

**THE EVALUATION OF METAL ION COMPETITION ON
THE FLUORIDE REMOVAL FROM SOLUTIONS USING
NATURAL MOLECULAR SIEVE AND CALCITE**

by

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DECLARATION

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

I hereby certify that the work embodied in this thesis contains published paper of which I am a joint author.

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TABLE OF CONTENTS

LIST OF FIGURES.....	VII
LIST OF TABLES.....	XIV
ABSTRACT	XVII
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 LITERATURE REVIEW	6
2.1 ALUMINUM SMELTING	6
2.2 SPENT POT LINING (SPL) WASTE	7
2.2.1 Chemical composition of SPL	7
2.2.2 Disposal and treatment of SPL.....	8
2.2.3 SPL contamination near Kurri Kurri.....	9
2.2.4 In situ remediation – permeable reactive barriers (PRBs)	14
2.3 FLUORIDE.....	16
2.3.1 Drinking water standards	17
2.3.2 Fluoride contamination.....	17
2.3.3 Methods of fluoride removal	18
2.4 THEORY OF REMOVAL MECHANISMS	20
2.5 SORBENT	23
2.5.1 Point of zero charge.....	24
2.5.2 Zeolite	26
2.5.2.1 Zeolite - point of zero charge.....	26
2.5.2.2 Cation (metal ions) removal.....	27
2.5.2.3 Anion (fluoride) removal.....	28
2.5.2.4 Organics removal	30
2.5.2.5 Clinoptilolite.....	31
2.5.3 Calcite	34
2.5.3.1 Metal ions removal	34

2.5.3.2 Fluoride removal	35
2.6 KINETICS	36
2.6.1 Rate law of chemical reaction.....	38
2.6.2 Kinetic models.....	41
2.6.2.1 First order kinetics	41
2.6.2.2 Second order kinetics.....	42
2.6.2.3 Pseudo-second order kinetics (PSO)	43
2.6.2.4 Intra-particle diffusion (IPD)	44
2.6.2.5 Power model.....	44
2.6.2.6 Elovich model.....	44
2.6.2.7 Hill models	45
2.6.2.8 Applications	47
2.7 CONTAMINANT TRANSPORT	48
2.7.1 Advection	49
2.7.2 Diffusion.....	50
2.7.3 Dispersion	51
2.7.4 Retardation.....	53
2.7.5 Transport modelling.....	55
2.7.5.1 ADE model	56
2.7.5.2 Other models	57
2.8 LABORATORY STUDIES.....	58
2.9 GEOCHEMICAL MODEL - PHREEQC.....	59
2.10 OBJECTIVES	59
CHAPTER 3 MATERIALS AND METHODS	61
3.1 MATERIALS.....	61
3.2 SYNTHETIC SOLUTIONS.....	62
3.3 EXPERIMENTAL METHODS.....	66
3.3.1 Zeolite surface charge.....	66

3.3.2 Batch reactor kinetics tests.....	67
3.3.3 Column tests	69
3.3.4 Chemical and pH analysis	71
3.4 MODELLING	72
3.4.1 Kinetic modelling	72
3.4.1.1 Model fitting evaluation	72
3.4.1.2 Error analysis.....	74
3.4.1.3 Confidence contour analysis	75
3.4.2 Transport modelling.....	76
3.4.3 Geochemical modelling.....	77
CHAPTER 4 BATCH REACTOR KINETICS TEST — ZEOLITE	78
4.1 ZEOLITE PORE SIZE DISTRIBUTION AND SURFACE AREA.....	78
4.2 SURFACE CHARGE	78
4.3 THE EFFECT OF Mn^{2+} , Cd^{2+} , Ba^{2+} METAL IONS ON DEFLUORIDATION	79
4.3.1 Mn^{2+}	79
4.3.2 Cd^{2+}	84
4.3.3 Ba^{2+}	86
4.3.4 Removal mechanism.....	89
4.4 KINETIC MODELLING	91
4.5 THE EFFECT OF STIRRING RATE	101
4.6 CONCLUSION	104
CHAPTER 5 BATCH REACTOR KINETICS TEST — CALCITE	106
5.1 SPECIATION MODELLING.....	106
5.2 CALCITE SURFACE AREA	108
5.3 KINETICS	109
5.4 CONFIDENCE CONTOUR ANALYSIS.....	115
5.5 EFFECT OF MINERAL IONS ON FLUORIDE REMOVAL KINETICS.....	116

5.6 PHREEQC MODELLING	122
5.7 CONCLUSION	123
CHAPTER 6 COLUMN TEST.....	125
6.1 ZEOLITE COLUMN TESTS	127
6.1.1 <i>Experimental observation and CXTFIT</i>	127
6.1.2 <i>PHREEQC Modelling: zeolite</i>	134
6.2 CALCITE COLUMN TESTS	141
6.2.1 <i>Experimental observation and CXTFIT</i>	141
6.2.2 <i>PHREEQ Modelling: Calcite</i>	151
6.3 CONCLUSION	161
CHAPTER 7 CONCLUSIONS AND FUTURE WORK	163
7.1 CONCLUSIONS.....	163
7.2 RECOMMENDATIONS FOR FUTURE WORK.....	165
REFERENCES	167
APPENDIX A. JOURNAL PAPER (PUBLISHED).....	181
APPENDIX B. MANUSCRIPT (UNDER REVIEW)	193
APPENDIX C. PHREEQC INPUT FILE FOR SPECIATION DISTRIBUTION.....	226
APPENDIX D. PHREEQC INPUT FILE FOR KINETIC MODELLING (BATCH TESTS)	229
APPENDIX E. RESULTS OF SAMPLE ANALYSIS BY ICP-MS	231
APPENDIX F. CXTFIT INPUT FILE.....	235
APPENDIX G. XRD ANALYSIS OF ZEOLITES	243

List of Figures

Figure 2. 1 Hall-Hérault aluminium electrolysis cell.....	7
Figure 2.2 SPL waste pile at Aluminium smelter at different time period: (A) 27 May 1975; (B) 3May 1978.....	12
Figure 2.3 The contaminant plume with groundwater flow vectors (July 2010) on Google Earth site map, the colour gets deeper in the place that has a higher contamination: (A) fluoride (mg.L^{-1}) contaminant map; (B) pH contaminant map	14
Figure 2.4 Schematic of a permeable reactive barrier (PRB) (GW flow, groundwater flow direction) (Powell et al., 1998)	16
Figure 2.5 (A) effects of dental fluorosis; (B) effects of skeletal fluorosis	17
Figure 2.6 Probability of fluoride contamination in the groundwater around the world (Amini et al., 2008).....	20
Figure 2.7 A schematic example of the zeolite exchange process between Ca^{2+} and the counter-balanced ions (Na^{+}) on the surface of zeolite (Lower, 2013)	21
Figure 2.8 Various mechanisms of sorption of an ion at the mineral/water interface: (1) adsorption of an ion via formation of an outer-sphere complex (a); (2) loss of hydration water and formation of an inner-sphere complex (b); (3) lattice diffusion and isomorphic substitution within the mineral lattice (c); (4) and (5) rapid lateral diffusion and formation either of a surface polymer (d), or adsorption on a ledge (which maximizes the number of bonds to the atom) (e). Upon the particle growth, surface polymers end up embedded in the lattice structure (f);	

finally, the adsorbed ion can diffuse back in solution, either as a result of dynamic equilibrium or as a product of surface redox reactions (g) (Sparks, 2003).....	23
Figure 2.9 Modified electrical double layer model for calcite surface. ϑ is the unsatisfied partial charge on the ions at the terminated surface of bulk solids; ζ stands for zeta potential; ψ_δ is the potential of the Stern layer (Stipp, 1999a).....	24
Figure 2.10 An example of PZC for a hypothetical mineral (Railsback, 2006) ...	25
Figure 2.11 The fundamental building block of zeolite (Margeta et al., 2013)	27
Figure 2.12 The exchange process between F^- and OH^- from zeolite surface (Liu et al., 2011).....	29
Figure 2.13 The distribution of zeolite (MerchantResearch&Consulting, 2014) .	33
Figure 2.14 Transport process in a solid – liquid system: (1) transport in the solution phase; (2) move across a liquid film at the solid – liquid interface; (3) transport in a liquid – filled macropore; (4) surface diffusion; (5) micropore diffusion; (6) diffusion in the bulk of the solid (Aharoni and Sparks, 1991).....	38
Figure 2.15 Simple rate laws for A converts to B (Appelo and Postma, 2005)....	40
Figure 2.16 Transport processes of contaminants versus time along a flow path (Merkel and Planer-Friedrich, 2008).....	49
Figure 2.17 Porosity and effective porosity (Hamdani, 2014).....	50
Figure 2.18 Diffusion process (KC, 2014).....	51
Figure 2.19 Longitudinal and transverse dispersion (Appelo and Postma, 2005)	52
Figure 2.20 Retardation caused by sorption. Case A: no adsorption occurs with retardation equals to 1; Case B: sorption occurs with half of total mass are lost, retardation is 2 (Appelo and Postma, 2005).....	54

Figure 3.1 (A) schematic diagram for kinetics test setup; (B) the experimental setup in the lab, the atmosbag is used for gas injection reactions (not in this study)	69
Figure 3.2 (A) schematic diagram for column test setup; (B) the experimental setup in the lab	71
Figure 4.1 Point of zero charge (pH_{pzc}) of natural zeolite ($<150 \mu\text{m}$)	79
Figure 4.2 The distribution of manganese speciation in the KF (200 mg.L^{-1}) and MnCl_2 solution: (a) initial $[\text{Mn}^{2+}]$ is 10 mg.L^{-1} ; (b) initial $[\text{Mn}^{2+}]$ is 100 mg.L^{-1} .	81
Figure 4.3 The effect of redox reactions on the concentrations of free Mn^{2+} : (a) and (b) initial $[\text{Mn}^{2+}]$ is 10 mg.L^{-1} ; (c) and (d) initial $[\text{Mn}^{2+}]$ is 100 mg.L^{-1}	81
Figure 4.4 Fluoride removal kinetics with model 95% CI's using zeolite ($<150 \mu\text{m}$) in the presence of manganese at 20°C and stirring rate of 200 rpm. Initial $[\text{F}^-] \sim 200 \text{ mg.L}^{-1}$, and initial concentrations of Mn^{2+} are 0 (blank), 10, 100 mg.L^{-1} respectively. Data sampled every 10 seconds, for clarity every 84 min points have been plotted. For $\text{Mn} \sim 100 \text{ mg.L}^{-1}$ data sampled every 10 seconds and plotted every 42 minutes (for $0 < t < 500 \text{ min}$) to show early part of curve	84
Figure 4.5 The distribution of cadmium speciation in the KF (200 mg.L^{-1}) and CdCl_2 solution: (a) initial $[\text{Cd}^{2+}]$ is 10 mg.L^{-1} ; (b) initial $[\text{Cd}^{2+}]$ is 100 mg.L^{-1}	85
Figure 4.6 The effect of redox reactions on the concentrations of free Cd^{2+} : (a) and (b) initial $[\text{Cd}^{2+}]$ is 10 mg.L^{-1} ; (c) and (d) initial $[\text{Cd}^{2+}]$ is 100 mg.L^{-1}	85
Figure 4.7 Impact of cadmium (Cd^{2+}) on fluoride removal with 95% CI's ($<150 \mu\text{m}$) at 20°C and stirring rate of 200 rpm. Initial $[\text{F}^-] \sim 200 \text{ mg.L}^{-1}$, and initial concentrations of metal ions are 0 (blank), 10, 100 mg.L^{-1} respectively. Data sampled every 10 seconds, for clarity every 84 min points have been plotted.....	86

Figure 4.8 The distribution of barium speciation in the KF (200 mg.L ⁻¹) and BaCl ₂ solution: (a) initial [Ba ²⁺] is 10 mg.L ⁻¹ ; (b) initial [Ba ²⁺] is 100 mg.L ⁻¹	87
Figure 4.9 The effect of redox reactions on the concentrations of free Ba ²⁺ : (a) and (b) initial [Ba ²⁺] is 10 mg.L ⁻¹ ; (c) and (d) initial [Ba ²⁺] is 100 mg.L ⁻¹	87
Figure 4.10 Impact of barium (Ba ²⁺) on fluoride removal by zeolite (<150 µm) at 200 rpm. Initial [F ⁻] ~200 mg.L ⁻¹ , and initial concentrations of metal ions are 0 (blank), 10, 100 mg.L ⁻¹ respectively. Data sampled every 10 seconds, for clarity every 84 min points have been plotted.....	88
Figure 4.11 Pseudo-second order model (PSO), Hill, and intra-particle diffusion (IPD) model fits (<150 µm zeolite, 20 ± 0.2 °C, 200 rpm): (a) blank; (b) 10 mg.L ⁻¹ Ba ²⁺ ; (c) 10 mg.L ⁻¹ Mn ²⁺ ; (d) 10 mg.L ⁻¹ Cd ²⁺ ; (e) 100 mg.L ⁻¹ Ba ²⁺ ; (f) 100 mg.L ⁻¹ Mn ²⁺ ; (g) 100 mg.L ⁻¹ Cd ²⁺ . The observed Data sampled every 10 seconds, for clarity every 84 min points have been plotted	92
Figure 4.12 Pseudo-second order model (PSO), Hill, and intra-particle diffusion (IPD) model fits for the 1 st removal steps of 100 mg.L ⁻¹ Ba ²⁺ samples (<150 µm zeolite, 200 rpm): (a) 20 ± 0.2 °C; (b) 26 ± 0.2 °C. The observed Data sampled every 10 seconds, for clarity every 84 and 31.5 min points have been plotted for (a) and (b) respectively	99
Figure 4.13 Fits of the experiments (<150 µm zeolite, 100 mg.L ⁻¹ Ba ²⁺ , 200 rpm) to biphasic dose response (BiDoseResp) model: (a) 20 ± 0.2 °C; (b) 26 ± 0.2 °C. The observed Data sampled every 10 seconds, for clarity any every 84 min points have been plotted.....	100

Figure 4.14 The first ~300 minutes fluoride removal in the 10 mg.L ⁻¹ Cd ²⁺ sample (Figure 4.7). Data sampled every 10 seconds, for clarity every 8.3 min points have been plotted	101
Figure 4.15 Impact of stirring rate on fluoride removal by zeolite (<150 µm) at 20 °C. Initial [F ⁻] ~200 mg.L ⁻¹ , and stirring rates are 100, 200, 300 rpm respectively. Data sampled every 10 seconds, for clarity every 84 min points have been plotted	102
Figure 5.1 The effect of redox reactions on the concentrations of free metals: (a) and (b) Ba ²⁺ ; (c) and (d) Cd ²⁺ ; (e) and (f) Co ²⁺ ; (g) and (h) Mn ²⁺ . Initial [F ⁻] = ~200 mg.L ⁻¹ ; initial [metal ²⁺] = ~0.1 mmol.L ⁻¹	107
Figure 5.2 The distribution of metal speciation: (a) Ba ²⁺ ; (b) Cd ²⁺ ; (c) Co ²⁺ ; (d) Mn ²⁺ . Initial [F ⁻] = ~200 mg.L ⁻¹ ; initial [metal ²⁺] = ~0.1 mmol.L ⁻¹	108
Figure 5.3 The effect of metal ions (Co ²⁺ , Mn ²⁺ , Cd ²⁺ and Ba ²⁺) and type of calcite (stonedust and Iceland spar) on (a) fluoride removal and (b) pH. Initial [F ⁻] = ~200 mg.L ⁻¹ ; initial [metal] = 0 or 0.101 ± 0.017 mmol.L ⁻¹ ; stirring rate of 200 rpm; initial pH=~6.6; temperature 20 ± 0.2°C. Data sampled every 10 seconds, for clarity any every 84 min points have been plotted. Note that all the tests conducted were using stonedust unless otherwise specified.....	110
Figure 5.4 Fits of experimental data to the pseudo-second order (PSO), Hill 4, Hill 5 and intra-particle diffusion (IPD) model: (a) blank (stonedust); (b) Iceland spar; (c) Ba ²⁺ ; (d) Cd ²⁺ ; (e) Co ²⁺ ; (f) Mn ²⁺ . The observed data sampled vary 10 seconds, for clarity any every 84 min points have been plotted. Initial [F ⁻] = 200 mg.L ⁻¹ ; [metal ²⁺] = 0.101 ± 0.017 mmol.L ⁻¹ ; temperature = 20 ± 0.2 °C; stirring rate = 200 rpm	111

Figure 5.5 Iceland Spar two-dimensional confidence contour plot showing the dependence of the normalised reduced sum of squares (RSS_{norm}) on parameters n and E . Cross (+) in centre represents best fit	116
Figure 5.6 Far from equilibrium effects of metal ions (Co^{2+} , Mn^{2+} , Cd^{2+} and Ba^{2+}) on fluoride removal by calcite (stonedust and Iceland spar): (a) system pH evolution during the first 20 minutes of reaction; (b) F^- removal during first 60 mins. Initial $[\text{F}^-] = \sim 200 \text{ mg.L}^{-1}$; initial $[\text{metal}] = 0$ or $0.101 \pm 0.017 \text{ mmol.L}^{-1}$; stirring rate of 200 rpm; initial $\text{pH} \sim 6.6$; temperature $20 \pm 0.2^\circ\text{C}$	122
Figure 5.7 PHREEQC modelling based on the parameters of pseudo-second order kinetics model (PSO): (a) blank (stonedust); (b) Iceland spar; (c) Ba^{2+} ; (d) Cd^{2+} ; (e) Co^{2+} ; (f) Mn^{2+} . For clarity any every 84 min points have been plotted for the PSO data	123
Figure 6.1 General framework of PHREEQC input file	126
Figure 6.2 Zeolite column test result of blank sample. Initial solution: $[\text{F}^-] = \sim 200 \text{ mg.L}^{-1}$; $[\text{Br}^-] = \sim 100 \text{ mg.L}^{-1}$. (a) effluent pH values; (b) breakthrough curve of fluoride (F/F_0 versus pore volume); (c) breakthrough curve of bromide (Br/Br_0 versus pore volume)	128
Figure 6.3 Zeolite column test result of Ba^{2+} sample. Initial solution: $[\text{F}^-] = \sim 200 \text{ mg.L}^{-1}$; $[\text{Br}^-] = \sim 100 \text{ mg.L}^{-1}$; $[\text{Ba}^{2+}] = \sim 10 \text{ mg.L}^{-1}$. (a) effluent pH values; (b) breakthrough curve of fluoride (F/F_0 versus pore volume); (c) breakthrough curve of bromide (Br/Br_0 versus pore volume)	129
Figure 6.4 Zeolite column test result of Cd^{2+} sample. Initial solution: $[\text{F}^-] = \sim 200 \text{ mg.L}^{-1}$; $[\text{Br}^-] = \sim 100 \text{ mg.L}^{-1}$; $[\text{Cd}^{2+}] = \sim 10 \text{ mg.L}^{-1}$. (a) effluent pH values; (b)	

breakthrough curve of fluoride (F/F_0 versus pore volume); (c) breakthrough curve of bromide (Br/Br_0 versus pore volume).....	130
Figure 6.5 Estimation of $t_{0.5-tracer}$ for zeolite column blank sample (no metals) by fitting observed Br^- BTC to the Hill 5 model ($R^2 = 0.99$).....	134
Figure 6.6 Calcite column test result of blank sample. Initial solution: $[F^-] = \sim 200$ $mg.L^{-1}$; $[Br^-] = \sim 100$ $mg.L^{-1}$. (a) effluent pH values; (b) experimental breakthrough curve of fluoride (F/F_0 versus pore volume); (c) experimental and CXTFIT fitted breakthrough curve of bromide (Br/Br_0 versus pore volume)....	143
Figure 6.7 Calcite column test result of Ba^{2+} sample. Initial solution: $[F^-] = \sim 200$ $mg.L^{-1}$; $[Br^-] = \sim 100$ $mg.L^{-1}$; $[Ba^{2+}] = \sim 10$ $mg.L^{-1}$. (a) effluent pH values; (b) breakthrough curve of fluoride (F/F_0 versus pore volume); (c) breakthrough curve of bromide (Br/Br_0 versus pore volume).....	144
Figure 6.8 Calcite column test result of Cd^{2+} sample. Initial solution: $[F^-] = \sim 200$ $mg.L^{-1}$; $[Br^-] = \sim 100$ $mg.L^{-1}$; $[Cd^{2+}] = \sim 10$ $mg.L^{-1}$. (a) effluent pH values; (b) breakthrough curve of fluoride (F/F_0 versus pore volume); (c) breakthrough curve of bromide (Br/Br_0 versus pore volume).....	145
Figure 6.9 SEM image (EDS spectra inset) of calcite exposed to tap water only	147
Figure 6.10 SEM image of calcite exposed to $5\text{ mg.L}^{-1} Cd^{2+}$. Arrow indicates $1000\times$ magnification	148
Figure 6.11 SEM image (back-scattered image, EDS spectra inset) of calcite exposed to $5\text{ mg.L}^{-1} Cd^{2+}$	148
Figure 6.12 The impact of $\log_k$ solubility on F/F_0 : (a) blank; (b) Ba^{2+} ; (c) Cd^{2+}	160

List of Tables

Table 2.1 Typical SPL compositions (Pong et al., 2000).....	8
Table 2.2 List of major metals and organics contaminants in the SPL leachate (July 2010)	12
Table 2.3 Fluoride limitation in drinking water and aquatic life (ANZECC, 2000; Canada, 1987; CEC, 1978; WHO, 2011).....	17
Table 2.4 Methodology for the measurement of pH_{pzc}	25
Table 2.5 Point of zero charge (pH_{pzc}) of zeolite via various methods.....	26
Table 2.6 Removal efficiency of metal ions from wastewater using natural zeolites (Margeta et al., 2013). Note that the removal efficiency depends on many factors such as initial concentration of metal ions in wastewater, pH value etc.....	32
Table 2.7 Differential forms and integrated forms of rate laws (Vallance, 2008).40	
Table 3.1 Experiment list	64
Table 3.2 Chemical composition of the zeolite.....	65
Table 3.3 Analysis result of groundwater from the Hydro Aluminium site. Metals are total concentration (including the metal content both dissolved in the solution and present in the particulates in the solution).....	65
Table 4.1 Hill model Monte Carlo 95% confidence intervals for zeolite (<150 μm), 20 ± 0.2 $^{\circ}\text{C}$, 200 rpm	83
Table 4.2 Intra-particle diffusion rate constants (results obtained under 20 ± 0.2 $^{\circ}\text{C}$, using <150 μm zeolite)	94
Table 4.3 Pseudo-second-order rate constants (results obtained under 20 ± 0.2 $^{\circ}\text{C}$, using <150 μm zeolite)	95

Table 4.4 Hill 4 rate constants (results obtained under 20 ± 0.2 °C, using <150 μm zeolite).....	96
Table 4.5 Hill 5 rate constants (results obtained under 20 ± 0.2 °C, using <150 μm zeolite). Note that the minimum removal was constrained $D = 0$ (mg.g^{-1}).....	97
Table 4.6 Intra-particle diffusion rate constants for the blanks (no metals, results obtained under 20 ± 0.2 °C, using <150 μm zeolite)	103
Table 4.7 Pseudo-second-order rate constants for the blanks (no metals, results obtained under 20 ± 0.2 °C, using <150 μm zeolite)	103
Table 4.8 Hill 4 rate constants for the blanks (no metals, results obtained under 20 ± 0.2 °C, using <150 μm zeolite)	103
Table 4.9 Hill 5 rate constants for the blanks (no metals, results obtained under 20 ± 0.2 °C, using <150 μm zeolite). Note that the minimum removal was constrained $D = 0$ (mg.g^{-1})	104
Table 5.1 Model selection criterion results (obtained under 20 ± 0.2 °C). The number of data points is 32017. p is the number of parameters	112
Table 5.2 Information criterion weights ($w_i(\text{AIC}) / w_i(\text{BIC})$) and evidence ratio (ER) results.....	112
Table 5.3 Parameters of PSO, Hill 4 and IPD models (all the results obtained under 20 ± 0.2 °C)	113
Table 5.4 Parameters of Hill 5 model (all the results obtained under 20 ± 0.2 °C)	114
Table 5.5 Upper (U) and lower (L) Monte Carlo 95% confidence intervals (CI) for the “best” model as identified in Table 5.1	114
Table 5.6 Sample pH (initial and equilibrium) and observed metal removal	117

Table 5.7 Metal ionic radius	117
Table 6.1 Laboratory column test conditions (conducted under the temperature of 25 ± 0.2 °C; column length = 29.4 cm; column cross section = 20.4 cm^2).....	127
Table 6.2 F/F_0 (the ratio of effluent F^- concentration and influent F^- concentration) at different pore volumes for three zeolite column tests. One pore volume time equals to $t_{0.5\text{-tracer}}$	133
Table 6.3 Fluoride transport parameters calculated from zeolite column tests...	134
Table 6.4 Transport parameters of tracer (Br^-) modelled by CXTFIT for the zeolite column tests.....	134
Table 6.5 Reactive and transport parameters from PHREEQC modelling for zeolite columns.....	141
Table 6.6 F/F_0 (the ratio of effluent F^- concentration and influent F^- concentration) at different pore volumes for three calcite column tests. One pore volume time equals to $t_{0.5\text{-tracer}}$	149
Table 6.7 Fluoride transport parameters calculated from calcite column tests...	150
Table 6.8 Transport parameters of tracer (Br^-) modelled by CXTFIT for the calcite column tests.....	150
Table 6.9 Reduced sum of squares (RSS) for calcite columns by changing log k solubility. Bold and italic represent best-fit	158
Table 6.10 Reactive and transport parameters from PHREEQC modelling for calcite columns.....	159

Abstract

Industrial wastewaters often consist of a complex chemical cocktail with treatment of target contaminants complicated by adverse chemical reactions. The impact of metal ions on the removal of fluoride by natural zeolite and calcite was investigated in the present study via laboratory batch reactor kinetics and column tests.

In order to better understand the kinetics, the intra-particle diffusion (IPD), pseudo-second order (PSO) and Hill (Hill 4 and Hill 5) models were applied on the basis of kinetics test results. As these models have different numbers of parameters, model fitting was compared using the Akaike Information Criterion (AIC) and the Schwarz Bayesian Information Criterion (BIC) methods capable of comparing models having different numbers of parameters. The Hill models (Hill 4 and Hill 5) were found to be superior in describing the fluoride removal processes which reflects the process of chemisorption during fluoride removal. Results indicate that the presence of Mn (100 mg.L^{-1}) and Cd (100 mg.L^{-1}) respectively increase the rate of fluoride sorption by zeolite by a factor of ~ 28.3 and ~ 10.9 , with the maximum sorption capacity increased by a factor ~ 2.2 and ~ 1.7 . The presence of Ba (100 mg.L^{-1}) in the zeolite sample initially inhibited fluoride removal and very poor fits were obtained for all models. Fitting was best described with a biphasic sigmoidal model with the degree of inhibition decreasing with increasing temperature suggesting at least two processes are involved with fluoride sorption onto natural zeolite in the presence of Ba.

With calcite, results reveal that the presence of Co^{2+} adversely affects the process of defluoridation resulting in a lowest amount of fluoride removal in the order $\text{Co}^{2+} < \text{stonedust}$ (a 99% pure natural calcite) $\approx \text{Cd}^{2+} < \text{Mn}^{2+} < \text{Ba}^{2+}$. Calculation of reaction half-lives ($t_{0.5}$), a measure of the length of time required to remove 50% of the initial fluoride mass, showed that $t_{0.5}$ increased in the order $\text{Ba}^{2+} \approx \text{stonedust} < \text{Cd}^{2+} < \text{Co}^{2+} < \text{Mn}^{2+}$, with Mn^{2+} and Co^{2+} requiring ~95 and ~140 minutes more to achieve half their respective predicted fluoride removal.

Column tests studying the effect of metal ions on fluoride transport in the presence of calcite or zeolite showed that the defluoridation efficiencies of zeolite and calcite are much lower than those in the batch tests, being only ~49% and ~20% respectively. This is attributed to the fact that the contact between sorbent and sorbate are temporal and spatial in column tests with the residence time much less than experienced during kinetics tests. The addition of Ba^{2+} and Cd^{2+} in the zeolite column sample respectively decreases the fluoride removal by ~13% and ~10% after four pore volumes had passed through the column while in the calcite sample, Cd^{2+} has similar defluoridation amount with the blank (no metals) and the presence of Ba^{2+} lowered the amount by ~8% at 4.5 PV. CXTFIT a program to model 1D transport processes was used to fit the tracer (Br^-) data from each column test. This allows the column characteristics such as the effective porosity, Darcy velocity, and dispersity to be calculated and used to assess the retardation of fluoride. PHREEQC geochemical modelling was also applied to both the kinetics data and the column experimental results. Modelling of the column tests using calcite required the addition of a hypothetical phase with a different solubility than calcite. By varying log k , calcite solubility can be changed with an

increasing log k indicating an enhanced calcite dissolution. It is found that the best match achieved between the observed and modelled calcite column data when log k is 1.1, 0.75, 1.2 for the blank, Ba^{2+} and Cd^{2+} samples respectively. This implies that calcite dissolution is suppressed by the presence of Ba^{2+} , which is inconsistent with the findings in the batch reactor kinetics tests. As for the zeolite columns, the log k of LinearF⁻ which defines the phases and the associated hypothetical reactions with F⁻ is altered by trial and error until the best fit is obtained. The log k of LinearF⁻ used in the zeolite blank column is -100.05, while it changes to -100.22 in the presence of Ba^{2+} and Cd^{2+} . Results show good fits with the observed data. Geochemical modelling of the kinetics data however was more problematic with the initial instantaneous sorption part of the model curves closely matching the observed data, however the final part of the model curves over predicted fluoride removal. The initial development of the PHREEQ geochemical model presented here shows potential in being able to be used as a predictive tool for the design of fluoride remediation strategies such as permeable reactive barriers.