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IN SITU REMEDIATION OF URANIUM CONTAMINATED GROUNDWATER

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ABSTRACT

In an effort to develop cost-efficient techniques for remediating uranium contaminated groundwater at DOE Uranium Mill Tailing Remedial Action (UMTRA) sites nationwide, Sandia National Laboratories (SNL) deployed a pilot scale research project at an UMTRA site in Durango, CO. Implementation included design, construction, and subsequent monitoring of an in situ passive reactive barrier to remove Uranium from the tailings pile effluent. A reactive subsurface barrier is produced by emplacing a reactant material (in this experiment - various forms of metallic iron) in the flow path of the contaminated groundwater. Conceptually the iron media reduces and/or adsorbs uranium in situ to acceptable regulatory levels. In addition, other metals such as Se, Mo, and As have been removed by the reductive/adsorptive process. The primary objective of the experiment was to eliminate the need for surface treatment of tailing pile effluent. Experimental design, and laboratory and field results are discussed with regard to other potential contaminated groundwater treatment applications.

INTRODUCTION

Until recently, remediation of contaminated groundwater utilized pump and treat or a related variation. Experience gained in this area has shown that pump and treat schemes are not cost effective in treating the majority of groundwater contamination problems. As an alternative to active pump and treat treatment systems efforts are being made to devise passive in situ treatment techniques. More specifically related to this project is the more than 230 million tons of uranium mill tailings at mill sites throughout the United States. (U.S. Environmental Protection Agency, 1987) Uranium and other metals in the mill tailings piles have contaminated subsurface soils and groundwater beneath many of these sites. Plumes migrating from mill tailings sites have been found to contain uranium concentrations on the order of several hundred parts per billion (ppb), which is in excess of the proposed drinking water maximum contaminant level of 20 ppb. Remediation costs of the existing contaminated groundwater associated with the 24 Uranium Mill Tailings Remedial Action (UMTRA) sites have been estimated at about $ 1 billion. Consequently, innovative improvements are necessary to lower the cost of cleaning up the remaining UMTRA sites.

This project demonstrated laboratory and field scale installation of a reactive barriers at the Durango, Colorado, UMTRA site. Conceptually a reactive barrier treatment system diverts contaminated groundwater with relatively impermeable vertical subsurface walls into a narrow higher permeability treatment zone. The treatment zone contains reactant materials or biota which selectively remove contaminants. Contaminant removal is achieved by one or a combination of the following mechanisms: (1) chemical, (2) physical, and (3) biological. Although the initial costs of a passive system will likely be more than an active system, the payback will be in the form of far less maintenance and operation costs over time.

TEST SITE: BODO CANYON DISPOSAL CELL, DURANGO, COLORADO - UMTRA SITE

Surface remedial action has been completed at the Uranium Mill Tailings Remedial Action Project site in Durango, Colorado. Contaminated soil and debris was moved to the Bodo Canyon

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Disposal site is in La Plata County, Colorado, approximately 1.5 miles from the town of Durango. The land within 1 mi surrounding the site is uninhabited. Movement of the mill/tailings to the Bodo Canyon disposal site was completed in the fall of 1990. A total of 2.5 million cubic yards (yd^3) of contaminated materials were relocated to the disposal cell. (Jacobs Engineering Group, 1994)

The disposal cell at Bodo Canyon was designed to limit the amount of new infiltrating precipitation. However, fluids disposed of with the contaminated tailings are currently draining from the disposal cell and UMTRA groundwater prediction models estimate three more years of drainage. The draining fluids (leachate), have been collected in a subsurface engineered collection gallery and drained via gravity to a lined retention basin for treatment. Previous treatment included conventional chemical flocculation/settling in a lined retention basin. Once confirmed clean, treated water is released into a nearby arroyo.

LABORATORY TESTING

For a reactive material to be effective in a passive barrier treatment system, the reactant must be capable of simultaneously removing metals from contaminated groundwater and maintaining sufficient hydraulic conductivity to facilitate the passage of fluid through the barrier for long periods of time. Table 1 shows the concentration of detectable metal constituents in Bodo Canyon tailings pile pore fluids and levels of metals acceptable to the Colorado Department of Public Health and Environment (CDPHE). Based on this information, uranium was chosen as the main target for chemical removal by the passive barrier design.

Table 1. Metal Concentrations in Bodo Canyon Tailings Pile Pore Fluids.

Element	Concentration (mg/L)	CDPHE Requirements
As	**0.16**	**0.5**
Se	**0.17**	**monitor**
Zn	**0.49**	**0.5**
U	**2.6**	**2.0**
Ra-226	**1.1 pCi/L**	**3.0 pCi/L**
Mo	**0.89**	**-**
Mn	**3.3**	**-**

Many inorganic reactive materials have been proposed for use in removing uranium and other contaminant metals from solutions similar to uranium mill tailings fluids. Some of these include: metallic iron (Cantrell, K.J., Kaplan, D.I., and Wietsma, T.W., 1995), ferric oxyhydroxide, clinoptilolite, coal, fly ash, peat, hydroxyapatite, sawdust, and titanium oxides (Morrison, S. J. and Spangler, R.R., 1992), (Morrison, S.J. and Spangler, R.R., and Tripathi, V.S., 1995); taconite and scoria (Jacobs Engineering Group, 1991), and sodium dithionite (Amonette, J.E., Szecsody, J.E., Schaer, H.T., Templeton, J.C., Gorby, Y.A., and Fruchter, J.S., 1994). In these studies, uranium and other metals were removed from solution primarily by sorption, reduction, and precipitation mechanisms.

Metallic iron, metallic iron in contact with a copper catalyst (copper screen), and a patented iron foam were selected for the Bodo Canyon passive barrier demonstration based on numerous laboratory successes in removing uranium and other metals from solutions similar to those at Bodo Canyon and from the actual tailing pond leachate. All of these reagents are environmentally benign in nature and should continue to react with metal contaminants for long periods of time without the need for outside intervention. Availability and cost were also primary considerations in the selection process, because substantial quantities will be required in many future field treatments. By testing multiple materials in the Bodo Canyon demonstration, information on longevity, cost, and effectiveness will be obtained for use in designing passive barriers for other sites.

Results from laboratory studies conducted by other researchers, on uranium and molybdenum removal by metallic iron are shown in Table 2. Metallic iron immobilizes uranium by chemical reduction and subsequent precipitation. AFO adsorbs uranium and other contaminants from groundwater without affecting the redox condition of the system. When metallic iron is in contact with a minor amount of catalytic metal such as copper, the rate of reduction is markedly increased (Sweeny, K.H., and Fischer, J.R., 1973). A bimetallic copper-iron reagent is being tested in order to see if metals such as Mo, V, and Se present in Bodo Canyon fluids (Table 1) can be removed more rapidly by reductive treatment than iron alone (Table 2).

Table 2. U and Mo Removal with Metallic Iron
(Data from: Cantrell et al., 1995 and Morrison et al., 1995)

	Reactant	Starting Concentration (mg/L)	Ending Concentration (mg/L)	Contact Time (hours)	CDPHE Requirements
U	**Metallic Iron**	**8.7**	**.040**	**2**	**2.0**
	Metallic Iron	**2.5**	**.002**	**2**	**2.0**
	AFO	**2.38**	**.001**	**4**	**2.0**
Mo	**Metallic Iron**	**26.0**	**2.5**	**88**	**-**
	Metallic Iron	**4.5**	**.09**	**88**	**-**

Although both reductive and adsorptive chemical treatment systems have been shown to remove uranium from solution in laboratory tests, it is also known that the removal efficiency can vary depending on site specific hydrogeochemical conditions such as pH, major element concentration, and mineralogy. In order to obtain engineering information on how site specific conditions at Bodo Canyon will affect reactivity of the permeable barrier a series of laboratory tests on chemical reactivity and hydraulic conductivity were conducted. Laboratory work determined the following characteristics of various potential treatment materials: (1) the capacity of the reactive material to remove target contaminants; (2) the capability of the reactive material to maintain sufficient hydraulic conductivity and to minimize flow losses because of plugging during the desired treatment interval; and (3) the compatibility of the treatment material with site specific geochemical conditions such as pH, redox, ionic strength, and major element concentrations. The laboratory experiments also aided in formulating the following engineering design parameters: (1) develop volume requirements and subsequent cost data for treatment material; (2) estimate treatment material capacity; and (3)estimate treatment material longevity.

PROJECT SCOPE

Demonstrate at a field scale that an in situ, passive geochemical barrier can be used to selectively remove contaminants from a plume. The entire experiment was conducted inside a 36 ft. X 60 ft. X 6 ft. deep pre-fabricated leak proof retention basin. In effect this treatment system simulates the flow and subsequent treatment of contaminated ground water in a controlled environment. Consequently, the risk of contaminant release during the experiment is eliminated. Figure 1 is a schematic of the general layout of the tailings pile, the old treatment retention pond, and the new treatment system.

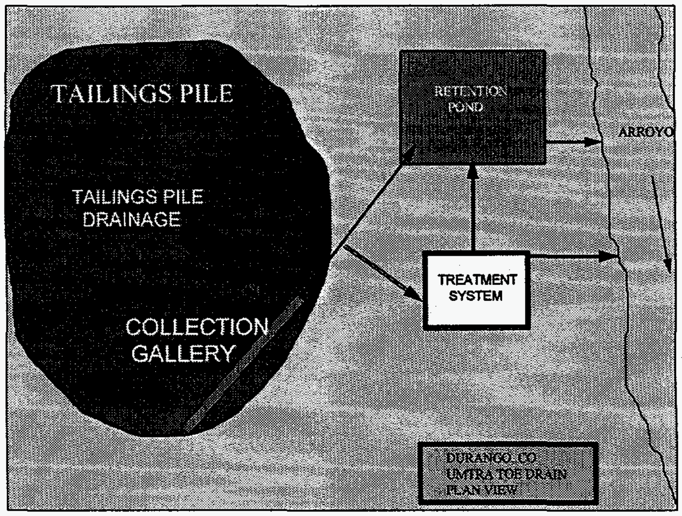

Figure 1. General location schematic.

OBJECTIVES

1. passive diversion of tailings pile effluent into treatment zone;
2. passive removal of selected contaminants from tailings effluent;
3. effective treatment of a simulated contaminated groundwater having representative (geochemistry and geohydrology) conditions of other UMTRA sites;
4. evaluate treatment efficiencies and associated costs for different treatment materials; and
5. extrapolate the longevity of each material.

Laboratory data was used to design treatment configurations 1 and 2 shown in Figures 3 and 4, respectively. More specifically: material saturated hydraulic conductivity and required residence time for contaminant removal were the primary parameters used to determine material volumes, thickness, and densities.

TREATMENT SYSTEM OPERATION

The new treatment system selectively transforms the unwanted contaminant (uranium) into a less toxic and mobile state, i.e., this is essentially a chemical filtration process. Treatment system chemistry is shown in Figure 2. The purified water is collected in the underdrain and diverted to the existing retention pond until treatment effectiveness is verified.

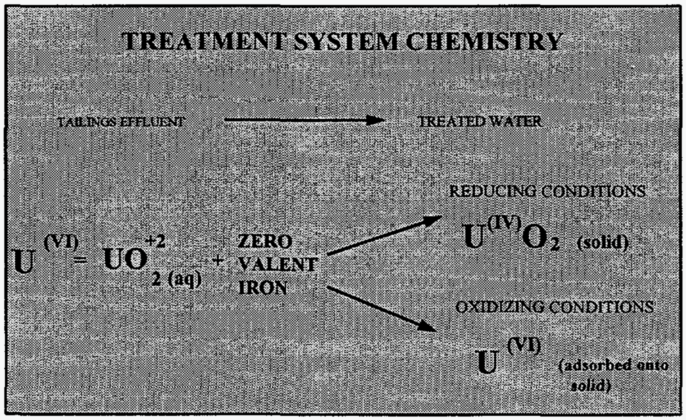

Figure 2. Treatment system chemistry.

Treatment Configuration 1 is an engineered ground water treatment system consisting of a subsurface drainfield similar to a residential septic leach field (Figure 3), that evenly distributes contaminated groundwater above a treatment zone was constructed inside of the retention basin. Contaminated groundwater percolates via gravity through the treatment zone where target contaminants (uranium, selenium, and molybdenum) are transformed and/or removed. The experiment tests three different materials (zero valent iron, iron foam, and a bimetallic iron/copper) using two different configurations in an effort to identify the optimum treatment media. In addition, field stability and form of the immobilized contaminants shall be evaluated for the duration of the project - 4 years. All test materials are completely benign, i.e., non-toxic. A second treatment configuration (Figure 4) utilizing a plug flow reactor design was used to evaluate an iron foam produced by Cercona, Inc. of Dayton, Ohio; and the zero-valent iron (steel wool).

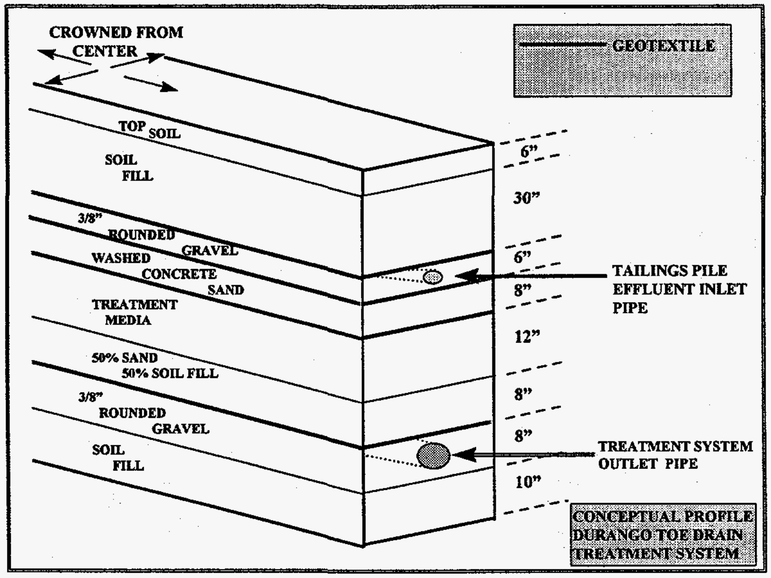

Figure 3. Configuration 1 - leach field cross section.

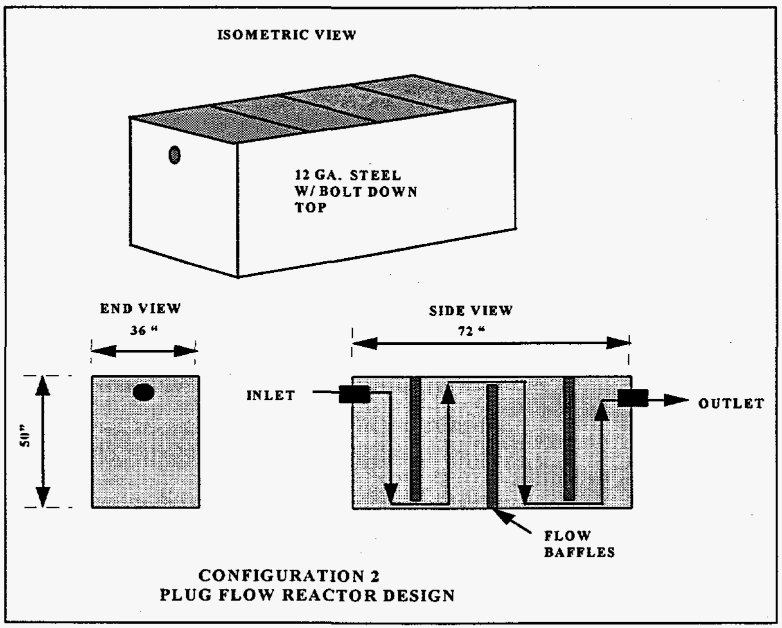

Figure 4. Configuration 2.

RESULTS

Operation of the field pilot test began in May, 1996 and is scheduled to continue through 1999. The results to date are very promising. Figures 5, 6, and 7 exhibit pilot test removal efficiencies of the iron foam treatment media. The field results essentially coincide with previous laboratory data. Previous research has shown that the rate of contaminant removal by metallic iron can be directly related to surface area of the reactant. Metallic iron foam could be the alternative reactive media that provides increased surface area for reaction as well as improved hydraulic conductivity. Metallic iron foam products have between .1 and 5 m^2/g of surface area. In comparison, steel wool has a surface area of about 5.6E-3 m^2/g. Batch experiments on the foam with Bodo Canyon water showed that uranium was removed to less than detectable levels within 10 hours of contact. A second parameter which will determine the feasibility of using zero valent iron as a long term solution is treatment effectiveness over time. Laboratory testing indicated that the metallic iron treatment media will maintain sufficient hydraulic conductivity during the desired treatment interval (4 years). Initial saturated hydraulic conductivity of the zero-valent iron (steel wool) was 6.4×10^{-3} cm/s; and the iron foam was 0.53 cm/s. Oxygenated water simulating a worst case plugging scenario was used to simulate changes that occur due to oxidation of the iron. After more than 700 pore volumes of water passed through the reactive zone the column still maintained its capacity.

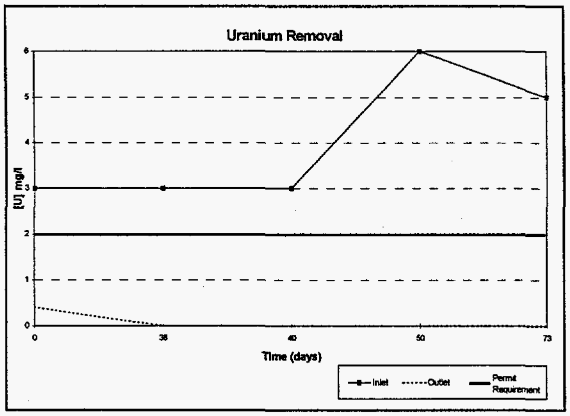

Figure 5. Uranium Removal.

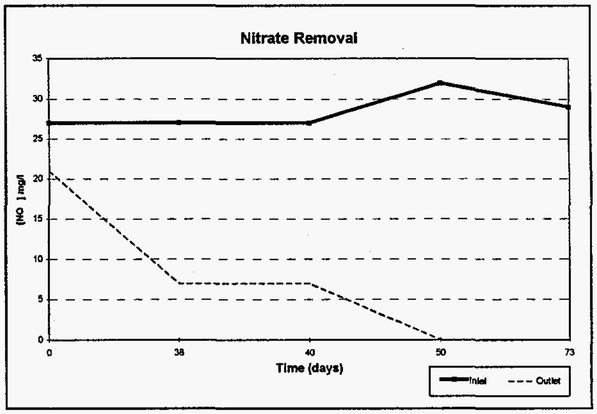

Figure 6. Nitrate Removal.

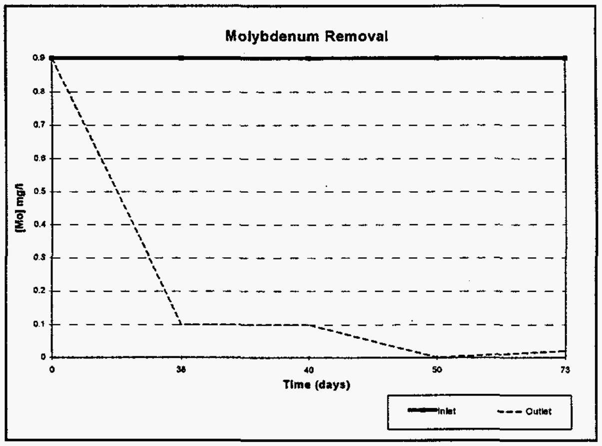

Figure 7. Molybdenum Removal.

CONCLUSIONS

Before reactive barriers can be accepted as a reliable and efficient method of addressing uranium mill tailing groundwater problems, field studies such as this Durango, CO pilot are needed to provide efficiency, longevity, and control information to interested parties. The nature of uranium mill sites, i.e., multiple contaminants, requires a technology capable of handling problematic contaminants using an in situ barrier.

Results from the Durango experiment have and will continue to be incorporated into reactive barrier designs for other uranium mill tailings remediation efforts. Information is being collected regarding removal efficiencies of uranium, selenium, molybdenum and other elements in an effort to broaden the technology application. During the expected project duration (3 more years), reactive zones will be examined to identify the long-term stability of the reaction products. This information will assist designers of future in situ reactive barrier installations. Finally, the costs and associated benefits of using this treatment approach will be determined.

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