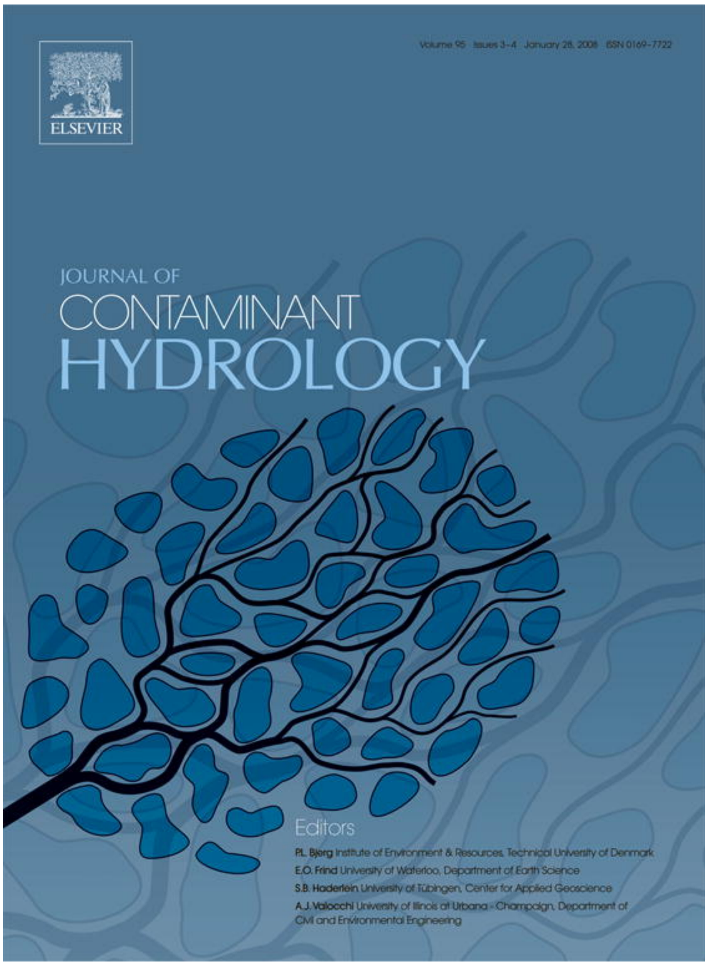
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A calcite permeable reactive barrier for the remediation of Fluoride from spent potliner (SPL) contaminated groundwater ☆

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Abstract

The use of calcite ($CaCO_3$) as a substrate for a permeable reactive barrier (PRB) for removing fluoride from contaminated groundwater is proposed and is illustrated by application to groundwater contaminated by spent potliner leachate (SPL), a waste derived from the aluminium smelting process. The paper focuses on two issues in the implementation of calcite permeable reactive barriers for remediating fluoride contaminated water: the impact of the groundwater chemical matrix and CO_2 addition on fluoride removal. Column tests comparing pure NaF solutions, synthetic SPL solutions, and actual SPL leachate indicate that the complex chemical matrix of the SPL leachate can impact fluoride removal significantly. For SPL contaminant mixtures, fluoride removal is initially less than expected from idealized, pure, solutions. However, with time, the effect of other contaminants on fluoride removal diminishes. Column tests also show that pH control is important for optimizing fluoride removal with the mass removed increasing with decreasing pH. Barrier pH can be regulated by CO_2 addition with the point of injection being critical for optimising the remediation performance. Experimental and model results show that approximately 99% of 2300 mg/L fluoride can be removed when CO_2 is injected directly into the barrier. This can be compared to approximately 30–50% removal when the influent solution is equilibrated with atmospheric CO_2 before contact with calcite.

Keywords: Spent potliner; SPL; Remediation; Calcite; Permeable reactive barrier; PRB

1. Introduction

Spent potliner (SPL), a by-product of the aluminium smelting process, is listed by various environmental bodies including the US EPA as a designated hazardous waste primarily due to the high levels of leachable fluoride and cyanide (Pong et al., 2000). Analysis of an SPL sample typically reveals the presence of fluoride (7.5–22% by weight), aluminium (4–22%), sodium (8.6–22%), carbon (13.7%), alumina (9.2–26%), cyanide (0.04–0.6%), iron (0.3–2.8%), calcium (0.5–6.4%) and sulfate, sulfur, magnesium and phosphorous (all <1%) (Kumar et al., 1992) Historically, SPL waste has been disposed of at many sites

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☆ *Scope*. This paper proposes the use of calcite/limestone in permeable reactive barriers for the remediation of fluoride contaminated groundwater and illustrates this for the particular case of leachate from spent potliner leachate (SPL) waste (a by-product of the aluminium smelting industry). Results from experiments designed to optimize fluoride removal are presented. The experiments consider both the potential competing reactions to reduce barrier performance and the injection of CO_2 to control pH.

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in unlined open dumps, resulting in the contamination of local groundwater aquifers with, among other contaminants, high levels of fluoride and complexed cyanide. At the Hydro Aluminium smelter near Kurri Kurri, NSW, Australia, SPL was dumped by previous owners in an unlined waste repository from 1969 to 1992 resulting in contamination of the local groundwater aquifer with high levels of fluoride, cyanide (complexed), sodium, sulfate and chloride. Hydro Aluminium, is now investigating remediation options for groundwater contaminated with SPL leachate, including *in situ* methods, primarily to control off-site contaminant impacts.

World wide it is estimated that the total amount of SPL produced is approximately 1 million tonnes per year (Pong et al., 2000) with the bulk of this being stored in purpose built storage facilities. With no definitive methods for destruction or re-use, the aluminum industry now recognizes the potential environmental liability of SPL and is actively pursuing many options for treatment or disposal (Silveira et al., 2002).

In situ remediation methods such as zero-valent iron permeable reactive barriers (PRB) are becoming increasingly popular because of their cost effectiveness (Ott, 2000). These barriers consist of a contaminant specific reactive material placed hydraulically downstream of a contaminant plume. The barrier transforms or removes the contaminant as the plume moves through the treatment zone (USEPA, 1998). Such *in situ* technologies are currently not available for remediation of fluoride contaminated groundwater (Ott, 2000).

A number of authors have published new approaches for removing fluoride from drinking water by fluorite (CaF_2) precipitation. Yang et al. (1999) used a fixed bed calcite reactor to examine the removal of fluoride from contaminated water and concluded that fluoride was removed via precipitation as CaF_2. Reardon and Wang (2000) examined methods of improving fluoride removal by calcite through the injection of CO_2 to control pH. Fluoride precipitation was enhanced by adding CO_2 to an influent solution containing 100 mg/L F^-.

Recently, Turner et al. (2004) proposed a calcite permeable reactive barrier for the removal of fluoride from groundwater. At approximately AUD$100 per m^3 calcite is a cheap, readily available material for this purpose. This paper reports the results from column experiments designed to assess the potential of calcite to be used as a permeable reactive barrier substrate for the removal of fluoride from SPL contaminated groundwater. In particular it is demonstrated that (a) the point of CO_2 injection is critical to the performance of the system; (b) an understanding of calcite chemistry is critical to interpret barrier performance; and (c) influent chemistry affects barrier performance (for example, an influent solution supersaturated with respect to fluorite enhances fluoride removal). The effect of the complex SPL leachate matrix is assessed by comparison to synthetic SPL leachate solutions as well as pure fluoride solutions and the results are used to assess aspects of barrier design.

2. Methods

Column experiments were conducted at room temperature (~25±2 °C) to assess the potential for fluoride removal in a calcite PRB. A column (41.0 cm × 4.75 cm)

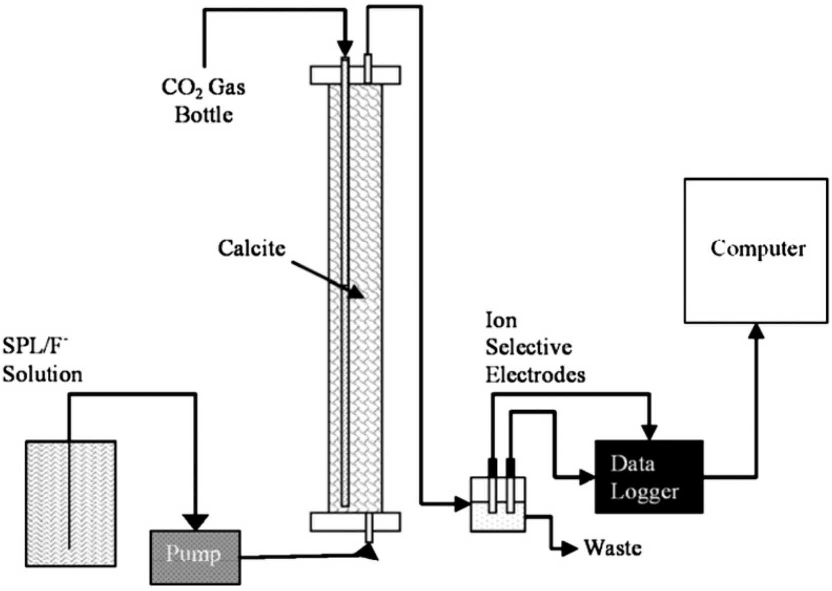

Fig. 1. Schematic diagram of the column experiment.

was constructed from polycarbonate with a 1.5 cm long mixing chamber at the column entrance to ensure uniform flow into the column (Fig. 1). Approximately 1.2 kg of pre-washed (with 18 $M\Omega cm^{-1}$ deionised water) and dried 1.18 mm diameter calcite was packed into the column. Approximately four pore volumes of 18 $M\Omega cm^{-1}$ deionised water were pumped through the column to ensure any loose calcite powder was washed out. Various fluoride solutions were then introduced into the column via a peristaltic pump at a constant flow rate. The flow rate was such that a residence time of between 2 and 6 h was achieved. The effluent pH and fluoride concentration were logged via a multi-channel Datataker™ (DT 50) connected to Orion ion selective electrodes (ISEs) located in a flow-through cell. In selected tests chloride concentrations were also logged.

The calcite tested in these experiments came from the areas of the Moore Creek & Sulcor Limestone members which is part of the Tamworth formation laid down in the late Devonian (Frasnian) period some 380 million years ago. Analysis with a Philips PW1404 Wavelength Dispersive Sequential XRF (X-Ray Fluorescence) analyzer showed that the limestone used in these experiments was 99% pure $CaCO_3$ with trace quantities of MgO (1%), strontium (168 ppm), barium (71 ppm), zirconium (40 ppm) and other trace elements at concentrations <40 ppm.

pH Analysis. pH was measured using an Orion 9165BN pH electrode connected to an Orion 720Aplus pH/ISE meter. Multipoint calibrations were done using pH 4, 7 and 10 NIST buffers (Orion) until a slope of between 92 and 102% was achieved.

Fluoride Analysis. All fluoride solutions were prepared with analytical grade NaF (BDH Chemicals) and diluted with deionised water (18 $M\Omega cm^{-1}$). Fluoride was measured with an Orion 9609BN fluoride ion-selective electrode (ISE) connected to an Orion 720Aplus pH/ISE meter. The fluoride ISE was calibrated using fluoride solutions adjusted to the ionic strength of the corresponding influent solution (as given below) with analytical grade KCl. Thus, at constant ionic strength the electrode measurements are directly proportional to concentration as the activity coefficient is constant. Calibration was carried out until a slope of 56±2 mV/decade was achieved. The calibration slope remains constant during analysis, resulting in a reproducibility of ±2% with a detection limit of 10^{-6} M.

A number of influent solutions were used in this study. Spent potliner leachate was taken from monitoring well E3 at the Hydro Aluminium field site. Historically, this monitoring well contains among the highest concentrations of contaminants at the site with approximately 1100 mg/L F^-, 3000 mg/L Cl^-, 950 mg/L NO_2^-, 50 mg/L Br^-, 4800 mg/L SO_4^{2-}, 8000 mg/L Na^+ and 300 mg/L NH_4^+ with around 200 mg/L total cyanide and 0.2 mg/L free CN^- with a pH of ~10.4. To reduce the risk associated with forming HCN gas, the leachate was diluted 1/5 with de-ionized water and spiked with NaF to bring the fluoride concentration to a level reflective of the highest concentrations found at the field site (~2300 mg/L F^-). Characteristically, the leachate is black in colour and analysis showed the leachate contains a number of volatile organic carbons (VOCs) such as phenols, phthalates, napthalenes and substituted napthalenes/benzenes characteristic of "black mud", a residue from the processing of SPL (USEPA, 1990). The effect of the SPL matrix on the removal of fluoride was investigated in control experiments using synthetic SPL solutions (consisting of the major inorganic ions and no organic contamination) made up to approximately 3000 mg/L Cl^-, 7200 mg/L Na^+, 5000 mg/L SO_4^{2-} and 2300 mg/L F^- by using analytical grade salts. To determine the effect of pH on fluoride removal, a pure NaF solution at ~1000 mg/L $F^-$was compared to a test using 1000 mg/L F^-in 0.06 M 2-Morpholinoethanesulfonic acid (MES) buffer. Carbon dioxide gas was also used to influence the system pH and optimize the fluoride removal.

CO_2 gas (pCO_2 ~ 1 atm) was bubbled through the influent solution or injected directly into the calcite column. The gas delivery tube was made from standard 0.7 mm outer diameter (0.3 mm internal diameter) stiff PVC tubing perforated with numerous pin sized holes. The holes were located in such a way so that the injected gas would exit the tubing over the interval running from the bottom to approximately half way up the column. Gas was injected into the top of the column so that no solution would be lost through leaks. The rate of CO_2 injection was kept constant during each test through the use of a flow regulator attached to the gas bottle. Where noted, the terms *injected* and *sparged* refer to CO_2 injection directly into calcite and injection into the influent solution respectively.

Experiment 1. *Spent Potliner Leachate (SPL) solution* $[F^-]_0$ *~2300 mg/L (I~0.35 M), pH ~10.4*. These column tests were done to determine the effects of the aqueous SPL leachate matrix on the removal of fluoride from SPL contaminated water. The influent solution consisted of the diluted SPL leachate spiked with NaF as described above. Two tests using SPL (test A and B) were run consecutively to test how column conditioning affects fluoride removal. Each test employed identical influent solutions and the column was flushed with a number of pore volumes of DI water between tests.

Experiment 2. *Synthetic SPL Leachate solution.* $[F^-]_0$ *~ 2300 mg/L with approximately 3000 mg/L* Cl^-*, 7200 mg/L*

Na^+, 5000 mg/L SO_4^{2-} and initial pH of 7.38. This test was run as a control experiment for comparison with experiment 1 to determine the effects of the major inorganic ions on fluoride removal by calcite.

Experiment 3. *High initial fluoride concentration with CO_2 injection and sparging ; $[F^-]_0 \sim 2300$ mg/L ($I \sim 0.33$ M) (with 3000 mg/L Cl^-, 7200 mg/L Na^+, 5000 mg/L SO_4^{2-} and initial pH of 7.38).* These tests determine the effect of fluoride removal from solutions having a high fluoride concentration (~2300 mg/L). The synthetic SPL solution was initially equilibrated with atmospheric CO_2 ($pCO_2 \sim 10^{-3.5}$ atm) by bubbling air through the solution during experiments. After fluoride breakthrough had occurred, CO_2 ($pCO_2 \sim 10^0$ atm) was then injected directly into the column over a period of ~15 min. For test B, CO_2 ($pCO_2 \sim 10^0$ atm) was injected into the influent solution for a number of hours after fluoride breakthrough was observed.

Experiment 4. *Low initial fluoride concentration. Pure NaF; $[F^-]_0 \sim 100$ mg/L; ($I \sim 0.005$ M).* The influent solution was equilibrated with atmospheric CO_2 ($pCO_2 \sim 10^{-3.5}$ atm) by bubbling air through the solution for the duration of the experiments. After fluoride breakthrough had occurred, CO_2 ($pCO_2 \sim 10^0$ atm) was either injected directly into the column (test A) for a few minutes or into the influent solution (test B) over a number of hours.

Experiment 5. *pH effects. Buffered (0.06 M MES) and unbuffered pure NaF solutions ; $[F^-]_0 \sim 1000$ mg/L.* To determine the effect of fluoride-calcite reactions on system pH, two column experiments (buffered and unbuffered) were done. Approximately three pore volumes of 0.06 M MES buffer (pH 6.08) was pumped through the column until a constant effluent pH was achieved. A solution of 1000 mg/L F^- in 0.06 M MES was then introduced. This was then compared to an identical, unbuffered, column test.

Experiment 6. *Pure NaF solution supersaturated with respect to CaF_2 ($I \sim 0.005$ M); $[F^-]_0 \sim 100$ mg/L.* To determine the effects of CaF_2 seeding on fluoride removal by calcite, experiment 5 was repeated with the influent solution supersaturated with respect to CaF_2.

The effect of the SPL matrix on fluoride removal by calcite can be assessed by comparing experiments 1 and 2. Experiments 3 and 4 highlight the importance of the point of CO_2 injection, while the effects of fluorite supersaturation on fluoride removal are seen by comparing experiments 4 and 5. The experimental results are shown together with the PHREEQ (Parkhurst and Appelo, 1999) model results.

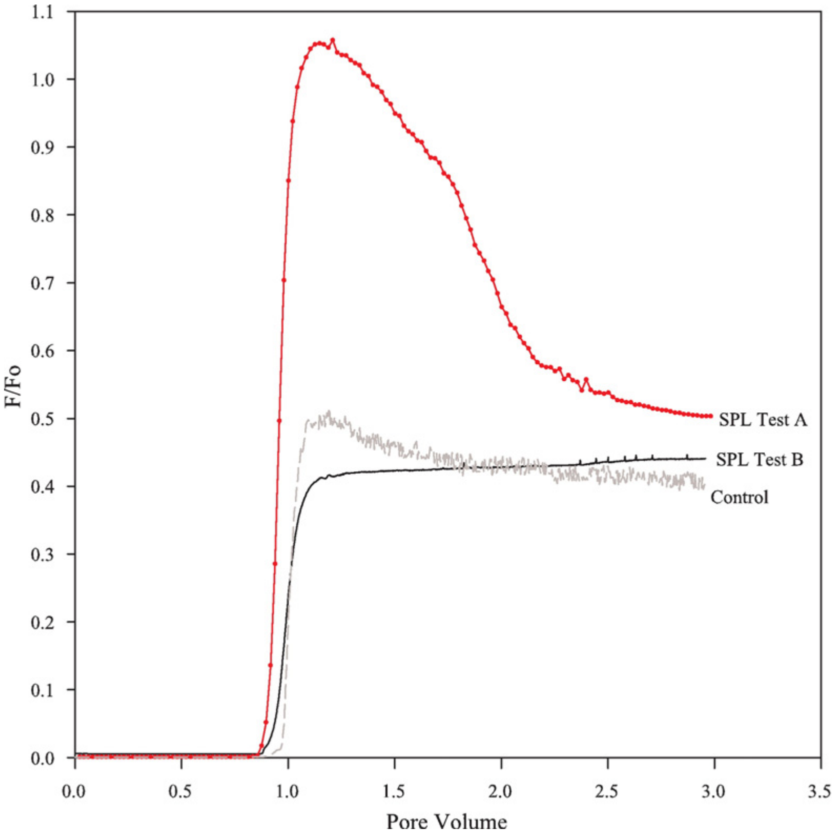

Fig. 2. Fluoride removal form SPL Leachate Column (Experiment 1; SPL tests A and B) and Synthetic SPL (control) tests (Experiment 2) Flow Rates ~0.6 mL/min. No $CO_{2(g)}$ injection. $[F^-]_0 \sim 2300$ mg/L.

The PHREEQ model uses advection to simulate one dimensional advective flow of the fluoride solution through the column with the model only accounting for fluoride removal via precipitation as fluorite. Model influent solutions contained Na^+ and F^-at concentrations identical to the experimental and were reacted with 1.2 kg of calcite within the modeled column. CO_2 was added either to the influent solution or allowed to equilibrate with calcite at the specified partial pressure. The model input file was altered to include the background matrix and mineral phase gypsum where necessary (e.g. experiments 1, 2 and 3).

3. Results and discussion

3.1. Impact of SPL matrix on fluoride removal rates (experiments 1 and 2)

SPL matrix effects can be seen by comparing results from experiment 1 with those of experiment 2, the control with a synthetic SPL leachate and $pCO_2 \sim 10^{-3.5}$ atm. Fig. 2 shows the results from two SPL leachate column tests (SPL test A and B), along with the synthetic leachate test results (experiment 2). In the figures, we define F/F_0 as the ratio of the measured fluoride concentration (F) to the initial fluoride concentration (F_0). For SPL test A it was observed that the carbon black component of the SPL matrix was deposited on the surface of the calcite in the column as soon as mixing occurred. Attempts to wash the carbon black from the calcite using water, detergent, acetone and hexane were all unsuccessful. The coating of the calcite appears to have an adverse effect on fluoride removal with little or no fluoride removal occurring in the initial stages of the column experiment ($F/F_0 \approx 1.0$; Fig. 2).

Synthetic SPL leachate contains all the major matrix components as SPL leachate with the exception of carbon black. Comparison of the synthetic SPL (experiment 2) experiment with SPL test A shows that in the absence of carbon black, fluoride removal is approximately 50%. Fig. 2 shows that even after 3 pore volumes in experiment 1A 50% fluoride removal are still not achieved. The observed initial inhibition of fluoride removal and the subsequent slow increase in removal during SPL test A are explained by Turner et al. (2005). The authors demonstrated that fluoride removal by calcite consists of an instantaneous adsorption

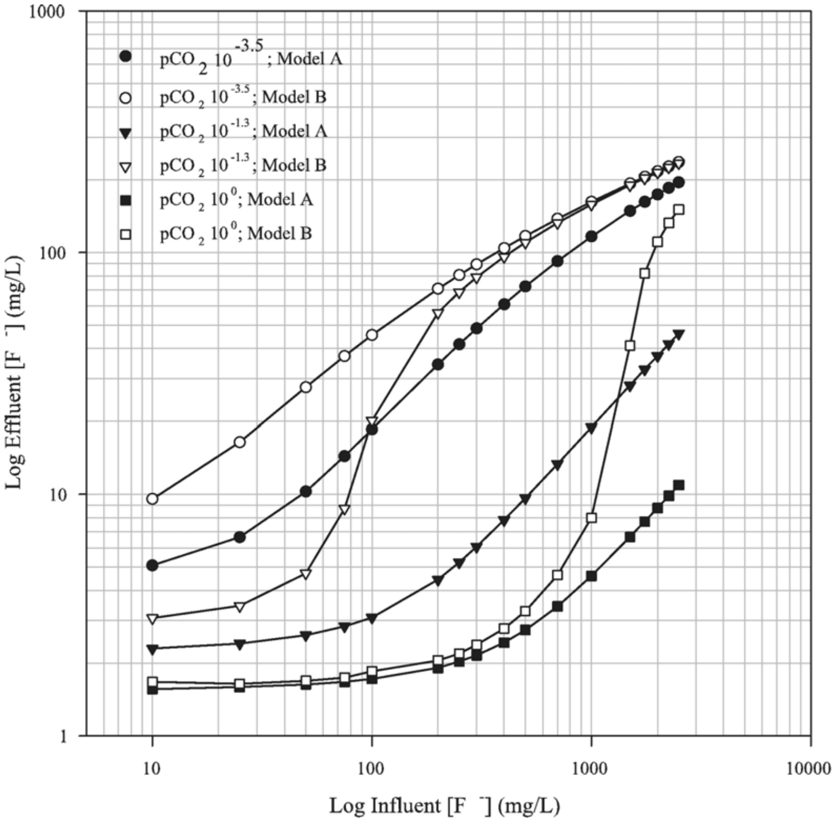

Fig. 3. PHREEQ predicted effluent [F^-] vs influent [F^-] for varying pCO_2 for CO_2 injected into calcite (Model A) and CO_2 injected into influent solution (Model B).

reaction followed by CaF_2 precipitation with nucleation and growth of fluorite crystals. It is hypothesized that carbon black coats the adsorption sites at the calcite surface and inhibits fluoride removal until the system shifts to precipitation mode.

In a subsequent experiment (SPL test B), using the same SPL leachate and calcite column as used in test A, fluoride removal at 1.0 pore volume (~60%) is much greater than removal experienced at the same time in SPL test A (0%). This is due to column conditioning attributed to the presence of CaF_2 nucleation centers (Reardon and Wang, 2000), thereby allowing the system to remove fluoride more rapidly than observed in SPL test A.

SPL test A and B (Fig. 2) appear to converge to approximately the same fluoride removal ($F/F_0 \sim 0.45$) at pH ~ 10.5 a change of only ~0.1 pH units. However the pH of the control test rises to ~11.4 and fluoride removal continues to (slowly) increase to ~60% at 3.0 PV. This further indicates that during SPL tests no surface adsorption is occurring because the carbon black in the SPL coats the calcite surface and inhibits fluoride exchange at the surface sites. Control test results can also be compared with batch test results where at pH >10.5, ~58% of the initial fluoride solution is removed (Turner et al., 2005). Clearly, the removal of only 58% of fluoride (at pH 10.5) is not sufficient to justify the choice of calcite as a material for the remediation of fluoride contaminated with SPL waste because the effluent fluoride concentration still exceeds 1300 mg/L. Consequently, pH control methods via CO_2 addition

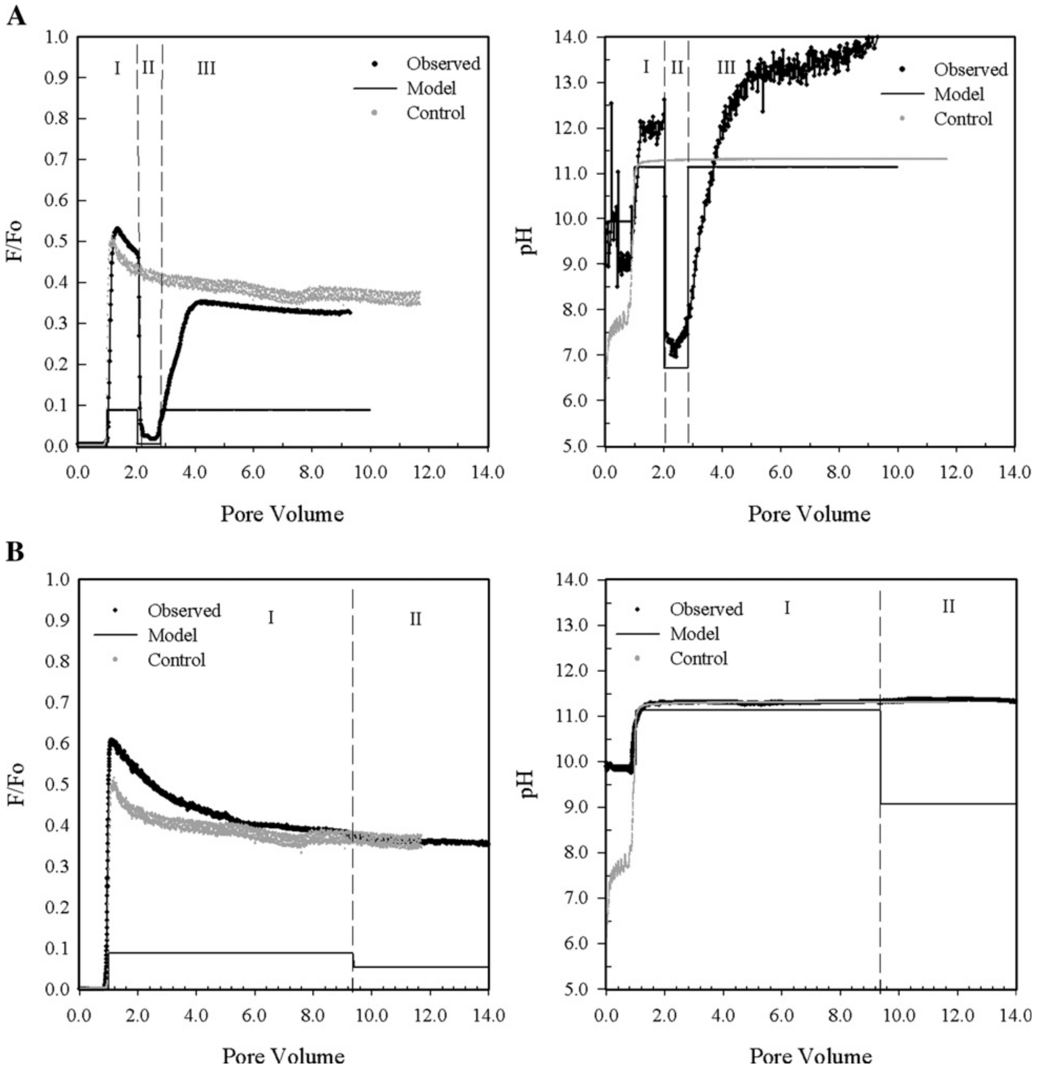

Fig. 4. Effluent fluoride concentration (F/F_0) and pH for experiment 3. (A) CO_2 injected directly into calcite and (B) CO_2 injected into influent solution using a synthetic SPL solution. $[F^-]_0 \sim 2300$ mg/L, $[Cl^-] \sim 3000$ mg/L, $[Na^+] \sim 7200$ mg/L and $[SO_4^{2-}] \sim 5000$ mg/L. Zone I and III $pCO_2 \sim 10^{-3.5}$ atm, Zone II $pCO_2 \sim 10^0$ atm. For comparison, results from a control experiment (no CO_2 injected or sparged) are also shown. In all zones model predicts that with respect to fluorite and calcite equilibrium is attained (SI = 0) and with respect to gypsum the system is undersaturated (SI < 0).

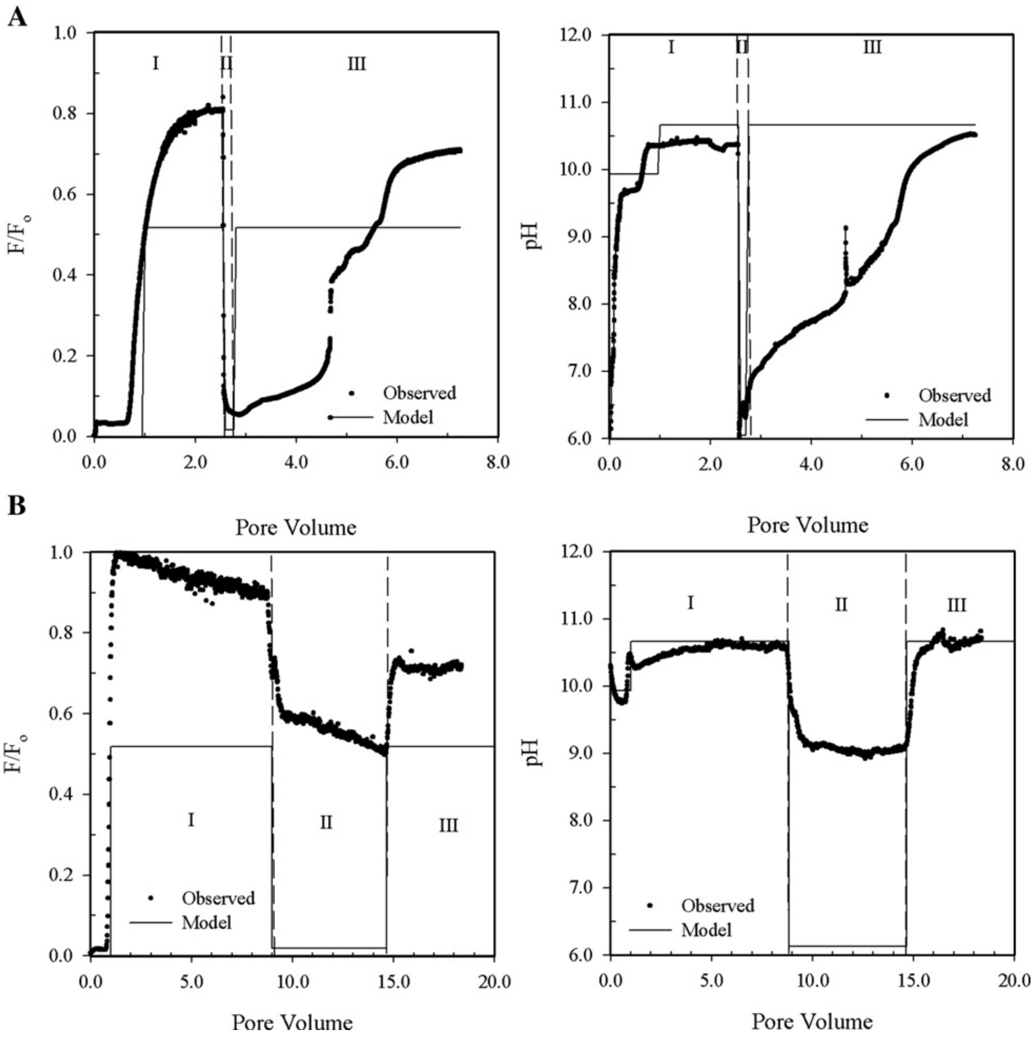

Fig. 5. Effluent fluoride concentration (F/F_0) and pH for experiment 4; (A) CO_2 injected into directly into calcite and (B) CO_2 injected into influent solution using a pure NaF solution. $[F^-]_0 \sim 100$ mg/L. Zone I and III $pCO_2 \sim 10^{-3.5}$ atm, Zone II $pCO_2 \sim 10^0$ atm.

were examined in an attempt to increase the efficiency of the removal process.

3.2. PHREEQ Model results to investigate the impact of CO_2 injection

PHREEQ can be used to assess how barrier performance varies with influent fluoride concentration and the results are shown in Fig. 3 as a function of initial fluoride concentration and pCO_2. Model A represents CO_2 injected into the calcite column replicating open system conditions and Model B represents CO_2 injected into the influent solution and therefore represents closed system conditions. The main difference between the open and closed systems is the availability of calcium to drive the fluoride precipitation reaction.

Fig. 3 shows that, at high initial fluoride concentrations, altering the point of injection can significantly affect the effluent concentration. For example, a solution with an initial fluoride concentration of ~2000 mg/L will have an effluent concentration of ~200 mg/L when CO_2 ($pCO_2 \sim 10^{-1.3}$ atm) is injected into the influent solution. If the same injection was made directly into the calcite the resultant effluent fluoride concentration would be ~40 mg/L. When fluoride concentrations exceed 2000 mg/L, effluent fluoride concentrations can be reduced to <20.0 mg/L by directly injecting $pCO_2 > 10^{-0.5}$ atm into the calcite (eg. $pCO_2 \sim 10^0$ atm). This is significant for Australian (NSW) conditions, since a fluoride concentration of 20 mg/L (mg/kg) is the maximum concentration permissible before the waste becomes a controlled liquid waste requiring a license for transport and disposal (EPA, 1999). As the initial fluoride concentration decreases below ~50 mg/L the point of injection becomes less important. However, the pCO_2 remains a significant influence on the final fluoride concentration.

3.3. Experiments to assess the impact of CO_2 injection (experiments 3 and 4)

Figs. 4 and 5 show results from experiments 3 and 4 and can be compared to illustrate the importance of the location of CO_2 injection. The following discussion will be divided into three parts describing the conditions before, during and after the CO_2 injection (zones I, II and III in the figures respectively).

Zone I in Fig. 4A and 5A defines the point before the addition of CO_2. Model predictions show that the pH after breakthrough (1.0 pore volumes) should be approximately 11.1 (Fig. 4) and 10.7 (Fig. 5) and that the fluoride removal should approach 90% ($F/F_0 \sim 0.1$; Fig. 4) and 48% ($F/F_0 \sim 0.52$; Fig. 5) for experiments 3 and 4 respectively. Observed pH values are slightly higher than model predictions, however, and F concentrations differ significantly from the predicted values with fluoride removal slowly increasing with pore volume (time) approaching 45–55%.

The significant differences between observed and modeled F removal can be explained by kinetics (Plummer and Parkhurst, 1979) or by the inhibition of calcite dissolution due adsorption at sites that are active to dissolution (Berner and Morse, 1974; Erga and Terjesen, 1956; Svensson and Dreybrodt, 1992). Plummer and Parkhurst (1979) studied calcite dissolution kinetics as a function of pCO_2 and pH and showed that calcite dissolution rates slow when CO_2 and H^+ concentrations are low. Under these conditions calcite dissolution is then controlled by the (slow) reaction with H_2O according to the hydrolysis reaction:

$$\begin{aligned} &CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^-; \\ &\log k = -5.86 - 317.0/T (T < 298.15^0 K) \end{aligned} \quad (1)$$

After breakthrough the observed pH exceeds 10.5 (Fig. 4 and 5) and the dissolution of calcite becomes controlled by Eq. (1) and its associated slow kinetics. The slow equilibration process can also be further inhibited by adsorption ions at calcite sites active to dissolution. It has been observed that the adsorption of Cu^{2+} (Erga and Terjesen, 1956) and PO_4^{3-} (Berner and Morse, 1974; Svensson and Dreybrodt, 1992) inhibits calcite dissolution by blocking sites that are active to dissolution. Furthermore, fluoride has also been shown to be adsorbed onto the calcite surface (Fan et al., 2003; Turner et al., 2005) thereby inhibiting calcite dissolution.

The slower reaction kinetics at high pH predicted above have been observed in batch experiments (Turner et al., 2005). With a fluoride concentration of 700 mg/L experiments were far from equilibrium at pH 10.5 with the given column residence times. However for pH <8, the experiments were >95% complete for the residence times employed in the column experiments presented in this paper.

The fact that the observed pH in Figs. 4 and 5 is slightly higher than the predicted model value indicates that an increase in pH is occurring due to another reaction. For example, OH^- exchange may occur during the exchange of $F^-$with surface OH^- bonded to the calcite as >CaOH (where >represents the solid surface). Stipp and Hochella (1991) have shown that such >CaOH surface sites exist with monolayer surface coverage (Fenter et al., 2000).

Zone II in Fig. 4 and 5 represents the period during CO_2 injection. Fig. 4A shows that direct injection of CO_2 into the calcite improves the removal efficiency of the system to ~99% in comparison to ~65% removal when CO_2 is injected into the influent solution (Fig. 4B). This equates to an effluent fluoride concentration of ~23 mg/L compared to ~805 mg/L, a result that clearly emphasizes the importance of the point of CO_2 injection. A similar conclusion can be made by examining Fig. 5A and B with ~94% and ~50% of F removal achieved for CO_2 injection into calcite (Fig. 5A) and influent solution (Fig. 5B) respectively.

During injection of CO_2 ($pCO_2 \sim 10^0$ atm) directly into the calcite (Fig. 4A and 5A) the observed pH drops to near neutral values resulting in a dramatic increase in F removal to levels exceeding 95%. According to Plummer et al. (1979) the calcite dissolution rate in the intermediate pH range depends on both pCO_2 and pH according to the equation

$$\begin{aligned} &CaCO_3 + H_2CO_3^0 = Ca^{2+} + 2HCO_3^-; \\ &\log k_2 = 2.84 - 2177.0/T \end{aligned} \quad (2)$$

Results presented in Fig. 4A and 5A (zone II) show good correspondence between observed and model results suggesting that the model/theory has correctly described the system.

When CO_2 is injected into the influent solution (zone II, Fig. 4B and 5B) the observed and model results do not agree. In Fig. 4B the observed pH is ~11.1 in zone II with F^-removal approaching 62%. In contrast, PHREEQ predicts a pH of ~9.1 when CO_2 ($pCO_2 \sim 10^0$ atm) is injected into the influent solution with ~94.6% F^-removed ($F/F_0 \sim 0.054$). As the influent solution container was open to the atmosphere the pH discrepancy between the observed and model results is most likely due to a pCO_2 drop during injection into the influent solution. If Fig. 2B is modeled as an open system with a $pCO_2 \sim 10^{-3.5}$ atm, then the experimental and model pH match, but the observed and model F^- results still differ with PHREEQ predicting 91.2% F^- removal. Similar discrepancies were obtained for the results shown in Fig. 5B.

Zone III in Fig. 4 and 5 corresponds to the point when CO_2 injection ceases. Model results show pH and fluoride concentrations return to values observed in zone I. However, the experimental results behave differently. In the early stages of zone III, Fig. 4A shows both experimental pH and F/F_0 rapidly increasing (i.e. fluoride removal decreasing). It is interesting to note that neither pH nor fluoride return to levels observed before the addition of CO_2 (pH ~ 12.0 and $F/F_0 \sim 0.5$). The system pH continues to rise above pH 13.0 and F^- removal plateaus at ~68% ($F/F_0 \sim 0.32$). The fact that pH and the removal of fluoride continue to increase in zone III is consistent with the notion of OH^-exchange during fluoride adsorption at the calcite surface. It is also possible that CO_2 addition has altered the calcite surface, perhaps adding more sorption sites. This is supported by van Cappellen et al. (1993) who suggested that CO_2 alters the pH of a calcite system and changes the speciation at the calcite surface.

For the low initial fluoride experiments (Fig. 5) it can be seen that the observed pH approximates the model prediction in zone III. Once again though, the observed F removal is less than predicted by the model, a result consistent with results observed in zone I. The experimental behaviour cannot be reproduced by the model as no surface sorption parameters for this system exist in the literature. This is attributed to the problems associated with separating adsorption from precipitation and desorption from dissolution in the calcite-fluoride system (Stipp, 1999).

3.4. Impact of CaF_2 seeding (experiments 4 and 5)

Fig. 6 compares experiments where the influent solution is undersaturated (experiment 4) and supersaturated (experiment 5) with respect to fluorite. The figure shows that fluorite supersaturation of the influent solution in experiment 5 increases the amount of fluoride removed initially by as much as 20% in zone I. This is attributed to the presence of fluorite particles in the influent solution acting as nucleation centers that effectively seed the

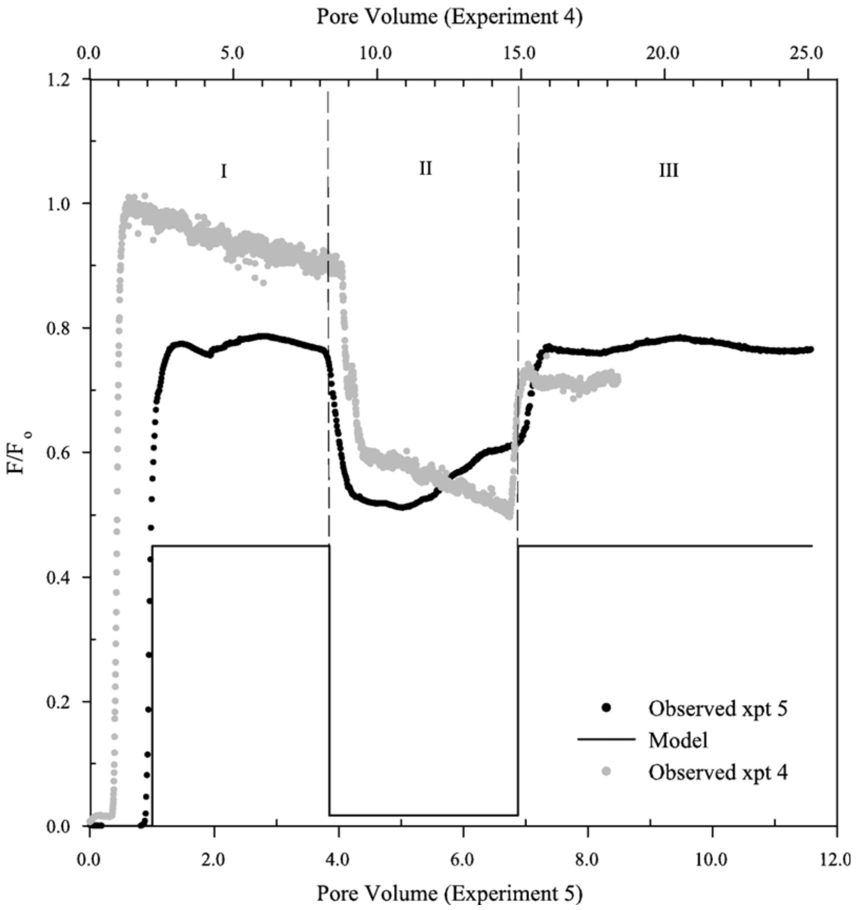

Fig. 6. Effluent Fluoride Concentration (F/F_0) for Experiment 5, pure NaF solution $SI_{fluorite} > 0$. $[F^-]_o \sim 100$ mg/L. CO_2 injected into influent solution. Zone I and III $pCO_2 \sim 10^{-3.5}$ atm, Zone II $pCO_2 \sim 10^0$ atm. Overlaid for comparison is Experiment 4, pure NaF solution, $SI_{fluorite} < 0$.

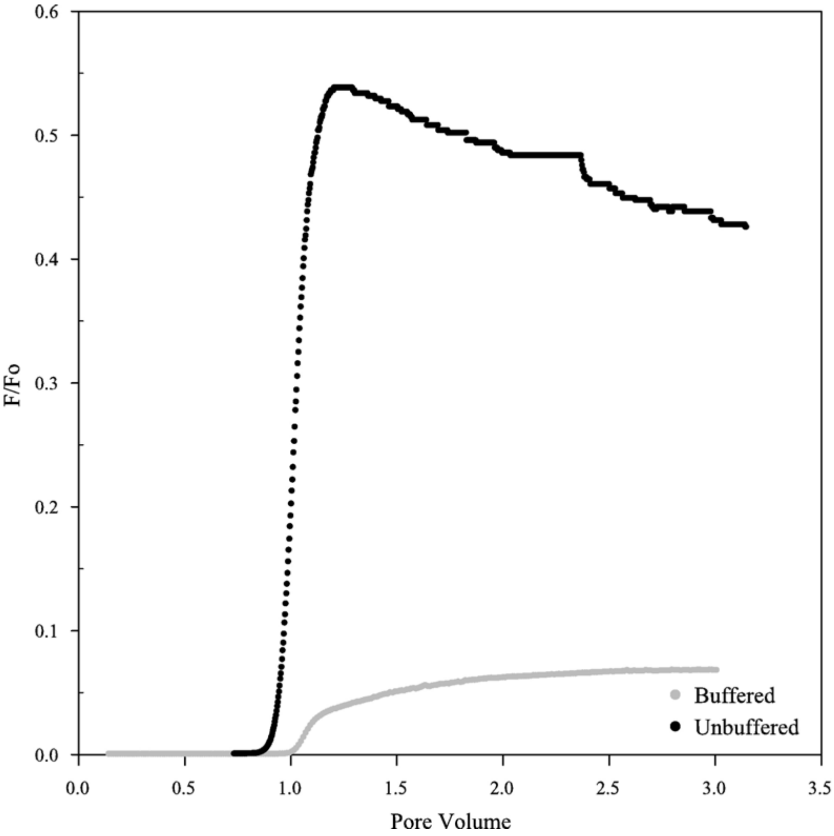

Fig. 7. Effluent fluoride concentration (F/F_0) for Buffered (0.06 M MES (2-Morpholinoethanesulfonic acid) buffer and unbuffered pure NaF column tests (experiment 6). $[F^-]_0 \sim 1000$ mg/L.

precipitation process. Differences in F^- removal after zone I are minimal (<7%) as the system is forced to precipitate CaF_2 during zone II when the concentration of dissolved CO_2 increases.

3.5. pH effects: buffered vs unbuffered systems (experiment 6)

Fig. 7 shows the results from experiment 6, a buffered and unbuffered column test ($[F^-]_0 \sim 1000$ mg/L). The unbuffered test shows an initial removal of ~45% at breakthrough with removal slowly increasing over time reaching ~55% at 3.0 pore volumes. The trend in fluoride removal with time is reflective of the continual increase in system pH from 6.1 (at PV ~ 0) to 10.93 (at PV ~ 3.0). In comparison, the column test buffered with 0.06 M MES and ~1000 mg/L F^- (initial pH 6.08) shows a removal of ~93% after ~3.0 pore volumes, a significant increase over the unbuffered system. In addition, the buffered system pH was found to have increased from 6.08 (at zero PV) to 6.9 (at PV ~ 1.0) and 7.8 (at PV ~ 3.0). The increase in pH in the buffered system supports the theory of F^- adsorption at the calcite surface (Turner et al., 2005) with F^- exchanging for OH^- as observed in Figs. 4 and 5. At the respective effluent pH values observed, the column test results are consistent with fluoride removal in batch test results. After the completion of the column experiment, the active medium was removed and visually inspected. No evidence of pore clogging was found in the column. The high removal rates and lack of pore clogging demonstrates the effectiveness of calcite as a substrate for the removal of fluoride and its potential for the use in an *in situ* permeable reactive barrier.

4. Conclusions

The findings presented in this paper show that calcite, a cheap and readily available material, can be used to remove fluoride from contaminated waters. Fluoride removal can be enhanced by injecting CO_2 into the calcite, and the performance is also good for complex chemical systems such as groundwater contaminated with SPL waste. Results show that the point of CO_2 injection is important in governing the mass of fluoride removed, with injection directly into the calcite being much more effective at removing fluoride (~99%) than equilibration of CO_2 with the influent solution (~50%). The additional benefit of injecting CO_2 into the calcite is that the effluent pH is approximately neutral in comparison to the alkaline effluent obtained by the latter method. Performance of the calcite permeable reactive barrier is good for a large range of fluoride concentrations, with high removal rates at both low and high concentrations. However, the addition of CO_2 is critical to system performance; for example, without gas injection mass removal falls from >95% to approximately 60% at high fluoride concentrations. Observed increases in system pH during fluoride removal can cause a decrease in the overall fluoride mass removed as well as increasing the residence time required in a potential calcite reactive barrier, however this can be overcome by direct injection of CO_2 with CaF_2 seeding also able to enhance fluoride removal by acting as potential nucleation centers for fluorite precipitation.

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