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Laboratory and Field Scale Demonstration of Reactive Barrier Systems

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LABORATORY AND FIELD SCALE DEMONSTRATION OF REACTIVE BARRIER SYSTEMS

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ABSTRACT

In an effort to devise a cost efficient technology for remediation of uranium contaminated groundwater, the Department of Energy's Uranium Mill Tailings Remedial Action (DOE-UMTRA) Program through Sandia National Laboratories (SNL) fabricated a pilot scale research project utilizing reactive subsurface barriers at an UMTRA site in Durango, Colorado. A reactive subsurface barrier is produced by emplacing a reactant material (in this experiment metallic iron) in the flow path of the contaminated groundwater. The reactive media then removes and/or transforms the contaminant(s) to regulatory acceptable levels. Experimental design and results are discussed with regard to other potential applications of reactive barrier remediation strategies at other sites with contaminated groundwater problems.

I. 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 remediation 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.[1] 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 barrier 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.

II. RELATED WORK

It appears that the development and application of in situ treatment wall technology, at the research level, is approaching "band wagon" proportions. The extensive laboratory research in this area has paved the way for the logical transition to field scale demonstrations. The environmental arena is ready for a careful move toward the implementation of the leading research concepts. Researchers from EPA's R.S. Kerr Environmental Research Laboratory[2] report the successful remediation of groundwater contaminated by reducible metal species with a metallic iron subsurface barrier in a field study at the U.S. Coast Guard Station near Elizabeth City, North Carolina. In their study, chromium was removed from groundwater by reduction and precipitation reactions with metallic iron in the barrier. Based on thermodynamic and preliminary laboratory studies,[3] metallic iron should also be able to reduce mobile uranium species to their more immobile counterparts.

III. OBJECTIVE

The primary aspects of a subsurface reactive barrier system are: (1) engineering/design, (2) system modeling, (3) installation methods, and (4) treatment materials. The engineering/design and installation techniques are adaptations of conventional civil engineering applications. The system modeling is simply modeling for a different reason, and the treatment materials have evolved from water treatment principles. The primary objective of this research project was to integrate these four individually mature technologies to demonstrate an in situ passive technique for remediation of contaminated groundwater. Engineering design and constructability were critical issues to be evaluated. Uranium is the primary contaminant of interest. Experimental results should provide the information necessary to determine adequacy of this technology at other sites with groundwater contamination problems.

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

A. Description

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 Disposal site 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.[4]

The disposal cell at Bodo Canyon was designed to limit the amount of new infiltrating precipitation. With time, alluvium below the disposal cell is expected to become dewatered and the vadose zone will attenuate any seepage from the bottom of the cell before it can move into the underlying bedrock. However, fluids disposed of with the contaminated tailings are currently draining from the disposal cell. The fluids, better known as leachate, have been collected in an engineered collection gallery and drained via gravity to a lined retention basin for treatment. Treatment included chemical flocculation/settling in this lined retention basin. Once confirmed clean, treated water was released into a nearby arroyo.

V. 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 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 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**	-
Co	**0.07**	-
Ni	**0.03**	-
V	**7.4**	-
Be	**0.02**	-

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[3], ferric oxyhydroxide, clinoptilolite, coal, fly ash, peat, hydroxyapatite, sawdust, and titanium oxides [5,6]; taconite and scoria [7], and sodium dithionite[8]. In these studies, uranium and other metals were removed from solution primarily by sorption, reduction, and precipitation mechanisms.

Metallic iron, metallic iron treated with a copper catalyst, 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.[9] 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. These tests are described in the following sections of this report.

B. Objectives

Determine the following characteristics of various potential treatment materials:

- the capacity of the reactive material to remove target contaminants;
- 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
- 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 provide estimates of the following engineering design parameters:

- develop volume requirements and subsequent cost data for treatment material;
- estimate treatment material capacity; and
- estimate treatment material longevity.

C. Laboratory Experiments

The laboratory experiments were divided into two related testing programs: 1) hydraulic conductivity measurements; and 2) contaminant removal efficiency.

1. Hydraulic Conductivity Measurements. Hydraulic conductivity of the reactive materials used in the Durango permeable barrier tests was measured using a bench scale flow through column setup. Changes in hydraulic conductivity over time were measured based on the knowledge that hydraulic conductivity might be adversely affected by rusting of the metallic iron reagents, or by washing away of the amorphous ferric oxyhydroxide under flow conditions. Results were incorporated into the engineering final design of the field system.

2. Contaminant Removal Efficiency. Batch tests to measure the capacity of reactant materials to remove uranium and other metals from Bodo Canyon fluids were completed. Actual tailings effluent samples and representative laboratory simulated sample solutions were used during the batch tests. The uranium removal capacity of various metallic iron sources were evaluated to determine the most effective iron material. That material was then combined with a second metal, copper, and tested for its ability to speed up the reduction of Mo, Se, and V. The rate of uranium removal at various fluid to filing ratios was measured; in addition, Eh, pH, and changes in the chemical composition of major and trace metals were recorded. Column tests that evaluated the rate of uranium immobilization in a flow through system assisted in extrapolating theoretical reactant longevities. The affect of solution chemistry and site-specific host material on the uranium reduction reaction was also evaluated.

VI. 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 pre-fabricated leak proof retention basin. The retention basin is a 36 ft. X 60 ft. X 6 ft. deep and is lined with a 2 ft. thick clay layer covered with two 40 mil HDPE (high density polyethylene) liners. In between the two 40 mil HDPE liners is a drainage net and monitoring system for verifying liner integrity. In effect this treatment system will simulate 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.

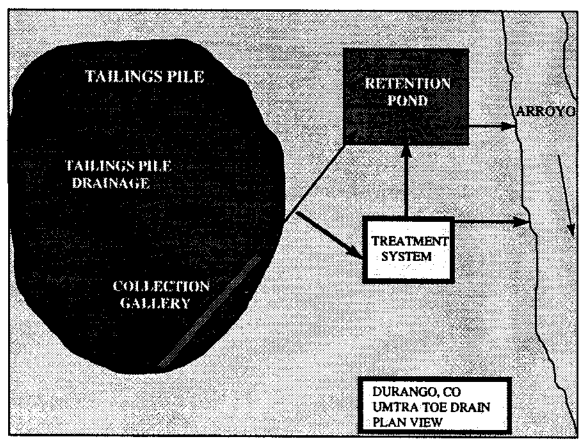

Figure 1. General location schematic.

Figure 2 shows the early stages of construction of the treatment system. In the foreground is the old retention pond (containing sludge residue), and to the right is the northeast edge of the tailings pile cover.

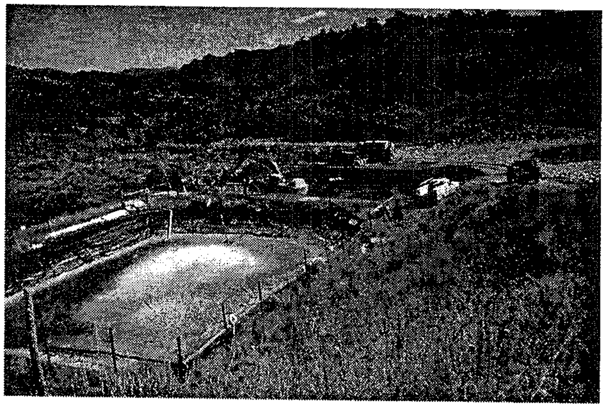

Figure 2. Early stages of treatment system construction.

Specific field scale demonstration objectives are:

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 5 and 6, 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.

A. Previous Operation

Tailings effluent was collected and diverted into the retention pond where it was held for treatment. The uranium was removed using conventional chemical/physical precipitation. The precipitated sludge accumulated at the bottom of the basin while the water was allowed to evaporate and/or be released down gradient. This project is directed at evaluating the effectiveness of a new treatment system that is more suitable to subsurface in situ treatment.

B. New 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 3. The purified water is collected in the underdrain and diverted to the existing retention pond until treatment effectiveness is verified.

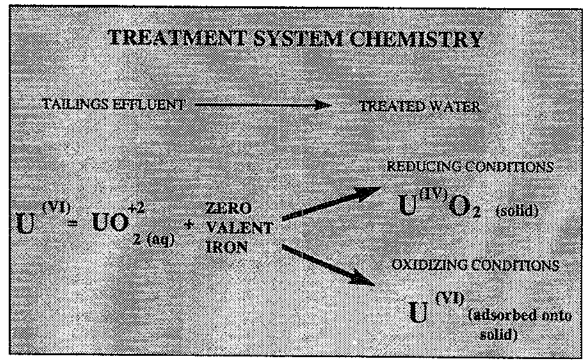

Figure 3. Treatment system chemistry.

An engineered ground water treatment system consisting of a subsurface drainfield (configurations A and B in Figure 5), similar to a residential septic leach field, 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 (Figure 5). 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.

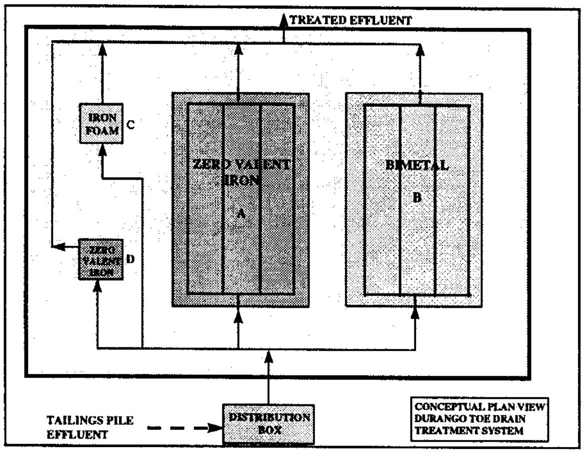

Figure 4. Plan view - Treatment system schematic.

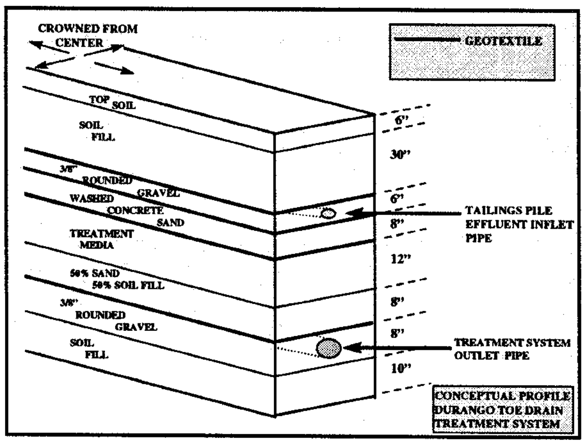

Figure 5. Configuration 1 - profile of treatments A and B.

A second treatment configuration (Figure 6) utilizing a plug flow reactor design was used to evaluate an iron foam (material C) produced by Cercona, Inc. of Dayton, Ohio; and the zero-valent iron (material D).

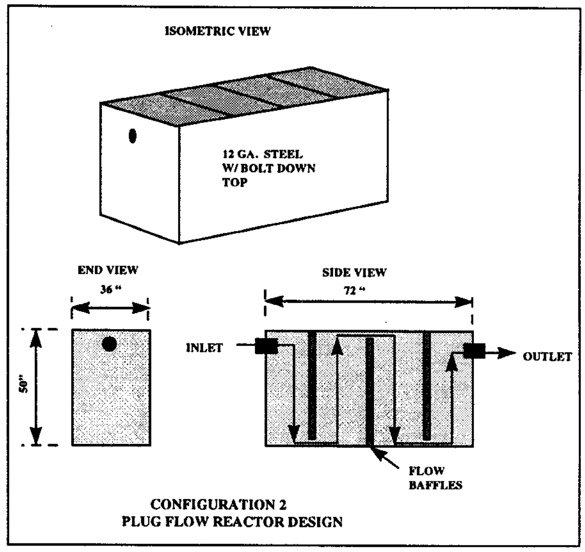

Figure 6. Configuration 2 - profile of treatment configurations C and D.

VII. RESULTS

Laboratory results verified that the metallic iron materials remove uranium from the Durango tailings leachate. Each metallic iron form reduced the uranium concentration from 6 ppm to less than 2 ppm (CDPHE requirement) in less than 24 hours, but the most effective was the iron foam, reduction in less than 5 hours. Metallic iron immobilizes uranium by chemical reduction and subsequent precipitation. When metallic iron is treated with a minor amount of catalytic metal such as copper, the rate of reduction is markedly increased. Results of batch tests with Durango water on catalyzed steel wool show uranium removal from solution to less than 1000 ppb in about 24 hours. 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 Durango water show that uranium was removed to less than detectable levels within 10 hours of contact.

Laboratory results have verified that the metallic iron materials can remove uranium from water derived from uranium mill tailing operations. In the laboratory, all of the metallic iron materials tested showed different reaction rate results. Long term performance of these materials in the field will be tested during the pilot study and evaluations made on efficiency and cost at the conclusion of the study.

Laboratory tests were also conducted on the capability of the steel wool material to maintain sufficient hydraulic conductivity during the desired treatment interval. 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.

VIII. FUTURE DESIGN CONSIDERATIONS

A treatment scheme that passively directs contaminated ground water into designated in situ treatment zones appears to be the most cost effective treatment alternative for many of the common subsurface contamination sources, i.e., slowly diffusing contaminants. The critical design parameters include: (1) the diversion wall material; (2) treatment zone materials, and (3) re-dispersion of the ground water.

- The diversion wall material must simultaneously:
  1. be installable in the local geology;
  2. stand up to the ground water chemistry
  3. provide adequate lateral hydraulic conductivity reduction so as to divert the ground water
  4. and meet the longevity requirements.

- The treatment material must simultaneously:
  1. be emplaceable in the local geology;
  2. adequately remove the target contaminant(s);
  3. be compatible with the ground water chemistry
  4. provide a higher conductivity than the surrounding formation;
  5. withstand the tendency of ground water to physically wash it away;
  6. and be environmentally benign.

- The dispersion wall must release the treated ground water back into the formation. This will avoid formation of a bottleneck due to the diversion wall.

IX. 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 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 will 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 (4 years), reactive zones will be examined to identify the long-term stability of the reaction products. Longevity of the reactive materials in the Durango test 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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