REACTIVE SANDPACKS FOR THE REMOVAL OF STRONTIUM-90 IN GROUNDWATER

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ABSTRACT

Reactive sandpacks have been proposed as an alternative treatment method for Sr-90 in groundwater. In concept, reactive sandpacks are installed around the screens of dewatering wells, replacing the non-reactive conventional sand pack, such that the contaminant is altered or sorbed in the ground during the dewatering process. While the concept appears to be useful, it has not been known whether reaction kinetics are fast enough in the fast moving water near the well-screen for satisfactory retention of contamination in a dewatering application. This study tested the concept of reactive sandpacks under realistic pumping conditions, by conducting in situ column experiments. Two sets of column experiments were conducted for the period of 49-55 days, with each set composed of two 10 cm columns placed in a well at the Chalk River site. The well was screened in an actual Sr-90 groundwater plume. Columns were filled with clinoptilolite (i.e., a natural zeolite), and groundwater was pumped through the columns at the velocities expected near the pumping well (33-200 m/day). Measurements of gross beta for the effluent water showed that the columns with higher flow velocities had effluents with greater radioactivities than the columns with lower velocities. The starting time and extent of the breakthrough of Sr-90 was proportional to the flow velocity. Distribution coefficients, determined by fitting the normalized aqueous gross beta data to the 1-D advection-dispersion equation, varied inversely with flow velocity, suggesting that the sorption of Sr-90 onto clinoptilolite is kinetically-controlled in this high velocity range. Radioactivities for the solid samples, retrieved from the columns after the operation, showed that sorption fronts were advancing in proportion to the flow velocity, consistent with the aqueous data. The results showed that the concept can be applied to dewatering projects if the sandpack is properly designed.

1. INTRODUCTION

At many industrial and nuclear sites, dewatering is necessary to facilitate building construction, the installation and repair of underground utilities, and the installation of subsurface remedial works in wet ground. When dewatering is required in areas where the groundwater contains contaminants, environmental guidelines and best practices require the careful handling, storage, and treatment of the dewatering effluent. However, the proper management of large quantities of contaminated dewatering effluent can be costly and onerous. If the contamination can remain in the ground, the problems and costs of surface storage and treatment would be much reduced.

Reactive sand packs, installed around the screens of dewatering wells, have been proposed as an alternative method to treat Sr-90 in groundwater [1]. The "reactive sand pack" concept would replace the non-reactive conventional sand pack of dewatering wells with a reactive material, such that the contaminant is altered or sorbed in the ground during the dewatering process. While the concept may appear useful, reaction kinetics may be too slow in the fast moving water near the well-screen for satisfactory retention of contamination in a dewatering application. The main purpose of this study was to test whether sorption is fast enough to treat Sr-90 under pumping conditions.

Naturally occurring and commercially-available granular clinoptilolite has proven effective in retaining Sr-90 in a Wall-and-Curtain permeable reactive barrier (PRB), Chalk River, Ontario, Canada, where groundwater flow is on the order of 1 m/day or less [2]. However, it is not clear whether this material will be effective under the velocities anticipated under pumping conditions. During the construction of the Wall-and-Curtain PRB in Chalk River, the well screens of three of the six dewatering wells were sandpacked with the reactive granular clinoptilolite, the same reactive material used in the Wall-and-Curtain PRB. The water pumped from the three wells showed decreased concentrations of Sr-90 in comparison with the other dewatering wells [3]. However, due to time limitations, the collection of water quality data from the three wells with reactive sandpacks was not well documented. Recently, Priebe [1] conducted laboratory column tests to investigate the attenuation capacity of clinoptilolite under the range of flow rates expected at various distances from a well screen during pumping. Priebe [1] estimated the K_d values ranged from 5,400 cm^3/g to 32,000 cm^3/g. The results supported the design of reactive sandpacks, which could be installed at the field sites. It was further suggested that a field trial would allow for evaluation of the concept in a natural geologic setting.

This study tested the concept of reactive sand packs for dewatering wells by conducting a field experiment where the contact time between contaminated groundwater and clinoptilolite is similar to that which would occur in an actual sand pack. The objectives of this study were to provide the design parameters for implementation of dewatering well reactive sandpacks under the field conditions at the Chalk River site and to identify underlying processes that control the efficiency of the technology.

2. METHODS

The design of the field (in situ) column tests was modified from the previous down-hole column tests at Chalk River Laboratories [4], [5]. Four columns in total were made from aluminum tubing. The columns had diameters of 5 cm and lengths of 10 cm. The columns were packed with 14×50 mesh clinoptilolite obtained from Teague Mineral Products of Oregon. The columns were saturated with de-ionized water after packing. Bulk densities and porosities of the clinoptilolite in each column were calculated by measuring the masses of unsaturated and saturated columns.

Because of the limited space in the well and available resources, two sets of the test (one set consisting of two columns at a time) were conducted between September 2010 and February 2011. First two columns (C1&C2) were installed in late September 2010 and operated until late November 2010, with the total operation period of 55 and 50 days for C1 and C2, respectively. The flow velocities of the columns were 60 and 120 mL/min, respectively (i.e., pore-water velocities of 100 and 200 m/day, respectively). Two additional columns (C3&C4) were set up at the same well and operated between late November 2010 and early February 2011, with the total operation period of 49 and 54 days for C3 and C4, respectively. The flow velocities of these additional columns were 20 and 40 mL/min, respectively (i.e., pore-water velocities of 33 and 66 m/day, respectively). Using the Theim equation [6], the average linear velocities of 33, 66, 100, and 200 m/day correspond to the radial distances of 1.6, 0.7, 0.4, and 0.2 m from a pumping well when pumping rate is 1.5×10^{-2} m^3/s and aquifer thickness is assumed to be 10 m.

For the installation at the field site, two columns were assembled together in a vertical orientation with a plastic baffle on top of the columns to minimize oxygen diffusion into the well (Figure 1). The assembly also included compression rods on the edges of the two columns to help keep the columns together and ¼ inch stainless steel tubing for the influent water and for each column effluent. This column assembly was installed into the 10-cm diameter well, which was screened in a Sr-90 groundwater plume in South Swamp

at the Chalk River site. The well yielded groundwater with a relatively high Sr-90 concentration (an average of 1750 Bq/L). The column assembly was suspended in the well beneath the water table by a steel rope. As a special precaution, pumped groundwater was pushed through a 5 gallon pail filled with clinoptilolite, such that the water was treated before it drained to the surface (Figure 1).

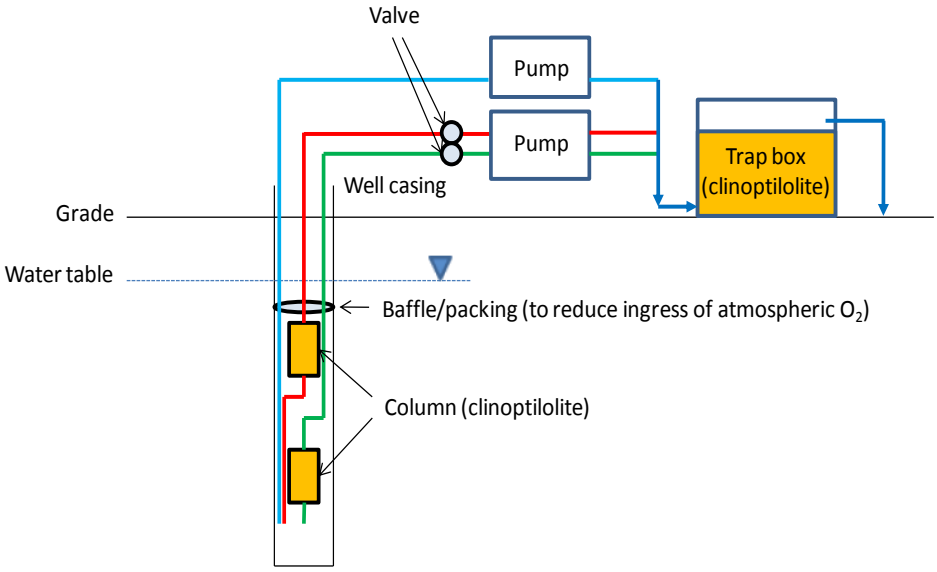

Figure 1. Schematic of in situ column set up.

Prior to the installation, conservative tracer tests were completed in the laboratory to ensure that columns were packed properly and to provide information on transport parameters for the columns. A solution of sodium chloride (600 mg/L) was pumped through the columns and the electrical conductivity (EC) of the effluent was measured and recorded. The tests were conducted at similar velocities targeted for each column. Transport parameters, such as effective porosity and dispersivity, were calculated by fitting the data (EC versus time) with an inverse numerical code CXTFIT [7]. The calculated effective porosities were similar to the porosity values calculated by measuring the masses of the columns before and after the saturation. The test results also confirmed that channeling of the flow did not occur even at the highest experimental flow rate of 200 m/day. After the tracer tests were completed, de-ionized water was run through the columns until the EC value returned to pre-tracer test levels.

Once the installation of the columns was completed in the field, pumping of groundwater through the columns was performed at the desired velocities for each column (20-120 mL/min). Either Geopump™ or ISMATEC® peristaltic pumps were used depending on the desired velocities. Beginning at the time of installation, effluent waters from the columns and influent groundwater were sampled on a regular basis (daily in the beginning and every 2 or 3 days thereafter) and were analyzed for gross beta. Samples were acidified with HNO_3 (to make 1%) and were added with H_2O_2 (10 mL of 30% Reagent Grade H_2O_2 to each 500 mL sample) to evolve the organic carbon to minimize the residual mass. Analysis of the effluents and influent was performed by evaporating a 250 to 300 ml sample to dryness on a stainless steel planchette and then using an OXFORD LB5100 Series IV Low Background Alpha/Beta Counting System to measure the gross beta radioactivity.

After completion of the tests, the columns were retrieved from the well, transferred to the laboratory, and sectioned to measure the solid phase radioactivity along the length of the columns. Each section of the column (1 cm interval) was measured with a Geiger-Mueller contamination ("pancake") meter to obtain a preliminary estimate of radioactivity. Subsamples of each section were prepared for gross beta counting by delivering a known amount (~0.1 g) of clinoptilolite onto planchettes and adding drops of 10% collodion and 90 % acetone solution onto the samples. Gross beta counting for the solid samples was performed using the same OXFORD LB5100 Series IV Low Background Alpha/Beta Counting System.

3. RESULTS

3.1 Flow rate and volume of treated water

The targeted flow rates for C3, C4, C1, and C2 were 20, 40, 60, and 120 mL/min, respectively. However, the actual velocities measured for the sampling events fluctuated for various reasons, particularly when Geopump™ pumps were used. Geopump™ pumps required frequent changes to the speed knob location for the same desired velocity and also frequent pump tube changes. Maintenance of the column system due to precipitation of iron oxides also affected the flow rate. Most importantly, precipitation of iron oxides resulted in significant reduction in permeability of the columns. Despite the use of the plastic baffle on top of the columns to minimize oxygen diffusion into the well (Figure 1), iron oxide formation occurred. Accumulation of iron oxides in the columns was visually obvious as a reddish color during sectioning of the columns, although reduction in permeability was not directly measured.

Cumulative volumes of treated water for each column were calculated based on the measured flow rates on the sampling days and time intervals between two adjacent sampling events. As expected, the volume of treated water for each column was proportional to the flow rate, except that C2 had a significant reduction in cumulative volume after day 31 because of the significant drop in flow rate. C3, C4, C1, and C2 had cumulative volumes of 1180, 2243, 3813, and 4285 L, respectively, which correspond to 14002, 26556, 44420, and 49158 pore volumes (PVs), respectively.

3.2 Gross beta for aqueous samples

To obtain reliable gross beta data, several quality assurance procedures were adopted. Because of decay of Sr-90 to Y-90 (29.1 y half-life) and Y-90 to Zr-90 (64.1 h half-life), quantifying radioactivity requires waiting ~30 days (~10 half lives of Y-90) to reach secular equilibrium, after which point half of the activity measured is from Sr-90 and half from Y-90 decay. Thus, measurement of radioactivity in the samples (both aqueous and solid) was conducted after 30 days. Laboratory blank, field blank and duplicates were analyzed on a routine basis. The typical method detection limit for aqueous gross beta was on the order of 1.0E-01 Bq/L, and the gross beta values for the laboratory and field blanks were in that range. The duplicate samples generally showed comparable results. Occasional analyses on the effluent samples from the trap box (Figure 1) confirmed that the effluent water out of the trap box did not contain any Sr-90. Because of the concern that some suspended solid particles might be dissolved during pre-treatment of the samples and could affect the measured radioactivity of aqueous samples, samples after day 18 for C1 and C2 and all samples for C3 and C4 were filtered using 0.45µm in-line filters at the time of sampling. However, on the selected occasions that both unfiltered and filtered samples were taken, the measured gross beta did not show significant differences between unfiltered and filtered samples.

The concentrations of the influent groundwater and effluents from the columns fluctuated during the course of column operation. Gross beta for the influent groundwater was 500-3500 Bq/L, with an average concentration of 1750 Bq/L. The cause of the fluctuation in the influent groundwater is not clear, although dilution by uncontaminated groundwater and rainfall could be a contributing factor. Variation in effluent concentrations, on the other hand, may be primarily due to the inconsistent flow rate for each column. To interpret the aqueous gross beta data on a more consistent basis, the effluent concentrations (C) were normalized to the influent concentration (C_0), as plotted in Figure 2. Although the fluctuating effluent concentrations are evident, particularly for C1 and C2, results show that the starting time and extent of the breakthrough is proportional to the flow velocity. C1 and C2 started to show partial breakthrough of Sr-90 from day 2, with C2 having slightly higher concentrations in the effluent until day 31, compared to C1. After day 31 (not plotted in Figure 2), the effluent concentration for C2 decreased significantly because of the drop in flow rate around this time period. C3 and C4 had a much longer time period before they experienced partial breakthrough (Figure 2). C4 started to have partial breakthrough from day 18 and C3 from day 33.

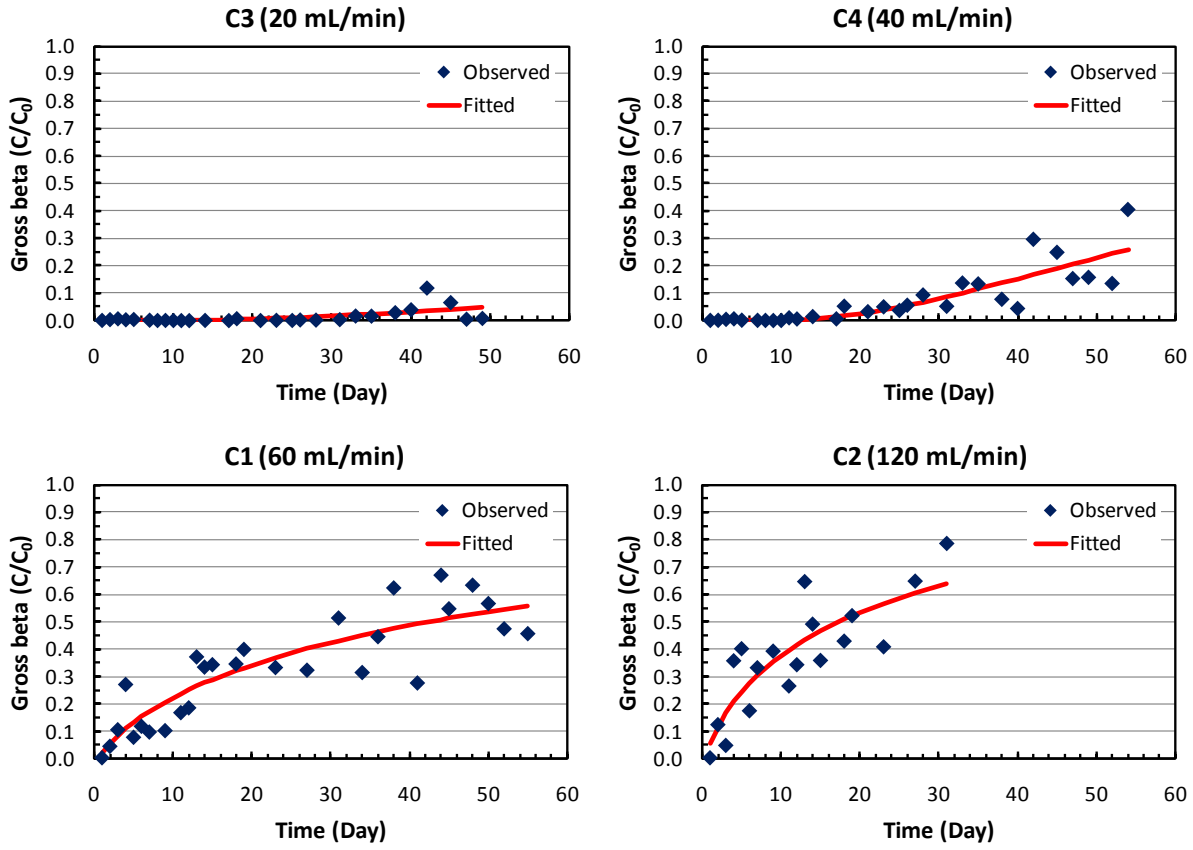

Figure 2. Observed and fitted breakthrough curves for the normalized aqueous gross beta concentration relative to the influent concentration (C/C_0).

3.3 Distribution coefficient (K_d)

The partitioning of the contaminant between the solid and aqueous phases is typically described by the distribution coefficient, K_d. The distribution coefficient is defined as the ratio of the mass of contaminant adsorbed per unit mass of sediment to the concentration of the contaminant in solution when the system is in equilibrium (commonly expressed as cm^3/g). When the velocity of the contaminant, v_c is known, the retardation equation can be used to determine the distribution coefficient. This equation can be expressed as:

$$R = \frac{v_g}{v_c} = 1 + \frac{\rho_b K_d}{n} \quad (1)$$

where R represents the retardation factor, v_g/v_c is the ratio of the average linear groundwater velocity to the transport velocity of the retarded contaminant, ρ_b is bulk density of the porous medium, and n is its porosity.

Assuming that the sorption of Sr-90 onto clinoptilolite is described by the K_d model for the column systems of this study (which is typically the case for other studies with slower groundwater velocities), sorption properties were determined by fitting the normalized aqueous gross beta data to the 1-D advection-dispersion equation (Figure 2). The numerical code CXTFIT was used for the fitting, assuming that sorption is in equilibrium (i.e., using the K_d model). For C2, only data up to day 31 were used because of the significant decrease in flow rate after that. The inverse modeling provided a retardation factor for each column. Then, K_d was calculated using Eq. (1), the retardation factor, and bulk density and porosity of each column. The retardation factors obtained from the model and calculated K_d values are listed in Table 1.

Despite the scattered aqueous gross beta data, the 1-D advection-dispersion equation was generally successful in fitting the observed breakthrough curves, indicating that the equilibrium sorption (K_d) model may be applicable to the data set at a given flow velocity. However, if the sorption was fast enough (i.e., instantaneous) to be explained with the equilibrium model for the entire range of flow velocity, the calculated K_d values should be similar regardless of the flow velocity. Figure 3 shows the relationship between the calculated K_d value and the flow velocity. It shows that the K_d values are decreasing as the flow velocity is increasing, suggesting that the sorption of Sr-90 onto clinoptilolite is kinetically-controlled in this high velocity range. It also suggests that rate expression may not be linear. While the equilibrium K_d model may still be useful to estimate sorption behaviour at a given flow velocity, sorption kinetics should be incorporated into reactive transport to adequately represent the entire system.

Table 1. Sorption properties determined by fitting the aqueous gross beta data to the 1-D advection-dispersion equation (using equilibrium sorption (K_d) model).

Column	C3	C4	C1	C2
Flow velocity	20 mL/min (33 m/day)	40 mL/min (66 m/day)	60 mL/min (100 m/day)	120 mL/min (200 m/day)
Retardation factor (-)	96,730	57,760	14,710	13,770
Distribution Coefficient (K_d) (cm^3/g)	46,386	27,756	7,186	6,913

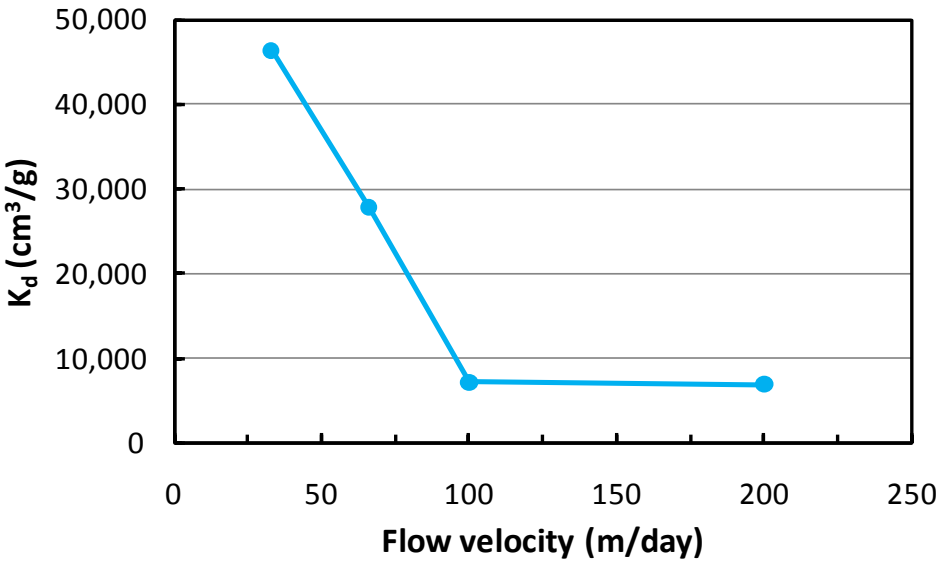

Figure 3. Flow velocity versus calculated K_d.

3.4 Solid samples from sectioned columns

Columns were sectioned to determine the amount of Sr-90 retained in the columns, to analyze spatial distribution of radioactivity along the lengths of the columns, and to visually identify the formation of iron oxide. A Geiger-Mueller contamination ("pancake") meter measurement for each section of the columns immediately after sectioning was compared with the gross beta counting by the Alpha/Beta Counter for the solid samples. Both measurements were consistent and showed that the columns with higher velocities had accumulated greater radioactivities than the columns with lower velocities. It suggests that the contamination meter readings are crude but useful, whereas the gross beta counting is quantitative. Accumulation of iron oxides in the columns was visible by reddish color.

Figure 4 shows gross beta counting values for the solid samples along the length of the columns. It indicates that sorption fronts are advancing in proportion to the flow velocity, consistent with the aqueous data. The general trends for the gross beta counting along the lengths of the columns (i.e., gradual decrease) suggest that the observed partial breakthrough of Sr-90 is due to exhaustion of sorption capacity in certain portions of the columns. The maximum gross beta counting value was 3.73E+04 Bq/g, observed at 1-2 cm of C2. Slightly lower value near the influent ends for C1 and C2 (Figure 4) may indicate that this portion of the columns already reached the maximum sorption capacity and experienced partial desorption. The gross beta values are generally decreasing after 3 to 4 cm distances for these columns, suggesting that this portion of the columns is still adsorbing the Sr-90 and has not reached the maximum sorption capacity. In contrast, with the relatively lower flow velocities, C3 and C4 showed gradual decreases in counting along the entire lengths of the columns, suggesting that the majority of clinoptilolite in these columns are still actively adsorbing the Sr-90, with the sorption fronts moving slowly toward the effluent ends.

Total radioactivities accumulated within each column were calculated using the gross beta counting and masses of solid samples in each section. The amount of accumulated radioactivity was proportional to the flow velocity. Each column had treated from 1.28E+06 to 5.13E+06 Bq of radioactivity (about one half believed to be Sr-90) for the operation period of 49-55 days. Using the maximum sorption capacity

(3.73E+04 Bq/g), it was calculated that clinoptilolite in a 10 cm column with a diameter of 5 cm can treat 3698 L of Sr-90 contaminated groundwater (with an average concentration of 1750 Bq/L).

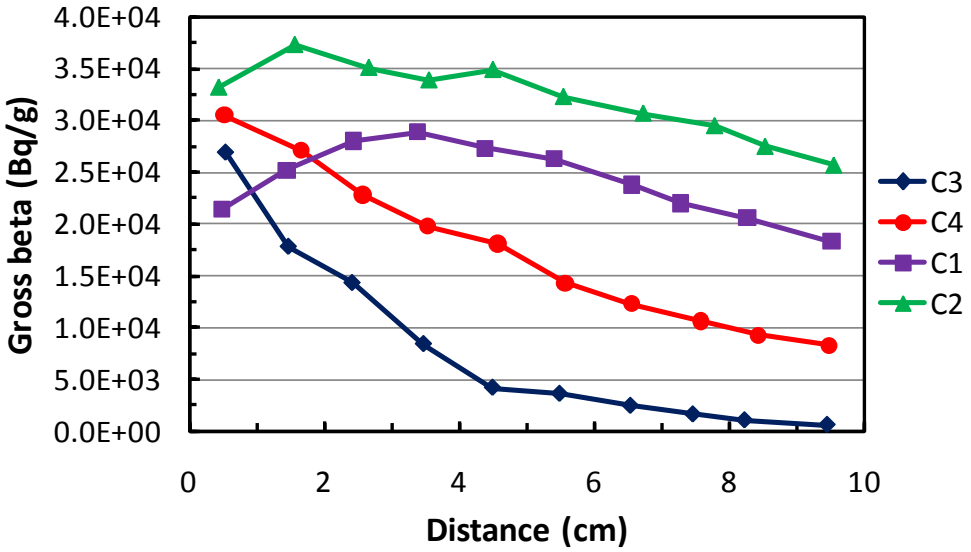

Figure 4. Gross beta for the solid samples along the length of the columns.

The total radioactivities accumulated in the solids were also compared with the values calculated from the aqueous data (Table 2). The differences in aqueous concentrations between the influent groundwater and effluent at a given sampling event were multiplied by the volume of treated water for that given period time. Summing up of these quantities for the entire period of the sampling should be equal to the amount accumulated in the solids. As shown in Table 2, the mass balances between the aqueous and solid samples are generally acceptable (with the maximum of 31% difference for C3), considering the inconsistent flow rates for the columns.

Table 2. Accumulated radioactivity and mass balance calculated from the aqueous and solid gross beta data.

Column	C3	C4	C1	C2
Flow velocity	20 mL/min (33 m/day)	40 mL/min (66 m/day)	60 mL/min (100 m/day)	120 mL/min (200 m/day)
Aqueous (Bq)	1.86E+06	3.19E+06	5.19E+06	5.78E+06
Solid (Bq)	1.28E+06	2.77E+06	3.83E+06	5.13E+06
% difference	30.86	13.06	26.33	11.33

4. SUMMARY AND CONCLUSIONS

In situ column tests were conducted to test the concept of dewatering well reactive sandpacks for the removal of Sr-90 in groundwater under field conditions. Two sets of column experiments were conducted, with each set composed of two 10 cm columns placed inside the pumping well. Columns filled with clinoptilolite were installed in a well at South Swamp of the Chalk River site and operated for the period of 49-55 days.

With pore-water velocities of 100 and 200 m/day, C1 and C2 removed Sr-90 in groundwater to concentrations lower than the influent (an average of 1750 Bq/L). However, the effluent waters showed partial breakthrough of Sr-90 through the clinoptilolite starting from day 2, which means that Sr-90 is not completely treated in these extremely high flow velocities. C3 and C4, which were operated at slower flow velocities (i.e., target velocities of 33 and 66 m/day, respectively), had a much longer time period before they experienced partial breakthrough of Sr-90. C4 started to have partial breakthrough from day 18 and C3 from day 33. Overall, the starting time and extent of the breakthrough was proportional to the flow velocity. Distribution coefficients were determined by fitting the normalized aqueous gross beta data to the 1-D advection-dispersion equation, assuming that the sorption of Sr-90 onto clinoptilolite can be described by the K_d model. The calculated K_d values varied inversely with velocity, suggesting that the sorption of Sr-90 onto clinoptilolite is kinetically-controlled in the velocity range tested. It thus suggests that sorption kinetics should be incorporated into reactive transport to adequately represent the entire flow range, which warrants further study.

Radioactivities for the solid samples, retrieved from the columns, were measured by a Geiger-Mueller contamination ("pancake") meter and the OXFORD LB5100 Series IV Low Background Alpha/Beta Counter. Both measurements were consistent and showed that the columns with higher flow velocities had effluents with greater radioactivities than the columns with lower velocities. Sorption fronts were advancing in proportion to the flow velocity, consistent with the aqueous data. Each column had treated from 1.28E+06 to 5.13E+06 Bq of radioactivity (about one half believed to be Sr-90) for the operation period of 49-55 days. Using the maximum sorption capacity (3.73E+04 Bq/g), it was calculated that clinoptilolite in a 10 cm column with a diameter of 5 cm can treat 3698 L of Sr-90 contaminated groundwater (with an average concentration of 1750 Bq/L).

The results of this study support the design of dewatering well reactive sand packs of clinoptilolite for dewatering projects at the field sites. Clinoptilolite will be effective under the velocities anticipated through a reactive sandpack of a construction dewatering well under pumping conditions, if properly designed. Design parameters will include thickness of the sandpacks, pumping rate, duration of the dewatering project, and concentrations of Ca and Sr.

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