# West Valley Demonstration Project

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| **Doc. ID Number** | WVDP-506 Addendum 1 |
| **Revision No.** | 0 |
| **Revision date** | 08/30/2010 |

## Update:
## Laboratory Testing of Zeolitic Materials

*Submitted by*
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*Submitted to*

West Valley Environmental Services, LLC

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State University of New York at Buffalo

**July 07, 2010**

# UPDATE

# LABORATORY TESTING OF ZEOLITIC MATERIALS

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# LABORATORY TESTING OF ZEOLITIC MATERIALS

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## INTRODUCTION

This report summarizes recent results of laboratory experiments performed as part of the study entitled "Laboratory testing of zeolitic materials," under West Valley Environmental Services (WVES) Purchase Order 19-001849-C-JK. The report includes results from ongoing column experiments conducted at the University at Buffalo (UB), as well as column experiments operated at the West Valley Demonstration Project (WVDP). Previous UB results were reported by Rabideau et al. (2009b).

The UB column experiments were performed by doctoral candidate Ms. Shannon Seneca at the Jarvis Hall Laboratory, under the direction of Dr. Alan J. Rabideau. The West Valley experiments were performed at the WVDP site by WVES personnel under the direction of Mr. Michael Pendl and Mr. David Scalise. For both studies, outside laboratories were utilized as noted to perform chemical analyses of water samples. The objectives and procedures described in this report are referenced to the approved Quality Assurance Project Plan (QAPP) of February 11, 2009 (Rabideau et al., 2009a). A DOE-WVDP surveillance reviewed adherence to the QAPP requirements and WVES oversight of the testing program. WVES responded to all surveillance findings and comments as documented by Biedermann (2009).

## METHODS

### Materials

Zeolite test materials were obtained directly from the suppliers: (1) Teague Mineral Products (TMP) of Adrian, OR and (2) Bear River Zeolite (BR) of Preston, ID. Because these natural materials are not pure minerals, they are commonly referred to as "zeolite-rich rock." However, for the purpose of this report, the simpler terms "zeolite" or "natural zeolite" are used. For both TMP and BR materials, the requested particle size was 14x40, which corresponds to standard sieve openings of 1.4 and 0.425 mm, respectively. Other properties of the TMP and BR zeolites used in the testing program were reported previously by Rabideau et al. (2009b).

Several of the column experiments were conducted with mixtures of material that included WVDP soil collected from a radiologically non-contaminated area during field characterization performed in fall 2008. Visual inspection indicated that the soil was comprised generally of silty-clay with a soft brown color and silky texture. The soil was first air-dried overnight, and then sieved to remove particles larger than 1.18 mm. Because the soil was available in limited quantity, further characterization was not performed.

### Analysis of water samples

The column test procedures described below required the analysis of aqueous samples for dissolved cations ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, nonradioactive strontium-88 [henceforth $Sr^{2+}$]and

radioactive strontium-90 [henceforth Sr-90]. Samples for the UB columns were shipped to Columbia Analytical Services (CAS, Rochester, NY) for analysis by Inductively Coupled Plasma (ICP, EPA Method 200.7). Aqueous sample handling and analytical procedures are summarized in the CAS Quality Assurance Manual, which was included in the QAPP. For the WVDP columns, nonradioactive cation analyses were performed by GEL Laboratories LLC (Charleston, SC) using the same method (ICP, EPA Method 200.7).
For the WVDP column tests, the analyses of aqueous samples for Sr-90 were performed by WVES personnel using Method EM-77, which utilizes 3M's Empore™ Strontium Rad Disks to separate Sr-90 from other isotopes present in the sample, followed by counting of the disk in a low-background proportional counter for beta activity.

Detection limits for the laboratories are summarized in Table 1. The various terminology used by the laboratories can be interpreted as follows:

- Concentrations reported at values below the Method Detection Limit (MDL) are considered to be statistically indistinguishable from zero.
- Concentrations reported at values above the MDL but below the Reporting Limit (RL) or Practical Quantitation Limit (PQL) are considered to be nonzero but less precise than values reported above the RL/PQL. For the purpose of this report, RL and PQL are considered as equivalent indicators of analytical precision, although individual laboratories may compute these thresholds differently.
- The Minimum Detectable Concentration (MDC) for Sr-90 is defined by a counting procedure that is sensitive to sample size and counting duration, which may vary by sample. The estimated MDC of 10 pCi/L was a typical value reported by WVES personnel, although some samples may be quantified at lower levels.

In general, only the aqueous concentrations of $Sr^{2+}$ and Sr-90 exhibited concentrations at or below any of the various threshold limits, primarily during the early stages of the column experiments. For the purpose of this report, all concentrations are displayed as reported.

**Column Testing**

For the UB experiments, ten experimental columns were operated beginning in February 2009 (Table 2), with four of the columns remaining in operation as of this writing. Columns denoted UB1, UB2, etc., correspond to the labels C1, C2, etc., that were reported previously by Rabideau et al. (2009b).

For the West Valley experiments, six experimental columns were operated beginning in May 2009 (Table 2, denoted WV1, WV2, etc.), with four of the columns operational at the time of this writing. Important differences between UB and WV experimental conditions include the use of on-site influent groundwater containing radioactive Sr-90 for the WV column, and variations in column media compositions. Two of the WV columns (WV3, WV4) contained an unrealistically high fraction (50 percent) of WVDP soil; these columns were terminated after approximately 175 days of operation.

Detailed descriptions and photographs of the experimental setup were included in Rabideau et al. (2009b). Both the UB and WVDP columns were constructed of Plexiglas. Each column was approximately 10 cm in length and 3.81 cm in diameter, with column dimensions selected to lessen the potential for substantive wall effects (e.g., Mehta and Hawley, 1969) and structural dispersive mixing (Li et al., 2009). Each column was equipped with a water inlet at the base of the column and a built-in diffuser to evenly distribute the flow of incoming water. Sampling ports located along the column length were not used in this study for aqueous sampling, but facilitated removal of column solids at the end of selected experiments. Further details of the column experimental procedures are provided in the project QAPP. Key experimental design components included:

- At both experimental sites, multi-channel peristaltic pumps were utilized to provide steady flow to the columns, with frequent gravimetric flow measurements used to support minor adjustment (if necessary) to the pump settings. The design flow rate of 0.2 ml/min was selected based on natural groundwater flow conditions observed at the site. The corresponding design Darcy velocity (flow per area) was approximately 0.23 m/day. Based on the results of previous work, this velocity, while near the high end of anticipated field conditions, were considered low enough such that the cation exchange process would achieve local geochemical equilibrium.
- For the UB tests, cation concentrations in the synthetic groundwater (Table 3) were prepared to represent the average concentrations observed in WVDP wells, with the exception of $Sr^{2+}$, which was increased to the approximate maximum observed value of 1 mg/L. After approximately 100 days of column operation, the source concentrations of $Ca^{2+}$ and $Na^{+}$ were increased to enhance the sensitivity of transport model parameters to the effluent data. For the long-running columns, the influent concentrations were subsequently returned to their initial value after approximately 155 days.
- WVDP test procedures were based on and thus similar to the UB experiments, except that the source groundwater was obtained from a well located on the WVDP North Plateau in the vicinity of the proposed PTW. The concentrations of relevant groundwater cations were similar to the UB study (Table 3), but the source water also contained Sr-90 at an activity of approximately 30,000 to 40,000 pCi/L. The influent groundwater was used as received throughout the experiments.

## RESULTS

### Interpretive Issues

The interpretation presented in this report is primarily graphical and qualitative, as summarized in the graphs of column effluent concentrations presented in Figures 1-10. Modeling of the UB columns was reported previously by Rabideau et al. (2009a). Additional interpretation of the 100 percent zeolite columns will be explored when final sorbed phase data are obtained after termination of the ongoing UB experiments. For all of the Figures, concentrations of $Sr^{2+}$ were plotted as μg/L to enhance visual clarity; concentrations of other nonradioactive cations were plotted as mg/L. For the WV columns, the effluent Sr-90 activity is shown on the right axis. It is noted that 1 pCi/L Sr-90 is equivalent to approximately 7 x $10^{-12}$ mg/L in mass units; on a mass basis, the amount of Sr-90 in the WVDP source water is on the order of $10^{-4}$ percent of the total exchangeable strontium (Sr-90 plus $Sr^{2+}$).

An approximate characterization of potential zeolite field behavior can be obtained by converting elapsed time (days) to dimensionless "pore volumes" (PVs) based on the measured or estimated flow rates and the flow-through length (or thickness) of the zeolite zone. However, such comparisons depend on an estimated effective porosity, which varies for different media and column/field emplacement, as well as the estimated groundwater flow conditions in the field, which will vary spatially. For this report, the following assumptions are adopted for illustrative purposes: (1) an effective porosity of 0.5 is assumed for 100% zeolite systems, (2) the average column flow per area was quantified at 0.23 m/day as described above, and (3) typical field velocities are assumed to fall within the range of 0.5 to 2 ft/day, (4) the installed PTW will be approximately 3 feet thick. These assumptions translate into an estimated normalized groundwater velocity of 4.6 PV/day for laboratory columns and 0.2-0.7 PV/day day for field conditions. Based on these ratios, the results from the longest running UB columns containing 100 percent zeolite (450 days reported here) represent approximately 8-28 years of field operation, while the WV zeolite columns (320 days reported here) represent approximately 6-20 years of field operation.

Columns containing soil mixtures are expected to have a much lower effective porosity, on the order of half of the pure zeolite value (0.25) due to the presence of smaller particles; these columns therefore generate a higher number of pore volumes per day of operation. However, because the complete mixing of soil/zeolite is unlikely to occur in the field, extrapolation of the mixture columns is not considered representative.

Although the column zeolite conditions are similar, the UB and WV columns have different influent concentrations, as summarized in Table 3. Of particular importance are differences in $Na^{+}$, $Ca^{2+}$, $Sr^{2+}$, and Sr-90. Also, UB influent conditions were adjusted during the experiment by increasing and decreasing the $Na^{+}$ and $Ca^{2+}$ concentrations. The overall effect of these differences on column behavior is difficult to characterize, but the UB columns probably represent a conservative representation of field conditions in terms of cation competition for exchange sites. In general, caution should be exercised in extrapolating column conditions to the field.

**General Observations**

Results from the six completed UB column tests (C2, C4, C6, C8, C9, and C10) were discussed previously in Rabideau et al. (2009b). Results for the ongoing UB columns (UB1, UB3, UB5, and UB8) are summarized in Figures 1-4, while results for all WV columns are shown in Figures 5-10.

Both the UB data and the WV data are consistent with a general conceptual model for PTW behavior that recognizes three distinct "stages" (trends) of effluent cation concentrations: (1) early-time dynamic behavior in which a significant exchange of groundwater and zeolite cations takes place, as expressed by crossing effluent curves influenced by the initial condition of the BR or TMP zeolite, (2) a "quasi-plateau" period in which effluent cation concentrations are similar to the influent concentrations, with the exception of $Sr^{2+}$ and Sr-90, which continue to be removed by the zeolite, and (3) a final equilibration period in which $Sr^{2+}$ and Sr-90 concentrations increase from the quasi-plateau level to the concentration of the influent groundwater. From a performance standpoint, the functional life of a zeolite PTW will be reached sometime during the third stage of operation, depending on the location of interest, source concentration, and target concentration.

The previous project report covered the first six months of the UB column operation, which corresponded to the completion of the first stage of dynamic ion exchange behavior and an extended period of the second stage "quasi-plateau" behavior. During the longer period of operation covered in this report, the ongoing UB columns and some of the WVDP columns began to exhibit the expected third stage increase in effluent Sr concentrations. None of the columns, however, have reached the point of "full breakthrough" in which Sr effluent concentrations reach the influent levels. Additional discussion of column behavior is provided below in the context of specific conditions.

BR zeolite columns

The experimental columns with the most direct correspondence to the planned PTW were assembled using 100 percent BR zeolite, including columns UB3, UB4, and WV5. UB4 was terminated after 75 days, as discussed in the previous report. For column UB3, effluent concentrations of $Sr^{2+}$ began to gradually increase after approximately 190 days of operation, indicative of the "third stage" of PTW operation, and reached approximately 50 percent of the influent level by day 450. The general pattern of behavior was expected and confirms the general conceptual model outlined above. Exploratory simulations indicated that timing of the $Sr^{2+}$ increase is generally consistent with predictions provided by the preliminary calibrated mathematical model reported in Rabideau et al. (2009b), although it is likely that minor adjustments of the cations selectivity coefficients will be required to better represent the new data. A more extensive model calibration would require post-experimental sorbed phase data and additional work to refine the data weighting scheme.

The WV5 column has exhibited qualitatively similar behavior to UB2, except that the expected increase in effluent $Sr^{2+}$ has not yet occurred, presumably because of the lower cumulative mass of cations contained in the column influent, which also results in a slightly lower $Sr^{2+}$ concentration for the stage 2 "quasi-plateau" period. The effluent activity of Sr-90 remained at or close to the detection limit (~10 pCi/L) until approximately 7-9 months of operation, at which point it began a very gradual increase to approximately 1000 pCi/L (less than 3 percent of the influent) at approximately 11 months of operation.

Taken together, the column results are consistent with expectations and indicate the BR zeolite has effectively removed both nonradioactive and radioactive Sr for extended periods of operation. Differences between the shapes of $Sr^{2+}$ and Sr-90 profiles for concentration WV5 are attributed primarily to the presence of initially sorbed $Sr^{2+}$ (but not Sr-90) on the BR zeolite. Although the effluent $Sr^{2+}$ concentration for UB3 reached approximately 50 percent of the influent level 450 days of column operation, the rate of increase is gradual and it is expected that "full breakthrough" will not be reached during the remaining experimental period.

The columns containing 100 percent TMP zeolite (UB1, WV6) have exhibited qualitatively similar cation behavior but are not discussed further here. Minor differences in effluent cation concentrations are attributed to different initial sorbed cations for the TMP zeolite, a smaller TMP clinoptilolite fraction, and a likely difference in effective porosity because of a higher fraction of fine particles in the TMP material.

Zeolite:soil mixtures

Columns containing zeolite:soil mixtures were originally designed to represent possible field mixing of emplaced zeolite with native soil. To provide consistent column conditions to support data interpretation, the zeolite and soil were thoroughly mixed prior to packing the columns. However, subsequent field investigations have indicated the anticipated PTW emplacement should produce a relatively homogenous core zone of near-100-percent zeolite, with much smaller zones of partial zeolite:soil mixing at the PTW edges. Thus, the columns containing zeolite:soil mixtures represent an unrealistic condition that likely overestimates the soil-related reduction in sorption capacity, and a detailed analysis of the mixture columns was not pursued for this report (see Rabideau et al., 2009b, for additional discussion). However, the overall behavior is consistent with the 3-stage PTW conceptual model described above, and the following observations are offered:

- Both nonradioactive and radioactive (WV) Sr effluent concentrations for columns containing soil began to increase at earlier times compared to the 100 percent zeolite columns.
- The columns containing 20 percent soil exhibited three stage behavior qualitatively similar to the pure zeolite columns, except that the "third stage" increases in effluent Sr concentrations began at significantly earlier times.
- Columns containing 50 percent soil (WV3, WV4) exhibited even earlier and more pronounced Sr increases compared to columns containing 20 percent soil (UB5, UB6, WV3, WV4), and the three stage transition behavior described above is less clearly distinguishable.

## SUMMARY

The column experiments described in this report represent a substantial expansion of the body of data available to assess the potential of natural zeolites to remove Sr in a PTW system. In particular, the extended duration of the WV and UB columns (320 to 450 days reported) relative to previously reported results (180 days) has yielded the first observations of "third stage" behavior in which effluent Sr begins to increase from a low-concentration plateau toward the influent level. Also, the WV columns provide the first experimental results confirming the removal of Sr-90 by natural zeolite; all previous work has utilized surrogate Sr compounds. As expected, columns containing zeolite:soil mixtures exhibited earlier and more significant increases in effluent Sr concentrations relative to pure zeolite columns, but the column conditions are not considered representative of field PTW conditions.

Of the results discussed in this report, the most relevant data are for the columns containing 100 percent BR zeolite (UB3, WV5). These results confirm previous observations that the BR zeolite will remove both radioactive and nonradioactive Sr by cation exchange over extended periods of operation, following a three stage conceptual model. For the UB column, a gradual increase in effluent $Sr^{2+}$ did not begin until approximately 190 days (approximately 960 pore volumes) of operation, and the effluent concentration did not reach 50 percent of the influent until approximately 450 days (2400 PV). For the WV column (WV5), significant increases in effluent Sr (radioactive and nonradioactive) were not exhibited during the entire 320 day (1472 PV) experimental period included in this report.

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Biedermann, C. A. (2009). Letter DW:11285 to B.C. Bower, Response to U.S. Department of Energy (DOE) West Valley Demonstration Project (DOE-WVDP) Surveillance S09-021E, North Plateau Plume Subcontract Oversight of Lab Work, dated September 3, 2009.

Mehta, D., and Hawley, M. C. (1969). "Wall effect in packed columns," *Industrial Engineering and Chemical Processes Design and Development*, 8 (2), 280-282, DOI: 10.1021/i260030a021.

Rabideau, A. J., Bronner, C. E., and Seneca, S. (2009a). "Quality Assurance Project Plan, Laboratory testing of zeolitic materials," Number 1, Revision 0, Department of Civil, Structural, and Environmental Engineering, University at Buffalo, Buffalo NY.

Rabideau, A. J., Bronner, C. E., and Seneca, S. (2009b). "Laboratory testing of zeolitic materials," Number 1, Revision 0, Department of Civil, Structural, and Environmental Engineering, University at Buffalo, Buffalo NY.

**Table 1. Typical laboratory detection limits**

| Cation | CAS MDL | CAS RL | GEL MDL* | GEL PQL* | WVES MDC* |
|---|---|---|---|---|---|
| $Ca^{2+}$ (mg/L) | 0.05 | 0.5 | 0.05 | 0.5 | |
| $Mg^{2+}$(mg/L) | 0.05 | 0.5 | 0.05 | 0.5 | |
| $K^{+}$(mg/L) | 0.20 | 2.0 | 0.20 | 2.0 | |
| $Na^{+}$(mg/L) | 0.05 | 0.5 | 0.05 | 0.5 | |
| $Sr^{2+}$(mg/L) | 0.01 | 0.1 | 0.01 | 0.1 | |
| $Sr^{90}$(pCi/L) | | | | | 10.0 |

CAS= Columbia Analytical Services, GEL = GEL Laboratories, LLC

MDL = Method Detection Limit, RL = Reporting Limit, PQL = Practical Quantitation Limit

WVES = West Valley Environmental Services, MDC = Minimum Detectable Concentration

* = typical value (sample specific values are subject to variation)

**Table 2: Scope of column experiments**

| Column | Description<br><br>(dup. = duplicate) | Duration<br><br>(days) | Samples<br><br>(* = not analyzed) |
|---|---|---|---|
| UB columns: ongoing (sample collection through May 26, 2010) | | | |
| UB1 | TMP zeolite only | 450 | 57 effluent |
| UB3 | BR zeolite only | 450 | 57 effluent |
| UB5 | 80% TMP zeolite, 20% WVDP soil | 450 | 57 effluent |
| UB8 | 80% BR zeolite, 20% WVDP soil | 450 | 57 effluent |
| UB columns: completed (reported in Rabideau et al., 2009) | | | |
| UB2 | TMP zeolite only (dup.UB1) | 142 | 31 effluent, 8 zeolite segments |
| UB4 | BR zeolite only (dup. UB3) | 142 | 31 effluent, 8 zeolite segments |
| UB6 | 80% TMP zeolite, 20% WVDP soil (dup. UB5) | 142 | 31 effluent, 8* zeolite segments |
| UB7 | 80% BR zeolite, 20% WVDP soil (dup. UB8) | 142 | 31 effluent, 8* zeolite segments |
| UB9 | WVDP soil only | 131 | 28 effluent |
| UB10 | 70% BR zeolite, 20% WVDP soil, 10% iron | 131 | 28 effluent |
| West Valley columns: completed | | | |
| WV3 | 50% BR zeolite, 50% WVDP soil | 175 | 32 effluent |
| WV4 | 50% BR zeolite, 50% WVDP soil (dup. WV3) | 175 | 32 effluent |
| West Valley columns: ongoing (sample collection through May 26, 2010) | | | |
| WV1 | 80% BR zeolite, 20% WVDP soil | 320 | 39 effluent |
| WV2 | 80% BR zeolite, 20% WVDP soil (dup. WV1) | 320 | 39 effluent |
| WV5 | BR zeolite only | 320 | 39 effluent |
| WV6 | TMP zeolite only | 320 | 39 effluent |

**Table 3: Influent cation concentrations**

| Cation | Groundwater conc. from 11 on-site wells | | UB synthetic groundwater 2/19 – 5/28/09 (mean) | UB synthetic groundwater 5/28 – 8/4/09 (mean) | UB synthetic groundwater 8/4/09 – current (mean) | WVDP 5/13/09 - current (mean) |
|---|---|---|---|---|---|---|
| | Mean | Maximum | | | | |
| $Ca^{2+}$ (mg/L) | 167 | 230 | 160.8 | 205.6 | 162.4 | 143.4 |
| $Mg^{2+}$(mg/L) | 26 | 36 | 26.5 | 25.4 | 26.7 | 22.1 |
| $K^{+}$(mg/L) | 3 | 6 | 5.0 | 5.0 | 5.0 | 3.0 |
| $Na^{+}$(mg/L) | 185 | 273 | 178.8 | 217.8 | 176.4 | 234.2 |
| $Sr^{2+}$(mg/L) | 0.3 | 1 | 1.0 | 1.0 | 1.0 | 0.32 |
| $Sr^{90}$(pCi/L) | | | | | | 34,088 |

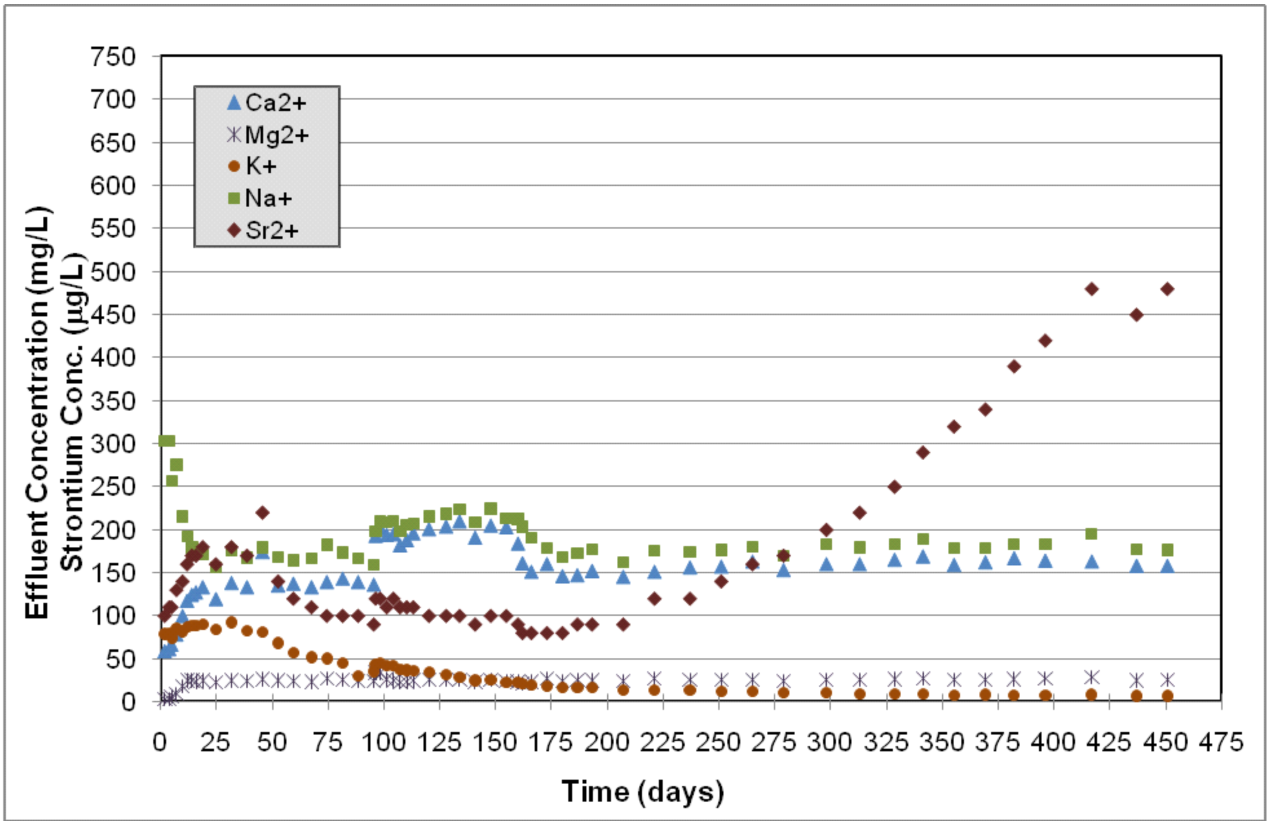


Figure 1. Effluent concentrations for column UB1 (100% TMP zeolite)

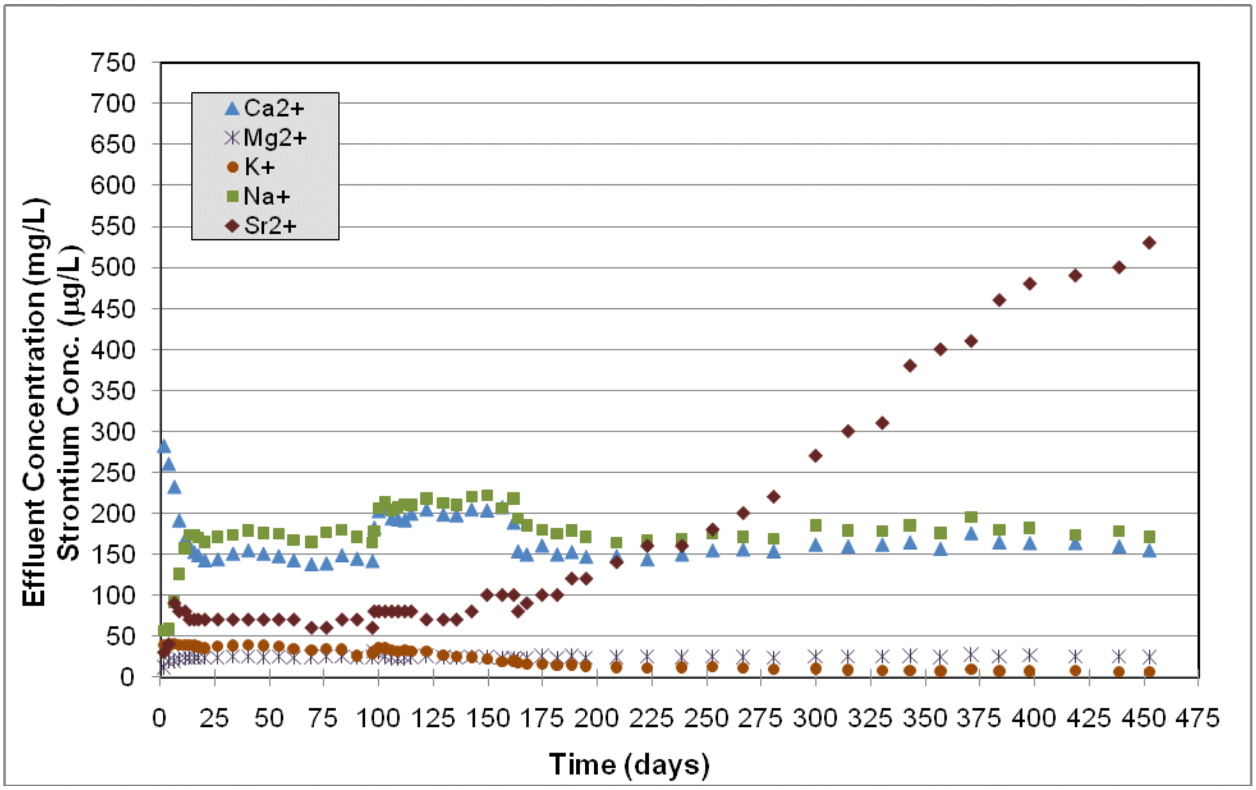


Figure 2. Effluent concentrations for column UB3 (100% BR zeolite)

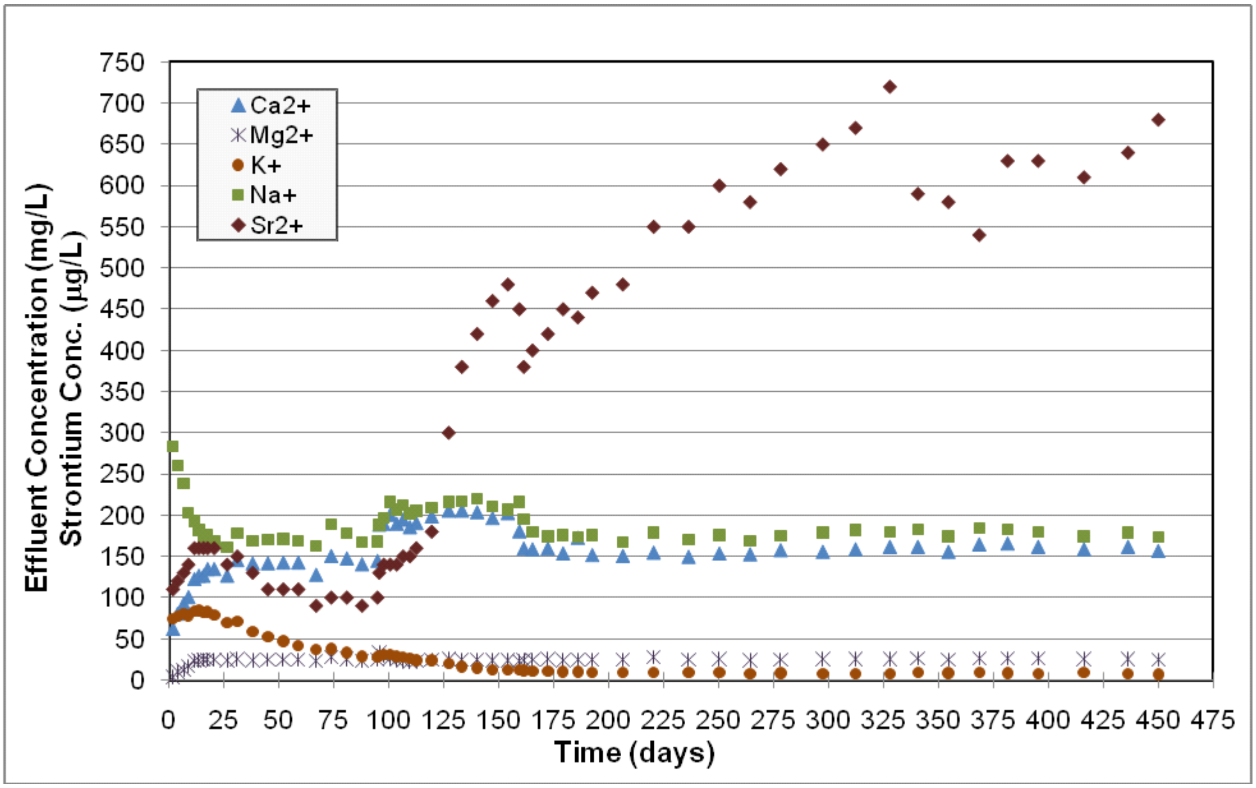


Figure 3. Effluent concentrations for column UB5 (TMP zeolite with 20% WV soil)

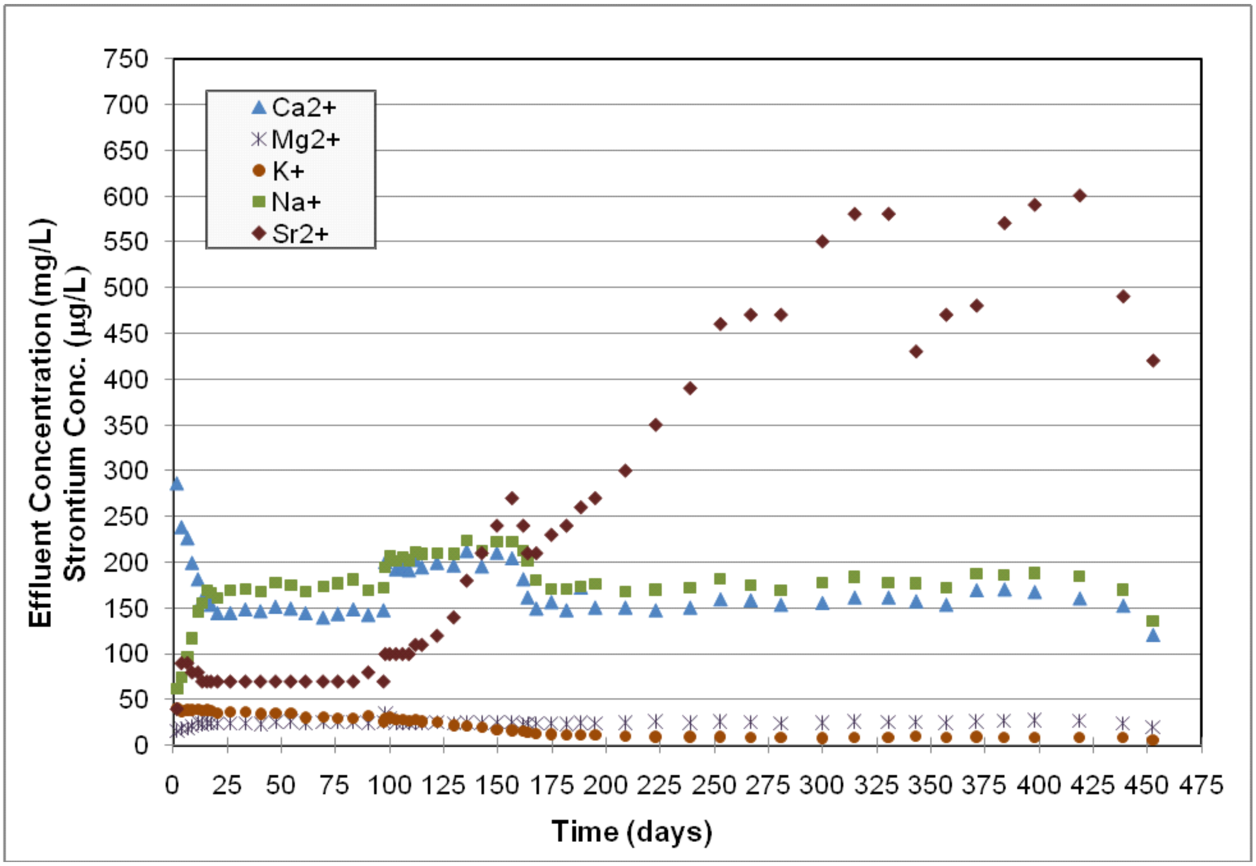


Figure 4. Effluent concentrations for column UB8 (BR zeolite with 20% WV soil)

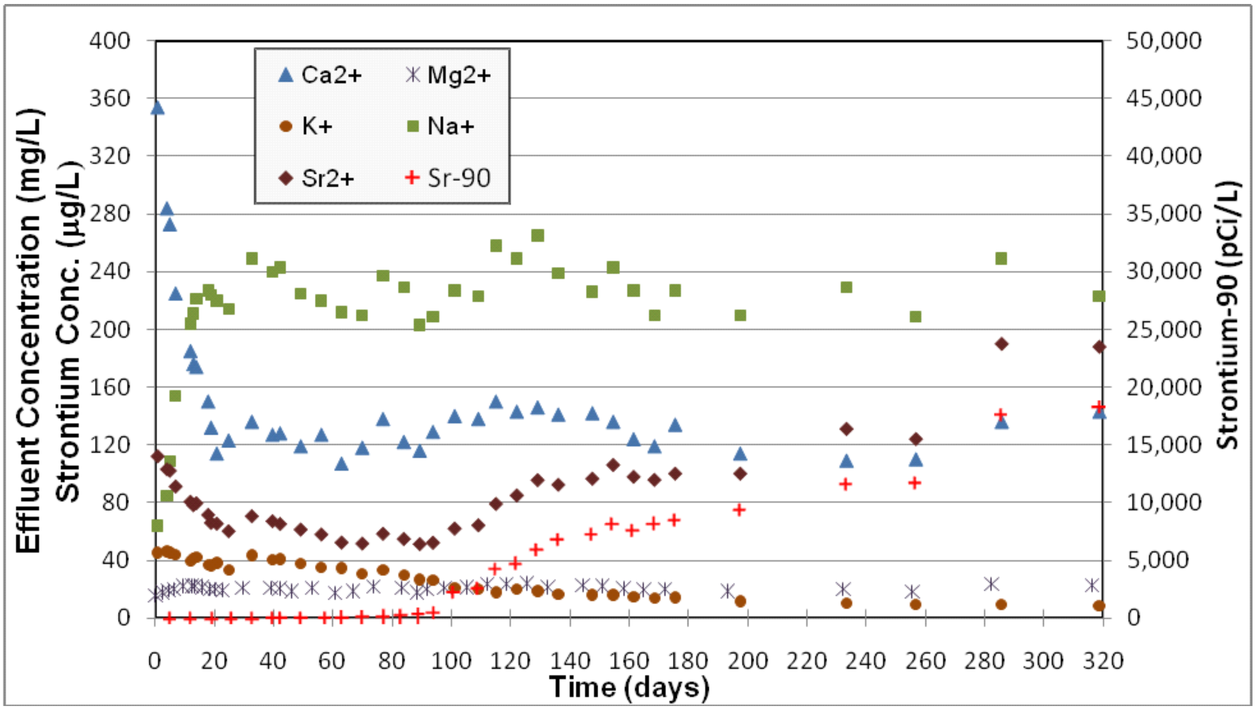


Figure 5. Effluent concentrations from column WV1 (BR zeolite with 20% WV soil)

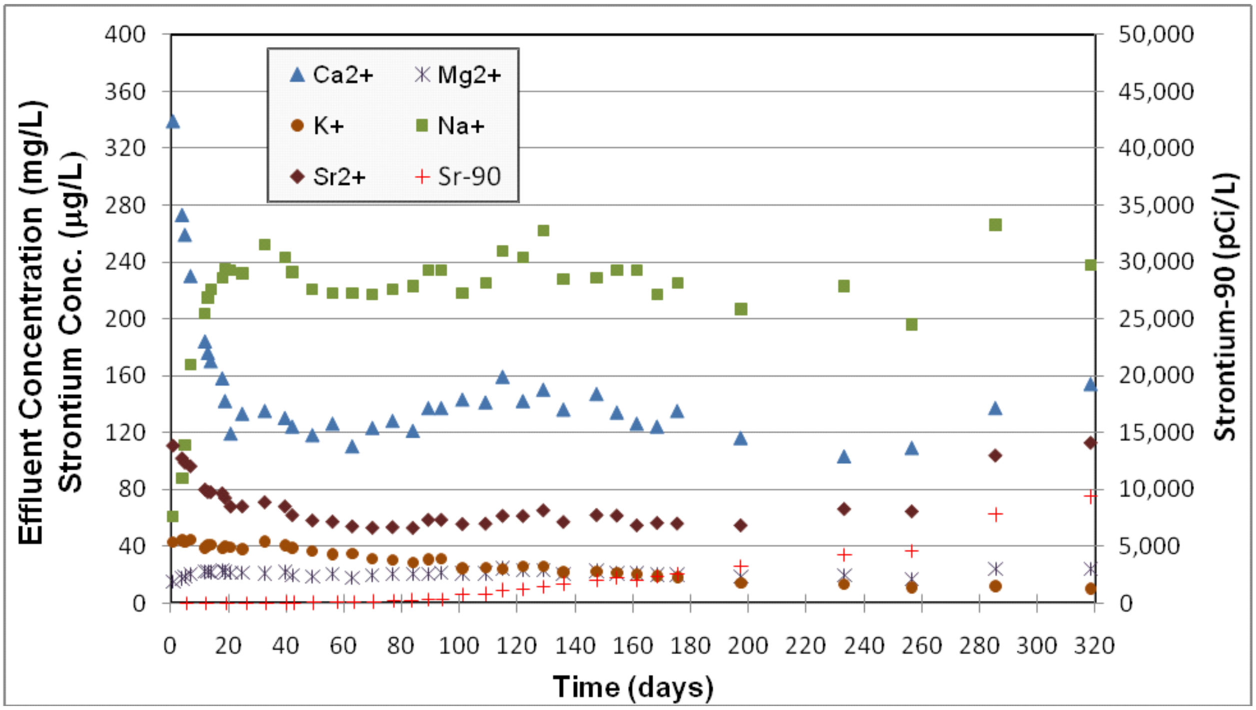


Figure 6. Effluent concentrations from column WV2 (BR zeolite with 20% WV soil)

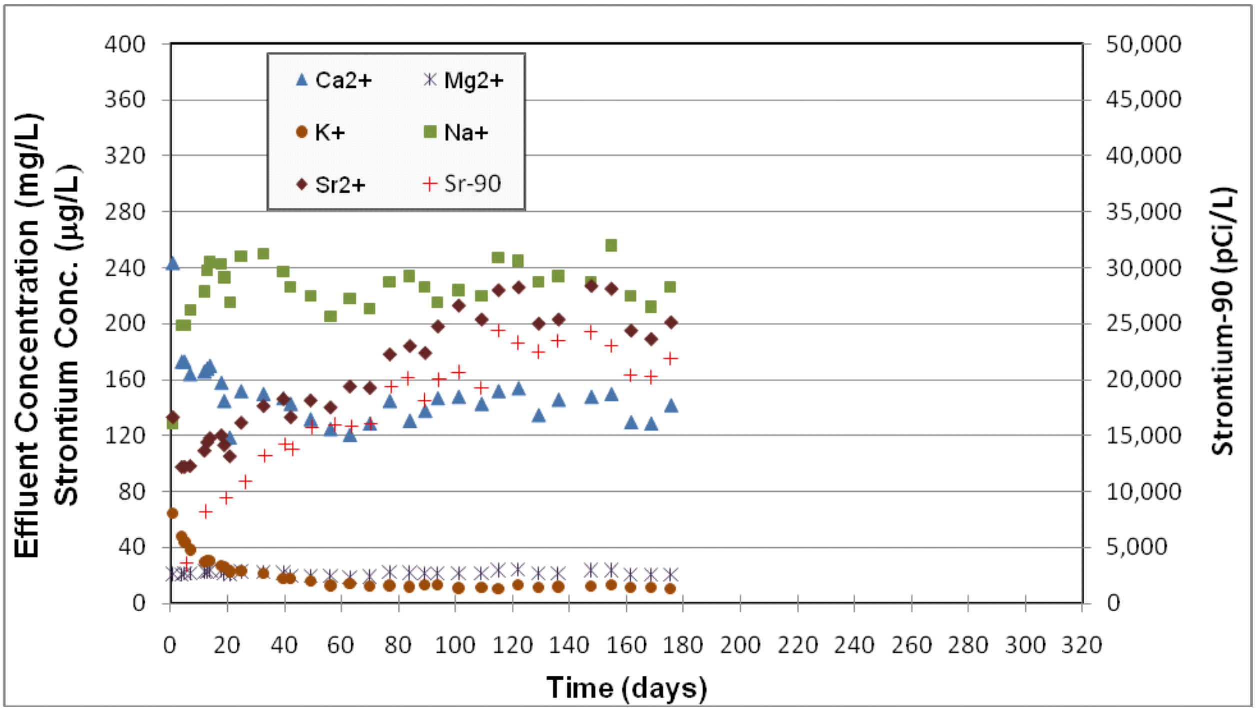


Figure 7. Effluent concentrations from column WV3 (BR zeolite with 50% WV soil)

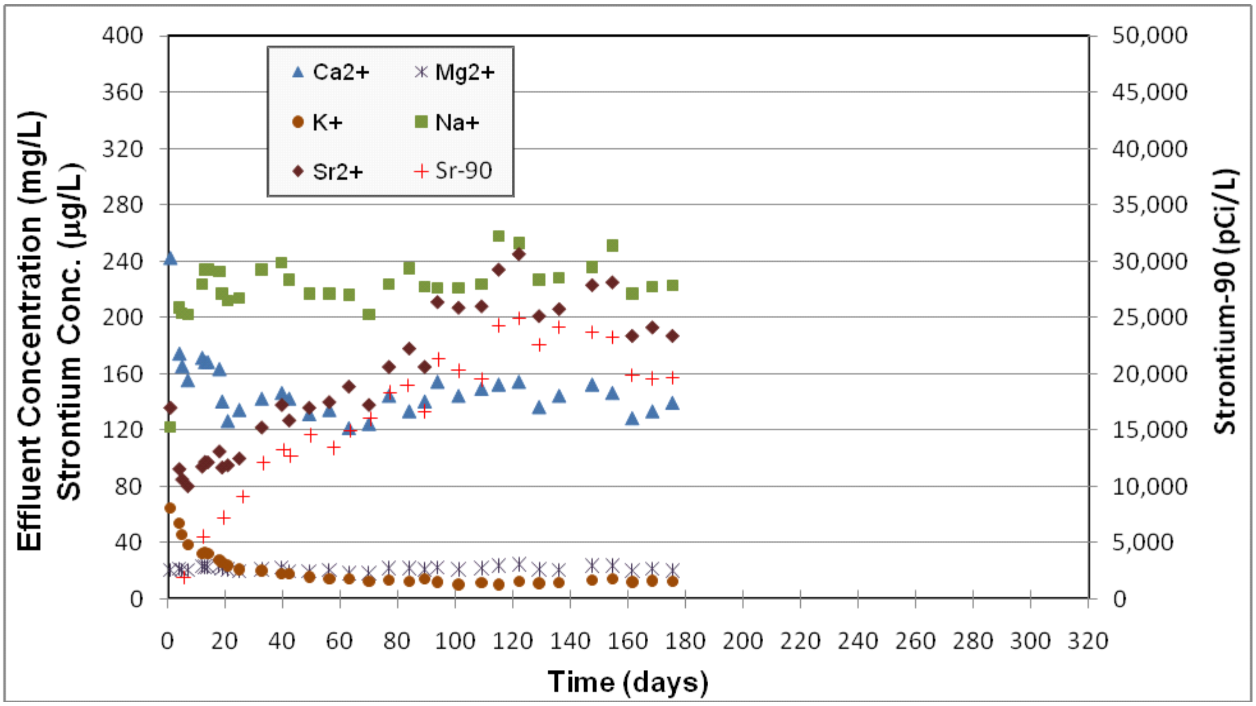


Figure 8. Effluent concentrations from column WV4 (BR zeolite with 50% WV soil)

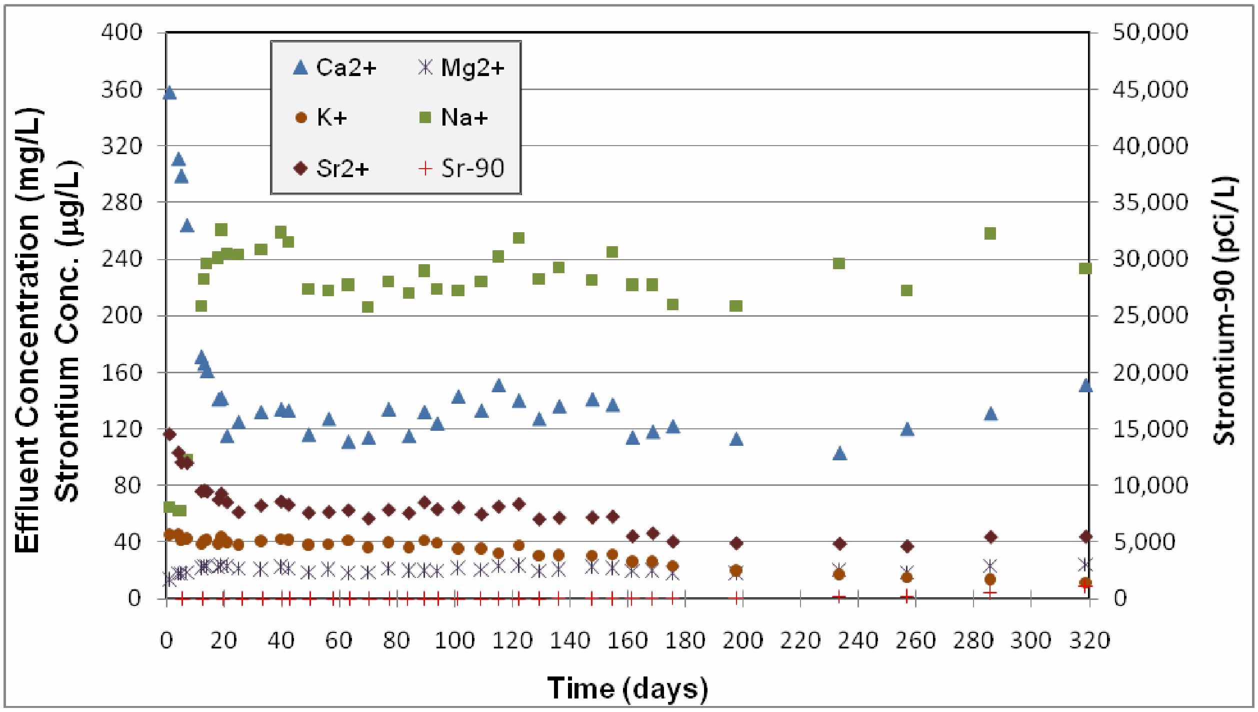


Figure 9. Effluent concentrations from column WV5 (100% BR zeolite)

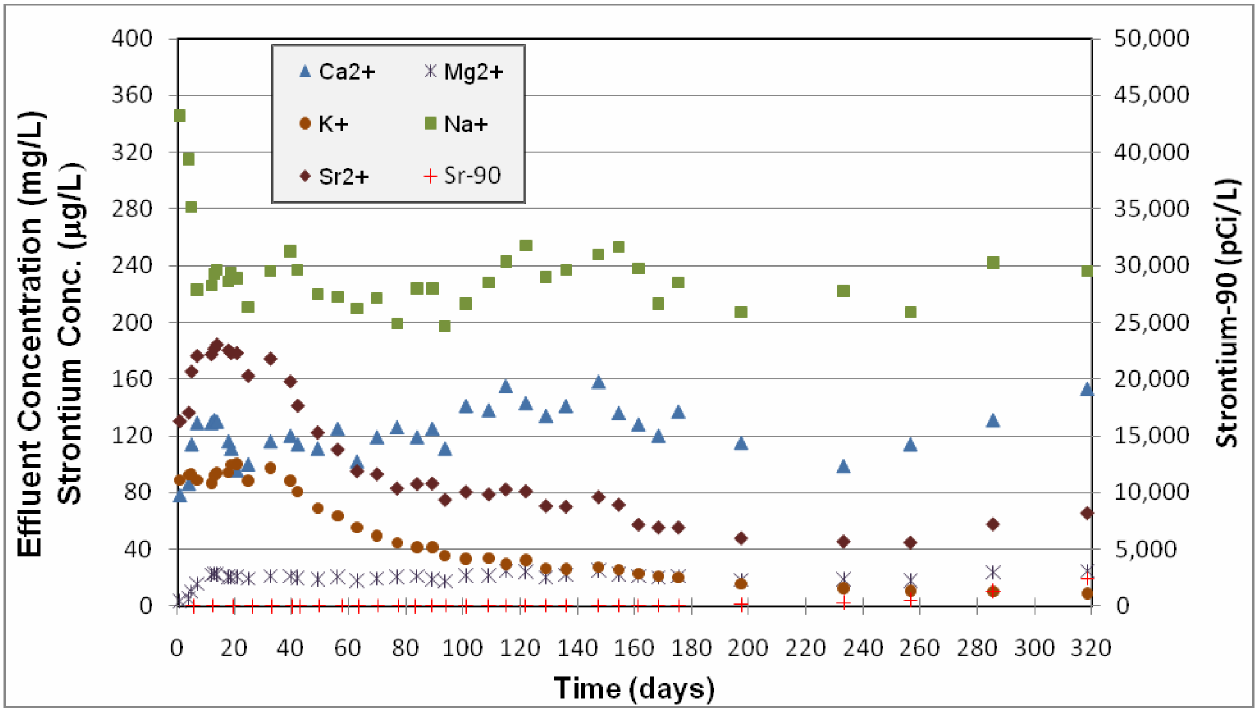


Figure 10. Effluent concentrations from column WV6 (100% TMP zeolite)

WVDP RECORD OF REVISION

| Rev. No. | Description of Changes | Revision On Page(s) | Dated |
|---|---|---|---|
| 0 | Original Issue<br>WVDP-506 provided and assessed results associated with the Laboratory Testing of Zeolitic Materials (covered first six months Of University of Buffalo column operation). Addendum 1 provides results of subsequent laboratory testing at the University of Buffalo and at the WVDP.<br><br>EA and QA are affected by this issue. | All | 08/30/10 |