Mobility of Radionuclides in Fractured Carbonate Rocks: Lessons from a Field-Scale Transport Experiment

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ABSTRACT: Current research on radionuclide disposal is mostly conducted in granite, clay, saltpine, or volcanic tuff formations. These rock types are not always available to host a geological repository in every nuclear waste-generating country, but carbonate rocks may serve as a potential alternative. To assess their feasibility, a forced gradient cross-borehole tracer experiment was conducted in a saturated fractured chalk formation. The mobility of stable Sr and Cs (as analogs for their radioactive counterparts), Ce (an actinide analog), Re (a Tc analog), bentonite particles, and fluorescent dye tracers through the flow path was analyzed. The migration of each of these radionuclide analogs (RAs) was shown to be dependent upon their chemical speciation in solution, their interactions with bentonite, and their sorption potential to the chalk rock matrix. The brackish groundwater resulted in flocculation and immobilization of most particulate RAs. Nevertheless, the high permeability of the fracture system allowed for fast overall transport times of all aqueous RAs investigated. This study suggests that the geochemical properties of carbonate rocks may provide suitable conditions for certain types of radionuclide storage (in particular, brackish, high-porosity, and low-permeability chalks). Nevertheless, careful consideration should be given to high-permeability fracture networks that may result in high radionuclide mobility.

1. INTRODUCTION

Despite continued reliance on nuclear energy worldwide, a permanent disposal solution for most spent nuclear fuel produced globally has yet to be determined. The current most viable disposal option is that of deep geological repositories, in which waste would be stored in caverns drilled into bedrock.1,2 Engineered barrier systems composed of bentonite clays are considered quite sorptive, which may effectively prevent radionuclides from being transported into the surrounding subsurface.3 However, over the half-lives of many radionuclides, these barriers may fail and erode, and the ultimate barrier between the waste and the surrounding environment is the geologic host rock in which the repository is located. Nuclear-waste generating countries such as Finland, Sweden, and France are currently exploring the disposal of waste in rocks consisting of granite, tuff, clay, or in some cases salt domes.1,2,4 Such rocks are known to have very low hydraulic permeability, minimal fracture networks, and high sorptivity. In countries where traditional repository rock types are unavailable or are located in populated areas, carbonate rocks containing sorptive clay components may be considered as an alternative. Presently, however, there is no evidence that carbonate rocks effectively immobilize any contaminants released from such a repository.

Groundwater rich in dissolved bicarbonate, found within carbonate rocks, has been shown to influence the speciation and mobility of soluble radionuclides such as UV,6 and other actinides, resulting in stable aqueous complexes such as the triscarbonato species AnO2(CO3)3m.7 Groundwater of high ionic strength and dissolved carbonate concentrations, therefore, provides unfavorable sorption conditions,8,9 leading to greater potential mobility of dissolved radionuclides.

Alternatively, actinides and their chemical analogs can also form sparingly soluble precipitates7,10 and/or sorb to mineral particles, which can result in migration as intrinsic and/or pseudocolloids or deposition through aggregation or filtration, depending on the groundwater’s ionic strength.11-13 In some arid regions, cycles of seasonal rains percolating into the groundwater and dissolving soluble minerals are followed by dry periods characterized by high evaporation, resulting in brackish groundwater.14 Under brackish conditions, radio-
nuclides which would otherwise be expected to migrate in association with colloids under freshwater conditions may be immobilized through flocculation and deposition. This differs sharply from migration of radionuclides in low ionic strength groundwater, where colloid presence and stability has been shown to significantly increase radionuclide transport.

Despite the fact that carbonate rock matrices may be relatively impermeable, fracture networks contained within may yield high permeabilities throughout the carbonate rock formations. The conductivity of such networks may increase with time because of the dissolution of calcite. Thus, from a purely hydrological standpoint, there is potential for radionuclides to migrate unrestricted through fractured carbonate rock formations. Transport of radionuclides through single fractures has previously been investigated on a laboratory benchtop scale. However, it is difficult to use these studies to predict field-scale processes, as they do not take into account the geochemical, physical, and hydrological heterogeneities of field-scale transport processes that are likely to impact radionuclide transport behavior.

The present study investigates the potential mobility of the radionuclide analogs (RAs) Ce, Re, Sr, and Cs through a chalk rock fracture network by use of a forced-gradient field-scale tracer experiment. Cerium was chosen as an analog for actinides, which readily precipitate with carbonates such as Am and Cm. Natural Sr and Cs were employed in this study as analogs for their radioactive counterparts relevant to nuclear waste disposal. Rhenium served two separate purposes: first, as an analog to radioactive Tc in the TcO$_4^-$ form, and second, as a conservative tracer. The objective of this field experiment was to determine the potential migration and mobile form of four geochemically distinct RAs through a highly permeable saturated chalk fracture network to help determine if fractured chalk rocks are geochemically appropriate for nuclear waste disposal. Field-scale transport studies such as this provide the basis for the safety assessment of geological nuclear repositories intended to house spent fuel.

2. MATERIALS AND METHODS

A forced-gradient tracer experiment was conducted between two boreholes previously drilled in an industrial zone in the northern Negev Desert, Israel (Figure 1A). The subsurface in the field site is saturated with brackish (272 mM) groundwater and is mainly composed of chalk from the Eocene-age Avdat Group, which ranges in thickness from 150 to 285 m. The porous chalk matrix (~40% porosity) is of low hydraulic conductivity (1 × 10$^{-3}$ m/day), but the bedrock contains an extensive fracture network through which water and contaminants in the area have been found to be highly mobile. In previous efforts to characterize the local aquifer, the local fracture network was investigated and mapped, and two main fracture systems were identified: one in the NE−SW direction (azimuth 50−60°) and one in the NW−SE direction (310−340°). Groundwater flow occurs almost entirely within these fracture systems and the bedding planes, while generally bypassing the low-permeability matrix. The field site is located next to a set of trenches, from which groundwater is pumped and treated at a pumping station (Figure 1C). Additional details of the groundwater characterization, natural particles, and boreholes are given in the Supporting Information Sections 1−3.

A tracer solution containing bentonite pre-equilibrated with the RAs along with the conservative fluorescent dye uranine was injected into injection borehole RH11C. A packer was inserted at 25 m depth to ensure that the injection solution would be forced to flow into the upper part of the formation (Figure 1D). It further prevented mixing of sediments from the...
bottom of the injection borehole during the experiment. A 3” submersible pump (Grundfos) was installed at a depth of 24 m for water recirculation. Water was pumped into the top 1 m of the water column (water level was 4.8 m below land surface) during the experiment to ensure tracer homogeneity in the injection borehole. Two sampling pumps (ECT Manufacturing, Inc.) were installed in the injection borehole at 10 and 20 m.

Pumping was conducted throughout the experiment from a down-gradient pumping borehole, RH11A (Figure 1D). A 2” pump (Grundfos) was installed at a depth of 17 m. The pump was set to a discharge of 8 L/min, which was previously shown to induce a drawdown of approximately 1.5 m. The pump was run for more than 24 h prior to the experiment start to ensure steady-state conditions were reached upon injection. Water levels in both boreholes were monitored using water level meters (Solinst) throughout the experiment. The natural gradient of 1.4 cm/m was thus increased to 6.3 cm/m, which remained constant throughout the experiment. A previous study carried out along the same flow path demonstrated an extremely high conductivity of 244 m/year between these two boreholes. A pH and EC logger (YSI) placed at a depth of 10 m in the pumping borehole recorded both parameters every 10 min.

Preparation of the tracer solution is described in detail in Supporting Information Section 4. To inject the tracer solution, the tap at the bottom of the continuously stirred tracer solution barrel was opened, allowing the solution to flow into three loosely fitted injection tubes. When the barrel was empty, it was removed along with the stand, and the injection tubing was pulled out of the borehole, allowing the tracer solution to homogenize along the length of the water column in the borehole. Sampling was started approximately 5 min prior to the injection from both sampling pumps (10 and 20 m depth) in the injection borehole and from the pumping borehole (17 m). Sampling continued at a rate of every 5 min from the injection borehole and every 2 min from the pumping borehole for the first hour after injection, and was gradually decreased to every 2–3 h as the experiment progressed.

After four days (95 h), 500 L of fresh tap water (EC = 0.35 mS/cm) mixed with naphthanate was injected into the injection borehole to observe the effects of lowering the ionic strength. Naphthanate was chosen as it exhibits different excitation and relaxation energies than urane, and therefore, the two dye concentrations can be measured simultaneously. A tank containing the fresh water injection was fitted with a tube, which was inserted into the injection borehole such that it reached the bottom of the 25 m water column. The tap was opened on the tank, and the entire fresh water solution was allowed to flow into the injection borehole. The water level in both injection and pumping boreholes, along with pH and EC at both boreholes, was monitored for the duration of the injection. Samples were taken at increased frequency before and for several hours immediately following the second injection, in a similar fashion to the initial tracer injection. Seven days after the initial injection (163 h), the experiment was terminated.

Samples were collected from the injection borehole at two depths (10 and 20 m) and from the pumping borehole throughout the experiment. Samples were filtered through 0.22 μm syringe filters to separate particulate from aqueous fractions, and all samples were then acidified in HNO3 to dissolve precipitates and stabilize metals for analysis. A size cutoff of 0.22 μm was chosen as an operational definition for the difference between “aqueous” matter and “particulate” matter in this study. This information was used to identify the impact of precipitates and/or bentonite on RA mobility and determine the most mobile form of each RA (i.e., particulate or aqueous). Fluorescent dyes were analyzed using spectrophotometry, and RAs were measured on an inductively coupled plasma mass spectrometer. Additional details of sample preparation and analysis are given in Supporting Information Sections 5 and 6.

3. RESULTS AND DISCUSSION

3.1. Injection Borehole Response. In the tracer solution prior to injection, most of the Ce (93 ± 0.5%), some of the Sr (34 ± 4%), and very little of the Cs and Re (6.0 ± 3 and 1.3 ± 9%, respectively) were associated with the particulate fraction (Table S3). In the presence of carbonates, Ce readily precipitates out of the solution as Ce(CO3)(2-)·8H2O, and these have been shown to heteroaggregate with bentonite. Similar bentonite–Ce heteroparticles were measured using dynamic light scattering in a filtered groundwater pumped from the same location as the present experiment, and sizes were found to range from 2.9 to 3.5 μm. These heteroaggregates account for the fractionation of aqueous and particulate Ce in the injection well (Figure S1). In the presence of dissolved carbonates, mixed hydroxycarbonate solids analogous to those of Ce may form through the precipitation of actinides in the (III) and (IV) redox states as An(OH)(CO3)(s) and An(OH)2(CO3)(s), respectively. It should be noted, however, that actinides in higher redox states may also form carbonate solids, especially in the presence of high Na concentrations where solubility is much lower. Under the conditions of this field experiment, these solids may be of relevance, as both the conditions of high ionic strength and high dissolved carbonate concentration are met.

Like Ce, geochemical analysis conducted with Visual Minteq suggests that Sr may also precipitate (strontianite; SrCO3) under the conditions of the injection borehole (Figure S2). Strontium is also known to sorb to bentonite, and thus the observed partitioning of Sr may be attributed to a combination of Sr precipitation and Sr association with bentonite. Cesium is not known to form stable complexes with other ligands in solution or to precipitate, and thus the small fraction of Cs measured in the particulate fraction (6%) in the injection borehole can be attributed to sorption to bentonite particles.

Concentrations of conservative tracers in the injection borehole at depths of 10 and 20 m were similar at every given sampling time throughout the experiment. This indicates that the recirculation pump maintained homogeneity throughout the water column in the injection borehole (Figure S3A). During the first 20 h after injection, the Re, Sr, and Cs concentrations declined at a similar rate in the injection borehole (~0.14 h⁻¹, Figure S4). Given the approximate injection borehole volume of 300 L, this means that the steady-state flux through the borehole was approximately 42 L/h. The rate at which the Ce concentration declined in the injection borehole was nearly twice that of the other tracers (Figure S4). Colloidal suspensions tend to flocculate and destabilize with increasing ionic strength, decreasing their mobility. As colloidal bentonite is unstable in brackish groundwater, bentonite–Ce heteroaggregates likely exhibited fast flocculation and deposition out of the water column in the injection
borehole without entering the fracture system, yielding a greater decay rate than more stable species. Visual Minteq models suggest that Sr precipitation would be less severe (Figure S2), which would limit the formation of bentonite−Sr heteroaggregates relative to Ce.

3.2. Pumping Borehole Response. Concentration data from the down-gradient pumping borehole were normalized to the injected mass, as defined by the measured concentrations in the injection solution multiplied by the injection volume according to the equation

\[ C_n = \frac{(C_m - C_i)}{m} \]

where \( C_n \) is the normalized concentration (μg/L per kg injected), \( C_m \) is the measured concentration in the pumped borehole sample (μg/L), \( C_i \) is the initial concentration in the pumping borehole prior to injection (μg/L), and \( m \) is the mass of the tracer injected (kg). This method normalizes the concentration at the pumping borehole to the mass injected rather than the concentration in the injection borehole and is, therefore, unaffected by the volume of water in which the tracers are mixed or the time it takes to inject the tracers.

The initial appearance of both conservative tracers Re and uranine occurred at the pumping borehole after approximately 22 min (Figure 2D, inset and Figure S5, inset). This is similar to results observed at the same field site in which an initial breakthrough was recorded after 23 min for uranine in the same flow path and at the same pumping rate. At the termination of the experiment, approximately 55% of the Re mass was recovered. The mass recovery of the reactive tracers was in the order Sr > Cs > Ce, corresponding to 63, 15, and 2% recovery, respectively. While Sr recovery appears to be somewhat greater than that of the conservative tracer, this may be attributed, in part, to the high Sr background at the site. Though this was accounted for in calculations, the drop in ionic strength potentially leads to artificially high Sr concentrations in samples, as discussed in detail in Supporting Information Section 7. This is further supported by the fact that the majority (89%) of the Re was recovered prior to the tap water injection, while only half (52%) of the Sr recovery can be accounted for prior to the freshwater injection (Table S5). The order of mass recovery also correlates with the maximum normalized concentrations measured in the pumping borehole, as both depend on the RA sorption affinity for the rock surface. Injection mass values used for mass normalization are given in Table S3.

Aluminum concentrations were used to track the bentonite breakthrough, and were not measurably elevated above the background levels in the pumping borehole throughout the duration of the test (Supporting Information Section 8). This suggests that the majority of the bentonite particles aggregated, which prevented them from reaching the pumping borehole.

In order to determine the nonreactive tracer transport parameters of the fracture system between the two boreholes, the RELAP code was used to model Re transport over the
first 95 h. The model successfully fits the data by assuming mass transport through three separate pathways (Figure 3), yielding the hydraulic parameters presented in Table S6.

Figure 3. Field and modeled data of Re breakthrough during the first 120 h, depicting the three contributing pathways used to achieve a reasonable fit.

To model the transport behavior of the reactive tracers, the mass fractions, mean residence times, and Peclet numbers (dispersivities) determined from modeling the Re breakthrough were assumed to apply to the reactive tracers, and the reactive tracer breakthroughs were fitted by adjusting the matrix retention factor for aqueous RAs and filtration and remobilization rate constants for RAs that migrated as particles (Table S7).

Nearly all of the Cs recovery was accounted for by the mobile aqueous fraction (Table S5). Indeed, the breakthrough of the Cs bulk and aqueous fractions are nearly identical (Figure 2A). A RELAP model that assumed no particulate Cs transport successfully reproduced the Cs transport data (Figure 4A), and the aqueous Cs was primarily retarded by strong sorption to the chalk matrix ($K_d = 622 \text{ mL/g}$, Table S6). In previous batch experiments investigating Cs sorption to crushed chalk in filtered groundwater solution pumped from the same site, a $K_d$ of 40−50 mL/g was reported. The lower $K_d$ reported for crushed chalk is because of the fact that most surface sites available for exchange are those on calcite, which exhibit low sorption potential for Cs. Natural fractures in the subsurface, meanwhile, are often coated with precipitated minerals (e.g., clays), which have greater sorption capacity, and therefore, are expected to yield a greater $K_d$. Furthermore, uncertainty in fracture aperture estimation impacts the deduced $K_d$ as described in detail in Supporting Information Section 9.

Cerium exhibited much lower mobility than Cs (1.9 and 14.9% total recovery, respectively; Table S5). Most of the mobile Ce was in the particulate fraction, as only 24.8% of the total recovered mass was aqueous (Table S5). The Ce breakthrough curve is consistent with this result, where the majority of the Ce that reaches the pumping borehole is particulate (Figure 2B). This is also consistent with geochemical analysis, which demonstrates that Ce in water in equilibrium with carbonate rock will likely precipitate as Ce$_2$(CO$_3$)$_3\cdot$8H$_2$O (Figure S2). The Ce data, fitted with the RELAP model, assumed that all the Ce was transported in the particulate form and uses a first-order filtration rate constant as the primary adjustable fitting parameter (Figure 4B). A filtration rate constant of 22 h$^{-1}$ (in all flow pathways) provided the best overall fit to the breakthrough curve. Such a filtration rate effectively means that nearly all Ce particulate material is immobilized within a day of injection, resulting in low overall recovery (1.9%, Table S5). While Ce carbonate intrinsic solids certainly account for at least part of the Ce particles detected in the pumping borehole, it is possible that some Ce-bentonite heteroaggregates also reached the borehole; however, as Al could not be measured effectively at low concentrations, it was not possible to definitively characterize the most mobile form of the Ce aside from distinguishing it solely as "particulate" or "aqueous."

Figures 4A and 4B are illustrative of the qualitative differences between reactive solute transport behaviors. Significant matrix diffusion/sorption of aqueous species results in a longer, more gently sloping tail (Figure 4A, Cs), and particle transport with significant filtration results in a truncated tail after a sharp peak (Figure 4B, Ce). The low, nearly flat tail of the Ce breakthrough curve is reproduced in the model by assuming a very slow remobilization rate of filtered particles (a rate constant of 0.0031 h$^{-1}$, Table S7). Laboratory transport studies have similarly shown that Ce migrates as an intrinsic colloid in the presence of bicarbonate, but may be filtered under brackish conditions.
Strontium appears to be mobile mainly as a dissolved species in the pumping borehole during the first four days following the initial injection, indicating that the particulate fraction observed in the injection borehole was immobile and was primarily filtered and deposited prior to reaching the pumping borehole. However, because 34% of the injected Sr was in the particulate form (Table S3), a combined model accounting for both particulate and aqueous transport was used to describe its transport. The vast majority of transport was attributed to aqueous Sr, but a small contribution from particulate Sr improves the fit for the early part of the Sr breakthrough curve (Figure 4C). The particle filtration rate constant was adjusted to fit the early Sr breakthrough, resulting in a best-fitting value of 8 h⁻¹, indicating that Sr precipitates are slightly more stable than Ce precipitates (filtration rate = 22 h⁻¹), but they are still likely to be immobilized within a matter of days. The best-fitting matrix sorption retardation factor for Sr is much smaller than that for Cs (Table S7), indicating that Sr sorption in the matrix was much weaker than for Cs. In fact, Cs has been shown to sorb strongly to sorptive clinoptilolite and smectite contained within the chalk matrix,⁴⁵,⁴⁷ which accounts for the significant Cs retardation in comparison to Sr. Furthermore, Cs has been shown to exhibit a greater sorption affinity for clays such as bentonite than Sr under similar conditions.⁴⁵,⁴⁹ It should be noted that the Sr particles observed here are mostly an artifact of the high Sr injection concentration (3302 mg/L) and are not likely to be found in the far-field of a repository under normal circumstances. However, if Sr was released into high-ionic strength groundwaters such as those found around the WIPP site in New Mexico,⁷ such precipitates may still form.

### 3.3. Second Injection: Fresh Water

Intrusion of low ionic strength waters may occur, for example, during seasonal high rainfall events in the area. In the Swedish Åspö underground laboratory, intrusion of low ionic strength waters during interglacial periods is postulated to potentially mobilize bentonite colloids and enhance radionuclide transport.⁵⁰,⁵¹ Therefore, fresh tap water (EC = 0.3 S m⁻¹) containing the fluorescent dye naphthionate was injected to explore the effect of low ionic strength water on the remobilization of RAs and/or deposited particles. The injection resulted in an EC drop of 50% within the injection borehole for half an hour, which then returned to its baseline after an additional 3.5 h. The decay constant calculated for naphthionate in the injection borehole was similar to that of uranium after the first injection (Figure S6), and no change was observed in the hydraulic gradient throughout the injection, confirming that any changes observed in the RA must result from chemical changes. Furthermore, the naphthionate exhibited a mass recovery of 40%, consistent with the 45% uranium recovery (Table S5). The salinity drop in the injection borehole was not observed at the pumping borehole (pH 6.95 ± 0.02, EC 14.9 ± 0.18 mS/cm), so remobilization of tracers was likely because of the processes that occurred in or near the injection borehole.

The response to the fresh water injection, observed at the pumping borehole, is plotted in Figure 5. The drop in ionic strength was likely insufficient to remobilize any deposited bentonite particles, as the water in the injection well remained above the critical coagulation concentration for montmorillonite⁵² throughout the freshwater injection period. Cesium did not appear to exhibit any remobilization. As Cs sorption to the chalk matrix would likely be increased at lower salinity rather than decreased⁸,⁵³ and Cs association with mobile particulates was found to be negligible, no remobilization through desorption would be expected. Contrary to Cs, Ce exhibited a concentration spike after the injection. This spike was only observed for the particulate fraction of Ce (Figure 5A), indicating that the drop in salinity caused dispersion and resuspension of the precipitated Ce particles but did not induce their dissolution at these timescales. The increase in the Ce concentration lasted approximately 1 h, after which Ce concentrations rapidly returned to the baseline measured immediately prior to the fresh water injection.

Geochemical speciation analysis showed that at pH 7 and a Sr concentration of 23.4 mg/L (the measured Sr concentration in the injection borehole at the time of the freshwater injection), strontianite is slightly below its saturation index (Figure S2). This suggests that some of the Sr precipitates dissolved as a result of the drop in salinity. Thus, the decrease in salinity appeared to affect Sr in two ways: first, any particulate Sr was partially remobilized, leading to an increase in bulk Sr at the pumping borehole (Figure 5A). These particles remained mobile until the termination of the experiment. Second, the dissolved portion of the particles leads to a spike in aqueous Sr detected at the pumping borehole (Figure 5B).

These results indicate that even small chemical perturbations near a contamination source may potentially mobilize deposited colloids and/or particles, thus increasing the transport of radionuclides away from the source. Thus, freshwater intrusion events can indeed induce particulate transport of certain radionuclides even when the impact on
bulk water chemistry is quite small. This also emphasizes that long-term waste repository performance must address potential climate shifts and their impact on groundwater chemistry, as it is clear that even transient shifts of geochemical conditions can induce remobilization of colloidal or particulate RAs.

3.4. Potential Transport of Radionuclides in Fractured Carbonate Rocks. The geochemistry of groundwater in equilibrium with carbonate rocks, especially in low transmissivity matrices and in arid environments, offers some advantages over other rock types for the immobilization of radionuclides in the subsurface. Because of seasonal rainfall, dissolution, and evaporation cycles, groundwater in such rocks is often brackish. These high ionic strength waters will tend to limit the potential for particulate and/or colloid-facilitated transport.

In the current experiment, Ce was nearly entirely present as a precipitate (93%). Water rich in bicarbonates found at circumneutral pH allow for the precipitation of Ce as an amorphous solid. At the investigated concentrations, 38% of Sr in the injection borehole was present in particulate form because of precipitation with bicarbonates. Because of the brackish conditions (272 mM), the particulate Ce and Sr were nearly completely immobilized prior to the freshwater injection. Furthermore, injected bentonite was entirely immobilized throughout the experiment, as none was detected at the pumping borehole. This is consistent with previous research showing the immobility of clay mineral colloids at high ionic strengths and suggests that under brackish conditions, colloid-facilitated transport is unlikely to play a significant role in radionuclide migration. While not directly studied in this experiment, it is worth mentioning here that other radionuclides complex readily with carbonate in the presence of high-dissolved carbonate concentrations. Examples include U(VI) and Np(V), which have been shown to form soluble complexes with calcium and carbonate, and therefore be mobilized as aqueous species in carbonate-rich environments. Carbonate rocks, therefore, may not serve as ideal host rocks for certain waste forms, and the contents of a particular waste type must be considered.

This study was carried out in a high-porosity (40%), low-permeability (~1 mDarcy) chalk, which allows for greater matrix diffusion of dissolved radionuclides than some other lower-porosity carbonate rocks. Relatively large matrix diffusion coefficients (3.46 × 10^-11 m^2/s) have previously been reported for uranium in the same chalk as that of this study. Under slower, natural groundwater flow velocities, diffusion of dissolved radionuclides into the rock matrix becomes significant. Within the pore space, radionuclides may come into contact with exchange sites on sorptive mineral components, increasing their retardation. Cesium is an example of such an aqueous radionuclide, which in the current study was able to diffuse into the matrix pore space, where it was immobilized by mineral components within the chalk. Other carbonate rocks exhibit a wide range of porosities ranging between 5 and 70% depending on their age, primary grain size and type, depositional energy, and burial depth. It has been shown that one high-porosity (45%) carbonate rock located at the surface decreases in porosity to 25–30% under pressure at a depth of 800 m. Therefore, the high porosities investigated here may be greater than those of rocks located at depths typical of nuclear waste repositories.

Porosity and permeability at the rock matrix scale, however, is not representative of porosity and permeability at the formation scale, mostly because of the presence of fractures. Because of the dissolution of calcite, carbonate rock fractures may have large apertures, resulting in fast transport times of radionuclides through the rocks on a formation scale. The present experiment was conducted in one such fracture set of extremely high conductivity (244 m/year), which represents an exceptional case of subsurface transport. Both Re and uranium, the conservative tracers, arrived at the pumping borehole after a mere 22 min, suggesting that Tc would flow nearly unrestricted in the subsurface. For comparison, the average permeability of fractures at this site has previously reported to be 1.5 m/year, and the chalk matrix permeability was reported at 0.06 m/year.

In the present experiment, particles that migrated as a result of the induced shear forces in this forced gradient experiment might be immobilized through deposition onto fracture surfaces at lower fluid velocities. Furthermore, under ambient gradients and along lower-permeability fracture networks over geological timescales, processes such as matrix diffusion would also be much more prominent. It should also be mentioned that this experiment was carried out close to the surface, where oxidizing conditions may allow species such as ReO_4^- to migrate more effectively than they otherwise might under reducing conditions more common at depths of planned nuclear repositories. However, this particular flow path and fluid velocity was chosen to ensure the greatest possible RA recovery over the time scale of this experiment. The field experiment examines the mobility of radionuclides under a “worst-case scenario” (i.e., in the existence of very high-permeability fractures) in order to assess the potential for radionuclide migration under similar conditions. The results suggest that matrix diffusion, sorption, and colloid filtration in carbonate rock brackish waters can effectively retard radionuclide migration, and such hydrogeologic conditions may be amenable to certain types of nuclear waste disposal.

Finally, geochemical perturbations such as changes in ionic strength or pH may result in remobilization of initially sorbed or precipitated radionuclides. In the event of even small geochemical changes, represented here by the drop in salinity of 50% for a half hour at the injection borehole, previously immobilized particles can become remobilized and make their way through the aquifer. This suggests that over long time scales, immobilized radionuclides within fractures may become remobilized upon changes in geochemical conditions resulting from climate change or anthropogenic activity (e.g., high rainfall events, anthropogenic intrusion events, etc.). Therefore, when conducting a safety assessment for a potential geological repository, the impact of climactic and transient geochemical perturbations on the groundwater transport must be addressed.

The geochemical characteristics of carbonate rocks, especially in brackish water in arid environments, can provide suitable conditions for certain types of waste isolation, especially that which might otherwise be mobile as colloids under lower ionic strengths. Nevertheless, this in-situ study suggests that physical fracture networks may provide fast pathways for radionuclide migration in the subsurface. Therefore, prior to locating a nuclear repository within a carbonate rock formation, extensive investigation should be conducted on fracture networks in the vicinity.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c03008.

Details of site groundwater characterization, naturally occurring colloids, borehole data, sample preparation and analysis, and model development (PDF)

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Notes

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