Paper 2A-05, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2002.* Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2002). ISBN 1-57477-132-9, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

PERMEABLE REACTIVE BARRIER TREATMENT TECHNOLOGY FOR REMEDIATION OF INORGANIC-CONTAMINATED GROUNDWATER

Tammy P. Taylor (taylort@lanl.gov), ***Patrick Longmire*** (plongmire@lanl.gov),
Dale A. Counce, Steve J. Chipera, John P. Kaszuba, and James L. Conca
(Los Alamos National Laboratory, Los Alamos, New Mexico, USA)

ABSTRACT: Permeable reactive treatment wall technology has been studied as a means to remediate inorganic-contaminated groundwater *in situ* at Los Alamos National Laboratory (LANL), New Mexico, USA. The prevalence of multiple contaminants, including $^{238,\ 239,\ 240}$Pu, ^{241}Am, ^{90}Sr, $^{234,\ 235,\ 238}$U, nitrate (NO_3^-) and perchlorate (ClO_4^-), has prompted utilization of novel types of reactive media to immobilize the contaminants. The objective of laboratory-scale treatability studies was to identify reactive media that could effectively reduce contaminant levels below regulatory limits for groundwater. Porous media were contacted with contaminants using a kinetically limited two-dimensional (2-D) aquifer cell. Previous 1-D column results indicated that a multiple layer treatment approach was necessary for optimal removal of the contaminants investigated. Two materials have shown significant propensity to remediate the contaminated groundwater: Apatite®II and pecan shells. Representative contaminants, monitored continuously during the 2-D experiment included ^{87}Sr (as a surrogate for ^{90}Sr), NO_3^- and ClO_4^-. On day 285 of the experiment influent and effluent samples, as well as solid materials from the 2-D cell, were collected for extensive analysis. These analytical results were used to model the behavior of contaminants within the cell during the experiment. Results of model simulations using MINTEQA2 suggested that dissolved strontium was stable as Sr^{2+}. Perchlorate and nitrogen were stable as ClO_4^- and NO_3^- in influent waters, however, reduction to intermediate compounds occurred based on complete reduction of ClO_4^- and NO_3^- during the first 305 pore volumes (282 days) of the experiment.

INTRODUCTION

Research at LANL has evaluated permeable reactive barrier (PRB) technology that can immobilize multiple contaminants *in situ* with low technological demand and cost. Reactive media were selectively identified for the removal of radionuclides, metals, NO_3^- and ClO_4^-. A shallow alluvial groundwater system at LANL has been identified for implementation of this technology. Radionuclides, including ^{90}Sr, $^{238,\ 239,240}$Pu, and ^{241}Am, have been detected in alluvial groundwater at this site since 1963 (Purtyman, 1995). These radionuclides are stable as free cations and hydroxo and carbonato complexes in the dissolved aqueous phase and as adsorbates associated with colloids consisting of calcium carbonate, silica, ferric hydroxide, and solid organic matter. Nitrogen (NO_3^- and total Kjeldahl nitrogen) is also prevalent in the groundwater, and with the impending EPA regulation of ClO_4^-, this contaminant has been identified as a significant concern.

The objective of laboratory-scale treatability studies was to identify reactive media that could effectively reduce contaminant levels below regulatory limits for a minimum of 10 years. Reactive materials will be replaced at the end of each 10-year cycle. The following materials were selected for investigation: polymer (Catfloc®) coated volcanic basalt for agglomerating colloids ($^{238, 239, 250}$Pu and ^{241}Am colloids), Apatite II for precipitating heavy metals and radionuclides and supplying reactive organic carbon to enhance microbial degradation of NO_3^- and ClO_4^-, pecan shells to adsorb metals and provide physical support for biofilm to further reduce NO_3^- and ClO_4^- and limestone to raise the pH of exiting pore waters and adsorb residual anionic complexes of ^{90}Sr, ^{241}Am, $^{238, 239, 250}$Pu and $^{234, 235, 238}$U. Porous media were contacted with contaminants using kinetically limited one-dimensional (1-D) columns and a 2-D aquifer cell. Column experiments have been previously describe by Taylor *et al.* (2001). Representative contaminants selected for study in the 2-D cell included ^{87}Sr (as a surrogate for ^{90}Sr), NO_3^- and ClO_4^-.

MATERIALS AND METHODS

Experimental. Concentrations of target contaminants in the groundwater after adding spikes were 2.0 mg/L ^{87}Sr (± 0.019), ~140 mg/L NO_3^- and ~350 mg/L ClO_4^-. Other contaminants present in the groundwater collected at the prospective field site will be presented in the results analysis. The cell packed with the reactive media was flushed at a constant flowrate of approximately 1.5 mL/min. This flowrate resulted in a resident contact time approximately equivalent to what will be observed within the PRB layers proposed to be installed at a LANL field site. Aliquots of effluent were retrieved manually for analysis of ^{87}Sr, NO_3^- and ClO_4^- on a daily basis from the effluent well and sample ports located between each layer within the cell. On day 285 of the experiment, a comprehensive analysis of metals, organic and inorganic carbon and alkalinity was conducted. Solid samples of each reactive medium in the 2-D cell were collected for analysis by X-ray diffraction (XRD).

Sample Preparation and Analytical Methods. Daily analysis of influent, effluent and samples collected from between the layers of the media in the 2-D cell were conducted by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for ^{87}Sr and by ion chromatography (IC) for NO_3^- and ClO_4^-. Influent and effluent water samples collected after 310 pore volume (285 days) for the 2-D aquifer cell were analyzed for inorganic and organic chemicals including anions, metals, and trace elements. Both filtered and non-filtered samples were collected for chemical analyses. An Orion meter with a Ross combination pH electrode was used to measure pH. Samples were filtered through 0.45-µm Gelman filters and acidified with analytical-grade HNO_3 to a pH of 2.0 or less for metal analyses. Water samples were analyzed using techniques specified in EPA method SW-846 including IC for bromide, chloride, fluoride, oxalate, NO_3^-, nitrite, ClO_4^-, phosphate, and sulfate, ICP optical emission spectroscopy (ICP-OES) for calcium, magnesium, silicon (silica), and sodium, and ICP mass spectrometry (ICP-MS) for aluminum, antimony, arsenic, boron, beryllium, barium, cadmium, cobalt, chromium, copper, iron, mercury, potassium, manganese, molybdenum, nickel, selenium, strontium, thallium, thorium, uranium, vanadium, and zinc. Alkalinity was determined using standard titration techniques. Total organic carbon (TOC) was determined by oxidation/combustion with infrared detection of carbon as carbon dioxide. Charge balance errors for analytical results were calculated for major and trace ions using the computer program MINTEQA2.

Geochemical Modeling. Calculations of solute speciation, PCO_2 gas, and solid phase saturation indices were made using the computer program MINTEQA2 (Allison et al., 1991), with single ion activity coefficients calculated using the Davies equation. MINTEQA2 quantifies possible medium-water and water-atmosphere reactions, but modeling results should be interpreted with caution and are limited by hydrologic flow conditions (saturated and unsaturated), possible reaction mechanisms, and kinetic constraints in a disequilibria-dominated system. A source of error with the computer program is the accuracy of the thermochemical data contained in the MINTEQA2 database. Errors are greater for trace solutes in which experimental data are inaccurate or incomplete. The uranium database contained in MINTEQA2 has been critically evaluated and summarized in Langmuir (1997). There are few errors associated with the major ions and solid phases consisting of carbonate, silicate, and sulfate minerals (Langmuir, 1997).

RESULTS

Experimental. Figure 1 provides a description of the 2-D aquifer cell. Figure 2 summarizes the concentrations of ^{87}Sr, NO_3^- and ClO_4^- eluted from the cell as a function of pore volume. Because Apatite II contains significant amounts of naturally abundant ^{87}Sr, its capacity to adsorb injected ^{87}Sr was limited. Consequently, this material leached ^{87}Sr continuously during early times in the experiment at a concentration of approximately 0.85 mg/L under the flow conditions simulated in this study. After 220 pore volumes of groundwater were introduced to the cell, ^{87}Sr concentrations began to approach the influent level, 2 mg/L. Apatite II will adsorb and precipitate significant concentrations of metals not abundant in its crystal structure. Results of a column experiment indicated that Apatite II could effectively adsorb ^{238}U (92 mg ^{238}U/kg Apatite II) and provided a substrate for microorganisms that continuously reduced NO_3^- and ClO_4^-, which were undetected during the column experiment (Taylor et al., 2001). Pecan shells adsorbed some ^{87}Sr (42 mg ^{87}Sr/kg shells) and the microorganisms that proliferated on the surface of the pecan shells, sustained by organic matter leaching from the Apatite II, reduced NO_3^- and ClO_4^- to undetectable levels for approximately 305 pore volumes (282 days of injection). Prior to detection of NO_3^- and ClO_4^- in effluent samples of the 2-D aquifer cell (<310 pore volumes), greater than 90% of the NO_3^- reduction and 70% of the ClO_4^- reduction was accomplished in the Apatite II layer, while the remainder was degraded during residence within the pecan shells.

Results of analytes measured in influent and effluent water samples collected on day 285 (310 pore volumes) are provided in Table 1. These waters had charge balance errors less than ±4%. The negative charge balance errors provided in Table 1 indicate slight excess anions from analytical results, a finding that is likely due to analytical errors associated with ion chromatography. Influent water was characterized by a mixed sodium-calcium-nitrate-bicarbonate ionic composition with calculated total dissolved solids of 623 mg/L. The effluent water was also characterized by a mixed sodium-calcium-nitrate-bicarbonate ionic composition with calculated total dissolved solids of 591 mg/L. Concentrations of dissolved sodium, barium, chromium, NO_3^-, ClO_4^-, fluoride, molybdenum, strontium, TOC, and uranium are higher in the influent water. Conversely, concentrations of alkalinity, calcium, sulfate, arsenic, manganese, and nickel were higher in the effluent water. Concentrations of Mn^{2+} increased from 0.0005 to 0.027 mg/L in the cell on day 285 suggesting reduction of Mn (+III, +IV) solids to Mn (+II) aqueous species. Oxidized states of manganese are electron acceptors from donors including Fe(II) and organic carbon. Influent and effluent concentrations of arsenic were 0.0009 and 0.0037 mg/L, respectively, which is possibly due to desorption reactions with Apatite II and/or limestone.

The total inorganic carbon (TIC) contents within fresh and 285 day-reacted Apatite II were 16.9% and 2.6% (wt.), respectively. Increasing concentrations of alkalinity within the pore water enhanced the precipitation of $CaCO_3$ and $SrCO_3$, which provided additional adsorption sites for barium, chromium, molybdenum, strontium and uranium. The TOC contents within the fresh and reacted Apatite II were 2.6% and 1.9% (wt.), respectively. Oxidation of organic carbon to CO_2 gas resulted in decreasing TOC within the Apatite II. This oxidation process was coupled with the reduction of both ClO_4^- to Cl^- and NO_3^- to N_2 gas based on the reductive capacity of reactive organic carbon in the presence of microbial populations. Total organic carbon in the water decreased by approximately 27% as the pore water reacted with surfaces of Apatite II particles. Perchlorate may have adsorbed onto mineral surfaces coated with reactive solid organic matter (SOM) under near-neutral pH conditions.

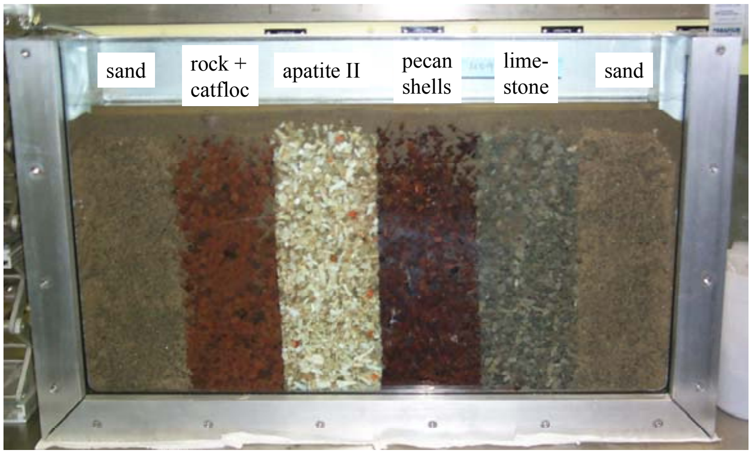

FIGURE 1. 2-D aquifer cell for treatment of ^{87}Sr-, NO_3^-- and ClO_4^--contaminated groundwater.

Reduction reactions of ClO_4^- to Cl^- and other aqueous species are provided in Table 2. Chlorate, a reduction intermediate of perchlorate, is observed in some groundwater at LANL in the part per billion range (Blake et al., 1995). Due to four strong covalent bonds between the O (-II) and Cl (+VII) atoms within the tetrahedral ClO_4^- molecule, this species does not become easily reduced to Cl^- without appropriate anaerobic microbial populations present. Strong reducing agents, such as reactive organic matter and hydrogen sulfide, however, are thermodynamically capable of reducing ClO_4^- to Cl^- under anaerobic conditions (Langmuir, 1997).

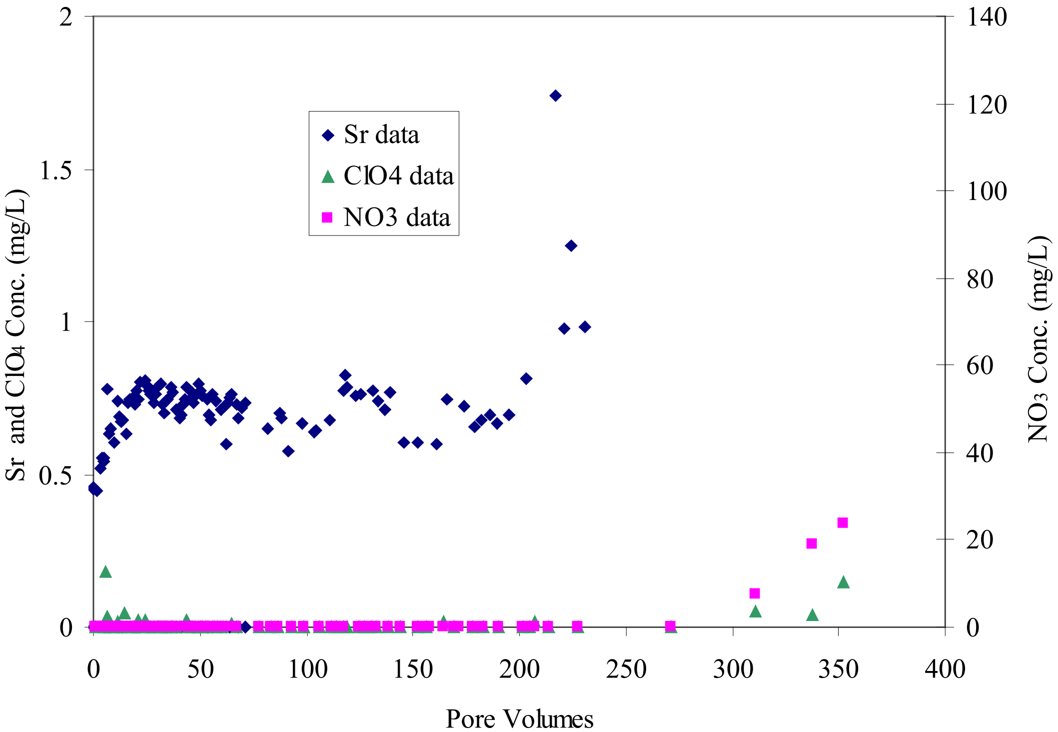

FIGURE 2. Effluent contaminant concentrations following contact with reactive media in 2-D cell.

Oxidation of organic carbon to carbonate alkalinity occurred in the 2-D aquifer cell as the pore water reacted both with Apatite II and the pecan shells (Table 1). Partial decomposition of Apatite II most likely released calcium to solution. The pore water was calculated to be in equilibrium with $CaCO_3$ as discussed in the modeling section of this paper. Concentrations of ClO_4^- and NO_3^- decreased by 71% and 75%, respectively, on day 285 of flow through the cell.

Speciation Modeling. Speciation calculations using the computer program MINTEQA2 (Allison et al., 1991) were performed to evaluate stable forms of dissolved solutes, which influence mineral precipitation and adsorption reactions occurring in the 2-D aquifer cell. Solutes of importance include major ions, ClO_4^-, NO_3^-, strontium, iron(II), and uranium(VI). Results of the speciation calculations are provided in Table 3.

The free or uncomplexed Sr^{2+} cation is available for adsorption and (co)precipitation reactions within the reactive 2-D aquifer cell. The adsorption capacity of the experimental system is limited, however, because of the presence of natural strontium in Apatite II. Nitrate and ClO_4^- are stable as soluble anions and concentrations of these two solutes are not significantly decreased by adsorption and precipitation processes. Nitrate and ClO_4^-, however, are reduced in the presence of reactive SOM and microbial populations as shown by concentration decreases of these two solutes in the effluent water (Figure 2 and Table 1).

TABLE 1. Aqueous Chemistry of Influent and Effluent Waters for the 2-D Aquifer Cell

Water Type	**Influent**	**Effluent**
Sample Treatment	**Filtered**	**Filtered**
Date Sampled (mo/dy/yr)	**08/15/01 (285 d)**	**08/15/01 (285 d)**
Temperature (°C)	25	25
pH	7.84	8.18
Alkalinity ($CaCO_3$ mg/L)	97.1	217
Ca (mg/L)	29.9	50.9
Mg (mg/L)	3.08	3.55
Na (mg/L)	85.0	75.5
K (mg/L)	14.8	15.0
Cl (mg/L)	26.8	27.0
SiO_2 (mg/L)	35.9	35.0
SO_4 (mg/L)	35.1	43.9
As (mg/L)	0.0009	0.0037
B (mg/L)	0.040	0.043
Ba (mg/L)	0.078	0.052
Cd (mg/L)	<0.001, U	<0.001, U
Cr (mg/L)	0.0027	0.0020
Co (mg/L)	<0.001, U	<0.001, U
ClO_4 (mg/L)	0.118	0.034
F (mg/L)	1.19	0.03
Fe (mg/L)	0.01	0.02
Mn (mg/L)	0.0005	0.027
Mo (mg/L)	0.089	0.030
Ni (mg/L)	0.0046	0.0064
NO_3 (as N) (mg/L)	34.1	8.6
Sr (mg/L)	2.12	1.54
PO_4 (total) (mg/L)	<0.02, U	<0.64, U
TOC (mgC/L), NF[b]	5.2	<1, U
U (mg/L)	0.0008	0.0005
MEQ[c] cations	5.789E-03	6.540E-03
MEQ anions	5.800E-03	6.944E-03
Charge Balance (%)	-0.10	-3.00

[a] U = not detected.

[b] NF = non filtered.

[c] MEQ = milliequivalents.

Saturation Index Calculations. Solid-solution phase calculations were performed with MINTEQA2 (Allison et al., 1991) using analytical results obtained from filtered (less than 0.45 µm membrane) influent and effluent water samples. The purpose of the calculations was to assess the importance of precipitation reactions. Table 4 shows the values of the saturation index (SI) for several key phases in the 2-D aquifer cell. The SI is a measure of the degree of saturation, undersaturation, or oversaturation of a solid phase in water [SI = $\log_{10}$ {activity product/solubility product}]; at equilibrium SI = 0 (± 0.05) (Langmuir, 1997).

TABLE 2. The Standard Potential[a], E^0, and Eh at pH = 7.0 and 25^{0}C of ClO$_4^-$ and Related Aqueous Species, Assuming Equilibrium

Reaction	E^0 (V)	Eh (V) at pH 7.0
$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$	1.39	1.306
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	1.23	0.816
$ClO_3^- + 2H^+ + e^- \rightarrow ClO_2^0 + H_2O$	1.13	0.301
$ClO_3^- + 2H^+ + 2e^- \rightarrow ClO_2^- + H_2O$	1.10	0.686
$ClO_2^0 + e^- \rightarrow ClO_2^-$	1.07	1.067
$ClO_2^- + 2H^+ + 2e^- \rightarrow ClO^- + H_2O$	1.51	1.096
$ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.72	1.306

[a] Thermochemical data used in calculations are from: Wagman et al., 1982, The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C$_1$ and C$_2$ organic substances in SI units: National Bureau of Standards, Washington DC.

TABLE 3. Results of Speciation Calculations Using MINTEQA2 for Influent and Effluent Waters of the Reactive 2-D Aquifer Cell

Solute	Influent Dominant Speciation and Percentage	Effluent Dominant Speciation and Percentage
Sr(II)	Sr^{2+}, 95.6	Sr^{2+}, 95.3
Sr(II)	$SrNO_3^-$, 1.0	not present
Sr(II)	$SrSO_4^0$, 3.1	$SrSO_4^0$, 3.7
Perchlorate	ClO_4^-, 100	ClO_4^-, 100
N(V)	NO_3^-, 100	NO_3^-, 100
U(VI)	$UO_2(CO_3)_2^{2-}$, 59.3	$UO_2(CO_3)_2^{2-}$, 37.4
U(VI)	$UO_2(CO_3)_3^{4-}$, 36.4	$UO_2(CO_3)_3^{4-}$, 60.5
U(VI)	$UO_2(OH)_2^0$, 3.1	$UO_2(OH)_2^0$, 1.4
Mo(VI)	MoO_4^{2-}, 100	MoO_4^{2-}, 100
As(V)	$H_2AsO_4^-$, 6.0	$H_2AsO_4^-$, 2.8
As(V)	$HAsO_4^{2-}$, 94.0	$HAsO_4^{2-}$, 97.1

TABLE 4. Results of Saturation Index Calculations Using MINTEQA2 for Influent and Effluent Waters of the 2-D Aquifer Cell

Solid or Gas Phase	Influent Water	Effluent water
Barite	-0.06	-0.16
Aragonite	-0.22	0.41
Calcite	-0.08	0.55
Hydroxyapatite	1.01	7.75
Fluorite	-0.85	-3.83
Gibbsite	-0.02	-0.44
Silica (ppt)	-0.52	-0.53
Silica (gel)	-0.21	-0.22
Strontianite	0.60	0.87
Siderite	-1.63	-0.93
Haiweeite	0.011	0.21
Soddyite	-3.07	-3.70
Log_{10} PCO_2	-2.78	-3.04

Influent water was calculated to be in equilibrium with $BaSO_4$ (barite), $CaCO_3$ (calcite), $Al(OH)_3$ (gibbsite), and $Ca(UO_2)_2(Si_2O_5)_3{\cdot}5H_2O$ (haiweeite) and undersaturated with respect to $CaCO_3$ (aragonite), $FeCO_3$ (siderite), silica (gel and precipitate), CaF_2 (fluorite), and $(UO_2)_2SiO_4{\cdot}2H_2O$ (soddyite). This solution, however, was calculated to be oversaturated with respect to $SrCO_3$ (strontianite) and $Ca_5(PO_4)_3OH$ (hydroxyapatite). Modeling results suggested that effluent water was oversaturated with respect to calcite, aragonite, strontianite, haiweeite, and hydroxyapatite and undersaturated with respect to barite, fluorite, gibbsite, silica phases, siderite, and soddyite. Calcite, quartz, kaolinite, smectite, aragonite, hydroxyapatite, and whewellite ($CaC_2O_2{\cdot}H_2O$) have been identified by quantitative XRD in materials used in the 2-D aquifer cell. Calcite and aragonite occurred within the Apatite II structure along with organic matter and whewellite is a constituent identified within the pecan shells. Strontianite and haiweeite have not been observed at abundances greater than 1% (wt.) in the materials, and precipitation of these phases is limited by kinetics. Overall, results of the modeling simulations support the identification of solid phases within the 2-D aquifer cell.

ACKNOWLEDGMENTS

LANL's Environmental Division and a Director's Postdoctoral Fellowship provided funding for this study. This manuscript summarizes recent research and does not represent the views of the funding agencies.

REFERENCES

Allison, J. D., D. S. Brown, and K. J. Novo-Gradac. 1991. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*. U.S. Environmental Protection Agency Technical Report, EPA/600/3-91/021, Office of Research and Development, Athens, GA, USA.

Blake, W. D., F. Goff, A. I. Adams, and D. Counce. 1995. *Environmental Geochemistry for Surface and Subsurface Waters in the Pajarito Plateau and Outlying Areas, New Mexico*. Los Alamos National Laboratory Report, LA-12912-MS, Los Alamos, NM, USA.

Langmuir, D. 1997. *Aqueous Environmental Geochemistry,* Prentice-Hall, Inc., Upper Saddle River, NJ, USA.

Purtyman, W.D. 1995. *Geologic and Hydrologic Records of Observation Wells, Test Holes, Test Wells, Supply Wells, Springs, and Surface Water Stations in the Los Alamos Area*. Los Alamos National Laboratory Report, LA-12883-MS, Los Alamos National Laboratory, Los Alamos, NM, USA.

Taylor, T.P., N.N. Sauer, J.L. Conca, B.A. Strietelmeier, J.P. Kaszuba, M.W. Jones and S.D. Ware. 2001. *Reactive Barrier Treatment Wall Technology for Remediation of Inorganic Contaminated Groundwater*. Groundwater Quality 2001 Conference, International Association of Hydrological Sciences (IAHS) and International Association of Hydrogeologists (IAH), Sheffield England, UK.