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In Situ Removal of Cadmium and Chromium from Groundwater Using ZeoTech Reactive Barriers

Final Report

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Project Summary

In this wok, it was demonstrated that it is economically and technically feasible to transform fly ash into a heavy metals (Cr and Cd) removing material. The objective of the research was to Alkali Fly Ash Permeable Reactive Barrier (AFA-PRB) Material to filter cadmium and chromium from contaminated water for use as an in-situ groundwater remediation material. The technology combines the recycling of an underutilized raw material, fly ash, with solving a difficult environmental problem, groundwater contamination.

AFA-PRB materials were fabricated with permeability ranging from 10^{-1} cm/sec to 10^{-4} cm/sec was created. 10 ppm and 1000 ppm of Cd and Cr were passed through the contamination barriers with various permeabilities. AFA-PRB material with permeability of 10^{-1} cm/sec was able to remove 99% of the heavy metals from solution. AFA-PRB materials were made with and without the addition of zeolite to determine if zeolite addition would improve the sorption ability of the barrier. AFA-PRB material with zeolite inclusion did not improve the removal of heavy metals from permeating solution.
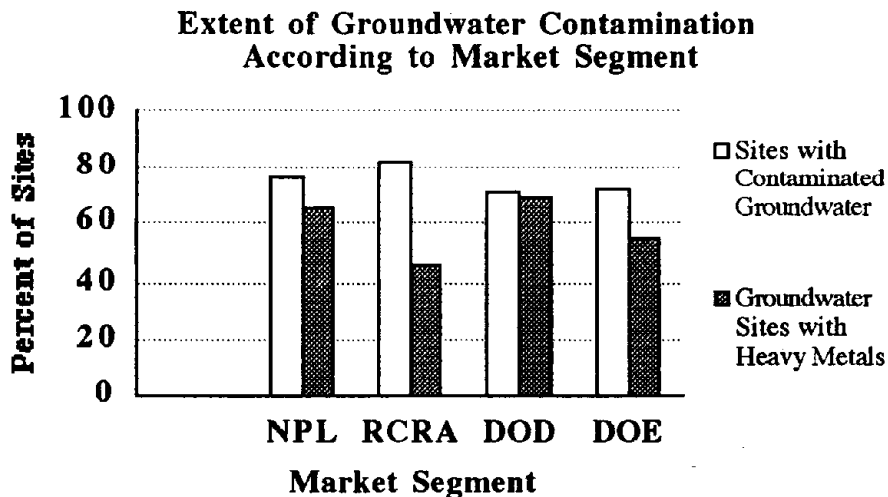
Potential applications of the technology are currently focused on in-situ groundwater remediation. The cost of the product is driven by the logistics of high volume material transportation. In general, the economics are very encouraging given use of non-saleable fly ash and commodity chemicals and the low cost of the processing.

Background and Significance

Need for Remediation of Contaminated Groundwater

There are over 200,000 contaminated sites in the United States which require remediation for an estimated cost of $ 200 billion (minimum), in 1999-2000 dollars and can take from 10 to 30 years or even longer. Groundwater contamination is involved in over 70% of the sites and of those, over 50% contain heavy metals contaminants as shown in Figure 1 [1].

Figure 1: Groundwater and Heavy Metal Contamination According to Market Segment.

Heavy metal pollution of ground water is an extremely serious environmental problem and a costly one to remediate. The Environmental Protection Agency is interested in new technologies which can economically and effectively remove heavy metals from groundwater or wastewater. Opportunities exist for adapting theoretical ideas in science to real world problems by developing the necessary technology.

Heavy Metal Contaminants

Groundwater polluted with heavy metals is perhaps the most dangerous because of the difficulty in treatment and the large percentage of the population which must rely on groundwater for consumption. The most frequently found metal contaminants are lead, zinc, barium, nickel, chromium, cadmium, and copper [1]. The effect on human health of several heavy metals is summarized in Table 1.

Table 1: Heavy Metal Contaminants in Wastewater

Metal	Species	Toxicity [2,3]
Cadmium	Cd (II)	Anemia; kidney damage; itai-itai, a skeletal disease. Elimination half-life may be as long as 30 years.
Chromium	Cr(VI), CrO_4^{2-}	Some Cr(VI) compounds are suspected carcinogens. Long term exposure can cause tubular proteinuria.
Lead	Pb(II)	Plumbism---lead poisoning
Arsenic	AsO_3^{3-} arsenite As (III) $As (V) AsO_4^{3-}$ arsenate As (V)	As(III) is the most toxic due to its ability to bind to sulfhydryl groups; As(V) can be reduced in the body to As(III).
Mercury	CH_3HgX (X is Cl or OH) $(CH_3)_2Hg$ $Hg°$, Hg(II)	Inorganic mercury (II) accumulates in the kidney. H_3HgX, is a more potent toxin than Hg salts because it accumulates in the fatty tissues of animals

The Phase I proposal concentrated on the development of barrier material from fly ash and tested for removal of two of the metals, cadmium, and chromium. Cadmium is used in industry in alloys and metal plating and chromium is produced from mines, quarries, metal-plating, welding, dye, and explosives [2]. However, the technology developed in the Phase I investigation with the current barrier material is not limited to these metals and was demonstrated to be applicable to a wide range of heavy metals. Phase II will extend and optimize the material development from fly ash and demonstrate its suitability for making pilot scale size barrier for emplacement in contaminated sites.

Background/Technical Approach
Permeable Reactive Barriers (PRB's)

Over 90% of the groundwater treatment strategies involve pump and treat remedies only. [1] Pump and treat can be effective in certain geologic and hydrologic situations with appropriate design, however, it is costly and labor intensive. Limitations of the pump and treat method have recently been recognized by the EPA and the National Research Council [1]. These studies cite in-situ groundwater remediation as the area most in need of innovative solutions.

A promising new emerging technology that can reduce the cost and increase the effectiveness of in-situ remediation of groundwater is the use of permeable reactive barriers (PRB's). PRB's are filled with reactive material to intercept and to decontaminate plumes in the subsurface. Permeable treatment walls are installed as permanent, semi-permanent, or replaceable units across the flow path of a contaminant plume. Natural gradients transport contaminants

through strategically placed treatment materials. See Figure 2 which shows a continuous plume flowing through a PRB.

In 1994, the first commercial application of permeable reactive barrier technology was installed in Sunnyvale, followed by at least a dozen other full-scale industrial facilities. The Sunnyvale installation is still operating and has proven itself in terms of cost effectiveness compared to pump and treat remediation. Most current full-scale PRB's are used for removal of chlorinated hydrocarbons and iron as the reactive material. However, a considerable amount of laboratory and field research has shown that many other trace metal contaminants could also be treated by selection of an appropriate reactive material. The prospects for PRB's as a cost effective alternative to pump and treat remediation are excellent.

The technology described here reduces the cost even further by constructing PRB's from fly ash, a product of the combustion of coal that would otherwise have to be landfilled. Phase I studies have already demonstrated that activated fly ash PRB's remove metals such as chromium and cadmium from contaminated water.
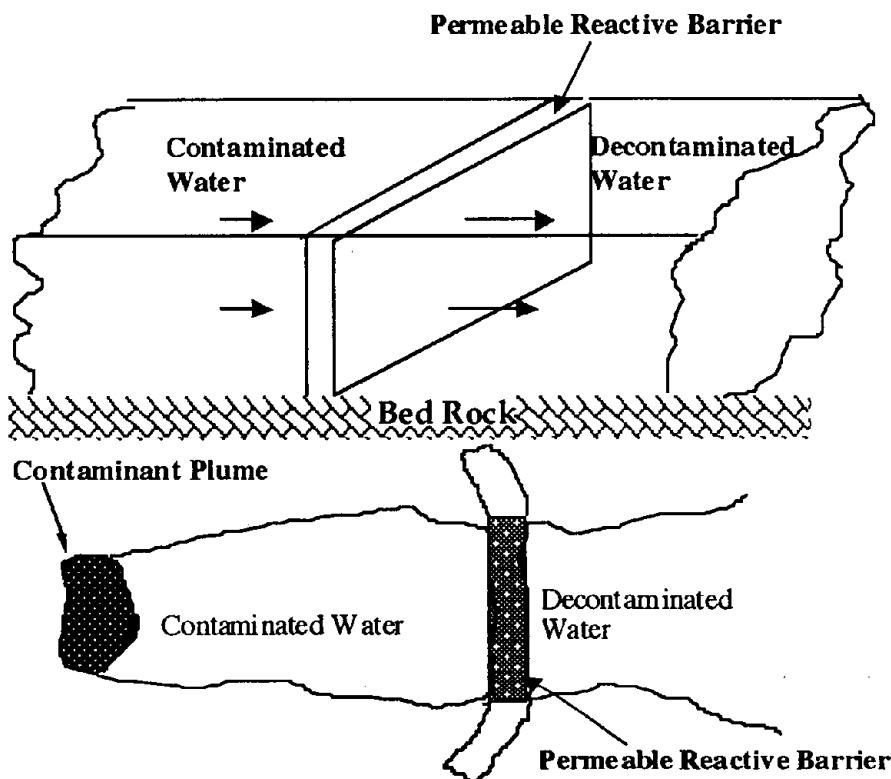

Figure 2: Diagram of a Permeable Reactive Barrier

Reactive Materials in PRB's

As contaminants move through the PRB material, reactions occur that transform them to less harmful or immobile environmentally acceptable species [4]. The reactive material in the PRB degrades, precipitates, or removes chlorinated solvents, metals, radionuclides, and other pollutants. These barriers may contain agents such as chelators for immobilizing metals. There exists a large body of literature on materials used in PRB technology. In general, the materials must cause no adverse chemical reactions nor produce any additional contaminants. They should have a long life-time and be available at low cost.

The materials are typically pelletized to provide relatively low head loss, ease of handling, and resistance to clogging. Pelletization can be carried out with relatively simple equipment. Drawbacks to this are difficulty in retrieval, limited depth of emplacement, and reduction in actively sorbing surface area. The various types of materials include clay minerals, synthetic zeolite from fly ash, organics, zero valent iron and metal oxides. (See Table 2)

Cost and effectiveness vary widely in laboratory scale experiments. Each material has advantages and disadvantages for certain applications. A considerable amount of effort is underway to investigate new inexpensive materials which can be used to create more effective PRB's with new functions.

Development of PRB material from activated fly ash (AFA-PRB's) with properties suitable for remediation of heavy metals has been demonstrated in the Phase I project for cadmium and chromium. .

Table 2: PRB Materials

Material (Ref)	Metal	Efficiency	Disadvantages
Zeolite Fly Ash [5-7] (Alkali Activated)	Cd	100 ppm reduced to 10 ppm @ pH 6 to 70 ppm @ pH 4	Cation removal disappears @pH <4; fine and powdery causing handling problems
Zero Valent Iron [8,9] [Fe° or Fe(0)]	U, Cr	1.24 ppm reduced to 0.02 ppm	Complex mechanism, pH dependent; large quantity needed
Pelletized Fly-Ash (High temperature activation) [10]	Cr	0.0254 meq/g	Expensive (forming pellets requires calcination at 400°C for 24 h), interference of sulfate, sulfide and cyanide, ineffective for Cr(VI) > 100 ppm
Clay Materials [11]	Cr	0.05 meq/g	Capacity decreases as pH decreases, from 20 ppm rate is slow, interference by Ca and Na cations
Zeolite Fly Ash [12]	Co	1.47 meq/g from 3000 ppm @ pH 1	Zeolites formed are unstable and collapse at low pH
Natural Zeolites [13, 14]	Sr	0.21 ppm reduced 0.002 ppm	Suitable only for low concentrations; < pH 5, negligible efficiency
Ferric [15-17] Oxyhydroxide, Lime, Gypsum, and others	U, Cr	20 ppm to 0.1 ppm @ pH 7	Below pH 5, negligible efficiency @ high pH. Most metals are insoluble, thus sorption of ferric oxyhydride is limited.
Activated Carbon [18]	Cd	10 ppm	Adsorption interfered with by Ca and Na, to almost zero effective at pH < 3
Red Mud and Fly Ash- Untreated [19]	Cu	10,000 ppm to 600 ppm	Adsorption capacity dependent on the insolubility of metal hydroxide. Ineffective @ low pH
AFA – PRB Phase I of Current Project.	Cd, Cr	1,000 ppm to 0.1 ppm	New and under investigation

Activated Fly Ash Permeable Reactive Barriers (AFA-PRB's)

In this work, permeable reactive barriers made from alkali activated fly ash (AFA-PRB's) are used to remove heavy metal ions from contaminated water. The material utilized in Phase I was made from fly ash consisting of fine particulates gathered from the flue gases of coal combustion. The particles have an average diameter of 20μ and range in size from less than 1μ to 100μ.

Fly ash has been used for the past four years in the production of AFA-PRB cementitious material [20-24]. There are two basic types of fly ash materials based on ASTM C 618:

Class C Fly Ash: Total SiO_2, Al_2O_3, Fe_2O_3 Content > 50% and < 70%
Class F Fly Ash: Total SiO_2, Al_2O_3, Fe_2O_3 Content > 70%

These classifications are an indication of the activity of the fly ashes. Class C fly ash typically originates from lignite coal and has a high calcium content. Class F fly ash originates from bituminous and subituminous coal and has a low calcium content. Oxide compositions of Class F and Class C fly ash are given in Table 3.

Table 3: Composition of Class F and Class C Fly Ash

Oxide Formula	% Oxide Class F	% Oxide Class C
SiO_2	45-59	20-40
Al_2O_3	15-34	8-15
Fe_2O_3	4-26	8-20
CaO	1-15	18-50
Na_2O and K_2O	1-8	2-8
MgO	1-2.5	1-5
Trace Metals	0.5-15	<4

In general, Class C fly ash has cementitious properties upon exposure to water whereas Class F fly ash does not. These classifications are not an entirely accurate description of the materials used in the investigation. Fly ash which meets ASTM C 618 standards has a market value and is bought and sold like a commodity product. Less than 30% of fly ash is recycled according to the American Coal Ash Association. The majority of fly ash needs to be landfilled because it does not meet consistency or performance requirements. Table 4 (on the next page) gives oxide content and sources of a selection of Class F fly ash materials used in the Phase I project. These are examples of materials which are *not* currently usable in portland cement concrete such as concrete pavement, and are landfilled.

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Table 4: Composition of Class F Fly Ash Materials from selected sources.

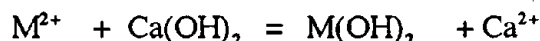| Ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Na_2O	LOI	Si+Al+Fe
Mojave	62.6	22.9	5.6	3.2	0.13	0.81	0.32	91.1
Gifford Hill	58.5	24.0	8.5	4.9	0.65	1.16	0.43	91.0
Hatfield	58.5	24.0	8.5	4.9	0.65	1.16	0.43	91.0
Ft. Martin	52.7	29.8	10.7	3.2	0.70	0.50	1.5	93.2
Montour 1	49.1	28.4	14.9	1.60	0.44	0.56	2.82	92.4
Montour 2	49.1	28.4	14.9	1.60	0.44	0.56	4.00	92.4
Miliken	45.4	23.7	18.0	4.00	0.83	0.65	3.16	87.1
PSEG&G 1	43.0	22.5	15.3	9.10	1.40	2.80	2.9	80.8
PSEG&G 2	43.0	22.5	15.3	9.10	1.40	2.80	4.9	80.8
Seward 1	49.1	24.8	17.1	1.8	0.09	0.37	4.0	91.0
Seward 2	47.0	23.0	21.4	2.1	0.03	0.39	14.0	91.4
FMC 1	53.5	11.9	17.1	17.3	1.9	1.3	1.1	82.5
FMC 2	49.1	16.7	6.9	16.2	1.7	1.25	0.44	72.7

Properties and chemical composition of fly ash, a product of coal burning operations, vary according to coal source and power plant operation. Thus fly ash varies from one part of the country to another. Fly ash used in this project was obtained from dozens of locations across the country. Based on the composition of the fly ash, there are a number of mechanisms which can be employed to remove heavy metals from solution. This variability makes activated fly ash barrier material even more versatile. By varying the ash type, different types of contamination can be removed.

Mechanisms for heavy metal removal

Knowing the dominant mechanism (or mechanisms) for removal of a given contaminant can be of value in many ways. Efficiency in removal of the contaminant can be optimized. In addition, mechanisms may suggest methods for increasing the longevity of the barrier (other than electrolytic recovery techniques which are impossible for Ni(II) and other metals with low reduction potentials). Brief descriptions of possible mechanisms for PRB materials are given below, including any associated recovery methods.
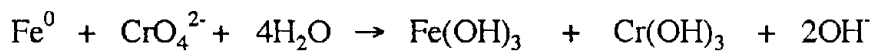
a. *Chemical Precipitation*

Heavy metals (M) can be chemically precipitated as insoluble nontoxic materials such as metal hydroxides. For this the most commonly used agent is calcium hydroxide:

$$M^{2+} + Ca(OH)_2 = M(OH)_2 + Ca^{2+}$$

Efficiency of the hydroxide precipitation depends on influent metal concentration, pH and the presence of competing metals. In addition, small particles of hydroxide precipitate may pass through the barrier. Coprecipitation can prevent this by adsorption of soluble ions of other metals onto precipitates. For example, the addition of aluminum salt in the hydroxide precipitation of arsenic can achieve optimum removal of arsenic by coprecipitation with aluminum hydroxide (at a pH close to 7).

Precipitation of chromium hydroxide requires pretreatment to obtain the Cr(III) ion. For example, oxidation-reduction precedes the precipitation of chromium hydroxide in PRB's that contain Fe(0) or Fe(II). The contaminant Cr(VI) in the form of chromate, CrO_4^{2-} is reduced by the iron.

$$Fe^0 + CrO_4^{2-} + 4H_2O \rightarrow Fe(OH)_3 + Cr(OH)_3 + 2OH^-$$
The Cr(III) is immobilized as the hydroxide [4,8].

b. *Solidification/Stabilization (S/S)* :
S/S uses binders and additives to reduce the mobility and toxicity of contaminants by limiting their solubility [25]. Inorganic binders include Portland cement, Portland cement/fly ash, Portland cement/soluble silicates, lime/fly ash, Portland cement/lime, and Portland cement/clay. It is not necessary for solidification to involve a chemical reaction between the contaminants and the solidifying agents. Solidification processes convert waste to a solid form by encapsulating the waste constituents. For instance, heavy metals can be encapsulated in a gel forming from cement particles physically entrapping the contaminants.

c. *Ion Exchange* :
Ion exchange reduces the concentration of a contaminant by converting a heavy metal waste into a form in which it can be reused, leaving a less toxic substance in its place [25]. Ion exchange is well-suited to the detoxification of large flows of wastewater containing relatively low levels of heavy metal contaminants. Some exchangers are selective for certain metals and can remove low concentrations of them from wastewater containing a high background level of a nontoxic metal. There are limitations on the concentration of what can be treated and produced. The contaminants are recovered from the ion exchanger by chemical regeneration with acids or alkali.

d. *Adsorption*
The adsorption can be physical (van der Vaal forces) or chemical. In chemisorption the contaminant attaches to charged reactive sites on surfaces of minerals forming chemical or ion-pair bonds. Metal oxides and clay minerals have net surface charges that can vary with pH, thus favoring either adsorption of cations or of anions depending upon the pH. The adsorbent should be a highly porous material . In cases where adsorption is reversible, thermal reactivation is the most widely used regeneration technique.

Permeable Reactive Barrier Emplacement Techniques
Installing the material for the creation of a PRB requires an appropriate emplacement technique. Cost will depend on the nature of the reactive material and funnel material (if needed) as well as construction costs. These costs depend on the size and expense of the equipment as well as the overall dimensions of the plume. Health and safety for workers must also be considered. Emplacement techniques including general method, depth, and cost estimates are described in Table 5 [4,26] (next page).

Tremie tube and high-pressure jetting appear to be cost-effective methods. It has been difficult for contractors to further develop emplacement technology suitable for PRB's in the current nebulous market. In general, the best emplacement method will depend upon the type of PRB. It is likely that many different methodologies will be used, and the availability of a variety of them is an advantage.

Table 5   Emplacement Methods

Method	Description	Depth (ft)	Estimated Cost
Slurry walls	Conventional excavation. Biodegradable material substituted for bentonite normally used.	50	$10/ft
Clamshell	Crane fitted with clamshell	>50	High transportation cost
Continuous trenching	Chain-saw device cuts a trench; can deliver reactive material	35-40	High transportation cost
Tremie tube (Mandel)	Hollow pipe which is pushed to depth; limited by geologies that can be pushed through	190	Relatively inexpensive
Deep-soil mixing	Utilizes large augers	150	Expensive due to transportation of large equipment
High pressure jetting	Injects grouts to make impermeable walls; minimizes damage to subsurface	200	Low cost due to small equipment
Vertical hydraulic fracturing (VHF)	Overcomes rocky soil	80-120	Can be emplaced at deep sites

Anticipated Benefits

Remediation of Wastewater

Remediation of heavy metal contamination in ground water, using the method of AFA-PRB's discussed here, will have obvious benefits for the public whose environmental quality will be restored. This translates into cleaner lakes, streams, and rivers at a minimal cost to taxpayers. Certain industries will benefit directly. The fishing industry has suffered as a result of the decline in the water quality in fish breeding areas. The Chesapeake Bay in particular has been worsening over the past 40 years. The primary reason is non-point source pollution which caused a decline in the shallow water plants in the bay. Shallow water plants are the breeding ground for over 95% of deep sea fish and 100% of coastal fish.

Developers of waste treatment technologies will be another beneficiary of the innovative AFA-PRB's proposed here. In addition, the businesses that generate the waste will benefit by having a new solution to an expense incurred by need to remediate waste water sites.

Alternative Uses for Fly Ash

There will be other benefits to the use of this new technology. Fly ash that would normally have to be landfilled will be put to use. In addition to its role in PRB's, there is a great deal of interest in a cost effective ion exchange system. The utilization of fly ash to create a zeolitic material has municipal, industrial, and agricultural applications. It is feasible that ion exchange materials produced from coal combustion fly ash will be a cost effective alternative to mined and synthetic zeolites. [27-30]

Accomplishment of Phase I Objectives

Task I: Construction of AFA with Desired Properties

Measuring Permeability and Mechanical Properties

The criteria for creating an acceptable barrier material are
- permeability, 10^{-4} cm/sec to 10^{-1} cm/sec
- strength of 50 psi to 500 psi
- reproducibility of the above measured properties.

Measurement of permeability was based on the constant head permeability procedure described in ASTM D-2434. The coefficient of permeability, k, reflects the permeability to water [31]. This test method was used to evaluate materials with a wide range of permeabilities. **Mix Designs**

AFA - PRB materials were prepared from a mixture of fly ash, sodium silicate, water, sand, and stone. Some of the parameters for making AFA-PRB materials with desirable properties were more readily determined, including the effect of selection of fly ash, curing temperature and the permeability control technique. Fly ashes for testing were Class F (low calcium) or Class C (high calcium) obtained from the major coal regions in the U.S. For oxide content of Classes F and C refer to Table 3. Processing methods were confined to heat cured materials (160°F) and the less costly ambient temperature curing. The permeability control techniques used were physical (gradation and compaction control) and chemical (foaming agents). Fillers were all inactive quartz. The optimal ratio of sodium silicate solution to fly ash had been determined in prior work on AFA-PRB cementitious material. The effect of these choices on AFA-PRB properties is summarized in Table 6. Class F fly ash under ambient curing, using chemical permeability control (foaming agent) provides materials with acceptable permeability and strength, as well as reproducible results

Table 6   Effect of Fly Ash Class, Curing Temperatures, and Permeability Control on AFA-PRB

AFA-PRB Barrier Materials	Permeability (cm/s)		Strength (psi)		Reproducibility	
	Using Foaming Agents	Using Gradation / Compaction	Using Foaming Agents	Using Gradation / Compaction	Using Foaming Agents	Using Gradation / Compaction
80°C Cure, Class F Fly Ash	10^{-7}- 10^{-4}	10^{-7}- 10^{-4}	100-1000	100-900	Poor	Average
Ambient Cure, Class F Fly Ash	10^{-7}- 10^{-1}	10^{-7}- 10^{-1}	50-500	100-500	Very good	Good
Ambient Cure, Class C Fly Ash	10^{-7}- 10^{-5}	10^{-7}- 10^{-5}	50-400	100-400	Poor	Average

*Chemical (using foaming agents) or Physical (using controlled gradation/compaction)

In addition to the properties included in the table, there are numerous other variables to be considered such as mixing proportions. In the Phase I project, a method was devised for

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producing barrier material with desired properties using a "matrix-based optimization method". A matrix of compositions was created to evaluate the impact on barrier properties of a variety of parameters. The mix design that produced materials with the most desirable combination of barrier properties is given in Table 7.

Table 7 Mix Design of a Powdered Pelletized sample

Constituent	% Weight	% Volume
NaOH	5.29	7.24
NaSiO$_2$	5.29	7.97
Water	7.41	15.52
Fly Ash*	79.37	69.27
Fine Aggregate	0.00	0.00
Coarse Aggregate	0.00	0.00
Aluminum	2.65	2.20

* The fly ash used came from the following sources: Pozzolannic , Blews Creek, Seward, Delmarva, PSE&G, Hatfield , Montour, Monex, Mojave, Mileken, Holtwood, Gifford Hill, and Ft. Martin

Using the mix design in Table 7, it is found that high strength materials have lower permeabilities and those with higher permeabilities have lower strength. Thus obtaining the desired strength and high permeability were mutually exclusive. Compromises were needed to produce material with suitable physical characteristics along with heavy metal removal capability.

Conclusion: Optimum Barrier Material
Based on Phase I results it was found that AFA-PRB materials containing Class F (low calcium) fly ash, cured at ambient temperature and made from the mix design shown in Table were effective in removal of heavy metals from contaminated water.

Task 2: Ability of AFA-PRB's to Reduce Cd and Cr Levels

Cd and Cr Removal using AFA-PRB's
AFA-PRB's made from Class F fly ash cured at ambient temperatures were prepared. The hardened material was formed into simulated barrier shapes. Compressive strengths ranged from 100 to 500 psi and permeabilities from 10^{-4} to 10^{-1} cm/s. Solutions contaminated with 1000 ppm Cd, and 1000 ppm Cr were used as influent solutions. Atomic absorption (AA) spectroscopy was used to determine the level of cadmium and chromium in the contaminated water before and after permeation through the AFA-PRB. Table 8 shows the heavy metal removal ability and permeability of barriers made from a variety of fly ashes. The test procedure was a batch test. Batch tests are quick testing methods that allow rapid comparison of varied parameter on the test results. The batch studies were performed by placing 5 to 25 gram of barrier material in a zero headspace extractor. To the barrier material was added 20 to 100 times by weight of contaminated water . The sample container was sealed and then was stirred (30 rpm). Water samples were periodically withdrawn for analysis by AA and pH measurement. However, batch testing does not involve flow of the water, it does not simulate the actual situation.

It can be seen that Mojave, Fort Martin, Hatfield and Holtwood reduced the heavy metal concentrations the most when the tests were repeated the same removal efficiencies were obtained) Among the five top performing mixes, barriers made from Mojave and Fort Martin ashes had the

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highest permeability. These materials were all prepared using the mix design shown in Table 7. The combination of high permeability and high heavy metal removal indicated that these two types of fly ash materials were selected for further investigation using both batch and column testing.

Table 8: Cd and Cr Removal by Simulated Barriers

Ash Type	Permeability cm/s	Cd 1000 ppm	Cr 1000 ppm
Mojave [68]*	10^{-1}	0.1	0.1
Mojave [193]	10^{-1}	0.1	0.1
Ft. Martin [176]	10^{-1}	0.1	0.1
Hatfield [39]	10^{-3}	0.1	0.1
Holtwood [91]	10^{-3}	0.1	0.1
Gifford Hill [154]	10^{-3}	0.4	0.3
Montour (4%) [62]	10^{-1}	2.4	3.1
Montour (2.9%) [62]	10^{-1}	2.4	3.1
Miliken [84]	10^{-2}	3.0	5.0
Holtwood [93]	10^{-3}	3.0	5.0
PSEG&G 1 [27]	10^{-1}	12	17
PSEG&G 2 [27]	10^{-1}	12	17
Pozzolanic [3]	10^{-4}	721	734
Seward I [19]	10^{-2}	753	851
Seward II [19]	10^{-2}	753	851
Monax 4% [62]	10^{-2}	821	807
Blews Cr (Monax?)	10^{-2}	843	906

* Numbers in [brackets] identify fly ash sample

Cd and Cr Removal using AFA-PRB's with Clinoptilolite Inclusion.

Contaminated barriers were constructed using a zeolitic material, clinoptilolite, as a partial replacement for ash and sand. There barriers were tested for their permeability and heavy metal removal ability (batch test) to find out whether or not clinoptilolite could enhance the efficiency of AFA-PRB barrier material. Mojave fly along with powdered clinoptilolite were used for this experiment. Permeabilities were all 0.1 cm/s. Table 9 shows the heavy metal removal of the zeolite enriched materials. There are two entries for each barrier substance, one for material made by adding the zeolite during the mixing of fly ash with activating chemicals, the other set when the zeolite was added prior to the mixing.

Table 9: Cd and Cr metal ability of AFA-PRB with clinoptilolite (clinop)
Permeabilities were 0.1 cm/s in every case.

Material	1000 ppm Cd	1000 ppm Cr	1000 ppm Cd	1000 ppm Cr
	clinop added after mixing	clinop added after mixing	clinop added during mixing	clinop added during mixing
99% AFA-PRB/1% clinop	0.3	0.2	0.3	0.3
95% AFA-PRB /5% clinop	1	1	1.5	0.5
90% AFA-PRB /10% clinop	4	3	43	53

The results indicate that there is no advantage obtained by including clinoptilolite to activated Mojave fly ash, since barriers made from activated Mojave fly ash by itself provided similar or better removal of both Cd and Cr, reducing 1000 ppm to 0.1 ppm (See Table 8). It was postulated that the presence of clinoptilolite could reduce the efficiency due to clogging of their micropores. Additional studies conducted with clinoptilolite blended with dry AFA-PRB of several compositions gave similar results.

In the final investigation AFA-PRB's were created by activating the solid with zeolite precursor solution. The dry barrier was placed in an excess of 2M NaOH solution at 100°C. Samples were removed periodically, dried and tested. The fly ash was Mojave as in the experiments above. The permeabilities of all materials sampled were 0.1 cm/s The results (measured using batch testing) can be seen in Table 10.

Table 10: Cd and Cr metal ability of AFA-PRB barrier activated with clinoptilolite solution
Permeabilities were 0.1 cm/s in every case

Material	Activation Time (h)	1000 ppm Cd	1000 ppm Cr
Mojave [68]	2	1.5	2
Mojave [68]	12	0.3	0.3
Mojave [68]	24	0.5	.4
Mojave [193]	2	1	1
Mojave [193]	12	0.3	0.4
Mojave [193]	24	0.5	0.4

Cd and Cr Removal : Column Testing

After selection of barrier material from batch test (screening purpose), column test experiment was conducted. Since column test involve flow of influent, it is closer to the real situation. Small column test is capable of accurately defining the heavy metal removal characterization of the barrier material for the contaminated water. The optimum column diameter should be at least 40 times greater than the average barrier particle material (particle size between 15 and 40 mesh). Therefore the column should be at least 2.5 cm in diameter or greater[32]. The optimum length of the column should be greater than or equal to four times the column diameter, indicating that the barrier column should be at least 10 cm in length. The volume of barrier material bed would thus be 50 cm³. AFA barrier material has a wet bulked density of 0.85 g/ml, indicating that the amount of material required to fill the optimum size column is 41 g (0.09 lb). A volume of 10 L of 10 ppm Cd and Cr and 7.5 L of 1000 ppm Cd and Cr. The flow rate through the column was 16 ml/min. Figures 5 and 6 show removal of Cd and Cr from 10 ppm solution using a column test.
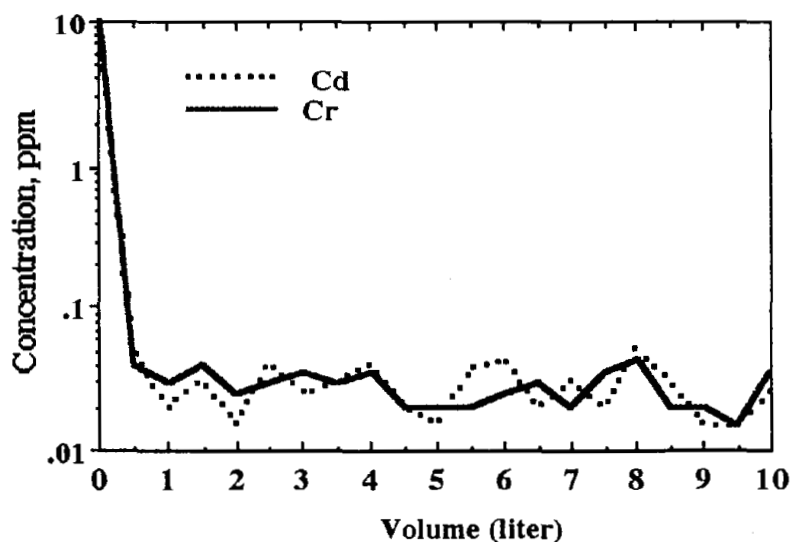
14

Figure (5): 10 ppm Cd and Cr passing through AFA – PRB

Figure 6 shows the removal of Cd and Cr using column testing from 1000 ppm solution.
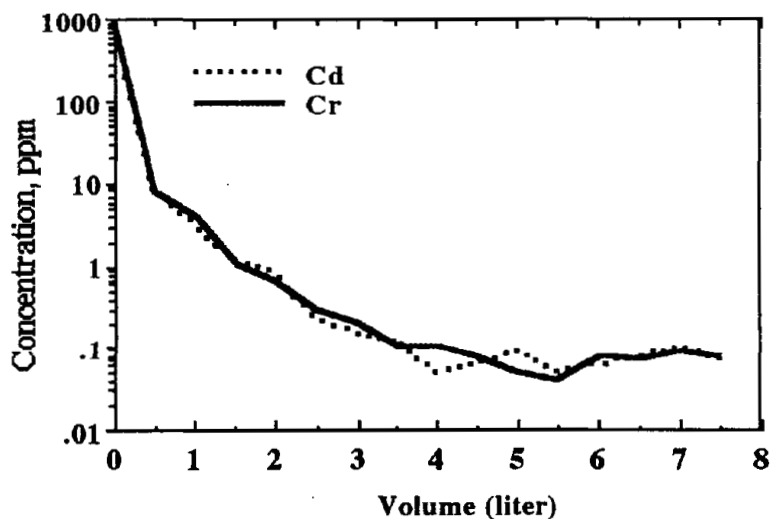

Figure (6): 1000 ppm Cd and Cr passing through AFA – PRB.

Conclusion: Heavy Metal Removal by AFA-PRB Materials with and without Added Clinoptilolite

The performance (using both batch and column testing) of the AFA-PRB Barrier Mojave [#68 and #193] was very good. The results on clinoptilolite-enriched Mojave ash materials were inconclusive. However, further efforts in this direction could yield improved selectivity of the barrier material.

Task 3: A Bench Scale Barrier was to be Constructed and Tested.

Construction of Bench Scale Model

A bench scale apparatus containing AFA- PRB was constructed (15 x 15 x 60 cm) with the AFA -PRB material plate (15 x 15 x 5 cm) placed 30 cm from the top of the container as shown in the figure below.
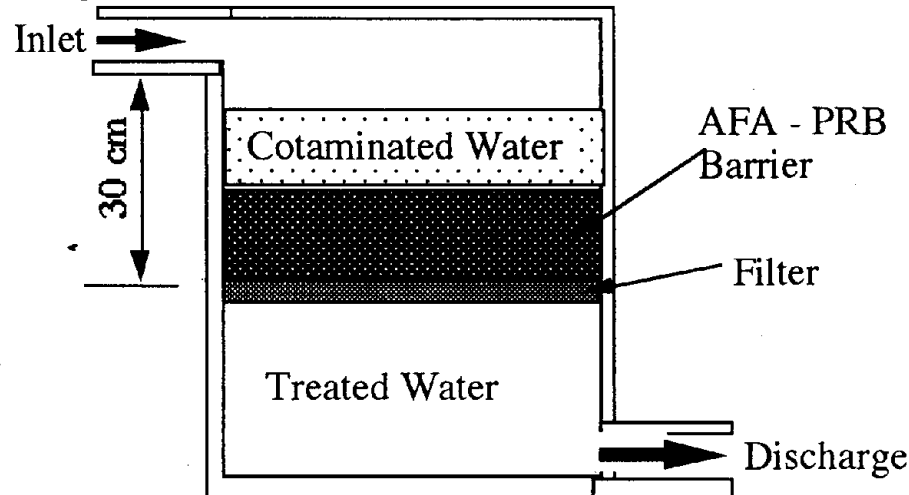

Figure 7 Bench Scale Model with AFA-PRB

Two different forms of AFA-PRB were used in this experiment, palletized and block (cartridge). The AFA-PRB was filled with permeable soil. Cadmium and chromium solutions of 10 ppm and 1000 ppm were poured from the top of the apparatus. The treated water was collected in the bottom of the test set up. Water samples were withdrawn every 0.5 liter for analysis by atomic adsorption

Heavy Metal Removal

The results obtained in this experiment were almost identical for both the palletized and block forms of the barriers. Results shown below are for the block form of the AFA-PRB's. The efficiency of removal of heavy metal was very similar to that obtained using simulated barriers in Task 2. Figure 8 shows the ability of AFA - PRB to remove Cd and Cr from contaminated water containing 1000 ppm. Results for the 10 ppm solutions and the 1000 ppm solutions, in which levels were reduced to about 0.1 ppm, were similar to those obtained using simulated barriers._
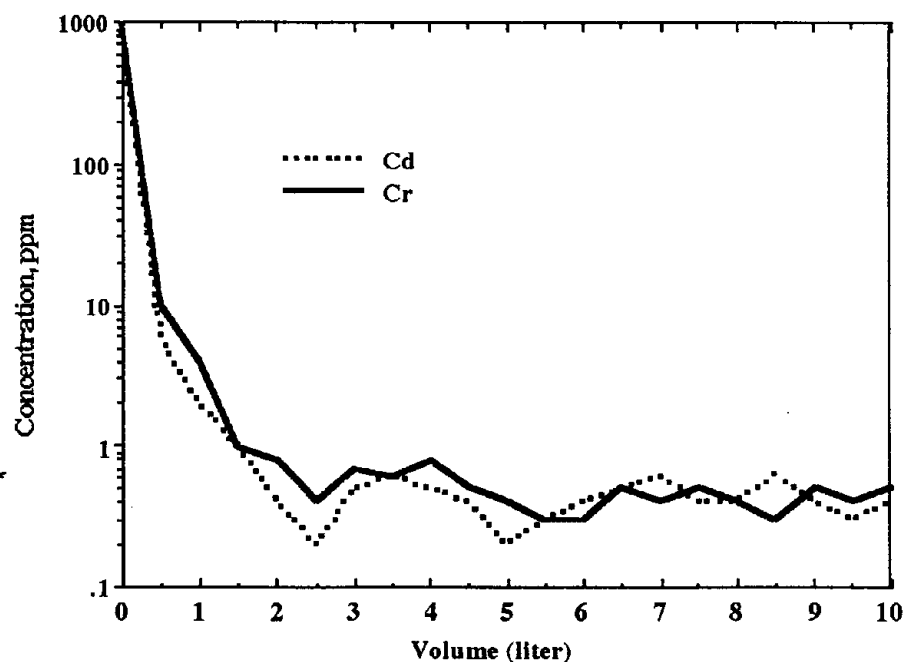
Figure 8: 1000 ppm Cd and Cr passing through AFA-PRB.

The ability of AFA - PRB to remove Cd and Cr from contaminated water from more dilute solutions containing 10ppm is shown below:
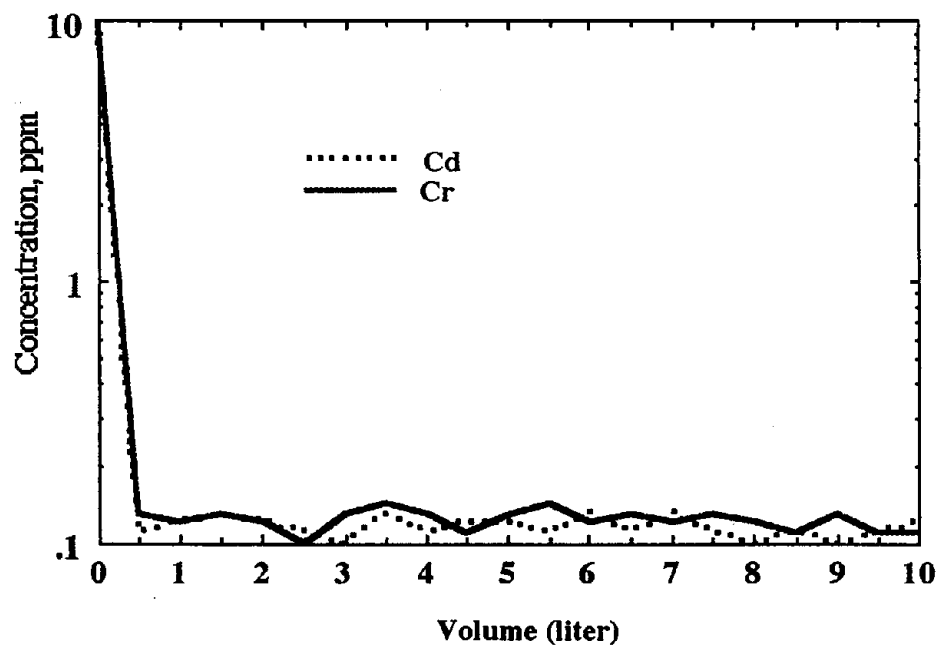

Figure 9 :   10 ppm Cd and Cr passing through AFA-PRB.

To determine the "breakthrough" quantity of contaminant, that is, the quantity which saturates all available sites allowing untreated contaminated water to pass, long term testing is needed.

However, due to time constraints accelerated tests were conducted using very concentrated solutions. A volume of 10 liters of !0,000 ppm Cd solution with increment of 0.5 L was passed through the bench scale barrier. The breakthrough was not reached, however, after passage of 8 L of 10,000 ppm AFA-PRB did become less effective. (See Figure 10)
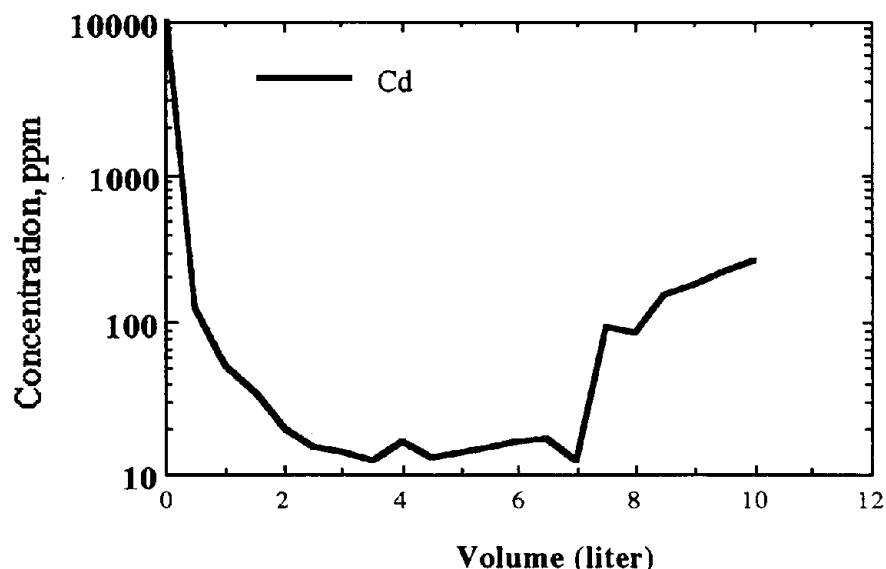

Figure 10: 10,000 Cd passing through AFA – PRB to determine breakthrough quantity

A similar experiment to find the breakthrough concentration was done using lead. Figure compares solutions with 1000 and 100,000 ppm lead solutions. For the 10,000 ppm solution the reduction was over 10, compared to as little as 0.1 for 1000 ppm. Again there was no breakthrough.

Conclusion: Heavy Metal Removal by AFA-PRB in Bench Model

Both the pelletized and block forms of the AFA-PRB's placed in a bench scale apparatus provided nearly identical results. Overall, the heavy metal removal efficiency for Cd and Cr was similar to that obtained using simulated barriers, reducing levels to around 0.1 ppm. No breakthrough was observed for Cd using accelerated testing (large concentrations of contaminant).

Task 4:   Investigation of Mechanisms

Surface Area and AFA-PRB's

Structural features, such as the surface area of the fly ash material, will help to illustrate the mechanism of removal of heavy metals. To reveal structural features of AFA-PRB's X-Ray Diffraction and BET surface area analysis were performed. Surface areas are given in Table 11.

Table 11: BET Specific Surface Area of AFA-PRB Barrier Materials:

Material	Results m²/ g
Fly ash	1.97
Fly ash; fine and coarse aggregates; solutions	1.82
Fly ash; fine aggregates; solutions	3.37
Fly ash; solutions	6.57

The X-Ray diffraction results indicate that activation of the fly ash results in the production of colloidal sodium aluminosilicate hydrate and a doubling of the surface area. In the next section the effect on mechanism of surface area will be discussed.

Surface Area vs Precipitation/Adsorption

Two mechanisms that depend upon surface area are precipitation and adsorption. The larger the surface area the more likely it is that the mechanism is adsorption rather than precipitation. Ratio of amount of heavy metals removed by precipitation vs adsorption was estimated by looking at SEM micrographs and the color of acid wash solutions. Precipitation resolubilizes more readily at pH below 4, according to SEM evidence. Results for precipitation vs adsorption at different pH values for the materials listed in Table 11 above, are estimated. Results are given in Table 12. As pH is varied the estimated percentages of removal by precipitation vs adsorption changes, as shown in the table below. However, to refine this data, standard SEM pictures are needed to support each mechanism.

Table 12. Estimated Removal Mechanism

pH	% Precipitate removed (app)	% Adsorbate removed (app)
5	0	0
4	75	0
3	100	0
2	100	100

Conclusion: Mechanism of Removal

Since Na is easily replaced with other metal ions, the ion exchange behavior of the AFA-PRB barrier can be studied by monitoring Na concentration. On the other hand, the total amount of heavy metal that is captured by the barrier can be measured by Atomic Absorption Spectroscopy (AAS). The difference between the results from ion exchange and AAS is the amount of metal removed by adsorption and precipitation. To further differentiate the difference between adsorption and precipitation, energy dispersion x-ray spectroscopy (EDXS) in TEM or SEM were used to characterize the distribution of the heavy metal in the barrier. The heavy metal-rich regions indicate precipitation.

In general, the ion exchange mechanism dominates at low heavy metal concentrations, whereas at higher, adsorption takes over.

Based on the results of Phase I, it is clear that the barrier materials prepared by different chemical composition result in different metal removal performance. The Si/Al ratio of barrier materials is critical for the extent of the negative charge on the surface of barriers. The higher negative surface charge of barrier material enhances the metal cation adsorption. The AFA-PRB

barrier material prepared with a systematic chemical composition will be tested and the optimum chemical composition for increasing metal removal efficiency and acid-resistance can be identified.

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