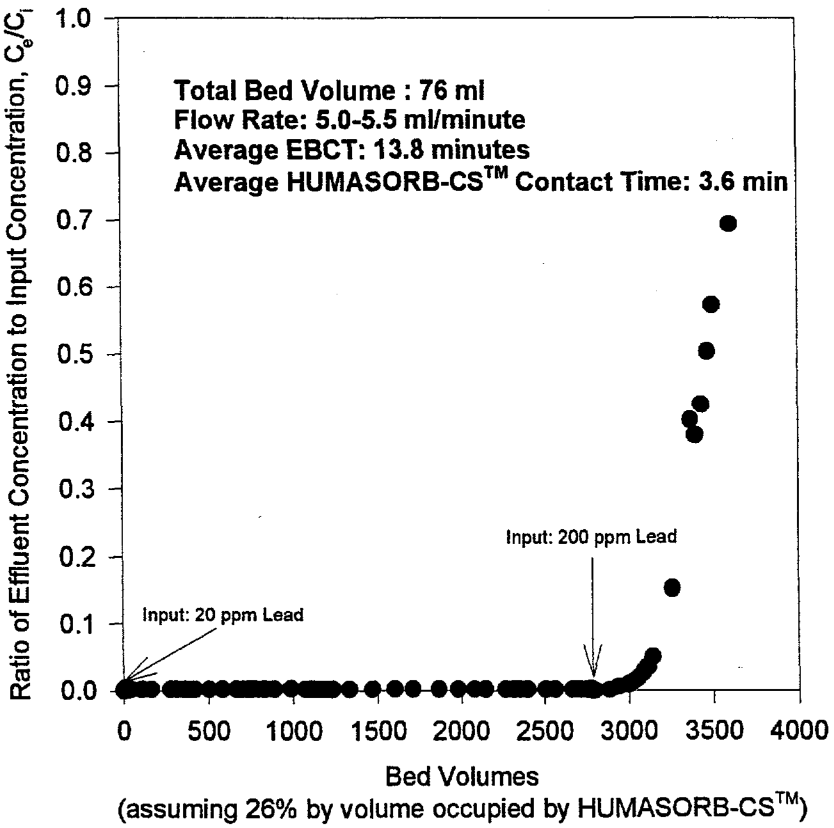


Figure 5.8. Column Breakthrough Curve for Copper

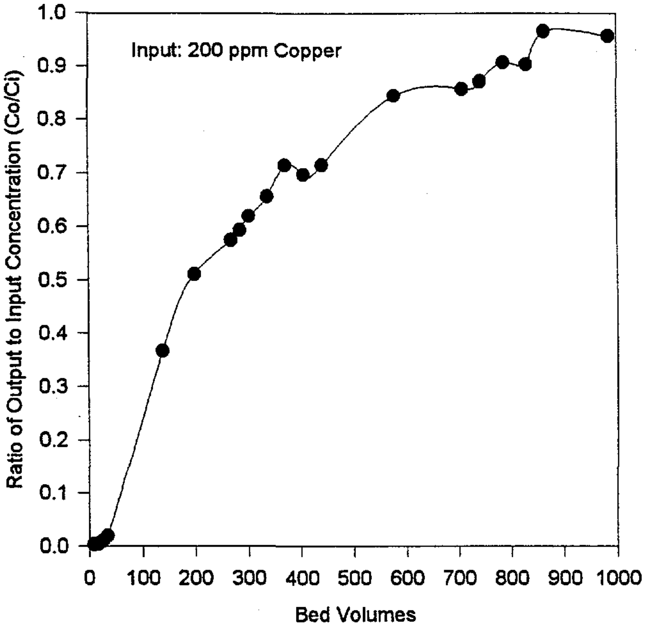


Figure 5.9. Column Breakthrough Curve for Chromium

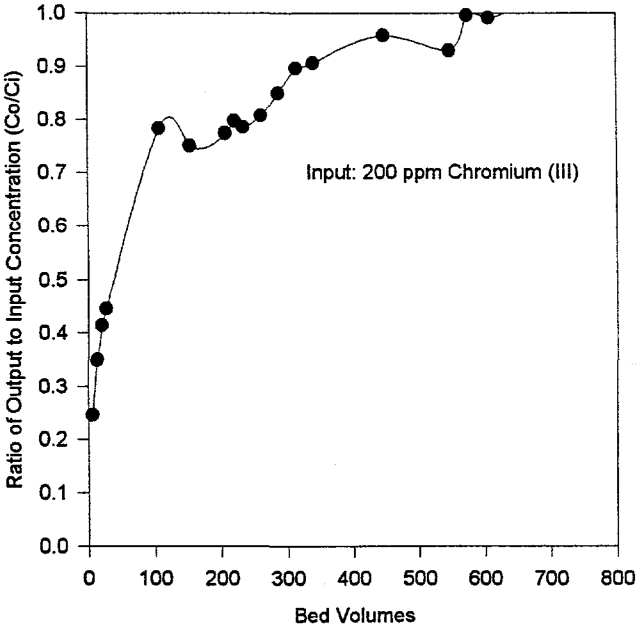
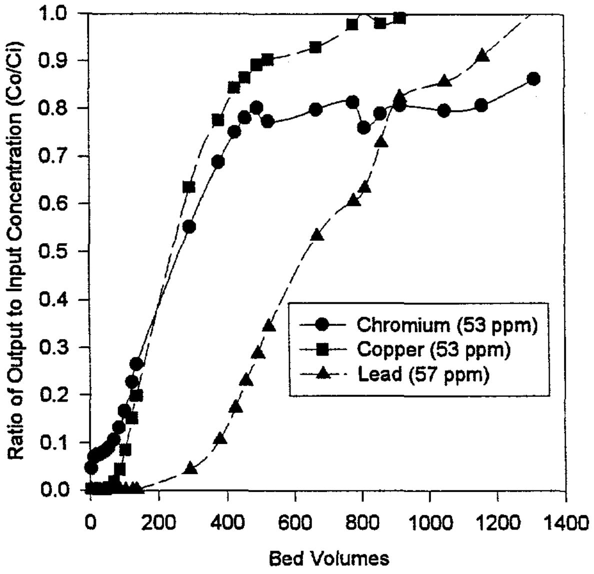


Figure 5.10. Column Breakthrough Curves from a Test with a Simulated Waste Stream Containing Multiple Contaminants



A column test was also conducted using a simulated waste stream containing cerium, a surrogate for radioactive plutonium. The input concentration of cerium in this test was 200 ppm. The breakthrough curve shown in Figure 5.11 indicates no breakthrough for at least 600 bed volumes; the column was saturated after nearly 1700 bed volumes.

The data from the various column tests was used to estimate the column performance parameters such as bed volumes treated at breakthrough and saturation, adsorption capacity at breakthrough and saturation. The capacities were estimated using mass balance analysis. The performance parameters are tabulated in Table 5.5.

5.3.3 Column Regeneration to Recover Metals

The columns used with simulated waste streams containing metals were regenerated using 1N sulfuric acid. During regeneration, 1000 mL of 1N H_2SO_4 was passed through the column followed by 1000 mL of distilled water. This procedure was followed for columns used with simulated waste streams containing copper and chromium. For the column used with simulated waste stream containing lead, 1000 mL of distilled water was passed through the column to evaluate if lead would be desorbed by water.

The results show that approximately 95% of the copper adsorbed was released during regeneration, but only 20% of chromium was released. The release of lead was negligible (less than 0.3%). This was expected since the column was treated only with water. The regenerated columns were used again to determine the ability of HUMASORB-CS™ to remove contaminants. A simulated waste stream containing 40 ppm copper was passed through the column. There was no breakthrough in this test after 800 bed volumes of simulated waste water had passed through the column (see Figure 5.12). The amount of copper adsorbed (determined from mass balance analysis) was approximately equal to 50% of the amount released during regeneration. For the chromium and lead columns, the regeneration was not complete as indicated earlier. However, the amount adsorbed after regeneration was greater than the amount released. This indicates possible activation of additional sites during regeneration. This effect needs further evaluation, but HUMASORB-CS™ can be successfully regenerated.

Column tests with a simulated waste stream containing chromium (VI) were also conducted. In this test, the column was pretreated with 1N sulfuric acid before passing the simulated waste stream containing chromium (VI). The empty bed contact time (EBCT) based on the HUMASORB-CS™ in the column was approximately 20 minutes

Figure 5.11. Column Breakthrough Curve for Cerium

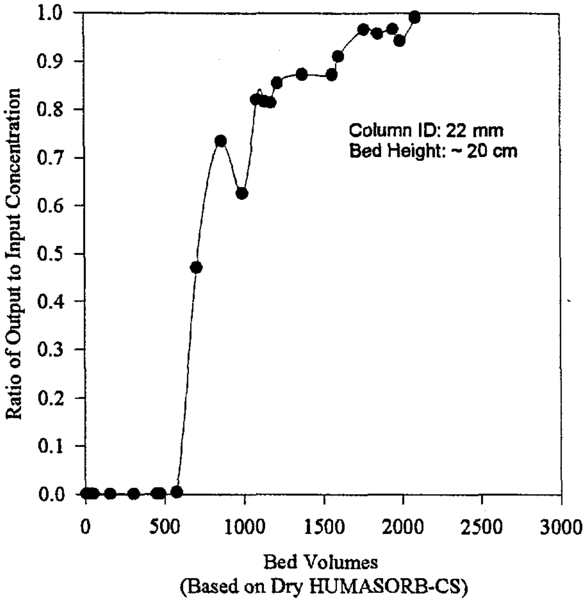


Table 5.5. HUMASORB-CS™ Performance Data from Column Tests

Input Concentration ppm	Bed Volumes Passed+++	Output Concentration ppm	Ratio (Output to Input)	Estimated Capacity mg/gm***
SIMULATED WASTE STREAM CONTAINING COPPER				
221	35	4.0	0.02	7.5
221	985	212	0.96	72.4
SIMULATED WASTE STREAM CONTAINING LEAD###				
222	3054###	4.0	0.02	112
222	3603###	154	0.69	196
SIMULATED WASTE STREAM CONTAINING COPPER, CHROMIUM AND LEAD				
53 (Copper)	82	2.3	0.043	3.23
57 (Lead)	290	2.6	0.046	16.13
53 (Copper)	1300	53.7	1.01	18.16
57 -71.3(Lead)	1300	71.6	1.00	35.31

+++: Bed Volumes based on HUMASORB-CS™ present in the column
***: Estimated from column study data using mass balance analysis
###: Includes approximately 2768 bed volumes of water containing 20 ppm lead passed through column before changing to 222 ppm lead containing water.

and the waste stream was passed through the column for approximately 50 hours (approximately 180 bed volumes). Chromium (VI) breakthrough occurred after 20 bed volumes (Figure 5.13). The concentration profile of chromium (VI) and total chromium is identical and the concentration difference remains constant. This indicates the rapid removal of chromium (III) formed by reduction of chromium (VI) by HUMASORB-CS™. The relatively quick removal of chromium (III) is similar to that observed in batch tests. It is anticipated that if the contact time is increased in the column test, the number of bed volumes treated at breakthrough will also be increased.

Figure 5.12. Column Breakthrough Curve for Copper after Regeneration

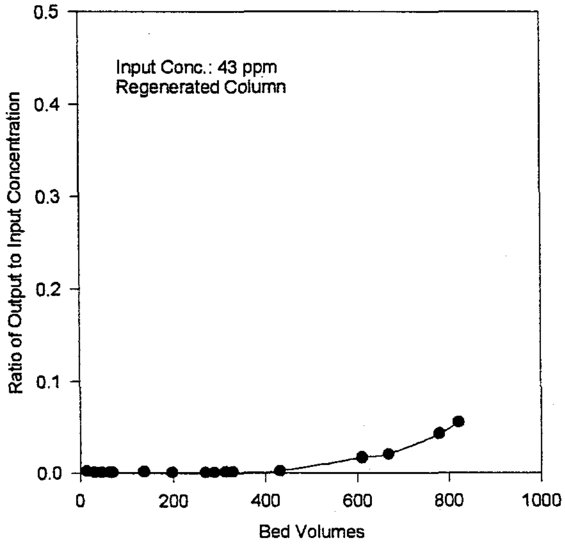
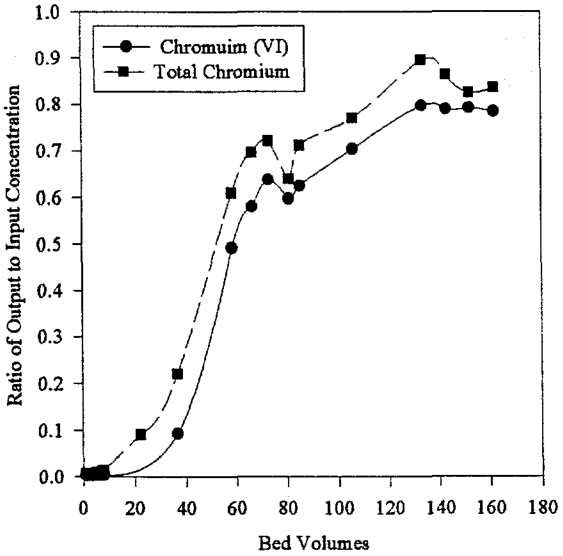


Figure 5.13. Column Breakthrough Curve for Chromium (VI)



5.3.4 Column Tests with Organics

In a column test with a simulated stream containing lead and PCE, Figure 5.7, there was no breakthrough of lead after 2500 bed volumes (based on the amount of HUMASORB-CS™ in the column). However, the organic contaminant (PCE) did breakthrough in these tests as shown in Figure 5.14. To generate the breakthrough curve for the organic contaminants, both input and output concentrations were measured at each sample point. The early breakthrough of the organic contaminant is believed to be due to the relatively lower empty bed contact time (EBCT) used in these studies (i.e., less than four minutes).

Column studies with relatively higher EBCT were also conducted with a simulated waste stream containing PCE. A simulated waste stream containing PCE was passed through a column packed with a mixture of 20% HUMASORB-CS™ and 80% sand on a weight basis. The EBCT in these tests was approximately 40 minutes. Two tests were conducted with one column being pretreated with 1 N sulfuric acid before the test. The tests were conducted for 48 hours (approximately 80 bed volumes) and the samples collected were analyzed. There was no breakthrough of the contaminant (PCE) as shown in Figure 5.15. However, since there was a time lag between the collection of samples and the analyses, the column could not be used again to continue the test. The results from the two columns are similar indicating no significant effect of pretreatment under the conditions of this test.

A simulated waste stream containing benzene was passed through a column packed with a mixture of 20% HUMASORB-CS™ and 80% sand on a weight basis. The breakthrough curve shown in Figure 5.16 shows saturation of the column after 50 bed volumes. The results are similar to that in the batch tests and indicate higher affinity for chlorinated organic contaminants compared to fuel hydrocarbons such as benzene.

Figure 5.14. Column Breakthrough Curve for PCE with Simulated Stream Containing Lead and PCE

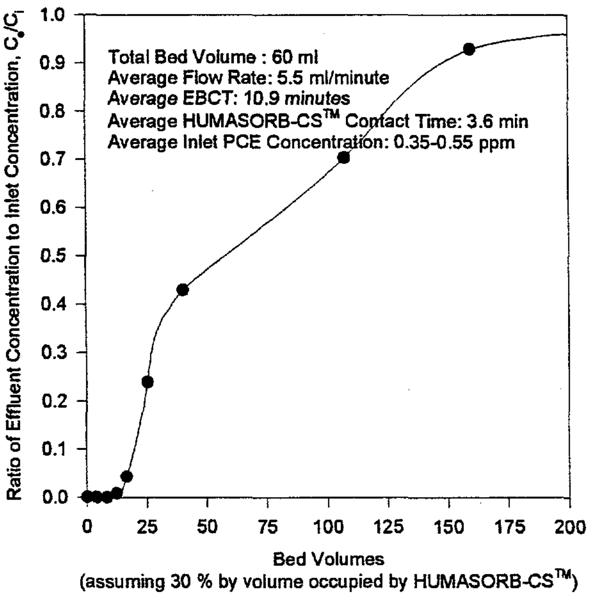


Figure 5.15. Column Breakthrough Curve for PCE with Simulated Waste Stream Containing PCE

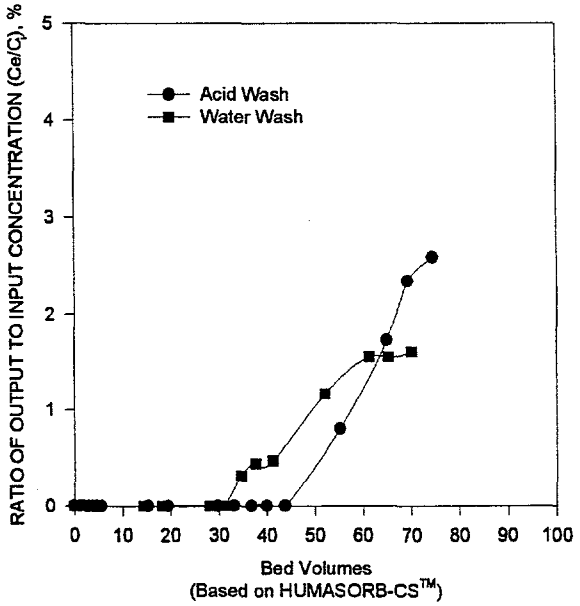
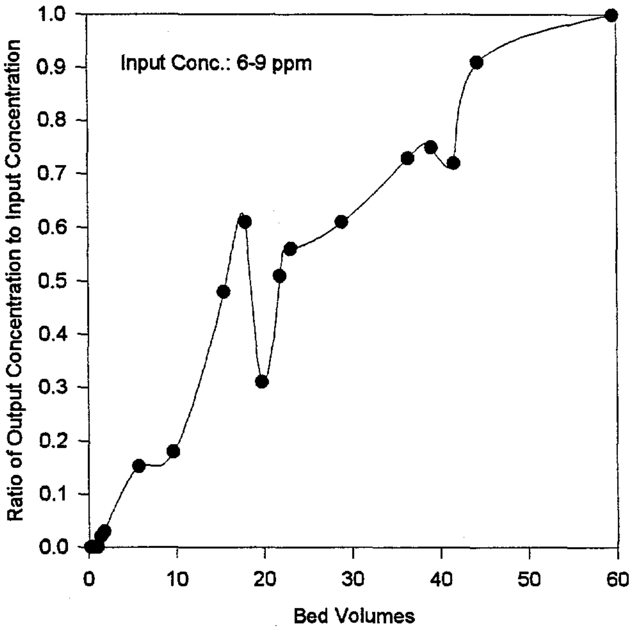


Figure 5.16. Column Breakthrough Curve for Benzene



5.4 Stability Tests

HUMASORB-CS™ was subjected to stability tests under various conditions. The objective of these tests was to evaluate the stability of HUMASORB-CS™ using solubility under various test conditions as a criterion. In addition, HUMASORB-CS™ was tested in batch mode to evaluate its effectiveness for removal of a target contaminant (chromium (III)) after the stability treatment.

5.4.1 Methodology

__Stability in water at different temperatures__: Approximately two grams of HUMASORB-CS™ was taken in centrifuge tubes. To this 10-mL of tap water was added. The mixture was then subjected to different temperatures for extended periods. The stability tests conducted are shown below. At the end of the test period, the mixture was centrifuged to separate the solid and liquid phases. The liquid phase was analyzed for humic acid by lowering the pH to below 2. The amount of dry humic acid obtained was used to estimate solubility of HUMASORB-CS™. The solid phase was then dried in an oven at 50°C and used in batch tests to evaluate removal of a target contaminant (Cr

(III)). Approximately 0.5 grams of the solid was mixed with 25 mL of spiked water containing chromium (III) at 300 rpm and 25°C for two hours. The solid and liquid phases were separated by centrifugation after the contact time and the liquid phase was analyzed for chromium (III).

The following stability tests in water at different temperatures were conducted:

- Ambient Conditions (1, 4, and 6 months)
- Temperature 50°C (1, 2, 3, and 4 Weeks)
- Temperature 4°C (3, 5.5, and 6.5 months).

Stability in water in the presence of anions: Tests were also conducted to evaluate stability of HUMASORB-CS™ in water in the presence of anions such as carbonate and sulfate. In these tests, spiked solutions were prepared containing carbonate or sulfate. The spiked solution (10-mL) was added to two grams of HUMASORB-CS™ in centrifuge bottles. The mixture was allowed to stand for extended period after which the solid and liquid phases were separated. The liquid phase from some of the samples was analyzed for humic acid by lowering the pH to below 2. The amount of dry humic acid obtained was used to estimate solubility of HUMASORB-CS™. In a few of the samples, the liquid phase was analyzed for the anions carbonate or sulfate. The solid phase was then dried in an oven at 50°C and used in batch tests to evaluate removal of a target contaminant (Cr (III)). Approximately 0.5 grams of the solid was mixed with 25 mL of spiked water containing chromium (III) at 300 rpm and 25°C for two hours. The solid and liquid phases were separated by centrifugation after the contact time and the liquid phase was analyzed for chromium (III).

The following stability tests were conducted in water in the presence of anions:

- 100 ppm Na_2SO_4 or 100 ppm Na_2CO_3 (1-day, 5 months)
- 100 ppm $CaSO_4$ or 100 ppm $CaCO_3$ (1-day, 5 months)
- 10,000 ppm Na_2SO_4 or 10,000 ppm Na_2CO_3 (3 month).

Biological stability: The biological stability of HUMASORB-CS™ was evaluated by adding 10 mL of a microbial stock suspension prepared in Peptone medium to approximately two grams of HUMASORB-CS™. The initial cell concentration in the microbial stock suspension was 1.0×10^6 cells/mL. In addition, control tests were conducted with HUMASORB-CS™ mixed with a solution that was filtered to remove microorganisms. The tests were conducted for one, three and four months. The samples were observed under microscope at the end of the tests to estimate the cell concentration and to determine if there was any attachment of microorganisms to HUMASORB-CS™. The biological stability tests were conducted for one, three and four months.

5.4.2 Results and Discussion

The solubility of HUMASORB-CS™ was less than 0.5 % in most of the stability tests indicating that HUMASORB-CS™ is stable under the conditions used in the study. However, HUMASORB-CS™ was soluble in the tests with 10,000 ppm sodium carbonate. HUMASORB-CS™ from the stability tests was used to evaluate chromium (III) removal from a simulated waste stream. More than 90% of chromium (III) was removed as shown in Figures 5.17-5.19. The tests clearly show that HUMASORB-CS™ is not only stable under the conditions evaluated in this study, but also retains it ability to remove contaminants (as shown with chromium (III)) from contaminated waste streams.

5.5 Summary

The results presented in this section demonstrate the improved solubility characteristics of HUMASORB-CS™ compared to HUMASORB-S™. The contaminant removal ability was either retained or enhanced with HUMASORB-CS™. Column tests were used to develop breakthrough curves for different types of contaminants including metals, radionuclide surrogates, oxo-anions and organics. The column performance was used to estimate parameters such as contaminant concentration on the media at breakthrough and at saturation. In addition, the ability to regenerate and re-use HUMASORB-CS™ was evaluated. The test results demonstrate that HUMASORB-CS™ can be used for removal of multiple types of contaminants (metals, radionuclides and organics) in a single-step process.

Figure 5.17. Chromium Removal by HUMASORB-CS™ after Stability Tests (Ambient and 4°C)

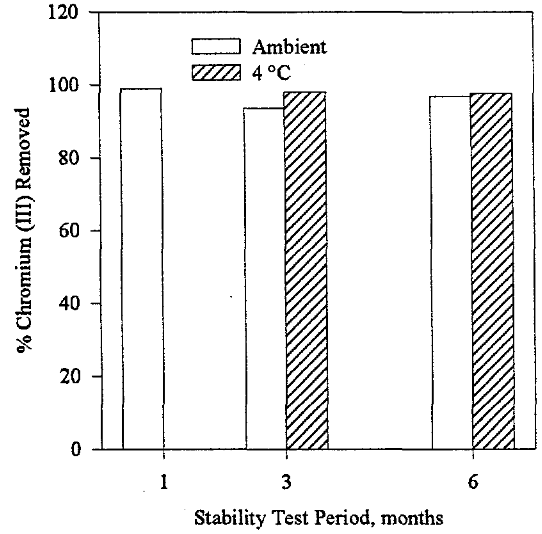


Figure 5.18. Chromium Removal by HUMASORB-CS™ after Stability Tests (50°C)

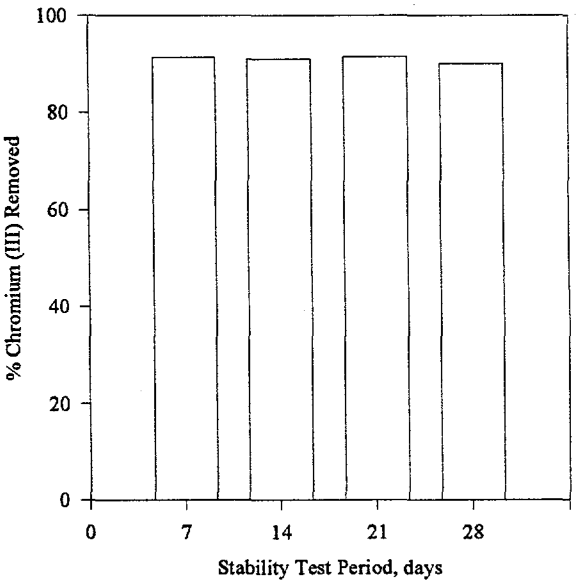
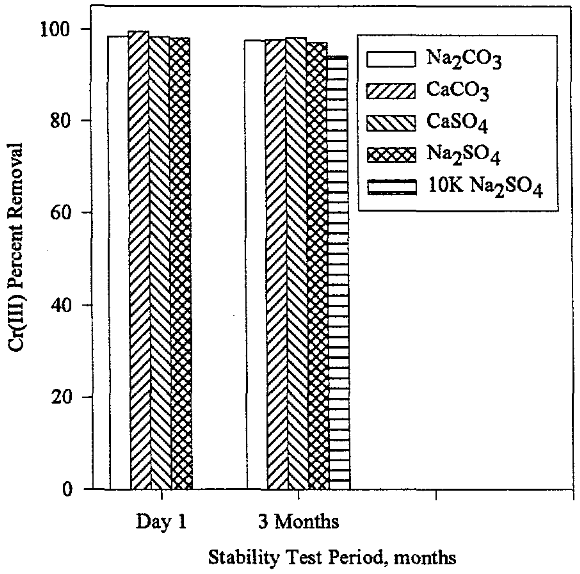


Figure 5.19. Chromium Removal by HUMASORB-CS™ after Stability Tests



6.0 HUMASORB-CS™ PERFORMANCE IMPROVEMENT

The results presented in earlier studies clearly show that HUMASORB-CS™ is effective for removal of multiple types of contaminants. In this section, the efforts made to improve HUMASORB-CS™ performance and enhance cost-effectiveness are documented. The approach used to improve HUMASORB-CS™ included possible incorporation of Zero-Valent Iron (ZVI) into HUMASORB-CS™, use of various drying techniques during HUMASORB-CS™ production and also the use of wet beads after storing for extended period of time for removal of multiple contaminants.

6.1 Incorporation of Zero-Valent Iron

The use of Zero-valent iron (ZVI) is a new approach for the removal of organic contaminants from contaminated groundwater. This new technology has been used at a number of sites contaminated with TCE and Chromium (VI). The mechanism of the removal is believed to be the reduction potential of the ZVI to reduce chlorinated hydrocarbons (such as TCE and PCE). The enhancement of performance of HUMASORB-CS™ to remove organic contaminants was evaluated after the incorporation of ZVI into its matrix. The objective of the tests discussed in this section was to test the organic removal capacity after the incorporation of the ZVI and compare it with the original HUMASORB-CS™.

6.11 Methodology

Chlorinated Organic Compounds Adsorption: Zero-valent iron was incorporated into the HUMASORB-CS™ by proprietary methods at two different percentages, namely 2.5 % and 7.5 % on a weight basis. Simulated waste stream containing 10 ppm of each of the chlorinated hydrocarbons TCE and PCE was prepared. The simulated waste stream was contacted in 35-ml zero-head space vials with 1.5 grams of the solid material (either HUMASORB-CS™ (H-CS) or HUMASORB-CS™ with 2.5 % zero-valent iron (2.5%ZVI+H-CS) or HUMASORB-CS™ with 7.5 % zero-valent iron (7.5%ZVI+H-CS). After contact time of 12 and 24 hours the vials were centrifuged at 2000 rpm to separate the solid and liquid phases. The liquid phase was then analyzed for both TCE and PCE using GC. Controls containing TCE and PCE were also analyzed.

Half-Life Determination: The tests to determine the half-life of TCE and PCE were conducted by contacting 25-mL of spiked water with one gram of various solid media under zero-headspace conditions for time periods between two hours and 24 hours. The solid media used were either 100% HUMASORB-CS™ or 2.5%ZVI+H-CS or (7.5%ZVI+H-CS) or 100% zero-valent iron (ZVI). The solid and liquid phases were separated after the desired contact time and the liquid phase was analyzed for TCE and PCE. Appropriate controls were used in all the tests.

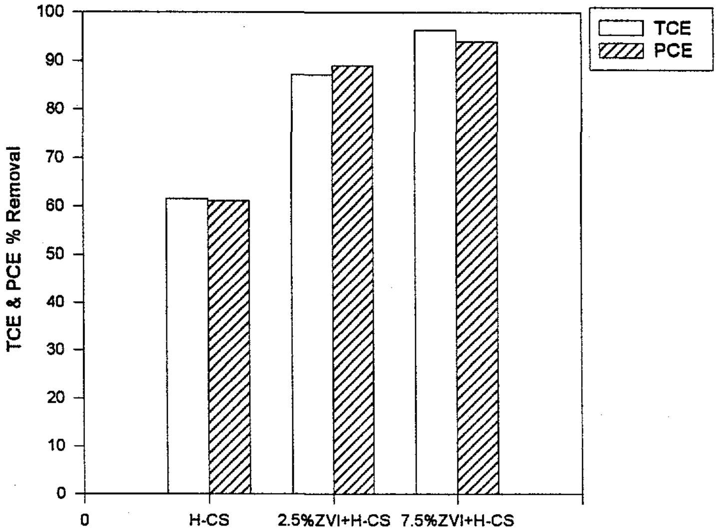
Adsorption and Possible Degradation of Chlorinated Organic Compounds: The ability of HUMASORB-CS™ to adsorb and destroy the chlorinated organics TCE and PCE was tested by contacting 3.0 grams of the different solid material with 38-mL of simulated stream containing 10 ppm of each TCE and PCE under zero-headspace conditions. The solid media used were either 100% HUMASORB-CS™ or 2.5%ZVI+H-CS or (7.5%ZVI+H-CS) or 100% zero-valent iron (ZVI). The solid and the liquid phases were analyzed for TCE and PCE and their reduced products (1,2-dichloroethylene and vinyl chloride). Controls containing TCE and PCE were also analyzed.

Column tests were also conducted to study the concentration profile of the chlorinated organic contaminants as they react with HUMASORB-CS™. The tests were conducted in a two-inch diameter and 46 inches long glass column, which was slurry packed with 1400 g of HUMASORB-CS™. The glass column was chosen to prevent any reaction with the TCE. The column has 11 sampling ports along the wall, which are 4 inches apart. The ports are equipped with valves for sample collection. A simulated stream containing TCE (15-20 ppm) was stored in a collapsible Teflon bag to provide a zero headspace. The simulated water was passed through the column at a flow rate of 2-mL/min with a peristaltic pump. Samples were collected on a regular basis from all the 11 ports in the column as well as from the inlet and outlet of the column. All samples collected were analyzed for TCE, vinyl chloride and cis 1,2-dichloroethylene using GC-MS.

6.12 Results and Discussions

Chlorinated Organic Compounds Adsorption: The test results show that TCE and PCE removal was improved with the incorporation of the zero-valent iron into the HUMASORB-CS™ matrix (Figure 6.1). The removal increased from about 60 % (H-CS) to about 90 % (2.5%ZVI+H-CS) and to approximately 93 % (7.5%ZVI+H-CS) when the contact time is 12 hours. At 24 hours contact time, however, the TCE and PCE removal was the same for all the three materials (Figure 6.2). The results indicate that the effectiveness of HUMASORB-CS™ is comparable to that of ZVI for TCE and PCE removal.

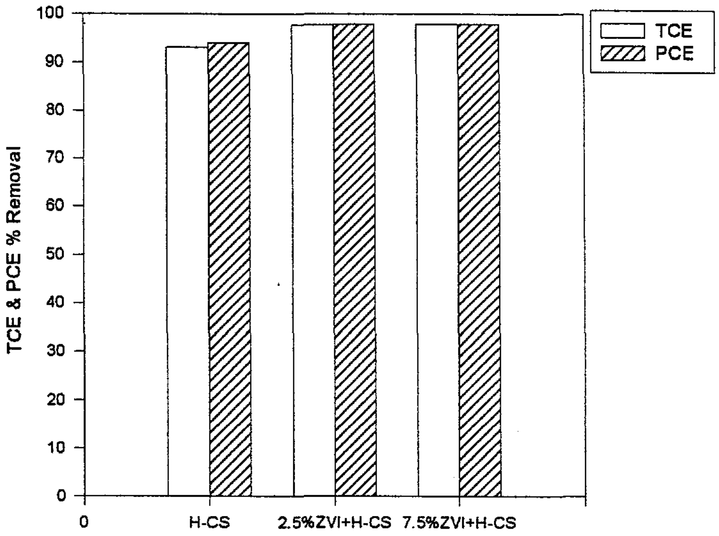
Figure 6.1. TCE and PCE Removal by HUMASORC-CS™ after the Incorporation of Zero-Valent Iron at 12 hours Contact Time



Half-Life Determination: The decrease in the concentration of TCE and PCE after treatment with the various media followed the 1st order kinetics as shown in Figures 6.3 & 6.4. The data from the tests was used to estimate the half-life for TCE and PCE, when treated with the media and are shown in the figures. The results clearly indicate that the half-life for TCE and PCE is significantly lower with HUMASORB-CS™ than with ZVI and the incorporation of ZVI into HUMASORB-CS™ does not have any beneficial effect.

Adsorption and Possible Degradation of Chlorinated Organic Compounds: The results from organics destruction tests are shown in Figure 6.5. The data for contaminants destroyed was calculated using the measured concentrations in the liquid and solid phases and by mass balance analysis. The results indicate that HUMASORB-CS™ is not only adsorbing the chlorinated organic contaminants, but potentially reducing them in the same way as zero-valent iron. The reduced products 1,2-dichloroethylene and vinyl chloride were however, not detected in both the liquid and solid phases.

Figure 6.2. TCE and PCE Removal by HUMASORC-CS™ after the Incorporation of Zero-Valent Iron at 24 hours Contact Time



The possibility of degradation of chlorinated compounds was evaluated in batch tests in cooperation with Temple University in Philadelphia. The tests were conducted with simulated waste stream containing TCE. The solid and liquid phases were analyzed using various techniques to evaluate the possible degradation of chlorinated organic compounds. The tests indicated that the reaction of TCE with HUMASORB-CS™ appears to follow the mechanism of reductive dehalogenation. The possibility of TCE destruction by reductive dehalogenation after being adsorbed by HUMASORB-CS™ was confirmed by a number of methods:

- The analysis of the headspace in the system after treatment of TCE contaminated water with HUMASORB-CS™ showed the presence of ethylene, an end product of reductive dehalogenation of TCE
- Ion-chromatography showed an increase in chloride concentration indicating destruction of TCE
- NMR studies showed that the vinylic proton (characteristic of TCE) disappeared completely from the reaction mixture after two hours of contact time. NMR spectra of spent HUMASORB-CS™ (dissolved in NaOD/D_2O), after treatment with TCE,

showed new peaks assigned to the adsorbed non-chlorinated degradation products, but no peaks for TCE.

Figure 6.3. TCE Half-Life Determination

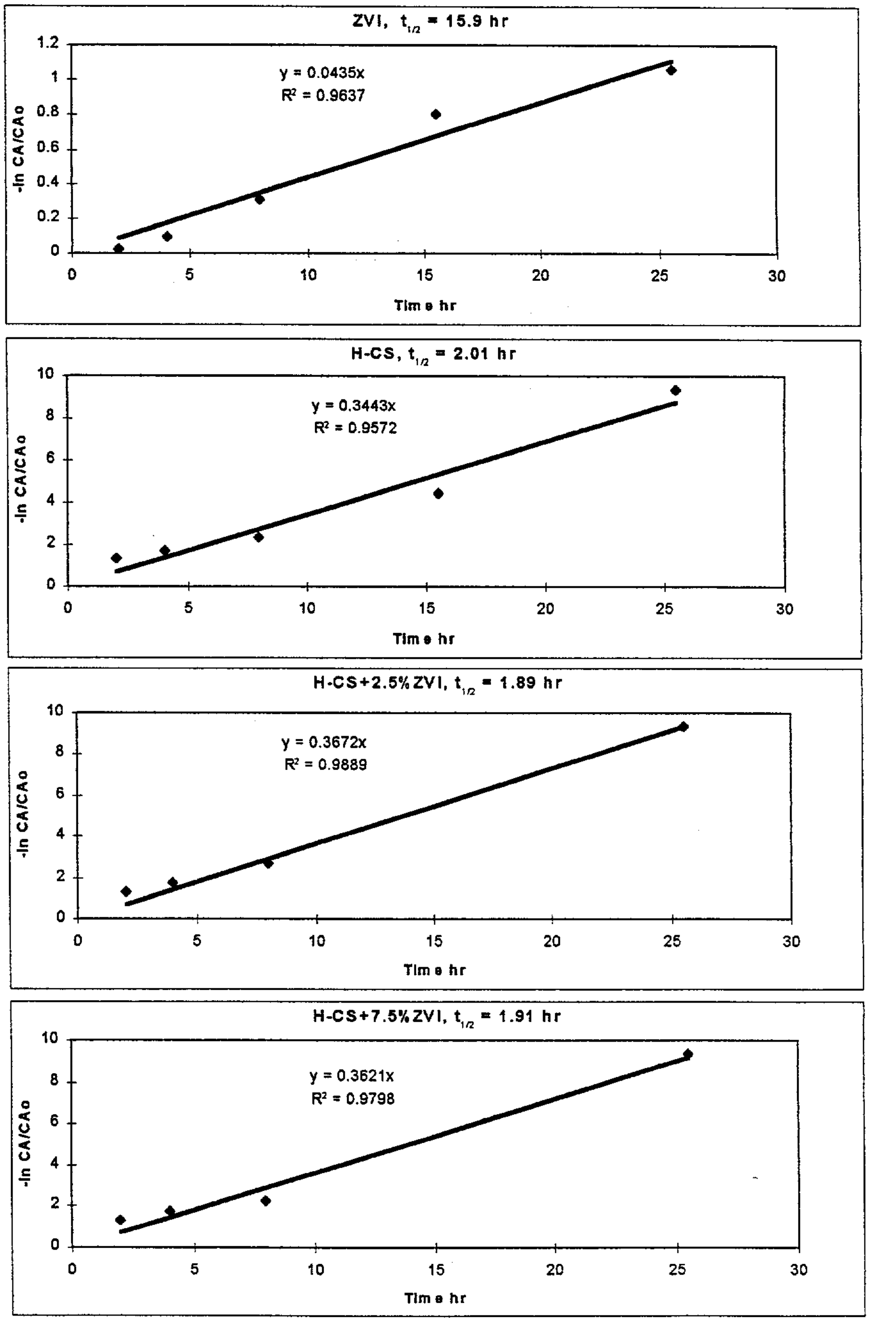
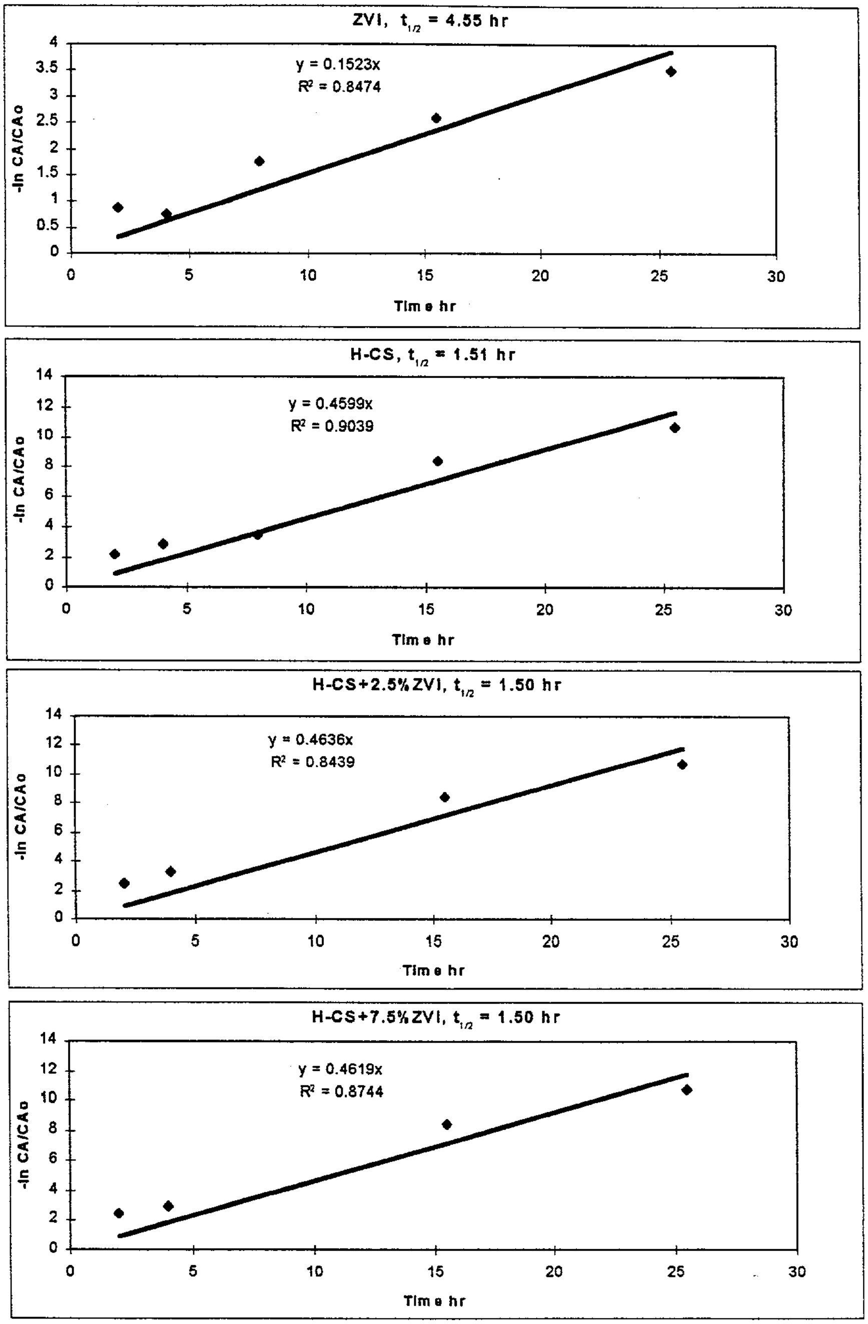
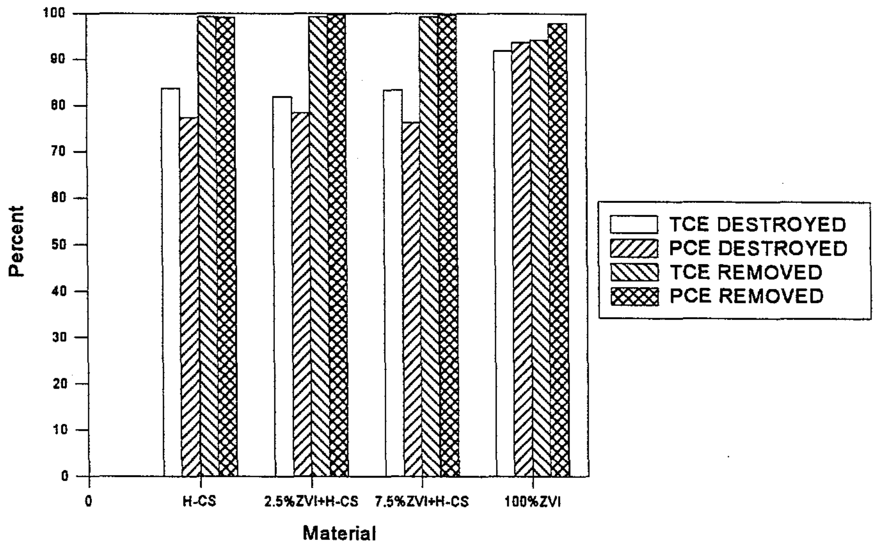


Figure 6.4. PCE Half-Life Determination



These results confirm that contaminants such as PCE, carbon tetrachloride, chloroform and other chlorinated hydrocarbons could be potentially degraded by reductive dehalogenation after being adsorbed by HUMASORB-CS™.

Figure 6.5. Destruction and Removal of TCE and PCE by HUMASORB-CS (H-CS) and Zero-Valent Iron (ZVI)



Column Tests: The samples collected in the column tests were analyzed for TCE, vinyl chloride, and cis 1,2-dichloroethylene. The results were used to develop concentration profiles along the length of the column. The TCE concentration profile along the length of the column as the water passes through the column is shown in Figure 6.6. The profiles show that column was slowly saturated with TCE after approximately 16 weeks. The results were also used to estimate TCE half-life and develop the TCE breakthrough curve, which is shown in Figure 6.7. The TCE half-life was estimated as 2.2 hrs, which is similar to that observed with the batch tests. The breakthrough curve (Figure 6.7) shows that TCE broke through the column after 105 bed volumes and was saturated after 250 bed volumes. The saturation capacity is estimated at 2.88 mg/g from the breakthrough curve

The analysis of the samples however, did not show any vinyl chloride, or cis 1,2-dichloroethylene. It is believed that the degradation products are adsorbed as they are formed and in addition, the degradation rate is believed to be much lower than the rate of adsorption.

Figure 6.6. TCE Concentration Profile in a Column Filled with HUMASORB-CS™

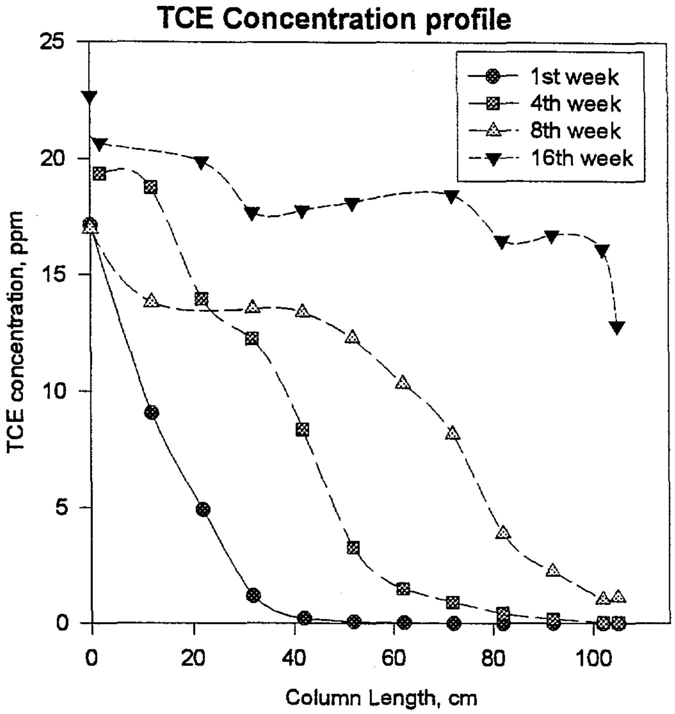
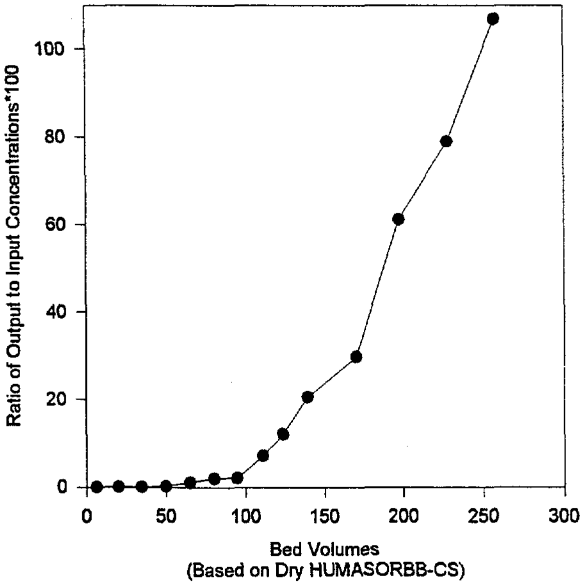
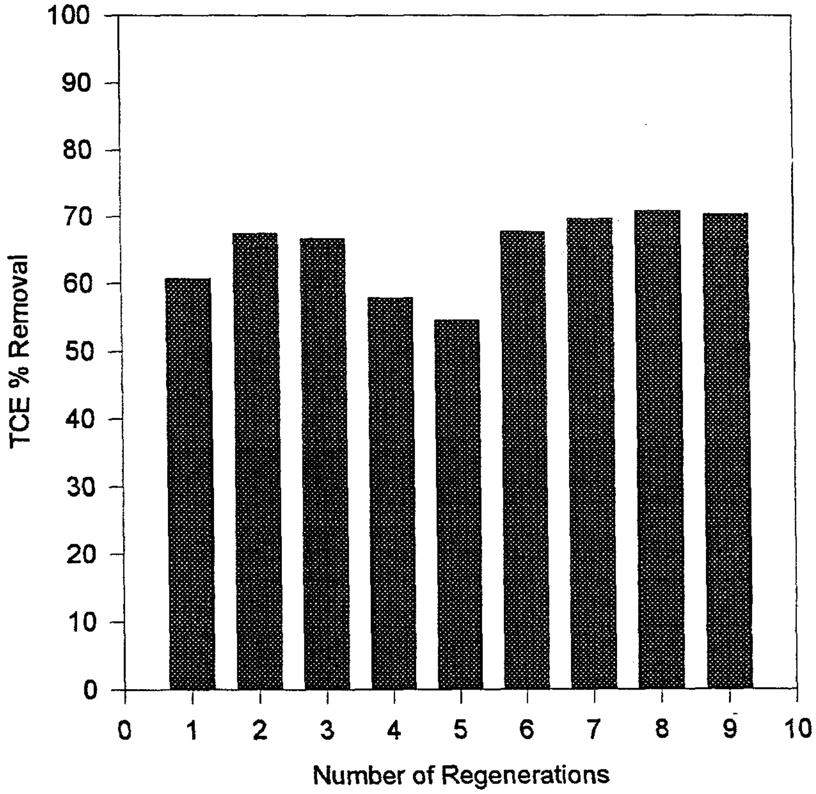


Figure 6.7: TCE Breakthrough Curve Developed from the Column Test with Multiple Sampling ports



Regeneration of HUMASORB-CS™: The regeneration of HUMASORB-CS™ after it was saturated with TCE was also evaluated in batch mode. HUMASORB-CS™ was contacted in 30-mL vials with simulated wastewater containing 50 ppm of TCE for 24 hours under zero-headspace conditions. The solid and liquid phases were separated and the liquid phase was analyzed for TCE. The solid phase was dried overnight in an oven at 50°C and reused in the test. The solid was used repeatedly to see the effect on TCE removal. The results are shown in Figure 6.8 and are expressed in terms of TCE removal percentage. The graph clearly indicates that HUMASORB-CS™ can be used effectively after repeated regeneration for TCE removal.

Figure 6.8. TCE Removal by HUMASORB-CS™ after Regeneration



6.2 Drying Techniques for Surface Area Improvement

The surface area of humic acid can be increased significantly depending on the drying method used as reported by Radwan et al. (J. Appl. Phycol., 9, 481-488, 1997). The use of various drying techniques was evaluated in a similar manner to increase the surface area of HUMASORB-CS™ and enhance the removal of various contaminants. The drying methods used include air-drying, oven drying, freeze-drying and supercritical drying using acetone to replace water in the matrix. The samples lost approximately 90% of their mass with the different drying methods and all were uniform materials with a spherical shape. The products were hard and not brittle, except for the freeze-dried product, which was very brittle and could be easily crushed. The surface area of the dried samples was measured at 77°K with liquid nitrogen as the adsorbate using the Branneur-Emmett-Teller (BET) method. The surface area of HUMASORB-CS™ produced by supercritical drying was the highest among the methods tested. The surface area of the freeze-dried sample was also relatively higher, but as indicated earlier, the beads are very brittle.

Samples produced from all methods of drying were evaluated for chromium and TCE removal in batch mode. The batch tests for chromium removal were conducted using one gram of HUMASORB-CS™ and 25-mL of water spiked with chromium at various concentrations. The chromium concentration levels were 10,000, 5,000, 2,000, 1,000 and 500 ppm. The tests were conducted by mixing the HUMASORB-CS™ and the solution in a 50-mL centrifuge bottles for two hours and 24 hours. The objective of the tests was to evaluate chromium removal at different concentrations, and also to estimate the saturation capacity based on the isotherms.

The results from the tests were used to develop isotherms for chromium removal using HUMASORB-CS™ produced by the different methods. The isotherms were then used to estimate the maximum capacity for uptake of chromium. The results of the maximum capacity for chromium and the corresponding surface area for the different products are tabulated in Table 1. The maximum capacity for chromium removal as estimated from the isotherms indicates that the capacity for contaminant removal with oven dried and supercritical dried samples is similar and is approximately twice that with the air-dried samples. The freeze-dried samples have the highest capacity as shown in Table 1. However, the freeze-dried samples are extremely brittle and are essentially in a powder form. The difference in the particle size of the freeze-dried samples and the other samples could be in part responsible for the higher capacity of the freeze-dried sample.

The results in Table 6.1 show that there is no correlation between the surface area as measured by the BET method and the capacity for chromium removal. However, when the air-dried sample was ground (increasing the external surface area), the capacity for chromium removal increased significantly. This indicates that an increase in the external surface area has a significant effect on the capacity for contaminant removal compared to the internal surface area. It is believed that this is because of the easier and better access to the functional groups and sites on the external surface, when the particle size is decreased.

Table 6.1. Chromium Removal Capacity for HUMASORB-CS™ Samples

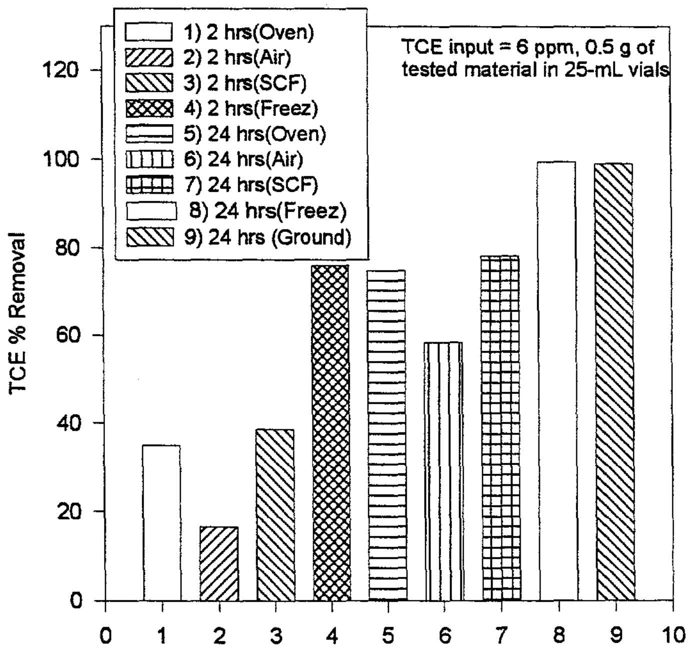
Drying Method	Maximum Capacity mg/gm	Surface Area, m^2/g
Freeze Drying	73.5	5.0
Supercritical Fluid Drying	36.4	15.8
Oven Drying	35.6	0.8
Air Drying	19.9	2.0
Air dried-Ground	74.6	1.3

In the batch tests with water contaminated with TCE, HUMASORB-CS™ (0.5 grams) was contacted with water contaminated with TCE (6 ppm) in 25-mL vials with zero headspace. The contact time was two hours and 24 hours. The mixture was centrifuged after the desired contact time and the liquid phase was analyzed using gas chromatography for TCE. The tests were conducted in duplicate and appropriate controls were used in the tests. The results in terms of TCE removal are shown in Figure 6.9 and show that the results are similar to that with metals (chromium). The removal of TCE is better with the samples dried by supercritical fluid drying and oven drying. The freeze-dried sample had the highest removal, but as indicated earlier, the particles are brittle and are in powder form.

6.3 Comparison of Wet and Dry HUMASORB-CS™ Beads

The use of different techniques did not have a significant impact on the removal of contaminants as discussed earlier. In order to reduce the overall costs, the wet beads of HUMASORB-CS™ (immediately after they were produced) were evaluated for contaminant removal. The objective of the tests was to determine the effect of storing the wet beads on the physical handling properties and the ability to remove contaminants. If the physical properties are not affected with extended storage periods of the wet beads and if the metal removal is not affected, it is possible to either reduce or eliminate the drying required to produce the beads, thereby enhancing the cost-effectiveness significantly. About 80 lbs of wet HUMASORB-CS™ beads were made and stored in two five-gallon sealed buckets for four months. The physical properties of the HUMASORB-CS™ beads were compared before and after storage and showed that the beads are preserving their shape and are strong.

Figure 6.9. TCE Removal Using HUMASORB-CS™ Samples



The HUMASORB-CS™ beads were tested for the removal of metals as wet beads and were compared to dry beads before and after storage. The tests were conducted in both batch mode and in column tests.

In batch tests, 25-mL of simulated waste stream containing chromium was contacted with HUMASORB-CS™ for two hours. The amount of HUMASORB-CS™ used was approximately 10 grams for wet beads and one gram for the dry beads. The 10 grams of wet beads will contain approximately one gram of the active component after drying. The tests were conducted in centrifuge tubes and chromium was analyzed after the test by using an ICP. The results from the batch tests for both the dry and wet beads (before and after storage) are shown in Table 2. Wet beads were still effective for chromium removal and are not affected by storing the beads for at least four months as wet beads.

Table 6.2. Chromium (III) removal with Wet and Dry HUMASORB-CS™ before and after storage

Sample	Before Storage	
	Input, ppm	Output, ppm
Dry HUMASORB-CS™	479	11.6
Wet HUMASORB-CS™	479	0.57
	After Four months Storage	
	Input, ppm	Output, ppm
Dry HUMASORB-CS™	464	5.35
Wet HUMASORB-CS™	464	0.68

The column tests were performed by slurry packing 150 g of wet beads in one column and 15 g of dried beads in another column. The simulated wastewater was prepared by dissolving Cr (III) salt (chromium nitrate) in water to obtain a concentration of approximately 25 ppm. The contaminated water was then passed through the column at a flow rate of 2-mL/min. A control sample was collected at the beginning of the test and samples were collected at the column effluent after every 50 to 100-bed volumes, based on the amount of dry HUMASORB-CS™ in the column. The control and collected samples were analyzed for Cr (III) using an ICP. The column tests were conducted with the wet beads that were used immediately and also with wet beads that were stored for an extended periof of time (four months). The results are shown as breakthrough curves in Figures 6.10 & 6.11.

The column tests results clearly show that the wet HUMASORB-CS™ beads are effective in removing chromium. The wet HUMASORB-CS™ is effective for chromium removal and can treat more than 400-500 bed volumes before breakthrough. The wet beads were physically intact during the course of the tests, but the water treated with the wet beads had significantly higher leaching of humic substances, indicating that the cross-linking was not complete. In addition, the tests showed that wet HUMASORB-CS™ can be stored for at least four months without any impact on the physical handling properties and without loosing the capacity to remove various contaminants.

Figure 6.10. Chromium Breakthrough Curves in Columns Packed with Fresh Wet and Dry HUMASORB-CS™

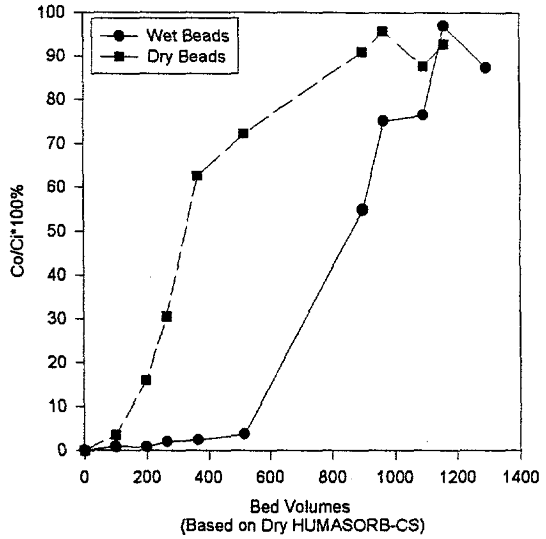
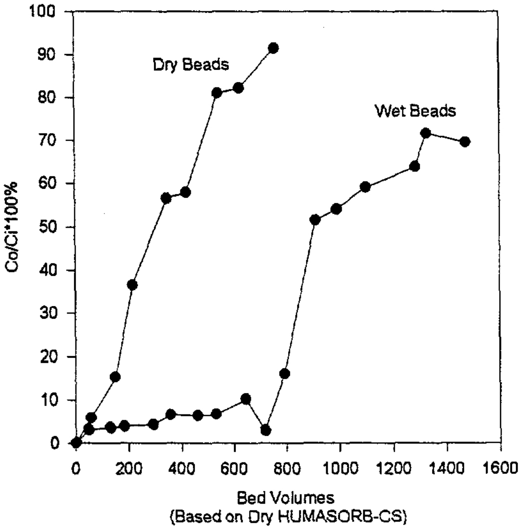


Figure 6.11. Chromium Breakthrough Curves in Columns Packed with Stored Wet and Dry HUMASORB-CS™



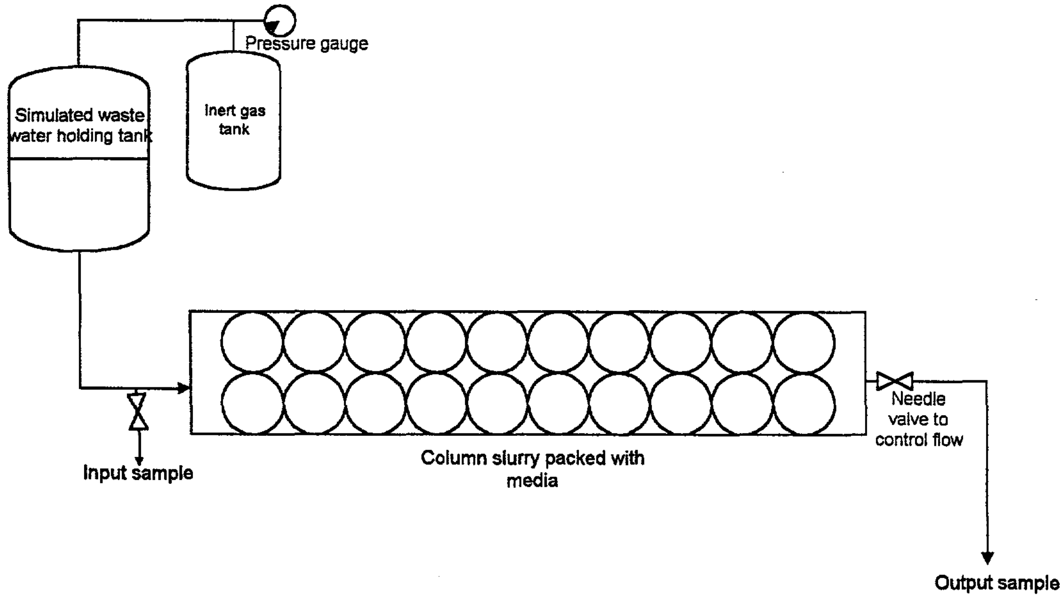
7.0 EVALUATION OF HUMASORB-CS™ UNDER SIMULATED BARRIER CONDITIONS

HUMASORB-CS™ was evaluated for contaminant removal under simulated barrier conditions at pressures of 10 psig and 100 psig. These conditions were used to simulate barrier installation depths of approximately 10 feet and 100 feet. The experiments were conducted using only HUMASORB-CS™ in the bed for shallow applications (pressure of 10 psig) and by mixing HUMASORB-CS™ with sand in the bed used to simulate deeper applications (pressure of 100 psig).

7.1 Methodology

The experiments were conducted using two large columns having an internal diameter of two inches and a length of 36 inches. The first column (A) was slurry packed with 100% HUMASORB-CS™ (870 grams) and was subjected to a pressure of 10 psig using nitrogen. The second column (B) was packed with a mixture of 50% sand and 50% HUMASORB-CS™ (750 grams) on a weight basis and was subjected to a pressure of 100 psig. Each column was connected to a pressurized tank, containing the simulated contaminated water under the desired pressure, as shown in the experimental setup of Figure 7.1. A simulated waste stream containing chromium (VI), cerium (surrogate for plutonium), copper, trichloroethylene, and tetrachloroethylene was prepared and passed at flow rate of approximately 1.0 ml/min and 0.5 ml/min through columns A and B respectively. The flow rates was maintained by controlling the output flow with a needle valve (column A) and a metering valve (column B). The flow rates were monitored and measured twice a day. Two samples were collected at the outlet and two at the inlet of each column every ten days for the metal and organic analyses, with the samples at the inlet acting as control. The samples were analyzed for organics and metals using calibrated methods by gas chromatography (GC) and inductively coupled plasma (ICP) respectively.

Figure 7.1. Experimental Setup to Evaluate HUMASORB-CS™ Under Simulated Barriers Conditions



7.2 Results and Discussions

The simulated barrier tests were conducted to evaluate the effectiveness of HUMASORB-CS™ to treat groundwater in-situ. The rate of groundwater flow is very low and the residence time in a permeable barrier is typically 1-2 days. The residence time in the simulated barrier tests, based on the amount of HUMASORB-CS™ present in the column was approximately 14 hours for Column A and 25 hours for Column B.

The breakthrough curves for the metals in columns A & B are shown in Figures 7.2 and 7.3. In this discussion, the breakthrough of the contaminants is assumed when the output concentration is more than 5% of the input. The simulated water was prepared on a regular basis throughout the nearly two-year study and the concentration of the contaminants in the input varied during the course of the study. The average input concentrations of the contaminants are shown in Figures 7.2 and 7.3. The breakthrough curves clearly indicate that there is no breakthrough of copper and cerium (surrogate for plutonium). The chromium (VI) concentration in the output is approaching breakthrough after 350 bed volumes, but does not increase till at least 700 bed volumes in Column A. The chromium (VI) output data is a little scattered, but the output concentration is very close to the breakthrough limit. For Column B, the concentration increased above the breakthrough limit after approximately 300 bed volumes, but gradually decreased after 350 bed volumes and remained lower than the 5% limit after more than 700 bed volumes. The anomaly in the chromium (VI) breakthrough between 300-350 bed volumes is primarily because of analytical issues and is also reflected to a certain extent in the breakthrough curves for Column A.

Figure 7.2. Column A Breakthrough Curves for Inorganic Contaminants
(Test Duration: 21 months)

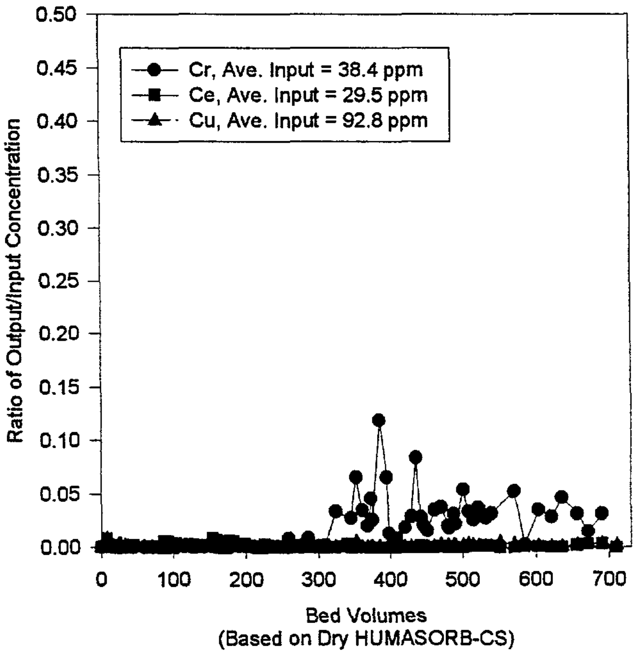
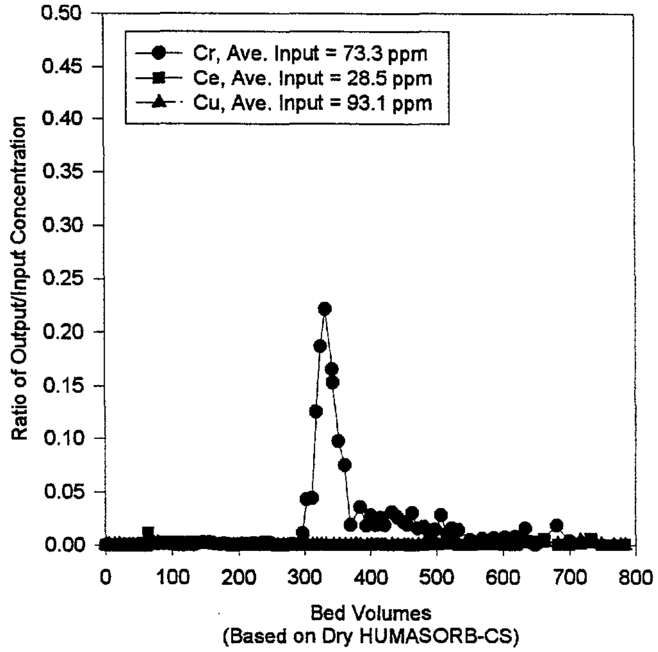


Figure 7.3. Column B Breakthrough Curves for Inorganic Contaminants

(Test Duration: 24 months and still running)



The breakthrough curves for PCE and TCE in columns A and B are shown in Figures 7.4 and 7.5. There is no breakthrough of PCE in Column A until approximately 400 bed volumes and the column was 30-40% saturated at 700 bed volumes. In Column B, PCE breakthrough occurs after 600 bed volumes and the column was nearly 60% saturated at 700 bed volumes. The higher amount of bed volumes passed through Column B before breakthrough is due to the longer residence time compared to that in Column A. TCE breakthrough occurs in both the columns at approximately 150 bed volumes and the output concentration continued to increase above the input concentration. This increase in the TCE concentration at the column output is believed to be the result of a number of factors. HUMASORB-CS™ has a higher affinity for PCE compared to TCE, resulting in possible preferential adsorption of PCE. In addition, there is some evidence to suggest the possible degradation of chlorinated organic compounds after adsorption by HUMASORB-CS™ (Section 6). TCE is a product of PCE degradation and the steady increase in TCE concentration could be a result of PCE degradation by HUMASORB-CS™.

Figure 7.4. Column A Breakthrough Curves for Organic Contaminants

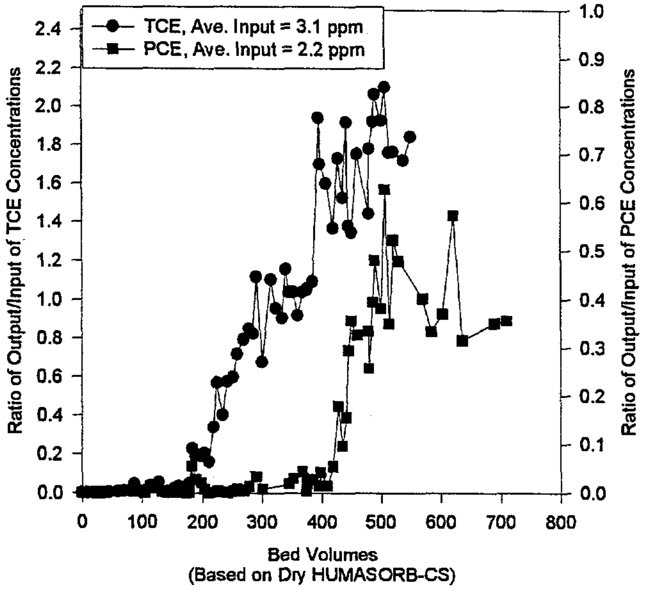
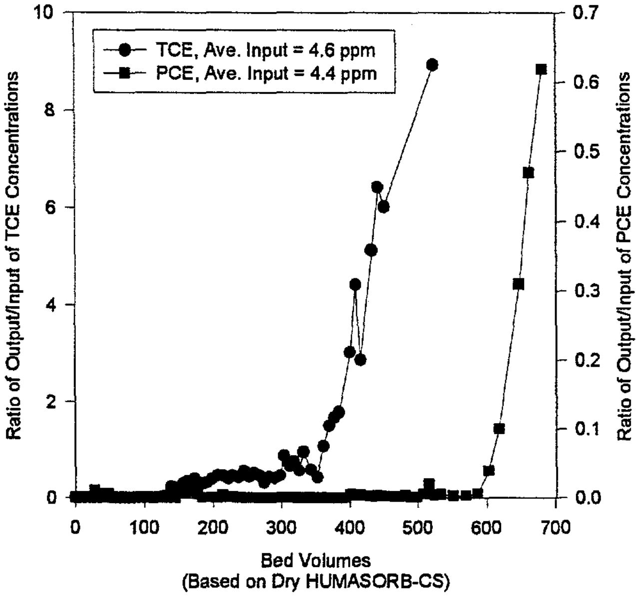


Figure 7.5. Column B Breakthrough Curves for PCE and TCE



The data used to generate the breakthrough curves was also used to estimate the capacity of HUMASORB-CS™ for the multiple inorganic and organic contaminants. The capacities were estimated at both breakthrough and percent saturation of the column at the time of this report and are tabulated in Table 7.1. The results clearly indicate that HUMASORB-CS™ has high capacity for the various contaminants and is effective in removing metals, organics and radionuclide surrogates from groundwater using a permeable reactive barrier system.

Table 7.1: Estimated Capacity of HUMASORB-CS™ for Various Inorganic and Organic Contaminants

	Estimated Bed Volumes and Capacity at Breakthrough			
	Column A		Column B	
Contaminant	Bed Volumes	Capacity, mg/g	Bed Volumes	Capacity, mg/g
Cu	710†	65.89	783†	72.9
Ce	710†	20.95	783†	22.3
Cr	352	13.52	318	23.3
PCE	419	0.92	618	2.72
TCE	177	0.55	244	1.12
	Estimated Bed Volumes and Capacity at the Time of the Report			
Cu	710†	65.89	783†	72.9
Ce	710†	20.95	783†	22.3
Cr	690‡	20.0	680‡	36.6
PCE	690&	1.22	682#	2.86
TCE	290*	0.92	361*	1.4

*: 100 % saturation, #: 60 % saturation, &: 30-40% saturation, ‡: 10 % saturation, † No breakthrough

8.0 CONCEPTUAL PROCESS DESIGN AND ECONOMIC ANALYSIS

Anticipated process economics for the production of HUMASORB-CS™ using the proprietary method developed at ARCTECH is presented in this section. The process economic analysis is based on currently available information. The proprietary process is being optimized to lower the capital and operating costs further. In addition, this section also includes comparison of life-cycle costs of HUMASORB™ based treatment systems with conventional approaches.

8.1 Basis for Cost Estimate

The basis for the cost analysis is HUMASORB-CS™ production rate of 150 tonnes per day (tpd) with 350 operating days per year. The analysis presented in this section is based on Standard Chemical Engineering Guidelines for Plant Design and Economics[23].

8.2 Capital Cost

Major process equipment in a full-scale plant will include tanks with agitators, conveyor-screen dryers and associated ancillary units such as storage tanks and pumps. The cost estimates for the various process equipment are shown in Table 8.1. The estimates for some of the equipment are based on vendor quotes for similar units. The cost estimates for the other process units are based on the *six-tenths-factor rule* used for estimation of equipment costs by scaling. The total process equipment costs are estimated to be $1.5 million.

In standard chemical engineering practice, purchased equipment cost will typically range from 15 to 40 % of the fixed-capital cost investment. In this analysis, purchased equipment was assumed to be 20 % of the fixed-capital investment. The fixed capital investment was thus estimated to be approximately $7.5 million. This value was then used to estimate costs associated with installation, instrumentation, piping, utilities and other costs by applying standard chemical engineering practices. The cost breakdown of the fixed-capital investment is shown in Table 8.2. The fixed capital investment was taken to be 80% of total capital investment. Working capital was then determined to be $ 1.9 million (or 20% of total capital investment).

8.3 Operating Cost

The estimated operating costs for a 150 tpd plant are summarized in Table 8.3. The raw material costs are based on current cost estimates to manufacture HUMASORB-L™ in large quantities. The costs of other chemicals are based on quotes from various suppliers and manufacturers. The total estimated raw material costs were used as the basis for the total operating costs. The other costs associated with operating costs displayed in Table 8.3 were estimated using standard chemical engineering guidelines and ARCTECH estimates.

8.4 Economic Analysis

The capital investment and the product cost were used to estimate the net present worth of the proposed conceptual plant. The analysis was performed using two different values for HUMASORB-CS™. In one analysis (Case I), the value of HUMASORB-CS™ was assumed to be $1.00/lb and in the second case (Case II), it was assumed to be $0.80/lb. Also, in the second case it was assumed that raw materials would be available at 25% discount due to the large volume. The life of the plant was assumed to be 20 years and the capital investment was assumed to be zero during the operation of the plant at the start of year one. The net present worth for the proposed full-scale plant is estimated at $ 44.56 million in Case 1 and $ 16.04 million in Case II. A summary of the analysis for the two cases is presented in Tables 8.4 and 8.5. As a comparison, the cost of HUMASORB-CS™ in a pilot scale production process is expected to be approximately $ 2/lb.

Table 8.1. Cost Estimates For Process Equipment (150 tpd plant)

Process Element	Number of Units	Unit Cost	Total Cost (in thousands)
Tanks (50,000 gallon) with agitators	2	90,000	180
Tanks (50,000 gallon)	1	55,000	55
Tanks (20,000 gallon) with agitators	1	60,000	60
Tanks (20,000 gallon)	1	35,000	35
Storage Tanks (35,000 gallons)	3	45,000	135
Storage Tanks (10,000 gallons)	1	40,000	40
Storage Tanks (5,000 gallons)	1	15,000	15
Conveyor-Screen dryers	3	250,000	750
Pumps	8	2,000	16
Contingency	-	-	214
TOTAL EQUIPMENT COST			1,500

Table 8.2. Cost Breakdown of Fixed-Capital Investment

Component	Assumed Percent of Total	Cost (in thousands)
DIRECT COSTS		
Total Equipment Costs	20	1,500
Equipment Installation	12	900
Instrumentation and Controls (installed)	4	300
Piping (installed)	10	750
Electrical (installed)	5	375
Buildings (including services)	5	375
Service Facilities	8	600
Land	1	75
TOTAL DIRECT COSTS		4,875
INDIRECT COSTS		
Engineering and Supervision	8	600
Construction Expense	10	750
Contractor's Fee	2	150
Contingency	15	1125
TOTAL INDIRECT COSTS		2,625
GRAND TOTAL (FIXED-CAPITAL INVESTMENT		7,500

Table 8.3. Cost Breakdown For Total Product Cost (150 tpd plant)

Component	Cost (in thousands)
MANUFACTURING COSTS	
Raw Materials	86,100
Operating Labor	2,000
Utilities	3,000
Maintenance and Repairs	380
Operating Supplies	40
Laboratory Charges	380
Fixed Charges	2,000
Plant Overhead	1,000
TOTAL MANUFACTURING COSTS	94,900
GENERAL EXPENSES	2,000
TOTAL PRODUCT COSTS	96,900

Table 8.4. Full-Scale Process Economic Analysis (150 tpd plant): Case I

										YEAR OF OPERATION (Dollar values are to the nearest million)											
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Fixed-capital investment		7.50																			
Working capital		1.90																			
Total capital investment		9.40																			
Annual Income (sales)		0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0	105.0
Direct Production Costs																					
Raw materials		0	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Cross-linking Chemicals			66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10	66.10
Labor		0	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Utilities		0	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Maintenance and repairs		0	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Operating supplies		0.00	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Laboratory charges		0	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Total Direct Production Costs		0	92	92	92	92	92	92	92	92	92	92	92	92	92	92	92	92	92	92	92
Fixed charges (local taxes, rent, insurance, etc)		0	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Plant Overhead		0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Manufacturing costs	**(Sum of 5, 6, 7)**	0	95	95	95	95	95	95	95	95	95	95	95	95	95	95	95	95	95	95	95
General Expenses		0	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Total Product Cost	**(Sum of 8,9)**	0	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97
Annual operating income (4-10-11)		0	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11
Annual depreciation		0	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Income before tax	(12-13)	0	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70	7.70
Income after 34% tax		0	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08	5.08
Annual Cash Income	(Sum of 15,13)	0	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46
Annual After-tax Cash Flow	**(Sum of 16,3)**	-9.40	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46	5.46

C ANALYSIS NOTES:

traight line depreciation of capital investment over 20 years

of HUMASORB-CS^{TM} is assumed to be $ 1.00/lb

INVESTMENT ANALYSIS

Capital Investment	**9.40**
Net Present Worth (8% interest)	**44.66**
Internal Rate of Return (After Tax)	**58%**
Payback Period, years	**1.374**

Table 8.5. Full-Scale Process Economic Analysis (150 tpd plant): Case II

								YEAR OF OPERATION (Dollar values are to the nearest million)										
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	Fixed-capital investment	7.50																		
2	Working capital	1.90																		
3	**Total capital investment**	9.40																		
4	**Annual income (sales)**	0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0	84.0
5	Direct Production Costs																			
	Raw materials	0	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
	Cross-linking Chemicals	0	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58
	Labor	0	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
	Utilities	0	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	Maintenance and repairs	0	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
	Operating supplies	0.00	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
	Laboratory charges	0	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
	Total Direct Production Costs	0	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75
6	Fixed charges (local taxes, rent, insurance, etc)	0	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
7	Plant Overhead	0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
8	**Manufacturing costs (Sum of 5, 6, 7)**	0	78	78	78	78	78	78	78	78	78	78	78	78	78	78	78	78	78	78
9	General Expenses	0	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
10	**Total Product Cost (Sum of 8,9)**	0	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80
12	Annual operating income (4-10-11)	0	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63	3.63
13	Annual depreciation	0	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
14	Income before tax (12-13)	0	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30
15	Income after 34% tax	0	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
16	Annual Cash Income (Sum of 15,13)	0	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55
17	**Annual After-tax Cash Flow (Sum of 16,3)**	-9.40	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55

ECONOMIC ANALYSIS NOTES:

Assumes straight line depreciation of capital investment over 20 years

The value of HUMASORB-CS™ is assumed to be $ 0.80/lb

INVESTMENT ANALYSIS

Capital Investment	**9.40**
Net Present Worth (8% interest)	**16.04**
Internal Rate of Return (After Tax)	**27%**
Payback Period, years	**2.938**

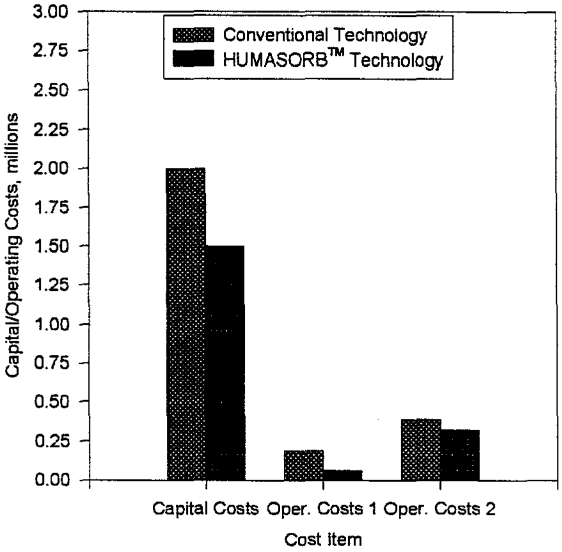
8.5 HUMASORB™ Treatment System Life-Cycle Costs

An analysis of the life-cycle costs for implementation of HUMASORB™ technology was conducted as part of this project. The life-cycle costs included estimates for both the capital and operating costs. The costs for the HUMASORB™ treatment system were then compared to the conventional treatment approaches reported in the literature.

One of the comparative analyses conducted was for surface treatment of water contaminated with multiple metal and organic contaminants. The conventional approach used here included a combination of electrochemical treatment, filtration and/or clarification. The rate of groundwater treatment was in the range 30-57 million gallons per year. The capital and operating costs of the conventional treatment approach are compared to the cost of potential HUMASORB™ treatment system in Figure 8.1. The comparison of life-cycle costs at the treatment rate of 30 million gallons per year is shown in Figure 8.2. It is clear that the use of a HUMASORB™ treatment system has significant cost advantages.

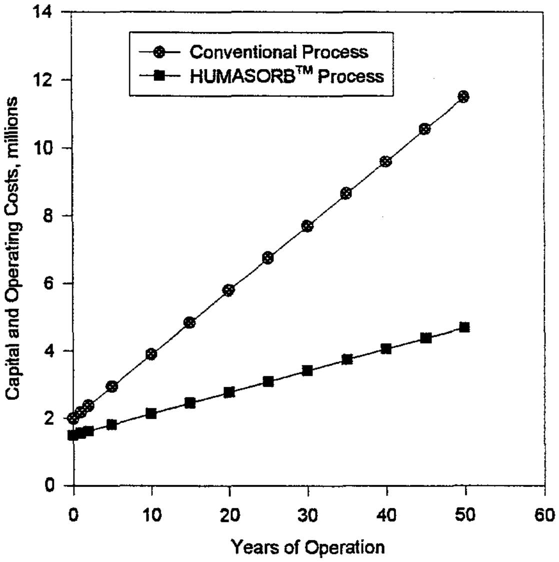
The use of HUMASORB™ in a permeable reactive barrier system will also result in cost benefits compared to a conventional pump and treat system. The life-cycle costs for treatment of a groundwater plume using HUMASORB™ are compared with the baseline pump and treat system in Figure 8.3. The use of permeable reactive barrier system based on HUMASORB™ will result in cost savings of approximately 60% over a 10 years.

Figure 8.1. Comparison of Capital and Operating Costs



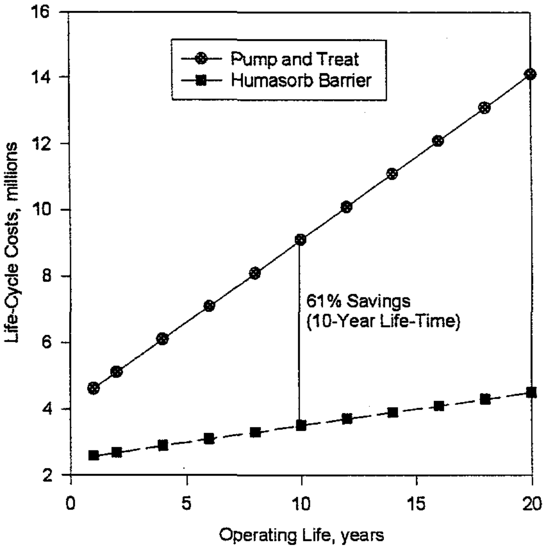
Oper. Costs 1: Annual Operating Costs for Water Treatment Rate of 30 million gallons per year
Oper. Costs 2: Annual Operating Costs for Water Treatment Rate of 57 million gallons per year

Figure 8.2. Life-Cycle Costs of HUMASORB™ Treatment System Compared to Conventional Approach for Surface Treatment



Conventional Process: Electrochemical treatment, filtration and clarification. Costs based on EPA Report 542-R-99-006
HUMASORB™ Process: Estimated Costs for water contaminated with multiple metals and organic compounds

Figure 8.3. Life-Cycle Costs of HUMASORB™ In-Situ Permeable Barrier System Compared to Conventional Approach for Groundwater Treatment



9.0 Feasibility Analysis for HUMASORB™ Application at DOE Sites

A large number of DOE weapons complex sites have soil and groundwater contaminated with mixed waste contaminants comprising of toxic organics, metals and radionuclides. A feasibility analysis was completed to identify the potential DOE sites for application of HUMASORB™. The analysis showed the broad applicability of HUMASORB™ for remediation of multiple contaminants present in various DOE waste streams. The results of the analysis are summarized in this section.

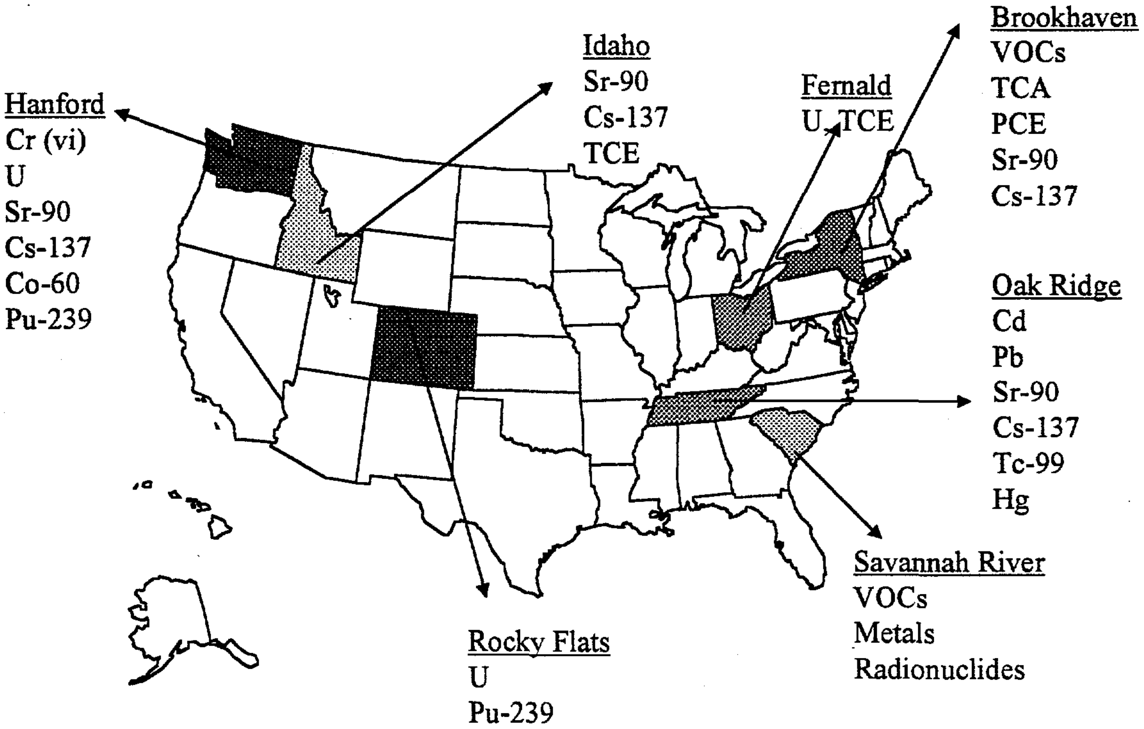
Contaminants at Waste Sites: The DOE estimates that more than 5,700 groundwater plumes have contaminated over 600 billion gallons of water and 50 million cubic meters of soil throughout the DOE complex. Mixed waste containing multiple hazardous and radioactive contaminants is a problem at a number of installations. The types of contaminants present at the sites include:

- Toxic metals such as lead, chromium, arsenic, cadmium, zinc, barium, nickel, copper, beryllium, mercury and others
- Organic chemicals such as benzene, toluene, xylenes, chlorinated hydrocarbons such as trichloroethylene, (TCE), perchloroethylene (PCE), energetic chemicals such as nitroesters and others
- Radioactive contaminants such as uranium, plutonium, thorium, cesium, strontium, technetium, tritium and others.

Decision Analysis for Remediation Technologies (DART): DART is a database developed at the Idaho National Engineering and Environmental Laboratory (INEEL) to provide analysis of the contaminants at various sites and the potential technologies for application. In addition, the database provides the cleanup criteria and goals, wherever applicable. The analysis of various sites represented in the database indicates that the waste streams are complex and contain multiple contaminants at a majority of the sites. The contaminants include metals, oxy-anions, radionuclides and organic compounds, including a number of chlorinated compounds. The cleanup criteria and the treatment requirements at the various sites indicates that HUMASORB™ technology is suitable for potential application at more than 90% of the sites in the DOE weapons complex.

DOE Sites for Potential HUMASORB™ Application: The analysis of the waste stream at various DOE sites was used to develop a short-list of potential sites for HUMASORB™ application. A few of the sites and the contaminants of concern at the sites are shown in Figure 9.1. The potential candidate sites identified in the figure for HUMASORB™ application contain metals, radionuclides and organic contaminants.

Figure 9.1. Potential HUMASORB™ Applications in the DOE Complex--A Few Selected Sites



9.1 Feasibility Analysis for Selected DOE Sites

HANFORD Site: Numerous DOE sites have high potential for application of a HUMASORB-CS™ Reactive Organic Barrier (ROB), including sites located in Pantex, Pinella, Fernald, Oak Ridge, INEL, Rocky Flats, Sandia, Savannah River, and Hanford. Of these candidate sites, the Hanford Site 100 Area is extensively characterized and key data for the site are published to enable engineering evaluations. Hanford 100 Area was therefore selected to illustrate the technical feasibility of engineering a ROB.

The interim remediation measures evaluated by the DOE at the site were: (1) no action, (2) institutional control/continue current action, (3) containment, (4) pump and reverse osmosis treatment and disposal, and (5) pump and ion exchange treatment and disposal.

None of the five options will remediate all of the plume contaminants. The two pump and treatment options will remove only selected contaminants. For example, the ion exchange treatment, the option selected by DOE, will remove only hexavalent chromium, zinc, and carbon-14. The other contaminants brought to the surface will therefore be re-injected into the plume. If the pumping operation continues, these same contaminants will ultimately be again extracted and re-injected. The ROB is a possible final site remedy at the Hanford 100-K area since it will remove all of the major plume contaminants.

The example ROB is compared with the existing Hanford pump and treatment operation in Figure 9.2. The specific ROB design used in this example is 5,000 feet in length, 3 feet in width, and with an active height of 30 feet. It is to be placed between the plume and the existing wells previously installed as a part of the interim remedial action plan. Information from these wells will provide a performance baseline and, at the same time, the wells will be used to monitor the performance of the ROB.

Pump-and-treat operations typically exceed 5 years in duration. Therefore, over an extended period, the ROB will generate significant cost savings as compared with the pump and treatment options. For example, assuming the ROB monitoring and maintenance will average $0.25 million per year, the 10-year life cycle savings will total $9 million, with the savings growing to $36 million if the ion exchange system continues to operate for 30 years. These costs and savings are summarized in Figure 9.3.

The ROB is designed to augment the natural attenuation of contaminants. Sufficient material will be emplaced to remediate all of the groundwater contaminants as compared with the Hanford interim remedial action that will treat only the chromium, zinc and carbon-14.

Fernald Site: HUMASORB™ is also suitable for application at sites where groundwater is treated on the surface. The cost benefit analysis for potential application of HUMASORB™ technology compared to conventional treatment approaches was performed using the Fernald, Ohio site as an example. An Advanced Wastewater Treatment System (AWWT) is used at the Fernald site to treat groundwater contaminated with uranium and TCE. AWWT is designed to treat a total of 1100 gallons per minute and uses activated carbon for the removal of TCE and an anion exchange resin is used to remove uranium.

Figure 9.2. HUMASORB™ Based ROB is a Viable Replacement for Pump and Treatment Operations

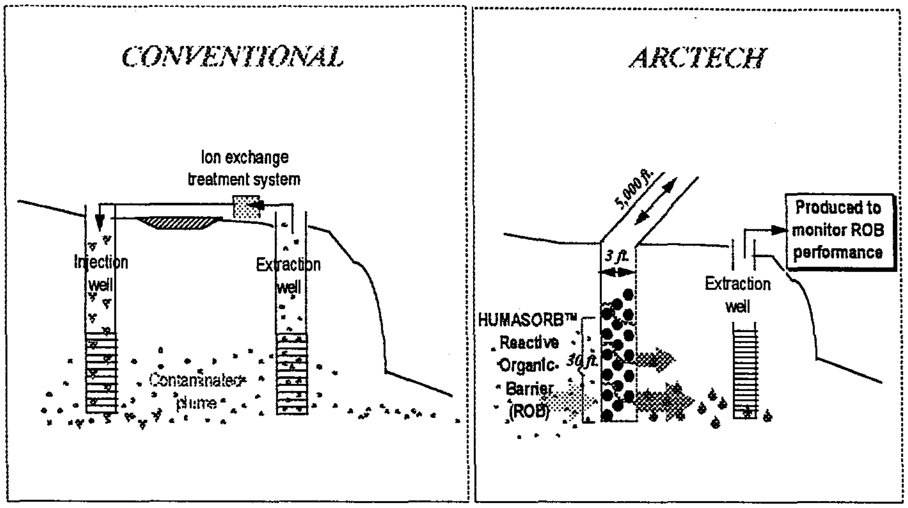
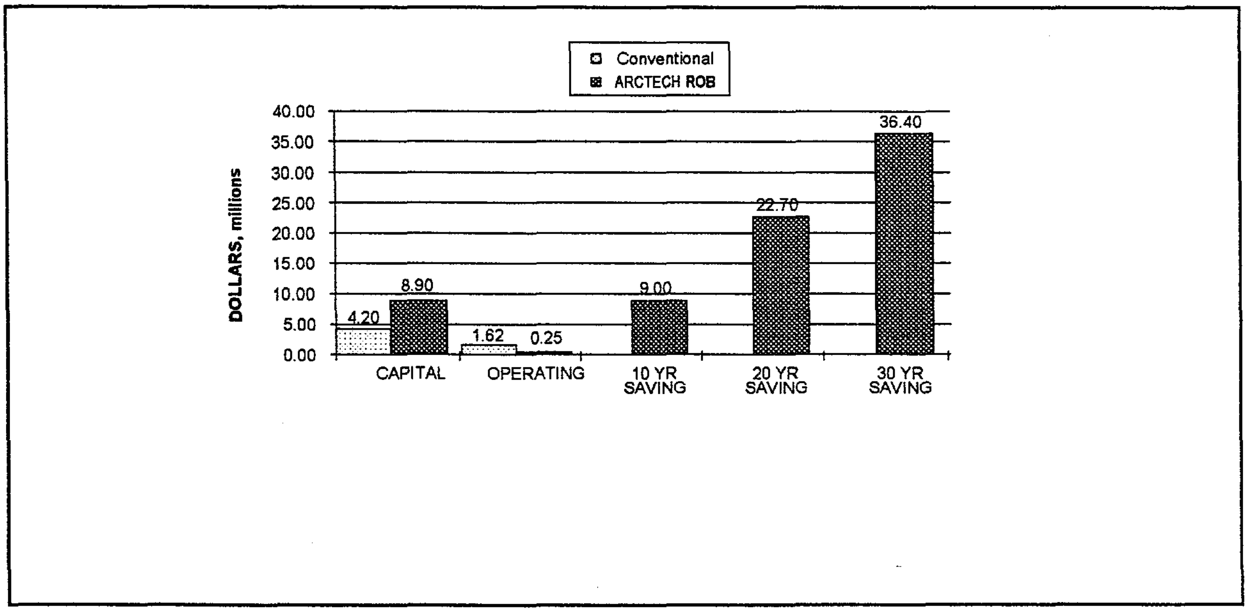


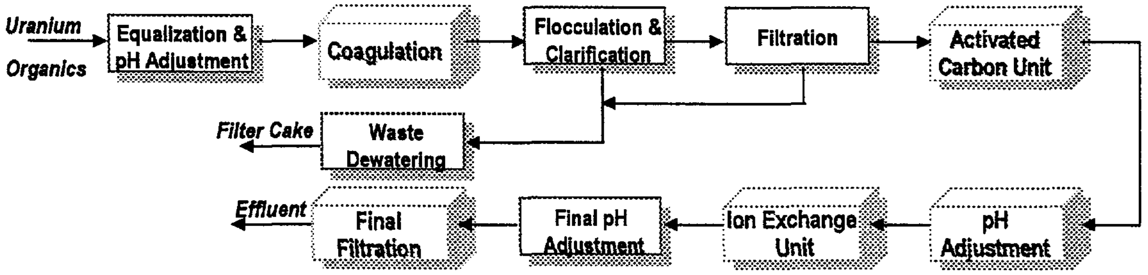
Figure 9.3. HUMASORB™ based ROB Will Generate Significant Life Cycle Cost Savings Over Conventional Approaches



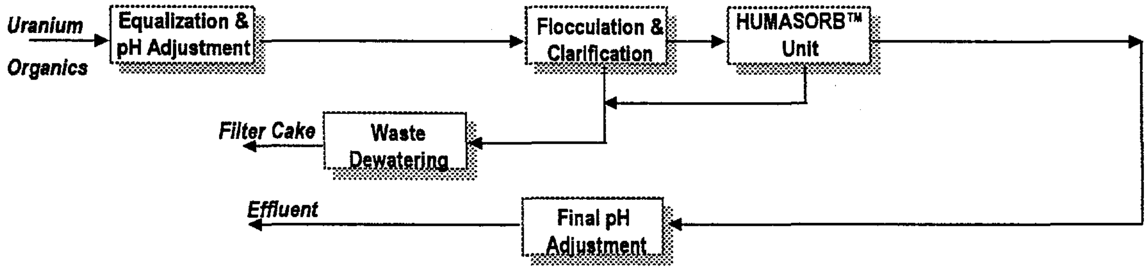
A HUMASORB™ based treatment system for the wastewater at the Fernald site would be simpler and result in significant cost advantages. The flow scheme and the unit operations in the existing AWWT are compared with a potential HUMASORB™ based system is shown in Figure 9.4. The use of a HUMASORB™ treatment system will reduce the number of processing steps because HUMASORB™ can removal multiple contaminants in a single treatment step. The capital and operating costs for the AWWT are compared with a HUMASORB™ treatment system in Figure 9.5. There are significant life-cycle cost savings with the use of a HUMASORB™ system as shown in Figure 9.5.

Figure 9.4. Comparison of Treatment Units in AWWT at Fernald Site with a HUMASORB™ Treatment System

Simplified Flow-Scheme for the AWWT at Fernald Site



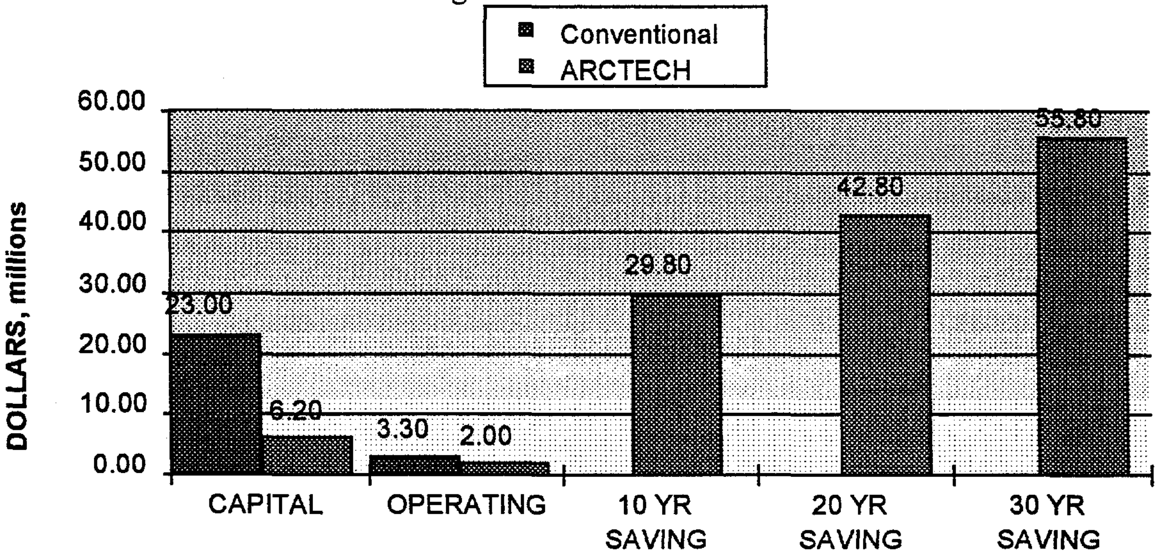
Simplified Flow-Scheme for a Potential HUMASORB™ Treatment System at Fernald Site



Oak Ridge Site: Tests were performed to establish the technical feasibility of the HUMASORB™ technology to capture and remove mercury from contaminated soils. The tests were performed with the multipurpose adsorbent HUMASORB-CS™. These tests were performed based on the data for soil contamination in the Y-12 Plant soil at Oak Ridge National Laboratory (ORNL). The mercury concentration in the Y-12 Plant soil ranges from 0 to 1000 ppm.

Test Description: A sand sample (300g each) was spiked with Hg (II) (up to 800 ppm) using mercuric chloride. The sand was divided into three portions (100 g each). To the first portion 10 g of HUMASORB-CS™ was added and mixed with the contaminated sand and then slurry packed in column # 1. In column # 2, 10 g of HUMASORB-CS™ was slurry packed at the bottom of the column, and 100 g of contaminated sand above it. The third portion of sand was used as a control, where only the contaminated sand was packed in column # 3. The tests were performed in glass columns (20 cm long and 2.5 cm diameter). 100-mL of water was passed through each column at a rate of about 2.0-mL per minute and were collected at the column outlet. In column # 2, water was first passing through the sand then through the HUMASORB-CS™. The collected samples were analyzed for mercury using ICP.

Figure 9.5. HUMASORB™ Treatment System is Cost-Effective Compared to the Existing AWWT at Fernald Site



Results: The results of the test are summarized in Table 9.1. The results confirm that HUMASORB™ is effective in capturing and containing mercury leached out from contaminated soil. The tests show that HUMASORB-CS™ can be deployed by mixing it with contaminated soil to capture and contain mercury that has been leached out. Alternatively, HUMASORB-CS™ can also be deployed by packing it into perforated pipes, which can be installed at an appropriate angle and depth so that the leached water will go through the pipes. After saturation of HUMASORB-CS™, these perforated pipes can be replaced with new ones.

Table 9.1. Mercury Removal from Contaminated Soil Using HUMASORB-CS™

Column Test #	Spiked Hg (II), ppm	Output, ppm
1 (HUMASORB-CS™ + Sand)	800	0.5
2 (HUMASORB-CS™)	800	0.2
3 (Control)	800	339

10.0 Conclusions and Recommendations

The objective of this project was to establish the applicability of a novel ion-exchange adsorbent polymer--HUMASORB™, which is based on the unique properties of humic acid for binding various types of contaminants. The goal of the project was to establish the potential for use of this economic and versatile material for use both in pump and treat systems and also for in-situ plume remediation.

Conclusions: The major conclusions from this project include:

- HUMASORB™, a humic acid based adsorber, is highly effective in removing multiple classes of contaminants such as metals, oxy-anions, organics and radionuclides from contaminated streams
- HUMASORB™ treatment systems are lower in capital and operating costs compared to conventional pump and treat systems and offer significant cost (50-60%) advantages
- HUMASORB™ is effective for application as a Permeable Reactive Barrier (PRB) material for in-situ treatment of groundwater. The use of HUMASORB™ in a PRB can result in life-cycle cost savings of 60%
- Metals are bound over a wide pH range. The cation-exchange capacity of HUMASORB™ is very high and can range between 1-5 meq/gram depending on the metal compared to 1-2 meq/gram for many ion-exchange resins
- Organic contaminants are adsorbed and removed from contaminated water. Chlorinated compounds are adsorbed and potentially reduced to less toxic compounds
- Toxic metals present as anions (such as hexavalent chromium) are reduced to less toxic state and removed from water
- HUMASORB™ is stable in the presence of anions such as sulfate, carbonate and in the presence of microorganisms. HUMASORB™ is stable up to pH 12
- HUMASORB™ is available in liquid and solid forms. The solid form can be regenerated easily for reuse
- HUMASORB™, in the solid form, has a particle density of approximately 1.6 gm/cc and a bulk (or packing) density of approximately 1.0 gm/cc)
- The projected cost of HUMASORB™ is estimated to be approximately $ 1/lb compared to commercial ion-exchange media which range from $3/lb to $135/lb or higher for very selective resins

- HUMASORB™ treatment systems have been demonstrated to be effective for various applications such as treatment of acid mine waters and removal of metals from waste brines.

Recommendations: The recommendations from the project activities include:

- Develop a pilot-scale system for production of HUMASORB™ with smaller particle size to further enhance contaminant removal efficiency and treatment costs
- Demonstration and deployment of a HUMASORB™ pump and treat system for treatment of mixed waste stream in the DOE complex
- Demonstration and deployment of a HUMASORB™ permeable reactive barrier for in-situ treatment of groundwater containing multiple contaminants.

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APPENDIX

HUMASORB™ TECHNOLOGY TREATABILITY & DEMONSTRATION AT CONTAMINATED SITES

HUMASORB™ technology is being evaluated for deployment at a number of contaminated sites under separately funded contracts. The evaluation includes conducting treatability tests for applications at three DOE sites (Savannah River site, Idaho National Engineering & Environmental Laboratory and Rocky Flats). The HUMASORB™ water treatment technology was adapted to the recovery of resource values from industrial sites (Berkeley Pit and Iron Mountain). Technology application studies using HUMASORB™ process on Spent Decontamination Solution (SDS) and brine samples received from Johnston Island. ARCTECH successfully completed treatment of approximately 24,000 gallons of SDS that contained RCRA hazardous levels of arsenic, lead and mercury. A brief description of the projects is included in this section.

Savannah River Site

The project was conducted using contaminated groundwater from the D-Area Coal Pile Runoff Basin at Savannah River site. The objective of the project was to establish the technical and economic feasibility of the HUMASORB™ technology to remove metals from contaminated groundwater and, simultaneously, recover the metals as a micronutrient for stimulating plant growth. The D-Area Coal Pile Runoff Basin groundwater sample was selected to demonstrate this new process. This Basin, located on the Savannah River Site, has a contaminated groundwater plume identified for treatment by the DOE. Groundwater sample from this basin was collected by the Westinghouse Savannah River Company (WSRC) and supplied to ARCTECH for this project. The D-Area groundwater is highly acidic (pH 1.8), contaminated with metals, and is high in sulfate concentration. This groundwater was treated with HUMASORB-L™ to form a iron humate complex. The iron humate complex was then formulated into *actosol*® for use as a plant growth enhancer. The details of the test conditions are provided in the final report titled "ARCTECH/FESCO PERFORMANCE TEST FOR SAVANNAH RIVER SITE GROUNDWATER REMEDIATION" which was submitted to WSRC in July 1997.

The HUMASORB™ technology is integrated into a single step process to remove metals from the D-Area groundwater, producing a valuable fertilizer product and clean water. The process flow is simple and straight-forward. First, the contaminated groundwater was rapidly mixed with HUMASORB-L™. Flocs were created by this mixing step whereby iron and other valuable micronutrients were removed from solution. Solids were separated from the liquids. The solids were formulated into actosol®. The liquids were passed through a filter for polishing prior to the release of the clean liquids.

The bench scale treatability test of the first task of this project was successfully completed and the test results verify the process design as a sound and effective way to convert contaminated water to clean water plus a useful fertilizer by-product. Comprehensive material balance calculations were made for each test. Over 95 percent of the material flow was accounted for in the bench-scale tests.

A comprehensive economic analysis for the capital and operating costs for the construction and operation of a 35 gpm (50,000 gallon per day) mobile unit was conducted. Capital costs are estimated at $410,000 and operating costs at $1.3 million per year. Revenues generated are based on a conservative product value. Using these assumptions, the net present value discounted at 10 percent is $908,000, or $471,000 in after-tax income. The commensurate internal rate of return is 35 percent before taxes and 23 % after taxes. Investment payback is 2.6 years using pre-tax dollars, or 3.8 years using after-tax income.

Idaho National Engineering & Environmental Laboratory Site

The project was conducted to establish the technically feasibility of HUMASORB-CS™ to remove the radioactive (hot) contaminants such as radioactive cesium and strontium from contaminated groundwater's at Idaho National Engineering & Environmental Laboratory (INEEL). Groundwater remediation efforts at INEEL are primarily focused at the Groundwater Treatment Facility (GWTF) near the TSF-05 injection well located at Test Area North (TAN). The decontamination of the water at GWTF was insufficient due to the presence of radioactive contaminants such as ^{137}Cs detected at higher concentrations than originally planned. HUMASORB-CS™ was evaluated in this project as a potential candidate radionuclide removal technology for ^{137}Cs and radioactive strontium^{85}Sr. The details of the test conditions are provided in the final report titled "ASSESSMENT OF A NOVEL HUMASORB-CS™ ADSORBENT FOR REMOVAL OF HOT CONTAMINANTS FROM DEPARTMENT OF ENERGY WASTE WATER" which was submitted to Global Environment & Technology Foundation in January 1998.

The tests with HUMASORB-CS™ were conducted in two phases. In the first phase, bench scale cold tests were performed at ARCTECH using simulated waste streams containing the contaminants present in the TAN groundwaters. The results from the column tests conducted at ARCTECH were used to design columns and establish treatment parameters for column tests with groundwater containing radioactive contaminants at INEEL.

The column tests conducted at INEEL show that HUMASORB-CS™ removed both ^{137}Cs and ^{85}Sr. The column breakthrough curves show ^{137}Cs breakthrough after approximately 100 bed volumes (assuming breakthrough at 5% of the input). The column was saturated with ^{137}Cs after nearly 600-700 bed volumes. In the case of ^{85}Sr, breakthrough did not occur until nearly 250 bed volumes had been passed through the column. The column was only 25% saturated with ^{85}Sr after nearly 700 bed volumes. The results show that HUMASORB-CS™ can effectively remove both ^{137}Cs and ^{85}Sr.

HUMASORB-CS™ is the only material other than IONSIV-IE911 (CST) evaluated by INEEL to date that is effective in removing both radioactive cesium and strontium. The results from the tests conducted in this project were compared with the results with CST. The amount of ^{137}Cs adsorbed per gram of the adsorbent is nearly two orders of magnitude higher with HUMASORB-CS™ compared to CST. In addition, HUMASORB-CS™ is significantly less expensive (with a projected commercial production costs of less than $ 1/lb) compared to CST (more than $ 135/lb).

Rocky Flats: Sandia National Labs evaluated HUMASORB-CS™ for application at Rocky Flats site. HUMASORB-CS™ was very effective for removal of multiple contaminants such as uranium, antimony and thallium in the column tests conducted with synthetic groundwater that was similar to the contaminated groundwater in the mound area of the Rocky Flats complex. HUMASORB-CS™ was more effective in removing the contaminants than the other media evaluated by Sandia National Laboratories.

Berkeley Pit Project

This project demonstrates that the HUMASORB™ technology can effectively translate new innovations into useful industrial applications. In this project, the HUMASORB™ water treatment technology was adapted to the recovery of resource values from a Superfund site. This project was undertaken to demonstrate the ability of the HUMASORB™ technology to remediate the waters of the Berkeley Pit.

This process consists of two stages. In stage one the acid mine drainage water of Berkeley Pit was treated with HUMASORB-L™ to remove iron and copper by formation of the humates, which was precipitated as flocs. The precipitated complex was easily separated from the water by a centrifuge. Metals remaining in the water from this stage and all the other toxic metals were removed in stage two using the water insoluble ion exchange material HUMASORB-CS™. The specific objectives were to remove heavy toxic metals (cadmium) while producing a chelated micronutrient-enriched fertilizer product for agriculture applications. In the bench scale demonstration, nearly 98% of the copper and iron in the Berkeley Pit water was captured for use as fertilizer micronutrients along with other important micronutrients (zinc, manganese, and magnesium). Toxic heavy metals (cadmium) were removed to levels below the detection limit of the standard laboratory tests before the water was discharged. The details of the test conditions are provided in the final report titled "RESOURCE RECOVERY OF BERKELEY PIT WATERS WITH THE ARCTECH HUMASORB-L™ TECHNOLOGY " which was submitted to MSE Technology Inc. in June 1996.

The *actosol*® Chelated Plus Iron fertilizer produced in this treatability study was evaluated by the Department of Plant, Soil, and Environmental Science at Montana State University. Wheat and alfalfa each responded with increased yield (biomass) of 30 to 50 percent at an application rate of 5 gallons/acre. The incremental benefits to the grower was estimated by University researchers to be $100/acre for wheat and $140/acre for alfalfa. Overall, the fertilizer enhanced with micronutrients from the Berkeley Pit waters is judged to be a promising material for agriculture use in Montana.

Treated water from the HUMASORB™ process could be potentially used for agricultural and irrigation applications. Toxic metals were below detection limits and the treated water contains nutrient metals (i.e., manganese and potassium) useful for plant and crop growth. Moreover, the pH of the treated water was about 5.5, a level suitable for agricultural applications.

This two-stage process was selected for scale up and demonstration. The bench scale treatability tests results produced the technical information needed to complete the equipment needed for the process demonstration unit. The unit is designed to treat 5 gpm (~7,000 gpd) of Berkeley Pit water. The equipment will be mounted to the mobile unit and then shipped to Butte, Montana for the process demonstration.

Iron Mountain Site

Contaminated water from this site was evaluated for treatment with HUMASORB-L™. The preliminary test results indicate that the concentration of most toxic metals in the treated water was either below detection limit or undetected. The results also indicate that the agricultural micronutrients present in the contaminated water can be recovered and formulated into ARCTECH's commercial products.

Johnston Island Project

The objective of this project was to treat approximately 33,000 gallons of Spent Decontamination Solution (SDS) at Johnston Island (JI) using ARCTECH's HUMASORB™ mobile unit and technology. UXB International completed the transfer of liquid wastes consisting of SDS from aging one-ton containers to 6,000-gallon ISO containers at Johnston Island. All of the wastes were analyzed for residual chemical agent and were found to be below the drinking water standards (DWS) for all agent types. However, much of the waste was found to contain levels of the metals, arsenic, lead and mercury exceeding those mandated under the Resource Conservation and Recovery Act (RCRA).

The original plan for treatment of the SDS was incineration. Two of the ISO containers (approximately 9,000 gallons) did not contain metals above the RCRA regulatory limits and could be incinerated at the Johnston Atoll Chemical Agent Disposal System (JACADS). However, the remaining 24,000 gallons (four ISO containers) of liquids could not be treated at JACADS because of the current RCRA permit limitations on the processing of such material.

The Program Manager for Chemical Demilitarization (PMCD) was asked by the U.S. Environmental Protection Agency (USEPA) to consider treatment of the liquid waste by some alternative technology to reduce the metals concentration to below the regulatory hazardous levels. ARCTECH conducted technology application studies using it's HUMASORB™ process on SDS samples received from Johnston Island. The results from the batch and column tests conducted by ARCTECH showed that the levels of arsenic, lead and mercury were below the RCRA treatment levels. The process was subsequently selected by the PMCD as a viable alternative for removal of the metal contaminants from the SDS waste based on the initial technology applications tests. ARCTECH was contracted by UXB International on behalf of PMCD and authorized to mobilize a process unit to treat approximately 33,000 gallons of SDS at Johnston Island. ARCTECH undertook minor modifications for the HUMASORB™ process mobile unit for treatment of SDS at Johnston Island. A filter press and a bag filter were incorporated into the treatment process train and shipped to the site.

ARCTECH successfully completed treatment of approximately 24,000 gallons of SDS that contained RCRA hazardous levels of arsenic, lead and mercury. The treated SDS was analyzed and concentrations of the toxic metals were determined to be below the required regulatory mandated levels. In addition, ARCTECH successfully processed an additional 10,000 gallons of SDS for solids removal. This project activity was completed ahead of schedule and all analytical activities for regulatory compliance were completed by an approved independent laboratory.

The successful treatment of SDS at Johnston Island clearly shows the benefits of the HUMASORB™ process for metals removal from brine solution. The successful treatment showed that the process can be implemented easily at various chemical agent disposal facilities under the jurisdiction of PMCD to not only treat SDS, but as a potentially effective and viable option for in-line treatment of waste brines generated at chemical agent disposal facilities.

Contaminants Removal from Brine Wastes

ARCTECH has successfully completed the evaluation for the treatment of brines received from Johnston Island (JI) using HUMASORB™ technology. The brines generated during the destruction of chemical warfare agents are complex and contain multiple toxic metals contaminants in cationic and anionic forms. In addition, the high concentration of sodium coupled with the suspended solids content in the brines present a challenge to selectively remove the metals using conventional treatment systems such as ion-exchange, membrane treatment or chemical precipitation. First, the suspended solids present in the brines require the use of a solid-liquid separation unit such as a filter press. Second, the presence of various metals in cationic and anionic forms requires the use of multiple resins and/or membranes to treat the brines, thereby increasing the complexity and cost of treatment. In contrast, the treatment studies show that the HUMASORB™ system can overcome the challenges of brine treatment.

The four brine samples received from JI were treated with HUMASORB-L™, a liquid form of HUMASORB™. The concentration of various metals, sodium concentration, pH and other characteristics of the four brines samples represent the broad range of brines generated during the destruction of chemical warfare agents. The four brine samples received at ARCTECH were analyzed for total metals, dissolved metals, total suspended solids content, settling characteristics, density and pH before treatment. One of the brine samples (# 6309), identified as typical brine was tested extensively after spiking with higher concentrations of metals such as chromium, copper, silver and vanadium and used in detailed tests.

The tests with HUMASORB-L™ using the spiked brine sample were conducted using a factorial experimental design approach and the results were analyzed statistically. The objective of the tests was to identify the optimum values of the process parameters such as pH, contact time and HUMASORB-L™ dosage. The analysis included development of surface and contour plots for various values of the parameters and regression analysis to help predict HUMASORB™ system performance as a function of the various parameter values. There was good agreement between the observed and predicted values from the regression analysis. The optimum conditions for the treatment of brines were identified based on the statistical analysis as pH of 4.5-5.0, contact time of five (5) minutes and HUMASORB-L™ dosage of 1% by wt. of the brine.

The confirmation tests were then completed using the optimum values of the parameters. The confirmation tests were conducted with the four brines samples received from Johnston Island and also with the spiked brine sample # 6309. The results of the confirmation tests were also analyzed independently by the Raytheon Laboratory in

Pennsylvania. The results show that the concentration of all the contaminants were reduced below the identified target limits in all of the tests.

There are a number of significant advantages to deploy a process based on HUMASORB-L™ for treatment of brines to remove multiple metals at Johnston Island. The advantages include:

Lower Cost: HUMASORB-L™ is a coal-derived liquid humic acid product, and is a low cost material. The production of HUMASORB-L™ does not require the use of various cross-linking and encapsulating chemicals and is therefore lower in cost compared to solid form, HUMASORB-CS™, that was used for treatment of Spent Decontamination Solution (SDS) at JI. This will result in a lower cost per unit of the active component and a lower processing cost for brine treatment compared to what was expected for brine treatment using HUMASORB-CS™.

Lower Waste Residuals: The amount of waste residuals generated is minimized by the use of HUMASORB-L™. The optimum dosage of HUMASORB-L™ has been identified as 1% by wt. of the brine treated. The lower dosage is effective because of the high capacity of HUMASORB-L™ for metal removal. HUMASORB-L™ incorporates the property of humic acid to bind multiple metals strongly. The metals stay bound to the humic acid complex, even as the humic acid precipitates from solution due to pH adjustment. Thus the amount of waste residuals will be lower than what was expected initially from the use of the solid HUMASORB-CS™.

Meets Treatment Criteria: HUMASORB-L™ is effective to treat the brines for metal removal to meet the requirements set by the permit at Johnston Island. The results show that the HUMASORB™ process is effective for various types of brines generated by the destruction of chemical warfare agents.

Simple Process: The process to remove multiple metals from the brines using HUMASORB-L™ is a simple and effective process, which can be operated by one person with minimal training. The steps in the treatment scheme include chelation/complexation and binding of the contaminants by HUMASORB-L™, followed by separation of the suspended and precipitated solids. The pH is adjusted to the desired level before separation of the solids using a filter press. The use of a filter press is not an additional unit operation that is unique to the HUMASORB™ treatment system. Any ion exchange and/or membrane treatment system would require the use of a solid-liquid separation unit such as a filter press.

Conclusions

HUMASORB™ technology has been successfully evaluated in bench-scale treatability tests using actual contaminated groundwater and on-site for remediation of complex waste streams. The results from these tests validate the results from the tests conducted with simulated waste streams during HUMASORB™ development.