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Column Study Results for the Permeable Reactive Barrier
by
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1.0 Introduction

Laboratory experiments were conducted in 2007 (LANL 2007, 096003) to evaluate the performance of six potential media for the pilot permeable reactive barrier (PRB): granular activated carbon (GAC), zero-valent iron (ZVI), apatite II, clinoptilolite, and gypsum. Bandelier Tuff was also studied to evaluate host rock attenuation of the two contaminants. From results of the earlier study, ZVI and the zeolitic mineral clinoptilolite were chosen as the two reactive media used in the pilot PRB. However, optimization of the media mix (sand plus media) was needed before the PRB was implemented. Further laboratory studies of isothermal batch sorption as well as isothermal flow-through columns were performed at room temperatures (~22°C) to optimize the media mixes as summarized in this report.

2.0 Media Description

The ZVI (**Image 1**) was provided by Connelly Iron Products, Chicago, Illinois. The material was received precleaned and size-differentiated from 0.0075 to 0.425 mm. The material was resieved to 0.075 to 0.250 mm. **Table 1** gives the report provided by Connelly Iron Products on its typical iron aggregate laboratory analysis.

Clinoptilolite (**Image 2**) was also provided by Connelly Iron Products. The material originated from Saint Cloud Mining Company in Winston, New Mexico. The company reports 75% to 85% clinoptilolite but does not provide information listing impurities. Similar to the ZVI, the material was received in the 0.0075- to 0.425-mm fractional size and was resieved to 0.075 to 0.25 mm.

Groundwater from Technical Area 16 (TA-16) at Los Alamos National Laboratory (LANL) was obtained from well purges collected between October 2006 and May 2009. Well CdV-16-02658, located near the pilot PRB, provided most of the water used in this study; however, well CdV-16-6295, located in Martin Canyon south of Cañon de Valle; well CdV-16-02657, located roughly one-half mile up from the PRB site; and well CdV-16-02659, located approximately one-half mile down from the PRB site, also supplied well water used in this study.

The well waters were combined and mixed together into four 20-L plastic carboys. Two of the carboys were individually spiked with 1 mL of 1000 µg/mL RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) standard purchased from Ultra Scientific Analytical Solutions with a 95% confidence-level accuracy of the standard. The RDX standard was stored in a base of acetonitrile. It was used to increase the concentration of the RDX from the natural water concentration <10 parts per billion (ppb) to a concentration of 103 ppb.

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The two spiked carboys of water were then pumped through a 0.45-µm inline Millipore GWSC water filter and named PWW16-MX2 (**Table 2**).

3.0 Analysis

Samples were analyzed in the Earth and Environmental Sciences (EES-14) laboratory at LANL. Cations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) using U.S. Environmental Protection Agency (EPA) Method 200.7. Ultra-high-purity nitric acid (Fisher Trace Metal Grade) was used in sample and calibration preparation prior to sample analysis. Internal standards (Sc, Ge, Bi, and In) were added to both samples and standards to correct for matrix effects.

RDX samples were analyzed by high-performance liquid chromatography (HPLC) using a Dionex Ultimate 3000 RS Variable Wave Length Detector following EPA Method 8330. Calibration was accomplished by evaluation of a dilution slope from an RDX standard purchased from Ultra Scientific Analytical Solutions (Product EPA-1233, lot CE-0126, expiration date of February 2012, concentration of 1000 µg/mL).

The pH measurements were performed using a Fisher Scientific Accumet combination pH probe with a 290A Orion meter.

Oxidation-reduction potential (ORP) measurements were made with an Erlich Industrial Development Corporation 120 mm platinum band probe and a 290A Orion meter. Calibration was performed using two pH buffers supersaturated with quinhydrone. Because the meter only allows a one-point calibration, mV reading was set to +89 with the pH 7.00 buffer supersaturated with quinhydrone and then compared to pH 4.00 buffer with quinhydrone which should register +265mV. Acceptable calibration was achieved when measurements were within plus or minus 3mV.

3.1 Batch Sorption

Batch sorption studies were performed to evaluate the performance of ZVI with RDX and Clinoptilolite with barium. The reactive media was placed in 125 mL plastic vials with 2 g of media to 100 mL of solution for a 1:50 ratio. Duplicates were run for each of the batch experiments. As a control, a sample of the experimental water was also placed in 125 mL plastic vials without any reactive media and run concurrently with the other samples. The samples were agitated on an orbital shaker at 120 revolutions per minute. Five mL aliquots were removed at each timed sample interval then centrifuged at 28,175 relative centrifugal force for 1 hr with the resulting supernate analyzed for barium concentration by ICP and RDX by HPLC.

Distribution coefficients were determined by calculating the ratio of the amount of contaminant sorbed by the reactive media to the amount of contaminant remaining in the solution (Freeze and Cherry 1979, 088742, p. 403):

$$K_d = \frac{dS}{dC}$$

where K_d = distribution coefficient
S = mass of the solute sorbed by reactive media
C = solute concentration remaining in solution

The following equation further clarifies how the K_d calculation was used in this summary:

$$K_d = \frac{C_i V_i - C_f V_f}{C_f M_s}$$

where K_d = distribution coefficient
C_i = initial solution concentration
C_f = final solution concentration
V_i = initial solution volume
V_f = final solution volume
M_s = sediment mass

3.2 Column Experiments

Column studies were performed with ZVI and clinoptilolite to assess constituent attenuation dynamics either from retarding or from breaking down barium and RDX under flow conditions that mimic environment applicable to the PRB. The columns were prepared by mixing the reactive media with sand. The sand was "Colorado Silica Sand" obtained from Oglebay Norton Company. The sand was received in a large 10/20 sieved fraction. The sand required size reduction where it was crushed and sieved to a 0.075–0.250mm grain size, followed by rinsing with deionized water and dried in a vacuum (~18" Hg) oven at 40° C.

Sixteen sets of column experiments were performed. The columns were customized using 3/8-in. inner diameter polyethylene tubing. The tubing was cut to lengths of 5 cm followed by tapping to a 1/8-in. 27 National Pipe Thread (NPT) allowing Luer fittings from Value Plastics, Inc., to be fitted to the small columns as endcaps. Therefore, inner column dimensions were approximately 1 × 5 cm, producing a volume ($\pi r^2 h$) of 3.93 mL for each column.

To minimize wall effects, where the tracer flows along the walls of the column avoiding flow and interaction with the column media, average particle diameter should be a fiftieth or smaller than the column diameter. Particle size of the column media was sieved to 0.075–0.250 mm for an average particle size of 0.15 mm, thus avoiding wall effects.

All experiments used the natural groundwater PWW16-mx2 containing 6.51 parts per million (ppm) barium that was also spiked to 103 ppb RDX. Columns were packed using

dry media gently poured in small sections, lightly tapped to induce compaction, with repeated pouring and tapping until filled followed by weighing.

The columns were purged of atmospheric gasses by subjecting columns to a vacuum pump (~20-in. Hg), then saturated by introducing deaerated Los Alamos municipal tap water to the columns while under static negative pressure achieved with Luer valves isolating the columns away from the vacuum pump. Chlorine, added as a sterilizing agent to the municipal water, was purged before column saturation by subjecting water to a vacuum for a minimum of 48 hr allowing sufficient time for chlorine to fully dissipate. Municipal water was used as a bicarbonate water source similar to the chemistry of PWW16-mx2 yet free of barium and RDX. This water was used to saturate and set flow conditions before saturating columns with PWW16-mx2 water. After column saturation, columns were weighed and compared to the dry weight to calculate column porosities. Hydraulic conductivity measurements were made for all the columns following EPA Method's 9100 constant head calculation using Darcy's law.

Column hydraulic conductivity measurements were taken at the start and at the end of the experiments after approximately 1 mo. Openings of the Luer endcap fittings were packed with loose polyester fiberfill to hold and retain column media. Attempts were made to use the same amount of material for each fitting and to pack them similarly; however, variation of conductivity measurements likely represented density packing variances of this material rather than differences in packing the sediment.

Columns were continually kept flowing; however, problems plagued the ZVI columns from the generation of hydrogen gas, particularly with higher weight percentage ZVI. Immediately before retesting the column hydraulic conductivities, each column was submerged in deaerated Los Alamos tap water and subjected to a vacuum to remove hydrogen gas so each column was in a similar saturation state.

Pore velocity was calculated using the following equation:

$$V_p = \frac{Q}{\pi r^2 \phi}$$

where V_p = pore velocity
Q = flow rate
π = 3.14
r = column internal radius
ϕ = column porosity

Column effluents were collected at timed intervals with test tube in a Gilson FC220 fraction collector. Flows to the columns were established using KD Scientific infusion KDS100 syringe pumps. All columns were subjected to flow at the experimental rate for at least 20 pore volumes before experimental start **(Image 3)**.

4.0 Results and Discussion

4.1 Batch Studies

Previous studies of potential reactive media for removal of RDX and barium focused the laboratory studies on clinoptilolite and ZVI as these were the two media selected for use in the pilot PRB field application. Clinoptilolite, a natural occurring zeolite with the chemical formula $(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12(H_2O)$, is readily available and locally found in New Mexico, providing an economically viable candidate for PRB media. Previously, clinoptilolite was found to have a strong affinity for sorption of barium. The earlier study found K_d value of 1827 mL/g after 100 hr; however, the study was not extended long enough to show the maximum K_d value after equilibration of the barium contaminated groundwater with clinoptilolite. Further studies carried over a longer period showed equilibration of the isotherm K_d plot of clinoptilolite with PWW16-mx2 water was achieved at approximately 288 hr with a maximum K_d value of 6930 mL/g. Equilibration is evidenced by the flattening section of the curve (**Plot 1**) where K_d values remained in the 6700 mL/g range after 288 hours.

Previous batch studies of ZVI were inconclusive because ZVI broke down rapidly, preventing estimation of the distribution coefficient. The previous tests were complicated by low natural RDX values (~15 ppb) in the groundwater that were close to detection level of the analytical instrumentation (~10 ppb). New test were performed with RDX spiked to 103 ppb. Using a higher RDX concentration with the groundwater, a distribution coefficient of 405 mL/g was found with ZVI after 68 hr; however, the next sample interval at 96 hr showed no measurable detection of RDX. Therefore, true K_d value is well in excess of the last measured assessment. However, it should be noted that K_d as a function of sorbtive behavior is not the correct characterization of RDX's degenerative, labile interaction in the presence of ZVI. A pseudo-first-order decay would better characterize the reaction (Wanaratna, et al., 2006, 095714; Venkatapathy, et al. 2002, 108726).

The ORP and pH measurements were taken concurrently with each sample for analysis for the batch studies (**Table 2**). It is interesting to note that for both ZVI and clinoptilolite, the water decreased in alkalinity with the most significant drop occurring with clinoptilolite. As can be expected, ORP values became most reduced with ZVI, but it is interesting to note that clinoptilolite also produced reducing conditions.

4.2 Column Studies

In the previous column studies, ZVI with RDX and clinoptilolite with barium demonstrated exceptional reaction kinetics hindering evaluation of breakthrough of the two contaminants. To enhance breakthrough observation, volume of reactive media was reduced by shrinking the columns to approximately ~4 mL while pore velocity was increased. Different flow rates were used with the columns by setting syringe pumps at a low of 2.5 mL/hr to a maximum of 30 mL/hr. Resulting pore velocities ranged from

~6.5 cm/hr to ~ 40 mL/hr. Average porosities of the microcolumns were ~47% with an average water volume of ~1.86 mL.

The columns were mixed with different weight ratios of sand to reactive media ranging from 75% of the media and 25% sand down to 10% media and 90% sand. Sediment mass varied because of ratio with sand, particularly because of the higher density of ZVI; however, on average, the sediment mass was about 5 g. Hydraulic conductivities of the columns were measured soon after saturation and before experiments were started and then remeasured approximately 1 mo after the experiments were finished. In all cases, hydraulic conductivity was found to have decreased in all the columns. On average, the clinoptilolite columns hydraulic conductivities declined by 18%; however, hydraulic conductivity decline was more noticeable with the ZVI columns where it decreased an average of 27%. It should be noted that because of the problem of hydrogen gas generated from water bonds being broken under the reducing conditions of ZVI, which was found in the previous set of experiments, all the columns were subjected to short exposure of 20-in. Hg vacuum to remove potential gas impediment of the columns hydraulic conductivity. Extrapolating these data to calculate an expected value of hydraulic conductivity decline for field application is difficult to model or assess but a decrease with time should be expected.

The 75% clinoptilolite and 25% sand columns showed a half-life residence time of 778 min for barium at a pore velocity of 6.6 cm/hr decreasing to 12.5 min half-life with a higher pore velocity of 81.6 cm/hr. At the 50% to 50% ratio, the half-life residence time at the slower pore velocity was 236 min, whereas at the higher velocity it was identical to the column with a higher percentage of clinoptilolite at 12.5 min, demonstrating half-life residence time is kinetically controlled. The breakthrough curves **(Plots 2 through 5)** also show notable differences in the time or amount of pore volume barium takes to breakthrough the columns with the 75% zeolitic columns demonstrating the highest amount of barium retardation.

The ZVI columns **(Plots 7 through 8)** had issues with generation of hydrogen gas as well as effectiveness in degrading RDX. Columns were run at 75%, 50%, 25% and finally 10% ZVI to 90% sand before breakthrough of RDX was noted at a pore velocity of 42 cm/hr. After the column had eluted 450 pore volumes, breakthrough had only reached ~2.5% of the inflow concentration of RDX. A rough prediction of the breakthrough curve was made by fitting a regression curve and extrapolating pore volume and half-life residence time for 50% and 75% mixed ratios of ZVI for these columns. The extrapolation calculated a half-life residence time of 2,500 hours at 50% ZVI and 3750 hr at 75% ZVI.

Column elutions were also collected to assess change in water chemistry through the columns and evaluate potential field chemistry of the water as it exits the barrier. Two sets of 5-cm-long columns were prepared and connected whereby one set of columns was configured so the inlet was comprised of a ZVI column connected to an outlet column of clinoptilolite and conversely rearranged for the second set. Flow through the columns was set at 0.5 mL/hr. Water chemistry showing major elemental analysis as well as total

dissolved solids (TDS), alkanlinity, pH and ORP are shown in **Table 2**. No significant change is observed when the water chemistries of the column elutants are compared with the inlet water. It is interesting to note that pH increased in alkalinity in comparison to samples taken with the batch sorption studies. It is also expected that ORP values reduced in the column discharge but it is surprising that the values are not even more reduced. Samples were collected and measured immediately, but it is likely that the water discharged from the columns quickly oxidized with the atmosphere. This is an indication that highly reduced waters exiting the field barrier will also quickly oxidize to ambient conditions and not affect the water chemistry downgradient of the barrier.

5.0 References

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Image 1: ZVI sieved to 0.075 to 0.25 mm

Image 2: Clinoptilolite sieved to 0.075 to 0.25 mm

Image 3: Setup and flow of microcolumns taped to fraction collector

Table 1: Typical Laboratory Analysis of Connelly Iron Products Iron Aggregate

Metallic Iron/Iron Oxide	87-93%
Total Carbon	2.85-3.23%
Manganese	0.14-0.6%
Sulphur	0.067-0.017%
Phosphorous	0-0.132%
Silicon	1.0-1.85%
Nickel	0.05-0.21%
Chromium	0.03-0.23%
Vanadium	ND
Molybdenum	0.08-0.15%
Titanium	0.004-0.1%
Copper	0.11-0.20%
Aluminum	0-0.005%
Cobalt	ND
Magnesium	0.01%
Boron	0.01%
Zinc	0.01%
Zirconium	0.01%

Table 2: Water Chemistry of PWW16-mx2 and Column Elutants

Description	PWW16-mx2	Column: ZVI inlet, Clinoptilolite outlet Flow: 0.5 mL/hr	Column: Clinoptilolite inlet, ZVI outlet Flow: 0.5mL/hr
RDX (mg/L)	0.103	non-detect	non-detect
Al (mg/L)	0.005	0.011	0.108
As (mg/L)	0.0005	0.0005	0.0005
B (mg/L)	0.066	0.153	0.108
Ba (mg/L)	6.14	0.581	0.185
Br (mg/L)	0.13	0.15	0.17
Ca (mg/L)	20.9	24	14
Cl (mg/L)	20.5	19.1	18.4
Cr (mg/L)	0.002	0.004	0.004
Cu (mg/L)	0.007	0.007	0.008
F (mg/L)	0.70	0.32	0.48
Fe (mg/L)	<0.01	0.26	0.64
K (mg/L)	2.17	10	23
Li (mg/L)	0.005	0.006	0.006
Mg (mg/L)	5	4	2
Mn (mg/L)	.001	0.247	0.085
Na (mg/L)	15.4	20	29
Ni (mg/L)	0.003	0.006	0.003
Pb (mg/L)	0.0009	0.0003	0.0006
Rb (mg/L)	0.002	0.030	0.050
Si (mg/L)	17	13	10
Sr (mg/L)	0.129	0.127	0.094
Ti (mg/L)	<0.02	<0.02	0.004
U (mg/L)	0.0002	0.0003	0.0002
V (mg/L)	0.002	0.004	0.003
Zn (mg/L)	0.045	0.015	0.009
pH	7.81	7.82	8.17
ORP (mV)	244	183.4	166.8
TDS (mg/L)	217	254	277
Alkalinity (mg/L) $CaCO_3$	76.5	99.2	119.7
HCO3 (mg/L)	93	121	146
Cation sum	2.25	2.67	2.76
Anion sum	2.48	3.04	3.31
Total cation and anion balance	-0.05	-0.07	-0.09

Table 3: Clinoptilolite Column Parameters

Column 1 x 5 cm	Sediment Mass (g)	Water Mass (g)	Porosity %	Hydraulic Conductivity Start (cm/min)	Hydraulic Conductivity End (cm/min)	Percent Change in Hydraulic Conductivity	Half-life residence time (min): barium	Pore Velocity cm/hr
Clinoptilolite 75%: Sand 25% 2.5mL/hr	4.88	1.91	48.6	0.33	0.28	15	778	6.5
Clinoptilolite 75%: Sand 25% 7.5 mL/hr	4.92	1.87	47.6	0.39	0.29	26	105	20.1
Clinoptilolite 75%: Sand 25% 15 mL/hr	4.97	1.87	47.6	0.29	0.24	17	35	40.1
Clinoptilolite 75%: Sand 25% 30 mL/hr	4.86	1.90	48.3	0.40	0.32	20	12.5	79.1
Clinoptilolite 50%: Sand 50% 2.5mL/hr	5.07	1.88	47.8	0.26	0.19	27	236	6.6
Clinoptilolite 50%: Sand 50% 7.5 mL/hr	5.03	1.85	47.1	0.41	0.33	20	50	20.3
Clinoptilolite 50%: Sand 50% 15 mL/hr	5.11	1.82	46.3	0.38	0.32	16	25	41.2
Clinoptilolite 50%: Sand 50% 30 mL/hr	5.08	1.84	46.8	0.28	0.23	18	12.5	81.6
Average	N/A	1.87	47.5	0.34	0.28	18	N/A	N/A

Table 4: ZVI Column Parameters

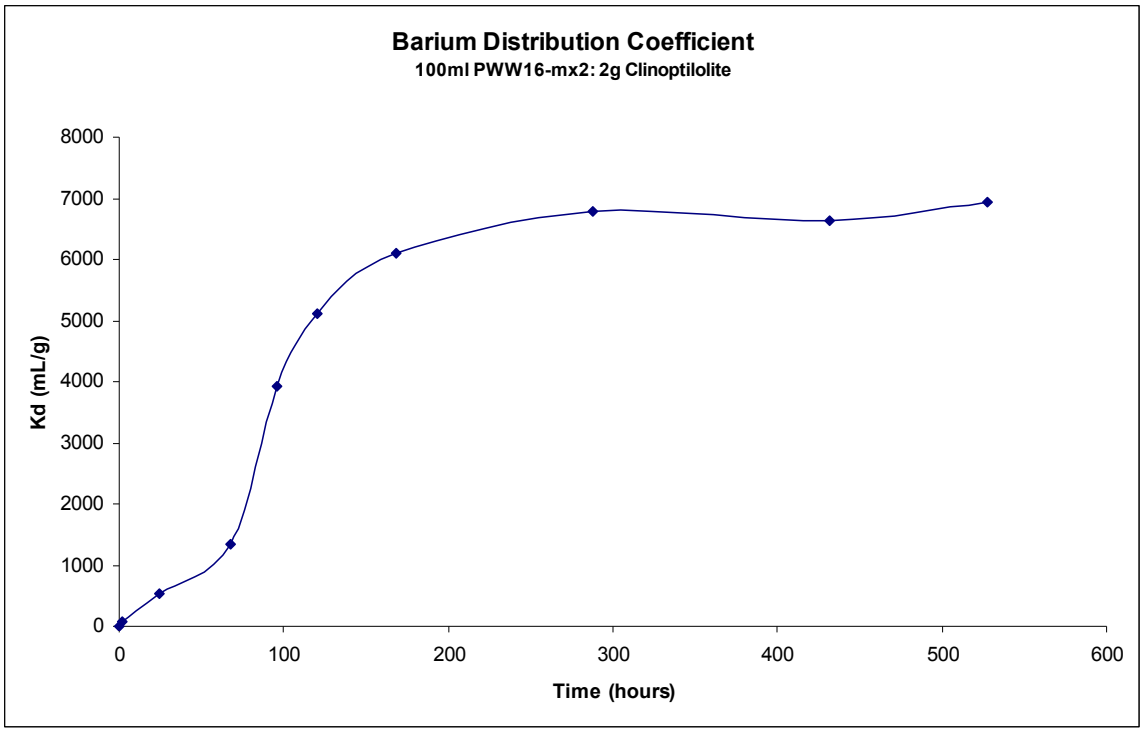
Column 1 x 5 cm	Sediment Mass	Water Mass	Porosity	Hydraulic Conductivity Start (cm/min)	Hydraulic Conductivity End (cm/min)	Percent Change in Hydraulic Conductivity	Half-life residence time (hrs): RDX	Pore Velocity cm/hr
ZVI 75%: Sand 25% 7.5 mL/hr	5.36	1.79	45.5	0.34	0.24	29	No Breakthrough	20.9
ZVI 75%: Sand 25% 15 mL/hr	5.33	1.83	46.6	0.42	0.29	31	No Breakthrough	40.1
ZVI 75%: Sand 25% 30 mL/hr	5.36	1.86	47.3	0.41	0.31	24	No Breakthrough	80.8
ZVI 50% Sand 50% 7.5 mL/hr	5.21	1.81	46.1	0.29	0.21	28	No Breakthrough	20.7
ZVI 50%: Sand 50% 15 mL/hr	5.24	1.91	48.6	0.37	0.26	30	No Breakthrough	39.3
ZVI 50%: Sand 50% 30 mL/hr	5.28	1.84	46.8	0.39	0.3	23	No Breakthrough	81.6
ZVI 25%: Sand 75% 15 mL/hr	5.19	1.86	47.3	0.36	0.25	31	No Breakthrough	40.4
ZVI 10%: Sand 90% 15 mL/hr	5.17	1.83	46.6	0.41	0.26	37	Regression estimated at 500	41.0
Average	N/A	1.84	46.9	0.37	0.27	27	N/A	N/A

Table 5: Batch Sorption Parameters of RDX (103ppb) with ZVI

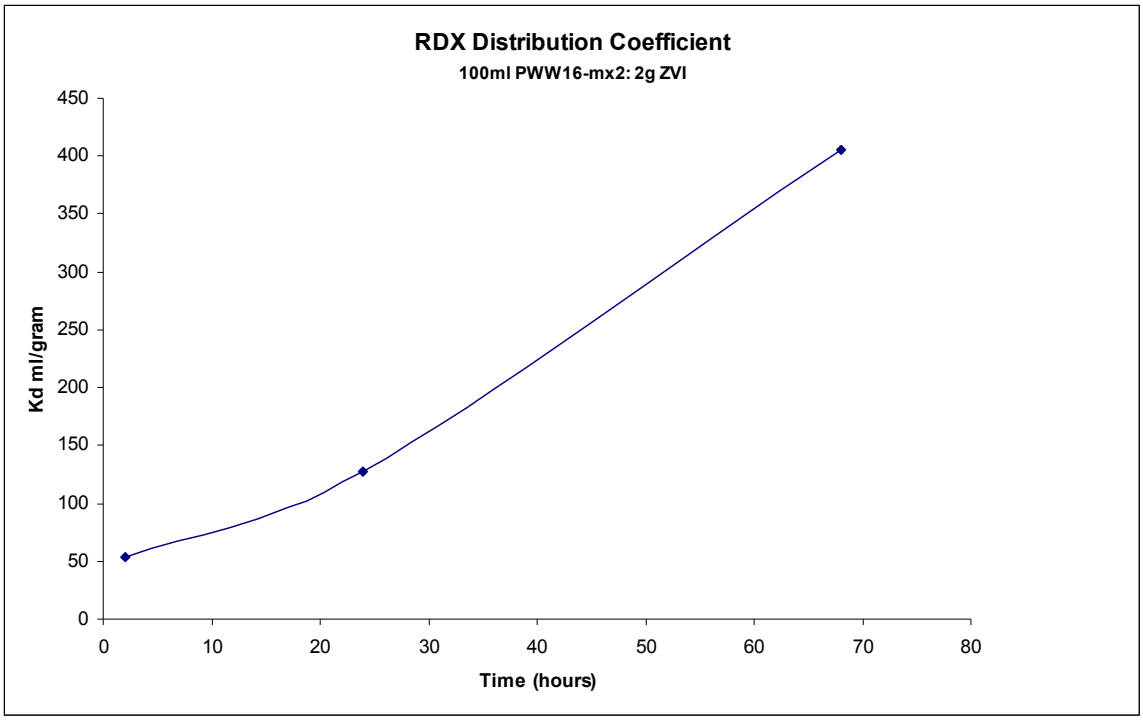
Time (hrs)	Kd (mL/g)	pH	ORP (mV)
0	0	8.23	244
2	53	8.12	167
24	127	7.65	140
68	405	7.99	124
96	Not Detectable	7.94	101

Table 6: Batch Sorption Parameters of Barium (6.14ppm) with Clinoptilolite

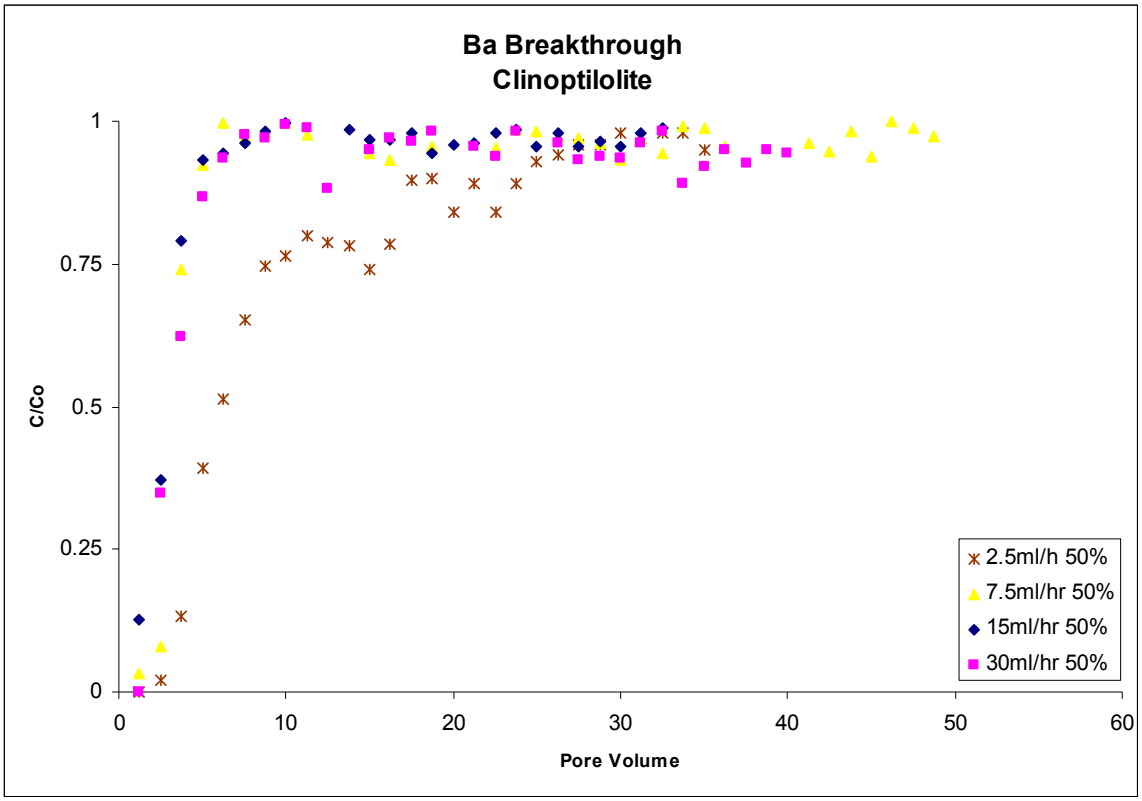
Time (hrs)	Kd (mL/g)	pH	ORP (mV)
0		8.23	244
2	85	8.217	164.7
24	520	7.696	184.3
68	1330	7.857	173.3
96	3917	6.972	189.2
120	5113	7.236	157.1
168	6092	7.148	163.4
288	6774	6.936	176.3
432	6626	7.027	168.6
528	6929	7.141	143.8

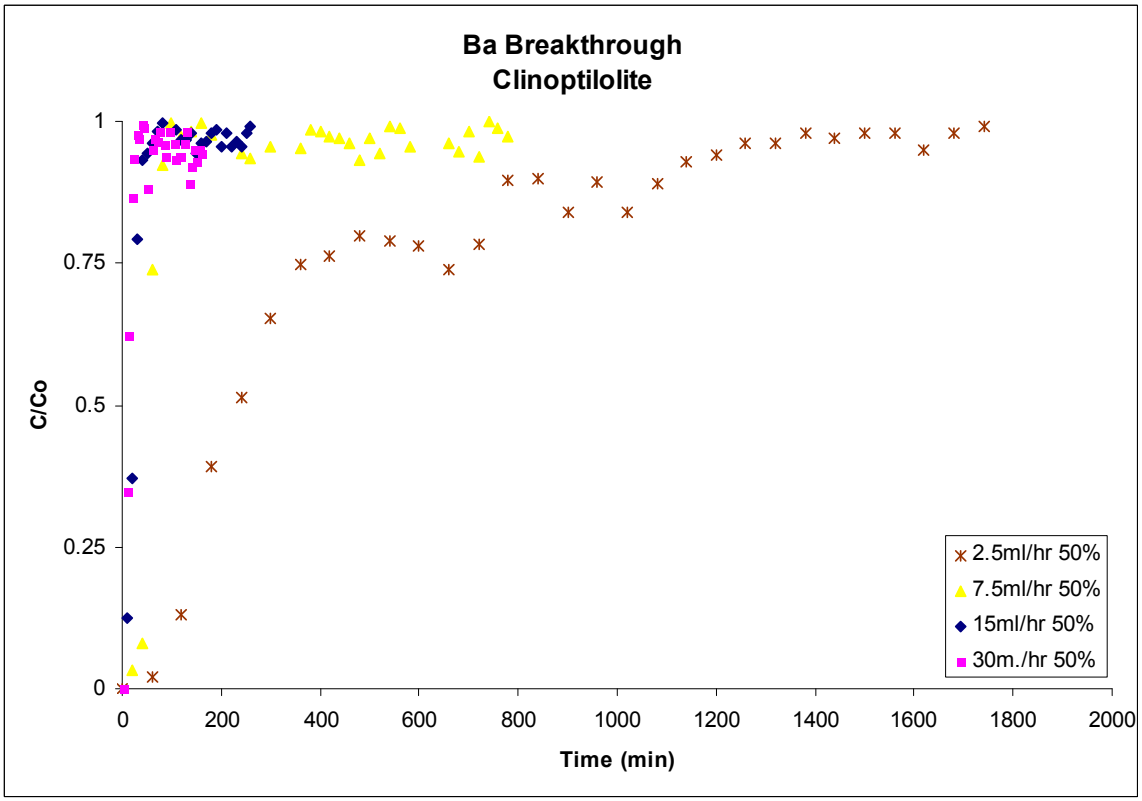


Plot 1: Batch sorption derived distribution coefficient for barium with clinoptilolite

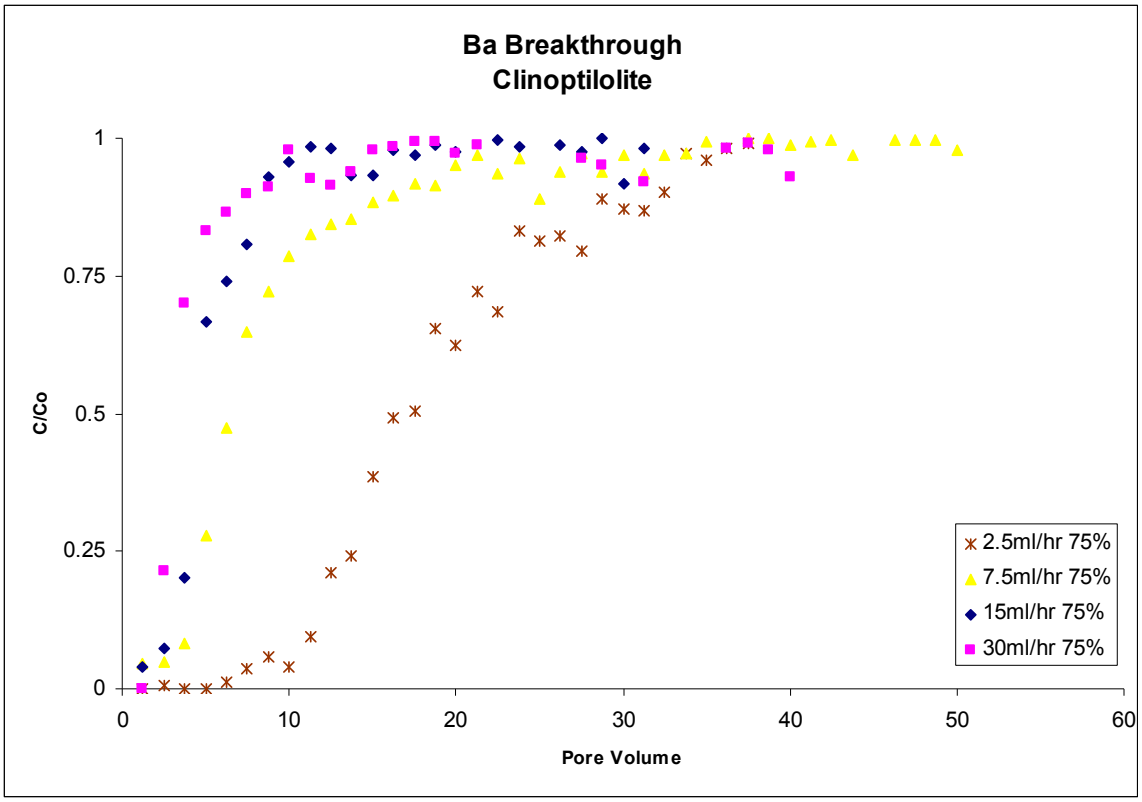


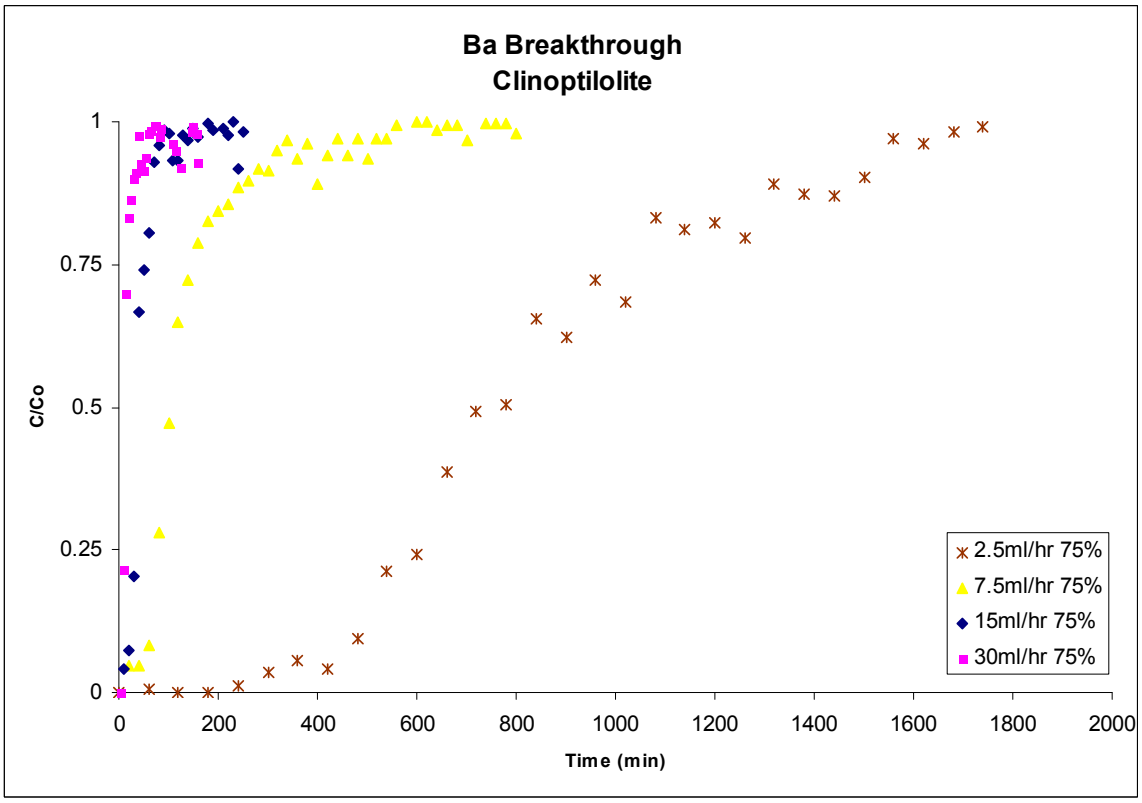
Plot 2: Batch sorption derived distribution coefficient for RDX with ZVI



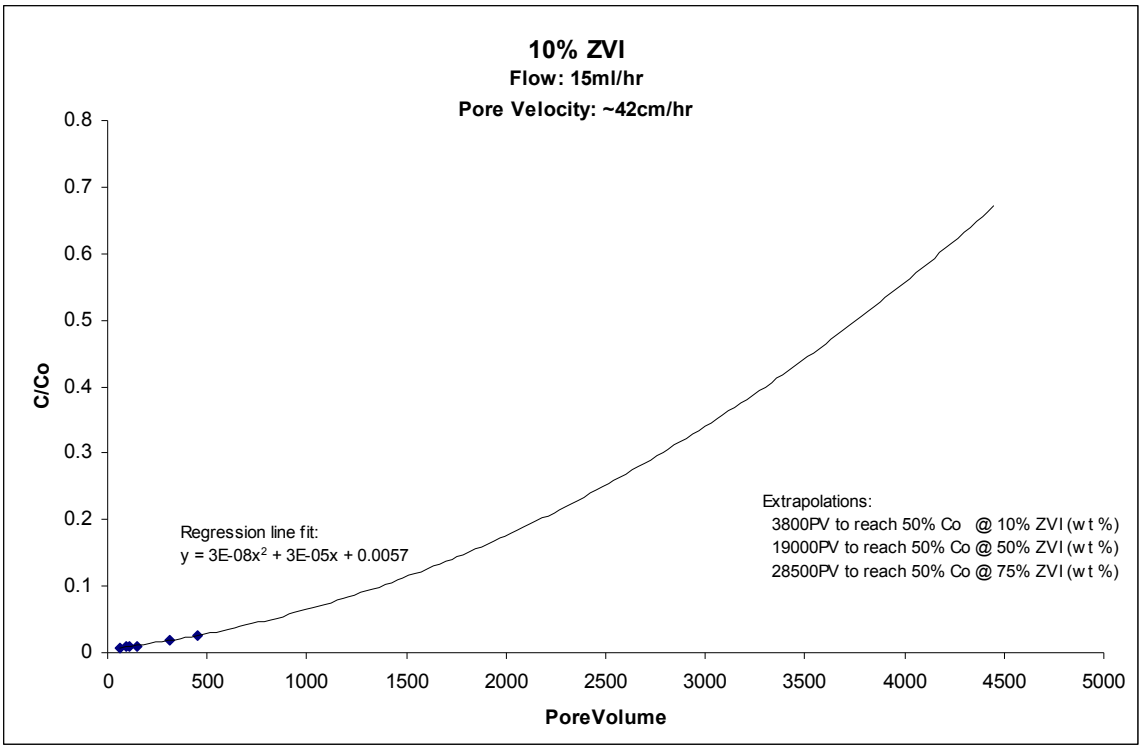


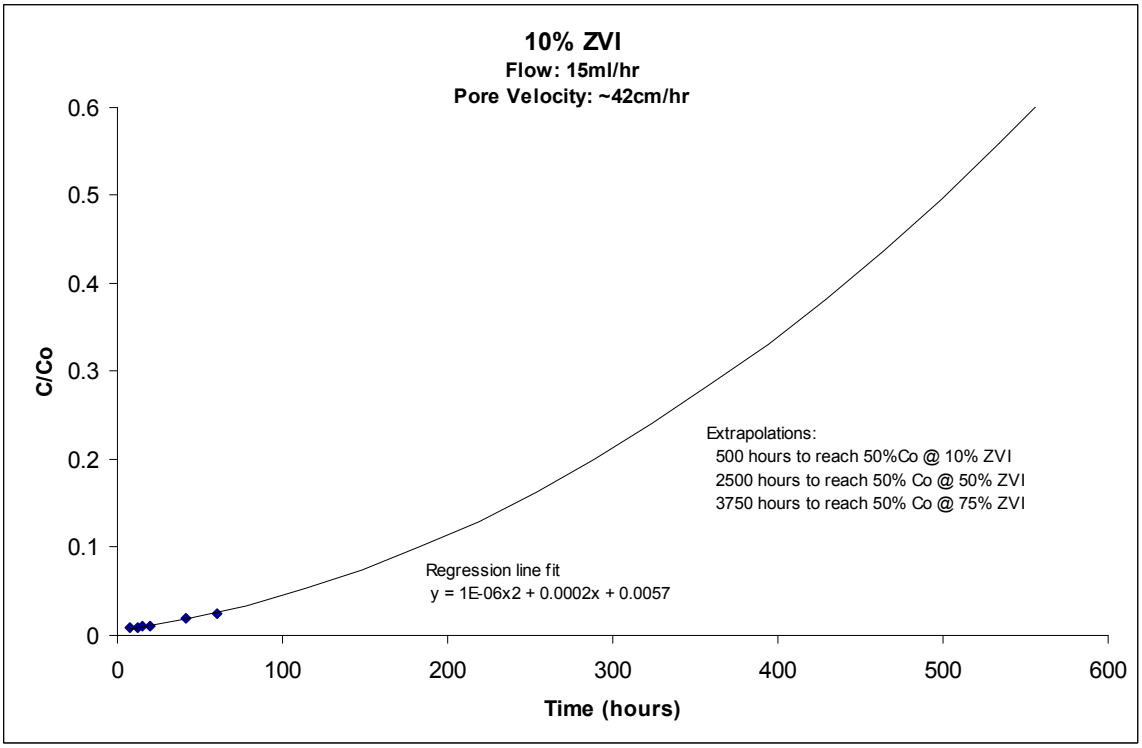
Plots 3 and 4: Barium breakthrough curve with 50% clinoptilolite





Plots 5 and 6: Barium breakthrough curve with 75% clinoptilolite





Plots 7 and 8: RDX breakthrough curve with 10% ZVI