Fluoride remediation with calcite as a function CO_2 partial pressure

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Abstract ——

At Hydro Aluminium located in the Hunter Valley, NSW, Australia, spent potliner (SPL) waste has contaminated the local ground water aquifer with concentrations of fluoride up to 2,000 mg/L. The ability of calcite ($CaCO_3$) to remove this fluoride was studied in a batch reactor as a function of CO_2 partial pressure and fraction size. Results show that fluoride removal at equilibrium is independent of fraction size, but the rate at which equilibrium is achieved is faster for smaller sized fractions (larger surface area). The optimum partial pressure of CO_2 was between 7% and 15% with ~95% & 98% F removal achieved respectively in experiments using pure fluoride solutions. Results using actual SPL contaminated groundwater indicate removal by calcite is dependent on at least two different chemical pathways (mechanisms) that can adversely affect defluoridation and that geochemical models require rigorously defined kinetic data before they can be used to accurately predict results in this system.

1 INTRODUCTION

Fluoride occurs naturally in the forms of sellatite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$3Ca_3(PO_4)_2 \cdot Ca(F,Cl_2)$] (Mohapatra et al. 2009). Despite these fluoride minerals generally having low solubilities, fluoride dissolution in groundwater can occur given the correct conditions. Generally fluoride concentrations in groundwater are low (<0.1−0.5 mg/L), however, if the rock formations are conducive to dissolution, concentrations of up to 10 mg/L are possible (NHMRC 1996). In potable waters, fluoride concentrations >1.5 mg/L have been associated with tooth mineralization (dental fluorosis) in young children and serious medical conditions such as skeletal fluorosis can occur with long term ingestion of high fluoride content drinking water (NHMRC 1996). Consequently, the World Health Organization (WHO 2004) and the Australia Drinking Standard Guidelines (NHMRC 1996) recommend that drinking water should not contain more than 1.5 mg/L. Despite fluoride occurring naturally in groundwater, increasing contamination due to anthropogenic activities has become a worldwide concern.

Anthropogenic fluoride contamination is associated with numerous industrial processes including, operating coal fired power stations, beryllium extraction, brick and iron processing, glass and ceramic production, electroplating, fertilizer production, electronics manufacture, and aluminium smelting.

The aluminium smelting process is performed in a steel vessel known as a 'pot' with a refractory brick and carbon cathode lining. The electrolytic cell developed in the pot has a limited life span and the pot lining material must be removed and replaced at the end of its operational life. During the smelting process metal and other chemicals are absorbed by the lining with sodium, fluoride and cyanide being the most common constituents being absorbed. The removed pot lining material with the absorbed chemicals known as spent potlining (SPL) is a major problem for the aluminium industry. For example, at the Hydro Aluminium smelter located in the Hunter Valley, NSW, Australia, SPL waste has contaminated the local ground water aquifer with concentrations up to 2000 mg/L F. The SPL was dumped by previous owners in an unlined waste repository from 1969 to 1992 and Hydro Aluminium is now investigating remediation options for ground water contaminated with SPL leachate.

The general composition of SPL is given in Table 1 with fluoride typically ranging from 7.5−22 per percentage weight. Approximately 22 kg of SPL is produced for every tonne of aluminium (Tetronics 2009). Worldwide primary aluminium production was ~50 million tonnes in 2009 with sustained growth predicted (USGS 2010). This equates to over 800,000 tonnes of SPL produced annually. The volume of SPL generated and its chemical composition creates potentially serious environmental concerns for the aluminium industry (Spigel and Pelis 1990).

Many different techniques have been developed and applied in order to remove fluoride from wastewater. These methods can be broadly divided into two main groups; precipitation and sorption. Precipitation

Table 1 General Composition of SPL (Kumar et al. 1992)

Constituent	Range, wt. %
Fluoride	7.5–22
Aluminium (total)	7.0–22
Sodium	8.6–22
Carbon (total)	13–69
Alumina	9.2–26
Cyanide	0.04–0.6
SiO_2 (as Si)	0.7–10.9
Fe_2O_3 (as Fe)	0.3–2.8
Calcium	0.5–6.4
Sulphate	0.1–0.18
Sulphur	0.1–0.18
Magnesium	0.01–0.17
Lithium	0.46–0.57
Phosphorous	0.0005–0.003

methods use the addition of chemicals in order to precipitate the fluoride out of an aqueous solution. Sorption methods remove the fluoride by sorption or ion exchange. The principal disadvantages of sorption or ion exchange methods are a high setup cost and the implementation of regular column regeneration procedures, which can interrupt the treatment process.

Various forms of lime [$Ca(OH)_2$, CaO, $CaCO_3$] or other calcium salts have been utilized to remove fluoride as fluorite (CaF_2). Calcite has been suggested as a fluoride removal medium with its main advantage being its cost. At approximately AUD$100 per m^3 calcite is cheap and abundant. Reardon & Wang (2000) 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. This fluoride removal process was limited by the solubility of the calcite in a closed reactor which limits the percentage of fluoride removal. Consequently, Reardon and Wang (2000) also examined ways of improving fluoride removal through the injection of CO_2 to lower pH. The injection of CO_2 (~96 mol%) enhanced the precipitation reaction by continually dissolving the calcite in solution, however only fluoride concentration up to ~100 mg/L were used.

The efficient and cost effective defluoridation of contaminated groundwater to <40 mg/L using a calcite/CO_2 system is the focus of this study. The use of CO_2 to enhance defluoridation is relatively expensive and the optimum conditions for CO_2 injection were determined through various stirred batch reactor tests. Results from pure fluoride only solutions and actual SPL contaminated groundwater are also compared to the geochemical model PHREEQc (Parkhurst and Appelo 1999).

2 MATERIALS & METHODS

Experiments were carried out using a free-drift batch reactor technique. This procedure was selected as it is superior to other methods, namely pH-stat. Free-drift requires less complicated apparatus than pH-stat and is excellent in obtaining multiple data acquisitions. All experiments were carried out in an inflatable gas glove box bag in a constant temperature (CT) room using various fixed partial pressures of CO_2 as outlined below.

2.1 Potassium Fluoride

Anhydrous potassium fluoride KF (Sigma-Aldrich) and demonized water was used in the preparation of F^- stock solutions. The demonized water was produced by a Millipore Milli-Q 185 water deionizer (18.2 $M\Omega/cm^{-1}$). A stock solution of 2000 mg/L of F standard was produced and all experiments used various dilutions of the pre-prepared stock solution. The exact concentration of F in the stock solution was determined by ion chromatography.

2.2 Calcite

The calcite used in these experiments was sourced 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. Crushed limestone was utilized in preference to commercial calcite powder to more closely represent conditions that will be experienced in the commercial treatment of the contaminated aquifer at Hydro Aluminium.

Analysis of the calcite with a Philips PW1404 Wavelength Dispersive Sequential XRF (X-Ray Fluorescence) analyzer, with less than ±2% error for elemental analysis, 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. The limestone was sieved into particle size fractions of 150–300 μm, 300–600 μm, 600–850 μm, 850 μm–1.18 mm, 1.18–2.36 mm and >2.36 mm, rinsed with demonized water and oven dried at 40°C. The 150–300 μm and 1.18–2.36 mm fractions were utilized for these experiments. The particle sizes of 150 μm and 1.18 mm are referred to for brevity. The 1.18 mm fraction was chosen as it is the dominant fraction size in the crushed limestone sample and 150 μm was used as it is known to dissolve quickly.

2.3 Spent Potlining Leachate (SPL)

SPL contaminated groundwater was sourced from the Hydro Aluminium field site and analyzed for major anions (F^-, Cl^-, SO_4^{2-}, and PO_4^{3-}) and cations (Ca^{2+}, Na^+, K^+) using a Dionex 2500C ion chromatograph. SPL was taken from a monitoring well known to have the highest concentrations of contaminants with approximately 1100 mg/L F^-, 3000 mg/L Cl^-, 950 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. 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 carbon black used in the production of the potliner materials.

2.4 CO$_2$ Partial Pressure

Carbon dioxide gas was added to an inflatable gas glove chamber at various partial pressures, (made up to 100% with N$_2$) of pCO_2 ~$10^{-3.5}$ atm (0.03 mol% i.e. atmospheric CO$_2$), ~$10^{-1.52}$ atm (3%), ~$10^{-1.16}$ atm (7%), ~$10^{-1.0}$ atm (10%), ~$10^{-0.82}$ atm (15%), ~$10^{-0.52}$ atm (30%), ~$10^{-0.30}$ atm (50%) and ~$10^{-0.18}$ atm (66%). The CO$_2$ gas was prepared and supplied by BOC Scientific. A certificate on analysis was provided with all gas bottles using ANA5024 standards which indicated an error of ±0.2% or less.

2.5 pH & Fluoride Analysis

pH was measured using an Orion 9165BN pH electrode connected to an Orion 720Aplus pH/ISE meter. Multipoint calibrations were completed using pH 4, 7 & 10 NIST buffers (Orion) until a slope of between 92 and 102% was achieved. Fluoride was measured with an Orion 9609BN fluoride ion-selective electrode (ISE) connected to an Orion 720Aplus pH/ISE meter. Multipoint calibrations were completed using 10, 100, 1000 and 2000 mg/L of potassium fluoride made up from stock solution, until a slope of -54 ± 2 mV/decade was achieved.

When using two or more electrodes within the same aqueous solution, interference in the millivolt values was observed. Consequently calibration was performed with both pH & fluoride electrodes present in the respective calibration solutions. Over the course of more than sixty calibrations it was determined that the induced interference did not affect the theoretical slope of the calibration curve with interference only causing a shift in the calibration offset (a constant) and therefore accurate and precise readings were taken.

Fluoride ISE potentials are also affected by changes in temperature. At the 10^{-3} M level, a 1°C difference in temperature results in a 2% error (TEC 2003). The experiments performed in the lab under atmospheric conditions indicated that temperature affected the resultant curve, however, it was not considered significant when compared to ion chromatograph results (independent of temperature) which showed an error in % F removal of 1.2 ± 2.6% RSD (relative standard deviation).

The fluoride ion selective electrode records the activity or "effective concentration" of free fluoride ion in solution. The fluoride ion activity, A, is related to free fluoride ion concentration, C_f, by the activity coefficient, γ_i

$$A = \gamma_y C_f \tag{1}$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ionic strength is defined as:

$$\text{Ionic strength} = 1/2 S C_i Z_i^2 \tag{2}$$

where:
  C_i = concentration of ion i
  Z_i = charge of ion i
and S symbolizes the sum of all the types of ions in solutions (TEC 2003).

All fluoride ion selective electrode calibration standards were analyzed by ion chromatography which gave true fluoride concentration values. These IC concentration values were then used to determine calibration curves for the fluoride ISE. Consequently, the problem of ionic strength effects (i.e. activity) is effectively eliminated.

2.6 Ion Chromatography

The anions (F$^-$, Cl$^-$, SO$_4^{2-}$, and PO$_4^{3-}$) from the samples were analysed using a Dionex 2500C ion chromatograph equipped with an AS18 analytical column in line with AS18G guard column with conductivity detection, a anion separator column (Dionex IonPac AS18A), and a suppressor column (Dionex ASRS-4 mm). The flow rate of the mobile phase, 30 mM KOH was set to 1.0 ml/min. The analytical run time was 15 minutes, which allowed excellent peak resolution.

Calibration standards were prepared from a Dionex Seven Anion Standard II solution by dilution, by mass, with 18.2 MΩ/cm^{-1} DI water. Calibration standards were run in duplicate at the start of every analysis. All analysis and control was achieved using Chromeleon 6.7 software.

To optimise ion chromatograph peak separation and resolution, the samples were filtered using 0.45 μm nylon membrane filter (Pall – Life Sciences), and diluted (1/400 by mass) with 18.2 Ω/cm^{-1} DI water.

3 RESULTS AND DISCUSSION

3.1 Fluoride Removal

During the experimentation process several parameters were assessed such particle size and stirring rate to determine their effect on percentage fluoride removal. Results obtained demonstrate that the percentage fluoride removal at equilibrium is independent of fraction size as reported by Sun et al. (2000), however the time taken to reach equilibrium, and therefore the kinetic reaction pathway, is highly dependent on particle size. No conclusions can be drawn as yet on the effect of stirring rate with further experimentation required.

3.2 CO$_2$ Partial Pressures

A range of partial pressures as described above, were used in experiments using an initial concentration of 2000 mg/L F, and reacted with 150 μm calcite fractions.

Figure 2 demonstrates that there is a clear relationship between partial pressure and time taken to reach equilibrium (assumed to be ~95% fluoride removal). It was also observed that at $pCO_2 > \sim 10^{-1.0}$ atm (10%) that there was no significant improvement in the time taken to reach equilibrium. This is a significant finding as the cost of CO_2 is a potentially prohibitive factor in the defluoridation of contaminated waters. At approximately AUD2500.00 per tonne for 100% CO_2, reducing the partial pressure to 10% or less with no significant reduction in the time to reach equilibrium greatly reduces one of the main input costs of this decontamination process. Other experiments (not shown) using $\sim 10^{-0.52}$ atm (30%), $\sim 10^{-0.30}$ atm (50%) and $\sim 10^{-0.18}$ atm (66%) partial pressures of CO_2 with 200 mg/L and 2000 mg/L stock solutions of fluoride reacted with 150 μm and 1.18 mm calcite fraction closely emulated these results.

3.3 Fraction Size

Batch tests performed on 150 μm and 1.18 mm calcite fractions under CO_2 partial pressures of pCO_2
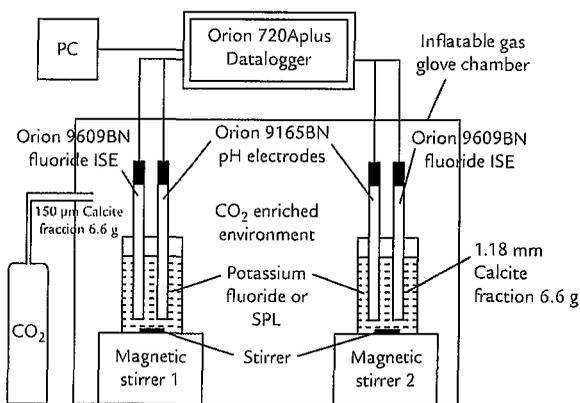
Figure 1 Schematic diagram of calcite/CO_2 reactor.
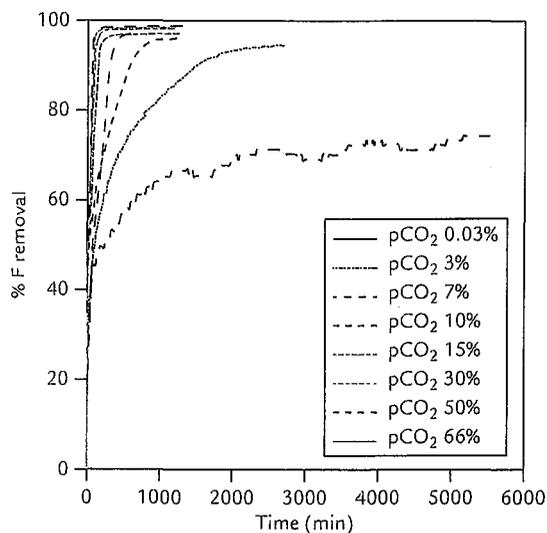
Figure 2 Fluoride removal (%), as a function of various partial pressures, 2000 mg/L initial fluoride and 150 μm calcite.

$\sim 10^{-1.16}$ atm (7 mol%), $\sim 10^{-1.0}$ atm (10%), $\sim 10^{-0.82}$ atm (15%) and $\sim 10^{-0.52}$ atm (30%), demonstrate that the % fluoride removal as a function of time is dependent upon calcite particle surface area.

Figure 3 shows that at various pCO_2, time to reach 95% fluoride removal was less for the 150 μm fraction than for the corresponding 1.18 mm fraction, and as expected, increasing the partial pressure of CO_2 decreased the time required to reach 95% F removal. This trend was observed for both 200 mg/L and 2000 mg/L concentrations of fluoride with the exception of the $\sim 10^{-1.16}$ atm (7%) pCO_2, 2000 mg/L, 1.18 mm experiment. Other experiments performed (not shown) also indicate that the smaller 150 μm fraction produces superior fluoride removal as a function of time. The results are supported by the findings of Sun et al. (2000) who report that the surface area of calcite effects dissolution rates as smaller particles present a larger surface area for solution reactions. As the 150 μm fraction provided superior fluoride removal for a given time, it was chosen as the preferred fraction for further experimentation.

3.4 Spent Potlining Leachate (SPL)

To determine the effects of the aqueous SPL leachate matrix on the removal of fluoride from SPL contaminated water using calcite, a solution of SPL leachate spiked with KF to ~2000 mg/L with pH ~10.4 was utilized in a series of stirred, free-drift, batch reactor tests. In these experiments the SPL as described above, was reacted with 150 μm calcite fraction with CO_2 partial pressures of pCO_2 $\sim 10^{-1.16}$ atm (7%), $\sim 10^{-1.0}$ atm (10%) and $\sim 10^{-0.82}$ atm (15%).

Figure 4 compares the pCO_2 (15% only) results for fluoride removal (and pH) for the SPL and
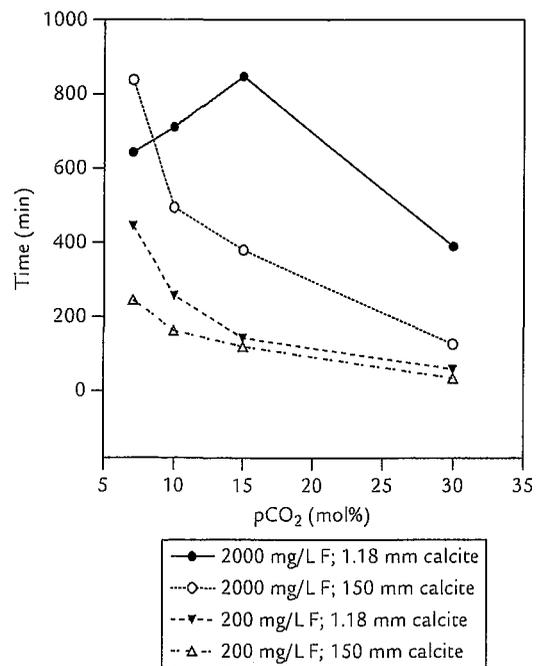
Figure 3 Time to reach 95% fluoride removal.

corresponding pure F solution experiments. Figure 4 shows that in the presence of SPL, an initial inhibition of fluoride removal and a subsequent slow increase in % fluoride removal is observed producing a distinctive S-Curve. It is interesting to note that at $t = 200$ minutes there is a sudden corresponding increase in the pH (7.6 to 9.3) in the SPL system indicating a change in the reaction mechanism. This phenomenon was also observed in other SPL experiments (not shown).

The observed initial inhibition of fluoride removal and the subsequent slow increase in removal is explained by Turner et al. (2005). The authors demonstrated that fluoride removal by calcite consists of an instantaneous adsorption reaction followed by CaF_2 precipitation with nucleation and growth of fluorite
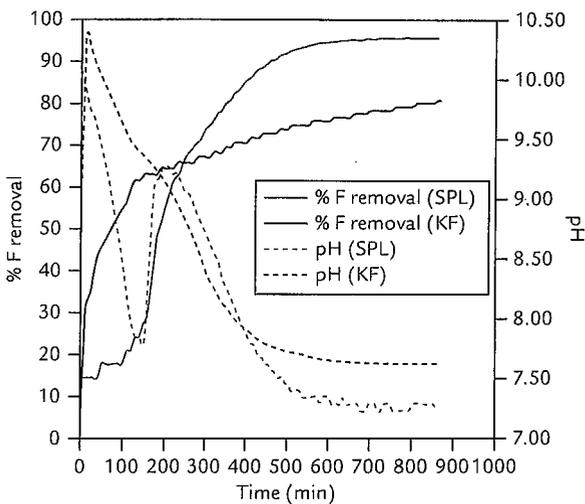
Figure 4 pH and F removal (%) from SPL and pure F (as KF) at pCO_2 $10^{-0.82}$ atm (15%) using 150 μm calcite with $[F]_i$ ~2000 mg/L.
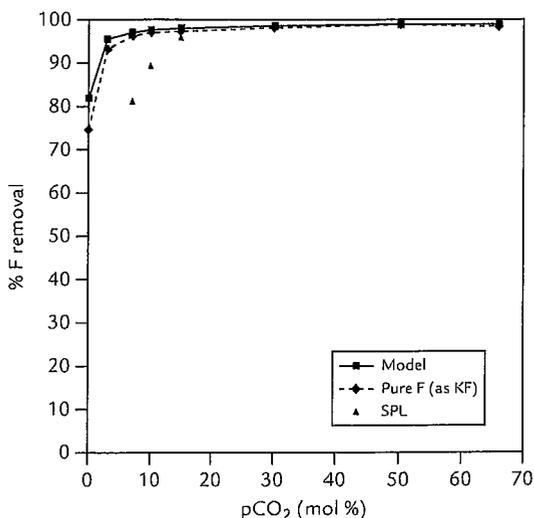
Figure 5 % F removal as a function of pCO_2 (mol%) for SPL & pure F (as KF) solutions in contact with 150 μm calcite. Predicted (Phreeq) % F removal is also shown.

crystals. They hypothesized that a component of the SPL matrix, carbon black, coats the adsorption sites at the calcite surface which inhibits fluoride removal until the system shifts to precipitation mode. However, it is possible that other anions in the SPL may be inhibiting the initial fluoride removal and additional experimentation is required.

Figure 4 shows that to reach the desired % F removal of ~95%, 650 minutes of contact time at pCO_2 ~$10^{-0.82}$ atm (15%) was required. However at ~$10^{-1.0}$ atm (10%) the curve had not reached equilibrium and the desired ~95% removal would require >1700 minutes as predicted by fitting a 5th order hyperbolic best-fit curve through the data and extrapolating to 95% F removal. At pCO_2 ~$10^{-1.16}$ atm (7%) that the required % fluoride removal was not obtained and therefore the time required to reach 95% removal would be cost prohibitive due to excessive CO_2 requirements.

3.5 PHREEQ Modeling

PHREEQ is an equilibrium geochemical model and as such it predicts the final geochemical speciation observed in a system. For the pure KF solution experiments it was found that all but the atmospheric pCO_2 ~$10^{-3.5}$ atm (0.03%) CO_2 results compared favourably with the model predictions of pH and % F removal. For the 1.18 mm (small surface area) calcite fraction, the atmospheric CO_2 experiments did not reach equilibrium even after 92 hours, only achieving 73.2% F removal (pH ~10.5) compared to the model prediction of 81.8% removal (pH ~9.8). Interestingly the higher surface area 150 μm calcite fraction similarly achieved 74.3% F removal, however, the pH far exceeded the model and 1.18 mm calcite fraction reaching pH~11.1 indicating the presence of OH^- exchange at the calcite surface as also found by Turner et al. (2005).

Experiments with the SPL leachate, however, indicate that the model cannot predict the equilibrium chemistry of the SPL/calcite/CO_2 system below 15% CO_2 (Fig. 5). As pCO_2 increases, the equilibrium % F removal and pH approaches that of the model, however it was observed that the time taken to reach equilibrium for the SPL experiments exceeds the time required for the corresponding pure F solution experiments. For example at 7% CO_2 the time required to reach 95% F removal was 640 minutes, in comparison the SPL system only achieved 39.7% F removal at 640 minutes. Similarly for 15% CO_2 the time required to reach 95% F removal was 400 minutes using the pure F solution whereas 650 minutes was required for the SPL solution.

4 CONCLUSIONS

As pure (100%) CO_2 is expensive, it is of benefit both financially and environmentally to optimize the

concentration (partial pressure) of CO_2 to give the most F removal. Our experiments show that the 150 μm calcite fraction in a $pCO_2 \sim 10^{-1.0}$ atm (10%) gives optimal conditions for defluoridation and at the same time decreasing the cost of CO_2 by a factor of 10.

Results show that calcite surface area is a dominant factor in the path taken for the system to reach equilibrium and that there is a significant disparity between the model and the SPL system results, a geochemical model based on kinetic reactions must be adapted for PHREEQ to be able to predict the reactions within the SPL/calcite/CO_2 system.

In most experiments 96% F removal can be routinely achieved, however, at 2000 mg/L F this leaves a residual of 80 mg/L. For discharge to the environment, a maximum of 20 mg/L F is required before the liquid waste is no longer deemed a hazardous liquid waste by the Department of Environment and Conservation consequently pre or post-dilution may also be required to achieve the final desired F level.

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