

Temperature Effects on Hydraulic and Buffering Performances of Soil-bentonite Mixture



YU Rongguang

July, 2024

ABSTRACT

Soil-bentonite mixture (SB) is one of the barrier materials for waste disposal and contamination managements, consisting of a small amount of sodium bentonite and on-site or off-site soil. SB possess characteristics of significantly low hydraulic conductivity and enhanced buffering capacity attributed to the added bentonite. Depending on the specific application, SB barriers is subjected to various thermodynamic conditions during operation, particularly under high-temperature conditions.

On the basis of lacking of comprehensive understanding of the barrier performances of SB under various temperature conditions. This research aims to clarify **the temperature effects on (1) adsorption behaviors of SB as a barrier material, (2) hydraulic performance of SB barrier under emulated in-situ conditions, and (3) buffering performance of SB barrier under emulated in-situ conditions by means of experimental methods against CaCl₂ solutions at various temperatures.**

To achieve the first objective of this research, batch tests were conducted under oscillating conditions at various constant temperatures (20°C to 50°C). A precise calculation method for the Ca²⁺ adsorbed amount (q_e) of in bentonite and SB batch systems considering the volume change of montmorillonite was proposed. Experimental results of adsorption/desorption kinetics, adsorption isotherms, and exchange (Ca-Na) isotherms were obtained. The ion exchange of SB showed characteristic of endothermal indicated by the increased amounts of Na⁺ desorption as the temperature increased. The direct adsorption without releasing Na⁺ was identified as the major process of Ca²⁺ adsorption and showed characteristic of exothermal indicated by the decreased q_e as the temperature increased. A concentration parameter named as internal Ca²⁺ molarity (c_{in}) was defined by dividing the q_e with the calculated volume of montmorillonite interlamellar space. Bulk Ca²⁺ molarity and c_{in} exhibited strong linear correlations, which could be utilized in calculating of standard enthalpy changes (ΔH^0) of direct adsorption process and $\Delta H^0(\text{dir}) = -6.49 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained.

To achieve the second objective of this research, falling-head hydraulic conductivity tests were conducted with modified flexible-wall permeameter, permeated with 0.1M (Set 1) and 1M (Set 2) CaCl₂, at constant temperatures of 20°C, 40°C, and 60°C, respectively. Experimental results of hydraulic conductivity (k) and intrinsic permeability (K) were obtained. The equilibrium k were found increased as the temperature increased, and the temperature dependencies of equilibrium k were found consistent with the estimation calculated with permeant densities and viscosities at corresponding temperatures. The K did not show significant temperature dependencies. Indicating that the changes of hydraulic performance of SB barrier in different constant temperature conditions were predominantly attributed to the changes of fluid viscosity and density. The temperature effects on the chemical compatibilities of prehydrated SB were insignificant, all obtained equilibrium k were lower than $10^{-9} \text{ m}\cdot\text{s}^{-1}$.

To achieve the third objective of this research, the chemical properties of the effluent samples collected in hydraulic conductivity tests introduced in last paragraph were analyzed. Experimental results of Ca²⁺ breakthrough curves, Na⁺ elution curves were obtained, and the

buffering performance of SB was characterized by Ca^{2+} sorbed amount (q_{sorb}) calculated from the Ca^{2+} breakthrough curves. The analytical expressions of Ca^{2+} breakthrough curves were obtained by fitting the experimental curve with the solution form of advection-dispersion equation and the corresponded retardation factor and dispersive coefficient were obtained. The temperature dependencies of the chemical properties of the effluents were found to differ at two different permeants. Specifically, the buffering performance of SB against Ca^{2+} decreased as the temperature increased when permeated with 0.1M CaCl_2 , while it slightly increased when permeated with 1M CaCl_2 . The concentration-dependent temperature dependencies of q_{sorb} indicated that most of the immobilized Ca^{2+} were highly possible to be sorbed onto the outer-surface space of montmorillonite, named as external sorption. The external sorption was inferred to have a nature of endotherm ($\Delta H^0(\text{ext}) > 0$).

The experimental results suggested that the increase of temperature have negative impacts to SB barrier in terms of hydraulic performance and the impacts were more significant when permeant Ca^{2+} concentration was higher. On contrast, the experimental results also suggested that the impacts of increasing temperature to SB barrier in terms of buffering performance depends on the permeant Ca^{2+} concentration, the impacts were significantly negative for 0.1M CaCl_2 while the impacts were insignificantly positive for 1M CaCl_2 .

ACKNOWLEDGMENTS

The research presented in this dissertation originated when the author was a PhD student at the Graduate School of Global Environmental Studies (GSGES), Kyoto University. The research could not have been completed successfully without the kind assistance and cooperation of many people.

Firstly, the author would like to express his sincere gratitude to his supervisor, Professor KATSUMI Takeshi, GSGES, Kyoto University, for his generosity in providing students with freedom to research, for his encouragement and insightful comments, and for his acceptance of me as one of his students.

The author would like to acknowledge his co-supervisor, Associate Professor TAKAI Atsushi, GSGES, Kyoto University, for his academically guidance in research theme, methodologies, discussions, and academic writings.

The author would like to acknowledge Assistant Professor KATO Tomohiro, GSGES, Kyoto University, who always show me his optimism and effort. The author, as a peer, holds the belief that Dr. KATO is a reputable researcher.

The author would also like to thank Professor HIGO Yosuke, Graduate School of Engineering, Kyoto University, for his examination and comments on this dissertation.

The author feels grateful to Dr. Lincoln W. Gathuka, Researcher, National Institute for Environmental Studies, for teaching the author on the operation of experimental equipment. This research could not be operated without his help.

The author feels fortunate to be a member of KATSUMI's research laboratory, and would like to extent his appreciations to the seniors PhD and graduated master students. Thanks to Dr. TANG Jiajie and Dr. ZHANG Yu, who kindly helped the author with daily life when he first arrived in Japan. Thanks to Dr. Aye Cho Cho Zaw, the author misses her candy. Acknowledgments are due to Mr. ISHIDA Michihiro and Mr. YOSHOMURA Hiro for their friendly accompanies.

Acknowledgement is also extended to the junior members, including Mr. TAYIMA Koichi, Mr. NAGAO Yuki, Mr. MIKI Yoshizane, Ms. OGATA Riho, Mr. SHIMIZU Ryosuke, Mr. TOMINAGA Iori, Mr. SHIMPO Tomoki, Ms. NISHIMURA Minami, and Mr. WEN Jiaming. Special thanks to the Mr. Town for his incredible dedication in disposing laboratory wastes.

The author extends congratulations to Mr. CHEN Ji on receiving his Ph.D. and wish him all the best in his future endeavors.

The author would also like to express his acknowledgement to his former supervisor, Professor ZHANG Huyuan, Graduate School of Civil Engineering and Mechanics, Lanzhou University, who is the enlightenment of the author's scientific research work when he was a master student and whom the author sincerely admires.

Finally, the author would like to acknowledge to his father, YU Genrui, and his mother LIN Xiaowei, for their great support and encouragement.

July, 2024

TABLE OF CONTENTS

ABSTRACT.....	i
ACKNOWLEDGMENTS	iii
TABLE OF CONTENTS	iv
LIST OF FIGURES	vii
LIST OF TABLES	ix
LIST OF EQUATIONS.....	x
CHAPTER 1 Introduction	1
1.1 General remarks	1
1.2 Soil barriers for waste disposal and contamination managements	2
1.3 Soil bentonite mixture (SB) as a barrier material	4
1.3.1 Swelling	5
1.3.2 Diffuse double layer (DDL).....	5
1.4 High-temperature conditions in soil barriers	8
1.4.1 Interior factors.....	8
1.4.2 Exterior factors.....	8
1.5 Objective and contents of the dissertation	9
References	10
CHAPTER 2 Temperature effects on adsorption behaviors of SB in aqueous system	13
2.1 Introduction.....	13
2.2 Literature review for Chapter 2	13
2.2.1 Adsorption behaviors of general soil in aqueous system.....	13
2.2.2 Adsorption behaviors of bentonite in aqueous system.....	14
2.2.3 Thermodynamics in adsorption processes	16
2.2.4 Thermodynamics in adsorption processes of bentonite	17
2.3 Experimental approaches to the temperature effects on adsorption behaviors of SB against Ca^{2+} in aqueous system	19
2.3.1 Materials.....	19
2.3.2 Discontinuous batch test at different temperatures	20
2.3.3 Assessments to the internal volume V_{in} by free swell test	25
2.4 Results.....	26
2.4.1 Adsorption/desorption kinetics of bentonite at different temperatures.....	26
2.4.2 Internal volume V_{in} of bentonite at different temperatures	27
2.4.3 Adsorption and exchange isotherms of B, S, and SB at different temperatures	29

2.4.4 Internal Ca^{2+} molarity (c_{in}) in bentonite and SB batch systems	36
2.5 Discussion	38
2.5.1 Interpretations to the systematic errors of adsorption/desorption amounts	38
2.5.2 Interpretations to the internal Ca^{2+} molarity (c_{in}) and the equilibrium state	39
2.5.3 Attempts in modeling of adsorption isotherms for bentonite and SB in a wide range of bulk concentration.....	43
2.6 Conclusions of Chapter 2.....	45
References	46

CHAPTER 3 Temperature effects on hydraulic performance of SB barrier..... 51

3.1 Introduction.....	51
3.2 Current studies concerning temperature effects on hydraulic performance of bentonite materials	52
3.3 Experimental approach to the temperature effects on hydraulic conductivity of SB against CaCl_2 solution.....	54
3.3.1 Materials.....	54
3.3.2 Falling-head hydraulic conductivity test with modified flexible-wall permeameter	55
3.4 Results.....	60
3.4.1 Profiles of hydraulic conductivity among with time and PVF.....	60
3.4.2 Temperature dependency of hydraulic conductivity and intrinsic permeability.....	63
3.5 Discussion.....	64
3.5.1 Temperature effects on chemical compatibility of prehydrated SB	64
3.5.2 Temporary changes of hydraulic conductivity at various temperatures	65
3.6 Conclusions of Chapter 3.....	66
References	67

CHAPTER 4 Temperature effects on buffering performance of SB barrier 71

4.1 Introduction.....	71
4.2 Evaluating buffering performance with hydraulic conductivity (column) test.....	71
4.2.1 Characterizing sorbed amount	71
4.2.2 Analytical solute transport	74
4.3 Results.....	76
4.3.1 Water chemistry of effluent sample	76
4.3.2 Cumulative amounts of effluent sample	78
4.3.3 Analytical solutions for Ca^{2+} breakthrough curves.....	82
4.4 Discussion.....	86
4.4.1 Concentration-dependent temperature dependencies of q_{sorb}	86
4.4.2 Differences and connections between adsorption and sorption in this dissertation...	90
4.5 Conclusions of Chapter 4.....	92
References	93

CHAPTER 5 Practical implications..... 97

5.1 Utilize the characteristics of endothermic reactions	99
--	----

5.2	Summarize the temperature effects on barrier performances	97
5.3	Accidental concerns and measures	99
	References	100
CHAPTER 6 Conclusions and future research needed		101
6.1	Conclusions.....	101
6.2	Further researches needed.....	104
APPENDIX A Chi-square test for variable correlations		105
APPENDIX B Attempts in calculating modified adsorption isotherm (q_e) from ordinary adsorption isotherm (Q_e)		107
APPENDIX C Vishnu, the god of Hinduism.....		111

LIST OF FIGURES

Figure 1.1 Global municipal solid waste (MSW) production and regional soil contaminations.	1
Figure 1.1 Common types of soil barriers.	3
Figure 1.2 Structure of dehydrated Na-montmorillonite lattice.	4
Figure 1.3 The swell of bentonite in SB (after Komine & Ogata, 2003).	5
Figure 1.4 Ionic distributions in interlamellar space of montmorillonite lattice according to the concept of DDL (after Mitchell, 1993).	6
Figure 1.5 High-temperature conditions in soil barriers caused by interior factors.	7
Figure 1.6 Historical and projected global warming (After Engel & Reid, 2019; IPCC, 2014).	8
Figure 1.7 Structure of this dissertation.	10
Figure 2.1 Adsorption behaviors of SB in aqueous system.	14
Figure 2.2 Adsorption of Ca^{2+} onto Wyoming bentonite (Sposito et al., 1981, 1983).	16
Figure 2.3 Adsorption been observed as exothermic (left) and endothermic (right) as the temperature increased (Cadaval Jr et al., 2016; Q. S. Liu et al., 2010).	17
Figure 2.4 SB mixing procedures.	19
Figure 2.5 Schematic of batch test.	20
Figure 2.6 Schematic for the bulk solution and internal solution in bentonite batch system.	22
Figure 2.7 Ca^{2+} adsorption (Q_t) kinetics of pure bentonite at two isothermal conditions.	26
Figure 2.8 Na^+ desorption ($-Q_t$) kinetics of pure bentonite at two isothermal conditions.	27
Figure 2.9 Results of V_{in}/m_s from free swell test.	28
Figure 2.10 Ca^{2+} adsorption (Q_e) of S at different temperatures.	29
Figure 2.11 Ca^{2+} adsorption isotherms of pure bentonite for bulk Ca^{2+} molarities (c_t) less than $50 \text{ mmol}\cdot\text{L}^{-1}$.	30
Figure 2.12 Ca^{2+} adsorption isotherms of SB for bulk Ca^{2+} molarities (c_t) less than $25 \text{ mmol}\cdot\text{L}^{-1}$.	30
Figure 2.13 Comparing Ca^{2+} adsorption isotherms q_e between pure bentonite and SB.	30
Figure 2.14 Ca^{2+} adsorption isotherms of pure bentonite at high concentration cases.	32
Figure 2.15 Na^+ desorption ($-Q_e$) of S at different temperatures.	33
Figure 2.16 Na^+ exchange isotherms of pure bentonite for bulk Ca^{2+} molarities (c_t) less than $50 \text{ mmol}\cdot\text{L}^{-1}$.	34
Figure 2.17 Na^+ exchange isotherms of SB for bulk Ca^{2+} molarities (c_t) less than $25 \text{ mmol}\cdot\text{L}^{-1}$.	34
Figure 2.18 Comparing Na^+ exchange isotherms ($-q_e$) between pure bentonite and SB.	34
Figure 2.19 Na^+ exchange ($-q_e$) isotherms at different temperatures	35
Figure 2.20 Relations between internal Ca^{2+} molarity (c_{in}) and bulk Ca^{2+} molarity (c_t).	37
Figure 2.21 Relations between c_{in} and c_t at different temperatures.	37
Figure 2.22 Difference between Q_e and q_e of Ca^{2+} adsorption related to bulk Ca^{2+} molarity.	38

Figure 2.23 Assessment to the thermodynamics parameters of Eq (2.27).....	40
Figure 2.24 Relation between Ca^{2+} adsorbed amount (q_e) and Na^+ desorbed amount ($-q_e$). .	42
Figure 2.25 Analytic description of adsorption isotherm of bentonite.	44
Figure 3.1 Temperature dependency of intrinsic permeabilities (K) in some studies. The values of K from Villar & Lloret (2004), Cho et al. (1999), and Towhata et al. (1993) were calculated based on their reported hydraulic conductivity or relative hydraulic conductivity, and the former are magnified by a hundred times to facilitate the comparison in the given range.....	53
Figure 3.2 Particle distributions of decomposed granite soil and mixed SB in this study.....	54
Figure 3.3 Schematic of modified flexible-wall permeameter.....	55
Figure 3.4 Monitored constant temperature conditions.	56
Figure 3.5 Hydraulic conductivity and volume ratio among with time and PVF of Set 0.....	61
Figure 3.6 Hydraulic conductivity, volume ratio, and EC among with time and PVF of Set 1.	61
Figure 3.7 Hydraulic conductivity, volume ratio, and EC among with time and PVF of Set 2.	62
Figure 3.8 Temperature dependency of hydraulic performance of SB.....	63
Figure 3.9 Relations between intrinsic permeability and permeant Ca^{2+} molarity.	64
Figure 3.10 Differences between initial k and equilibrium k	65
Figure 4.1 Schematic drawing of solute transport in column test.	73
Figure 4.2 Ionic compositions and pH of effluents among with time and PVF (Set 0, Set 1).76	
Figure 4.3 Ionic compositions and pH of effluents among with time and PVF (Set 2).	77
Figure 4.4 Cumulative amounts of Ca^{2+} and Na^+ in effluents of Set 0 and Set 1.	79
Figure 4.5 Cumulative amounts of Ca^{2+} and Na^+ in effluents of Set 2.	79
Figure 4.6 Profiles of Ca^{2+} sorbed amount (q_{sorb}) among with time and PVF (Set 1).	81
Figure 4.7 Profiles of Ca^{2+} sorbed amount (q_{sorb}) among with time and PVF (Set 2).	81
Figure 4.8 Ca^{2+} sorption isotherms derived from the results of column test, the fittings were operated on the plots where the bulk Ca^{2+} molarity above 10% and below 100% of permeant concentrations.	83
Figure 4.9 Ca^{2+} breakthrough curves fitted by analytical solution.....	84
Figure 4.10 Verifying the temperature dependency of D	85
Figure 4.11 Exchange fractions in profiles of q_{sorb} among with PVF.	87
Figure 4.12 Ca-Na exchange paths in column test.....	87
Figure 4.13 Pore water in SB specimen (after Wersin et al., 2004).	88
Figure 4.14 Relations between Ca^{2+} adsorbed amount and Na^+ desorbed amount in this dissertation.	91

LIST OF TABLES

Table 2-1 Thermodynamic parameters of cation exchanges in montmorillonite at 25°C and of H ₂ O sorption at 30°C.	18
Table 2-2 Physical properties of soil materials.	19
Table 2-3 Target results of batch test, required values and calculations.....	22
Table 2-4 Conditions for adsorption/desorption kinetics of bentonite.....	23
Table 2-5 Conditions for batch tests with 24 h oscillation for bentonite (B), decomposed granite soil (S), and soil-bentonite (SB).	24
Table 2-6 Conditions for free swell test.	25
Table 2-7 Detail of fitted curves of V_{in}/m_s expressed by c	28
Table 2-8 Parameters of linear fitting shown in Figure 2.14 (b).....	32
Table 2-9 Parameters of linear fitting shown in Figure 2.23 (a).....	40
Table 2-10 Obtained thermodynamic parameters of Eq (2.27).....	40
Table 3-1 Temperature effects on bentonite or clay materials' k by various investigators	52
Table 3-2 Physical properties of soil materials.	54
Table 3-3 Conditions for hydraulic conductivity tests of SB with 30 kPa confined pressure.	58
Table 3-4 Fluid density and viscosity at different temperatures.	58
Table 3-5 Hydraulic conductivities of GCLs.	64
Table 4-1 Simplified conditions for the tests and obtained Ca ²⁺ sorbed amounts q_{sorb} until the last effluent samples collected in each case.	73
Table 4-2 Comparison between the last Ca ²⁺ sorption amounts per unit mass of bentonite ($q_{sorb}/m_{bent.}$) and the equilibrium Ca ²⁺ adsorption amounts (q_e).	82
Table 4-3 Parameters of linear fitting in Figure 4.8 and obtained retardation coefficients. ...	83
Table 4-4 Significant levels of Chi-square test, obtained coefficients of normalized dispersive (D^*) and dispersive (D).	84
Table 4-5 Apparent D at room temperature in various studies.	85
Table 5-1 Summarized temperature effects on barrier performances of SB.	98

LIST OF EUQATIONS

Eq (1.1)	4	Eq (2.34)	43
Eq (1.2)	5	Eq (2.35)	43
Eq (1.3)	6	Eq (2.36)	43
Eq (2.1)	13	Eq (2.37)	44
Eq (2.2)	15	Eq (2.38)	44
Eq (2.3)	15	Eq (2.39)	44
Eq (2.4)	15	Eq (3.1)	52
Eq (2.5)	15	Eq (3.2)	57
Eq (2.6)	16	Eq (3.3)	57
Eq (2.7)	16	Eq (3.4)	63
Eq (2.8)	16	Eq (4.1)	72
Eq (2.9)	16	Eq (4.2)	72
Eq (2.10)	18	Eq (4.3)	74
Eq (2.11)	20	Eq (4.4)	74
Eq (2.12)	20	Eq (4.5)	74
Eq (2.13)	21	Eq (4.6)	74
Eq (2.14)	21	Eq (4.7)	74
Eq (2.15)	22	Eq (4.8)	74
Eq (2.16)	22	Eq (4.9)	75
Eq (2.17)	22	Eq (4.10)	75
Eq (2.18)	22	Eq (4.11)	75
Eq (2.19)	25	Eq (4.12)	75
Eq (2.20)	36	Eq (4.13)	75
Eq (2.21)	36	Eq (4.14)	84
Eq (2.22)	38	Eq (4.15)	85
Eq (2.23)	38	Eq (4.16)	86
Eq (2.24)	39	Eq (4.17)	86
Eq (2.25)	39	Eq (4.18)	90
Eq (2.26)	39	Eq (4.19)	90
Eq (2.27)	39	Eq (4.20)	90
Eq (2.28)	39		
Eq (2.29)	41		
Eq (2.30)	41		
Eq (2.31)	41		
Eq (2.32)	43		
Eq (2.33)	43		

CHAPTER 1

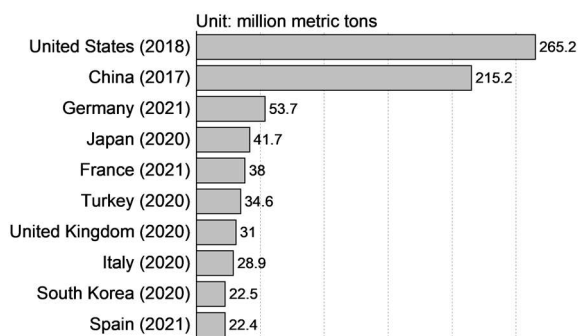
Introduction

1.1 General remarks

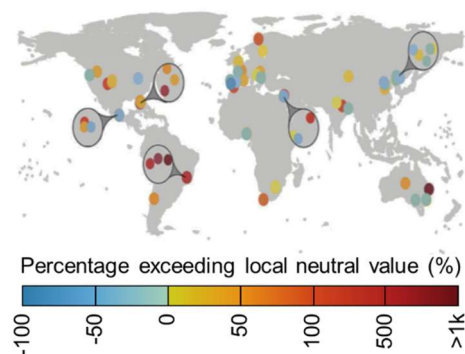
Pollution stands out as a significant environmental issue affecting humans, animals, plants, and the Earth in the contemporary era, necessitating collaborative efforts from all individuals to address. In 2015, the Food and Agriculture Organization of the United Nations (FAO) provided a precise definition of the term pollution as: the presence of a chemical or substance out of place and/or present at a higher than normal concentration that has adverse effects on any non-targeted organism (Rodríguez-Eugenio et al., 2018). For centuries, the massive release of wastes and contaminants by human civilization's industrial, agricultural, and life activities in pursuit of “abundance” and “convenience” have directly contributed to the escalation of pollution levels. Figure 1.1 shows the current status of global municipal solid waste production and soil contaminations by heavy metals.

From a motivational standpoint, pollution has never been a goal of civilization, but rather a deliberate action in exchange for the material or economic progress (e.g. developing countries vigorously develop industry and invest less in environmental conservation, as developed countries have done in the past). Along with the ozone depletion, climate change, biological extinction, and human diseases caused by contaminants, the adverse impacts of the exchange have become increasingly serious in recent decades.

As J. Robert Oppenheimer had said after he witnessing the successful test of atomic bomb he had designed, “Vishnu¹ takes on his multi-arms from and says, ‘Now, I am become Death, the destroyer of worlds.’ I suppose we all thought that one way or another” (Bird & Sherwin, 2005). The humans are becoming the Death of the Earth if the issues relate to pollution cannot be effectively addressed.



(a) Primary MSW generated in recent years
(www.statista.com)



(b) Regional soil contaminations by Cr, Cd, Pb, As, and metalloids (Y. R. Liu et al., 2023)

Figure 1.1 Global municipal solid waste (MSW) production and regional soil contaminations.

¹ God of Hinduism

The huge amounts of MSW, accompanied with toxic chemicals, polluted fields and other hazardous wastes rises the urgent requirements for suitable and environmentally friendly governances. Consequently, researches and practical methods for waste disposal and contamination management have received more and more attentions from research institutions and administrative departments. By far the main economical and feasible methods of waste disposal are landfilling and in-situ isolation, both require constructing barriers to separate waste from the ecological environments. Therefore, the performance of those barriers become the key to effective waste disposal and contamination managements, which is in the realm of this dissertation.

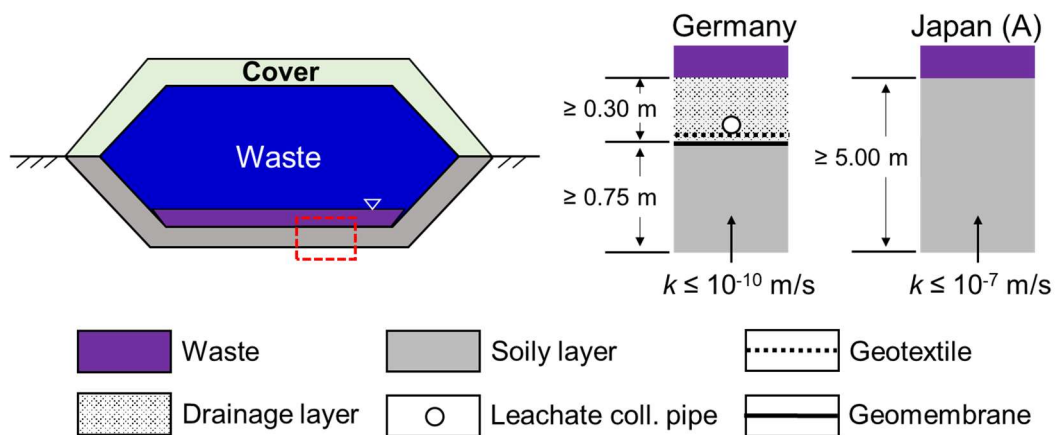
1.2 Soil barriers for waste disposal and contamination managements

In order to prevent the ecological environments from being polluted, soil barriers are designed based on two basic principles: containment and attenuation (Chai, 2002; Kamon, et al., 2002; Komine & Ogata, 1999; Rowe, 1998, 2020). These barriers are commonly possessing very low hydraulic conductivity and effective buffering capabilities. Hence, the environmentally harmful chemicals can be isolated within the barriers. Bentonite has been utilized as a material for soil barriers due to its extremely low hydraulic conductivity. The special characteristics of bentonite are introduced in Section 1.3.

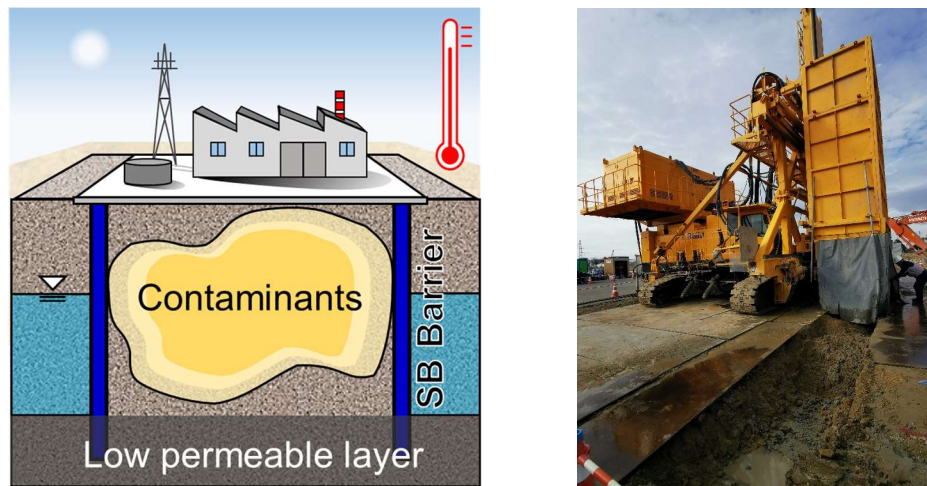
Figure 1.1 shows common soil barriers of 3 application scenarios. In Figure 1.1 (a), soil barriers are designed as bottom liner system in waste landfills. The systems include one or more low permeable layers of clay soils. The standard of the liner varied in different centuries. In Japan, natural clay ≥ 5 m in thickness with hydraulic conductivity $\leq 10^{-7} \text{ m}\cdot\text{s}^{-1}$ can be utilized as a liner while ≥ 0.75 m in thickness with hydraulic conductivity $\leq 10^{-10} \text{ m}\cdot\text{s}^{-1}$ was regulated in Germany (Chai, 2002). Recently, geosynthetic materials contained bentonite are also been widely used as the main composition of the liner system.

As shown in Figure 1.1 (b), the cut-off wall is an in-situ containment technique that around the field been contaminated to isolating it from ground water (Evans, 1993). The cut-off walls are constructed by mixing the clay soil (usually bentonite) with in-situ soils without uptake of excavated soil. In Japan, the methods of Trench cutting and Remixing Deep wall (TRD) (Evans, 2007; Takai et al., 2013) is commonly used as the construction process. The TRD methods allows the construction been finished by one TRD machine shown in Figure 1.1 (b) (Raito Kogyo Co. Ltd. HP) without separate excavation processes. The hydraulic conductivity of the cut-off wall was reported to be in the reported in the range of 10^{-10} to $10^{-8} \text{ m}\cdot\text{s}^{-1}$ (Malusis et al., 2009), effectively hindering water flow and advective contaminant transport.

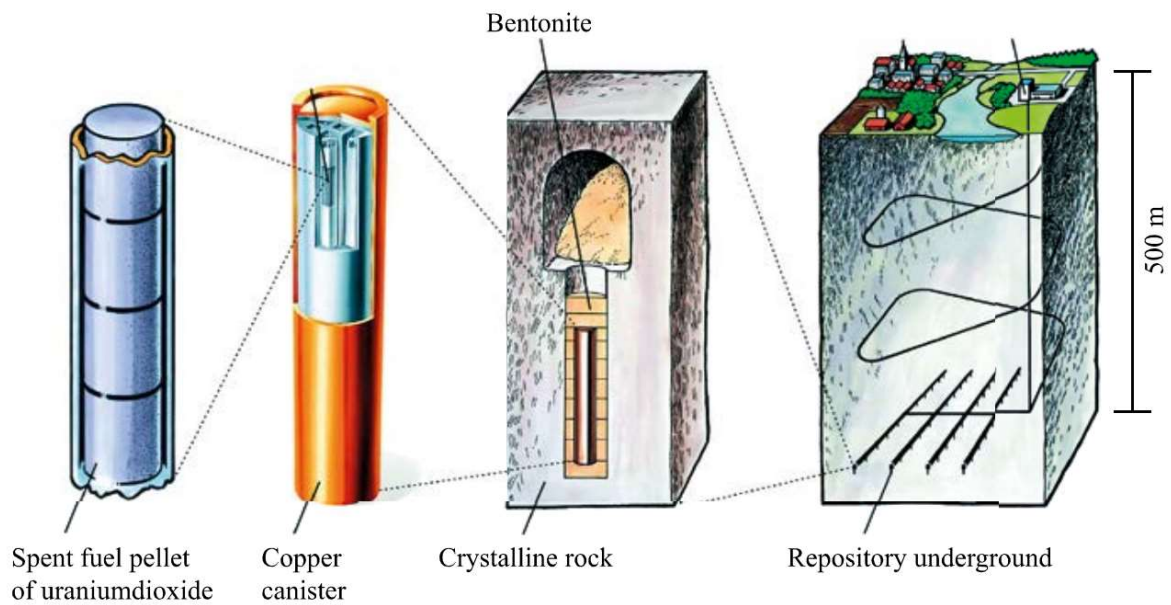
Deep geological repository is the most probable option to permanently isolate high-level waste (typically nuclear waste) from the human environment. As shown in Figure 1.1 (c), the repository is built hundreds of meters underground, where the barrier should meet the requirements of both impermeability and resistance to geologic processes (i.e. seismic activity). To achieve permanent isolation the barrier is usually made directly from high purity and highly compacted bentonite materials. The hydraulic conductivity of this kind of barrier can be lower than $10^{-11} \text{ m}\cdot\text{s}^{-1}$ (Villar & Lloret, 2004).



(a) Designs of bottom liner systems for landfills (After Chai, 2002).



(b) Design and construction of vertical cut-off walls for contaminated field.



(c) High-level waste deep geological repository (Svensson et al., 2017).

Figure 1.1 Common types of soil barriers.

1.3 Soil bentonite mixture (SB) as a barrier material

The term SB does not denote a specific material, where the S could be any in-situ or off-situ soils while B specifically refers to sodium bentonite. Although the mass ratio of bentonite in SB is typically less than 10% (Kamon et al., 2006), the barrier performances of SB are primarily determined by the unique properties of bentonite.

Bentonite is a versatile natural clay with a wide range of industrial and commercial applications. Named after the discovery of Benton Shale formation in Wyoming, USA, where it was officially identified in modern geology (Sutherland, 2014). It is primarily composed of montmorillonite, a member of the smectite group of clay minerals, and is formed from volcanic ash deposits that have weathered over time. Despite slight differences among mineral veins worldwide, a basic chemical formula for a unit of sodium montmorillonite lattice can be written as below (Ross & Hendricks, 1945):



where Na is exchangeable that can be replaced by other metal elements (Ca, Mg, etc.). Figure 1.2 shows the structure of the Na-montmorillonite lattice. Montmorillonite has a 2:1 micro-structure that consists of an octahedral sheet sandwiched between two silica sheets. The micro-structures extend horizontally and overlap each other to form layered structures. Such 2:1 structure leads to the accumulations of additional negative charges at top and bottom of the lattice, allowing exchangeable cations to occupy the interlamellar space in a state close to precipitation when the mineral is dehydrated (McBride, 1994).

The relatively weak electrostatic bonds between montmorillonite lattices facilitate the separation of layers during hydration as water molecules enter the interlamellar space (Grim, 1953). The primary cause of the decrease in SB's permeability is the decrease in effective pore volume resulting from the processes of bentonite hydration.

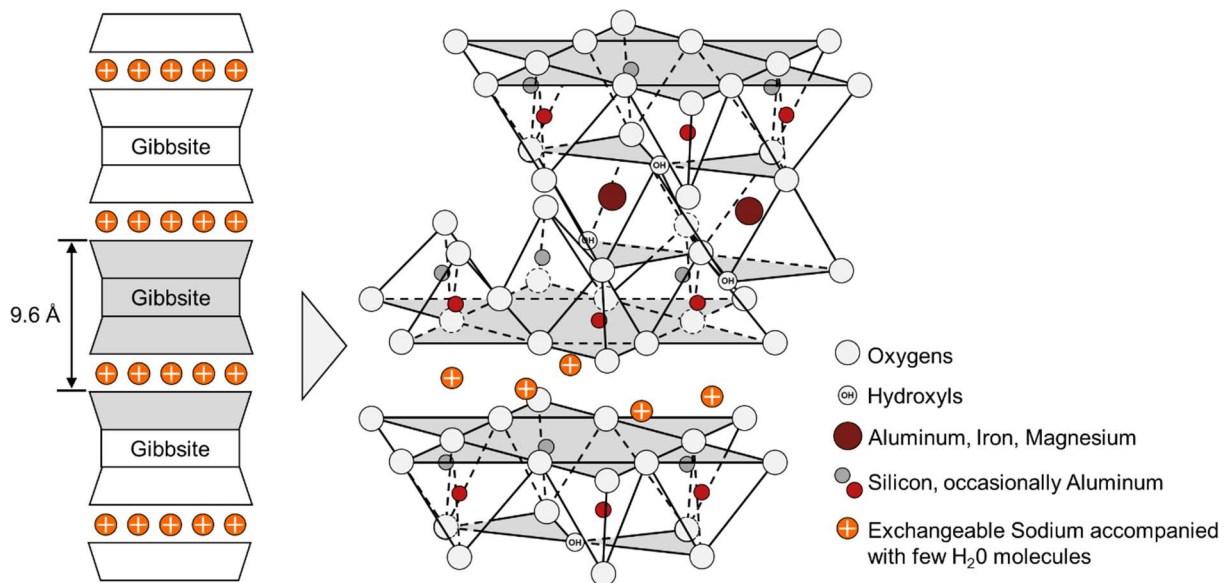


Figure 1.2 Structure of dehydrated Na-montmorillonite lattice.

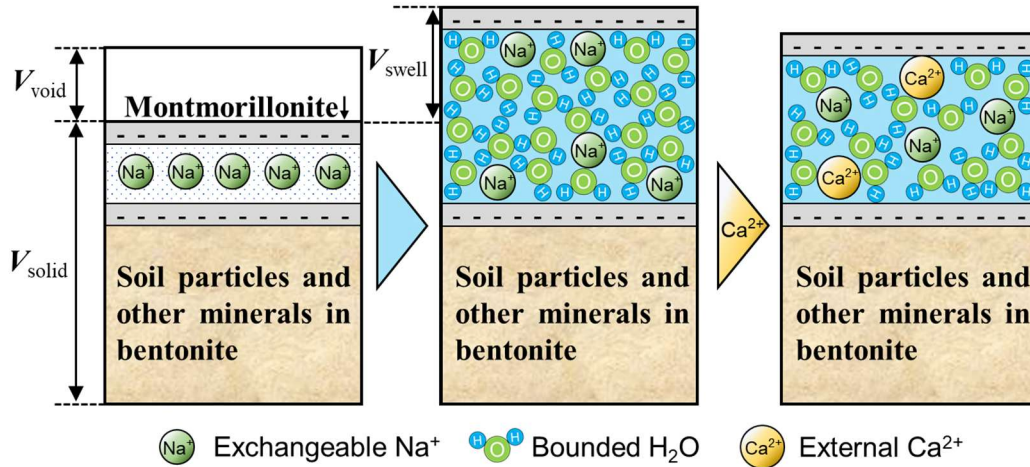


Figure 1.3 The swell of bentonite in SB (after Komine & Ogata, 2003).

1.3.1 Swelling

Swelling is widely recognized macroscopic characteristic of bentonite. As shown in Figure 1.3, the increased volume of montmorillonite after water uptake occupies or even exceeds the initial pore volume. The swelling of bentonite is considered driven by, initially, the osmotic pressure between the interlamellar space and bulk water or solution (Bolt, 1955). The fundamental equation for estimating osmotic pressure was introduced by Van't Hoff in 1886:

$$\Pi = \frac{\Delta nRT}{V} \quad (1.2)$$

where Π is the osmotic pressure between the interfaces (Pa); $\Delta n/V$ is the concentration difference between the interfaces ($\text{mol} \cdot \text{L}^{-1}$); T is the absolute temperature (K). According to Eq (1.2), the higher osmotic pressure, the stronger the tendency of the water molecule movements from low concentration phase to high concentration phase will be. Therefore, water molecules will spontaneously, be attracted, entering the interlamellar space, and the osmotic process will be intensified if the temperature is increased.

The description above refers to the osmotic process of the swelling. However, since H_2O is polar molecule, it is also subjected to the electrostatic forces from the electrical potential of the interlamellar space directly. Thus, the water molecules are driven by both osmotic pressure and electrostatic forces, it is more realistically to treat the swell of bentonite a combination of osmotic process and electrostatic process. The latter allows bentonite to exhibit some special properties after hydration.

1.3.2 Diffuse double layer (DDL)

The water molecules and ions (including original exchangeable cations and ions previously dissolved in water) around clay surface will eventually form specific distribution with electrostatic equilibrium. The special structure of the distribution is called diffuse double layer (DDL) in colloid science and soil mechanics. The DDL theory for ionic distribution was developed independently by Gouy (1910) and Chapman (1913). Subsequently, further extended by Derjaguin and Landau (1941) and Verwey and Overbeek (1948) (J. Hunter, 1981).

As the description of DDL, because the exchangeable ions exist in the interlamellar will gain tendency to diffuse away from the clay surface when they are “dissolved” while the tendency is still restricted by the electrostatic attraction from negative charged surface. An ideal ionic distribution of DDL adjacent to flat plates model of clay surface is given in Figure 1.4. According to Coulomb’s law, it can be inferred that the electrostatic constraints experienced by cations and oriented water molecules near the clay surface are higher. There is a certain distance to the clay surface at which electrostatic attraction and diffusive tendency are balanced. Farer than that distance, ions and water molecules are free to diffuse and possess liquidity; Closer than that distance, ions and water molecules are strongly constrained and lost liquidity to a certain extent. The distance is the thickness of DDL in the interlamellar space.

Though it is almost impossible to practically measure such distance, it is allowed that the thickness of DDL to be characterized based on the ionic and electrostatic parameters of the interlamellar space. Such “thickness” of the DDL in double flat plate model can be obtained (Mitchell, 1993) by:

$$\frac{1}{\kappa} = \left(\frac{\varepsilon k_B T}{2n_0 e^2 v^2} \right)^{1/2} \quad (1.3)$$

where κ is called Debye-Hückel parameter in colloid science (m^{-1}), $1/\kappa$ is defined as the “thickness” of DDL (m); ε is the permittivity of the fluid medium ($\text{F}\cdot\text{m}^{-1}$); T is the absolute temperature (K); k_B is Boltzmann constant ($= 1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$); n_0 is the electrolyte concentration of ions (m^{-3}); e is the unit electronic charge ($= 1.602 \times 10^{-19} \text{ C}$); v is the valence of ions. Although the solution within DDL is still in a liquid phase, its illiquidity exhibits properties closer to solid. The decrease of “free space” for fluid to passing through is the critical reason of impermeability of bentonite materials. Eq (1.3) indicating that the “thickness” of DDL will decrease when the temperature is decreased, the bulk concentration is increased, and the valence of cation is increased.

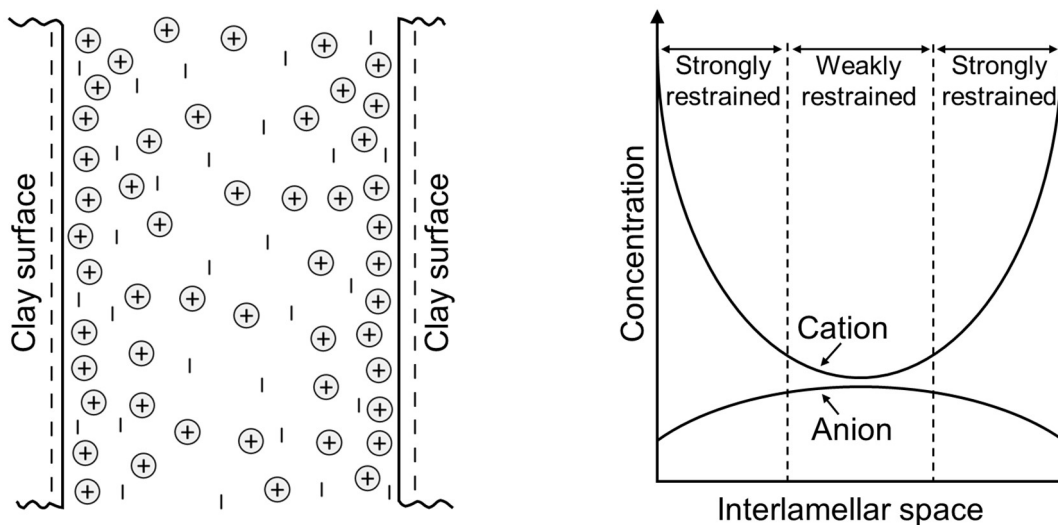
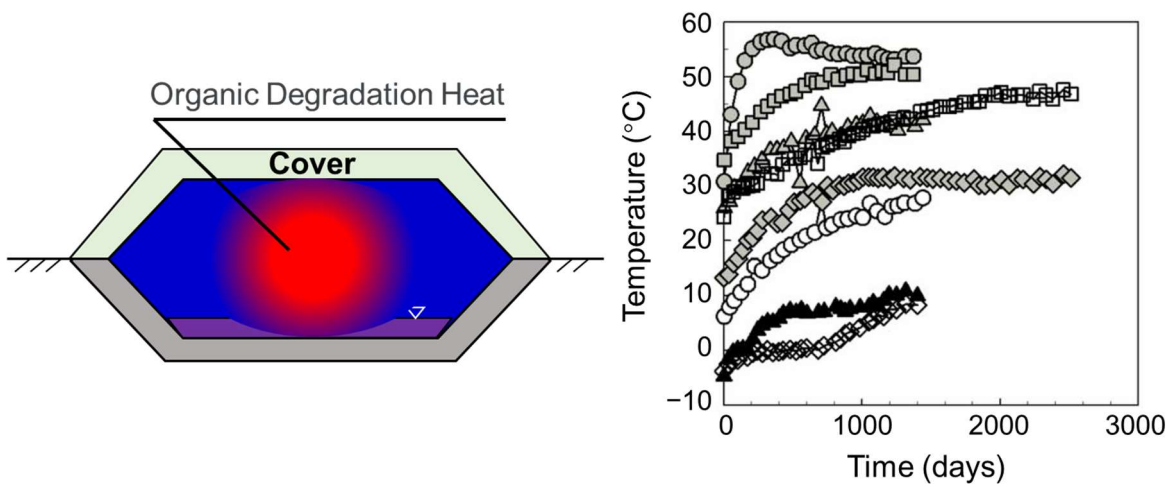
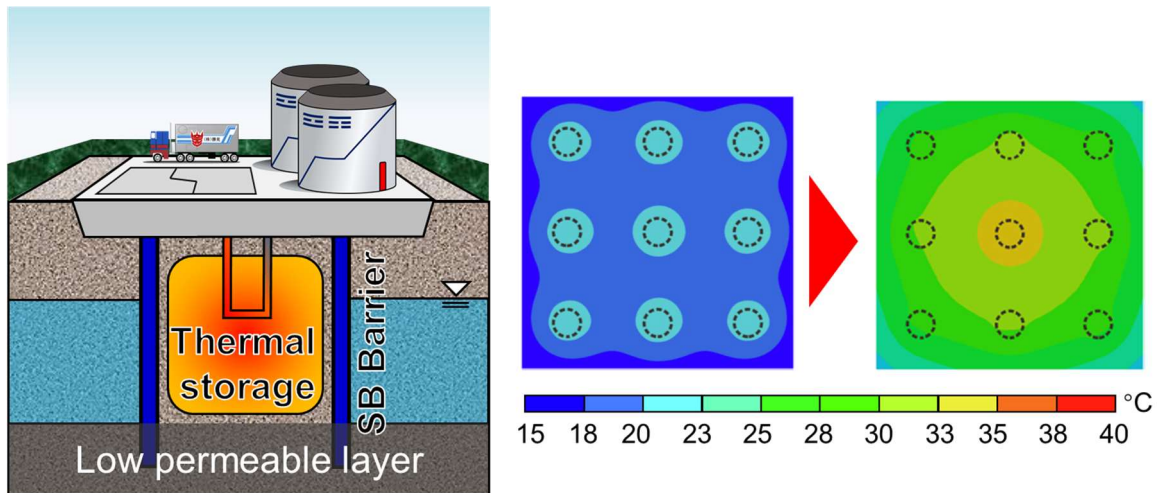


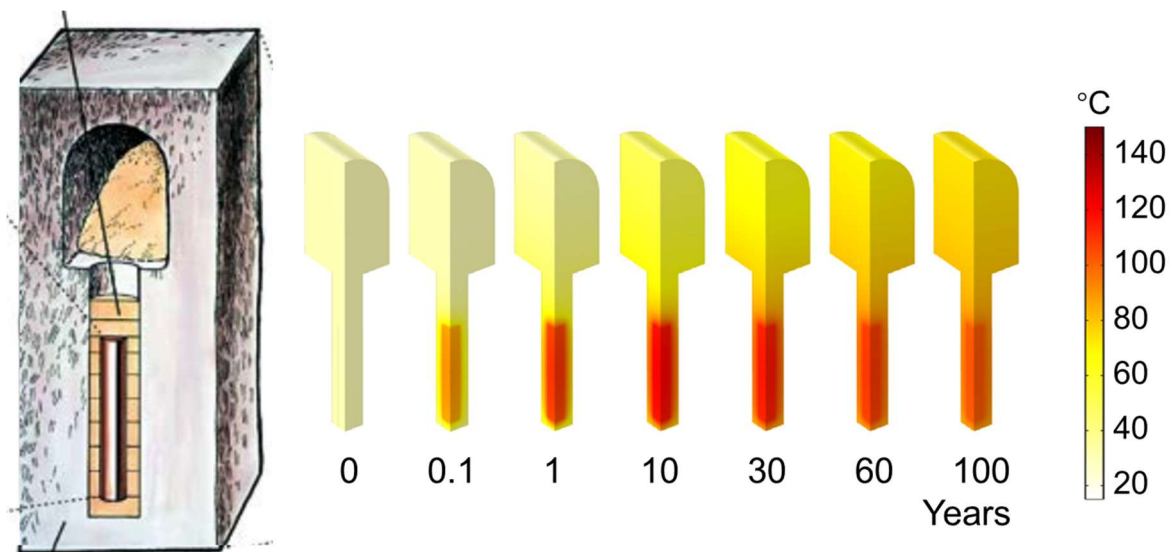
Figure 1.4 Ionic distributions in interlamellar space of montmorillonite lattice according to the concept of DDL (after Mitchell, 1993).



(a) Elevated temperatures in MSW landfills (Hanson et al., 2010).



(b) Cut-off wall for underground thermal storage facilities (Ma & Wang, 2020).



(c) Decay heat in HLW deep geological repository (J. O. Lee et al., 2017).

Figure 1.5 High-temperature conditions in soil barriers caused by interior factors

1.4 High-temperature conditions in soil barriers

1.4.1 Interior factors

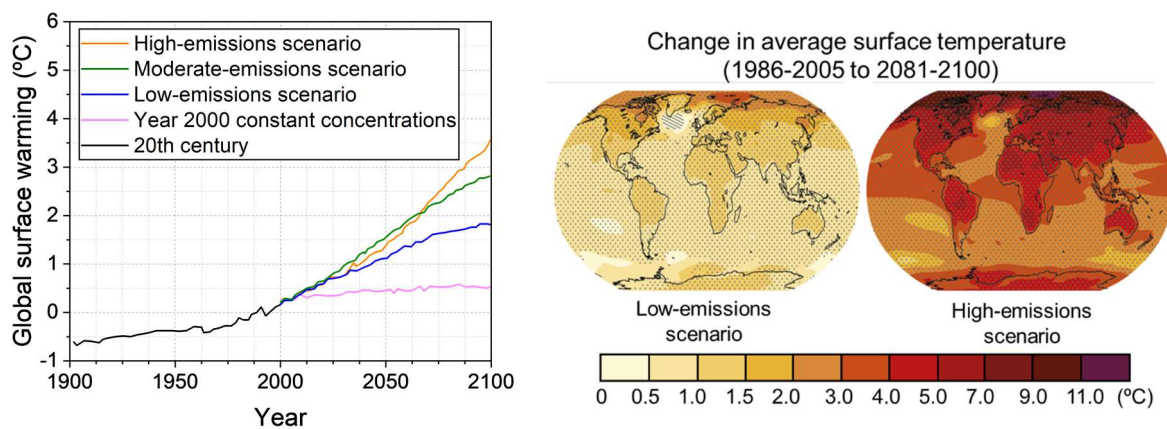
Depending on the application scenarios, the soil barriers are expected to be subjected to various thermodynamic conditions during operation, as shown in Figure 1.5. For instance, the subsurface ground temperature alongside degradable municipal waste landfill sites or underground thermal storage facilities could be heated by elevated temperatures over 60°C in those sites (Jafari et al., 2017; Tveit et al., 2009). When in-situ thermal remediation (Horst et al., 2021) is applied to the ground contaminated by organic compounds, the vertical cut-off walls, which are often supplementary constructed, are also heated. In high-level waste deep geological repository, the decay heat generated by nuclear waste can raise the temperature of the repository barrier to more than 100°C (Gibb et al., 2008).

1.4.2 Exterior factors

“The era of global warming has ended and the era of global boiling has arrived,” said by the UN secretary general António Guterres in 2023. The impacts of Climate Change to the performances of soil barriers can no-longer be neglect especially in long-term considerations.

Figure 1.6 shows the historical and projected global warming. Reported data shows that the development of global warming will dependent on the emission amount of CO₂ in the future. Predictions of global temperature based on different emission scenarios indicated that the average global temperature will increase over 0.5°C (Lowest) to over 3.5°C (High-emission) by the end of 2100 compared to the late 20th century, among which some of the predicted regional temperatures at high latitudes might increase over 10°C.

Accompanying with ongoing Climate Change, the soil barriers will experience more serious daily and seasonal fluctuations in temperature, and average temperature continues to rise. With introduced interior and exterior factors, it is necessary to evaluate the temperature effects to the hydraulic and buffering performances of SB barriers.



(a) Global surface warming for years 1900 to 2000 and projected to 2100

(b) Increase in temperature on a regional scale for 2 scenarios of greenhouse gas emissions

Figure 1.6 Historical and projected global warming (After Engel & Reid, 2019; IPCC, 2014).

1.5 Objective and contents of the dissertation

The objective of this dissertation is to quantitatively evaluate the temperature effects on hydraulic and buffering performances of soil-bentonite mixture (SB) by means of experimental methods. The experimental works including the batch test to evaluate the basic properties of materials and column type hydraulic conductivity test to evaluate the barrier performances of SB by emulating in-situ conditions.

The structure of this dissertation is shown in Figure 1.7. The dissertation is divided into 6 chapters, where the current chapter contains the introductions of necessary background information and the main components of the study. Chapter 2 to Chapter 4 contain all experimental works. Followed the practical implications in Chapter 5, and end with conclusions and prospects in Chapter 6.

In Chapter 2, the adsorption behaviors of SB are studied based on batch tests with CaCl_2 solutions. The batch tests are carried out with different initial CaCl_2 concentrations and different constant temperature conditions. The Ca^{2+} adsorption isotherms, and Na^+ exchange isotherms of SB, as well as pure decomposed granite soil (S) and pure bentonite (B) are obtained. The comparison of these isotherms at different temperatures are carried out. The discussions and interpretations on the temperature dependencies of adsorption and ion exchange processes, and on the modelling of Ca^{2+} adsorption isotherms in a wide range of bulk concentration SB and B are given.

In Chapter 3, the hydraulic performance of consolidated SB specimens at different temperatures are evaluated. The hydraulic conductivity tests using modified flexible-wall permeameter that carried out in this study is introduced in this chapter. The hydraulic performance in this study refers to the values of hydraulic conductivity and intrinsic permeability. The comparison of hydraulic behaviors at different temperatures and their dynamic changes during the tests are given. The physical meaning and impact of the observed hydraulic behaviors are also evaluated.

In chapter 4, the buffering performances of consolidated SB specimens at different temperatures are evaluated. The results of Ca^{2+} breakthrough, and Na^+ elution from the tests introduced on chapter 4 are shown in this chapter. The buffering performances of SB against Ca^{2+} are quantitatively characterized by Ca^{2+} sorbed amount, and the temperature dependencies of Ca^{2+} sorption at different test conditions are evaluated. In addition, the intrinsic correlation between the Ca^{2+} sorption in hydraulic conductivity tests and the Ca^{2+} adsorption in batch tests are discussed.

Chapter 5 uses the results obtained in chapters 2 to chapter 4 to provides practical implications of the temperature effects on hydraulic and buffering performance of SB in specific application scenarios. In addition, possible improvement to the SB are proposed, and several accidental concerns are discussed.

Chapter 6 summarizes all results and discussions obtained in each chapter as the conclusions of entire dissertation. In the last, several unidentified problems that required further researches are pointed out as the prospects of the dissertation.

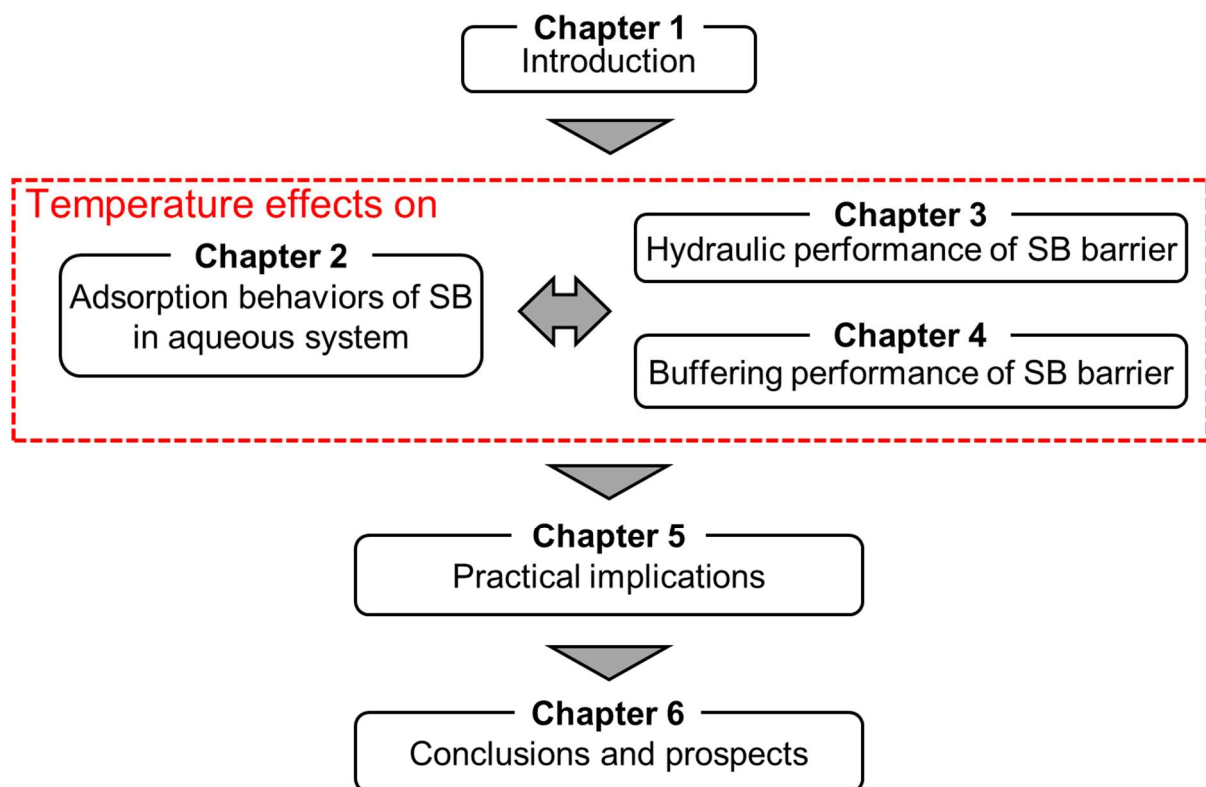


Figure 1.7 Structure of this dissertation.

References

- Bird, K., & Sherwin, M. J. (2005). *American Prometheus: the triumph and tragedy of J. Robert Oppenheimer*. Knopf.
- Bolt, G. H. (1955). Analysis of the validity of the Gouy-Chapman theory of the electric double layer. *Journal of Colloid Science*, 10(2), 206–218. [https://doi.org/10.1016/0095-8522\(55\)90027-1](https://doi.org/10.1016/0095-8522(55)90027-1)
- Chai, J. N. M. (2002). Comparing the performance of landfill liner systems. *J Mater Cycles Waste Manag*, 4, 135–142.
- Engel, T., & Reid, P. (2019). *Thermodynamics, statistical thermodynamics, and kinetics: physical chemistry* (4th editio). Pearson education.
- Evans, J. C. (1993). Vertical cutoff walls. In *Geotechnical Practice for Waste Disposal* (pp. 430–454). Springer US. https://doi.org/10.1007/978-1-4615-3070-1_17
- Evans, J. C. (2007). The TRD method: slag-cement materials for in situ mixed vertical barriers. In *Soil Improvement* (pp. 1–11).
- Gibb, F. G. F., Travis, K. P., McTaggart, N. A., Burley, D., & Hesketh, K. W. (2008). Modeling temperature distribution around very deep borehole disposals of HLW. *Nuclear Technology*, 163(1), 62–73. <https://doi.org/10.13182/NT08-A3970>
- Grim, R. E. (1953). *Clay mineralogy* (Vol. 76, Issue 4). LWW.
- Hanson, J. L., Yeşiller, N., & Oettle, N. K. (2010). Spatial and Temporal Temperature Distributions in Municipal Solid Waste Landfills. *Journal of Environmental Engineering*, 136(8), 804–814. [https://doi.org/10.1061/\(asce\)ee.1943-7870.0000202](https://doi.org/10.1061/(asce)ee.1943-7870.0000202)
- Horst, J., Munholland, J., Hegele, P., Klemmer, M., & Gattenby, J. (2021). In Situ Thermal Remediation for Source Areas: Technology Advances and a Review of the Market From 1988–2020. *Groundwater Monitoring and Remediation*, 41(1), 17–31.

- <https://doi.org/10.1111/gwmmr.12424>
- IPCC. (2014). IPCC, 2014: Climate Change 2014 Synthesis Report. In IPCC (Vol. 218, Issue 2). [https://doi.org/10.1016/S0022-0248\(00\)00575-3](https://doi.org/10.1016/S0022-0248(00)00575-3)
- J. Hunter, R. (1981). Zeta potential in colloid science: Principles and applications. In Academic Press.
- Jafari, N. H., Stark, T. D., & Thalhamer, T. (2017). Spatial and temporal characteristics of elevated temperatures in municipal solid waste landfills. *Waste Management*, 59, 286–301. <https://doi.org/10.1016/j.wasman.2016.10.052>
- Kamon, M., Katsumi, T., Inui, T., Ogawa, Y., & Araki, S. (2006). Hydraulic Performance of Soil-Bentonite Mixture Barrier. In 5th ICEG Environmental Geotechnics: Opportunities, Challenges and Responsibilities for Environmental Geotechnics (pp. 733–740). <https://doi.org/10.1680/ieg.34747.0733>
- Kamon, M., Zhang, H., Katsumi, T., & Sawa, N. (2002). Redox Effect on the Hydraulic Conductivity of Clay Liner. *Soils and Foundations*, 42(6), 79–91. https://doi.org/10.3208/sandf.42.6_79
- Komine, H., & Ogata, N. (1999). Experimental Study on Swelling Characteristics of Sand-Bentonite Mixture for Nuclear Waste Disposal. *Soils and Foundations*, 39(2), 83–97. https://doi.org/10.3208/sandf.39.2_83
- Komine, H., & Ogata, N. (2003). New equations for swelling characteristics of bentonite-based buffer materials. *Canadian Geotechnical Journal*, 40(2), 460–475. <https://doi.org/10.1139/t02-115>
- Lee, J. O., Choi, H., & Kim, G. Y. (2017). Numerical simulation studies on predicting the peak temperature in the buffer of an HLW repository. *International Journal of Heat and Mass Transfer*, 115, 192–204. <https://doi.org/10.1016/j.ijheatmasstransfer.2017.07.039>
- Liu, Y. R., van der Heijden, M. G. A., Riedo, J., Sanz-Lazaro, C., Eldridge, D. J., Bastida, F., Moreno-Jiménez, E., Zhou, X. Q., Hu, H. W., He, J. Z., Moreno, J. L., Abades, S., Alfaro, F., Bamigboye, A. R., Berdugo, M., Blanco-Pastor, J. L., de los Ríos, A., Duran, J., Grebenc, T., ... Delgado-Baquerizo, M. (2023). Soil contamination in nearby natural areas mirrors that in urban greenspaces worldwide. *Nature Communications*, 14(1), 1–12. <https://doi.org/10.1038/s41467-023-37428-6>
- Ma, Q., & Wang, P. (2020). Underground solar energy storage via energy piles. *Applied Energy*, 261(December 2019), 114361. <https://doi.org/10.1016/j.apenergy.2019.114361>
- Malusis, M. A., Barben, E. J., & Evans, J. C. (2009). Hydraulic Conductivity and Compressibility of Soil-Bentonite Backfill Amended with Activated Carbon. *Journal of Geotechnical and Geoenvironmental Engineering*, 135(5), 664–672. [https://doi.org/10.1061/\(asce\)gt.1943-5606.0000041](https://doi.org/10.1061/(asce)gt.1943-5606.0000041)
- McBride, M. B. (1994). Environmental chemistry of soils. In Suparyanto dan Rosad (2015. Oxford university press.
- Mitchell, J. K. (1993). Fundamentals of Soil Behavior. In Soil Science Society of America Journal (3rd ed.). John Wiley & Sons, Inc.
- Ross, C. S., & Hendricks, S. B. (1945). Minerals of the montmorillonite group: Their origin and relation to soils and clays (Issue 205). US Government Printing Office.
- Rowe, R. K. (1998). Geosynthetics and the minimization of contaminant migration through barrier systems beneath solid waste Hydraulic Performance of GCLs in containment of brine and landfill applications View project Long-term performance of geomembranes View project. March 1998. <https://www.researchgate.net/publication/291698097>
- Rowe, R. K. (2020). Geosynthetic clay liners: Perceptions and misconceptions. *Geotextiles and Geomembranes*, 48(2), 137–156. <https://doi.org/10.1016/j.geotexmem.2019.11.012>
- Sutherland, W. M. (2014). Wyoming bentonite. Catalysis from A to Z, September 2014. <https://doi.org/10.1002/9783527809080.cataz18044>

- Svensson, D., Lundgren, C., Johannesson, L.-E., & Norrfors, K. (2017). Developing strategies for acquisition and control of bentonite for a high level radioactive waste repository. Svensk Kärnbränslehantering AB, Swedish Nuclear Fuel and Waste Management~....
- Takai, A., Inui, T., Katsumi, T., Kamon, M., & Araki, S. (2013). Hydraulic barrier performance of soil bentonite mixture cutoff wall. *Coupled Phenomena in Environmental Geotechnics: From Theoretical and Experimental Research to Practical Applications - Proceedings of the International Symposium, ISSMGE TC 215, December, 707–714.* <https://doi.org/10.1201/b15004-96>
- Tveit, T. M., Savola, T., Gebremedhin, A., & Fogelholm, C. J. (2009). Multi-period MINLP model for optimising operation and structural changes to CHP plants in district heating networks with long-term thermal storage. *Energy Conversion and Management, 50*(3), 639–647. <https://doi.org/10.1016/j.enconman.2008.10.010>
- Villar, M. V., & Lloret, A. (2004). Influence of temperature on the hydro-mechanical behaviour of a compacted bentonite. *Applied Clay Science, 26*(1-4 SPEC. ISS.), 337–350. <https://doi.org/10.1016/j.clay.2003.12.026>

CHAPTER 2

Temperature effects on adsorption behaviors of SB in aqueous system

2.1 Introduction

Adsorption is a nature that one substance becomes attached to another. In geoenvironmental and geotechnical concerns, adsorption is one of the crucial processes for removing priority inorganic pollutants, notably heavy metals like Mercury, Cadmium, Copper, and Zinc, from aqueous systems (Bonilla-Petriciolet et al., 2017; Dias et al., 2007).

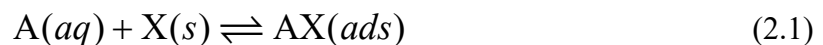
SB's adsorption behaviors against metal ions largely determine its capability to prevent the migration of contaminants when function as a barrier. Therefore, laboratory evaluation to the adsorption behavior of SB can provide good reference for predicting the interactions between contaminant and SB barrier, and guiding dimensional design, and estimating operational lifespans of the barrier. As a mixed material, the adsorption process of SB is the overlay of two kinds of adsorption behaviors of parent soil and bentonite, where the latter plays the main role of adsorption. Although studies showed the adsorption capabilities of bentonite in removing metal ions in aqueous system (Kaya & Ören, 2005; Meneguín et al., 2017; Sposito et al., 1981), less attention has been paid to its adsorption as SB mixture. Therefore, one concern of this study is to determine whether the bentonite can fully utilize its adsorption capacity as SB, and another concern is to evaluate the effects of temperature on the adsorption behaviors.

In this study, Ca^{2+} was choose as the indicator of adsorption. Studies (Bradshaw et al., 2013; Kolstad, Benson, & Edil, 2004; Lange et al., 2009; Rowe et al., 2005) have shown that the concentrations and valences, rather than species, of cations effects the barrier performances of bentonite materials most significantly. Therefore, results of Ca^{2+} adsorption have reference significance for the temperature effects of adsorption of other multivalent cations. Also, from a safety perspective, the non-toxic Ca^{2+} allows a large number of tests, as well as tests with high-concentration solutions to be carried out.

2.2 Literature review for Chapter 2

2.2.1 Adsorption behaviors of general soil in aqueous system

As shown in Figure 2.1 (a), for a spherical soil particle, the main adsorption is a process that the solute bonded to the surface of the particle, which is a consequence of surface energy in principle (Ng et al., 2017). An adsorption process that solute A be adsorbed onto activate site X on surface of a soil particle can be written as a reaction:



where the “ads” in brackets indicated an adsorbed phase. The equilibrium of adsorption is the state that the surface energy is lowest at the equilibrium external condition, where the rates of adsorption and desorption are equal. Therefore, adsorption capability of soil particle as well as most adsorbent are characterized by the relation between equilibrium sorbed amount ($\text{mol}\cdot\text{g}^{-1}$) and equilibrium bulk concentration ($\text{mol}\cdot\text{L}^{-1}$), known as adsorption isotherm (Giles et al., 1960; Tipping, 1995).

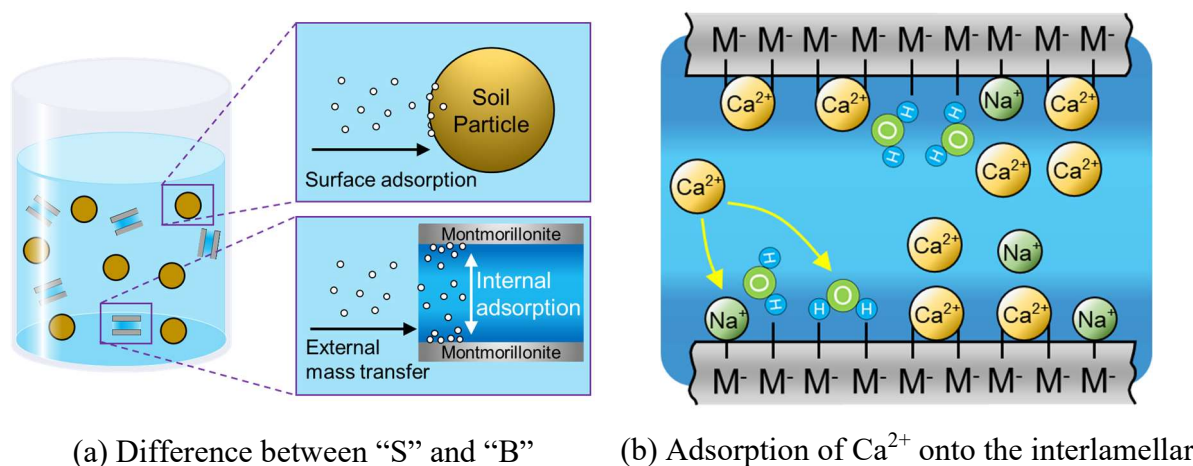


Figure 2.1 Adsorption behaviors of SB in aqueous system.

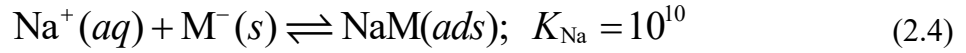
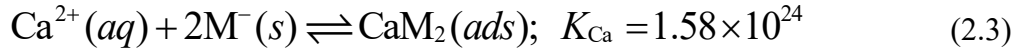
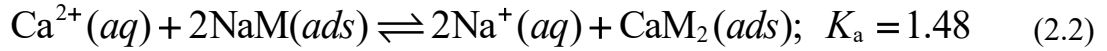
2.2.2 Adsorption behaviors of bentonite in aqueous system

In Figure 2.1 (a), the adsorption of bentonite is not as simple as the adsorption of spherical soil particle in principle. As the solute is not bonded to the out-surface of bentonite but move into the interlamellar of montmorillonite (Bourg et al., 2003; Torikai et al., 1996), where they are subject to strong electrostatic forces and participate in the formation of the diffuse double layer (DDL) (J. Hunter, 1981). As a result, the cations are restrained in the interlamellar and become immobilized.

Figure 2.1 (b) shows the behavior of Ca^{2+} when the DDL formed according to the Guoy-Chapman's theory. When the Ca^{2+} moves into the interlamellar, it is subjected to the attractions from two inter-surfaces. Ca^{2+} might be directly adsorbed onto one surface with ionic bond, or be adsorbed onto the first layer without ionic bond with the surface. In the meantime, the Na^+ in the interlamellar could be replaced by the Ca^{2+} and moved into bulk solution, known as the ion exchange behavior. Furthermore, if the bulk concentration is not very dilute, the distance between the two surface is going to decrease as the increase of total positive charges in the interlamellar (Mitchell, 1993). The change of the available space for the adsorbed cations generate difficulties for comprehensive modelling of bentonite adsorption.

Results from spectroscopy and molecular dynamics models showed that the distinguish of ions adsorbed onto the surfaces or onto the second layer is difficult (F.-R. C. Chang et al., 1998; Papelis & Hayes, 1996; Sposito et al., 1999). The two (or more) layers of immobilized cations were usually treated as in same adsorbed state. Also, the related chemical-physical parameters for the adsorption are the effective values for the overall process. Therefore, several (major)

ionic behaviors of during the process of Ca^{2+} been adsorbed onto montmorillonite inter-surface of Na-bentonite can be equivalently written as (Fletcher & Sposito, 1989):



where M^- is the negatively charged active site on the inter-surface; K_a , K_{Ca} , and K_{Na} are the corresponded equilibrium constants at 25°C. Eq (2.2) is the well-known ion exchange reaction of clay materials (Bouazza et al., 2007; Kaya & Ören, 2005; Naka et al., 2019). Eq (2.3) and (2.4) are complexation reactions derived from the ion exchange reaction, they represent the processes of adsorption of Ca^{2+} and desorption of Na^+ independently. K_a is absolute value, while K_{Ca} and K_{Na} are relative values, they are related by:

$$K_a = \left(\frac{f_{\text{Ca}}}{f_{\text{Na}}^2} \right) \cdot \left(\frac{K_{\text{Ca}}}{K_{\text{Na}}^2} \right) \cdot (m_{\text{CaM}_2} + m_{\text{NaM}}) \quad (2.5)$$

where f is the ionic activity coefficient at adsorbed phases (-); m_{CaM_2} and m_{NaM} are the relative molalities of adsorbed phases on the surface (-). The obtaining of chemical equilibrium constants above were carried out at Na-saturated bentonite (McBride, 1994), where the bentonite was pretreated by solutions with high concentrations of NaCl or NaClO₄. From a practical perspective, when bentonite is applied to barrier construction, it is not common to pretreated by Na^+ solution for it might inhibits its property of swell. Therefore, for “Na-unsaturated” bentonite, reactions of Eq (2.2) and (2.3) proceeded simultaneously when Ca^{2+} is adsorbed.

On the perspective of adsorption, the concern is the amounts of ions that get into the interlamellar and become immobilized rather than the specific processes. However, in clay-solution systems, the application of mass conservation is difficult since the water is also retained by clays. Efforts have been made to correctly measure the volumes of bulk solutions in clay-solution systems by Hutcheon (1966), Sposito et al. (1981, 1983), Tertre et al. (2011), and Robin et al. (2015). In those studies, terms or correction factors to characterize the changed solution volume were added into the mass conservation equations in the adsorption/exchange systems. Also, sometimes the adsorption capability was characterized with ionic concentrations in the interlamellar named as ρ_{clay} or C_{dl} ($\text{mol} \cdot \text{L}^{-1}$) by Kraepiel et al. (1999) and Bourg et al. (2003) respectively. The interlamellar concentration is linked with the adsorption amount ($\text{mol} \cdot \text{g}^{-1}$) in principle. After all, the Ca^{2+} adsorption isotherm in a wide range of bulk Ca^{2+} concentration given by Sposito et al., (1983) showed a trend of decreasing in Figure 2.2 (b), which is difficult to be characterized by regular adsorption models.

Still, when the bulk solution is dilute enough, the adsorption of bentonite against metal ions can be well characterized by adsorption models that did not take the volume change into account. Chang et al. (2020) reported that the adsorption of Cu^{2+} and Ni^{2+} onto bentonite can be well characterized by Langmuir and Freundlich isotherms when the bulk concentrations were below

400 mg·L⁻¹. Ranges of bulk concentrations less than 10 mmol·L⁻¹ have been obtained by Meneguín et al. (2017) and Wang et al. (2009) for adsorption of Pb²⁺ onto bentonite. Kaya & Ören (2005) also reported the adsorption isotherm of Zn²⁺ onto bentonite can be fitted by Langmuir model. In those studies, the adsorption isotherms were obtained through the mass conservation in batch systems, where the volumes of bulk solutions were treated as constant.

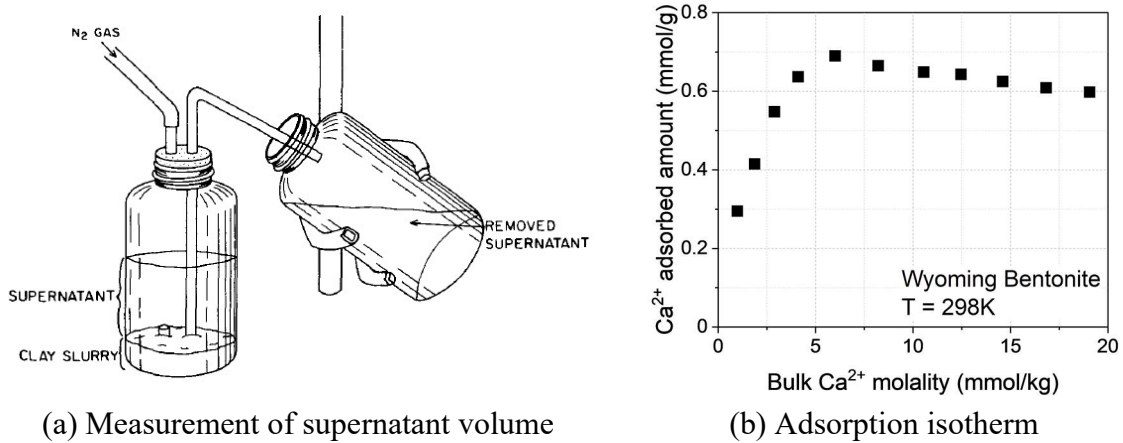


Figure 2.2 Adsorption of Ca²⁺ onto Wyoming bentonite (Sposito et al., 1981, 1983).

2.2.3 Thermodynamics in adsorption processes

In perspective of thermodynamics, the direction of adsorption process is government by the change of Gibb's free energy ΔG (J·mol⁻¹) (Engel & Reid, 2019). $\Delta G < 0$ indicates the process becomes favorable, $\Delta G > 0$ indicates the process becomes unfavorable, and $\Delta G = 0$ indicates the reaction reaches equilibrium.

For any condition, the ΔG of a reaction can be calculate from its value of that reaction at standard condition:

$$\Delta G = \Delta G^0 + RT \ln(K_e) \quad (2.6)$$

where ΔG^0 is the standard free energy of the reaction (J·mol⁻¹); R is gas constant ($= 8.314$ J·K⁻¹·mol⁻¹); T is absolute temperature (K); K_e is the equilibrium constant of the reaction (-), same as K_a in Eq (2.5). The ΔG^0 is intrinsic relates to the standard enthalpy change ΔH^0 (J·mol⁻¹) and standard entropy change (J·K⁻¹·mol⁻¹), showing in the following equation:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (2.7)$$

At equilibrium, $\Delta G = 0$, substituting Eq (2.6), Eq (2.7) becomes:

$$\ln(K_e) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (2.8)$$

Equation (2.8) is known as Van't Hoff expression, herein:

$$\frac{d \ln(K_e)}{dT} = \frac{\Delta H^0}{RT^2} \quad (2.9)$$

If the reaction is exothermic, $\Delta H^0 < 0$, the reaction is inhibited as the temperature increased; If the reaction is endothermic, $\Delta H^0 > 0$, the reaction is promoted as the temperature increased.

In practice, K_e of adsorption process is obtained based on the parameters of adsorption isotherm, and ΔH^0 and ΔS^0 are found on the plot of $\ln(K_e)$ versus $(1/T)$. However, the correct calculation for K_e is still a discussed topic without common sense (Zhou et al., 2012). Furthermore, if the adsorption behavior is accompanied with other physical process that release/consume energy, e.g. in bentonite batch system, the obtain of accurate K_e is more difficult. In general, an adsorption reaction is usually exothermic but there are exceptions, Figure 2.3 shows two results that indicating exothermal adsorption and endothermal adsorption, showing the necessity of experimentally finding the nature of adsorption processes.

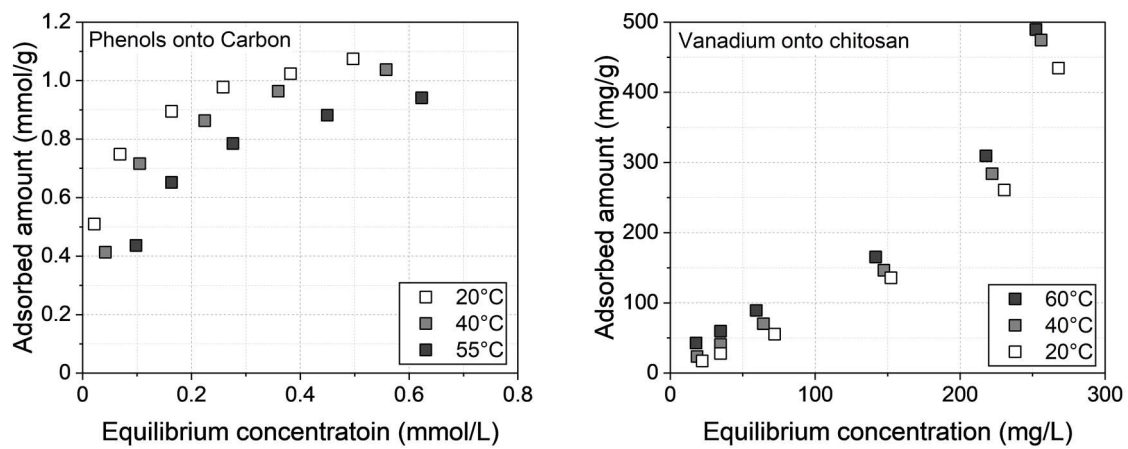


Figure 2.3 Adsorption been observed as exothermic (left) and endothermal (right) as the temperature increased (Cadaval Jr et al., 2016; Q. S. Liu et al., 2010).

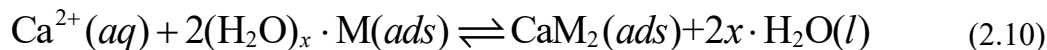
2.2.4 Thermodynamics in adsorption processes of bentonite

As Eq (2.2) and (2.3) showed, the Ca^{2+} is adsorbed onto montmorillonite inter-surface either accompanied by the release of Na^+ or directly. For the convenience of narrative, the former is called ion exchange and the latter is called direct adsorption in this study. Naturally, the thermodynamics of adsorption attributed to the ion exchange and direct adsorption need to be considered separately.

The thermodynamics of ion exchanges in bentonite clay have been comprehensively studied since 1960s. The representative results of Laudelout et al. (1968) and Gilbert & Van Bladel (1970) had revealed the nature of ion exchange that the spontaneous exchange of low-charge by high-charge cations on clays is an endothermic process (McBride, 1994). Table 2-1 summarized thermodynamic parameters of several cation exchanges. The positive ΔH^0 for exchanges from No 1 to No 6 predicting that the equilibrium shifts further in the direction that the ion exchange reactions are written as the temperature is raised. The increase in entropy, ΔS^0 , when high charge cations displace low charge cations from the surface into solution indicates the increase of disorder in the exchange system. Explained by the greater rotational mobility of divalent cations have more configurational entropy (Everett, 1964; Hnizdo & Gilson, 2010).

The direct adsorption showed in Eq (2.3) was written as a complexation form. It should be

noted that the assumed “empty” active site on the montmorillonite is not complete empty, but occupied by oriented H₂O molecule in aqueous system. So, the Ca²⁺ are actually exchanged with those “adsorbed” H₂O, and Eq (2.3) can be written as:



where H₂O on the left is in adsorbed phase and on the right is in liquid phase. The phase change of H₂O in the direction of reaction is found endothermic and increase entropy (Hutcheon, 1966), corresponding values of ΔH^0 and ΔS^0 were approximately one order less than other exchange reactions, shown in Table 2-1. Hardly any studies have given the thermodynamic parameters when cations are exchanged with H₂O (ads). However, the symbols of the thermodynamic parameters of the reaction shown in Eq (2.10) is predictable in principle. Firstly, the entropy of H₂O (ads) is probably higher than the Ca²⁺ (ads) for its polarity, and there are more possibilities for the orientation and position of H₂O molecules when they are adsorbed, shown in Figure 2.1 (b). Hence the ΔS^0 is negative for the reaction. Since adsorptions of metal ions onto bentonite occurs spontaneously (driven by Coulomb force) at room temperature, ΔH^0 of the reaction is likely to be negative according to the Eq (2.7). Therefore, it can be predicted that as the temperature increased, the reaction in the direction of Eq (2.10) is likely to be inhibited.

Since the signs ΔH^0 of ion exchange (Eq (2.2)) and direct adsorption (Eq ((2.10)) are likely to be different, the temperature dependency to the adsorbed amount of Ca²⁺ could be complicated and attributed by the proportion of the two reactions. The two reactions should be carefully separated to analyze the temperature effects to the adsorption behaviors of SB against Ca²⁺ comprehensively. According to the Eq (2.2), Na⁺ can be considered as an indicator of ion exchange reaction. Herein with the comparing between desorbed amount of Na⁺ and adsorbed amount of Ca²⁺, the distinguish of the two reactions is possible.

Table 2-1 Thermodynamic parameters of cation exchanges in montmorillonite at 25°C and of H₂O sorption at 30°C. The adsorbed substances exist on the left sides of chemical formula and the replaced substances on the right (after Hutcheon, 1966; Laudelout et al., 1968).

No.	Adsorbed	Replaced	ΔG^0 (kJ·mol ⁻¹)	ΔH^0 (kJ·mol ⁻¹)	ΔS^0 (J·mol ⁻¹ ·K ⁻¹)
1	Mg ²⁺	2NH ₄ ⁺	+4.29	+10.67	+24.78
2	Ca ²⁺	2NH ₄ ⁺	+4.17	+10.47	+23.94
3	Ba ²⁺	2NH ₄ ⁺	+3.91	+7.74	+13.81
4	Ba ²⁺	2Na ⁺	-0.23	+2.85	+10.67
5	Ca ²⁺	2Na ⁺	-0.61	+5.58	+20.80
6	-	H ₂ O(l)	0	+0.63	+2.09
7	Ca ²⁺	H ₂ O(l)	-	< 0	< 0

(1) No 6 is calculated from No 2, No 3, No 4 according to Hess's law

(2) No 7 is estimated after analyzing with current data

2.3 Experimental approaches to the temperature effects on adsorption behaviors of SB against Ca^{2+} in aqueous system

2.3.1 Materials

The physical properties of soil materials are listed in Table 2-2. Decomposed granite soil, which is a sandy soil widely distributed in the subsurface throughout Japan, was used as the parent soil of SB in this study. Decomposed granite soil possesses low Atterberg limits and weak adsorption properties (Mo et al., 2020); Kunigel V1, one of the sodium bentonites mined and produced in Japan was used as the bentonite added to the parent soil. The procedures of SB preparation are given in Figure 2.4. Bentonite was added to the decomposed granite soil with a mass proportion of 7.5% compared to the dry mass of SB, which kept propinquity as previous studies (Katsumi, et al., 2008; Takai et al., 2016). The decomposed granite soil was first passed through 2 mm sieve and then oven dried at 110°C, while the bentonite powder was air dried with 7.2% initial moisture content, and the 5% bentonite slurry was prepared by mixing bentonite powder with distilled water at a mass ratio of 1:20 for 20 minutes. To emulate the construction procedures of SB walls on-site, the slurry was first added to the soil to improve workability and mixability. Then, the bentonite powder was added in several times. After all bentonite powder were inputted, the soil mixer continued to run for 5 minutes to ensure uniform mixing. The initial moisture content of mixed SB was controlled at approximately 29%.

Table 2-2 Physical properties of soil materials.

		Bentonite	Dec. granite soil	SB	Method
Particle density	($\text{Mg}\cdot\text{m}^{-3}$)	2.79 ⁽¹⁾	2.65	2.66	JIS A 1202
Plastic limit	(%)	26.6	NP	NP	JIS A 1205
Liquid limit	(%)	522.0	NP	25.0	JIS A 1205
Montmorillonite content	(%)	48 ⁽¹⁾	-	3.6	
Cation exchange capacity	($\text{meq}\cdot\text{g}^{-1}$)	0.732 ⁽¹⁾	-	-	
Na^+ exchange capacity	($\text{meq}\cdot\text{g}^{-1}$)	0.405 ⁽¹⁾	-	-	
Ca^{2+} exchange capacity	($\text{meq}\cdot\text{g}^{-1}$)	0.287 ⁽¹⁾	-	-	

(1) Komine et al., 2009

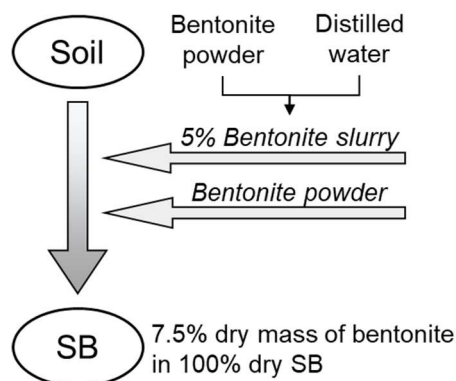


Figure 2.4 SB mixing procedures.

2.3.2 Discontinuous batch test at different temperatures

In this study, batch tests shown in Figure 2.5 were performed with different initial concentrations of CaCl_2 , and fixed adsorbent dosages of bentonite (B), decomposed granite soil (S), and soil-bentonite (SB) respectively. B, S, or SB were added into 250 mL-PP bottles contain 200 mL neutral CaCl_2 , then the bottles were subjected to 200 Hz oscillation at constant temperature conditions using a thermostat shown in Photo 2.1. For some cases where the water contained by soil prior to the test was not 0, the initial concentration and volume of solution were corrected with following two equations:

$$c_0 = c_{\text{initial}} \cdot \frac{V_{\text{initial}}}{V_0} \quad (2.11)$$

$$V_0 = V_{\text{initial}} + \frac{w \cdot m_s}{\rho_w} \quad (2.12)$$

where c_{initial} is the prepared molarities of Ca^{2+} solution ($\text{mmol} \cdot \text{L}^{-1}$); V_{initial} is the volume of solution input into the bottle (L); c_0 is the effective initial molarity of Ca^{2+} ($\text{mmol} \cdot \text{L}^{-1}$); V_0 is the effective initial volume of solution (L); w is the moisture content of soil (%); m_s is the dry mass of soil (g); ρ_w is the density of pure water ($\text{Mg} \cdot \text{m}^{-3}$).

After the end of oscillation, the bottle was left undisturbed for 15 minutes in a water bath controlled at same temperature, the separation between clay and solution was clearly observed. The supernatant in the batch system was then extracted with a syringe, and the supernatant in the syringe was carefully filtrated through $0.2 \mu\text{m}$ filter without squeezing forcefully and moved into a centrifuge tube. The centrifuged tube was then subject to 3000 rpm centrifuge for 10 min and filtrated through $0.2 \mu\text{m}$ filter again. Next, the supernatant was diluted according to the instrument's range of measurement, and 1% volume of $13.5 \text{ mol} \cdot \text{L}^{-1} \text{HNO}_3$ was added to the diluted supernatant to lower the pH to keep Ca^{2+} and Na^+ exist in ionic phase. Last, the molarities of Ca^{2+} and Na^+ in the supernatant were measured by an atomic emission spectrometer (SHIMADZU, ICPE-9800, see Photo 2.2).

The same procedures from oscillation to supernatant extraction were also carried out at same conditions where the adsorbent dosage is 0, the measured concentrations at these cases were treated as the true values of c_{initial} , where the effects of oscillation and evaporation to the mass conservation of the batch system were eliminated.

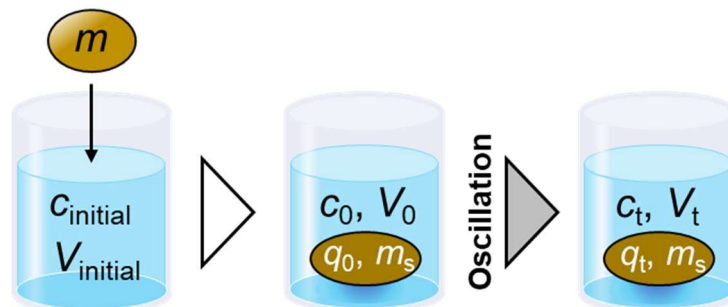


Figure 2.5 Schematic of batch test.



Photo 2.1 Bottle, oscillator, and thermostat for batch test.

Photo 2.2 ICPE-9800 for molarities of Ca^{2+} and Na^{+} measurements.

In a batch system shown in Figure 2.5, the adsorbed/desorbed amounts of Ca^{2+} and Na^{+} can be obtained through mass conservation. Two kinds of calculation were introduced in this study, showing as the following equations:

$$Q_t = (c_0 - c_t) \cdot \frac{V_0}{m_s} \quad (2.13)$$

$$q_t = \frac{c_0 \cdot V_0 - c_t \cdot V_t}{m_s} \quad (2.14)$$

where Q_t and q_t are the adsorbed/desorbed amounts calculated by two methods respectively ($\text{mmol} \cdot \text{g}^{-1}$); c_t is the molarity of bulk solution at the end of test ($\text{mmol} \cdot \text{L}^{-1}$); V_t is the volume of bulk solution at the end of test (L). The Q_t was obtained on the premise that the volume of bulk solution was constant during the test ($V_t = V_0$), the Eq (2.13) is mostly common used in the studies in concerns of adsorption or sorption in liquid phase. The q_t was obtained on the premise that the volume of bulk solution actually decreased during the test ($V_t < V_0$) after the water molecules be retained by montmorillonite. For distinguish, Q_t is called **ordinary ads/des amount**, and q_t is called **modified ads/des amount**.

Q_t and q_t are generally positive values when represent Ca^{2+} adsorbed amounts, because usually $c_t < c_0$ if the Ca^{2+} is adsorbed from the solution (the exception exist in this study). Q_t and q_t are negative values when represent Na^{+} desorbed amounts since $c_0 = 0$. In order to avoid conceptual confusion, a minus sign “−” is added to the Q_t and q_t when they represent desorption amounts (i.e. $-Q_t$ and $-q_t$). In addition, the difference between Q_t and q_t were compared and

their respective scopes of applicability were discussed in this study.

The internal concentration c_{in} ($\text{mol}\cdot\text{L}^{-1}$) characterized the average Ca^{2+} molarity in the interlamellar of montmorillonite was also introduced (Bourg et al., 2003; Kraepiel et al., 1999). As shown in Figure 2.6, the liquids in a batch system contents bentonite are divided into two phases of bulk solution and internal solution. The total amounts of ions are constant in the system, herein a mass conservation stands as:

$$c_{in} \cdot V_{in} + c_t \cdot V_t = c_0 \cdot V_0 + q_0 \cdot m_s \quad (2.15)$$

where c_{in} is the internal Ca^{2+} molarity in the interlamellar ($\text{mmol}\cdot\text{L}^{-1}$); V_{in} is the volume of interlamellar (L); q_0 is the Ca^{2+} amount in the interlamellar prior to the test ($\text{mmol}\cdot\text{g}^{-1}$). The total volume of liquid in the system is constant:

$$V_t + V_{in} = V_0 \quad (2.16)$$

Substitute Eq (2.16) into Eq (2.15), c_{in} can be solved as:

$$c_{in} = \frac{1}{V_{in}} \cdot [c_0 \cdot V_0 - c_t \cdot (V_0 - V_{in}) + q_0 \cdot m_s] \quad (2.17)$$

Also, it is possible to characterize the c_{in} with Ca^{2+} adsorbed amounts Q_t or q_t as:

$$c_{in} = (Q_t + q_0) \cdot \frac{m_s}{V_{in}} + c_t = (q_t + q_0) \cdot \frac{m_s}{V_{in}} \quad (2.18)$$

Table 2-3 summarized the target results of this study, the required values and calculations. The required values except V_{in} is available from batch test. In principle, the V_{in} of per unit bentonite is constant under the same equilibrium conditions, which allows the measurement of V_{in} independent to the batch test. The assessments to the V_{in} are introduced in Subsection 2.3.3.

Table 2-3 Target results of batch test, required values and calculations.

Target results	Required values	Calculations
Ordinary ads/des amount Q_t	c_0, c_t, m_s, V_0	$Q_t = (c_0 - c_t) \cdot V_0 / m_s$
Modified ads/des amount q_t	$c_0, c_t, m_s, V_0, V_{in}$	$q_t = [c_0 \cdot V_0 - c_t \cdot (V_0 - V_{in})] / m_s$
Internal Ca^{2+} molarity c_{in}	$c_0, c_t, V_0, V_{in}, q_0$	$c_{in} = [c_0 \cdot V_0 - c_t \cdot (V_0 - V_{in}) + q_0 \cdot m_s] / V_{in}$

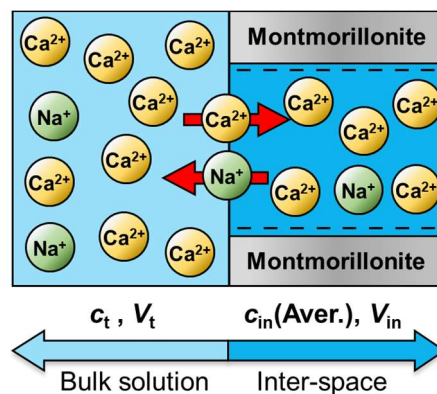


Figure 2.6 Schematic for the bulk solution and internal solution in bentonite batch system.

2.3.2.1 Test conditions for adsorption/desorption kinetics of bentonite

One major premise to analyze the nature of adsorption/desorption is the equilibrium need to be archived in a batch system (Giles et al., 1960; Ng et al., 2017). The equilibrium state will be reached if the time for the interactions between adsorbent and solution is sufficient, and the adsorption/desorption kinetics before the equilibrium are also discussed topics. Dependent on the type of adsorbent, the required time for a batch system to achieve equilibrium varies from minutes to days (Bonilla-Petriciolet et al., 2017; Chen et al., 2023; Liu et al., 2010; S. Gupta & Bhattacharyya, 2011). Considering the bentonite plays the main role in adsorption/desorption of SB, it is important to evaluate the adsorption/desorption kinetics of bentonite, and to determine the time for batch system content bentonite to reach equilibrium state.

Table 2-4 summarized the test conditions for bentonite adsorption/desorption kinetics. The input dosage of bentonite is controlled at 0.75 ± 0.01 g for each batch systems. At two temperature conditions and two initial Ca^{2+} molarities, the oscillations were continued 0 to 72 h. All procedures are in consist with the narration at the beginning of Subsection 2.3.2 (the 0 h oscillation cases also subject to 15 min undisturbed water bath), all cases carried out twice.

Table 2-4 Conditions for adsorption/desorption kinetics of bentonite.

Temperature (°C)	Initial Ca^{2+} molarity (mmol/L)	Oscillation time (h)									
		0	1	3	5	6	8	24	36	48	72
20	0.5		√		√		√	√		√	√
	20	√	√	√		√		√	√	√	√
50	0.5		√			√		√		√	√
	20	√	√	√		√		√	√	√	√

2.3.2.2 Test conditions for adsorption/desorption isotherms of B, S and SB

The test conditions are summarized in Table 2-5. Bentonite and SB batch system is assumed to reach equilibrium state in 24 h. All batch tests in this subsubsection were oscillated for 24 h. Batch tests for bentonite (B), decomposed granite soil (S), and soil-bentonite (SB) were operated independently in order to verify whether bentonite can fully utilize its capability of Ca^{2+} adsorption as SB. The initial Ca^{2+} molarities from 0.5 to 1000 $\text{mmol}\cdot\text{L}^{-1}$ (c_{initial}) were designed considering the wide range of metal ion concentrations in waste leachate (Bradshaw et al., 2013; Kolstad et al., 2004). Four temperatures from 20°C to 50°C were operated.

Several dosages of adsorbents were designed based on the type of adsorbent and c_{initial} . For B, 0.75 ± 0.01 g were added to the batch system when c_{initial} was less than 50 $\text{mmol}\cdot\text{L}^{-1}$, such dosage was enough to generate significant concentration changes, but not sufficient to create suspension that was difficult to separate. When c_{initial} was over 100 $\text{mmol}\cdot\text{L}^{-1}$, the dosage of B increased to 10 ± 0.1 g. Because at such high concentrations, more bentonite is needed to generate measurable adsorbed amount (i.e. if $q_t = 1 \text{ mmol}\cdot\text{g}^{-1}$ is estimated, then 1 g bentonite in 200 mL of 1000 $\text{mmol}\cdot\text{L}^{-1}$ CaCl_2 solution will resulted in a supernatant molarity of Ca^{2+} higher than 995 $\text{mmol}\cdot\text{L}^{-1}$, the accuracy of the calculation results cannot be guaranteed with such a small concentration difference).

Table 2-5 Conditions for batch tests with 24 h oscillation for bentonite (B), decomposed granite soil (S), and soil-bentonite (SB). All cases were triplicated.

Temperature (°C)	Designed initial Ca ²⁺ molarity <i>c</i> _{initial} (mmol·L ⁻¹)													
	0.5	1	5	10	15	20	25	30	40	50	100	200	500	1000
20	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B	B	B	B	B	B	B
30	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B/S/SB	-	-	-	B	B	B	B
40	B/SB	B/SB	B/S/SB	B/SB	B/S/SB	B/SB	B/SB	-	-	-	B	B	B	B
50	B	B	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B/S/SB	B	B	B	B	B	B	B
<i>c</i> _{initial} ≤ 50											<i>c</i> _{initial} ≥ 100			
Adsorbent dosage	B: 0.75 ± 0.01 g; S: 10 ± 0.1 g; SB: Equivalent mass contained 0.75 ± 0.1 g B										B: 10 ± 0.1 g			

For S, the dosage was controlled at 10 ± 0.1 g for all conditions considering the slight adsorption capability of S compare to the B.

For SB, the dosage was designed as 10 g of dry SB which contained equivalent 0.75 g of B. The actual input mass fluctuated according to the measured water content after the mixing procedures (see Figure 2.1), approximately around 12.9 ± 1.0 g.

2.3.3 Assessments to the internal volume V_{in} by free swell test

As introduced in Subsection 2.3.2, the internal volume V_{in} of bentonite is required for the calculations of q_t and c_{in} , and V_{in} can be measured independently at same equilibrium state. The free swell tests correspond to ASTM D5890 (2019) were conducted in order to characterize the V_{in} of bentonite under different CaCl_2 concentrations and temperatures.

The procedures of the free swell test in this study are as follows. The tests were conducted in 100 mL graduated cylinders. Initially, the cylinders and solutions were subjected to target temperatures 24 h. Each cylinder was then filled with solution up to half, and the cylinder was tilted and rotated to wetted the side below 100 mL scale line. Next, 2 g bentonite powder was carefully added to the cylinder using a glass funnel. The powder remained on the funnel was rinsed with the target solution. The cylinder was then topped up to 100 mL, then returned to target temperature for 3 to 6 h (the evaporation was allowed in this step). When there was no bentonite floated on the surface, the cylinder was then refilled to 100 mL with distilled water (to cover the evaporation), and 2 mL silicon oil was added to the top to eliminate further evaporation. The cylinder was left undisturbed for 24 h at target temperature, and then the cylinder was shaken slightly to reduce the free voids at the bottom of cylinder. After another 24 h, the volume of bentonite was obtained from the reading of cylinder, at which the supernatant was also collected and Ca^{2+} molarity was measured.

After all, the internal volume V_{in} of bentonite per unit mass can be approximately calculated by:

$$\frac{V_{in}}{m_s} = \frac{V_{FS}}{m_s} - \frac{1}{\rho_s} \quad (2.19)$$

where V_{in}/m_s is the approximate internal volume per gram ($\text{mL} \cdot \text{g}^{-1}$); V_{FS}/m_s is the free swell volume observed from the test ($\text{mL} \cdot \text{g}^{-1}$); ρ_s ($\text{Mg} \cdot \text{m}^{-3}$) is the particle density of bentonite. Table 2-6 summarized the conditions for free swell test, the temperature and initial Ca^{2+} molarity covered the ranges of batch test.

Table 2-6 Conditions for free swell test.

Temperature (°C)	Designed initial Ca^{2+} molarity ($\text{mmol} \cdot \text{L}^{-1}$)										
	5	10	15	20	25	30	40	50	100	500	1000
20	√	√	√	√	√	√	√	√	√	√	√
30	√	√		√		√			√		√
40	√	√		√		√			√		√
50	√	√	√	√	√	√	√	√	√	√	√

2.4 Results

2.4.1 Adsorption/desorption kinetics of bentonite at different temperatures

In this subsection, the adsorption kinetics of Ca^{2+} and desorption kinetics of Na^+ were characterized with ordinary ads/des amount Q_t because the kinetics of V_{in} were not measured.

The Q_t of Ca^{2+} adsorption kinetics when initial molarity of Ca^{2+} was $0.5 \text{ mmol}\cdot\text{L}^{-1}$ are shown in Figure 2.7 (a). Q_t were observed approximately $0.13 \text{ mmol}\cdot\text{g}^{-1}$ over time, indicating the equilibrium of Q_t was achieved soon after the batch test started.

The Q_t of Ca^{2+} adsorption kinetics when the initial molarity of Ca^{2+} was $20 \text{ mmol}\cdot\text{L}^{-1}$ are shown in Figure 2.7 (b). Initial “pulses” were observed on the profiles. Q_t rapidly exceeded $0.3 \text{ mmol}\cdot\text{g}^{-1}$, continued to increase for hours, and exceeded $0.4 \text{ mmol}\cdot\text{g}^{-1}$. The decreases in Q_t was observed then, and “pulses” ceased 6 h, with Q_t returning to approximately $0.3 \text{ mmol}\cdot\text{g}^{-1}$ at 24 h. Subsequently, Q_t showed slight increase up to 72 h. One possible explanation to the “pulses” is time needed for the changes in V_{in} of bentonite, as the swelling of bentonite is inhibited in solution with high ionic concentration, requiring time to stabilize. At first, the V_{in} was relatively large and allowed more Ca^{2+} to be adsorbed. Accompanied with the decrease of V_{in} , some of the adsorbed Ca^{2+} lost its space in V_{in} and be released. Therefore, considering that the swell of montmorillonite can reach stability within 24 hours in most cases (Ishimori & Katsumi, 2012), the “pulse” of Q_t is unlikely to last over 24 h in other conditions.

Regarding to the equilibrium of Ca^{2+} adsorption. The sight differences between Q_t at initial, at 24 h, and at 72 h shown in Figure 2.7 indicated the process of adsorption was proceeded almost instantaneously after the start of batch test. In that case, 24 h can be approximately considered enough to achieve the equilibrium of Ca^{2+} adsorption.

The temperature effects to the kinetics of Q_t was insignificant when initial Ca^{2+} molarity was $0.5 \text{ mmol}\cdot\text{L}^{-1}$, the profiles of Q_t at 20°C and at 50°C were nearly overlapped in Figure 2.7 (a). In contrast, as shown in Figure 2.7 (b), temperature showed two effects to the profiles of Q_t . The first is the timing of the “pulse” peak arrived faster and the “pulse” decreased faster at 50°C ; The second is the Q_t at 50°C was generally lower than the Q_t at 20°C at same time.

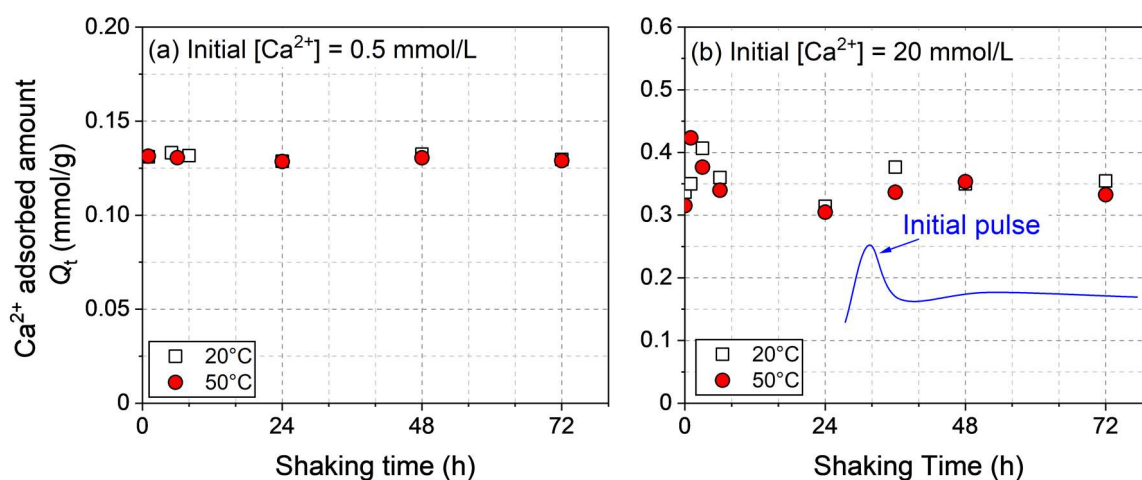


Figure 2.7 Ca^{2+} adsorption (Q_t) kinetics of pure bentonite at two isothermal conditions.

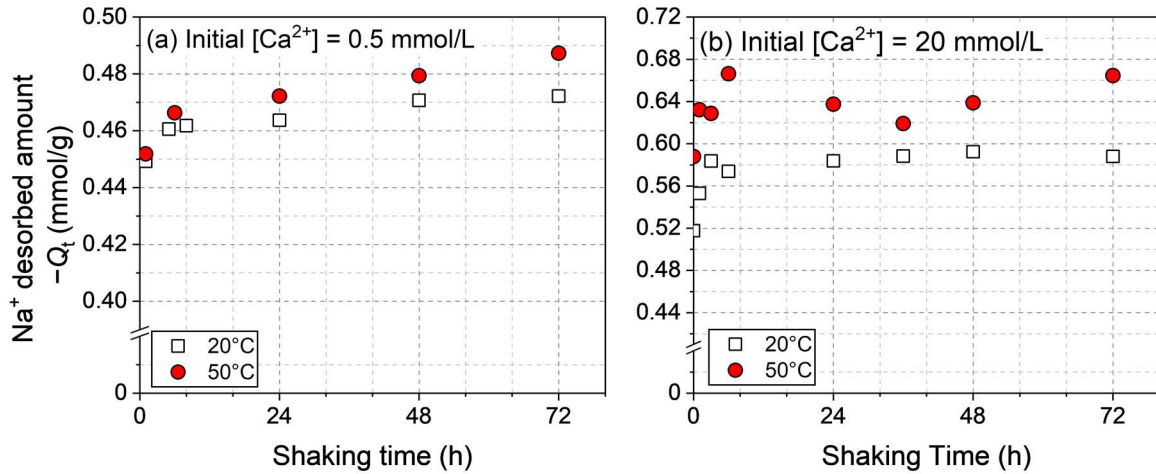


Figure 2.8 Na⁺ desorption ($-Q_t$) kinetics of pure bentonite at two isothermal conditions.

The $-Q_t$ of Na⁺ desorption kinetics when initial molarity of Ca^{2+} $0.5 \text{ mmol} \cdot \text{L}^{-1}$ are shown in Figure 2.8 (a). The $-Q_t$ immediately exceeded $0.44 \text{ mmol} \cdot \text{g}^{-1}$ and showed continuously slight increase until 72 h. This was due to insufficient Ca^{2+} in bulk solution to allow thoroughly ion exchange reaction, and the $-Q_t$ showed more characteristics of leaching behavior that the equilibrium was difficult to be completely achieved in short time (Kato et al., 2021). Still, the increase of $-Q_t$ were slight, from 24 h to 72 h, Na⁺ were further released by approximately $0.02 \text{ mmol} \cdot \text{g}^{-1}$ at 20°C and by approximately $0.03 \text{ mmol} \cdot \text{g}^{-1}$ at 50°C.

The $-Q_t$ of Na⁺ desorption kinetics when initial molarity of Ca^{2+} $20 \text{ mmol} \cdot \text{L}^{-1}$ are shown in Figure 2.8 (b). The $-Q_t$ immediately exceeded $0.50 \text{ mmol} \cdot \text{g}^{-1}$ at 20°C and exceeded $0.58 \text{ mmol} \cdot \text{g}^{-1}$ at 50°C. The profiles of $-Q_t$ became stable after 6 h, while $-Q_t$ exhibited more fluctuations at 50°C than at 20°C. Indicating that ion exchange reaction reached equilibrium faster when Ca^{2+} in bulk solution is sufficient. Therefore, in most cases shown in Table 2-5, 24 h is enough for Na⁺ desorption to achieve equilibrium.

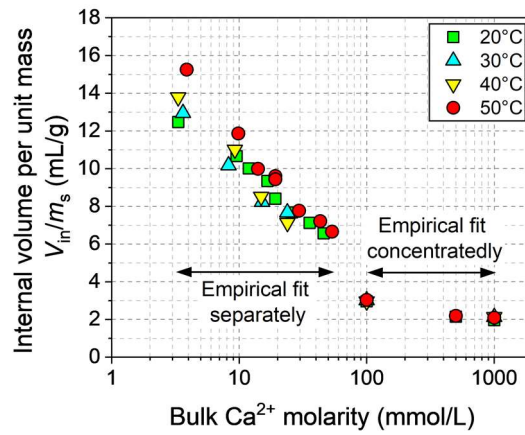
The temperature effects to the kinetics of $-Q_t$ were clearly observed in Figure 2.8. Generally, more Na⁺ were released at 50°C than at 20°C. When Ca^{2+} was insufficient, more Na⁺ were released by leaching behavior (written as reverse of Eq (2.4)) at high temperature; when Ca^{2+} was sufficient, more Na⁺ were released by ion exchange behavior at high temperature. Both the leaching and ion exchange processes that released Na⁺ were indicated to be endothermic ($\Delta H^0 < 0$), which is in consistent with the researches in thermodynamics (McBride, 1994).

2.4.2 Internal volume V_{in} of bentonite at different temperatures

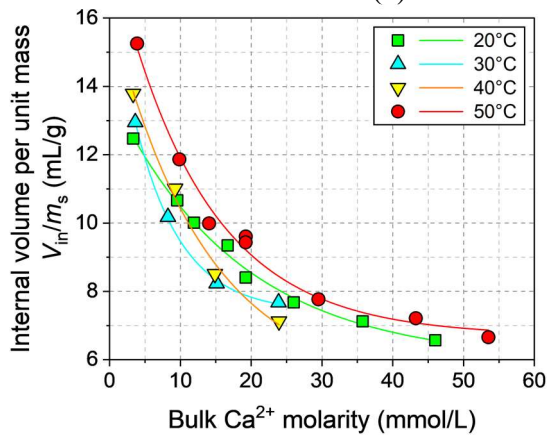
The results of free swell test were given as V_{in}/m_s calculated by Eq (2.19). Figure 2.9 (a) shows the relation between V_{in}/m_s and bulk Ca^{2+} molarity. As the increase of Ca^{2+} molarity, V_{in}/m_s decreased significantly at low Ca^{2+} molarity ($< 100 \text{ mmol} \cdot \text{L}^{-1}$) and decreased slightly when it was higher than $100 \text{ mmol} \cdot \text{L}^{-1}$. The temperature generated measurable differences of V_{in}/m_s at low Ca^{2+} molarity, however, regular temperature dependency was not observed. Temperature changes had little effect on test results at high Ca^{2+} molarity ($\geq 100 \text{ mmol} \cdot \text{L}^{-1}$), where V_{in}/m_s hardly changed from 20°C to 50°C.



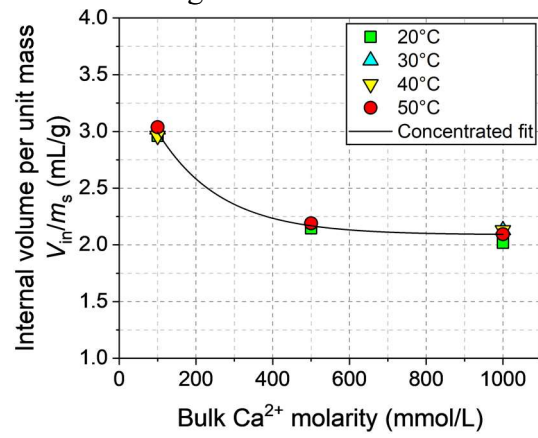
Photo 2.3 Appearances of free swell test.



(a) Measured V_{in}/m_s in entire range



(b) Measured and fitted V_{in}/m_s at low c_t



(c) Measured and fitted V_{in}/m_s at high c_t

Figure 2.9 Results of V_{in}/m_s from free swell test.

Table 2-7 Detail of fitted curves of V_{in}/m_s expressed by c .

No.	T (°C)	Available c_0 (mmol·L ⁻¹)	Empirical Fitted	D of freedom	Chi- square	Sig. level
1	20	(0, 50]	$V_{in} / m_s = 5.96 + 7.90 \cdot \exp(-c / 17.92)$	5	0.11	> 0.995
2	30	(0, 30]	$V_{in} / m_s = 5.19 + 11.13 \cdot \exp(-c / 13.27)$	1	0.18	> 0.900
3	40	(0, 30]	$V_{in} / m_s = 4.37 + 11.88 \cdot \exp(-c / 15.53)$	1	0.02	> 0.950
4	50	(0, 50]	$V_{in} / m_s = 6.70 + 11.47 \cdot \exp(-c / 12.68)$	5	0.03	> 0.995
5	All	[100, 1000]	$V_{in} / m_s = 2.09 + 1.66 \cdot \exp(-c / 164.4)$	6	0.002	> 0.995

Empirical fittings for the relations between bulk Ca^{2+} molarity (c) and internal volume per unit mass (V_{in}/m_s) were operated in order to quantitatively estimate the values of V_{in}/m_s at any c_t after the batch test. Exponential function with natural logarithm as base was chosen as the model function. For $c < 100 \text{ mmol}\cdot\text{L}^{-1}$, the fitting was operated separately for results at different temperatures. For $c \geq 100 \text{ mmol}\cdot\text{L}^{-1}$, the fitting was operated concentratedly for all obtained data. The details of the empirical fitting are summarized in Table 2-7, the fitted curves were tested by Chi-square method (Elderton, 1902), the significance levels of all curves were above 0.90. Notably since the curves were completely empirical, the parameters in the functions had no physical meaning and the obtained function can only apply to the batch tests with correspond ranges of initial Ca^{2+} molarities.

2.4.3 Adsorption and exchange isotherms of B, S, and SB at different temperatures

The results in subsection 2.4.1 indicated that 24 h of oscillation was enough for batch tests to achieve equilibrium in most cases. Therefore, from this subsection, subscript “e” was used for ads/des amounts for 24 h oscillation instead of “t” (i.e. Q_e and q_e). For Ca^{2+} adsorption, the results were given as adsorption isotherms (Q_e or q_e vs bulk Ca^{2+} molarity). For Na^+ desorption, the results were given as exchange isotherms ($-Q_e$ or $-q_e$ vs bulk Ca^{2+} molarity).

2.4.3.1 Ca^{2+} adsorption isotherms

The Q_e of decomposed granite soil (S) is shown in Figure 2.10, the q_e was not calculated because the internal volume in its soil particle can be approximated to 0 compare to the bentonite, hence $q_e = Q_e$. Negative values were observed when bulk Ca^{2+} molarity was lower than $5 \text{ mmol}\cdot\text{L}^{-1}$, indicating the S contained a certain amount of Ca^{2+} (ads) prior to the batch test. Those Ca^{2+} (ads) were released as the reverse of reaction showed in Eq (2.1) because of redundant products. Q_e became positive values as the increase of bulk Ca^{2+} molarity, and became stable when bulk Ca^{2+} molarity exceeded $10 \text{ mmol}\cdot\text{L}^{-1}$. All the observed Q_e of S were lower than $0.01 \text{ mmol}\cdot\text{g}^{-1}$ ($0.4 \text{ mg}\cdot\text{g}^{-1}$) in the range showed in the Figure. Temperature showed insignificant effect to the Q_e of S, where Q_e were observed slightly higher when temperature was raised from 20°C to 50°C .

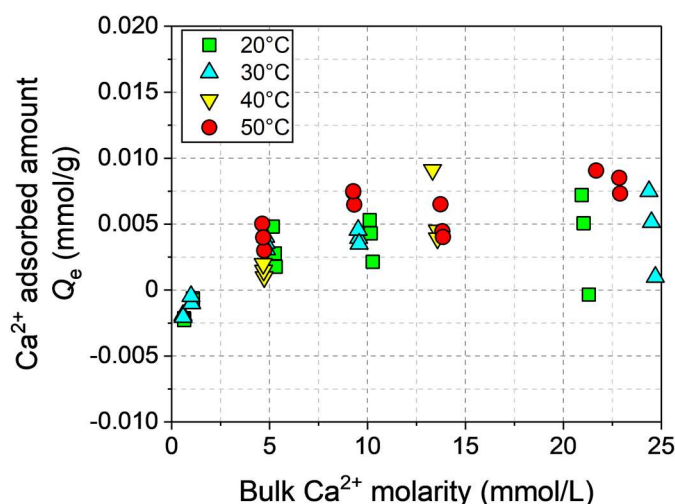


Figure 2.10 Ca^{2+} adsorption (Q_e) of S at different temperatures.

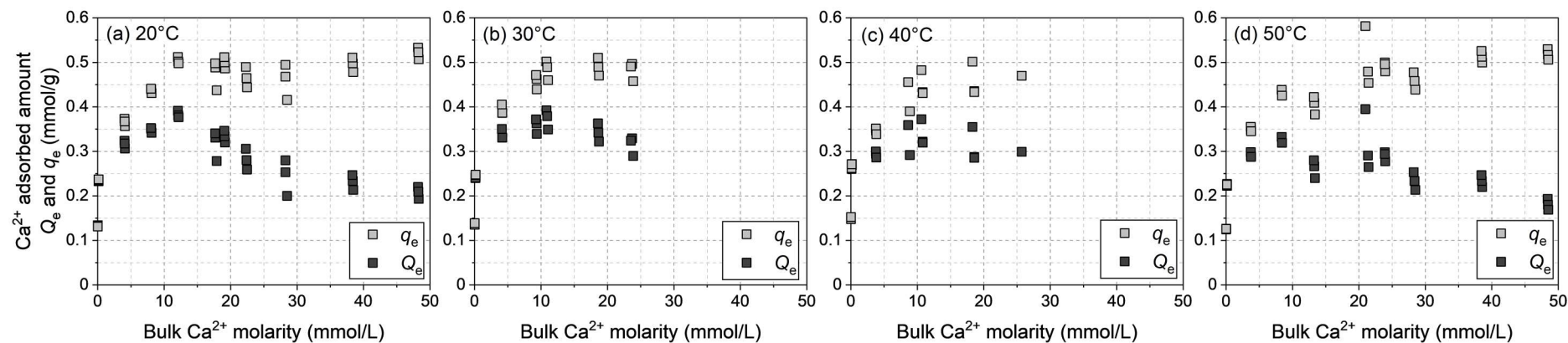


Figure 2.11 Ca^{2+} adsorption isotherms of pure bentonite for bulk Ca^{2+} molarities (c_i) less than $50 \text{ mmol}\cdot\text{L}^{-1}$.

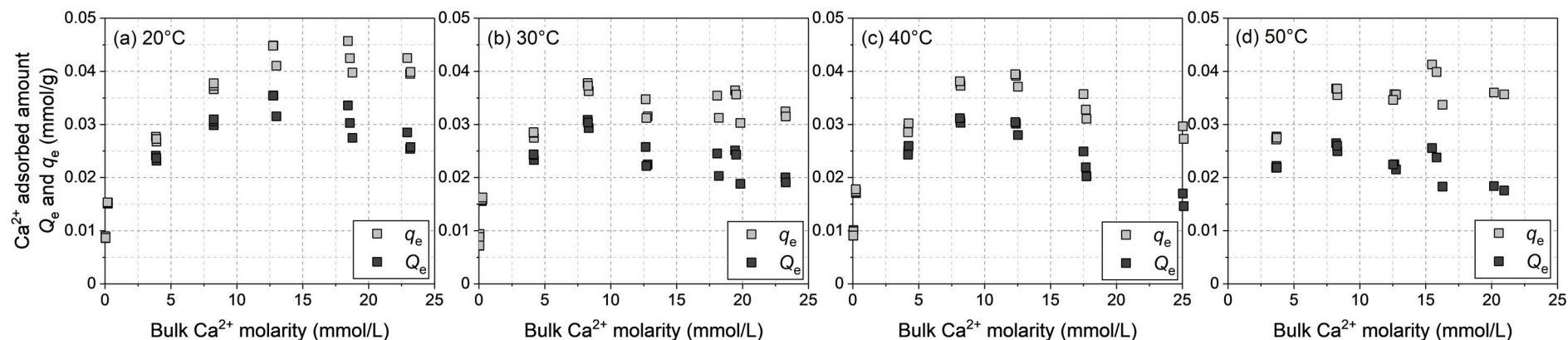


Figure 2.12 Ca^{2+} adsorption isotherms of SB for bulk Ca^{2+} molarities (c_i) less than $25 \text{ mmol}\cdot\text{L}^{-1}$.

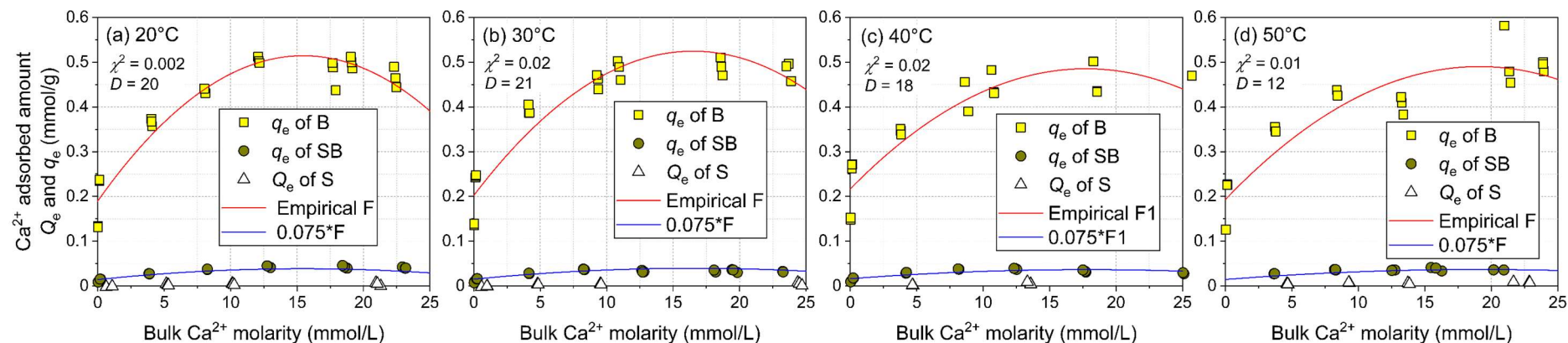


Figure 2.13 Comparing Ca^{2+} adsorption isotherms q_e between pure bentonite and SB.

Figure 2.11 shows the Q_e and q_e of pure bentonite (B) for bulk Ca^{2+} molarities less than $50 \text{ mmol}\cdot\text{L}^{-1}$. The values of Q_e always lower than the values of q_e , and the differences between them increased as the increase of bulk Ca^{2+} molarity. When bulk Ca^{2+} molarity exceeded a certain value, the profiles of Q_e and q_e showed different trends. For example, in Figure 2.11 (a), Q_e and q_e were nearly identical when bulk Ca^{2+} molarity was less than $1 \text{ mmol}\cdot\text{L}^{-1}$, started to exhibit significant difference in values at approximately $5 \text{ mmol}\cdot\text{L}^{-1}$; Q_e was observed to decline significantly and continuously when bulk Ca^{2+} molarity exceeded $12 \text{ mmol}\cdot\text{L}^{-1}$ while the profile of q_e exhibited slightly trend of decrease, but increase again when bulk Ca^{2+} molarity exceeded $30 \text{ mmol}\cdot\text{L}^{-1}$. When Ca^{2+} molarity closed to $50 \text{ mmol}\cdot\text{L}^{-1}$, q_e was higher than twice as much as Q_e , meanwhile the calculated V_{in} for 0.75 g bentonite in the batch system was less than 5 mL, which was less than 2.5% of the V_0 . Such differences between Q_e and q_e indicated that when the calculation of bentonite adsorption based on mass conservation of batch system was proceeded, the ignorance of tiny volume changes of bulk solution when bulk solution is not very dilute (at least for $\text{Ca}^{2+} > 5 \text{ mmol}\cdot\text{L}^{-1}$) would highly underestimated the adsorption capabilities of bentonite.

The profiles of Q_e and q_e in Figure 2.11 (b), (c), and (d) maintained similar characteristics when temperature was changed. However, the timings of Q_e started to decrease and of q_e restarted to increase were shifted leftward as the temperature increased. Comparing Figure 2.11 (a) and (d), 20°C and 50°C , the bulk Ca^{2+} molarity for Q_e started to decrease shifted from around $12 \text{ mmol}\cdot\text{L}^{-1}$ to less than $10 \text{ mmol}\cdot\text{L}^{-1}$ and for q_e restarted to increase shifted from approximately $30 \text{ mmol}\cdot\text{L}^{-1}$ to less than $20 \text{ mmol}\cdot\text{L}^{-1}$.

Figure 2.12 shows the Q_e and q_e of SB for bulk Ca^{2+} molarities less than $25 \text{ mmol}\cdot\text{L}^{-1}$. The differences between Q_e and q_e of SB were similar to those of B. These differences demonstrated the importance of accurate measurement of V_t when evaluating the adsorption of bentonite and soil-bentonite. In addition, the timing of Q_e started to decrease also shifted leftward as the temperature increased.

The values of q_e between batch systems of bentonite and SB are compared in Figure 2.13. The q_e of B were empirically fitted in the Figure in order to compare with the q_e of SB, notably the quantitative comparison was the only reason for those fittings, and the modelling of q_e was discussed in section 2.5. The mixing procedures shown in Figure 2.4 ensured 7.5% solid mass of SB was made up by bentonite, herein the adsorption capability of SB should around 7.5% of pure bentonite (the adsorption of S is too weak comparing to the bentonite). The comparison was operated by multiplied the fitted curve with 0.075, and the correlations between q_e of SB and calculated curves were tested by Chi-square method (Elderton, 1902). The test between calculated curves q_e of SB resulted in significant levels higher than 0.99, indicated that the calculated values were highly correlated with the measured q_e of SB.

The results verified that there are no interactions between soil and bentonite that significantly interference with adsorption behaviors, bentonite can fully utilize its adsorption capability as SB regardless the temperature change from 20°C to 50°C . This also indicated that the mixing procedures shown in Figure 2.4 ensured the uniformity of SB, for q_e of SB in all cases were approximately 7.5% of q_e of B under the same test conditions. Therefore, the adsorption behaviors of SB can be characterized by the adsorption behaviors of pure bentonite.

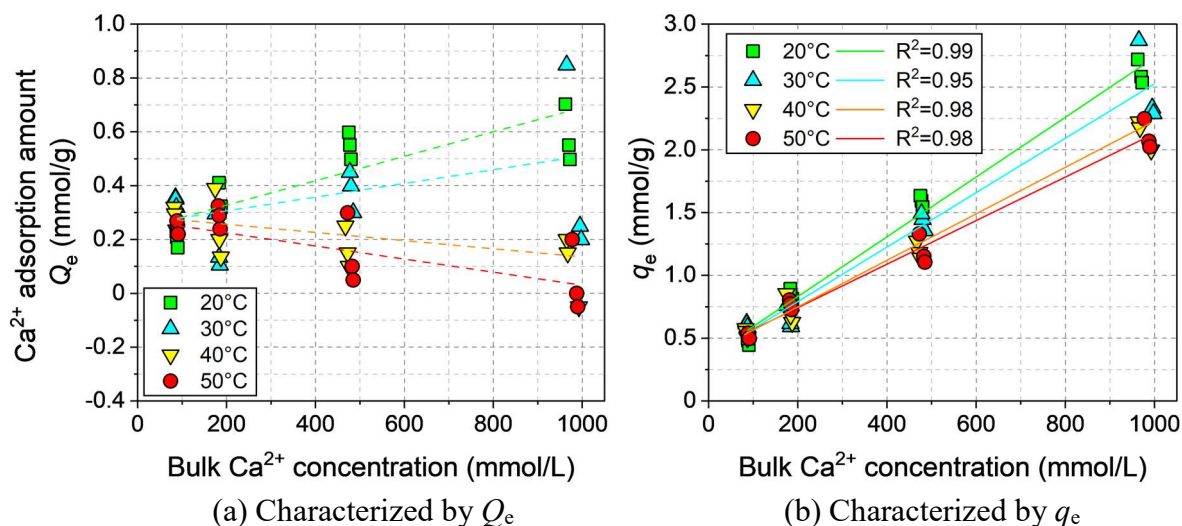
Figure 2.14 Ca^{2+} adsorption isotherms of pure bentonite at high concentration cases.

Table 2-8 Parameters of liner fitting shown in Figure 2.14 (b).

Temperature (°C)	Slope $\times 10^3$ ($\text{L}\cdot\text{g}^{-1}$)	Intercept ($\text{mmol}\cdot\text{g}^{-1}$)	R^2
20	2.38	0.355	0.99
30	2.17	0.358	0.95
40	1.85	0.380	0.98
50	1.73	0.397	0.98

Figure 2.14 shows the Q_e and q_e of pure bentonite (B) for initial bulk Ca^{2+} molarities from 100 to 1000 $\text{mmol}\cdot\text{L}^{-1}$. The differences between Q_e and q_e increased further as the increase of bulk Ca^{2+} molarities. In Figure 2.14 (a), the profiles of Q_e differed as temperature changing, where Q_e kept increasing at 20°C but lacked monotonicity at 30°C, 40°C and 50°C. Furthermore, some counter-intuitive results were observed at 40°C and 50°C, where the Q_e were observed as negative values. The bulk Ca^{2+} molarities at the end of those counter-intuitive cases were measured even higher than their initial molarities. If Q_e is treated as the correct calculation for adsorption in bentonite batch system, then this result means when temperature is high enough, after a certain threshold of bulk Ca^{2+} molarity, bentonite will begin to release Ca^{2+} which will further increase the Ca^{2+} amount in bulk solution.

In Figure 2.14 (b), the profiles of q_e were similar at different temperatures. q_e kept increasing as the increase of bulk Ca^{2+} molarities. The temperature effects to q_e became more and more significant as the bulk Ca^{2+} molarities increased, less q_e were observed at higher temperatures. The profiles of q_e were well fitted by linear model and the related parameters are summarized in Table 2-8. The fitted slopes decreased as the temperature increased, indicated the adsorption of Ca^{2+} became unfavorable. The fitted intercepts increased as the temperature increased, ranged from 0.355 to 0.397 $\text{mmol}\cdot\text{g}^{-1}$, equivalently 0.710 to 0.794 $\text{meq}\cdot\text{g}^{-1}$. Comparing the values of intercepts and the cation exchanged capacity (CEC) of the bentonite used in this study which was reported as 0.732 $\text{meq}\cdot\text{g}^{-1}$ (Komine, 2004). There is a possibility that those intercepts are intrinsically related to the CEC of bentonite.

Overall, the results of Ca^{2+} adsorption isotherms shown in Figure 2.11, Figure 2.12, and

Figure 2.14 indicated that Q_e and q_e were identical only when the bulk Ca^{2+} concentration were less than $1 \text{ mmol}\cdot\text{L}^{-1}$. Otherwise, Q_e and q_e showed significant differences. In some cases, shown in Photo 2.4, the volume change of bulk solution can even be observed visually. Therefore, the volume change of bulk solution should be carefully considered and calculated when batch test was operated, the modified adsorbed amount q_e were more accurate than ordinary adsorbed amount Q_e when characterizing the adsorption capabilities.

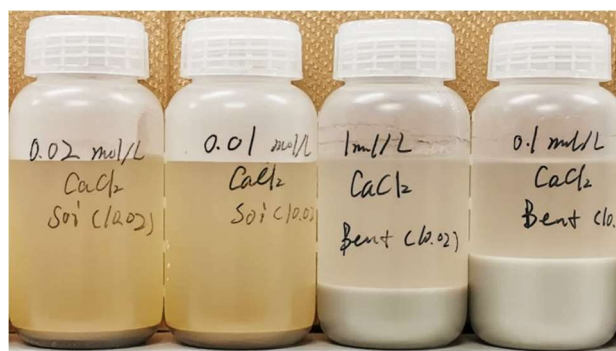


Photo 2.4 Batch systems 15 min after the end of oscillation, the separation of supernatant, and change of bulk volumes in bentonite batch system were observed.

2.4.3.2 Na^+ exchange isotherms

The $-Q_e$ ($\mu\text{mol}\cdot\text{g}^{-1}$) of decomposed granite soil (S) is shown in Figure 2.15, and $-q_e = -Q_e$ for non-swell soil particles of S. Positive values of $-Q_e$ were observed throughout the range of bulk Ca^{2+} molarity, indicating the S contained a certain amount of Na^+ (ads) prior to the batch test. The $-Q_e$ increased as the increase of bulk Ca^{2+} molarity. The changes of temperature from 20°C to 50°C showed positive effects to the Na^+ desorption, $-Q_e$ were observed higher at higher temperatures. Indicating that the ion exchange in S is also an endothermal process ($\Delta H^0 < 0$). All the observed $-Q_e$ were less than $2 \mu\text{mol}\cdot\text{g}^{-1}$ ($0.046 \text{ mg}\cdot\text{g}^{-1}$) in the range of bulk Ca^{2+} molarity showed in the figure. Hence the ion exchange behavior of S was unlikely to affect the behavior of SB.

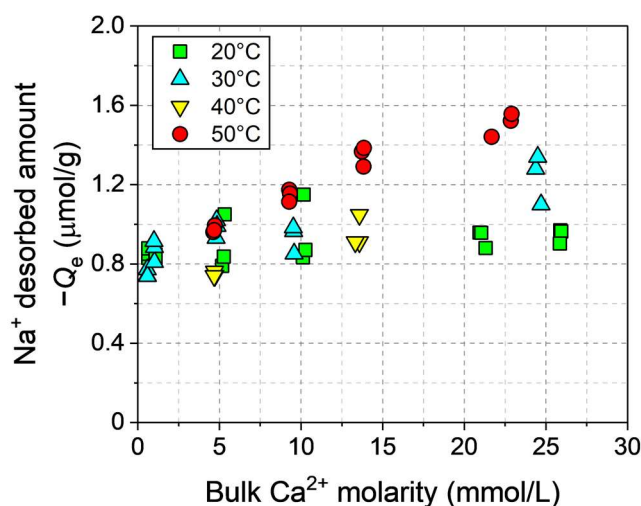


Figure 2.15 Na^+ desorption ($-Q_e$) of S at different temperatures.

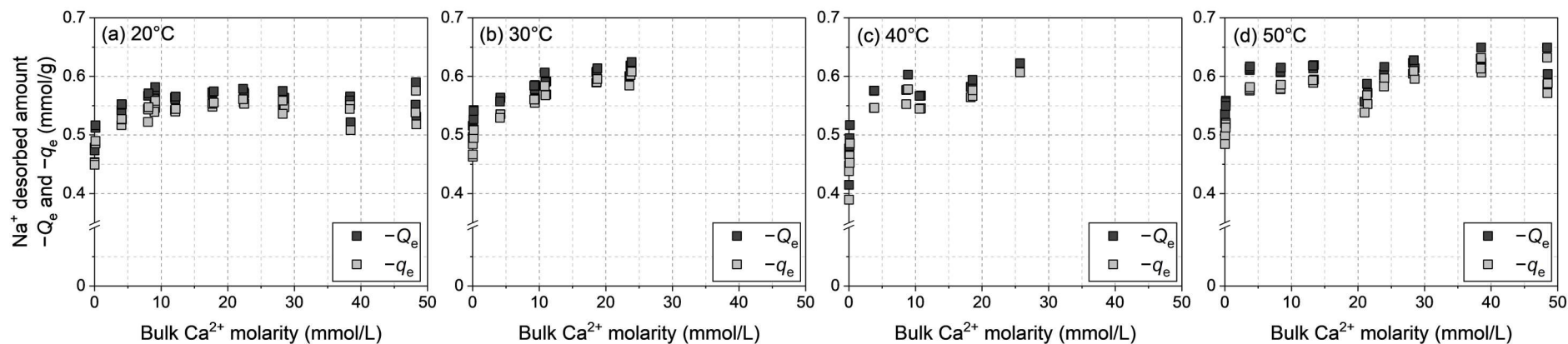


Figure 2.16 Na⁺ exchange isotherms of pure bentonite for bulk Ca²⁺ molarities (c_i) less than 50 mmol·L⁻¹.

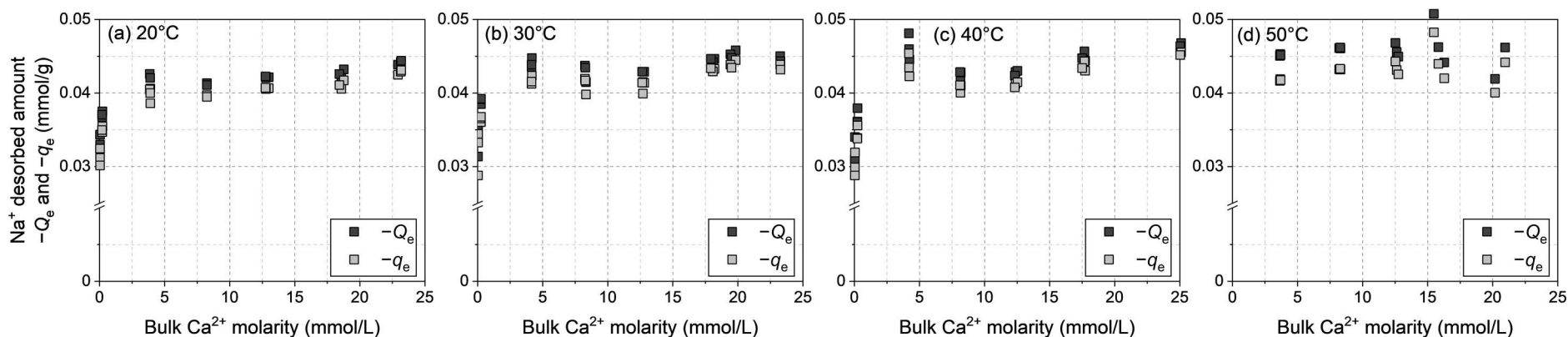


Figure 2.17 Na⁺ exchange isotherms of SB for bulk Ca²⁺ molarities (c_i) less than 25 mmol·L⁻¹.

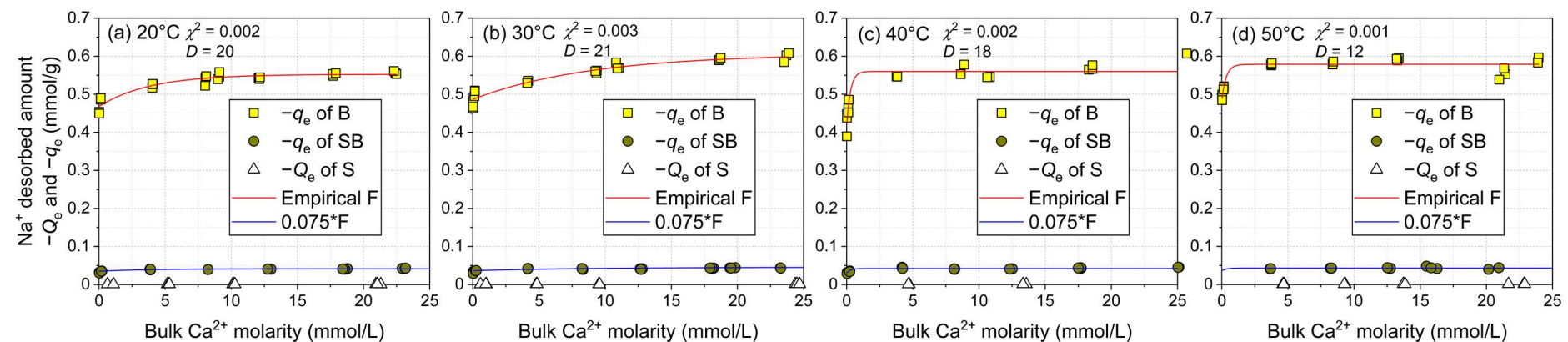


Figure 2.18 Comparing Na⁺ exchange isotherms ($-q_e$) between pure bentonite and SB.

Figure 2.16 and Figure 2.17 show the exchange isotherms of Na^+ of pure bentonite and SB where the desorbed amounts were characterized by $-Q_e$ and $-q_e$. The profiles of $-Q_e$ and $-q_e$ have same characteristics with apparent initial values that gradually increase before plateauing. The values of $-Q_e$ were always slightly higher than the values of $-q_e$, suggesting that neglecting small volume changes in the bulk solution could lead to slight overestimations of the desorption amounts of Na^+ from bentonite.

The values of $-q_e$ of pure bentonite and SB are compared in Figure 2.18, the comparison was operated the same as the way shown in Figure 2.13 and the results of Chi-square tests were given in the figure. The $-q_e$ of SB of all cases also were approximately 7.5% of $-q_e$ of B under the same test conditions.

Figure 2.19 shows the Na^+ exchange isotherms ($-q_e$) at different temperatures, with the x-axis using both linear scale and logarithmic scale. In the wide range of bulk Ca^{2+} molarity, $-q_e$ only varied slightly, remaining below $0.8 \text{ mmol}\cdot\text{g}^{-1}$. The profiles of $-q_e$ in four temperatures suggested that the release of major of exchangeable Na^+ were achieved when bulk Ca^{2+} molarity was very low ($< 0.1 \text{ mmol}\cdot\text{L}^{-1}$) and increasing bulk Ca^{2+} molarity had limited effect on further Na^+ desorption.

Basically, $-q_e$ increased as the temperature increased. The temperature effects to the $-q_e$ observed in this study were consistent with the related thermodynamics studies that Na^+ desorption by ion exchange is an endothermal process (Gilbert & Van Bladel, 1970; Laudelout et al., 1968). Temperature dependency on Na^+ desorption was more significant when bulk Ca^{2+} molarity was lower than $50 \text{ mmol}\cdot\text{L}^{-1}$, where differences approximately to $0.05 \text{ mmol}\cdot\text{g}^{-1}$ could be found between $-q_e$ at 20°C and at 50°C . However, when the bulk Ca^{2+} molarity was higher than $100 \text{ mmol}\cdot\text{L}^{-1}$, the temperature effects became insignificant. The decrease in significant level of temperature effects to Na^+ desorption as the increase of the bulk Ca^{2+} molarity could be explained by the limited amounts of Na^+ presents in montmorillonite. More Na^+ were remained in montmorillonite when the bulk Ca^{2+} molarity was low, increase in temperature can promote the endothermic process and release more Na^+ . While less Na^+ were remained when bulk Ca^{2+} molarity was high, and the temperature effects were limited.

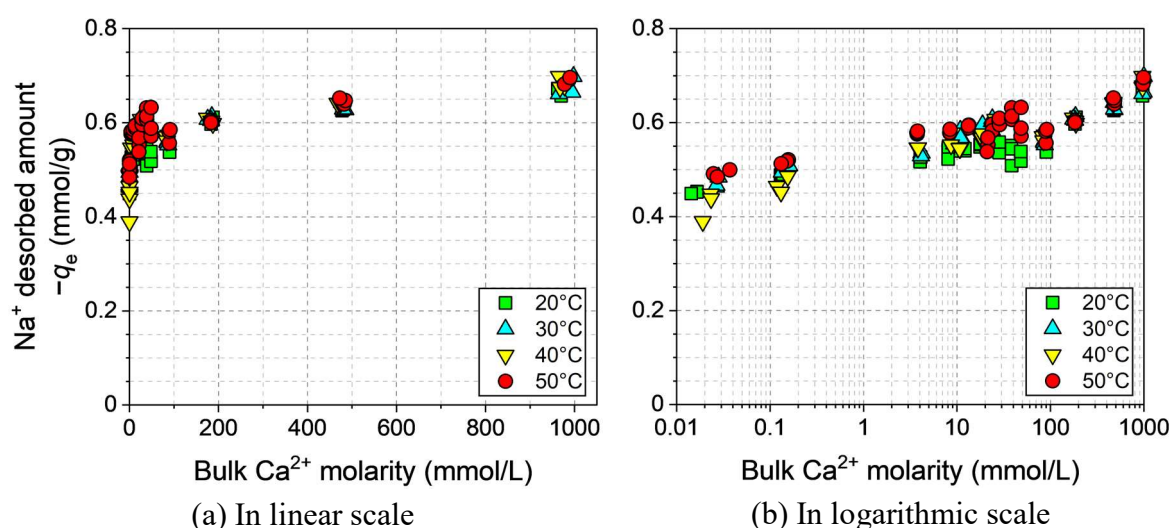


Figure 2.19 Na^+ exchange ($-q_e$) isotherms at different temperatures

2.4.4 Internal Ca^{2+} molarity (c_{in}) in bentonite and SB batch systems

After the modified ads amount q_e and internal volume per unit mass V_{in}/m_s were given, the internal Ca^{2+} molarity c_{in} ($\text{mmol}\cdot\text{L}^{-1}$) can be obtained as (or by Eq (2.17)):

$$c_{\text{in}} = (q_e + q_0) \cdot \frac{m_s}{V_{\text{in}}} \quad (2.20)$$

$$c_{\text{in}} = \left(\frac{q_e}{n_{\text{bent.}}} + q_0 \right) \cdot \frac{m_s}{V_{\text{in}}} \quad (2.21)$$

where $n_{\text{bent.}}$ is the mass ratio of bentonite in dry SB ($= 7.5\%$); q_0 was treated the same as the Ca^{2+} exchange capacity of bentonite ($= 0.144 \text{ mmol}\cdot\text{g}^{-1}$). Eq (2.20) and Eq (2.21) are applied to batch systems of B and SB respectively. Notably c_{in} is the average molarity of entire space of what is treated to be the montmorillonite interlamellar space in this study.

Figure 2.20 shows the relations between c_{in} and bulk Ca^{2+} molarity in this study. The profiles of c_{in} for B and for SB basically matched to each other, which is the consequence of the comparison shown in Figure 2.13. This result implied that in batch systems of B and of SB, the bentonite was approximately in same equilibrium state as long as the bulk Ca^{2+} molarity was the same. Therefore, in this subsection, no more distinction will be made between c_{in} of B and c_{in} of SB.

The profiles of c_{in} in Figure 2.20 increased monotonically as bulk Ca^{2+} molarity increased. Indicating the ionic density in the internal space and the tendency of one Ca^{2+} been adsorbed into the internal space were kept increasing as the increased of bulk concentration. The values of c_{in} were always higher than bulk Ca^{2+} molarity also suggested the unchanged nature of bentonite to attract the Ca^{2+} in the bulk solution. Otherwise, the internal solutions would be lighter than the bulk solutions, and bentonite may float on the liquid surface, which did not occur.

According to the profiles of c_{in} , it can be verified that the decreases in profiles of q_e shown in Figure 2.10 and Figure 2.11 were predominantly attributed to the rapid volume changes in corresponding bulk Ca^{2+} molarities shown in Figure 2.9. The mechanism for the decrease of q_e at some bulk concentrations should be appropriately explained as the bentonite lost its space to contain more Ca^{2+} rather than lost its nature of attraction to the Ca^{2+} .

Figure 2.21 shows the temperature effects to the c_{in} . When the bulk Ca^{2+} molarity was lower than $50 \text{ mmol}\cdot\text{L}^{-1}$, in Figure 2.21 (a), the temperature effects were relatively insignificant between 30°C and 40°C for their values were very close. However, it could be clearly observed that c_{in} at 20°C were basically higher than c_{in} at 50°C . When the bulk Ca^{2+} molarity was higher than $50 \text{ mmol}\cdot\text{L}^{-1}$, in Figure 2.21 (b), the profiles of c_{in} as well as the temperature effects were analogous to the results of q_e shown in Figure 2.14 (b). The analogousness between c_{in} and q_e when bulk concentration was high could be inferred be attributed to the stabilized internal volumes V_{in} . The observed c_{in} in wide a range exhibited approximately linear correlations with bulk Ca^{2+} molarities, the temperature effects to c_{in} also became more and more significant as the bulk Ca^{2+} molarities increased, and c_{in} were observed decreased as the temperature increased.

Therefore, the processes transferring Ca^{2+} from the bulk solution into the internal space of

montmorillonite, the superposition of adsorption and inhibition of swell, exhibited characteristics of exothermal when characterized by the average Ca^{2+} molarity (c_{in}) in this study.

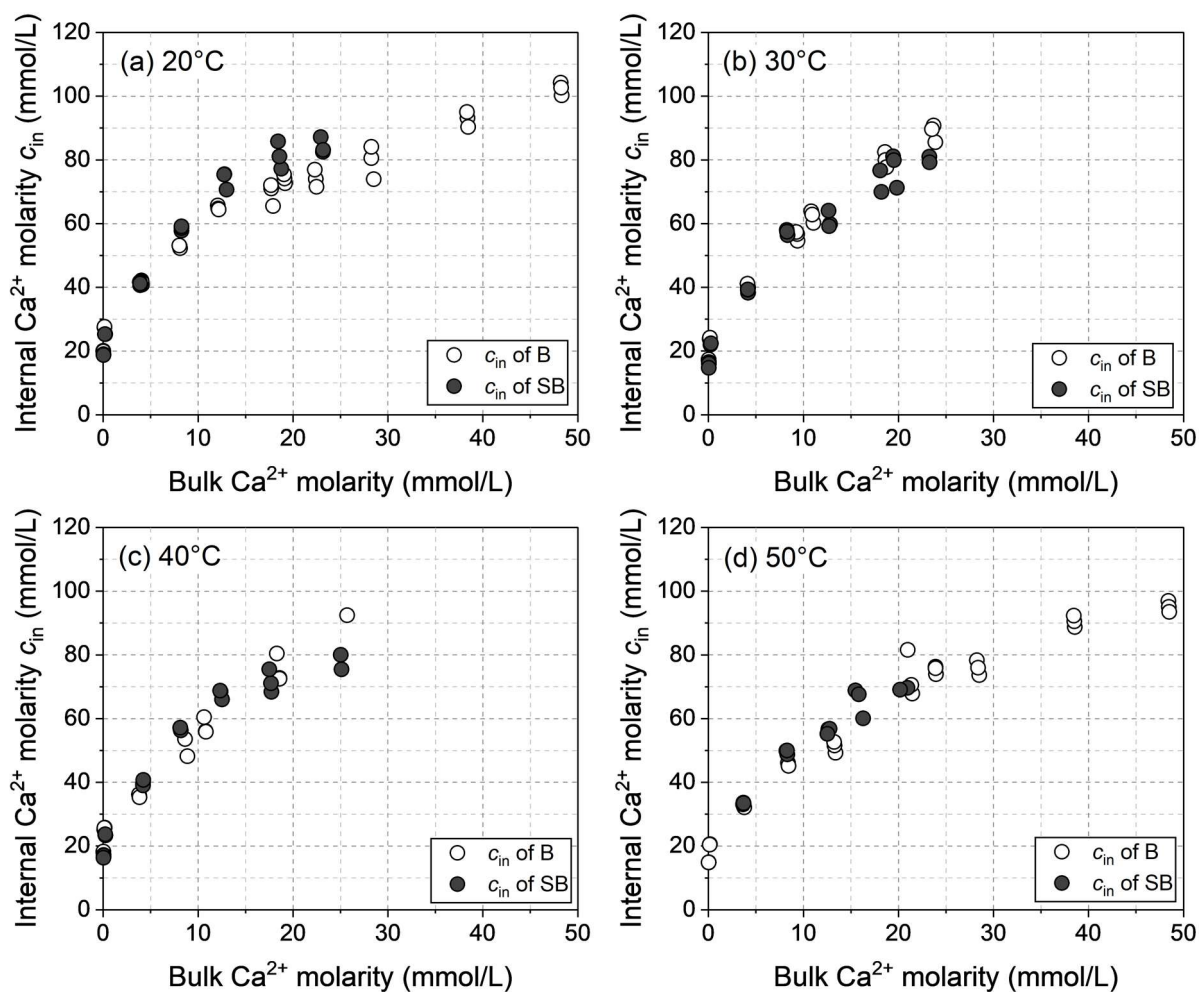


Figure 2.20 Relations between internal Ca^{2+} molarity (c_{in}) and bulk Ca^{2+} molarity (c_{t}).

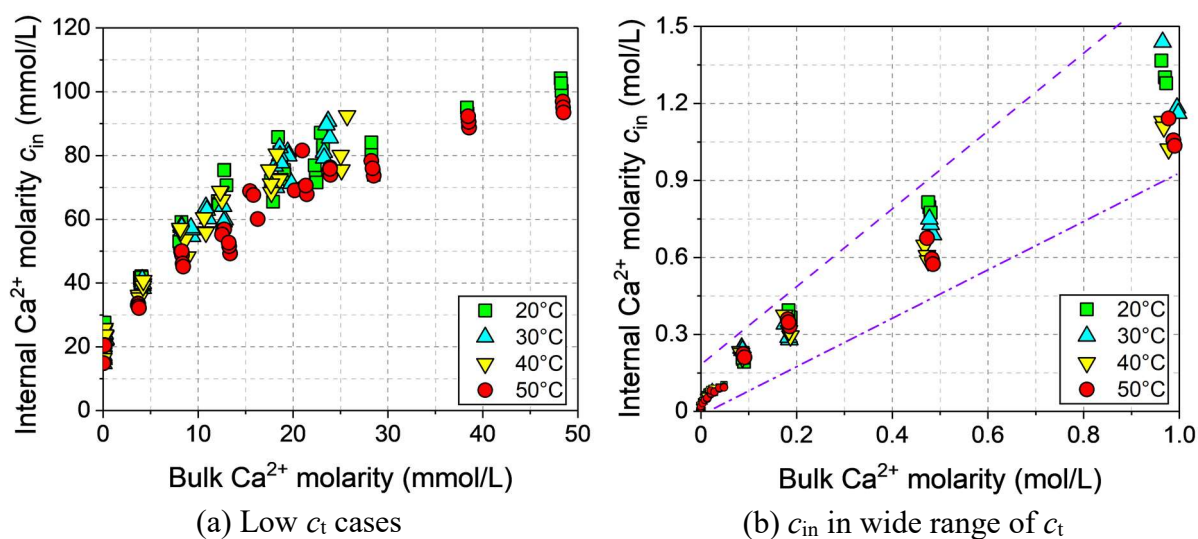


Figure 2.21 Relations between c_{in} and c_{t} at different temperatures.

2.5 Discussion

2.5.1 Interpretations to the systematic errors of adsorption/desorption amounts

In this study, the results have showed in batch systems contained bentonite, the volume change of bulk solution need be considered to ensure the accuracy of the calculated ads/des amounts. However, the results also showed in some cases, the volume change only generated very tiny differences to the calculation results. Hence it is necessary to compare the differences between q_e and Q_e in principle. The differences between q_e and Q_e are defined as the systematic error of ads/des amounts in this subsubsection.

For Ca^{2+} adsorption, recalling Eq (2.13) and (2.14), the systematic error can be obtained as:

$$q_e - Q_e = c_t \cdot \frac{V_0 - V_t}{m_s} = c_t \cdot \frac{V_{in}}{m_s} \quad (2.22)$$

Substitute the empirical model used in Table 2-7 to characterize the V_{in}/m_s into Eq (2.22), the systematic error of adsorption can be approximated as a function of c_t

$$q_e - Q_e = c_t \cdot (i_1 \cdot e^{-c_t/i^*} + i_2) \quad (2.23)$$

where i_n and i^* are numerical parameters. The exponential term in Eq (2.23) converges to 0 at high concentrations, and there will be a systematic error proportional to c_t . At very dilute concentrations, the values of c_t are approximately to zero and the error can be neglect.

A schematic drawing is given in Figure 2.22 to show the differences between q_e and Q_e along with c_t . The systematic error of adsorption was categorized into four types based on different ranges of c_t according to the results shown in Figure 2.10. In range (I), q_e and Q_e are nearly identical. In range (II), observable systematic error occurs to the value, while the profiles of q_e and Q_e remain the same. In ranges (III) and (IV), systematic errors are significant, and the profiles obtained from the two calculations may show different trends.

Therefore, in ranges (I) and (II), the calculation of Q_e can characterize the adsorption isotherm characteristics, but the accurate values can only be ensured in range (I). In ranges (III) and (IV), the calculation of Q_e failed to characterize the adsorption behaviors of bentonite, and the volume change in the batch system must be considered.

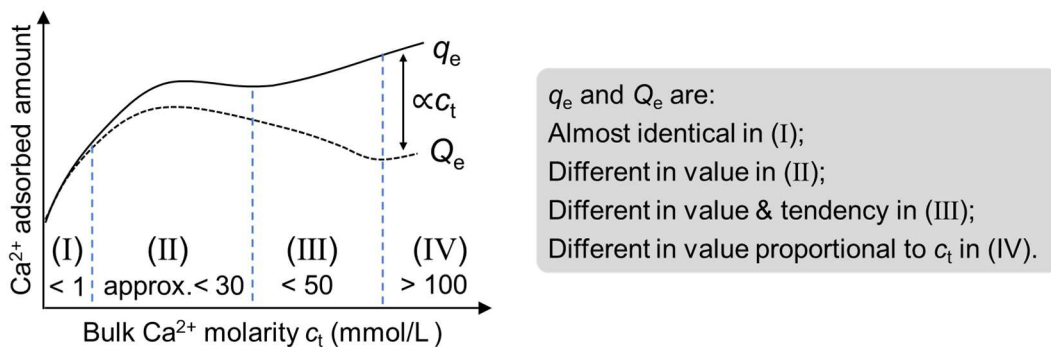


Figure 2.22 Difference between Q_e and q_e of Ca^{2+} adsorption related to bulk Ca^{2+} molarity.

For Na^+ desorption, since $c_0 = 0$, the calculations of $-q_e$ and $-Q_e$ were simplified as:

$$-q_e = \frac{c_t(\text{Na}^+) \cdot V_t}{m_s} \quad (2.24)$$

$$-Q_e = \frac{c_t(\text{Na}^+) \cdot V_0}{m_s} \quad (2.25)$$

where $c_t(\text{Na}^+)$ refers to the molarity of Na^+ in bulk solution. The results in Figure 2.17 have showed that the systematic error of desorption was very small, hence $-q_e$ and $-Q_e$ are compared by division:

$$\frac{-q_e}{-Q_e} = \frac{V_0 - V_{in}}{V_0} \quad (2.26)$$

Apparently, the systematic error of desorption depends on the volume change of the bulk solution, specifically the swelling of bentonite. Therefore, the accuracy of $-Q_e$ can be ensured as long as the dosage of input bentonite is low enough (i.e. 0.75 g in 200 mL), and the systematic error should be corrected based on the volume change of bulk solution when the dosage is very high (i.e. 10 g in 200 mL).

2.5.2 Interpretations to the internal Ca^{2+} molarity (c_{in}) and the equilibrium state

Subsection 2.4.4 has revealed that at the equilibrium states of batch systems, the internal Ca^{2+} molarity was significantly correlated with the bulk Ca^{2+} molarity and indicated the nature of bentonite attracting Ca^{2+} from bulk solution. Suggesting that although the distribution of cations in the interlayer space of bentonite is not uniform in reality (J. Hunter, 1981; McBride & Baveye, 2002), it is practicable to treat the solute and solvent in the internal space as an equivalent internal solution with molarity different to the bulk solution when describing the interaction between bentonite and solution macroscopically. Naturally, the equivalent internal solution possesses equivalent chemical properties. This subsection will explore how these properties can be used to characterize the equilibrium state in bentonite and SB batch systems.

Since the internal solution was assumed, the adsorption of Ca^{2+} becomes the process that transfer the bulk solution into the internal solution. In that case, the reaction for the Ca^{2+} been adsorbed could be equivalently written as:



where $\text{Ca}^{2+}(in.aq)$ is the phase of the internal solution ($\text{mol} \cdot \text{L}^{-1}$); The reactants and products in the chemical formula are both in solution phase, hence the chemical equilibrium constant K_e can be easily obtained as:

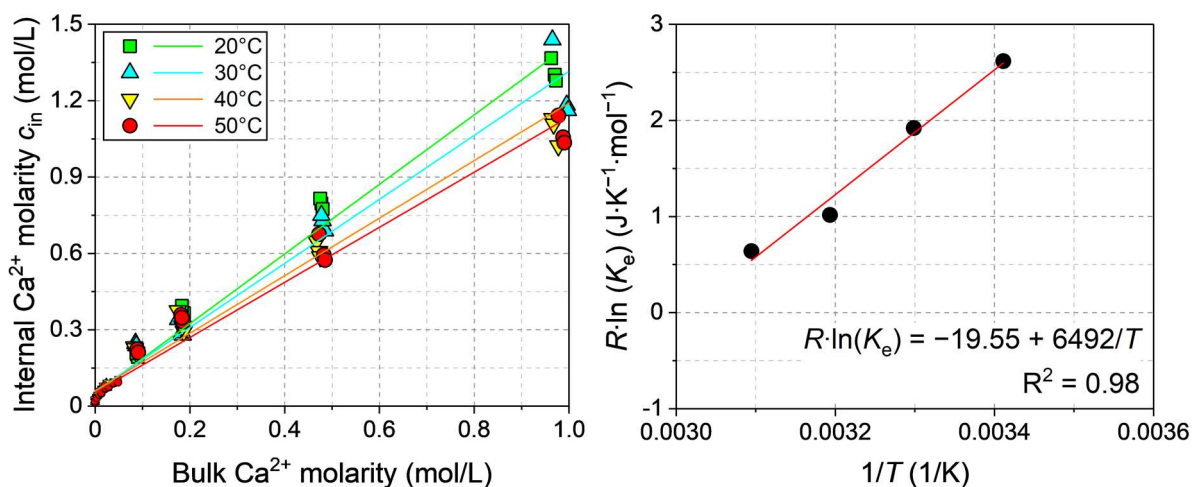
$$K_e = \frac{[\text{Ca}^{2+}(in.aq)]}{[\text{Ca}^{2+}(aq)]} = \frac{c_{in}}{c_t} \quad (2.28)$$

For a given chemical reaction in solution phase, the value K_e only depends on temperature (Engel & Reid, 2019). So, Eq (2.28) suggests that at the same temperature, c_{in} and c_t should

have a linear correlation to each other at the equilibrium state in principle, which provides a sufficient reason to operate linear fitting in relations between c_{in} and c_t .

Figure 2.23 (a) shows the results of linear fitting for c_{in} vs c_t and the parameters of the fitting are summarized in Table 2-9. It could be seen that within the wide range of c_t , the linear correlations were significant at different temperatures, with $R^2 > 0.97$. The slopes, which equals to the values of K_e of Eq (2.27), decreased as the temperature increased. With the K_e at different temperatures, the thermodynamic parameters of the reaction are also available through Van't Hoff relation as Eq (2.8) showed. The Van't Hoff plot is shown in Figure 2.23 (b), the intercept and the opposite of slope of the fitted curve indicated the standard entropy change ΔS^0 and standard enthalpy change ΔH^0 in the direction of reaction was written, respectively. Summarized in Table 2-10, both ΔH^0 and ΔS^0 for the reaction in Eq (2.27) were found negative, meaning the reaction was exothermic and decreased the disorder of the batch system.

The negative ΔH^0 is reasonable for the transfer of Ca^{2+} which is predominantly driven by electrostatic forces that release electrical potential energy. The negative ΔS^0 can be explained as the configurational entropy of Ca^{2+} that characterize the possibility of position and rotational mobility was decreased when $Ca^{2+} (aq)$ became $Ca^{2+} (in.aq)$ and be constrained by the inter-surface of montmorillonite.



(a) Linear fitting for c_{in} vs c_t (b) Van't Hoff plot for equilibrium Eq (2.27)

Figure 2.23 Assessment to the thermodynamics parameters of Eq (2.27)

Table 2-9 Parameters of linear fitting shown in Figure 2.23 (a)

Temperature (°C)	Slope (-)	Intercept (mmol·L ⁻¹)	R ²
20	1.37	50.88	0.99
30	1.26	57.67	0.99
40	1.13	60.67	0.98
50	1.08	53.51	0.99

Table 2-10 Obtained thermodynamic parameters of Eq (2.27).

ΔG^0 at 20°C (kJ·mol ⁻¹)	ΔH^0 (kJ·mol ⁻¹)	ΔS^0 (J·K ⁻¹ ·mol ⁻¹)
-0.76	-6.49	-19.55

The reaction written in Eq (2.27) focuses on the interaction between Ca^{2+} and montmorillonite only. Hence its standard thermodynamic parameters are only available for the fraction of adsorbed Ca^{2+} that interact solely with montmorillonite, referred to the direct adsorption named in subsection 2.2.2. The other fraction of adsorbed Ca^{2+} is the amount that exchanged with Na^+ by ion exchange reaction. The two fractions can be distinguished by using desorbed Na^+ as an indicator because the exchange ratio of Ca^{2+} and Na^+ is always 1:2 in the reaction shown in Eq (2.2), hence:

$$q(\text{exc}) = 0.5 \cdot (-q_e^{\text{Na}}) \quad (2.29)$$

$$q(\text{dir}) = q_e + q_0 - q(\text{exc}) \quad (2.30)$$

where $q(\text{exc})$ and $q(\text{dir})$ are exchange and direct adsorption fractions ($\text{mmol} \cdot \text{g}^{-1}$), respectively; q_0 is the Ca^{2+} exist in bentonite prior to the test ($= 0.144 \text{ mmol} \cdot \text{g}^{-1}$). For $q(\text{exc})$, the temperature effects follow the thermodynamic parameters shown in Table 2-1. While for $q(\text{dir})$, the temperature effects follow the thermodynamic parameters shown in Table 2-10. With the values of the two fractions and corresponding thermodynamic parameters, the equivalent changes of standard enthalpy and entropy of Ca^{2+} adsorption in bentonite and SB batch systems can then be calculated. For ΔH^0 :

$$\Delta H^0(\text{eqv}) = \frac{q(\text{exc}) \cdot \Delta H^0(\text{exc}) + q(\text{dir}) \cdot \Delta H^0(\text{dir})}{q(\text{exc}) + q(\text{dir})} \quad (2.31)$$

where $\Delta H^0(\text{eqv})$ is the equivalent standard enthalpy change of Ca^{2+} adsorption ($\text{kJ} \cdot \text{mol}^{-1}$); $\Delta H^0(\text{exc})$ is the standard enthalpy change of ion exchange ($= +5.58 \text{ kJ} \cdot \text{mol}^{-1}$); $\Delta H^0(\text{dir})$ is the standard enthalpy change of direct adsorption ($= -6.49 \text{ kJ} \cdot \text{mol}^{-1}$). Since the signs of $\Delta H^0(\text{exc})$ and $\Delta H^0(\text{dir})$ are different, the sign of $\Delta H^0(\text{eqv})$ depends on the proportions of $q(\text{exc})$ and $q(\text{dir})$. By calculations, $\Delta H^0(\text{eqv}) > 0$ when $q(\text{dir}) < 0.85q(\text{exc})$, $\Delta H^0(\text{eqv}) = 0$ when $q(\text{dir}) = 0.85q(\text{exc})$ and $\Delta H^0(\text{eqv}) < 0$ when $q(\text{dir}) > 0.85q(\text{exc})$.

Notably, although the ΔH^0 of H_2O was also introduced in subsection 2.2.4, its value is significantly smaller compared to others. Additionally, when the direct adsorption fraction was characterized by the behavior of the solution phase, the behavior of H_2O was also part of that characterization. Hence, the ΔH^0 of H_2O is not added to the calculation of $\Delta H^0(\text{eqv})$.

Figure 2.24 shows the relation between Ca^{2+} adsorbed amount (q_e) and Na^+ desorbed amount ($-q_e$). Equilibrium curves can be derived from data collected in adsorption and exchange isotherms, with each temperature having its own curve, but the diagram only shows an approximate curve for all data. The equilibrium curves can be used as a criterion to determine whether the batch system (same untreated bentonite in neutral CaCl_2 solution) has achieved equilibrium. For example, if one test result is somehow obtained as the dummy point shown in the figure, then that batch system is not in equilibrium, and the equilibrium is likely to be achieved by releasing Ca^{2+} and Na^+ until the dummy point reaches the equilibrium curve.

In Figure 2.24, the $q(\text{exc})$ is showed as a line with slope of 0.5. All the test results were above or approximately on the $q(\text{exc})$ line, indicating that the ion exchange reaction took the precedence over the direct adsorption reaction in bentonite and SB batch systems. Specifically,

the direct adsorption reaction became favorable after the ion exchange reaction achieved equilibrium. This result is consistent with the theories of selectivity (Sposito et al., 1983).

The $q(\text{dir})$ is above the $q(\text{exc})$, and the line which $q(\text{dir}) = 0.85q(\text{exc})$ is plotted in Figure 2.24. The area above the $q(\text{dir}) = 0.85q(\text{exc})$ line is in blue color and the area below is in yellow color. The theoretical calculations in Eq (2.31) indicated $\Delta H^0(\text{eqv}) < 0$ in blue area and $\Delta H^0(\text{eqv}) > 0$ in yellow and orange area. The data in the blue area showed differences of q_e at different temperatures which decreased as the temperature increased. The differences are more significant at the top of blue area, where $q(\text{dir})$ is much higher than $q(\text{exc})$, the characteristics of exothermal is predominate by direct adsorption process. On contrast, the data in the yellow area where $q(\text{exc})$ was the major fraction showed insignificant differences of q_e at different temperatures and reversals of temperature dependency at some points, indicating the characteristics of endothermal.

The effects of temperature on Ca^{2+} adsorption in the equilibrium state obtained from the test is consistent with the results calculated using thermodynamic parameters in terms of trends. The imperfect compatibility between test results and thermodynamic calculations was observed when $q(\text{exc})$ and $q(\text{dir})$ were close. The reasons for the imperfect compatibility are numerous. For example, the ion exchange and direct adsorption might interact to each other when the $q(\text{dir})$ was very low, leading to the errors of thermodynamic calculation. Or, the Ca^{2+} amount prior exist in the bentonite was underestimated, which seems likely given that the reported Na^+ exchange capacity was $0.405 \text{ mmol} \cdot \text{g}^{-1}$ but the measured desorbed amount exceeded $0.6 \text{ mmol} \cdot \text{g}^{-1}$ in many cases. In that case, the initial value of Y-axis in Figure 2.24 should be lower, so as should the yellow area.

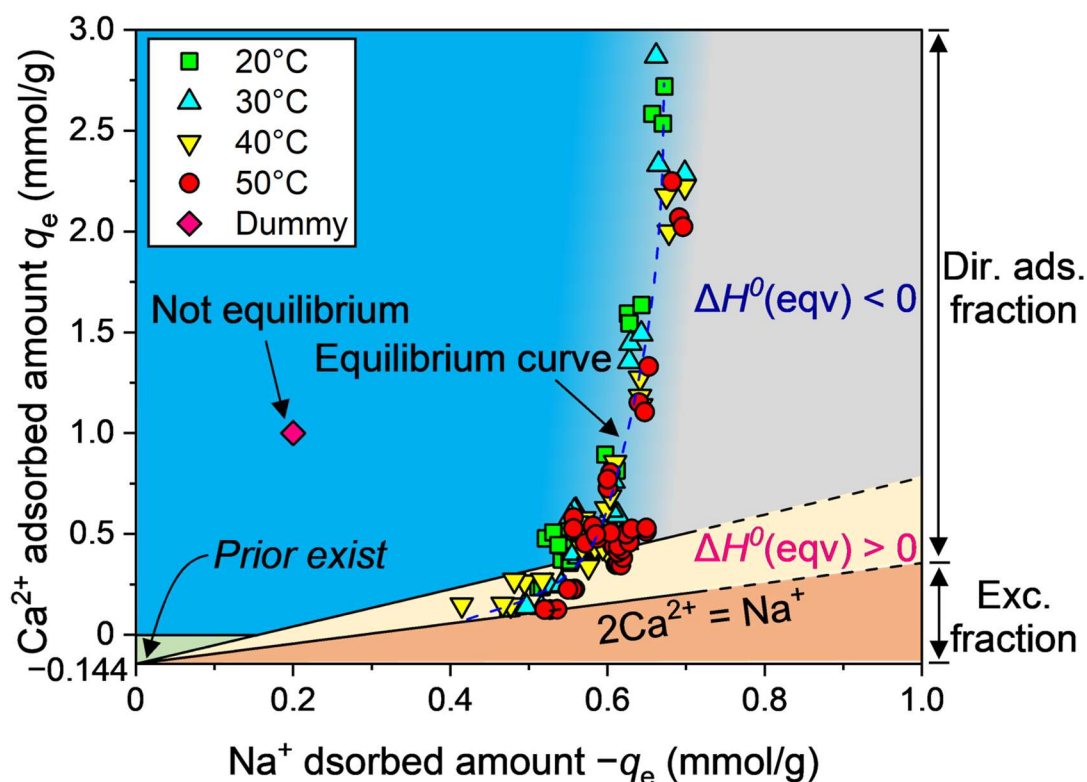


Figure 2.24 Relation between Ca^{2+} adsorbed amount (q_e) and Na^+ desorbed amount ($-q_e$).

2.5.3 Attempts in modeling of adsorption isotherms for bentonite and SB in a wide range of bulk concentration

In engineering practice, adsorption isotherms are more often used when quantified the adsorption capability. The models of the adsorption isotherms implied the key parameters like adsorption capacity, partition coefficient, and chemical equilibrium constant (Mohan & Gandhimathi, 2009; Ng et al., 2017; Ruiz et al., 2012). The biggest difference between bentonite and other adsorbents is the volume change of bentonite accompanied with adsorption when bulk concentration is not very dilute. This principle interferes the intrinsic relation between the adsorbed amount (q_e) and bulk concentration (c). Consequently, q_e is no longer a sufficient description in bentonite batch system for there could be several c corresponded to one q_e .

Still, q_e can be expressed as a function of c . In order to obtain the numerical expression of q_e , the intrinsic relations between parameters when q_e was obtained needs to be excluded. Rearrange Eq (2.18), q_e can be written as function of internal concentration c_{in} and unit internal volume V_{in}/m_s :

$$q_e = c_{in} \cdot \frac{V_{in}}{m_s} - q_0 \quad (2.32)$$

Results in subsections 2.4.2 and 2.5.2 have showed that V_{in}/m_s can be empirically given as exponential function of c , and c_{in} is intrinsically related to the c linearly:

$$\frac{V_{in}}{m_s} = i_1 \cdot e^{-c/i^*} + i_2 \quad (2.33)$$

$$c_{in} = j_1 \cdot c + j_2 \quad (2.34)$$

where i_n and j_n are sets of numerical parameters, i^* is the parameter for the index. Substitute Eq (2.33) and Eq (2.34) into Eq (2.32), the form of the function to characterize q_e becomes:

$$\begin{aligned} q_e &= [(K_{11} \cdot c + K_{12}) \cdot e^{-c/i^*}] + [K_{21} \cdot c + K_{22}] - q_0 \\ &= [\text{linear} \times \text{exponential}] + [\text{linear}] \end{aligned} \quad (2.35)$$

where K_{ij} are another sets of parameters derived from i_n and j_n as:

$$K_{ij} = [i]_{2 \times 1} \cdot [j]_{1 \times 2} \quad (2.36)$$

Notably “[]” in Eq (2.36) mean matrix, but are simply brackets in Eq (2.35). The first term in the function of q_e describes the effects of volume change, it is given as the product of linear and exponential functions, but it can have other forms depend on the empirical function for V_{in}/m_s . The rests in the function of q_e is in the form of linear.

Equation (2.35) has a general shape shown in Figure 2.25, which could well express the adsorption isotherms with characteristics that first rises, then falls, and rises again. The initial value of q_e depends on K_{11} , K_{22} , and q_0 . As the exponential term converges to 0, q_e is simplified into a linear function characterized by K_{21} and K_{22} , which is corresponded to the fitting curves shown in Figure 2.14(b). Therein the values of K_{21} and K_{22} can be determined using measured

q_e when c is very high, and the value of K_{22} can then be determined with initial value. The exponential term equals to 1 when $c = 0$, therefore the initial slope of q_e is equal to $K_{11} + K_{21}$. After all, K_{ij} could all be obtained from the shape of adsorption isotherm, only the i^* cannot be directly obtained.

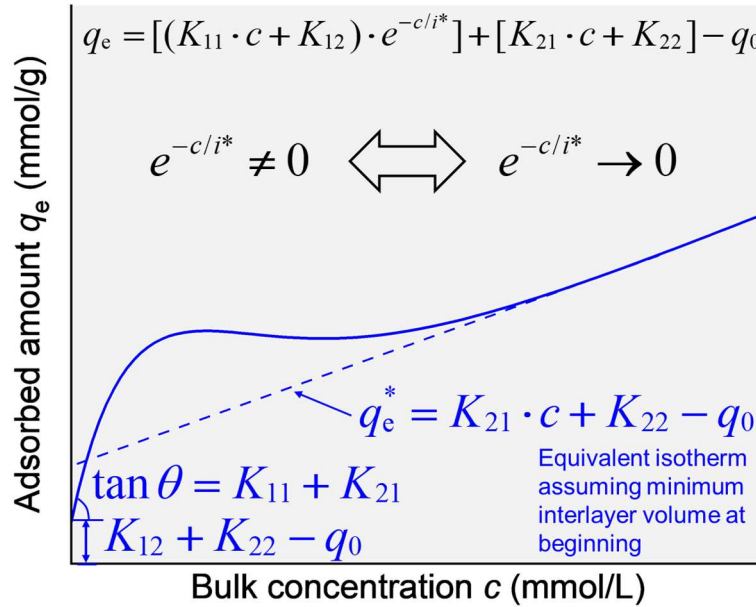


Figure 2.25 Analytic description of adsorption isotherm of bentonite.

The same sequence can also apply to the ordinary ads amount Q_e despite it is not the correct value of adsorption of bentonite batch system in principle. Rearrange Eq (2.18) as:

$$Q_e = (c_{in} - c) \cdot \frac{V_{in}}{m_s} - q_0 \quad (2.37)$$

Analogy to Eq (2.34), $c_{in} - c$ can be characterized without changing parameters:

$$c_{in} - c = (j_1 - 1) \cdot c + j_2 \quad (2.38)$$

Substitute Eq (2.33) and Eq (2.38) into Eq (2.32), Q_e becomes:

$$Q_e = [(K_{11}^* \cdot c + K_{12}) \cdot e^{-c/i^*}] + [K_{21}^* \cdot c + K_{22}] - q_0 \quad (2.39)$$

The differences between Q_e and q_e now can be strictly quantified as the differences between K_{11} and K_{11}^* , and between K_{21} and K_{21}^* that effect the in initial slopes and final slopes, respectively. As long as the $[i]_{2 \times 1}$ and $[j]_{1 \times 2}$ can be solved from K_{ij} , then the obtaining the adsorption isotherm of q_e only need to replace the j_{1-1} by j_1 .

Assuming the j_{1-1} can be solved from K_{ij} . Then the measuring of the volume change will become unnecessary as the form of Eq (2.33) is known. For the K_{ij} of Q_e isotherm can be obtained from its shape, and the only unknown parameter i^* can be obtained by fitting, then replace the j_{1-1} by j_1 , K_{ij} of q_e isotherm can be achieved. However, it seems the solving of j_{1-1} is not an easy task, and the practicality of the mathematical method for calculating q_e given above needs to be verified and required further research (Appendix B).

2.6 Conclusions of Chapter 2

In this Chapter, the temperature effects to the adsorption behaviors of bentonite (B), decomposed granite soil (S), and soil-bentonite (SB) against Ca^{2+} were evaluated by operating batch tests of B, S, and SB in 200 mL natural CaCl_2 solutions with different initial Ca^{2+} molarities (0.5 to $1000 \text{ mol}\cdot\text{L}^{-1}$) and with different constant temperatures (20°C to 50°C), respectively. The equilibrium amounts of adsorption and desorption were characterized by ordinary ads/des amounts (Q_e) and modified ads/des amounts (q_e) where the latter considered the volume change of bulk solution and is more correct in principle. The following conclusions could be summarized supported by the test results and discussions:

- (1) The kinetics of Ca^{2+} adsorption and Na^+ desorption by bentonite were observed to occur rapidly in batch system. The ads/des amounts instantaneously reached considerable values, and showed characteristics of stabilization after several hours. The tests were operated with a longest period of 72 h of oscillation, with no significant differences in Ca^{2+} adsorption and Na^+ desorption amounts compared to the 24 h. The 24 h oscillation was approximately sufficient to achieve the equilibrium for Ca^{2+} adsorption and Na^+ desorption.
- (2) The free swell test was carried out to assess the unit volumes of interlamellar space of bentonite in aqueous system (V_{in}/m_s). The V_{in}/m_s was defined as the difference between the free swell volume and particle volume of unit mass bentonite. The V_{in}/m_s was found can be empirically fitted by exponential model as a function of equilibrium Ca^{2+} bulk molarity (c_t).
- (3) When characterizing adsorption isotherms, Q_e were lower than q_e and the differences increased significantly as the increased of c_t . When characterizing exchange isotherms, $-Q_e$ were higher than $-q_e$ while the differences between Q_e and q_e were relatively insignificant. Test results indicated that the Q_e underestimated the adsorption amounts, and overestimated the desorption amounts of bentonite. Except for very dilute bulk solution, the volume change of bulk solution in batch system contains bentonite should not be ignored.
- (4) The Ca^{2+} adsorption (q_e) isotherms obtained in this study showed characteristics of decreasing at about $10 \text{ mol}\cdot\text{L}^{-1}$ of c_t , which were attributed to the rapidly decreasing of V_{in}/m_s . When c_t exceeded $100 \text{ mol}\cdot\text{L}^{-1}$, the adsorption isotherms were observed increased linearly as the c_t increased, q_e exceeded $2 \text{ mmol}\cdot\text{g}^{-1}$ at approximate $1000 \text{ mmol}\cdot\text{L}^{-1}$ of c_t .
- (5) The Na^+ exchange ($-q_e$) isotherms showed characteristics of initial values of approximately $0.4 \text{ mmol}\cdot\text{g}^{-1}$, and continuously slight increasing as the c_t increased. At approximate $1000 \text{ mmol}\cdot\text{L}^{-1}$ of c_t , $-q_e$ reached $0.7 \text{ mmol}\cdot\text{g}^{-1}$.
- (6) The adsorption/exchange isotherms of bentonite and SB shared same characteristics. The q_e of SB were approximately equal to the q_e of B multiplied by the bentonite mass ratio of SB at various temperatures. Bentonite can fully utilize its adsorption capability as SB regardless of the temperature changes. Also, the mixing procedures ensured the uniformity of SB.
- (7) The temperature effects to Ca^{2+} adsorption (q_e) isotherms were relatively insignificant when c_t were lower than $50 \text{ mmol}\cdot\text{L}^{-1}$, and were significantly observed when c_t were higher than $100 \text{ mmol}\cdot\text{L}^{-1}$, where q_e decreased as the temperature increased, exhibited characteristics of exothermal. On contrast, the temperature effects to Na^+ exchange ($-q_e$) isotherms were

more significantly observed when c_t were lower than $50 \text{ mmol}\cdot\text{L}^{-1}$, where $-q_e$ increased as the temperature increased, exhibited characteristics of endothermal.

- (8) The Ca^{2+} adsorbed amount can be characterized by the molarity of Ca^{2+} in the internal space (c_{in}), which is calculated from q_e and V_{in}/m_s . The c_{in} increased monotonically as the c_t increased and c_{in} were always higher than c_t . Suggesting the nature of bentonite to attract Ca^{2+} in bulk solutions remained unchanged. The observed c_{in} exhibited approximately linear correlations with c_t in a wide range.
- (9) The Ca^{2+} adsorption by bentonite is the consequences of ion exchange and direct adsorption processes. The standard thermodynamic parameters of the direct adsorption process were calculated by analyzing the relation between c_{in} and c_t . The direct adsorption was found to be an exothermal reaction with $\Delta H^0 = -6.49 \text{ kJ}\cdot\text{mol}^{-1}$, which is different with the reported ΔH^0 of ion exchange reaction in sign. The sign of the equivalent ΔH^0 of Ca^{2+} been adsorbed depends on the proportions of the two reactions. Which explained the results that adsorption showed more significant exothermic characteristics when q_e were relatively high, with direct adsorption fractions ($q(\text{dir})$) significantly higher than ion exchange fractions ($q(\text{exc})$). The endothermic or exothermic nature of the equivalent reaction for Ca^{2+} adsorption can be determined using a diagram showing relations between Na^+ desorbed amount and Ca^{2+} adsorbed amount.

References

- ASTM D5890. (2019). Standard Test Method for Swell Index of Clay Mineral Component of Geosynthetic Clay Liners has been revised to D5890-11. *American Society for Testing and Material*.
- Bonilla-Petriciolet, A., Mendoza-Castillo, D. I., & Reynel-Ávila, H. E. (2017). Adsorption processes for water treatment and purification. In *Springer International Publishing AG*.
- Bouazza, A., Jefferis, S., & Vangpaisal, T. (2007). Investigation of the effects and degree of calcium exchange on the Atterberg limits and swelling of geosynthetic clay liners when subjected to wet-dry cycles. *Geotextiles and Geomembranes*, 25(3), 170–185. <https://doi.org/10.1016/j.geotexmem.2006.11.001>
- Bourg, I. C., Bourg, A. C. M., & Sposito, G. (2003). Modeling diffusion and adsorption in compacted bentonite: A critical review. *Journal of Contaminant Hydrology*, 61(1–4), 293–302. [https://doi.org/10.1016/S0169-7722\(02\)00128-6](https://doi.org/10.1016/S0169-7722(02)00128-6)
- Bradshaw, S. L., Benson, C. H., & Scalia, J. (2013). Hydration and Cation Exchange during Subgrade Hydration and Effect on Hydraulic Conductivity of Geosynthetic Clay Liners. *Journal of Geotechnical and Geoenvironmental Engineering*, 139(4), 526–538. [https://doi.org/10.1061/\(asce\)gt.1943-5606.0000793](https://doi.org/10.1061/(asce)gt.1943-5606.0000793)
- Cadaval Jr, T. R. S., Dotto, G. L., Seus, E. R., Mirlean, N., & de Almeida Pinto, L. A. (2016). Vanadium removal from aqueous solutions by adsorption onto chitosan films. *Desalination and Water Treatment*, 57(35), 16583–16591.
- Chang, F.-R. C., Skipper, N. T., Refson, K., Greathouse, J. A., & Sposito, G. (1998). *Interlayer molecular structure and dynamics in Li-, Na-, and K-montmorillonite-water systems*. ACS Publications.
- Chang, Y. S., Au, P. I., Mubarak, N. M., Khalid, M., Jagadish, P., Walvekar, R., & Adbullah, E. C. (2020). Adsorption of Cu (II) and Ni (II) ions from wastewater onto bentonite and bentonite / GO composite. *Environmental Science and Pollution Research*, 27, 33270–33296.

- Chen, J., Chen, Y., Zhou, Y., Luo, X., & Tang, Q. (2023). Insight into Adsorption of Cesium Ion in Aqueous Solution Based on Inorganic Modified Bentonite. *Polish Journal of Environmental Studies*, 32(2), 1565–1580. <https://doi.org/10.15244/pjoes/158763>
- Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Rivera-Utrilla, J., & Sánchez-Polo, M. (2007). Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. *Journal of Environmental Management*, 85(4), 833–846. <https://doi.org/10.1016/j.jenvman.2007.07.031>
- Elderton, W. P. (1902). Tables for testing the goodness of fit of theory to observation. *Biometrika*, 1(2), 155–163. <https://doi.org/10.1093/biomet/1.2.155>
- Engel, T., & Reid, P. (2019). *Thermodynamics, statistical thermodynamics, and kinetics: physical chemistry* (4th editio). Pearson education.
- Everett, D. H. (1964). Thermodynamics of adsorption from solution. Part 1.—Perfect systems. *Trans. Faraday Soc.*, 60, 1803–1813. <https://doi.org/10.1039/TF9646001803>
- Fletcher, P., & Sposito, G. (1989). The Chemical Modelling of Clay/Electrolyte Interactions for Montmorillonite. *Clay Minerals*, 24(2), 375–391. <https://doi.org/10.1180/claymin.1989.024.2.14>
- Gilbert, M., & Van Bladel, R. (1970). Thermodynamics and thermochemistry of the exchange reaction between NH_4^+ and Mn^{2+} in a montmorillonite clay. *Journal of Soil Science*, 21(1), 38–49.
- Giles, C. H., MacEwan, T. H., Nakhwa, S. N., & Smith, D. (1960). 786. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society (Resumed)*, 846, 3973. <https://doi.org/10.1039/jr9600003973>
- Hnizdo, V., & Gilson, M. K. (2010). Thermodynamic and differential entropy under a change of variables. *Entropy*, 12(3), 578–590. <https://doi.org/10.3390/e12030578>
- Hutcheon, A. T. (1966). Thermodynamics of cation exchange on clay: Ca-K-montmorillonite. *Journal of Soil Science*, 17(2), 339–355. <https://doi.org/10.1111/j.1365-2389.1966.tb01478.x>
- Ishimori, H., & Katsumi, T. (2012). Temperature effects on the swelling capacity and barrier performance of geosynthetic clay liners permeated with sodium chloride solutions. *Geotextiles and Geomembranes*, 33, 25–33. <https://doi.org/10.1016/j.geotexmem.2012.02.005>
- J. Hunter, R. (1981). Zeta potential in colloid science: Principles and applications. In *Academic Press*.
- Japanese Industrial Standards. (2020a). Test method for density of soil particles. *JIS A 1202*.
- Japanese Industrial Standards. (2020b). Test method for liquid limit and plastic limit of soils. *JIS A 1205*.
- Kato, T., Gathuka, L. W., Okada, T., Takai, A., Katsumi, T., Imoto, Y., Morimoto, K., Nishikata, M., & Yasutaka, T. (2021). Sorption-desorption column tests to evaluate the attenuation layer using soil amended with a stabilising agent. *Soils and Foundations*, 61(4), 1112–1122. <https://doi.org/10.1016/j.sandf.2021.05.004>
- Katsumi, T., Kamon, M., Inui, T., & Araki, S. (2008). Hydraulic barrier performance of SBM cut-off wall constructed by the trench cutting and re-mixing deep wall method. In *GeoCongress 2008: Geotechnics of Waste Management and Remediation* (pp. 628–635).
- Kaya, A., & Ören, A. H. (2005). Adsorption of zinc from aqueous solutions to bentonite. *Journal of Hazardous Materials*, 125(1–3), 183–189. <https://doi.org/10.1016/j.jhazmat.2005.05.027>
- Kolstad, D. C., Benson, C. H., & Edil, T. B. (2004). Hydraulic Conductivity and Swell of Nonprehydrated Geosynthetic Clay Liners Permeated with Multispecies Inorganic Solutions. *Journal of Geotechnical and Geoenvironmental Engineering*, 130(12), 1236–1249.

- [https://doi.org/10.1061/\(asce\)1090-0241\(2004\)130:12\(1236\)](https://doi.org/10.1061/(asce)1090-0241(2004)130:12(1236))
- Komine, H. (2004). Simplified evaluation for swelling characteristics of bentonites. *Engineering Geology*, 71(3–4), 265–279. [https://doi.org/10.1016/S0013-7952\(03\)00140-6](https://doi.org/10.1016/S0013-7952(03)00140-6)
- Komine, H., Yasuhara, K., & Murakami, S. (2009). Swelling characteristics of bentonites in artificial seawater. *Canadian Geotechnical Journal*, 46(2), 177–189. <https://doi.org/10.1139/T08-120>
- Kraepiel, A. M. L., Keller, K., & Morel, F. M. M. (1999). A model for metal adsorption on montmorillonite. *Journal of Colloid and Interface Science*, 210(1), 43–54. <https://doi.org/10.1006/jcis.1998.5947>
- Lange, K., Rowe, R. K., & Jamieson, H. (2009). Diffusion of metals in geosynthetic clay liners. *Geosynthetics International*, 16(1), 11–27. <https://doi.org/10.1680/gein.2009.16.1.11>
- Laudelout, H., Van Bladel, R., Bolt, G. H., & Page, A. L. (1968). Thermodynamics of heterovalent cation exchange reactions in a montmorillonite clay. *Transactions of the Faraday Society*, 64, 1477–1488. <https://doi.org/10.1039/TF9686401477>
- Liu, Q. S., Zheng, T., Wang, P., Jiang, J. P., & Li, N. (2010). Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. *Chemical Engineering Journal*, 157(2–3), 348–356. <https://doi.org/10.1016/j.cej.2009.11.013>
- McBride, M. B. (1994). Environmental chemistry of soils. In *Suparyanto dan Rosad* (2015). Oxford university press.
- McBride, M. B., & Baveye, P. (2002). Diffuse Double-Layer Models, Long-Range Forces, and Ordering in Clay Colloids. In *Soil Science Society of America Journal* (Vol. 66, Issue 4, pp. 1207–1217). <https://doi.org/10.2136/sssaj2002.1207>
- Meneguín, J. G., Moisés, M. P., Karchiyappan, T., Faria, S. H. B., Gimenes, M. L., de Barros, M. A. S. D., & Venkatachalam, S. (2017). Preparation and characterization of calcium treated bentonite clay and its application for the removal of lead and cadmium ions: Adsorption and thermodynamic modeling. *Process Safety and Environmental Protection*, 111, 244–252. <https://doi.org/10.1016/j.psep.2017.07.005>
- Mitchell, J. K. (1993). Fundamentals of Soil Behavior. In *Soil Science Society of America Journal* (3rd ed.). John Wiley & Sons, Inc.
- Mo, J., Flores, G., Inui, T., & Katsumi, T. (2020). Hydraulic and sorption performances of soil amended with calcium-magnesium composite powder against natural arsenic contamination. *Soils and Foundations*, 60(5), 1084–1096. <https://doi.org/10.1016/j.sandf.2020.05.007>
- Mohan, S., & Gandhimathi, R. (2009). Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent. *Journal of Hazardous Materials*, 169(1–3), 351–359. <https://doi.org/10.1016/j.jhazmat.2009.03.104>
- Naka, A., Flores, G., Inui, T., Sakanakura, H., & Katsumi, T. (2019). Hydraulic performance and chemical compatibility of a powdered Na-bentonite geosynthetic clay liner permeated with mine drainage. *Soils and Foundations*, 59(5), 1128–1147. <https://doi.org/10.1016/j.sandf.2019.02.005>
- Ng, K. C., Burhan, M., Shahzad, M. W., & Ismail, A. Bin. (2017). A Universal Isotherm Model to Capture Adsorption Uptake and Energy Distribution of Porous Heterogeneous Surface. *Scientific Reports*, 7(1), 1–11. <https://doi.org/10.1038/s41598-017-11156-6>
- Papelis, C., & Hayes, K. F. (1996). Distinguishing between interlayer and external sorption sites of clay minerals using X-ray absorption spectroscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 107, 89–96. [https://doi.org/10.1016/0927-7757\(95\)03370-X](https://doi.org/10.1016/0927-7757(95)03370-X)
- Robin, V., Tertre, E., Beaufort, D., Regnault, O., Sardini, P., & Descostes, M. (2015). Ion exchange reactions of major inorganic cations (H⁺, Na⁺, Ca²⁺, Mg²⁺ and K⁺) on beidellite: Experimental results and new thermodynamic database. Toward a better prediction of contaminant mobility in natural environments. *Applied Geochemistry*, 59, 74–84.

- <https://doi.org/10.1016/j.apgeochem.2015.03.016>
- Rowe, R. K., Mukunoki, T., & Sangam, H. P. (2005). BTEX diffusion and sorption for a geosynthetic clay liner at two temperatures. *Journal of Geotechnical and Geoenvironmental Engineering*, 131(10), 1211–1221. [https://doi.org/10.1061/\(ASCE\)1090-0241\(2005\)131:10\(1211\)](https://doi.org/10.1061/(ASCE)1090-0241(2005)131:10(1211))
- Ruiz, A. I., Fernández, R., Sánchez Jiménez, N., Rodríguez Rastrero, M., Regadío, M., de Soto, I. S., & Cuevas, J. (2012). Improvement of attenuation functions of a clayey sandstone for landfill leachate containment by bentonite addition. *Science of the Total Environment*, 419, 81–89. <https://doi.org/10.1016/j.scitotenv.2011.11.054>
- Sen Gupta, S., & Bhattacharyya, K. G. (2011). Kinetics of adsorption of metal ions on inorganic materials: A review. *Advances in Colloid and Interface Science*, 162(1–2), 39–58. <https://doi.org/10.1016/j.cis.2010.12.004>
- Sposito, G., Holtzclaw, K. M., Charlet, L., Jouany, C., & Page, A. L. (1983). Sodium-Calcium and Sodium-Magnesium Exchange on Wyoming Bentonite in Perchlorate and Chloride Background Ionic Media. *Soil Science Society of America Journal*, 47(1), 51–56. <https://doi.org/10.2136/sssaj1983.03615995004700010010x>
- Sposito, G., Holtzclaw, K. M., Johnston, C. T., & LeVesque-Madore, C. S. (1981). Thermodynamics of Sodium-Copper Exchange on Wyoming Bentonite at 298°K. *Soil Science Society of America Journal*, 45(6), 1079–1084. <https://doi.org/10.2136/sssaj1981.03615995004500060014x>
- Sposito, G., Holtzclaw, K. M., Jouany, C., & Charlet, L. (1983). Cation selectivity in sodium-calcium, sodium-magnesium, and calcium-magnesium exchange on Wyoming bentonite at 298 K. *Soil Science Society of America Journal*, 47(5), 917–921.
- Sposito, G., Skipper, N. T., Sutton, R., Park, S. H., Soper, A. K., & Greathouse, J. A. (1999). Surface geochemistry of the clay minerals. *Proceedings of the National Academy of Sciences of the United States of America*, 96(7), 3358–3364. <https://doi.org/10.1073/pnas.96.7.3358>
- Takai, A., Inui, T., & Katsumi, T. (2016). Evaluating the hydraulic barrier performance of soil-bentonite cutoff walls using the piezocone penetration test. *Soils and Foundations*, 56(2), 277–290. <https://doi.org/10.1016/j.sandf.2016.02.010>
- Tertre, E., Prêt, D., & Ferrage, E. (2011). Influence of the ionic strength and solid/solution ratio on Ca(II)-for-Na⁺ exchange on montmorillonite. Part 1: Chemical measurements, thermodynamic modeling and potential implications for trace elements geochemistry. *Journal of Colloid and Interface Science*, 353(1), 248–256. <https://doi.org/10.1016/j.jcis.2010.09.039>
- Tipping, E. (1995). Chemical kinetics and process dynamics in aquatic systems. In *Environmental Pollution* (Vol. 87, Issue 1). [https://doi.org/10.1016/s0269-7491\(99\)80016-5](https://doi.org/10.1016/s0269-7491(99)80016-5)
- Torikai, Y., Sato, S., & Ohashi, H. (1996). Thermodynamic properties of water in compacted sodium montmorillonite. *Nuclear Technology*, 115(1), 73–80. <https://doi.org/10.13182/NT96-A35276>
- Wang, S., Dong, Y., He, M., Chen, L., & Yu, X. (2009). Characterization of GMZ bentonite and its application in the adsorption of Pb(II) from aqueous solutions. *Applied Clay Science*, 43(2), 164–171. <https://doi.org/10.1016/j.clay.2008.07.028>
- Zhou, X., Liu, H., & Hao, J. (2012). How to Calculate the Thermodynamic Equilibrium Constant using the Langmuir Equation. *Adsorption Science & Technology*, 30(7), 647–649. <https://doi.org/10.1260/0263-6174.30.7.647>

CHAPTER 3

Temperature effects on hydraulic performance of SB barrier

3.1 Introduction

The hydraulic conductivity (k) is a crucial parameter to characterize the hydraulic performance of soil barriers. An effective soil barrier should have a low k to inhibit the movement of contaminant leachate. For bentonite barriers, $k < 10^{-9} \text{ m}\cdot\text{s}^{-1}$ were reported in many previous studies (Bradshaw et al., 2013; Kamon et al., 2006; Kolstad, Benson, & Edil, 2004; J.-M. Lee & Shackelford, 2005; Norris et al., 2018; R. Alther, 1982; Rowe, 1998; Tan et al., 2021). Soil-bentonite mixtures (SB), which consisting of a small amount of sodium bentonite (less than 10% in mass ratio), also showed characteristics of extremely low k (Evans, 1993; Kamon et al., 2002; Katsumi et al., 2008b; Malusis et al., 2009).

The decreasing of effective voids volume due to bentonite swelling has been identified as a dominant cause of low k (Komine & Ogata, 1999; H. Wang et al., 2022; Ye et al., 2013). Consequently, factors that negatively affect the swelling characteristics of bentonite also hinder the hydraulic performance of bentonite barriers (Katsumi et al., 2007; Komine, 2004; Naka et al., 2019; Rowe, 2020). Chemical effects are the main factors that primarily inhibit the swelling of bentonite (Gleason et al., 1997; Shackelford, 1994a) because the thickness of diffused double layer (DDL) decreased in high-concentration solutions due to the accumulation of multivalence cations in the montmorillonite interlamellar (J. Hunter, 1981; McBride, 1994), as introduced in Chapter 1 and Chapter 2. Since the multivalence cations are commonly found in contaminant leachates (Bradshaw & Benson, 2014), chemical compatibility of bentonite materials must be taken into account when applying to barrier constructions.

Prehydrating bentonite materials before permeating them with chemical solutions is reported as an effective and practical method to enhance their chemical compatibility, typically resulting in lower k compared to direct permeation with the chemical solutions (Katsumi et al., 2008a; Sato et al., 2017; Shackelford et al., 2000). In principle, the prehydration allows polar H_2O molecules to occupy the montmorillonite interlamellar space initially. Once water molecules are tightly adsorbed, cations in the permeant have fewer chances to enter and be adsorbed. It has been reported that the pre-hydration also increased the chemical compatibility of SB (Malusis & McKeehan, 2013; Takai et al., 2013) that prehydrated SB showed $k < 10^{-9} \text{ m}\cdot\text{s}^{-1}$ when permeated with 1M CaCl_2 .

This study focused on the temperature effects on the hydraulic performance of SB barrier. Based on the above reported results, the SB were prehydrated with distilled water and permeated with Ca^{2+} solutions. The k of SB were experimentally measured at various temperatures, and the mechanisms of temperature effects to k were discussed.

3.2 Current studies concerning temperature effects on hydraulic performance of bentonite materials

Previous studies have evaluated the temperature effects on the hydraulic performance of materials such as pure bentonite, sand-bentonite mixtures, geosynthetic clay liners (GCLs), and other types of clays using various methods. Table 3-1 summarizes some information on relevant studies, the research has gradually evolved from single-temperature studies to investigating a combination of temperature and chemical conditions. In recent years, the researches have evolved from single-temperature studies to investigating a combination of temperature and chemical conditions, and the research methods have also transitioned from using rigid wall permeameters to employing flexible wall permeameters. Limited focus has been given to the temperature effects of hydraulic performance of SB.

Numerous studies have demonstrated that an increase in temperature leads to a corresponding increase in the hydraulic conductivity (k) of bentonite materials, which is unfavorable to the hydraulic performance of soil barriers. In principle, the effects of temperature on the k of bentonite materials can be divided into the effects on the solid matrix (including the parts of pore that no longer holds the properties of pore e.g. the DDL) and the effects on the fluidity of the liquid. An analytical method to separate the two kinds of effects is using intrinsic permeability K (m^2) as an indicator of hydraulic performance (Bear, 1973). The K can be calculated using the following equation:

$$K = k \cdot \frac{\mu}{\rho g} \quad (3.1)$$

where $\mu/\rho g$ ($\text{m}\cdot\text{s}$) represents the fluid's fluidity; ρ ($\text{Mg}\cdot\text{m}^{-3}$) is the fluid's density; μ ($\text{Pa}\cdot\text{s}$) is the fluid's dynamic viscosity; g ($\text{m}\cdot\text{s}^{-2}$) is the gravitational acceleration. The significant decreases in μ as the temperature increases were mostly contributed to the increase of k in relevant studies. But the temperature dependencies of K in clay materials did not exhibit a clear regular pattern in the reported results.

Table 3-1 Temperature effects on bentonite or clay materials' k by various investigators

Investigators	Year	Material	Permeameter	T ($^{\circ}\text{C}$)	Permeants
Cho et al.	1999	Ca-bentonite	Rigid-wall	20, 40, 60, 80	Demineralized water
Villar & Lloret	2004	FEBEX bentonite	Rigid-wall	20, 60, 80	Deionized water
Lloret & Villar	2007	FEBEX bentonite	Rigid-wall	20, 40, 60, 80	Distilled water
Bouazza et al.	2008	GCL	Rigid-wall	30, 40, 50, 60	Pure water
Ishimori & Katsumi	2012	GCL	Large column	20, 60	0.1 & 0.4M NaCl
Ye et al.	2014	GMZ bentonite	Rigid-wall	25, 60, 80	NaOH
S. Wang et al.	2017	Compacted clay	Flexible-wall	25, 35, 50, 60	Deionized water
Ozhan	2018	Polymer-treated GCL	Flexible-wall	20, 40, 60	0.1 & 0.5M MgCl_2

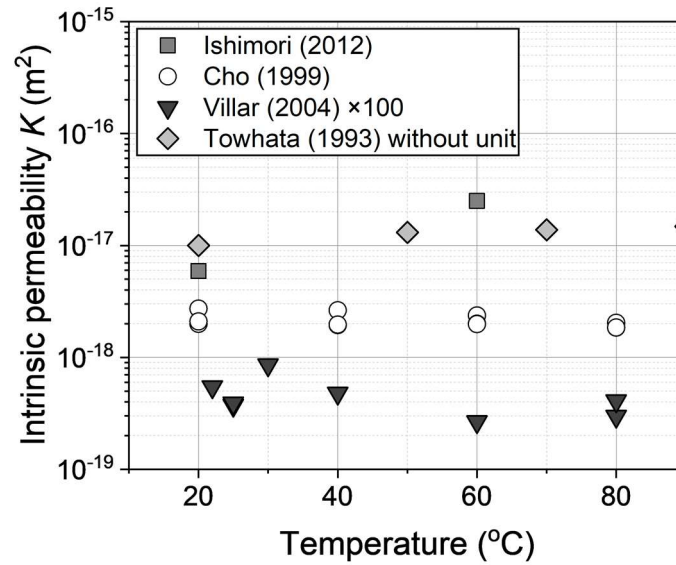


Figure 3.1 Temperature dependency of intrinsic permeabilities (K) in some studies. The values of K from Villar & Lloret (2004), Cho et al. (1999), and Towhata et al. (1993) were calculated based on their reported hydraulic conductivity or relative hydraulic conductivity, and the former are magnified by a hundred times to facilitate the comparison in the given range.

Figure 3.1 summarizes the reported positive, negative, and insignificant temperature dependencies of K from several studies. The variations in the figure suggest that the temperature dependency of the bentonite materials' K depends on the specific materials, methods, and testing conditions.

Cho et al. (1999) investigated the permeability of compacted Ca-bentonite against demineralized water at temperatures ranging from 20 °C to 80°C. They reported that the increase in k for specimens at high temperatures attributed solely to the change in the fluid's kinematic viscosity. Consequently, their K did not change with temperature. The results are supported by the studies of Delage et al. (2000) for Boom clay, Bouazza et al. (2008) and Ozhan (2018) for GCL containing Na-bentonite. Villar & Lloret (2004) reported that in their results of FEBEX bentonite against deionized water, showed that as temperature changes, the measured k were lower than predicted when only fluid property changes were considered. It can be inferred that K were decreased with temperature. The same trend was noted by Ye et al. (2013) for GMZ bentonite and by S. Wang et al. (2017) for compacted clay. Towhata et al. (1993) noted that the measured k of consolidated bentonite at various temperatures were higher than the prediction only considered the changes in fluid properties, where the K of the bentonite increased with temperature. Ishimori & Katsumi (2012) also reported a significant increase in GCL's K between 20°C and 60°C when exposed to NaCl solutions.

For bentonite materials, as the theories related to the effective voids (Komine et al., 2009) indicated, the values of K also related to the thickness of DDL. Therefore, the changes of K at various temperatures were not only attributed to the mechanical reasons such as aggregation expand or particle crushing that effects the real voids, but also to the changes in the swelling characteristics of bentonite that effects the effective voids.

3.3 Experimental approach to the temperature effects on hydraulic conductivity of SB against CaCl_2 solution

3.3.1 Materials

The decomposed granite soil (S) and the Kunigel V1 sodium bentonite (B) were used as parent soil and additive in this study, the mass ratio of B in SB was controlled as 7.5%. The physical properties of the soil materials, and the mixing procedures of SB in this study align with Chapter 2. Figure 3.2 shows the particle distribution curves of decomposed granite soil (S) and SB, where the latter was calculated with 7.5% bentonite mass ratio. Some additional information is summarized in Table 3-2. Although the swelling characteristics of bentonite are mostly attributed to the barrier properties of SB, the particle distribution curves indicated that the input of clay particles also physically enhanced the soil's particle composition, significantly improved the uniformity coefficient and curvature coefficients.

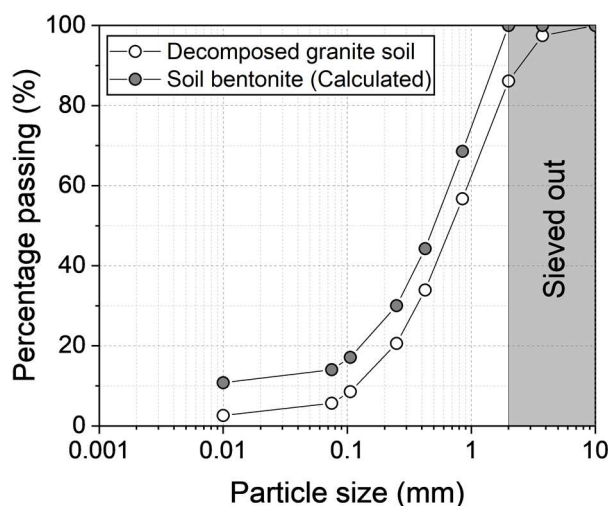


Figure 3.2 Particle distributions of decomposed granite soil and mixed SB in this study.

Table 3-2 Physical properties of soil materials.

		Bentonite	Dec. granite soil	SB	Method
Particle density	(Mg/m^3)	2.79 ⁽¹⁾	2.65	2.66	JIS A 1202
Particle size					JIS A 1204
Gravel [2.00 ~ mm]	(%)	0	13.9	0	
Sand [0.075 ~ 2.00 mm]	(%)	0	80.5	86.0	
Fine [$\sim$ 0.075 mm]	(%)	100	5.7	14.1	
Uniformity coefficient	-	-	8.18	75	
Curvature coefficient	-	-	1.24	8.33	

(1) Komine et al., 2009

3.3.2 Falling-head hydraulic conductivity test with modified flexible-wall permeameter

In order to operate the hydraulic conductivity test at various temperature conditions, a temperature control module was installed on the flexible-wall permeameter, the modified device is shown in Figure 3.3. The test temperature was controlled via a silicon rubber heater covering the outer face of the acrylic cylinder, and an external thermoregulator was connected to the heater to maintain the temperature of the cell water constant. The temperature of the cell water was measured and recoded with temperature sensor and logger, the monitored temperature was treated as the temperature condition of the test. The sensor was regularly calibrated with an analog thermometer to ensure the credibility of the temperature data. The appearance of the modified permeameters are shown in Photo 3.2.

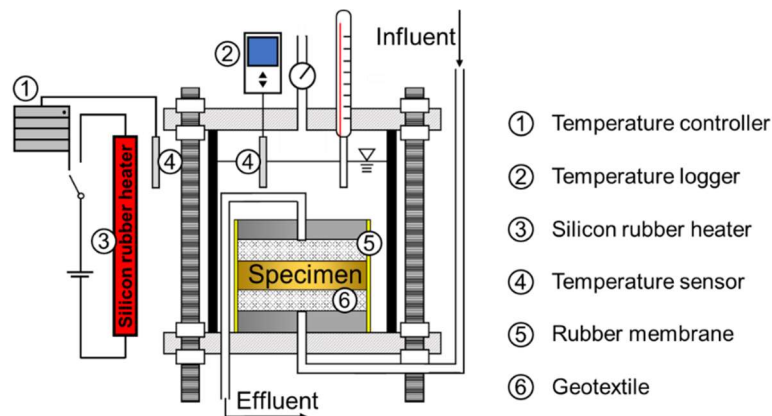


Figure 3.3 Schematic of modified flexible-wall permeameter.



Photo 3.1 Data logger, temperature regulator, and rubber heater used in this study



Photo 3.2 On-going hydraulic conductivity test with modified flexible-wall permeameter

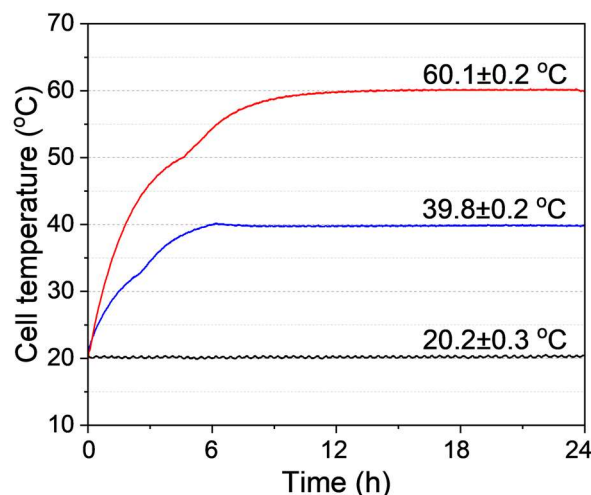


Figure 3.4 Monitored constant temperature conditions.

Figure 3.4 shows three cases of monitored temperatures which were targeted at 20°C, 40°C, and 60°C, respectively. The 20°C was controlled via laboratory air conditioning system. After the heating process started, the cell temperature increased continuously and eventually stabilized at $39.8 \pm 0.2^\circ\text{C}$ and $60.1 \pm 0.2^\circ\text{C}$ within 6 and 12 h, respectively. Considering the accuracy of temperature control and slight differences exist in individual devices, the temperature data were given with an accuracy of 1 degree Celsius in this study.

The falling-head hydraulic conductivity test in this study was operated followed the introduction of ASTM D 5084 “Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter” (ASTM, 2010). The SB specimens for the hydraulic conductivity test were prepared by the following steps:

(i) Consolidation: The SB was firstly placed in a mold measuring 60 mm in diameter and 70 mm in height. Then, a pressure of 39.2 kPa was applied to the top of the mold until no vertical displacement for a duration of 12 hours was observed. The consolidation resulted in a dry density range of 1.46 to 1.47 Mg/m³. **(ii) Saturation:** The consolidated SB was then cut into molds measuring 60 mm in diameter and 20 mm in height. These smaller samples as well as the molds were immersed in distilled water and subjected to vacuum saturation for a period of 48 hours. This procedure also allowed the bentonite to perhydrate and increased the specimens’ chemical compatibility. **(iii) Assembling:** After saturation, the specimens were carefully removed from the molds and placed onto the flexible-wall permeameter between water-saturated geotextiles and filter papers.

After the permeameter was installed, the burette at influent side was firstly filled with distilled water (DW), and the influent tube and heater were turned on after the confining pressure of 30 kPa was applied. When the constant temperature condition in the cell was maintained for 24 h, the influent tube was switched to another burette filled with target solution and the effluent tube was opened. The test started at the timing the effluent tube was opened. The hydraulic gradients provided by the water head in the burettes were initially 50 and gradually decreased as the test proceeded, the burettes were refilled before hydraulic gradient lower than 30.

The evaporation in the burettes was evaluated with closed burettes filled with solutions. Less than 0.1 mL evaporation for 1 week was confirmed in the burettes. Such small error was unmeasurable between the 2 intervals of water head measurements during the test (usually 1 or 2 d), and the systematic errors accumulated by evaporation was eliminated every time the burettes were refilled. Therefore, the effects of evaporation to the test results can be neglect.

The k in falling head hydraulic conductivity test is calculated with:

$$k_i = \frac{al}{A(t_i - t_{i-1})} \ln \frac{H_i}{H_{i-1}} \quad (\Delta t \ll t_{\text{total}}) \quad (3.2)$$

where a is cross area of burette (m^2); l is thickness of specimen (m); A is cross area of specimen (m^2); t_i is the time of i th measurement (s); H_i is water head at side of influent at t_i (m); k_i is hydraulic conductivity ($\text{m}\cdot\text{s}^{-1}$) at t_i .

The effluents were collected by 15 mL centrifuge tubes with 0.1 mL in accuracy, the centrifuge tubes were exchanged after one or several intervals of water head measurements. The cumulated volumes of effluents were obtained and characterized by pore volumes of flow (PVF) as the following equation:

$$\text{PVF} = \frac{V_{\text{out}}}{V_{\text{void}}} \quad (3.3)$$

where V_{out} is the cumulated volume of effluent (L); V_{void} is the pore volume of consolidated SB specimen (L). The PVF calculations were accurate to one digit after the decimal point. The exchanged centrifuge tubes then stored at 4°C after the electrical conductivity and pH of effluents were measured by HORIBA, LAQUAtwins pH-22B & EC-33B, with accuracy of 0.01 in pH and 0.001 S/m in EC.

The terminations of the test met the criteria recommended by ASTM D 6766 “Standard Test Method for evaluation of Hydraulic Properties of Geosynthetic Clays” (ASTM, 2014). Test were terminated after the steady hydraulic conductivity were observed at last 3 values, the EC ratio of effluent to influent was within 1.0 ± 0.1 , and 3 PVF of effluent had been collected.

Summarized in Table 3-3, 14 cases were operated in this study. Set 0 was operated as empty references in this study where distilled water was choose as permeant and the temperature was controlled at 20°C. Set 1 was operated in order to evaluate the temperature effects the on the hydraulic performance of SB when the concentration of multivalence cation was relatively low, where 0.1M CaCl_2 was choose as permeant and temperature was controlled at 20°C, 40°C, and 60°C. Set 2 was operated in order to evaluate the temperature effects on the hydraulic performance of SB when the concentration of multivalence cation was relatively high, where 1M CaCl_2 was choose as permeant and the temperature was controlled at 20°C, 40°C, and 60°C. In Set 1, the 20°C and 60°C cases were duplicated, and 40°C was operated once; In Set 2, the 20°C and 60°C cases were triplicated, and 40°C was operated once. The cases were named as “Permeant-Temperature-No.” (e.g. DW-20°C-1 and 0.1M-60°C-2). The 0.1M-40°C-1 and 0.1M-60°C-1 in Set 1 failed to meet the termination criteria, the terminated PVF of the two cases were 0.6 and 1.1, respectively.

Table 3-3 Conditions for hydraulic conductivity tests of SB with 30 kPa confined pressure, obtained values of hydraulic conductivity (k) and intrinsic permeability (K). The initial k is the averages of the first 5 values, equilibrium k is the average of values when PVF > 3 or average of last 3 values when terminated before 3 PVF. The K were calculated using fluid parameters of the corresponding permeant for each case at equilibrium.

Set	Name	Permeant	T (°C)	ρ_d (Mg·m ⁻³) after		Void ratio after		Terminate PVF	k (m·s ⁻¹)		K (m ²)	Terminate criteria
				Pre-consol.	Test	Pre-consol.	Test		Initial	Equilibrium		
0	DW-20°C-1	DW	20	1.47	1.46	0.84	0.86	3.1	4.6×10 ⁻¹¹	3.9×10 ⁻¹¹	4.0×10 ⁻¹⁸	Yes
	DW-20°C-2	DW			1.48		0.83	4.3	6.6×10 ⁻¹¹	6.0×10 ⁻¹¹	6.1×10 ⁻¹⁸	Yes
1	0.1M-20°C-1	0.1M CaCl ₂	20	1.47	1.47	0.83	0.83	4.9	3.4×10 ⁻¹¹	2.6×10 ⁻¹¹	2.7×10 ⁻¹⁸	Yes
	0.1M-20°C-2	0.1M CaCl ₂			1.47		0.83	4.9	3.3×10 ⁻¹¹	2.8×10 ⁻¹¹	2.9×10 ⁻¹⁸	Yes
	0.1M-40°C-1	0.1M CaCl ₂	40	1.47	1.47	0.84	0.84	0.6	2.7×10 ⁻¹¹	8.7×10 ⁻¹²	-	No
	0.1M-60°C-1	0.1M CaCl ₂	60	1.46	1.46	0.85	0.85	5.8	6.2×10 ⁻¹¹	4.3×10 ⁻¹¹	2.2×10 ⁻¹⁸	Yes
	0.1M-60°C-2	0.1M CaCl ₂			1.44		0.86	1.1	8.0×10 ⁻¹¹	4.7×10 ⁻¹¹	-	No
2	1M-20°C-1	1M CaCl ₂	20	1.47	1.46	0.83	0.84	8.4	5.0×10 ⁻¹¹	1.2×10 ⁻¹⁰	1.5×10 ⁻¹⁷	Yes
	1M-20°C-2	1M CaCl ₂			1.46		0.84	8.1	5.4×10 ⁻¹¹	1.1×10 ⁻¹⁰	1.5×10 ⁻¹⁷	Yes
	1M-20°C-3	1M CaCl ₂			1.46		0.84	8.0	5.9×10 ⁻¹¹	9.6×10 ⁻¹¹	1.2×10 ⁻¹⁷	Yes
	1M-40°C-1	1M CaCl ₂	40	1.47	1.46	0.84	0.85	4.1	1.1×10 ⁻¹⁰	1.7×10 ⁻¹⁰	1.4×10 ⁻¹⁷	Yes
	1M-60°C-1	1M CaCl ₂	60	1.46	1.45	0.84	0.85	16.1	3.2×10 ⁻⁹	2.6×10 ⁻¹⁰	1.7×10 ⁻¹⁷	Yes
	1M-60°C-2	1M CaCl ₂			1.44		0.86	12.9	1.3×10 ⁻⁹	2.3×10 ⁻¹⁰	1.4×10 ⁻¹⁷	Yes
	1M-60°C-3	1M CaCl ₂			1.45		0.85	13.0	9.9×10 ⁻¹⁰	2.0×10 ⁻¹⁰	1.3×10 ⁻¹⁷	Yes

DW = Distilled water; M = 1 mol/L at 25°C

Table 3-4 Fluid density and viscosity at different temperatures, referenced from Wimby & Berntsson (1994), Lide (2004), and Abdulagatov & Azizov, (2006).

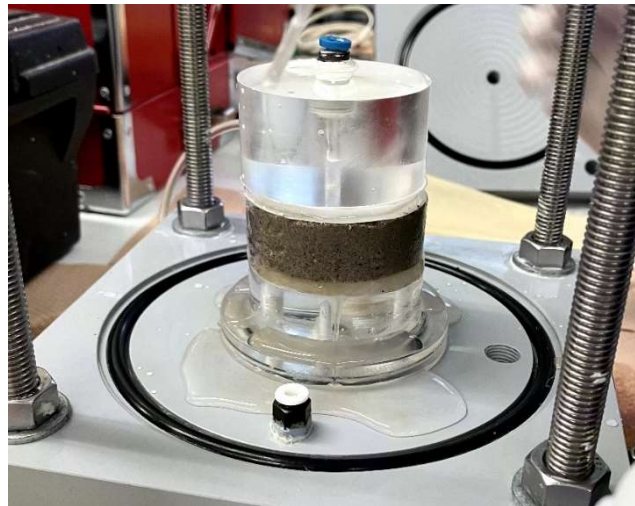
	DW			0.1M CaCl ₂			1M Ca Cl ₂		
	20	40	60	20	40	60	20	40	60
ρ (Mg/m ³)	1.00	0.99	0.98	1.01	1.00	1.00	1.08	1.07	1.07
μ (mPa·s)	1.00	0.65	0.47	1.03	0.70	0.49	1.33	0.91	0.68
$\rho g/\mu$ (10 ⁶ m ⁻¹ ·s ⁻¹)	9.80	14.93	20.43	9.61	14.08	19.80	7.96	11.20	15.42



(a) Pre-consolidation



(b) After vacuum saturation



(c) Placing specimen onto permeameter



(d) Specimen covered by rubber membrane.

Photo 3.3 Procedures of specimen preparing and installing.

The deformation of the specimens during the test periods were not accurately measured due to the obstruction of view by covered rubber heater, shown in Photo 3.2. As an alternative, the volumes of influent (V_{in}) and effluent (V_{out}) were compared in each case. The changes in void ratio were also measured after the test terminated, with a maximum difference of 0.02. Such changes were unable to generate calculation errors in PVF which accurate to one digit after the decimal point. Therefore, the V_{void} were considered as constant in this study.

3.4 Results

3.4.1 Profiles of hydraulic conductivity among with time and PVF

The relations between hydraulic conductivity (k) and time or PVF of Set 0, 1, 2 are showed in Figure 3.5 to Figure 3.7. The profiles of V_{in}/V_{out} for each Set, and profiles of EC for Set 1, 2 serve as indicators of the accuracy of the calculated k . Because fluctuations in k were observed initially in many cases, values of initial k and equilibrium k were defined individually in this study. The initial k was determined as the mean of the first 5 measured values, whereas the equilibrium k was determined as the average of values of PVF > 3.

In Figure 3.5 (a) and (b), the profiles of k of Set 0 were nearly constant among with time and PVF, the equilibrium k were $5 \times 10^{-11} \text{ m} \cdot \text{s}^{-1}$ on average. The equilibrium k is consistent with the value obtained by Takai et al. (2013) using SB with same mass ratio of bentonite under same test condition, indicating that the basic hydraulic performance of the SB used in this study is consistent with previous study. In addition, the V_{in}/V_{out} approximately equaled to 1 were observed in Figure 3.5 (c) and (d).

Figure 3.6 (a) and (b) shows the relations between k and time or PVF of Set 1. At 60°C, the initial values of k were relatively high, and the profiles of k showed characteristics of stable before 1 PVF, or approximately before $3 \times 10^6 \text{ s}$. At 40°C, the profile of k showed significant decreasing, and lower than $1 \times 10^{-11} \text{ m} \cdot \text{s}^{-1}$ before 0.5 PVF. At 20°C, the profiles of k showed slight increases at approximately 1 PVF, or at $2 \times 10^6 \text{ s}$, and followed by slight decreases until terminations.

The profiles of effluents' EC of Set 1 are shown in Figure 3.6 (c) and (d). The EC of effluents gradually approached and converged to the values of the influent ($1.96 \text{ S} \cdot \text{m}^{-1}$) as test proceeded, following the well-known “breakthrough” process (Shackelford et al., 1999). Although 0.1M-40°C-1 and 0.1M-60°C-2, did not met the criteria of termination, their profiles showed similarity to the others. The temperature effects to the EC were discussed in Chapter 4.

In Figure 3.6 (e) and (f), V_{in}/V_{out} of Set 1 were observed approximately equaled to 1 before 1 PVF, or before $2 \times 10^6 \text{ s}$, indicated the validity of measured k . As summarized in Table 3-3, the obtained initial k were 3.4×10^{-11} , 2.7×10^{-11} , and $7.1 \times 10^{-11} \text{ m} \cdot \text{s}^{-1}$ on average at 20°C, 40°C, and 60°C, respectively. Equilibrium k were 2.7×10^{-10} , 8.7×10^{-12} , and $5.7 \times 10^{-10} \text{ m} \cdot \text{s}^{-1}$ on average at 20°C, 40°C, and 60°C, respectively. The equilibrium k of 0.1M-40°C-1 and 0.1M-60°C-2 was given as the average of last 3 values, where the former was treated invalid for the irregular observed in profiles of k and the latter was treated valid considering the similarity of the k profiles between 0.1M-60°C-1 and 0.1M-60°C-2.

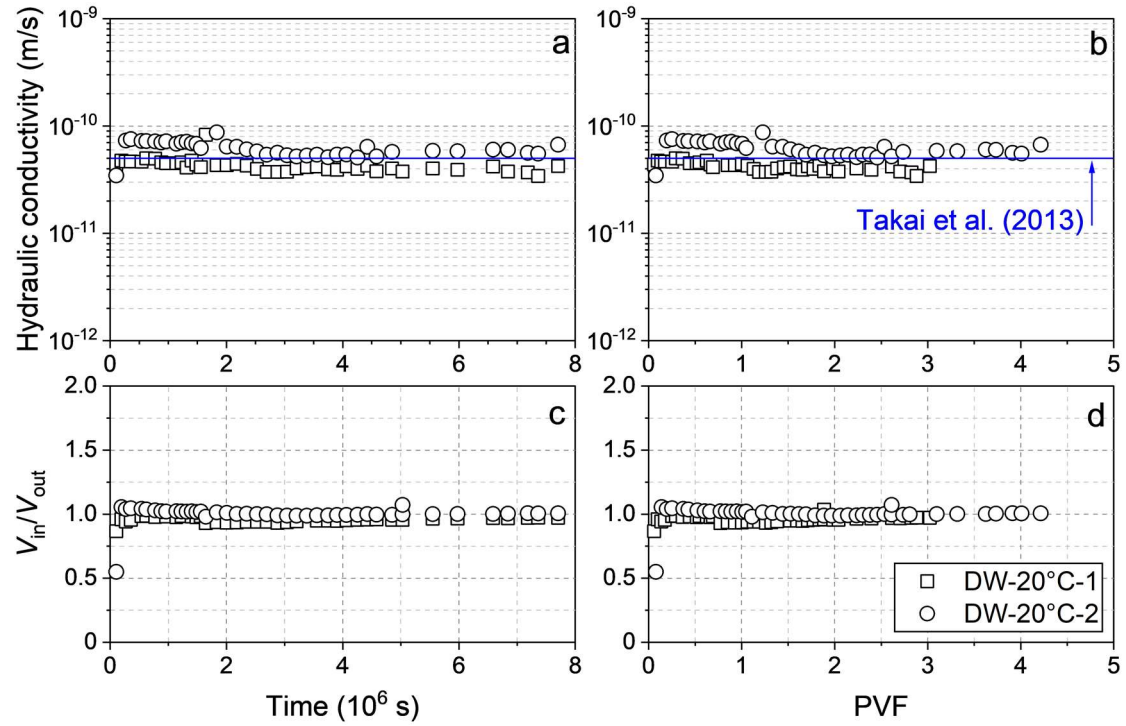


Figure 3.5 Hydraulic conductivity and volume ratio among with time and PVF of Set 0.

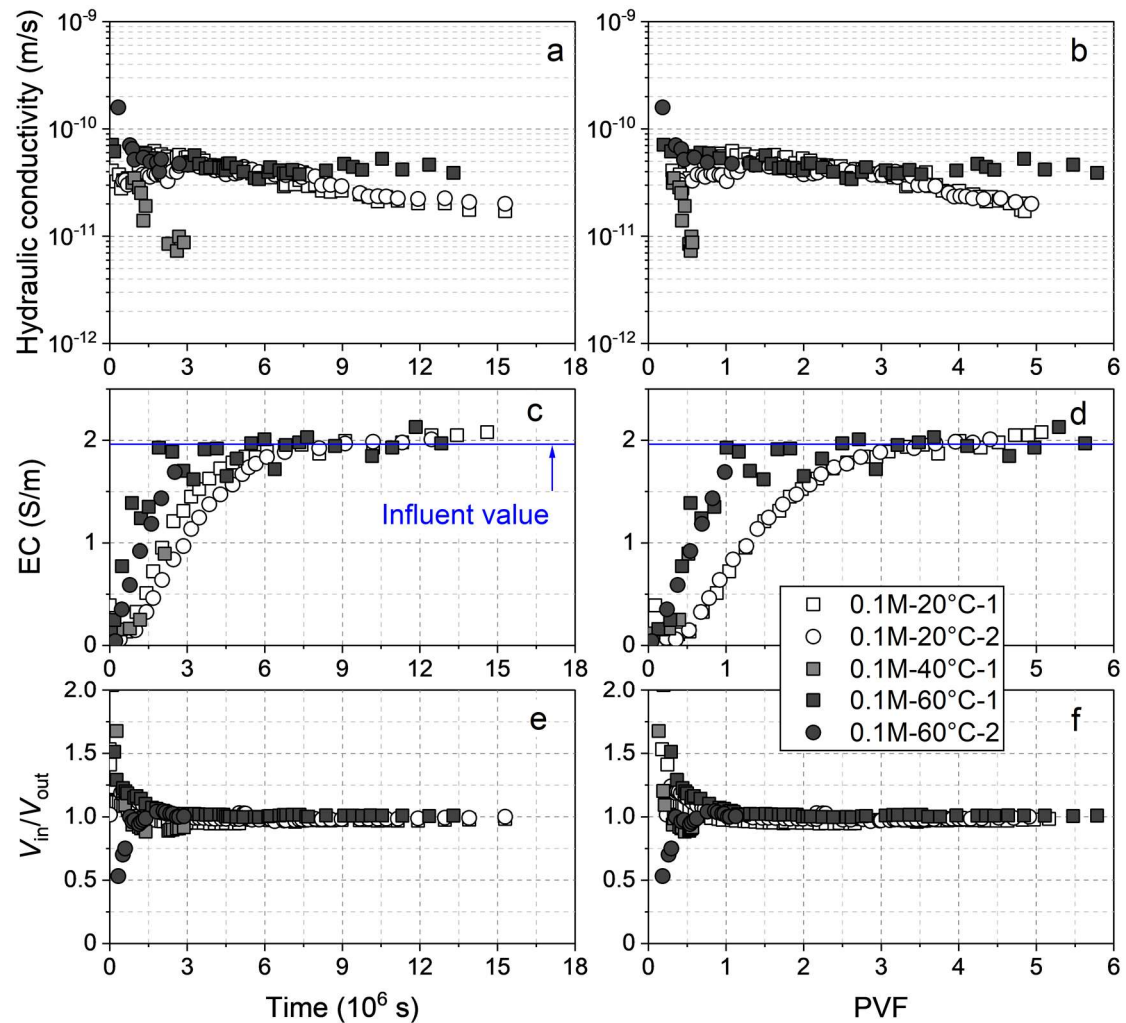


Figure 3.6 Hydraulic conductivity, volume ratio, and EC among with time and PVF of Set 1.

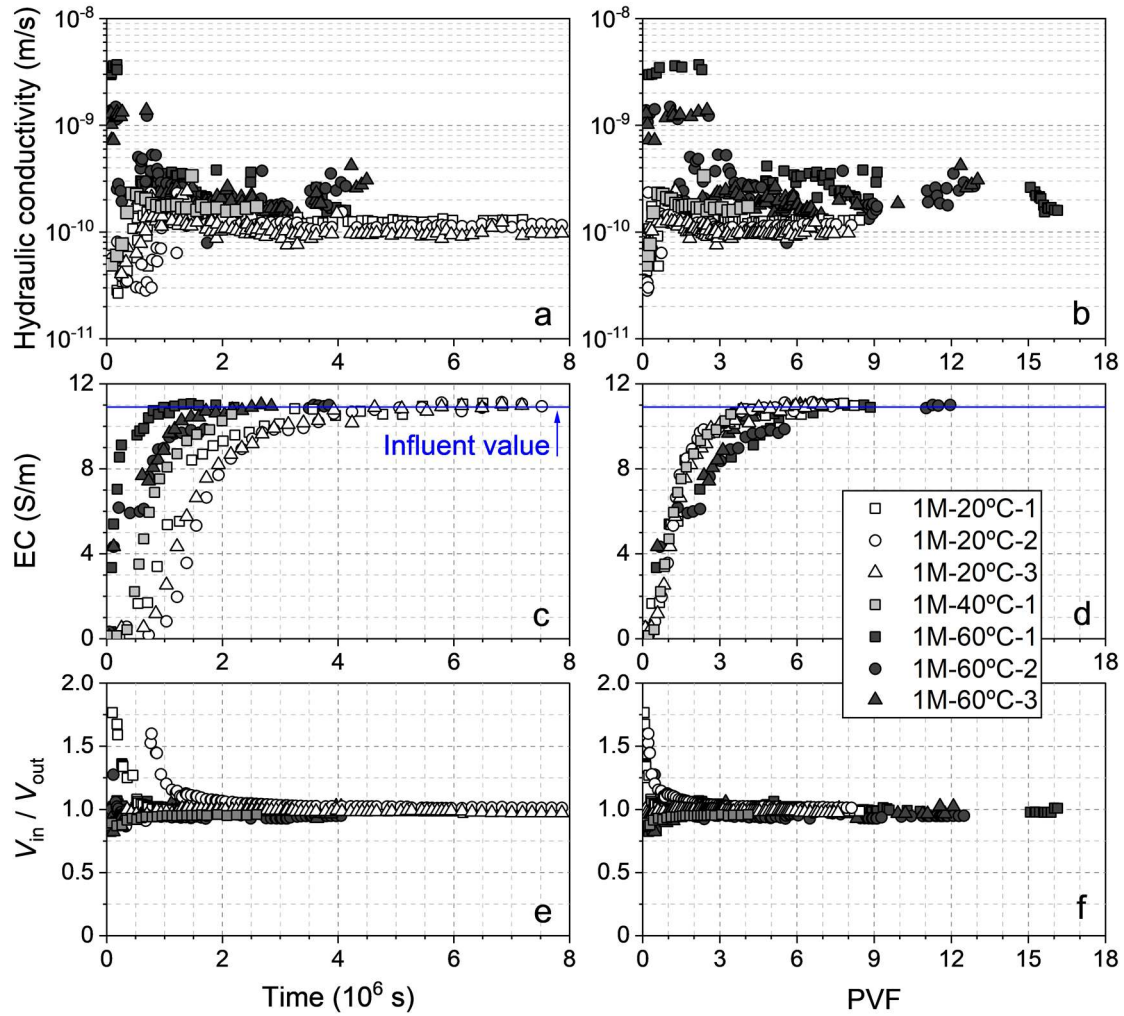


Figure 3.7 Hydraulic conductivity, volume ratio, and EC among with time and PVF of Set 2.

Figure 3.7 (a) and (b) shows the relations between k and time or PVF of Set 2. At 60°C, the profiles of k exhibited brief high values initially, during which the values of k temporarily exceeded 10^{-9} m/s. The k decreased at approximately 3 PVF, or before 1×10^6 s, and then became stable but showed minor fluctuations until the terminations. At 20°C and 40°C, the profiles of k slightly increased initially and then became stable at approximately 1 PVF.

The profiles of effluents' EC of Set 2 are shown in Figure 3.7 (c) and (d). The EC finally converged to the influent value ($10.9 \text{ S} \cdot \text{m}^{-1}$) were observed in all cases of Set 2, indicating that the tests met the termination criteria. The impact of temperature on the EC breakthrough varied depending on whether time or PVF was the X-axis. As temperatures increased, effluent EC reached convergence faster, but the volumes of effluent at convergence also increased. The temperature effects to the EC were discussed in Chapter 4.

Among all cases in Set 2, as shown in Figure 3.7 (e) and (f), the cumulative volumes of effluent V_{out} eventually, approximately, equaled to the cumulative volumes of influent V_{in} before 1 PVF, indicated the validity of measured k . As summarized in Table 3-3, the obtained initial k were 5.4×10^{-11} , 1.1×10^{-10} , and $1.8 \times 10^{-9} \text{ m} \cdot \text{s}^{-1}$ on average at 20°C, 40°C, and 60°C, respectively. Equilibrium k were 1.1×10^{-10} , 1.7×10^{-10} , and $2.3 \times 10^{-10} \text{ m} \cdot \text{s}^{-1}$ on average at 20°C, 40°C, and 60°C, respectively.

3.4.2 Temperature dependency of hydraulic conductivity and intrinsic permeability

The temperature dependencies of equilibrium k of Set 1 and Set 2 are shown in Figure 3.8 (a), where the obtained equilibrium k were compared with calculated hydraulic conductivity ($k_{\text{Calc.}}$). The $k_{\text{Calc.}}$ in Figure 3.8 (a) is obtained by equation, derived from Eq (3.1) with assuming K is constant, as below:

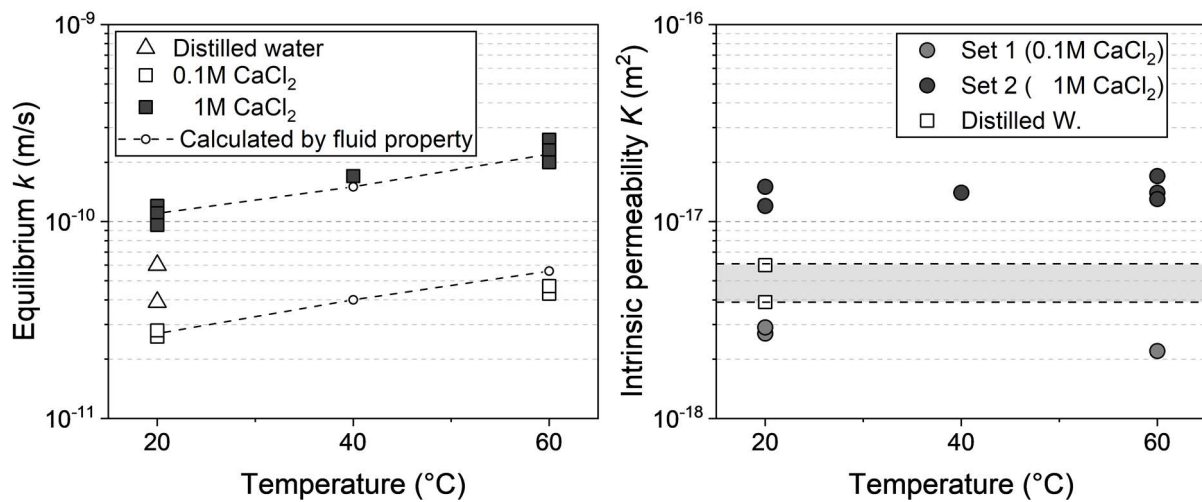
$$\frac{k_{\text{Calc.}}}{k_{20}} = \frac{(\rho g / \mu)_T}{(\rho g / \mu)_{20}} \quad (3.4)$$

where $(\rho g / \mu)_T$ is the fluid property of permeant at specific temperatures ($\text{m}^{-1} \cdot \text{s}^{-1}$). The pore solutions in the specimens at equilibrium were treated the same as the permeant, as indicated from the EC of the effluents shown in Figure 3.6 and Figure 3.7, relevant values are summarized in Table 3-4.

In this study, the values of intrinsic permeability (K) were determined using Eq (3.1) with equilibrium k , and the K of cases failed to meet the terminate criteria were not calculated. The temperature dependencies of K of Set 0, 1 and 2 are shown in Figure 3.8 (b).

In Figure 3.8 (a), both the equilibrium k of Set 1 and Set 2 were observed increased with temperature, and the differences between equilibrium k and $k_{\text{Calc.}}$ were insignificant, and were smaller than their corresponding magnitude (maximum differences of $0.9 \times 10^{-11} \text{ m} \cdot \text{s}^{-1}$ in Set 1 and $0.4 \times 10^{-10} \text{ m} \cdot \text{s}^{-1}$ in Set 2). In Figure 3.8 (b), the temperature effects to the values of K were also insignificant, the average K were 5×10^{-18} , 2.6×10^{-18} , and $1.4 \times 10^{-17} \text{ m}^2$ in Set 0, 1, and 2, respectively. The K of Set 2 were higher than the K of Set 1, however, the K of Set 1 were slightly lower than the K of cases permeated with distilled water.

The insignificant temperature dependencies of K are consistent with some previous studies using other materials (Bouazza et al., 2008; Cho et al., 1999; Ozhan, 2018b). Indicating the temperature dependency of SB's hydraulic conductivity was predominantly attributed to the variations in fluid density and viscosity.



(a) Characterized by hydraulic conductivity (b) Characterized by intrinsic permeability

Figure 3.8 Temperature dependency of hydraulic performance of SB

3.5 Discussion

3.5.1 Temperature effects on chemical compatibility of prehydrated SB

As it was introduced in Section 3.1, the prehydration effectively increased the chemical compatibility of bentonite materials to prevent significantly changes in hydraulic performance when permeated with chemical solutions. The results in Section 3.4 have showed that the equilibrium k of all cases were lower than $10^{-9} \text{ m}\cdot\text{s}^{-1}$, indicated that the hydraulic performance of prehydrated SB can be maintained to a large extent between 20°C to 60°C .

One confusing result is both k and K in Set 1 (0.1M CaCl_2) were even lower than k and K in Set 0 (DW), which indicated that the hydraulic performance of SB were even slightly increased when attacked by chemical solutions with relatively low concentration. Though strange, similar results have been reported by Kolstad et al. (2004) that the prehydrated GCL had lower k when permeated with 2M CaCl_2 than permeated with deionized water. The reason for the slight decrease of k and K is unclear, but it did not negatively impact the SB's hydraulic performance.

Figure 3.9 shows the relation between intrinsic permeability and permeant Ca^{2+} molarity. The K of SB showed relatively significant increase when permeant Ca^{2+} molarity changed from 0.1M to 1M. However, this change is still minimal when chemical solution attacked to non-prehydrated materials. The hydraulic conductivity of largest K still lower than the criterion of most soil barriers (Chai, 2002; Takai et al., 2013). The temperature effects in Figure 3.9 were insignificant. Therefore, chemical compatibility of prehydrated SB barrier is unlikely to be significantly affected by the change of temperature from 20°C to 60°C .

Table 3-5 Hydraulic conductivities of GCLs (Kolstad et al., 2004).

Permeant	Prehydrated GCL		Conventional GCL	
	$k \text{ (m}\cdot\text{s}^{-1}\text{)}$	k/k_{DI}	$k \text{ (m}\cdot\text{s}^{-1}\text{)}$	k/k_{DI}
1M NaCl	4.2×10^{-12}	1.02	7.9×10^{-7}	65800
2M CaCl_2	3.7×10^{-12}	0.90	8.1×10^{-7}	67500
Deionized water	4.1×10^{-12}	1.00	1.2×10^{-11}	1.00

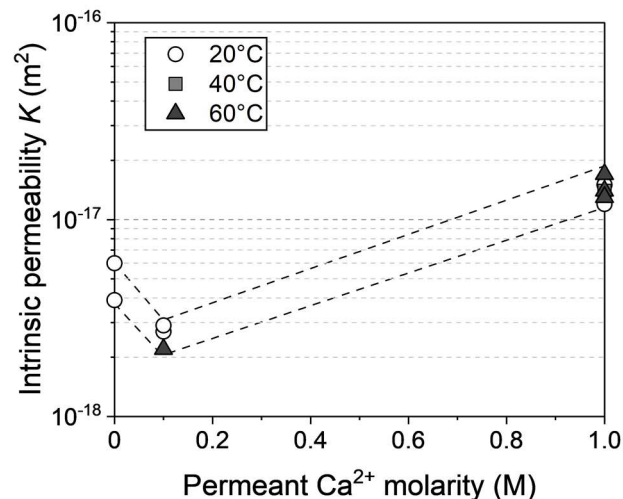


Figure 3.9 Relations between intrinsic permeability and permeant Ca^{2+} molarity.

3.5.2 Temporary changes of hydraulic conductivity at various temperatures

As shown in Figure 3.6 and Figure 3.7, the profiles of hydraulic conductivity (k) exhibited different characteristics at different temperatures. Specifically, the temporal changes of k can be quantified from the differences between values of initial k and equilibrium k that summarized in Table 3-3.

The differences between initial k and equilibrium k are shown in Figure 3.8. When permeated with distilled water (Set 0), the differences between initial k and equilibrium k were insignificant; When permeated with 0.1M CaCl_2 (Set 1), initial k were higher than equilibrium k at 20°C and 60°C; When permeated with 1M CaCl_2 (Set 2), initial k were lower than equilibrium k at 20°C, but higher than equilibrium k at 40°C and 60°C. Overall, the impacts of temperature on the initial k were more significant than on the equilibrium k .

At 20°C, the initial values of the three Sets were concentrated within 3×10^{-11} to $6 \times 10^{-11} \text{ m}\cdot\text{s}^{-1}$, which is consistent with the same initial state of all specimens that the pore water were approximately pure water when test started. The decrease of k of Set 1 at 20°C has been discussed in Subsection 3.5.1. Then, the rest differences between initial k and equilibrium k can be divided into: (i) the k increased slightly and reached equilibrium, as 20°C and 40°C of Set 2; (ii) the k decreased and reached equilibrium, as 20°C of Set 1, and 60°C of Set 1 and Set 2.

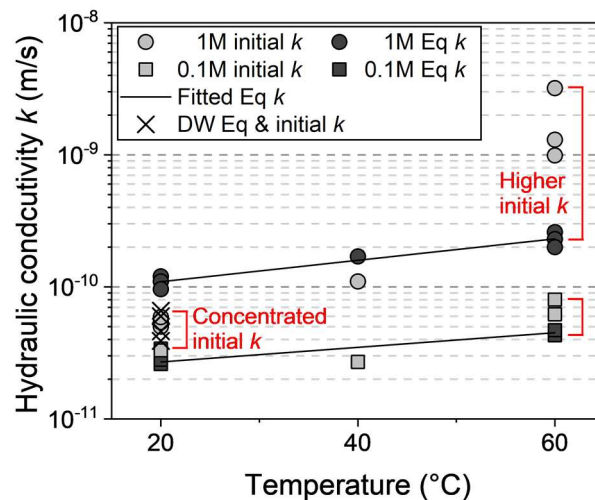


Figure 3.10 Differences between initial k and equilibrium k .

The slight increases in k can be explained as the increase of pore concentration as the breakthrough of CaCl_2 reduced the DDL thickness. Similar behavior has been observed in some prior studies (Jo et al., 2005; Katsumi et al., 2007). In addition, the changes of k were . Indicating the chemical compatibility of SB obtained from the prehydration (Kolstad et al., 2004; Shackelford et al., 2000) during the specimen preparation.

The decreases in k at 60°C were unusual. The presence of initial high values in Set 1 (relatively insignificant) and in Set 2 (significant) suggests that it was unlikely to be caused by chance factors. Considering all specimens at equilibrium had proximate values of intrinsic permeability, it is reasonable to infer that at 60°C, the initial k were “too high” rather than the equilibrium k were “too low”, and the k of SB specimens were somehow increased initially.

The most possible reason for such phenomenon is the heating procedure, the only variable. Heating the specimen to 60°C within 24 h might generated some damages to the specimen by reasons like aggregate expansion and particle extrusion. There must be a threshold between 40°C and 60°C where such damages were capable to exhibit significant changes in initial k . While there is no solid evidence to support this claim, similar decreases in k have been reported in studies concerning curing processes of bentonite materials (Egloffstein, 2001; Flessati et al., 2023; Y. Wang et al., 2021) that materials were intentionally damaged initially and then self-healed and sealed to recover from the damage. In this study, although the increased k were finally recovered, it reveals the possibility that k may temporarily increase when there are rapid temperature changes, highlighting the need to monitor the temperature changes during the operation of the SB barrier.

3.6 Conclusions of Chapter 3

In this Chapter, the temperature effects to the hydraulic performance of soil-bentonite mixtures (SB) were evaluated by operating falling-head hydraulic conductivity tests at constant temperatures of 20°C, 40°C, and 60°C with modified flexible-wall permeameter. The SB barriers were emulated by consolidated SB specimens with 20 mm initial height and 1.46 to 1.47 Mg·m⁻³ initial dry densities. The hydraulic performance was characterized by hydraulic conductivity (k) and intrinsic permeability (K). The following conclusions could be summarized supported by the test results and discussions:

- (1) A temperature control module was installed on the flexible-wall permeameter. The test temperature was heated via a silicon rubber heater covering the outer face of the acrylic cylinder, and maintained via a thermoregulator connected to the heater. The device enables the falling-head hydraulic conductivity test to be operated accurately within a temperature range of 20°C to 60°C with a precision of 1°C.
- (2) The equilibrium k were determined as the average of obtained values when PVF > 3. The equilibrium k of all cases were < 10⁻⁹ m/s. The equilibrium k were observed increase with increased temperature when permeated with 0.1M CaCl₂ (Set 1) and 1M CaCl₂ (Set 2). Equilibrium k were 2.7×10⁻¹⁰ and 5.7×10⁻¹⁰ m·s⁻¹ on average at 20°C and 60°C in Set 1. Equilibrium k were 1.1×10⁻¹⁰, 1.7×10⁻¹⁰, and 2.3×10⁻¹⁰ m·s⁻¹ on average at 20°C, 40°C, and 60°C, respectively, in Set 2.
- (3) The temperature dependencies of equilibrium k of Set 1 and Set 2 were found consistent with the estimation calculated with permeant densities and viscosities at corresponding temperatures. The K was calculated by eliminate the fluid density and viscosity from equilibrium k . The K did not show significant temperature dependencies, which were 2.6×10⁻¹⁸ and 1.5×10⁻¹⁷ m² on averages in Set 1 and Set 2, respectively. Indicating that the changes of equilibrium k in different temperatures were predominantly attributed to the changes of fluid viscosity and density in this study.
- (4) The prehydrated SB specimens exhibited good chemical compatibility. The increases of the K when permeated with 1M CaCl₂ were less than one magnitude compared to the cases permeated with distilled water. The temperature effects on the chemical compatibilities

gained from prehydration were insignificant. The chemical compatibility of prehydrated SB barrier is unlikely to be significantly affected by a temperature change of temperature from 20°C to 60°C during practical functioning.

- (5) Temporary changes of k were observed in profiles of k among with time and PVF. The temporary changes were characterized by the differences between initial k and equilibrium k , where initial k were determined as the first 5 values obtained in the test. The initial k increased as temperature rose, with temperature having a more significant impact on the initial k than on the equilibrium k .
- (6) The test results showed the hydraulic performance of SB barrier met the criterion of soil barriers when equilibrium k were achieved. The test results also reveal the possibility that k may temporarily increase when there are rapid temperature changes, highlighting the need to monitor the temperature changes during the operation of the SB barriers.

References

- Abdulagatov, I. M., & Azizov, N. D. (2006). Viscosity of aqueous calcium chloride solutions at high temperatures and high pressures. *Fluid Phase Equilibria*, 240(2), 204–219. <https://doi.org/10.1016/j.fluid.2005.12.036>
- ASTM:D5084-16a. (2010). Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter. *ASTM International, West Conshohocken, PA, USA, C*, 1–23. <https://doi.org/10.1520/D5084-03.1.3.2>
- ASTM:D6766-12. (2014). Standard Test Method for Evaluation of Hydraulic Properties of Geosynthetic Clay. *ASTM International, West Conshohocken, PA, USA, i*, 1–9. <https://doi.org/10.1520/D6766-20A.2>
- Bear, J. (1973). Dynamics of Fluids in Porous Media. In *Dover publications* (Vol. 37, Issue 4). Dover.
- Bouazza, A., Abuel-Naga, H. M., Gates, W. P., & Laloui, L. (2008). Temperature effects on volume change and hydraulic properties of geosynthetic clay liners. *The First Pan American Geosynthetics Conference & Exhibition, C*(January), 102–109.
- Bradshaw, S. L., & Benson, C. H. (2014). Effect of Municipal Solid Waste Leachate on Hydraulic Conductivity and Exchange Complex of Geosynthetic Clay Liners. *Journal of Geotechnical and Geoenvironmental Engineering*, 140(4). [https://doi.org/10.1061/\(asce\)gt.1943-5606.0001050](https://doi.org/10.1061/(asce)gt.1943-5606.0001050)
- Bradshaw, S. L., Benson, C. H., & Scalia, J. (2013). Hydration and Cation Exchange during Subgrade Hydration and Effect on Hydraulic Conductivity of Geosynthetic Clay Liners. *Journal of Geotechnical and Geoenvironmental Engineering*, 139(4), 526–538. [https://doi.org/10.1061/\(asce\)gt.1943-5606.0000793](https://doi.org/10.1061/(asce)gt.1943-5606.0000793)
- Chai, J. N. M. (2002). Comparing the performance of landfill liner systems. *J Mater Cycles Waste Manag*, 4, 135–142.
- Cho, W. J., Lee, J. O., & Chun, K. S. (1999). The temperature effects on hydraulic conductivity of compacted bentonite. In *Applied Clay Science* (Vol. 14).
- Delage, P., Sultan, N., & Cui, Y. J. (2000). On the thermal consolidation of Boom clay. *Canadian Geotechnical Journal*, 37(2), 343–354. <https://doi.org/10.1139/cgj-37-2-343>
- Egloffstein, T. A. (2001). Natural bentonites - Influence of the ion exchange and partial desiccation on permeability and self-healing capacity of bentonites used in GCLs. *Geotextiles and Geomembranes*, 19(7), 427–444. [https://doi.org/10.1016/S0266-1144\(01\)00017-6](https://doi.org/10.1016/S0266-1144(01)00017-6)

- Evans, J. C. (1993). Vertical cutoff walls. In *Geotechnical Practice for Waste Disposal* (pp. 430–454). Springer US. https://doi.org/10.1007/978-1-4615-3070-1_17
- Flessati, L., Vecchia, G. Della, & Musso, G. (2023). Effects of curing on the hydro-mechanical behaviour of cement-bentonite mixtures for cut-off walls. *Construction and Building Materials*, 383(January), 131392. <https://doi.org/10.1016/j.conbuildmat.2023.131392>
- Gleason, M. H., Daniel, D. E., & Eykholt, G. R. (1997). Calcium and Sodium Bentonite for Hydraulic Containment Applications. *Journal of Geotechnical and Geoenvironmental Engineering*, 123(5), 438–445. [https://doi.org/10.1061/\(ASCE\)1090-0241\(1997\)123:5\(438\)](https://doi.org/10.1061/(ASCE)1090-0241(1997)123:5(438))
- Ishimori, H., & Katsumi, T. (2012). Temperature effects on the swelling capacity and barrier performance of geosynthetic clay liners permeated with sodium chloride solutions. *Geotextiles and Geomembranes*, 33, 25–33. <https://doi.org/10.1016/j.geotexmem.2012.02.005>
- J. Hunter, R. (1981). Zeta potential in colloid science: Principles and applications. In *Academic Press*.
- Japanese Industrial Standards. (2020a). Test method for density of soil particles. *JIS A 1202*.
- Japanese Industrial Standards. (2020b). Test Methods for Particle Size Distribution of Soils. *JIS A 1204*.
- Jo, H. Y., Benson, C. H., Shackelford, C. D., Lee, J.-M., & Edil, T. B. (2005). Long-Term Hydraulic Conductivity of a Geosynthetic Clay Liner Permeated with Inorganic Salt Solutions. *Journal of Geotechnical and Geoenvironmental Engineering*, 131(4), 405–417. [https://doi.org/10.1061/\(asce\)1090-0241\(2005\)131:4\(405\)](https://doi.org/10.1061/(asce)1090-0241(2005)131:4(405))
- Kamon, M., Katsumi, T., Inui, T., & Morimoto, T. (2002). Suitability Assessment of Bentonite-Soil Mixtures as the Landfill Bottom Liner Material. *Journal of the Society of Materials Science, Japa*, 51(1), 36–41.
- Kamon, M., Katsumi, T., Inui, T., Ogawa, Y., & Araki, S. (2006). Hydraulic Performance of Soil-Bentonite Mixture Barrier. In *5th ICEG Environmental Geotechnics: Opportunities, Challenges and Responsibilities for Environmental Geotechnics* (pp. 733–740). <https://doi.org/10.1680/ieg.34747.0733>
- Katsumi, T., Ishimori, H., Ogawa, A., Maruyama, S., & Fukagawa, R. (2008). Effects of Water Content Distribution on Hydraulic Conductivity of Prehydrated GCLS against Calcium Chloride Solutions. *Soils and Foundations*, 48(3), 407–417. <https://doi.org/10.3208/sandf.48.407>
- Katsumi, T., Ishimori, H., Ogawa, A., Yoshikawa, K., Hanamoto, K., & Fukagawa, R. (2007). Hydraulic Conductivity of Nonprehydrated Geosynthetic Clay Liners Permeated with Inorganic Solutions and Waste Leachates. *Soils and Foundations*, 47(1), 79–96. <https://doi.org/10.3208/sandf.47.79>
- Katsumi, T., Kamon, M., Inui, T., & Araki, S. (2008). Hydraulic barrier performance of SBM cut-off wall constructed by the trench cutting and re-mixing deep wall method. In *GeoCongress 2008: Geotechnics of Waste Management and Remediation* (pp. 628–635).
- Kolstad, D. C., Benson, C. H., & Edil, T. B. (2004). Hydraulic Conductivity and Swell of Nonprehydrated Geosynthetic Clay Liners Permeated with Multispecies Inorganic Solutions. *Journal of Geotechnical and Geoenvironmental Engineering*, 130(12), 1236–1249. [https://doi.org/10.1061/\(asce\)1090-0241\(2004\)130:12\(1236\)](https://doi.org/10.1061/(asce)1090-0241(2004)130:12(1236))
- Kolstad, D. C., Benson, C. H., Edil, T. B., & Jo, H. Y. (2004). Hydraulic conductivity of a dense prehydrated GCL permeated with aggressive inorganic solutions. *Geosynthetics International*, 11(3), 233–241. <https://doi.org/10.1680/gein.11.3.209.44488>
- Komine, H. (2004). Simplified evaluation for swelling characteristics of bentonites. *Engineering Geology*, 71(3–4), 265–279. [https://doi.org/10.1016/S0013-7952\(03\)00140-6](https://doi.org/10.1016/S0013-7952(03)00140-6)
- Komine, H., & Ogata, N. (1999). Experimental Study on Swelling Characteristics of Sand-Bentonite Mixture for Nuclear Waste Disposal. *Soils and Foundations*, 39(2), 83–97.

- https://doi.org/10.3208/sandf.39.2_83
- Komine, H., Yasuhara, K., & Murakami, S. (2009). Swelling characteristics of bentonites in artificial seawater. *Canadian Geotechnical Journal*, 46(2), 177–189. <https://doi.org/10.1139/T08-120>
- Lee, J.-M., & Shackelford, C. D. (2005). Impact of Bentonite Quality on Hydraulic Conductivity of Geosynthetic Clay Liners. *Journal of Geotechnical and Geoenvironmental Engineering*, 131(1), 64–77. [https://doi.org/10.1061/\(asce\)1090-0241\(2005\)131:1\(64\)](https://doi.org/10.1061/(asce)1090-0241(2005)131:1(64))
- Lide, D. R. (2004). *CRC handbook of chemistry and physics* (Vol. 85). CRC press.
- Lloret, A., & Villar, M. V. (2007). Advances on the knowledge of the thermo-hydro-mechanical behaviour of heavily compacted “FEBEX” bentonite. *Physics and Chemistry of the Earth*, 32(8–14), 701–715. <https://doi.org/10.1016/j.pce.2006.03.002>
- Malusis, M. A., Barben, E. J., & Evans, J. C. (2009). Hydraulic Conductivity and Compressibility of Soil-Bentonite Backfill Amended with Activated Carbon. *Journal of Geotechnical and Geoenvironmental Engineering*, 135(5), 664–672. [https://doi.org/10.1061/\(asce\)gt.1943-5606.0000041](https://doi.org/10.1061/(asce)gt.1943-5606.0000041)
- Malusis, M. A., & McKeehan, M. D. (2013). Chemical Compatibility of Model Soil-Bentonite Backfill Containing Multiswellable Bentonite. *Journal of Geotechnical and Geoenvironmental Engineering*, 139(2), 189–198. [https://doi.org/10.1061/\(asce\)gt.1943-5606.0000729](https://doi.org/10.1061/(asce)gt.1943-5606.0000729)
- McBride, M. B. (1994). Environmental chemistry of soils. In *Suparyanto dan Rosad* (2015). Oxford university press.
- Naka, A., Flores, G., Inui, T., Sakanakura, H., & Katsumi, T. (2019). Hydraulic performance and chemical compatibility of a powdered Na-bentonite geosynthetic clay liner permeated with mine drainage. *Soils and Foundations*, 59(5), 1128–1147. <https://doi.org/10.1016/j.sandf.2019.02.005>
- Norris, A., Di Emidio, G., Malusis, M. A., & Replogle, M. (2018). Modified bentonites for soil-bentonite cutoff wall applications with hard mix water. *Applied Clay Science*, 158(November 2017), 226–235. <https://doi.org/10.1016/j.clay.2018.03.030>
- Ozhan, H. O. (2018a). Effects of Temperature Increase in 0.5 M MgCl₂ Solution on Hydraulic Capability of Anionic Polymer-Treated Geosynthetic Clay Liners Used as Barriers. *Journal of Environmental Engineering*, 144(10), 1–11. [https://doi.org/10.1061/\(asce\)ee.1943-7870.0001451](https://doi.org/10.1061/(asce)ee.1943-7870.0001451)
- Ozhan, H. O. (2018b). Hydraulic capability of polymer-treated GCLs in saline solutions at elevated temperatures. *Applied Clay Science*, 161, 364–373. <https://doi.org/10.1016/j.clay.2018.05.007>
- R. Alther, G. (1982). The Role of Bentonite in Soil Sealing Applications. *Environmental & Engineering Geoscience*, xix(4), 401–409. <https://doi.org/10.2113/gsegeosci.xix.4.401>
- Rowe, R. K. (1998). *Geosynthetics and the minimization of contaminant migration through barrier systems beneath solid waste Hydraulic Performance of GCLs in containment of brine and landfill applications View project Long-term performance of geomembranes View project. March 1998.* <https://www.researchgate.net/publication/291698097>
- Rowe, R. K. (2020). Geosynthetic clay liners: Perceptions and misconceptions. *Geotextiles and Geomembranes*, 48(2), 137–156. <https://doi.org/10.1016/j.geotexmem.2019.11.012>
- Sato, K., Barast, G., Razakamanantsoa, A. R., Djeran-Maigre, I., Katsumi, T., & Levacher, D. (2017). Comparison of prehydration and polymer adding effects on Na activated Ca-bentonite by free swell index test. *Applied Clay Science*, 142, 69–80. <https://doi.org/10.1016/j.clay.2016.10.009>
- Shackelford, C. D. (1994). Waste-soil interactions that alter hydraulic conductivity. *Hydraulic Conductivity and Waste Contaminant Transport in Soil*, 1142, 111.
- Shackelford, C. D., Benson, C. H., Katsumi, T., Edil, T. B., & Lin, L. (2000). Evaluating the

- hydraulic conductivity of GCLs permeated with non-standard liquids. *Geotextiles and Geomembranes*, 18(2–4), 133–161. [https://doi.org/10.1016/S0266-1144\(99\)00024-2](https://doi.org/10.1016/S0266-1144(99)00024-2)
- Shackelford, C. D., Malusis, M. A., Majeski, M. J., & Stern, R. T. (1999). Electrical Conductivity Breakthrough Curves. *Journal of Geotechnical and Geoenvironmental Engineering*, 125(4), 260–270. [https://doi.org/10.1061/\(ASCE\)1090-0241\(1999\)125:4\(260\)](https://doi.org/10.1061/(ASCE)1090-0241(1999)125:4(260))
- Takai, A., Inui, T., Katsumi, T., Kamon, M., & Araki, S. (2013). Hydraulic barrier performance of soil bentonite mixture cutoff wall. *Coupled Phenomena in Environmental Geotechnics: From Theoretical and Experimental Research to Practical Applications - Proceedings of the International Symposium, ISSMGE TC 215, December*, 707–714. <https://doi.org/10.1201/b15004-96>
- Tan, Y., Zhang, H., Zhang, T., Zhang, G., He, D., & Ding, Z. (2021). Anisotropic hydro-mechanical behavior of full-scale compacted bentonite-sand blocks. *Engineering Geology*, 287(May 2020), 106093. <https://doi.org/10.1016/j.enggeo.2021.106093>
- Towhata, I., Kuntiwattanaku, P., Seko, I., & Ohishi, K. (1993). Volume change of clays induced by heating as observed in consolidation tests. *Soils and Foundations*, 33(4), 170–183.
- Villar, M. V., & Lloret, A. (2004). Influence of temperature on the hydro-mechanical behaviour of a compacted bentonite. *Applied Clay Science*, 26(1-4 SPEC. ISS.), 337–350. <https://doi.org/10.1016/j.clay.2003.12.026>
- Wang, H., Ito, D., Shirakawabe, T., Ruan, K., & Komine, H. (2022). On swelling behaviors of a bentonite under different water contents. *Geotechnique*. <https://doi.org/10.1680/jgeot.21.00312>
- Wang, S., Zhu, W., Qian, X., Xu, H., & Fan, X. (2017). Temperature effects on non-Darcy flow of compacted clay. *Applied Clay Science*, 135, 521–525. <https://doi.org/10.1016/j.clay.2016.09.025>
- Wang, Y., Zhang, H., Tan, Y., & Zhu, J. (2021). Sealing performance of compacted block joints backfilled with bentonite paste or a particle-powder mixture. *Soils and Foundations*, 61(2), 496–505. <https://doi.org/10.1016/j.sandf.2021.01.005>
- Wimby, J. M., & Berntsson, T. S. (1994). Viscosity and Density of Aqueous Solutions of LiBr, LiCl, ZnBr₂, CaCl₂, and LiNO₃. 1. Single Salt Solutions. *Journal of Chemical and Engineering Data*, 39(1), 68–72. <https://doi.org/10.1021/je00013a019>
- Ye, W. M., Wan, M., Chen, B., Chen, Y. G., Cui, Y. J., & Wang, J. (2013). Temperature effects on the swelling pressure and saturated hydraulic conductivity of the compacted GMZ01 bentonite. *Environmental Earth Sciences*, 68(1), 281–288. <https://doi.org/10.1007/s12665-012-1738-4>
- Ye, W. M., Zheng, Z. J., Chen, B., Chen, Y. G., Cui, Y. J., & Wang, J. (2014). Effects of pH and temperature on the swelling pressure and hydraulic conductivity of compacted GMZ01 bentonite. *Applied Clay Science*, 101, 192–198. <https://doi.org/10.1016/j.clay.2014.08.002>

CHAPTER 4

Temperature effects on buffering performance of SB barrier

4.1 Introduction

The buffering performance of barrier materials is their capability to impede contaminant migration through mechanisms such as adsorption, ion-exchange, precipitation, and redox reactions (Evans et al., 1997; Kamon, et al., 2002; Masindi et al., 2017; Masuda et al., 2006; Pivato & Raga, 2006; Ruiz et al., 2012; Vhahangwele & Mugeru, 2015; Zhang et al., 2004). In the case of bentonite barriers, the buffering performance is primarily linked to the electrostatic interactions of montmorillonite and fluids, leading to the formation of diffuse double layer (DDL) (Appelo, 2013; J. Hunter, 1981; Mojid & Cho, 2006; Tripathy et al., 2004; H. Wang et al., 2022) that also contribute to the low hydraulic conductivity. As a result, the cations present in the bulk solution are attenuated (sorbed). The thickness of DDL is theoretically characterized by the Debye-Hückel parameter, which is positively related to the temperature (Mitchell, 1993), as is the buffering performances of bentonite. In Chapter 2, SB showed significant adsorption behaviors against Ca^{2+} in aqueous system, and the adsorption behaviors showed significant characteristics of exothermic when bulk Ca^{2+} molarity were higher than $100 \text{ mmol}\cdot\text{L}^{-1}$. However, **there is a lack of experimental data demonstrating the direct impact of temperature on the buffering performance of SB barrier.**

In this study, the buffering performance of SB barrier was characterized by Ca^{2+} sorption capability of consolidated and prehydrated SB specimen in a flexible-wall permeameter, introduced in Chapter 3, during hydraulic conductivity test. The temperature effects to the Ca^{2+} sorption capability were evaluated by comparing the corresponding results at 20°C , 40°C , and 60°C . In addition, the results obtained in this Chapter were compared with those from Chapter 2, and a comprehensive discussion on the temperature effects on the buffering performance of SB barriers were conducted.

4.2 Evaluating buffering performance with hydraulic conductivity (column) test

4.2.1 Characterizing sorbed amount

The materials, methods, and procedures of the hydraulic conductivity test were consistent with Chapter 3. For the intuitiveness of narration, the hydraulic conductivity test was called **column test** in this Chapter. The direction of solute transport in column test is shown in Figure 4.1 (a). As the test proceeded, the influent was continuously replenished, maintaining a constant concentration (c_0), while the volume and concentration (c) of effluent gradually increased.

The typical profile of concentration changes in effluent among with the cumulated effluent volume is shown in Figure 4.1 (b), where the smooth curve is generally called “breakthrough curve”. The concentrations of effluent indicate Phases of I, II, III during the test. In Phase I, the solute in influent is transport by advection, dispersion processes, and is subjected to the sorption while the solute does not reach the effluent; In Phase II, the solute reaches the effluent but all the processes are still proceeding in the specimen; In Phase III, the dispersion and sorption processes are finished, leading to complete breakthrough of specimen.

During the test, the effluent was obtained as discrete effluent samples in 15 mL centrifuge tubes. Corrections were applied to the “timings” of values obtained from effluent samples. For directly measured values (e.g. concentration and pH), the values were treated corresponding to the PVF or time when half of the effluent sample were collected (e.g. c_i is corresponded to $(V_{i-1}+V_i)/2$) on the basis of those values represented the average during sampling period (Finkel & Grathwohl, 2017). For cumulative values (e.g. Ca^{2+} sorbed amount), the corresponding PVF or time were treated as the end of that sampling period (V_i).

As introduced in Chapter 2, the sorption of Ca^{2+} by SB is accompanied with the desorption of exchangeable Na^+ and the amounts of released Na^+ could be used as an indicator to the ion-exchange reactions. Therefore, both the molarities of Ca^{2+} and Na^+ in effluents were measured to comprehensively analyze the sorption processes. The cumulative amounts of Ca^{2+} and Na^+ in effluents that were collected by discrete effluent samples were obtained by:

$$n_{\text{Ion}} = \sum_i \Delta V_i \cdot [\text{Ion}] \quad (4.1)$$

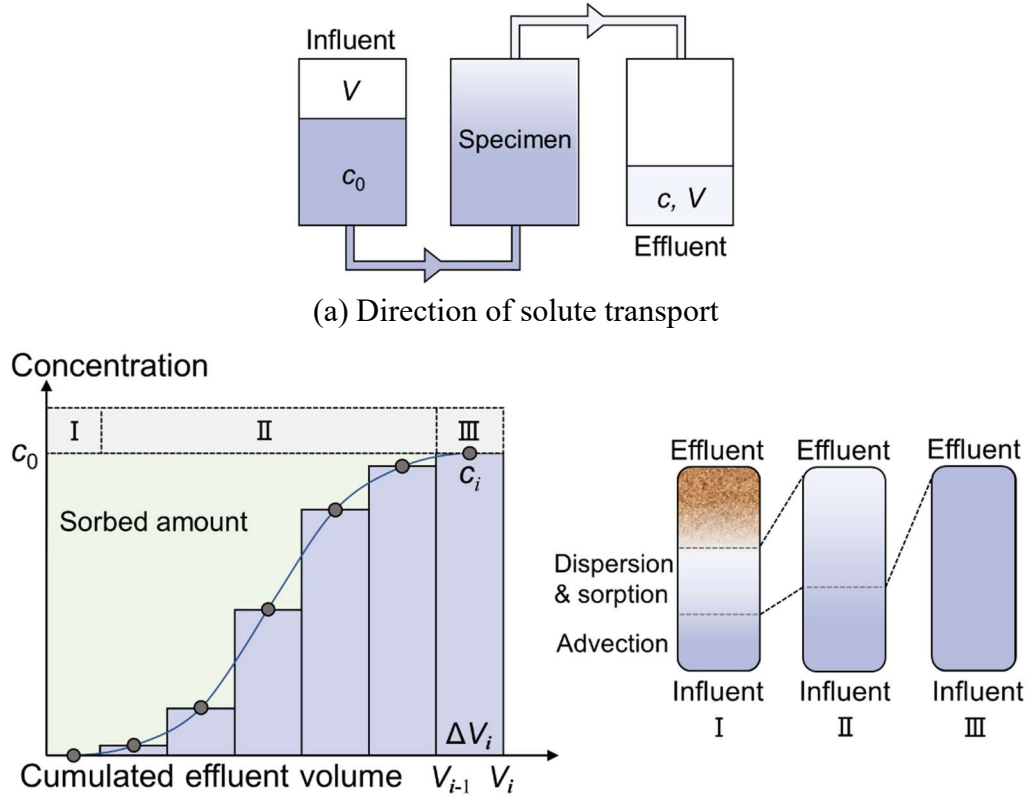
where n_{Ion} is the cumulative amount of Ca^{2+} or Na^+ in effluent (mmol); $[\text{Ion}]$ is the measured molarity of Ca^{2+} or Na^+ in effluent sample ($\text{mol} \cdot \text{L}^{-1}$); ΔV_i is the volume of effluent collected in one centrifuge tube (L). For convenience, the ion valence is omitted in the symbol n (e.g. n_{Ca}).

As shown in Figure 4.1 (b), the reduced amount of Ca^{2+} can be obtained and treated as the sorbed amount when the sorption process played the main role of reduction. The Ca^{2+} sorbed amount in this study was calculated with (Kato et al., 2021; Mo et al., 2020; Patel, 2019):

$$q_{\text{sorb}} = \frac{c_0 \cdot V_i - n_{\text{Ca}}}{m_{\text{SB}}} \quad (4.2)$$

where q_{sorb} is the sorbed amount of Ca^{2+} ($\text{mmol} \cdot \text{g}^{-1}$); m_{SB} is the dry mass of specimen (g); V_i is the cumulated volume of effluent (L); ΔV_i is the collect volume of individual effluent sample. the 1st term on the right side is the amount that have entered the specimen, and the 2nd term on the right side is the amount that have been collected in discrete effluent samples.

The test conditions are summarized in Table 4-1. Distilled water was permeated in Set 0 at 20°C as empty reference. 0.1M CaCl_2 was permeated in Set 1 at 20°C and 60°C; 1M CaCl_2 was permeated in Set 1 at 20°C, 40°C and 60°C. The conditions of all specimens are approximately the same (Table 3-3). The pH of effluent samples was measured by HORIBA, LAQUAtwins pH-22B with a accuracy of 0.01. The molarities of Ca^{2+} and Na^+ were measured by an atomic emission spectrometer (SHIMADZU, ICPE-9800, see Photo 2.2), the procedures of the measurments are inconsistent with the introduction in subsection 2.3.2.



(After Bonilla-Petriciolet et al., 2017)

Figure 4.1 Schematic drawing of solute transport in column test.

Table 4-1 Simplified conditions for the tests and obtained Ca^{2+} sorbed amounts q_{sorb} until the last effluent samples collected in each case (Test conditions with more details were shown in Table 3-3).

Set	Name	Permeant	Dry mass (g)	T (°C)	Aver. k ($\text{m}\cdot\text{s}^{-1}$)	Last q_{sorb} (mmol/g)	PVF at last q
0	DW-20°C-1	DW	83.0	20	4.0×10^{-11}	-	2.7
	DW-20°C-2	DW	83.0	20		-	3.7
1	0.1M-20°C-1	0.1M CaCl_2	83.1	20	2.7×10^{-11}	0.072	4.8
	0.1M-20°C-2	0.1M CaCl_2	83.1	20		0.071	4.4
	0.1M-60°C-1	0.1M CaCl_2	82.6	60	4.5×10^{-11}	0.052	5.5
	0.1M-60°C-2	0.1M CaCl_2	82.6	60			0.7
2	1M-20°C-1	1M CaCl_2	83.2	20	1.1×10^{-10}	0.62	6.4
	1M-20°C-2	1M CaCl_2	83.2	20		0.59	5.7
	1M-20°C-3	1M CaCl_2	83.2	20		0.59	5.8
	1M-40°C-1	1M CaCl_2	83.1	40	1.7×10^{-10}	0.59	3.5
	1M-60°C-1	1M CaCl_2	82.5	60		0.58	8.8
	1M-60°C-2	1M CaCl_2	82.5	60	2.3×10^{-10}	0.71	12.1
	1M-60°C-3	1M CaCl_2	82.5	60		0.71	7.1

4.2.2 Analytical solute transport

The physical transport of solute in fluids is driven by the flow and concentration difference. In a system that transport is one dimensional and in a steady state flow, as in flexible-wall permeameter, the transport can be described by advection-dispersion equation (ADE) in the form (Fetter et al., 2017; Kaluarachchi & Morshed, 1995; Runkel, 1996):

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} - \frac{\rho_d}{\phi} \cdot \frac{\partial q_{\text{sorb}}}{\partial t} \quad (4.3)$$

where c is the concentration ($\text{mol} \cdot \text{L}^{-1}$); D is the dispersive coefficient ($\text{m}^2 \cdot \text{s}^{-1}$); v_x is the flow velocity ($\text{m} \cdot \text{s}^{-1}$); x is the distance from the source (m); t is the time (s); q_{sorb} is the amounts reduced by sorption ($\text{mol} \cdot \text{g}^{-1}$); ρ_d is the dry density of specimen ($\text{g} \cdot \text{m}^{-3}$); ϕ is the porosity of specimen (-).

The third term in the right side of Eq (4.3) represents the effect of soil sorption, it can have other forms for different physical and chemical processes (Celia et al., 1989; Silavwe et al., 2019). According to the principal of soil sorption that sorbed amount q is related to the bulk concentration c at equilibrium state (Bonilla-Petriciolet et al., 2017; Giles et al., 1960; Tipping, 1995), and flow velocities during the test were low enough to maintain approximate equilibrium states. For example, more than 50 h are needed for a flow with hydraulic gradient of 50 to penetrate the 20 mm SB specimen with hydraulic conductivity lower than $10^{-9} \text{ m} \cdot \text{s}^{-1}$. Therefore, the q can be replaced by c with substitution, and Eq (4.3) can be rewritten as:

$$R \cdot \frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} \quad (4.4)$$

$$R = 1 + \frac{\rho_d}{\phi} \cdot \frac{dq_{\text{sorb}}}{dc} \quad (4.5)$$

where R is called retardation coefficient (-), which characterizes the sorption capability of the SB specimens in this study.

For the convenience of analysis, the c , x , and t in Eq (4.4) can be transferred into dimensionless C , X , and PVF with relations below:

$$\partial \text{PVF} = \frac{1}{V_{\text{void}}} \cdot \partial V = \frac{A \cdot k \cdot i}{V_{\text{void}}} \cdot \partial t \quad (4.6)$$

$$X = x / L \quad (4.7)$$

$$C = c / c_0 \quad (4.8)$$

where V_{void} is the voids volume of specimens (m^3); A is the cross area of specimen (m^2); k is hydraulic conductivity ($\text{m} \cdot \text{s}^{-1}$); i is hydraulic gradient (-); L is the height of specimen (m); c_0 is the concentration of the influent solution.

The term $k \cdot i$ in Eq (4.6) represent the average velocity of flow across the specimen's area in Darcy's law, real flow velocity should be corrected with porosity of specimen ϕ :

$$v_x = \frac{k \cdot i}{\phi} \quad (4.9)$$

Substituting Eq (4.6) (4.7) (4.8) and (4.9) into Eq (4.4), a dimensionless form of ADE can be written as:

$$R \cdot \phi \cdot \frac{A \cdot L}{V_{void}} \cdot \frac{\partial C}{\partial PVF} = \phi \cdot \frac{D}{k \cdot i \cdot L} \cdot \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} \quad (4.10)$$

Equation (4.10) could be further simplified as:

$$R \cdot \frac{\partial C}{\partial PVF} = D^* \cdot \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} \quad (4.11)$$

$$D^* = \frac{D}{k} \cdot \frac{\phi}{i \cdot L} \quad (4.12)$$

ADE is mathematically transferred into dimensionless form with: unchanged retardation coefficient R , and a normalized dispersive coefficient D^* which can be obtained with original D . The D^* is defined in this study to keep the symmetricity of the ADE forms, its reciprocal is also called column Peclet number (P_L) in other studies (Shackelford, 1994b).

When the concentration of influent is constant, the analytical solution of dimensionless ADE at $X = 1$ is given by (Bear, 1973; Kaluarachchi & Morshed, 1995; Shackelford et al., 1999; Van Genuchten, 1982):

$$C(PVF)|_{X=1} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{R - PVF}{2\sqrt{D^* R \cdot PVF}} \right) + \exp\left(\frac{1}{D^*}\right) \cdot \operatorname{erfc} \left(\frac{R + PVF}{2\sqrt{D^* R \cdot PVF}} \right) \right] \quad (4.13)$$

Therefore, the analytical description of the breakthrough curve can be determined after the R and D^* are obtained. Also, it is possible to determine the values of R and D^* with the breakthrough curve obtained from experimental results.

The premise that Eq (4.13) could be an analytical solution of ADE is that R and D^* are, or could be approximated as, constants. As it was shown in Eq (4.5), R is constant value only when the Ca^{2+} sorbed amount (q_{sorb}) and bulk concentration (c) are linearly correlated, indicating the Ca^{2+} sorption isotherms of SB can be characterized by Henry's model (Giles et al., 1960; Ruthven, 1984).

A practical assessment to the R is to use the slopes in linear (ad)sorption isotherms obtained from batch test, mostly written as K_d (Bouchard et al., 1988; Kato et al., 2021; Martínez-Lladó et al., 2011), as the values of term dq_{sorb}/dc in Eq (4.5). The results in Chapter 2 showed that the Ca^{2+} adsorption isotherms were approximately linear when bulk Ca^{2+} molarity was larger than $50 \text{ mmol} \cdot \text{L}^{-1}$. But whether the slopes in the adsorption isotherms are capable to characterize the Ca^{2+} sorption in column test needed to be verified. In this Chapter, the dq_{sorb}/dc , as well as the R were determined after q_{sorb} were calculated from the methods introduced in Subsection 4.2.1, and after the comparison between q_{sorb} and q_e obtained in Chapter 2. Then, the D^* and D were obtained the by fitting methods.

4.3 Results

4.3.1 Water chemistry of effluent sample

The measured pH and molarities of Ca^{2+} and Na^+ of collected effluent samples are shown in Figure 4.2 and Figure 4.3 as the profiles among with time and PVF.

Figure 4.2 (a) and (b) show the breakthrough curves of Set 1 with permeants of 0.1M CaCl_2 . The profiles of Ca^{2+} reached the influent value faster at 60°C compared to 20°C when time and PVF was the X-axis. The complete breakthrough of Ca^{2+} were observed at approximately 12×10^6 s or 4.5 PVF at 20°C, and at approximately 5×10^6 s or 2.5 PVF at 60°C. The complete breakthrough of 0.1M-60°C-2 was not observed but its profiles are highly overlapped to the profiles of 0.1M-60°C-1.

Figure 4.2 (c) and (d) show the profiles of Na^+ molarities of Set 0 and Set 1. The profiles of Na^+ showed characteristics of single peak which increased first and then gradually decreased. The peaks were approximately ranged from 15 to 30 $\text{mmol} \cdot \text{L}^{-1}$ in Set 0, while more than 60 $\text{mmol} \cdot \text{L}^{-1}$ in Set 1. The peaks at 60°C were observed higher the peaks at 20°C.

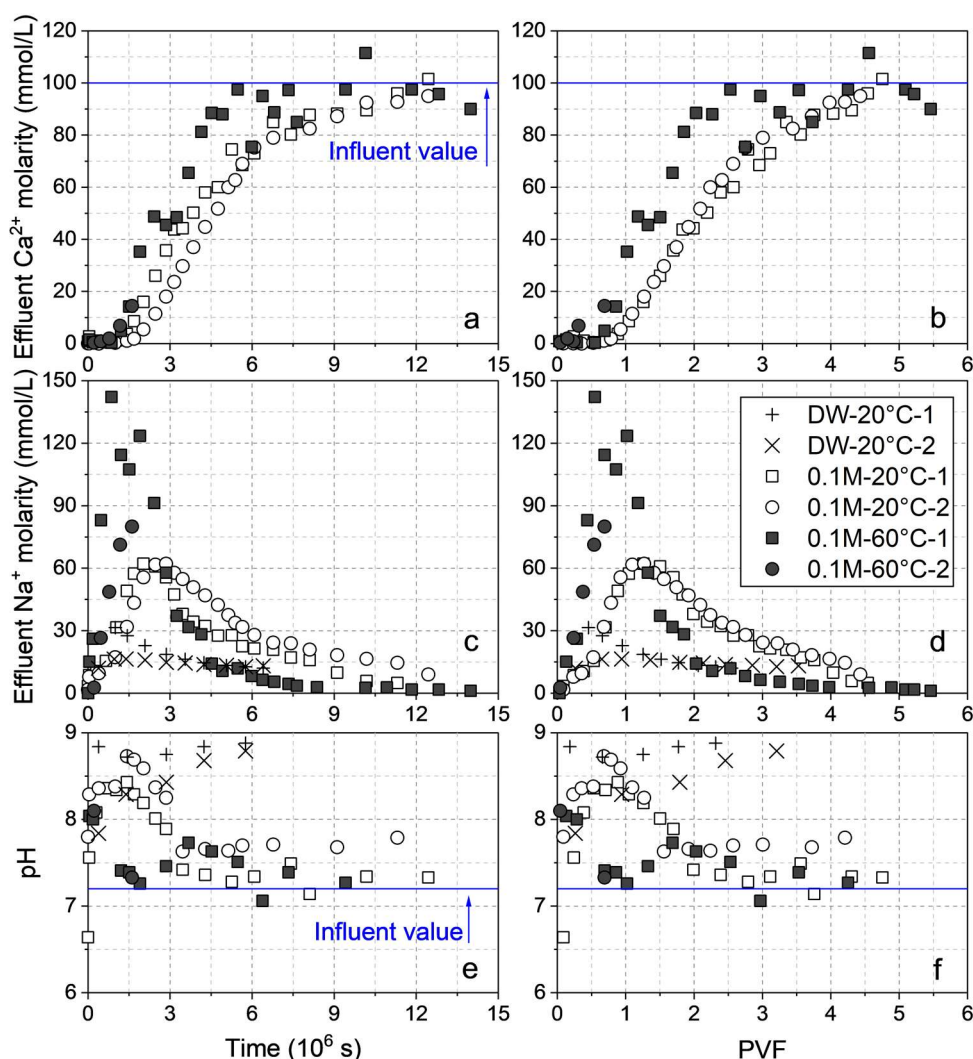


Figure 4.2 Ionic compositions and pH of effluents among with time and PVF (Set 0, Set 1).

Figure 4.3 (a) and (b) show the breakthrough curves of Set 2 with permeants of 1M CaCl_2 . The temperature dependencies of the breakthrough curves varied when time or PVF was the X-axis. At higher temperature, the Ca^{2+} increased and reached influent value faster in time, but the PVF for complete breakthrough increased. The complete breakthrough of Ca^{2+} were observed at approximately 5×10^6 s or 5 PVF at 20°C , and at approximately 3×10^6 s or >6 PVF at 60°C . The complete breakthrough of 1M- 40°C -1 was not observed, its profiles are positioned between the profiles at 20°C and 60°C .

Figure 4.3 (c) and (d) show the profiles of Na^+ molarities of Set 2. The profiles of Na^+ molarity showed single peaks consistently. Lower peaks were observed at higher temperatures, which is different with the results of Set 1 shown in Figure 4.2 (c) and (d). The peak molarities over $100 \text{ mmol}\cdot\text{L}^{-1}$ were observed at 20°C while the peak molarities less than $60 \text{ mmol}\cdot\text{L}^{-1}$ were observed at 60°C .

The profiles of pH are shown in (e) and (f) of Figure 4.3 and Figure 4.4. For Set 0, the pH ranged from 7.8 to 8.9, effluents consistently exhibited slight basicity throughout the test. For Set 1 and Set 2, the pH showed initial values approximately to 8, and decreased to approximately 7. The effluents of Set 1 and Set 2 eventually exhibited neutrality as the test proceeded.

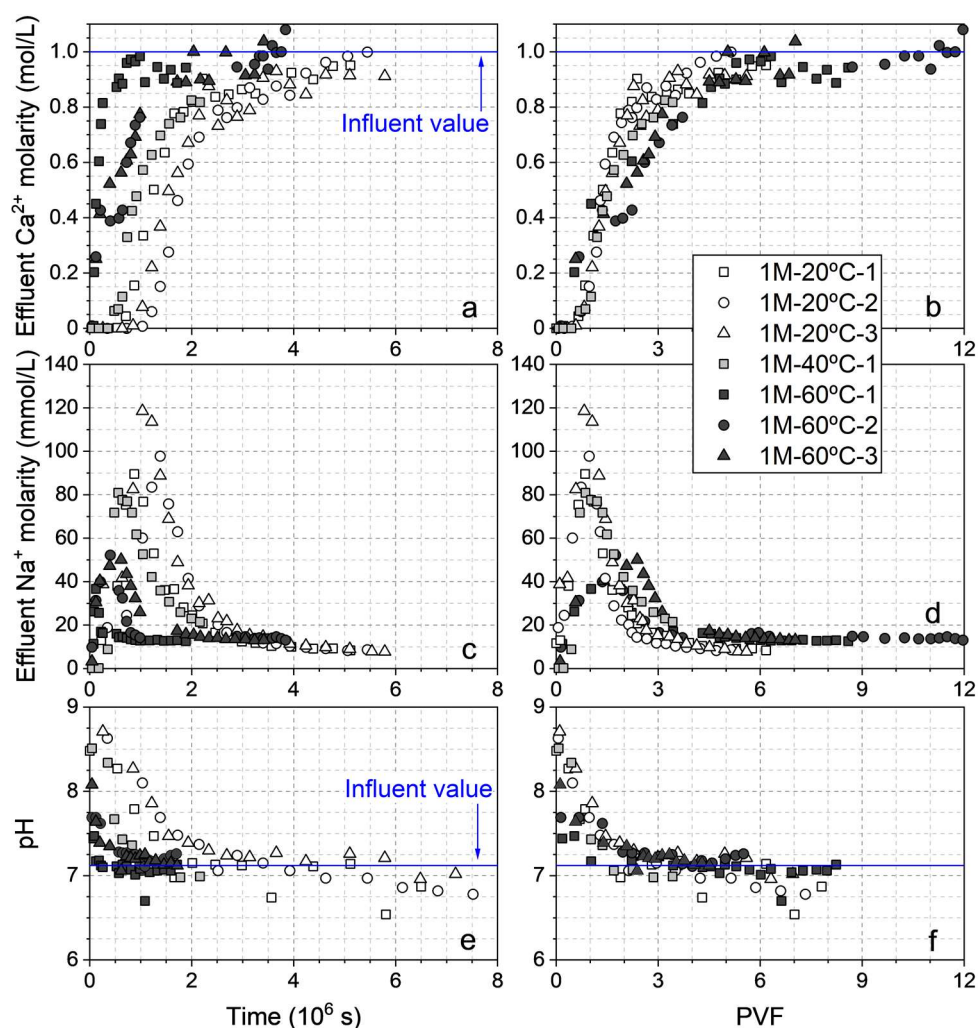


Figure 4.3 Ionic compositions and pH of effluents among with time and PVF (Set 2).

The temperature effects to the profiles of Ca^{2+} and Na^+ were significant, as shown in Figure 4.2 and Figure 4.3. However, the temperature dependencies on profiles of Ca^{2+} breakthrough, Na^+ elution, and pH were also dependent on the selection of independent variables (time or PVF) and the concentration of permeant (0.1M or 1M).

The varying temperature dependencies of profiles among with time and PVF were attributed to the changes of the hydraulic performance of SB specimen. When time was used as the X-axis, the extents of processes proceeded faster with higher flow velocities. Therefore, though invisible, temperature was not the only variable in diagrams with X-axis of time in Figure 4.2 and Figure 4.3. The PVF, in contrast, represents the volume of effluent regardless the hydraulic properties, is a normalized variable that the variations in flow velocity were eliminated to a large extent. Hence the variations of the profiles above the X-axis of PVF can better indicate the changes of chemical and physical processes between specimen and permeant at different temperatures.

Consequently, the profiles among with PVF shown in Figure 4.2 and Figure 4.3 indicated that the temperature dependencies of Ca^{2+} sorption and Na^+ elution reversed as the permeant concentration increased.

4.3.2 Cumulative amounts of effluent sample

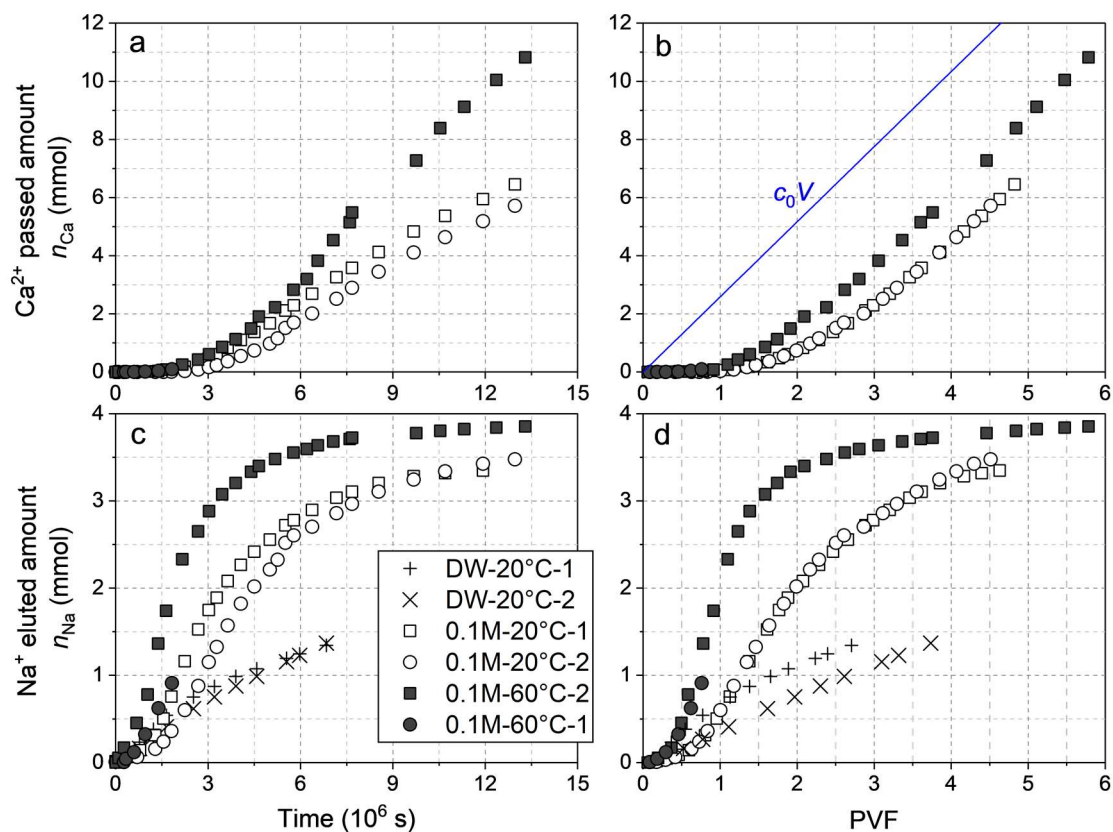
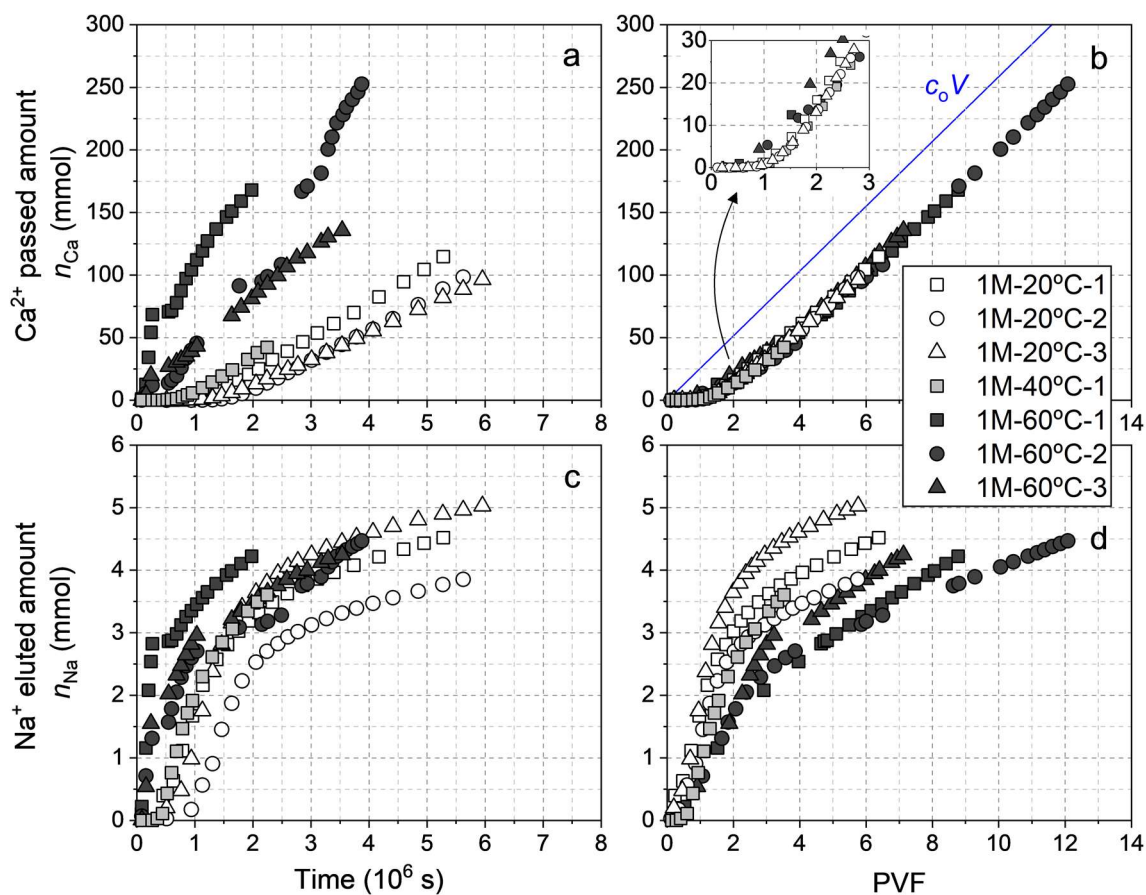
4.3.2.1 Cumulative Ca^{2+} and Na^+ in effluents

Figure 4.4 and Figure 4.5 show the profiles of cumulative Ca^{2+} (n_{Ca}) and Na^+ (n_{Na}) among with time and PVF. As explained above, the temperature dependencies of n_{Ca} and n_{Na} when time was the X-axis were subjected to the attribution of hydraulic performance. In order to focus on the temperature effects on the buffering performance of SB, the following explanations and discussions were focused on the profiles among with PVF.

Figure 4.4 (b) shows the profiles of n_{Ca} among with PVF of Set 1. The profiles of n_{Ca} were lower than the calculated Ca^{2+} inflow amount $c_0 \cdot V_{\text{out}}$, suggesting that Ca^{2+} was reduced due to the interactions between permeant and SB specimens. The temperature dependency of n_{Ca} was initially insignificant, and became significant after approximately 1 PVF. Higher n_{Ca} were observed at 60°C compared to 20°C. Indicating the Ca^{2+} sorption became less favorable at higher temperatures when permeated with 0.1M CaCl_2 .

Figure 4.4 (d) shows the relations between n_{Na} and PVF of Set 0 and Set 1. The profiles of Set 0 and Set 1 were initially overlapped, and started to show differences at approximately 0.5 PVF. The n_{Na} of Set 1 exceeded the n_{Na} of Set 0 as the permeant flowed into the specimens, which is consistent with the theory that ion-exchange is the primary reason for the Na^+ elution. Higher n_{Na} were observed at 60°C compared to 20°C. Indicating the Na^+ elution from SB became more favorable at higher temperatures when permeated with 0.1M CaCl_2 .

Figure 4.5 (b) shows the relations between n_{Ca} and PVF of Set 2. The temperature dependency of n_{Ca} was not significant, as profiles at different temperatures nearly overlapped. Despite variations in Ca^{2+} breakthrough curves at different temperatures in Figure 4.3 (b), it did not significantly affect the cumulative amounts, and n_{Ca} were predominantly determined by PVF. The differences in the reduced amounts at different temperatures were insignificant in the scale in Figure 4.7 (b).

Figure 4.4 Cumulative amounts of Ca^{2+} and Na^+ in effluents of Set 0 and Set 1.Figure 4.5 Cumulative amounts of Ca^{2+} and Na^+ in effluents of Set 2.

Although the temperature dependency of n_{Ca} in Figure 4.5 (b) was eventually insignificant. But it can be observed in the zoom-in profiles that the n_{Ca} at 60°C were higher than the n_{Ca} at 20°C initially, which is consistent with the profiles of n_{Ca} of Set 1. This suggested that the different temperature dependency of n_{Ca} will either eventually disappeared or eventually exist as the furthering proceeding of Set 1. The former indicated that it is the extent or scale rather than permeant concentration that fundamentally determined the observable temperature dependency of n_{Ca} ; And the latter indicated that the permeant concentration primary determined the observable temperature dependency of n_{Ca} .

Figure 4.7 (d) shows the relations between n_{Na} and PVF of Set 2. As the temperature increased, more PVF of effluent was collected for a certain amount of n_{Na} . The profiles suggest that the elution of Na^+ from SB specimens became less favorable at higher temperatures when permeated with 1M $CaCl_2$. As the test proceed, the slopes of the profiles eventually converged to the non-zero values, differing from the n_{Na} profiles of Set 1. Indicating the elution of Na^+ was continuously proceeded when the breakthrough of Ca^{2+} was basically complete.

4.3.2.2 Ca^{2+} sorbed amounts (q_{sorb})

Figure 4.6 and Figure 4.7 show the profiles of q_{sorb} of Set 1 and Set 2, respectively. As explained in subsection 4.3.1. The temperature dependencies of q_{sorb} when time was the X-axis were greatly attributed to the flow velocities in the SB specimens. In order to focus on the temperature effects on the buffering performance of SB, the following explanations and discussions were still focused on the profiles among with PVF.

Figure 4.6 (b) shows the profiles of q_{sorb} among with PVF of Set 1. The temperature effects to the q_{sorb} were insignificant initially, where $PVF < 1$ and the profiles showed characteristics of linear. When $PVF > 1$, the profile of q_{sorb} at 60°C (0.1M-40°C-1) was below the profiles of q_{sorb} at 20°C. The profiles were divided into Stage a and Stage b corresponded to the fast and slow increases respectively. Summarized in Table 4-1, until the last collected effluent samples, the last q_{sorb} (those reached Stage 2) of Set 1 were 0.072 and 0.052 $mmol \cdot g^{-1}$ at 20°C and 60°C, respectively. The results of Set 1 suggest the buffering performance of SB against Ca^{2+} decreased as temperature increased when permeated with 0.1M $CaCl_2$.

Figure 4.7 (b) shows the profiles of q_{sorb} among with PVF of Set 2. The profiles exhibited characteristics that increased rapidly initially and then slowed down at approximately 3 to 5 PVF. The fast and slow increases indicated the Ca^{2+} were possibly sorbed by several different processes. The temperature effects on the profiles of q_{sorb} of 7 cases were observed insignificant. Summarized in Table 4-1, until the last collected effluent samples, the last q_{sorb} of 7 cases of Set 2 were ranged from 0.58 to 0.71 $mmol \cdot g^{-1}$, with the lowest and highest values both observed at 60°C. Focusing on average values, the last q_{sorb} were 0.60, 0.59, and 0.67 $mmol \cdot g^{-1}$ on average at 20°C, 40°C, and 60°C, respectively. Considering the q_{sorb} of 1M-40°C-1 has more potential to increase where its last effluent sample was collected at 3.5 PVF, it seems the Ca^{2+} sorption capability slightly increased as the temperature increased, in Set 2. But at least, it can be concluded that temperatures changes from 20°C to 60°C did not significantly reduce the Ca^{2+} sorption amount, and the buffering performance of SB against Ca^{2+} could be maintained when permeated with 1M $CaCl_2$.

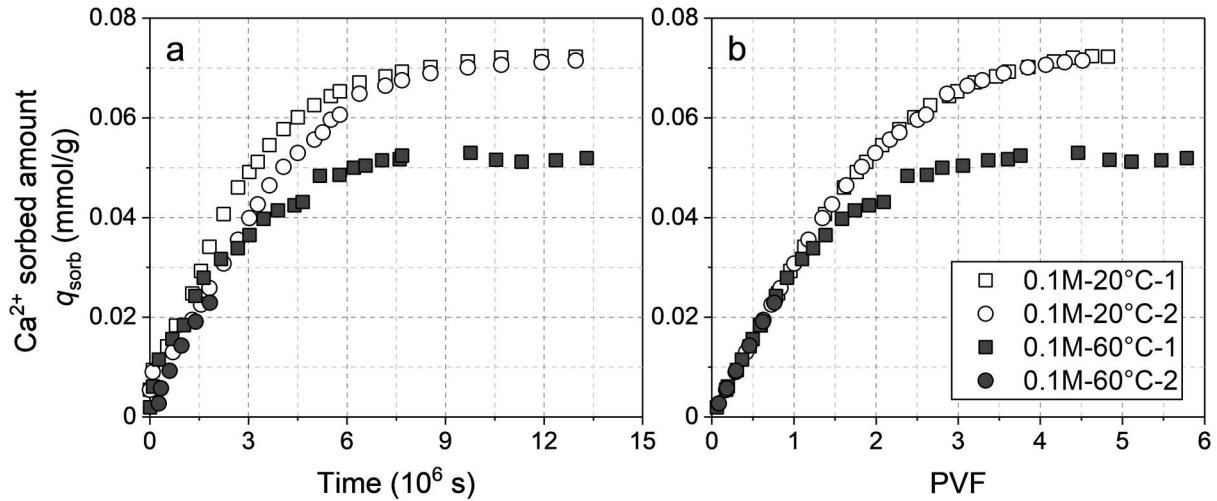


Figure 4.6 Profiles of Ca^{2+} sorbed amount (q_{sorb}) along with time and PVF (Set 1).

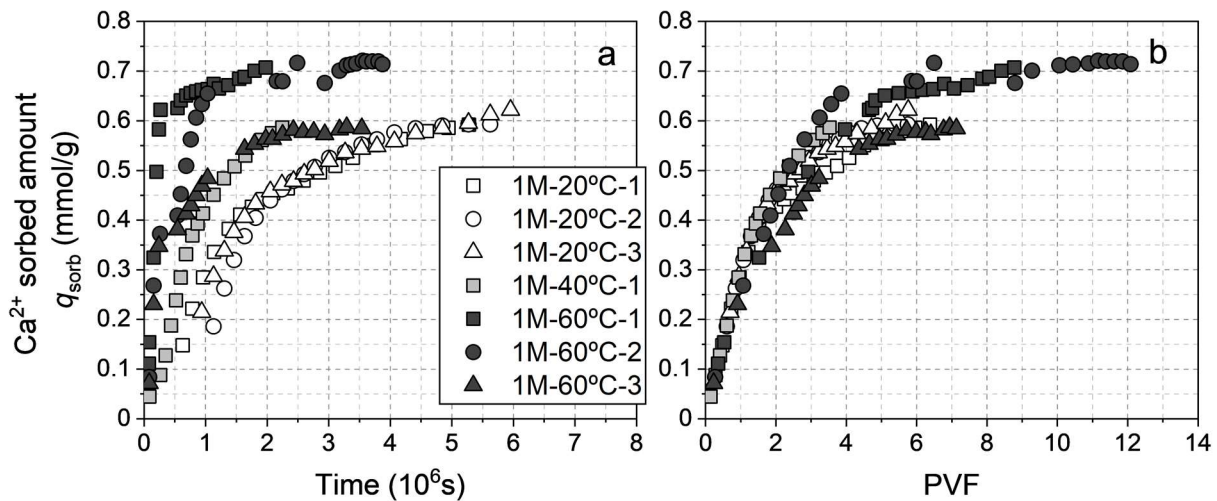


Figure 4.7 Profiles of Ca^{2+} sorbed amount (q_{sorb}) along with time and PVF (Set 2).

In Figure 4.6 (b) and Figure 4.7 (b), the profiles of q_{sorb} showed similar characteristics. However, the correlated processes that contributed to the q_{sorb} in Set 1 and Set 2 might be different considering their different temperature dependencies. The details of interactions between SB and permeant at the 2 Stages and the reason reasons for the different temperature dependencies in Set 1 and Set 2 were discussed in Section 4.4

Although PVF is a normalized variable that indicating the extents of physical and chemical processes between SB and permeant in column test, the results characterized by PVF may not intuitively enough to guide practical situations. For example, it is too abstractionism to state that “This barrier will continue to function and the migration of contaminates will be inhibited until 3 PVF of leachate have passed the barrier”. Therefore, the time variable is more suitable to be applied to practical situations. In Figure 4.7 (a), the profiles of q_{sorb} at 60°C were above the q_{sorb} at 20°C throughout, which means the sorption capacity were reached faster at 60°C. Despite a slight increase in the q_{sorb} values of Set 2 at higher temperatures, it is more appropriate to consider that temperature increases have an overall negative impact on the inhibition of contaminant migration of SB barrier if considering practical implications.

4.3.3 Analytical solutions for Ca^{2+} breakthrough curves

It was introduced in Subsection 4.2.2 that the values of retardation coefficient (R) and coefficients of dispersive (D) and normalized dispersive (D^*) in advection-dispersion equation (ADE) can be determined with the breakthrough curve obtained from experimental results (Shown in Figure 4.2 and Figure 4.3). A method to assess the R of SB barrier was proposed in this Subsection, D and D^* were obtained by fitting methods. After that, the validity of D and D^* were verified in principle.

4.3.3.1 Obtaining retardation coefficient (R)

Table 4-2 summarizes the obtained Ca^{2+} (ad)sorption amounts in two kinds of test at complete breakthrough and at equilibrium at 20°C , differences were observed in the (ad)sorption amounts between the results of batch test and column test. More Ca^{2+} were sorbed in the column test in addition to the adsorbed amounts in the batch test, and the differences were more significant at high concentration cases. Therefore, the application of slopes in adsorption isotherms as K_d will result in underestimations of sorption amounts in column test. Such differences suggest that there may be a difference in the mechanisms of adsorption in batch test and sorption in column test.

On the basis that the difference in test conditions between batch type and column type brought the different results of Ca^{2+} (ad)sorption amounts of SB. Another approach to determined dq_{sorb}/dc was used in this study. In this Chapter, the Ca^{2+} sorbed amounts (q_{sorb}) were calculated as the cumulative amounts with Eq (4.1) and Eq (4.2), and correlated c were also recorded. Naturally, relations between q_{sorb} and c can be directly given, and dq_{sorb}/dc can be derived from the relations.

Figure 4.8 shows the Ca^{2+} sorption isotherms in Set 1 (0.1M CaCl_2) and Set 2 (1M CaCl_2). The profiles of q_{sorb} shared characteristics of rapid initial increase, reaching a significant initial value, followed by continuously steady increase. The initial values were observed decreased as the temperature increased in both Set 1 and Set 2. The steady increases were more significant at 20°C than at 60°C in Set 1, while were more significant as temperature increased in Set 2. The values of q_{sorb} in the sorption isotherms were significantly different in Set 1 and Set 2. For example, when bulk Ca^{2+} were $100 \text{ mmol}\cdot\text{L}^{-1}$ at 20°C , approximately $0.07 \text{ mmol}\cdot\text{g}^{-1}$ of q_{sorb} was obtained in Set 1, while approximately $0.3 \text{ mmol}\cdot\text{g}^{-1}$ of q_{sorb} was obtained in Set 2. Such differences suggest that the mechanisms leading to additional sorption amounts compared to adsorption amounts were highly dependent on the permeant concentration.

Table 4-2 Comparison between the last Ca^{2+} sorption amounts per unit mass of bentonite ($q_{\text{sorb}}/n_{\text{bent.}}$) and the equilibrium Ca^{2+} adsorption amounts (q_e) obtained in Chapter 2 at 20°C .

Bulk Ca^{2+} molarity ($\text{mol}\cdot\text{L}^{-1}$)	Last $q_{\text{sorb}}/n_{\text{bent.}}$ ($\text{mmol}\cdot\text{g}^{-1}$)	q_e ($\text{mmol}\cdot\text{g}^{-1}$)
0.1	0.96	0.59
1.0	8.00	2.74

*The values of q_e were calculated through fitted adsorption isotherm shown in Table 2-8

* $n_{\text{bent.}} = 0.075$

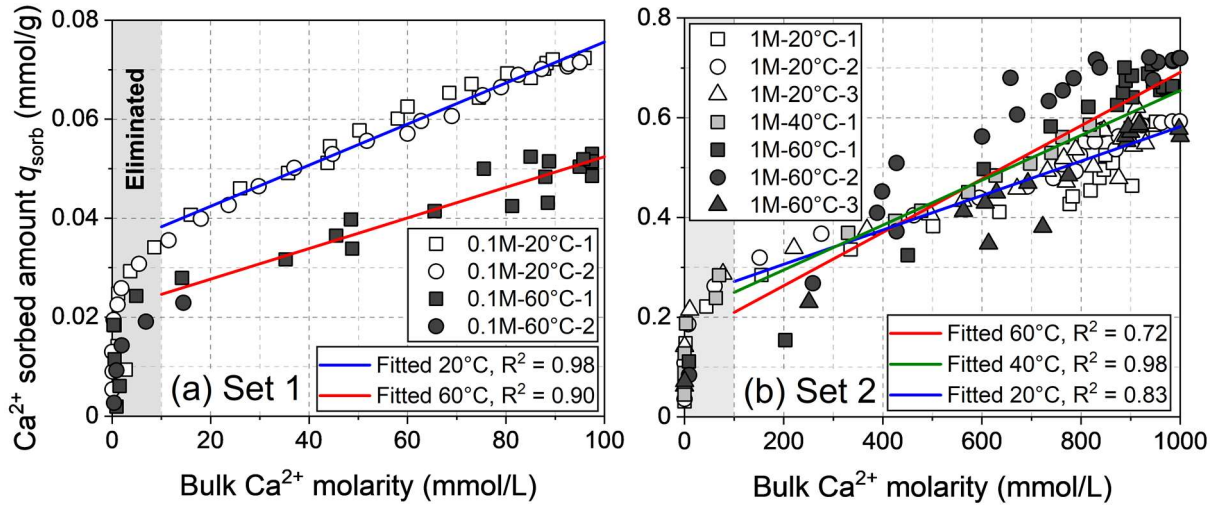


Figure 4.8 Ca^{2+} sorption isotherms derived from the results of column test, the fittings were operated on the plots where the bulk Ca^{2+} molarity above 10% and below 100% of permeant concentrations.

Table 4-3 Parameters of linear fitting in Figure 4.8 and obtained retardation coefficients.

Temperature	Set 1		Set 2		
	20°C	60°C	20°C	40°C	60°C
Slopes ($\text{L}\cdot\text{g}^{-1}$)	4.15×10^{-4}	3.09×10^{-4}	3.45×10^{-4}	4.50×10^{-4}	5.35×10^{-4}
Intercepts ($\text{mmol}\cdot\text{g}^{-1}$)	0.034	0.022	0.23	0.20	0.16
R² (Determination)	0.98	0.90	0.83	0.98	0.72
R (Retardation)	2.36	1.98	2.13	2.43	2.70

Linear fitting was operated in Figure 4.8 in order to obtain the constant values of dq_{sorb}/dc . The operations eliminated the plots in profiles of q_{sorb} with bulk Ca^{2+} molarities below 10% and above 100% of permeant concentrations to ensure the precise characterizations of the linear parts in profiles of q_{sorb} . The selection of data also on the basis that the initial values in profiles of q_{sorb} only determined the initial parts in Ca^{2+} breakthrough curves where the effluent Ca^{2+} molarity was very low. After all, the concern is whether the obtained R can well characterize the profiles of Ca^{2+} breakthrough curves. In Figure 4.8 (a), the fitted line of 60°C was below the fitted line of 20°C with lower slope. In Figure 4.8 (b), the fitted lines crossed when bulk Ca^{2+} was between 400 to 500 $\text{mmol}\cdot\text{L}^{-1}$, the slopes increased as the temperature increased.

Table 4-3 summarized the parameters of linear fitting in Figure 4.8 and obtained values of R . The linear fitting showed coefficients of determination (R^2) higher than 0.90 in Set 1. R^2 of fitted lines of 20°C and 60°C in Set 2 were relatively lower than R^2 of others, which were attributed to the larger fluctuations among individual cases under same test condition. Overall, the data showed well correlations with the fitted lines. The intercepts of the fitted lines decreased as the temperature increased in both Set 1 and Set 2. The obtained R was ranged from 1.98 to 2.70. The R decreased as the temperature increased in Set 1 where the permeant was 0.1M CaCl_2 , while the R increased as the temperature increased in Set 2 where the permeant was 1M CaCl_2 .

4.3.3.2 Obtaining coefficients of dispersive (D) and normalized dispersive (D^*)

As long as the values of R were determined in each test condition. The D^* became the only free parameter in the analytical solution of breakthrough curve shown in Eq (4.13). Therefore, the values of D^* can be iteratively calculated without changing their physical meaning. In this study, the D^* were computed with Levenberg-Marquardt algorithm (Moré, 2006), which is available in many software applications for solving generic curve-fitting problems. The principle of the algorithm is to find parameters in a given function that the sum of square error (SSE) is minimum:

$$\text{SSE} = \sum (\hat{y} - y_i)^2 \quad (4.14)$$

where y_i is the experimental value; $\hat{y}$ is predicted value.

Figure 4.9 shows the fitted breakthrough curves, the fitted curves were tested by Chi-square (χ^2) method (Elderton, 1902). Table 4-4 summarized the significant levels corresponding to the χ^2 values and the obtained values of D^* and D . The significant level exceeded 0.99 in each condition indicated the fitted results were highly correlated with the experimental results. The dispersive coefficients (D) were calculated with Eq (4.12), the D were ranged from 6.96×10^{-12} to $2.40 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ and increased with the temperature increased.

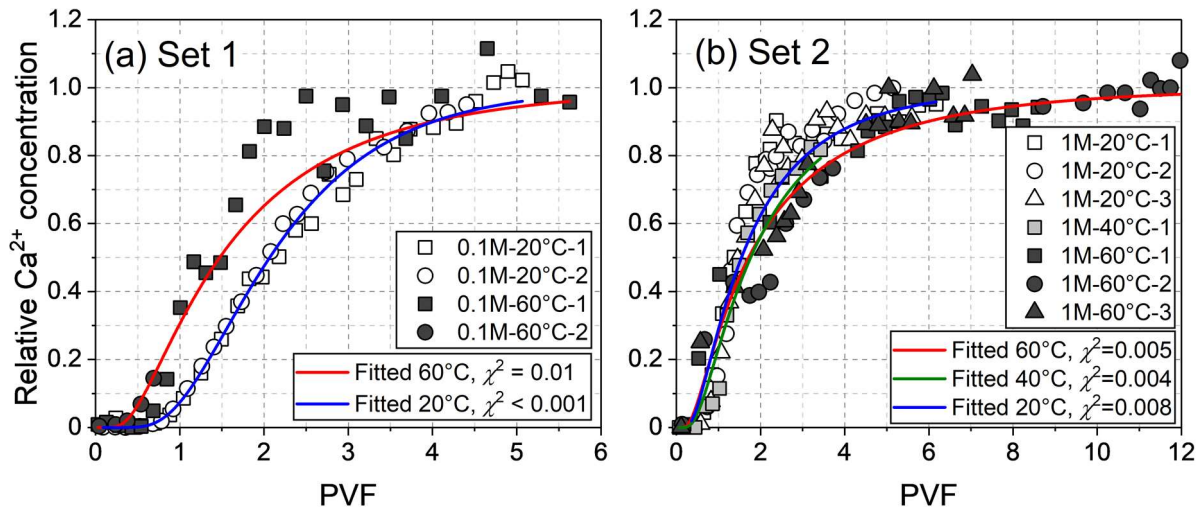


Figure 4.9 Ca^{2+} breakthrough curves fitted by analytical solution.

Table 4-4 Significant levels of Chi-square test, obtained coefficients of normalized dispersive (D^*) and dispersive (D).

Temperature	Set 1		Set 2		
	20°C	60°C	20°C	40°C	60°C
χ^2	< 0.001	0.01	0.008	0.004	0.005
Deg. of freedom	49	29	56	15	55
Sig. level	> 0.99	> 0.99	> 0.99	> 0.99	> 0.99
D^*	0.145	0.356	0.392	0.391	0.600
$D (\text{m}^2 \cdot \text{s}^{-1})$	6.96×10^{-12}	2.79×10^{-11}	7.67×10^{-11}	1.16×10^{-10}	2.40×10^{-10}

4.3.3.3 Verification of the obtained dispersion coefficient (D)

When cations diffuse in bentonite materials, they are inevitably subject to complex electrostatic interactions even if they were not eventually sorbed (Appelo, 2013). As a result, the measured apparent D in bentonite materials is usually lower than its diffusion coefficient in solution. Table 4-5 summarizes the measured apparent D (also named as global D or effective D) of bentonite materials at room temperature as reported by some researchers. The ranges of the D in this study are basically consistent with the reported values ($10^{-10} \sim 10^{-12} \text{ m}^2\cdot\text{s}^{-1}$). Also, the D of 0.1M Ca^{2+} was comparable to the reported D of Sr^{2+} , divalent cation, at similar porosities. The reported data also verified concentration dependency of D that permeant with higher concentration leading to a larger D .

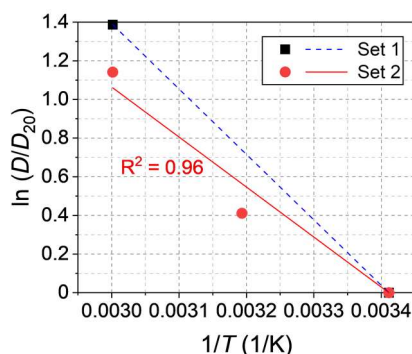
In terms of temperature effects, the variations of D are characterized by Arrhenius expression in principle (Krynicky et al., 1978):

$$D_T = D_{T_0} \cdot \exp\left[\frac{E}{R_{\text{gas}}} \cdot \left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \quad (4.15)$$

where E is activation energy of dispersive process ($\text{kJ}\cdot\text{mol}^{-1}$); R_{gas} is the gas constant ($= 8.314 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); T is Kelvin temperature (K). Taking T_0 as 293.15K (20°C), the temperature dependency of D can be verified by plotting relations between $\ln(D_T/D_{T_0})$ and $1/T$ as long as the relations are approximately linear. In Figure 4.10, the plots of Set 2 showed significant linear correlation with $R^2 = 0.96$. The obtained E of dispersive process of 0.1M and 1M CaCl_2 were 28.0 and 23.8 $\text{kJ}\cdot\text{mol}^{-1}$, which is comparable to the $E = 24.7 \text{ kJ}\cdot\text{mol}^{-1}$ of Na^+ self-diffusion in compacted bentonite reported by Kozaki et al. (1998).

Table 4-5 Apparent D at room temperature in various studies (after Dominijanni et al., 2018).

	Specimen	Apparatus	Porosity	Permeant molarity ($\text{mol}\cdot\text{L}^{-1}$)	Apparent D ($\text{m}^2\cdot\text{s}^{-1}$)
Malusis & Shackelford (2002)	GCL	Rigid-wall	0.80	0.0039 (K^+)	7.05×10^{-11}
			0.76	0.047 (K^+)	2.34×10^{-10}
Dominijanni et al. (2014)	Indian Na-bent.	Rigid-wall	0.81	0.01 (Na^+)	2.54×10^{-10}
			0.81	0.11 (Na^+)	4.60×10^{-10}
This study	SB	Flexible-wall	0.45	0.1 (Ca^{2+})	6.96×10^{-12}
			0.45	1 (Ca^{2+})	7.67×10^{-11}
Sato et al. (1992)	Kunipia-F	Rigid-wall	0.48	Very dilute (Sr^{2+})	5.40×10^{-12}



Supplementary information

	Set 1	Set 2
Slopes (K)	-3387	-2588
R^2	-	0.96
E ($\text{kJ}\cdot\text{mol}^{-1}$)	28.0	23.8

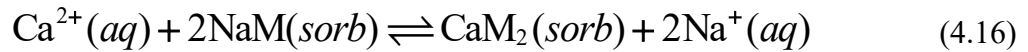
Figure 4.10 Verifying the temperature dependency of D .

4.4 Discussion

4.4.1 Concentration-dependent temperature dependencies of q_{sorb}

The results shown in Subsection 4.3.2 and 4.3.3 have indicated that the temperature dependency of the q_{sorb} in column test was dependent on the permeant Ca^{2+} molarity. As the temperature increased, the q_{sorb} significantly decreased when permeant was 0.1M CaCl_2 , while it slightly increased when permeant was 1M CaCl_2 . Also, the different values of q_{sorb} in the two sets at the same bulk Ca^{2+} molarity indicate the differences in sorption mechanisms.

It has been identified in Chapter 2 that the Ca^{2+} adsorption by bentonite was attributed to processes of ion exchange and direct adsorption. Likewise, the Ca^{2+} sorption of SB specimens in column test could be attributed to several processes. A comprehensive explanation to the temperature effects to the Ca^{2+} sorption can be given after the sorption processes been identified. One definitely identical process in batch test and column test is the ion exchange that the only source of Na^+ is the montmorillonite inter-surface. The process was governed by charge conservation (Bouazza et al., 2007; Kaya & Ören, 2005; Naka et al., 2019):



where M refers to the activate site on montmorillonite inter-surface. Eq (4.16) indicates that the exchange between Ca^{2+} and Na^+ should follows the ratio of 1:2, specifically one Ca^{2+} been sorbed resulted in two Na^+ been released. Therefore, the fraction of q_{sorb} that was attributed to ion exchange reaction could be identified, analogous to Eq (2.29), as:

$$q(\text{exc}) = \frac{0.5 \cdot n_{\text{Na}}}{m_{\text{SB}}} \quad (4.17)$$

where the $q(\text{exc})$ was the exchange fraction in the q_{sorb} ($\text{mol} \cdot \text{g}^{-1}$). Eq (4.17) indicates that the profiles of $q(\text{exc})$ can be derived from the profiles of n_{Na} as shown in Figure 4.4 and Figure 4.5.

Figure 4.11 shows the profiles of $q(\text{sorb})$ and $q(\text{exc})$ among with PVF, linear Y-axis is used in Figure 4.11 (a) while logarithmic Y-axis is used in Figure 4.11(b) for intuitive comparisons. In Set 1, the $q(\text{exc})$ increased as the increased of temperature while q_{sorb} decreased, the values of $q(\text{exc})$ were comparable with other fractions are in the same order of magnitude. In Set 2, the $q(\text{exc})$ decreased as the increased of temperature while q_{sorb} slightly increased, the values of $q(\text{exc})$ were smaller than 1/10 of q_{sorb} .

The temperature dependencies of q_{sorb} and $q(\text{exc})$ observed in Set 1 are consistent with the temperature dependency of q_e observed in batch test (Chapter 2) and are consistent with the principles that ion exchange is endothermic reaction and direct adsorption is exothermic reaction. On contrast, in Set 2, the ion exchange reaction became unfavored at higher temperatures. Since the nature of a reaction is unlikely to change, it can be inferred the ion exchange reaction in Set 2 were somehow been inhibited or interacted. Furthermore, the reversed temperature dependencies of q_{sorb} from Set 1 to Set 2 suggests a fraction other than $q(\text{exc})$ and $q(\text{dir})$ which possess the nature of endothermic.

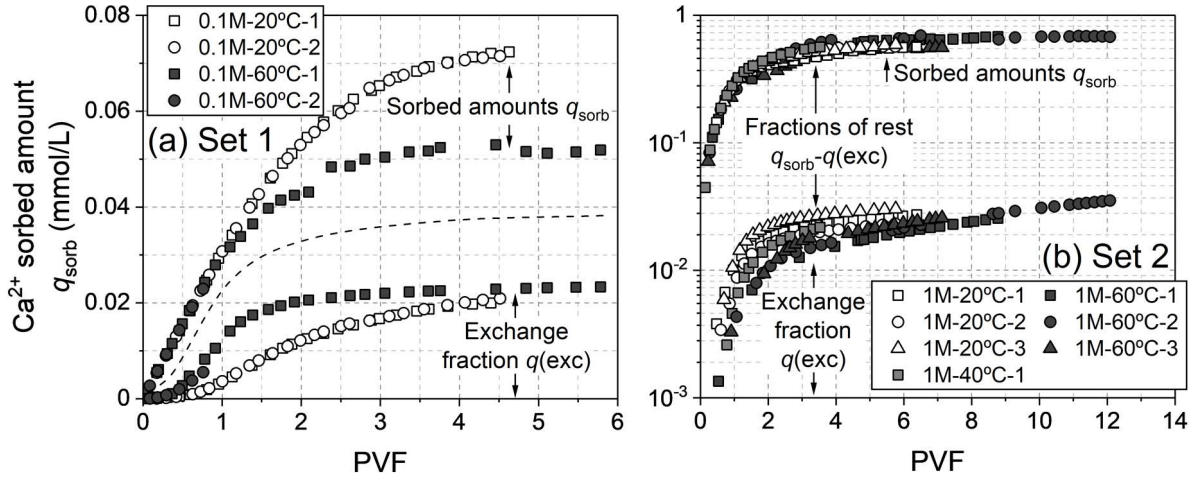
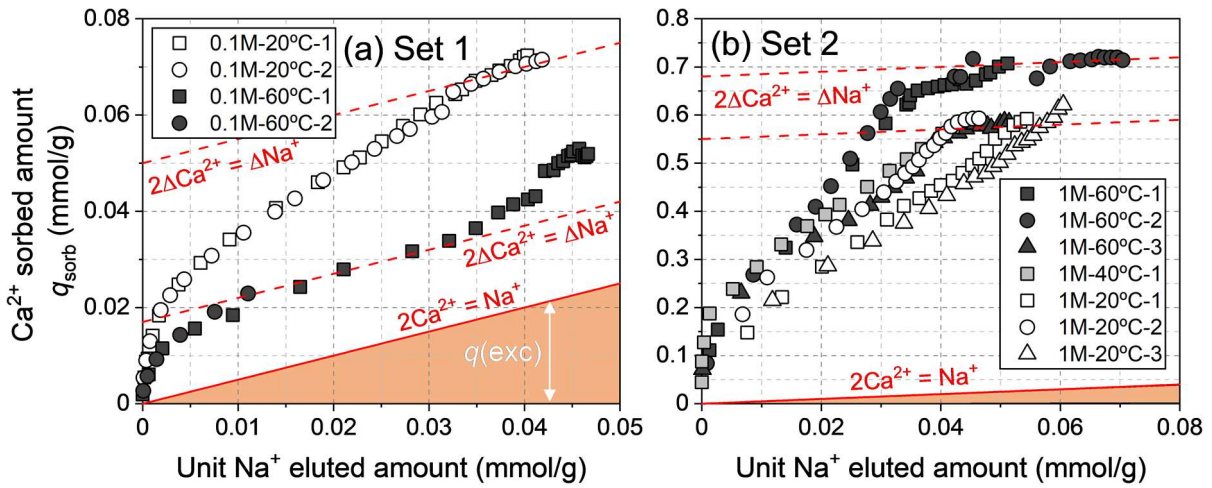
Figure 4.11 Exchange fractions in profiles of q_{sorb} along with PVF.

Figure 4.12 Ca-Na exchange paths in column test.

Before identifying the third fraction in q_{sorb} , its nature can be further inferred. Figure 4.12 shows the profiles q_{sorb} along with and unit Na⁺ eluted amount ($n_{\text{Na}}/m_{\text{SB}}$), the profiles are named as **exchange paths** rather than **exchange isotherms** for isotherms required equilibrium states but the elution (desorption) of Na⁺ will not reach equilibrium in column test because the product is continuously been transport out of the system by the flow. The $q(\text{exc})$ in the figure were exhibited as blue areas and the dashed lines indicated the 1:2 exchange ratio. The slopes of 1:2 were found in the central of the profiles for 0.1M-60°C-1 and 0.1M-60°C-2, while they were located at the terminus of the remaining profiles. Overall, the majority of q_{sorb} in all profiles were utilized before observing the 1:2 slopes, indicating that other sorption mechanisms played a more significant role in q_{sorb} prior to ion exchange taking the charge. Given the principle of selectivity (McBride, 1994; Sposito, Jouany, et al., 1983) and the results in Chapter 2, it is evident that ion exchange should be prioritized over direct adsorption in the interlamellar spaces of montmorillonite. Hence, the majorities of the rest fractions q_{sorb} indicated in Figure 4.11 (b) were unlikely to have occurred in the interlamellar region. Then, it can be indicated that, the remaining option of places for the majority of sorption processes to occur is the outer-surface space of montmorillonite in SB specimens.

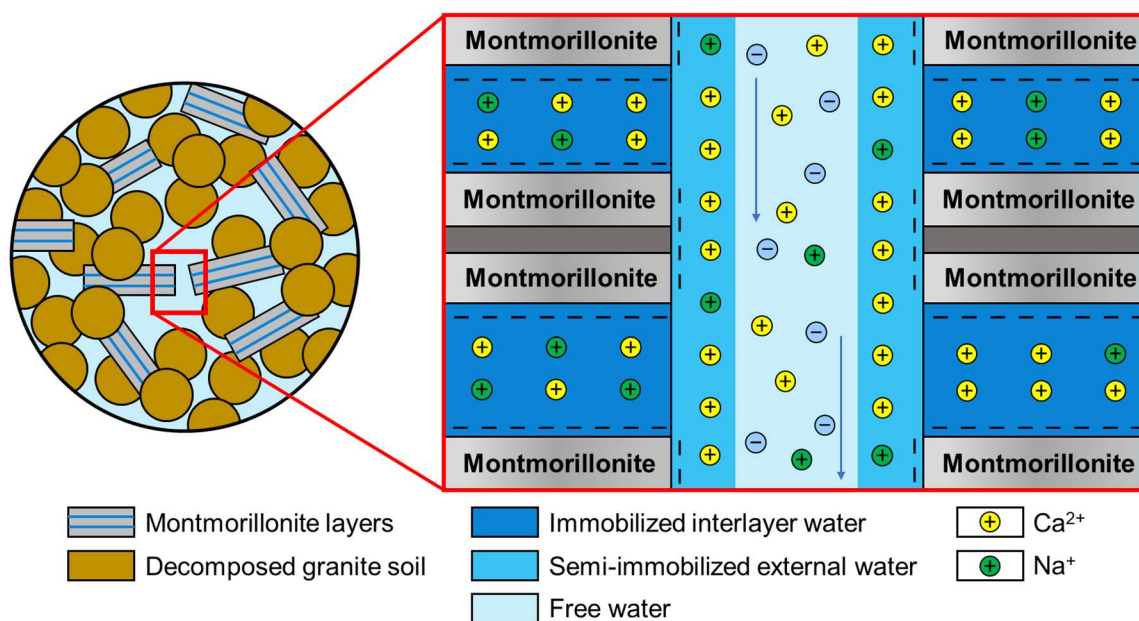


Figure 4.13 Pore water in SB specimen (after Wersin et al., 2004).

Figure 4.13 shows schematic of the pore water in the SB specimen. It was assumed that the outer-surface space of montmorillonite is also significantly affected by the DDL in stable aqueous environments. This model was proposed by Wersin et al. (2004). Sorption at the outer-surface space is permissible when the interlayer water and external water are treated separately. As Figure 4.13 showed, when permeant flowed into the SB specimen, physically, the Ca²⁺ will initially encountered with the semi-immobilized external water and be sorbed. Since the majority of Na⁺ is located at the interlayer space initially, the sorption at out-surface space can proceeds prior to ion exchange without following the rule of selectivity. This explained why the majority of q_{sorb} were achieved before the slopes of 1:2 were observed in Figure 4.12.

The fraction of the Ca²⁺ sorbed amount at the outer-surface space is symbolled as $q(\text{ext})$ in this study. On the basis that the q_{sorb} were primary attributed to the $q(\text{ext})$, the concentration-dependent temperature effects to the q_{sorb} indicating that the $q(\text{ext})$ was highly dependent on the Ca²⁺ molarity of permeant. Specifically, as can be inferred from Figure 4.13, the $q(\text{ext})$ significantly increased when permeant bulk Ca²⁺ molarity increased from 0.1M to 1M.

Notably, the $q(\text{ext})$ was fundamentally derived from the contradiction between observed profiles of q_{sorb} and principle of selectivity. Consequently, the concentration dependency of $q(\text{ext})$ was an inevitable deduction derived from the obtained Ca-Na exchange paths. Experimental data of this study supported the model shown in Figure 4.13, and microscopic evidence for the external sorption was also provided by Papelis & Hayes (1996). Therefore, $q(\text{ext})$ is considered to be inherently present for the subsequent discussions. It can be inferred that the temperature dependencies of q_{sorb} are dependent on the (i) states of semi-immobilized external water that contains the $q(\text{ext})$ and (ii) the temperature dependency of $q(\text{ext})$ itself.

The states of semi-immobilized external water can be comprehensively analyzed through a comparative assessment of extreme scenarios. Firstly, assuming the absence of any semi-immobilized external water. Then, the sorption processes will be consistent with the adsorption

processes (Chapter 2) that took place in the interlamellar space, which showed equivalent characteristic of exothermal in most cases (See Figure 2.24). In contrast, assuming the external water is highly stable and fully immobilized. Then, it will be difficult for the sorbed Ca^{2+} in the outer-surface space to across the layer of external water and been adsorbed onto the inter-surface. Consequently, the temperature dependency of q_{sorb} will exhibit fewer characteristics of adsorption processes in the interlamellar space and will show more characteristics of $q(\text{ext})$.

The aforementioned inferences can also be obtained from the perspective of particle movements. It has been introduced Subsection 2.1.2 that all particles including H_2O molecules and Cations located in the interlamellar space are in unfree states that restrained by electrostatic interactions, the adsorption of extra Ca^{2+} onto the inter-surface must be accompanied by the releasing of Na^+ or H_2O (the corresponding reactions were given as Eq (2.2) and Eq (2.10)). However, in the model shown in Figure 4.13, the interlamellar space becomes enclosed to a certain extent. The movements of particles into and out of the interlamellar are physically constrained by the semi-immobilized external water that covers the edges of the layers. Therefore, as the accumulation of $q(\text{ext})$, the ionic density in the semi-immobilized external water is also increased, and the tendency of sorbed Ca^{2+} on the outer-surface space to move inwards by electrostatic attraction is conflict with the fact that particles of Na^+ and H_2O in the interlamellar are physically restricted from moving outwards. As a result, the adsorption processes occurring in the interlamellar space are inhibited. This kind of “traffic jam” is inferred to occur at the boundaries between immobilized interlayer water and semi-immobilized external water.

Up to this point, the temperature dependencies shown in Figure 4.11 and Figure 4.12 can be explained. When permeant was 0.1M CaCl_2 (Set 1), the $q(\text{ext})$ were relatively low and the inhibition of the adsorption processes were relatively weak. Hence, the temperature dependency of q_{sorb} showed characteristics of exothermal in Figure 4.12 (a), which was consistent with the equivalent temperature dependency of adsorption behaviors obtained in Chapter 2. When the permeant was 1M CaCl_2 (Set 2), the $q(\text{ext})$ were relatively high and the inhibition of the adsorption processes were relatively strong. Hence, the temperature dependency of q_{sorb} was attributed to the temperature dependency of $q(\text{ext})$, which was indicated as endothermal in Figure 4.12 (b). It is important to highlight that the categorization of inhibition as “weak” or “strong” in adsorption processes was based on the relative estimated $q(\text{ext})$ values, the fractions of q_{sorb} that were attributed to adsorption processes in Set 2 were still higher than those in Set 1, resulting in a greater elution of Na^+ in Set 2.

The endothermic nature of $q(\text{ext})$ indicates that and the standard entropy of external sorption must be positive ($\Delta S^0(\text{ext}) > 0$) to ensure its spontaneity according to the theory of thermodynamics introduced in Subsection 2.2.1. So, it turns out that the process of external sorption consumes energy and increases the disorder of the system. These natures can be explained but lacking solid evidence: Since the tendency of sorbed Ca^{2+} on the outer-surface space to move inwards is hindered by the particles in the interlayer, the electric potential energy is accumulated at the interface as the increase of $q(\text{ext})$, which consumes energy. The increase of disorder can be explained as the results of mutual repulsion between sorbed Ca^{2+} , or the polarity and orientation of the complex formation between sorbed Ca^{2+} and hydroxyl sites on

the external surface (Katz & Hayes, 1995).

By the way, the inference that $q(\text{ext})$ was the majority of q_{sorb} also supports the chemical compatibility of the hydraulic performance of prehydrated SB specimens. For less Cations were adsorbed onto the inter-surface of montmorillonite due to the physical barrier of the semi-immobilized external water, the distances between montmorillonite layers did not exhibit a significant decrease with the increased of q_{sorb} . Hence, the SB specimens maintained very low hydraulic conductivity against permeants contained high concentrations of Ca^{2+} .

4.4.2 Differences and connections between adsorption and sorption in this dissertation

In this dissertation, the Ca^{2+} that underwent immobilizations were deliberately labeled as “**adsorbed**” in batch tests and “**sorbed**” in column tests to account for the varying states or locations of the immobilizations. In Chapter 2, the specimens of batch tests were not prehydrated and were subjected to oscillations with frequency of 200 Hz. Hence, the Ca^{2+} were more freely to move into the montmorillonite and been **adsorbed**, the total amount of immobilizations at equilibrium was symbolled as q_e . In Chapter 4, the specimens of column test were prehydrated and were in stable conditions. Hence, more Ca^{2+} were **sorbed** on the outer-surface of montmorillonite layers, the total amount of immobilizations was symbolled as q_{sorb} .

The q_e and q_{sorb} both included all processes of immobilization in their cases, they can be characterized with the fractions of the processes respectively:

$$q_e + q_0 = q(\text{exc}) + q(\text{dir}) \quad (4.18)$$

$$q_{\text{sorb}} + q_0 = q(\text{exc}) + q(\text{dir}) + q(\text{ext}) \quad (4.19)$$

where q_0 is the amount of Ca^{2+} exist in montmorillonite interlayers prior to the tests, which was treated equal to the Ca^{2+} exchange capacity of bentonite in this dissertation ($= 0.144 \text{ mmol} \cdot \text{g}^{-1}$); $q(\text{exc})$ is the fraction of ion exchange ($\text{mmol} \cdot \text{g}^{-1}$); $q(\text{dir})$ is the fraction of direct adsorption introduced in Subsection 2.5.2 ($\text{mmol} \cdot \text{g}^{-1}$); $q(\text{ext})$ is the fraction of external sorption ($\text{mmol} \cdot \text{g}^{-1}$). Therefore, following Eq (2.31), the equivalent standard enthalpy change of q_{sorb} can be calculated with the standard enthalpy changes of every fraction:

$$\Delta H^0(\text{eqv}) = \frac{q(\text{exc}) \cdot \Delta H^0(\text{exc}) + q(\text{dir}) \cdot \Delta H^0(\text{dir}) + q(\text{ext}) \cdot \Delta H^0(\text{ext})}{q(\text{exc}) + q(\text{dir}) + q(\text{ext})} \quad (4.20)$$

where $\Delta H^0(\text{eqv})$ is the equivalent standard enthalpy change of Ca^{2+} sorption in column test ($\text{kJ} \cdot \text{mol}^{-1}$); $\Delta H^0(\text{exc})$ is the standard enthalpy change of ion exchange ($= +5.58 \text{ kJ} \cdot \text{mol}^{-1}$); $\Delta H^0(\text{dir})$ is the standard enthalpy change of direct adsorption ($= -6.49 \text{ kJ} \cdot \text{mol}^{-1}$); $\Delta H^0(\text{ext})$ is the standard enthalpy of external sorption ($\text{kJ} \cdot \text{mol}^{-1}$). The value of $\Delta H^0(\text{ext})$ is not measured in this study, but $\Delta H^0(\text{ext}) > 0$ can be inferred from the endothermic nature of q_{sorb} shown in Figure 4.12 (b) where $q(\text{ext})$ were the major fraction. Notably the $q(\text{dir})$ and $q(\text{ext})$ cannot be quantitatively identified in column tests for there was no indicator showing the location a Ca^{2+} became immobilized, but the $q(\text{dir})$ in column test was less than it in batch test with same test condition because the adsorption processes were inhibited in column test.

The relations between Ca^{2+} (ad)sorbed amount and Na^+ desorbed amount obtained from batch tests and column tests are shown in Figure 4.14, which is analogous to Figure 2.24. In the figure, the results of batch tests at 20°C and 50°C were showed as plots of equilibriums, the results of column tests at 20°C, 40°C, and 60°C were given as plots of paths which showing the profiles of development before equilibriums; The background colors indicated the sign of $\Delta H^0(\text{eqv})$ at different areas, and the grey area was assumed had no physical meaning in principle; The equilibrium curves were given as the extensions of the plots of equilibrium obtained in batch tests; The values of q were all converted to (ad)sorbed amount per unit mass bentonite, the initial value of Y-axis was set same as the Ca^{2+} exchange capacity of bentonite ($= -0.144 \text{ mmol}\cdot\text{g}^{-1}$), the ranges of $q(\text{exc})$, $q(\text{dir})$, and $q(\text{ext})$ were showed.

As shown in Figure 4.12, the profiles of q_{sorb} were generally above the estimated equilibrium curves. The last q_{sorb} approximately approached to the equilibrium curves but the values between last q_{sorb} and q_e at the same test condition differed (e.g. 1M Ca^{2+}). The last q_{sorb} is notably always not the exact equilibrium point in the column test. However, as the molarities of Ca^{2+} and Na^+ in effluent samples converged to those in the influents, the exchange paths will progressively become more and more difficult to move forwards. In theory, it might be possible to determine whether the column is close to a true equilibrium state based on the position of last q_{sorb} , but it required the completeness of the equilibrium curves. Last but not least, suggested by the reversed temperature dependencies in the diagram, a permeant concentration ranged in 0.1M to 1M might exist, and there will be no temperature dependency in column test when permeated with that permeant.

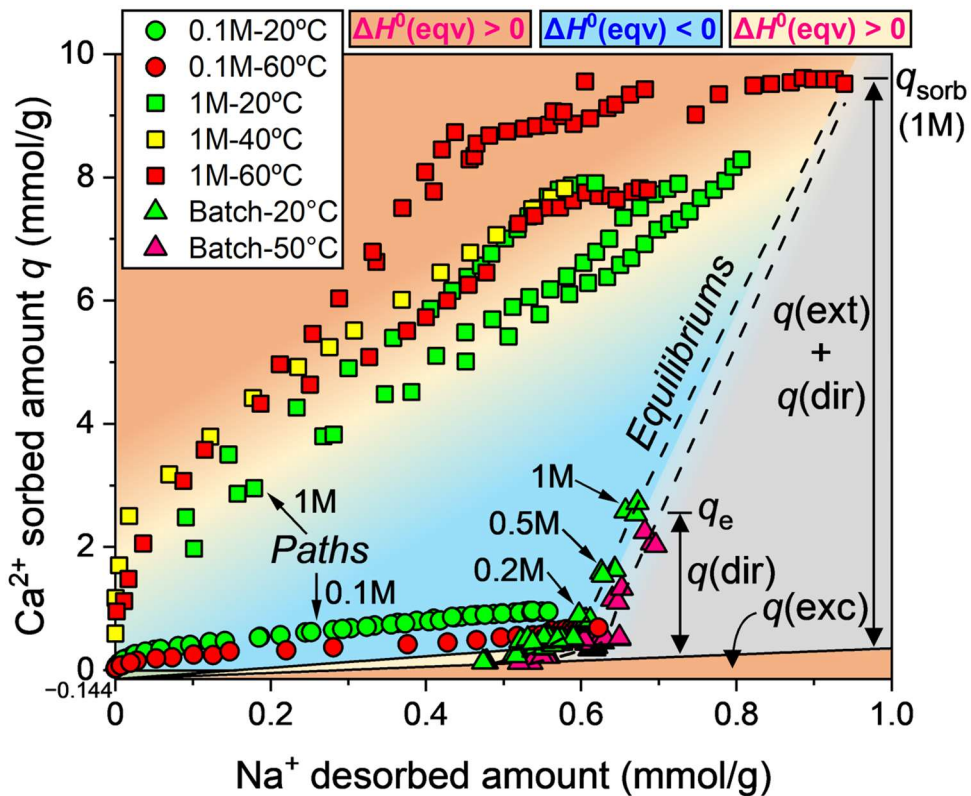


Figure 4.14 Relations between Ca^{2+} adsorbed amount and Na^+ desorbed amount in this dissertation.

4.5 Conclusions of Chapter 4

In this Chapter, the temperature effects to the buffering performance of soil-bentonite mixtures (SB) were evaluated by operating column test at 20°C, 40°C, 60°C with modified flexible-wall permeameter and permeated with 0.1M (Set 1) and 1M (Set 2) CaCl_2 . The buffering performance was characterized by Ca^{2+} sorbed amount (q_{sorb}). The following conclusions could be summarized supported by the test results and discussions:

- (1) The temperature dependencies on the molarities and cumulative amounts of ionic compositions in effluent samples exhibited consistent profiles over time or PVF in Set 1, but exhibited significant variations in Set 2. The variations observed in Set 2 were attributed to the more significant changes in hydraulic conductivity (changes in Set 1 were same but insignificant) that flow rates were faster at higher temperatures. When Ca^{2+} molarity was relatively low (Set 1), the temperature effects to the buffering performance were largely dependent on the temperature dependencies of physical-chemical interactions between SB and permeant; When Ca^{2+} molarity was very high (Set 2), the temperature effects to the buffering performance were predominantly dependent on the temperature dependency of SB's hydraulic performance (Shown in Chapter 3) if considering practical implications.
- (2) The profiles of q_{sorb} were showed rapid initial increases and then gradually slowed down. The temperature dependency of q_{sorb} was obtained by comparing the last q_{sorb} at the last collected effluent samples. In Set 1, the last q_{sorb} were 0.072 and 0.052 $\text{mmol}\cdot\text{g}^{-1}$ on average at 20°C and 60°C, respectively. Suggesting the buffering performance of SB against Ca^{2+} decreased as the temperature increased when permeated with 0.1M CaCl_2 ; In Set 2, the last q_{sorb} were 0.60, 0.59, and 0.67 $\text{mmol}\cdot\text{g}^{-1}$ on average at 20°C, 40°C, and 60°C, respectively. Suggesting that the buffering performance of SB against Ca^{2+} did not significantly decrease but even slightly increased as temperature increased when permeated with 1M CaCl_2 .
- (3) The breakthrough curves of Ca^{2+} observed in column test were analytically expressed with coefficients of retardation (R) and dispersive (D) derived from the Advection-dispersion equation (ADE). The R were obtained by linear fitting the profiles of q_{sorb} among with Ca^{2+} molarity in effluent sample. The D were obtained by fitting the experimental curves to the analytical solution of ADE at position of effluent after the R were obtained. The values of R were 2.36 and 1.98 at 20°C and 60°C in Set 1, and were 2.13, 2.43, and 2.70 at 20°C, 40°C, and 60°C, respectively in Set 2. The values of D ($\text{m}^2\cdot\text{s}^{-1}$) were 6.96×10^{-12} and 2.79×10^{-11} at 20°C and 60°C in Set 1, and were 7.67×10^{-11} , 1.16×10^{-10} , and 2.40×10^{-10} at 20°C, 40°C, and 60°C, respectively in Set 2.
- (4) The different temperature dependencies in profiles of q_{sorb} over PVF in Set 1 and Set 2 can be explained with an assumption that most of the immobilized Ca^{2+} were sorbed onto the outer-surface space of montmorillonite, named as external sorption and the fraction that was symbolled as $q(\text{ext})$. The external sorption was inferred to has a nature of endotherm ($\Delta H^0(\text{ext}) > 0$), and the external sorption increased the entropy of the system ($\Delta S^0(\text{ext}) > 0$). The external sorption possibly, indicated from test results, inhibited the processes of ion exchange and direct adsorption in the interlamellar space of montmorillonite by physically

constraining the particles within the interlamellar space, preventing their movement outward.

- (5) The q_{sorb} was assumed to consist of three fractions: $q(\text{exc})$, $q(\text{dir})$, and $q(\text{ext})$, which varied with q_e containing $q(\text{exc})$ and $q(\text{dir})$. The $q(\text{ext})$ significantly increased the values of q_{sorb} in column test compare to q_e in batch test under the same bulk Ca^{2+} molarity. However, the equilibriums of q_{sorb} in column tests and the equilibriums adsorption amounts (q_e) in batch tests are likely to share the same equilibrium curves in a diagram showing the relations between Ca^{2+} sorbed amount and Na^+ desorbed amount.

References

- Appelo, C. A. J. (2013). A review of porosity and diffusion in bentonite. *POSIVA Working Report 29*, 29(October), 36.
- Bear, J. (1973). Dynamics of Fluids in Porous Media. In *Dover publications* (Vol. 37, Issue 4). Dover.
- Bonilla-Petriciolet, A., Mendoza-Castillo, D. I., & Reynel-Ávila, H. E. (2017). Adsorption processes for water treatment and purification. In *Springer International Publishing AG*.
- Bouazza, A., Jefferis, S., & Vangpaisal, T. (2007). Investigation of the effects and degree of calcium exchange on the Atterberg limits and swelling of geosynthetic clay liners when subjected to wet-dry cycles. *Geotextiles and Geomembranes*, 25(3), 170–185. <https://doi.org/10.1016/j.geotexmem.2006.11.001>
- Bouchard, D. C., Wood, A. L., Campbell, M. L., Nkedi-Kizza, P., & Rao, P. S. C. (1988). Sorption nonequilibrium during solute transport. *Journal of Contaminant Hydrology*, 2, 209–223.
- Celia, M. A., Kindred, J. S., & Herrera, I. (1989). Contaminant transport and biodegradation: 1. A numerical model for reactive transport in porous media. *Water Resources Research*, 25(6), 1141–1148. <https://doi.org/10.1029/WR025i006p01141>
- Dominijanni, A., Guarena, N., & Manassero, M. (2018). Laboratory assessment of semi-permeable properties of a natural sodium bentonite. *Canadian Geotechnical Journal*, 55(11), 1611–1631. <https://doi.org/10.1139/cgj-2017-0599>
- Dominijanni, A., Manassero, M., & Puma, S. (2014). Coupled chemical-hydraulic-mechanical behaviour of bentonites. *Bio-and Chemo-Mechanical Processes in Geotechnical Engineering: Géotechnique Symposium in Print 2013*, 57–71.
- Elderton, W. P. (1902). Tables for testing the goodness of fit of theory to observation. *Biometrika*, 1(2), 155–163. <https://doi.org/10.1093/biomet/1.2.155>
- Evans, J. C., Prince, M. J., & Adams, T. L. (1997). *Metals attenuation in mineral-enhanced slurry walls*.
- Fetter, C. W., Boving, T., & Kreamer, D. (2017). *Contaminant hydrogeology*. Waveland Press.
- Finkel, M., & Grathwohl, P. (2017). Impact of pre-equilibration and diffusion limited release kinetics on effluent concentration in column leaching tests: Insights from numerical simulations. *Waste Management*, 63, 58–73. <https://doi.org/10.1016/j.wasman.2016.11.031>
- Giles, C. H., MacEwan, T. H., Nakhwa, S. N., & Smith, D. (1960). 786. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society (Resumed)*, 846, 3973. <https://doi.org/10.1039/jr9600003973>
- Hutcheon, A. T. (1966). Thermodynamics of cation exchange on clay: Ca-K-montmorillonite. *Journal of Soil Science*, 17(2), 339–355. <https://doi.org/10.1111/j.1365-2389.1966.tb01478.x>
- J. Hunter, R. (1981). Zeta potential in colloid science: Principles and applications. In *Academic*

Press.

- Kaluarachchi, J. J., & Morshed, J. (1995). Critical assessment of the operator-splitting technique in solving the advection-dispersion-reaction equation: 1. First-order reaction. *Advances in Water Resources*, 18(2), 89–100. [https://doi.org/10.1016/0309-1708\(95\)00001-Y](https://doi.org/10.1016/0309-1708(95)00001-Y)
- Kamon, M., Zhang, H., Katsumi, T., & Sawa, N. (2002). Redox Effect on the Hydraulic Conductivity of Clay Liner. *Soils and Foundations*, 42(6), 79–91. https://doi.org/10.3208/sandf.42.6_79
- Kato, T., Gathuka, L. W., Okada, T., Takai, A., Katsumi, T., Imoto, Y., Morimoto, K., Nishikata, M., & Yasutaka, T. (2021). Sorption-desorption column tests to evaluate the attenuation layer using soil amended with a stabilising agent. *Soils and Foundations*, 61(4), 1112–1122. <https://doi.org/10.1016/j.sandf.2021.05.004>
- Katz, L. E., & Hayes, K. F. (1995). Surface complexation modeling: II. Strategy for Modeling Polymer and Precipitation Reactions at High Surface Coverage. In *Journal of Colloid and Interface Science* (Vol. 170, Issue 2, pp. 491–501). <https://doi.org/10.1006/jcis.1995.1128>
- Kaya, A., & Ören, A. H. (2005). Adsorption of zinc from aqueous solutions to bentonite. *Journal of Hazardous Materials*, 125(1–3), 183–189. <https://doi.org/10.1016/j.jhazmat.2005.05.027>
- Kozaki, T., Fujishima, A., Sato, S., & Ohashi, H. (1998). Self-diffusion of sodium ions in compacted sodium montmorillonite. *Nuclear Technology*, 121(1), 63–68. <https://doi.org/10.13182/nt98-a2819>
- Kraepiel, A. M. L., Keller, K., & Morel, F. M. M. (1999). A model for metal adsorption on montmorillonite. *Journal of Colloid and Interface Science*, 210(1), 43–54. <https://doi.org/10.1006/jcis.1998.5947>
- Krynicky, K., Green, C. D., & Sawyer, D. W. (1978). Pressure and temperature dependence of self-diffusion in water. *Faraday Discussions of the Chemical Society*, 66, 199–208. <https://doi.org/10.1039/DC9786600199>
- Laudelout, H., Van Bladel, R., Bolt, G. H., & Page, A. L. (1968). Thermodynamics of heterovalent cation exchange reactions in a montmorillonite clay. *Transactions of the Faraday Society*, 64, 1477–1488. <https://doi.org/10.1039/TF9686401477>
- Malusis, M. A., & Shackelford, C. D. (2002). Coupling effects during steady-state solute diffusion through a semipermeable clay membrane. *Environmental Science and Technology*, 36(6), 1312–1319. <https://doi.org/10.1021/es011130q>
- Martínez-Lladó, X., Valderrama, C., Rovira, M., Martí, V., Giménez, J., & de Pablo, J. (2011). Sorption and mobility of Sb(V) in calcareous soils of Catalonia (NE Spain): Batch and column experiments. *Geoderma*, 160(3–4), 468–476. <https://doi.org/10.1016/j.geoderma.2010.10.017>
- Masindi, V., Gitari, M. W., Tutu, H., & DeBeer, M. (2017). Synthesis of cryptocrystalline magnesite–bentonite clay composite and its application for neutralization and attenuation of inorganic contaminants in acidic and metalliferous mine drainage. *Journal of Water Process Engineering*, 15, 2–17. <https://doi.org/10.1016/j.jwpe.2015.11.007>
- Masuda, R., Asano, H., Tada, H., Nishimura, T., Amemiya, K., & Komine, H. (2006). Evaluation of Attenuation of Impact on Bentonite-Based Buffer Under Construction. *Doboku Gakkai Ronbunshuu C*, 62(2), 292–304. <https://doi.org/10.2208/jscejc.62.292>
- McBride, M. B. (1994). Environmental chemistry of soils. In *Suparyanto dan Rosad (2015)*. Oxford university press.
- Mitchell, J. K. (1993). Fundamentals of Soil Behavior. In *Soil Science Society of America Journal* (3rd ed.). John Wiley & Sons, Inc.
- Mo, J., Flores, G., Inui, T., & Katsumi, T. (2020). Hydraulic and sorption performances of soil amended with calcium-magnesium composite powder against natural arsenic contamination.

- Soils and Foundations*, 60(5), 1084–1096. <https://doi.org/10.1016/j.sandf.2020.05.007>
- Mojid, M. A., & Cho, H. (2006). Estimating the fully developed diffuse double layer thickness from the bulk electrical conductivity in clay. *Applied Clay Science*, 33(3–4), 278–286. <https://doi.org/10.1016/j.clay.2006.06.002>
- Moreé, J. J. (2006). The Levenberg-Marquardt algorithm: implementation and theory. *Numerical Analysis: Proceedings of the Biennial Conference Held at Dundee, June 28--July 1, 1977*, 105–116.
- Naka, A., Flores, G., Inui, T., Sakanakura, H., & Katsumi, T. (2019). Hydraulic performance and chemical compatibility of a powdered Na-bentonite geosynthetic clay liner permeated with mine drainage. *Soils and Foundations*, 59(5), 1128–1147. <https://doi.org/10.1016/j.sandf.2019.02.005>
- Papelis, C., & Hayes, K. F. (1996). Distinguishing between interlayer and external sorption sites of clay minerals using X-ray absorption spectroscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 107, 89–96. [https://doi.org/10.1016/0927-7757\(95\)03370-X](https://doi.org/10.1016/0927-7757(95)03370-X)
- Patel, H. (2019). Fixed-bed column adsorption study: a comprehensive review. *Applied Water Science*, 9(3), 1–17. <https://doi.org/10.1007/s13201-019-0927-7>
- Pivato, A., & Raga, R. (2006). Tests for the evaluation of ammonium attenuation in MSW landfill leachate by adsorption into bentonite in a landfill liner. 26, 123–132. <https://doi.org/10.1016/j.wasman.2005.03.009>
- Ruiz, A. I., Fernández, R., Sánchez Jiménez, N., Rodríguez Rastrero, M., Regadío, M., de Soto, I. S., & Cuevas, J. (2012). Improvement of attenuation functions of a clayey sandstone for landfill leachate containment by bentonite addition. *Science of the Total Environment*, 419, 81–89. <https://doi.org/10.1016/j.scitotenv.2011.11.054>
- Runkel, R. L. (1996). Solution of the Advection-Dispersion Equation: Continuous Load of Finite Duration. *Journal of Environmental Engineering*, 122(9), 830–832. [https://doi.org/10.1061/\(ASCE\)0733-9372\(1996\)122:9\(830\)](https://doi.org/10.1061/(ASCE)0733-9372(1996)122:9(830))
- Ruthven, D. M. (1984). *Principles of adsorption and adsorption processes*. John Wiley & Sons.
- Sato, H., Ashida, T., Kohara, Y., Yui, M., & Sasaki, N. (1992). Effect of dry density on diffusion of some radionuclides in compacted sodium bentonite. *Journal of Nuclear Science and Technology*, 29(9), 873–882. <https://doi.org/10.1080/18811248.1992.9731607>
- Shackelford, C. D. (1994). Critical Concepts for Column Testing. *Journal of Geotechnical Engineering*, 120(10), 1804–1828. [https://doi.org/10.1061/\(ASCE\)0733-9410\(1994\)120:10\(1804\)](https://doi.org/10.1061/(ASCE)0733-9410(1994)120:10(1804))
- Shackelford, C. D., Malusis, M. A., Majeski, M. J., & Stern, R. T. (1999). Electrical Conductivity Breakthrough Curves. *Journal of Geotechnical and Geoenvironmental Engineering*, 125(4), 260–270. [https://doi.org/10.1061/\(ASCE\)1090-0241\(1999\)125:4\(260\)](https://doi.org/10.1061/(ASCE)1090-0241(1999)125:4(260))
- Silavwe, D. D., Brink, I. C., & Wallis, S. G. (2019). Assessment of some numerical methods for estimating the parameters of the one-dimensional advection–dispersion model. *Acta Geophysica*, 67(3), 999–1016. <https://doi.org/10.1007/s11600-019-00293-3>
- Sposito, G., Jouany, C., Holtzclaw, K. M., & LeVesque, C. S. (1983). Calcium-Magnesium Exchange on Wyoming Bentonite in the Presence of Adsorbed Sodium. *Soil Science Society of America Journal*, 47(6), 1081–1085. <https://doi.org/10.2136/sssaj1983.03615995004700060004x>
- Tipping, E. (1995). Chemical kinetics and process dynamics in aquatic systems. In *Environmental Pollution* (Vol. 87, Issue 1). [https://doi.org/10.1016/s0269-7491\(99\)80016-5](https://doi.org/10.1016/s0269-7491(99)80016-5)
- Tripathy, S., Sridharan, A., & Schanz, T. (2004). Swelling pressures of compacted bentonites from diffuse double layer theory. *Canadian Geotechnical Journal*, 41(3), 437–450. <https://doi.org/10.1139/T03-096>

- Van Genuchten, M. T. (1982). *Analytical solutions of the one-dimensional convective-dispersive solute transport equation* (Issue 1661). US Department of Agriculture, Agricultural Research Service.
- Vhahangwele, M., & Muger, G. W. (2015). The potential of ball-milled South African bentonite clay for attenuation of heavy metals from acidic wastewaters: Simultaneous sorption of Co^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} ions. *Journal of Environmental Chemical Engineering*, 3(4), 2416–2425. <https://doi.org/10.1016/j.jece.2015.08.016>
- Wang, H., Ito, D., Shirakawabe, T., Ruan, K., & Komine, H. (2022). On swelling behaviors of a bentonite under different water contents. *Geotechnique*. <https://doi.org/10.1680/jgeot.21.00312>
- Wersin, P., Curti, E., & Appelo, C. A. J. (2004). Modelling bentonite-water interactions at high solid/liquid ratios: Swelling and diffuse double layer effects. *Applied Clay Science*, 26(1-4 SPEC. ISS.), 249–257. <https://doi.org/10.1016/j.clay.2003.12.010>
- Zhang, H., Kamon, M., & Katsumi, T. (2004). Effect of Acid Buffering Capacity on the Long-Term Mobility of Heavy Metals in Clay Liner. *Soils and Foundations*, 44(6), 111–120. https://doi.org/10.3208/sandf.44.6_111

CHAPTER 5

Practical implications

5.1 Summarize the temperature effects on barrier performances

The temperature effects on the hydraulic and buffering performances of emulated SB specimens were evaluated by hydraulic conductivity test with modified flexible-wall permeameter in Chapter 3 and Chapter 4. The results indicated that temperature dependencies of barrier performances of SB vary between the two permeants, suggesting that the temperature effects differ under distinct application scenarios. Such results might lead to confusion. Therefore, it is important to make it clear that how exactly the temperature effects on the hydraulic and buffering performances of SB under specific conditions of application in order to propose targeted countermeasures.

Table 5-1 summarize the temperature effects on hydraulic and buffering performances of SB and corresponding applications. In practice, the different concentration of CaCl_2 solutions as permeant refers to the different ionic concentrations of leachate. Naturally, the classification focus on the potential concentrations, the low-concentration leachate refer to those with properties equivalent to and with concentrations close to or less than those of 0.1M CaCl_2 solution, and 1M CaCl_2 for the high-concentration leachate.

In terms of hydraulic performance, experimental results have shown that the impact of temperature to SBs' equilibrium k was attributed to changed fluid viscosity and density in constant temperature conditions. Therefore, when SB barrier is applied to high-temperatures, the change of leachate fluidity should be considered as a main factor that effect the k of the barrier, independent to the concentration of CaCl_2 . After all, the k of barrier has its criterion, its appropriateness can be intuitively judged. It is showed that under test conditions, the equilibrium k were all less than $10^{-9} \text{ m}\cdot\text{s}^{-1}$.

In terms of buffering performance, temperature dependencies of Ca^{2+} sorbed amounts (q_{sorb}) of SB were found differently when permeated with 0.1M or 1M CaCl_2 solutions. If the barrier is exposed to low-concentration leachate, an increase in temperature may lead to a significant decrease in q_{sorb} . Conversely, when the barrier is exposed to high-concentration leachate, a temperature increase may result in a slight increase in q_{sorb} , insignificantly, which seems appears to have a not-bad impact. However, it has to be noted that the buffering performance is actually not independent to the hydraulic performance. As discussed in subsubsection 4.3.2.1, in practice, it is more appropriate to judge based on the result of q_{sorb} characterized by time rather than PVF. Therefore, with a higher hydraulic conductivity, the sorption capacity will still be depleted faster at a higher temperature (see Figure 4.7 (a)) even if it has higher q_{sorb} . Consequently, the buffering performance of SB barrier is indeed decreasing with the increasing

Table 5-1 Summarized temperature effects on barrier performances of SB.

	With low-concentration leachate (Equivalent to or less than 0.1M CaCl ₂)	With high-concentration leachate (Higher than 0.1M CaCl ₂)
Application scenarios	• Conventional cut-off wall⁽¹⁾ • Barriers for soils contain geogenic contaminations⁽²⁾ • Barriers for underground thermo-storage facilities⁽³⁾	• Barriers alongside marine landfills⁽⁴⁾ • Barriers for degradable municipal solid waste landfills⁽⁵⁾ • Barriers for highly contaminated fields applied with in-situ thermal remediation⁽⁶⁾
Temperature effects	Predominate by the changes in buffering performance • The hydraulic conductivity (k) increased with the temperature increased, which is attributed to the changes of fluidity of the permeant. The initial k were slightly higher than equilibrium k. All k were observed lower than $1 \times 10^{-10} \text{ m} \cdot \text{s}^{-1}$. • The Ca²⁺ breakthrough in effluents among with PVF proceeded faster as the temperature increased. The Ca²⁺ sorbed amount (q_{sorb}) significantly decreased as the temperature increased. The Ca²⁺ sorption showed an equivalent characteristic of exotherm, which was mostly attributed to the process of direct adsorption.	Predominate by the changes in hydraulic performance • The hydraulic conductivity (k) increased with the temperature increased, which is attributed to the changes of fluidity of the permeant. The initial k were significantly higher than equilibrium k, values higher than $1 \times 10^{-9} \text{ m} \cdot \text{s}^{-1}$ were temporary observed right after the heating process. • The Ca²⁺ breakthrough in effluents among with PVF proceeded slower as the temperature increased. The Ca²⁺ sorbed amount (q_{sorb}) slightly increased as the temperature increased. The Ca²⁺ sorption showed an equivalent characteristic of endotherm, which was mostly attributed to the process of external sorption.

(1) Evans (1993); (2) Mo et al. (2020); (3) Tveit et al. (2009); (4) Jones (2010); (5) Jafari et al. (2017); (6) Horst et al. (2021)

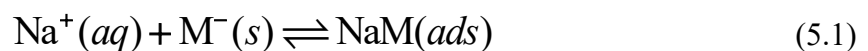
of temperature, regardless the change of permeant. Hence, when designing a SB barrier for high-temperature conditions, it may be necessary to enhance the standards for the sorption properties of the barrier materials to guarantee long-term safety.

Specific measures to raise the hydraulic and buffering performances of SB are, in a sense, the primary concern of field work. There is no doubt that increasing the ratio of bentonite in SB will resulted in lower hydraulic conductivity and higher sorption capacity both. Nevertheless, this approach may not be optimal due to cost considerations. In order to lowering the hydraulic conductivity, there is not much efficient choice other than adding more bentonite. But when the barrier is expected to be exposed to low-concentration leachate, where the hydraulic conductivity is lower enough while the temperature have significantly negative affect to the sorption capacity, incorporating additional adsorbent material might potentially offer a more cost-effective alternative.

5.2 Utilize the characteristics of endothermic reactions

In terms of sorption capability, when a barrier is applied to a condition with high temperatures, higher sorption amounts can be expected if the main reactions for its sorption are endothermal. According to the results shown in Chapter 2 and Chapter 4, the Ca^{2+} sorption processes of SB against CaCl_2 were identified as ion exchange (endothermal), direct adsorption (exothermal), and external sorption (endothermal). Therefore, the sorption behavior of SB will be inhibited with an increase in temperature if direct adsorption is the major reaction (e.g. Ca^{2+} molarity from 0.1M to 1M in batch test and 0.1M in hydraulic conductivity test).

Since the direct adsorption is available due to the exist of additional activate sites with negative charges in montmorillonite interlamellar (McBride, 1994), one affective way to decrease the fraction of direct adsorption process is to intentionally filled the activate sites with exchangeable Na^+ with following reaction:



where M^- is the negatively charged active site on the inter-surface; *ads* indicates the adsorbed phase. If the additional activate sites are saturated with Na^+ to their full capacity, the predominant sorption mechanisms of Ca^{2+} in SB against CaCl_2 will be the endothermal processes of ion exchange and external sorption.

A practicable approach is to add sodium in phases of powder or solution (e.g. NaCl or Na_2CO_3) during the mixing process of SB or in the pre-hydration process of SB post-mixing. Significantly, this type of pretreatment can also influence on the hydraulic performance of SB. The significance of the pretreatment is evident only when the hydraulic conductivity of the soil bentonite meets the specified requirements.

5.3 Accidental concerns and measures

The results in Chapter 3 showed that the initial values of hydraulic conductivity (k) right after the heating process were higher than the equilibrium k at some isothermal conditions, the

heating increased the cell temperature to the target values in 24 h. There is a noticeable trend indicating that as the temperature and concentration of permeant increase, the disparity between the initial k and equilibrium k also increases. Such phenomenon indicates a risk of decreased hydraulic performance in SBs' barrier performances in dynamic temperature conditions, e.g. when in-situ thermal remediation (Horst et al., 2021) is applied to contaminated sites surrounded by SB cut-off wall. Therefore, when SB barrier is meeting dynamic temperature conditions, k should be verified by in-situ methods, e.g. Piezocone or CPTU (Britton et al., 2004; Takai et al., 2016), and methods of drainage might needs to be considered.

External sorption was identified as the main process of Ca^{2+} sorption SB in hydraulic conductivity test in Chapter 4, which the Ca^{2+} were inferred been sorbed on the out-surface of montmorillonite accompanied with semi-immobilized water layers. The concern is how much the semi-immobilized water can hold the sorbed Ca^{2+} . Since no signs of external sorption were observed in batch test where the specimens were subject to oscillation of 200 Hz, it can be indicated that the semi-immobilized water layers as well as the sorbed Ca^{2+} are possibly desorbed if subjected to the oscillation. Consequently, when a functional barrier is exposed to severe seismic conditions, there is a possibility of temporary desorption of sorbed contaminants. This risk is seldom be mentioned and necessitates additional investigation.

References

- Britton, J. P., Filz, G. M., & Herring, W. E. (2004). Measuring the Hydraulic Conductivity of Soil–Bentonite Backfill. *Journal of Geotechnical and Geoenvironmental Engineering*, 130(12), 1250–1258. [https://doi.org/10.1061/\(asce\)1090-0241\(2004\)130:12\(1250\)](https://doi.org/10.1061/(asce)1090-0241(2004)130:12(1250))
- Evans, J. C. (1993). Vertical cutoff walls. In *Geotechnical Practice for Waste Disposal* (pp. 430–454). Springer US. https://doi.org/10.1007/978-1-4615-3070-1_17
- Horst, J., Munholland, J., Hegele, P., Klemmer, M., & Gattenby, J. (2021). In Situ Thermal Remediation for Source Areas: Technology Advances and a Review of the Market From 1988–2020. *Groundwater Monitoring and Remediation*, 41(1), 17–31. <https://doi.org/10.1111/gwmr.12424>
- Jafari, N. H., Stark, T. D., & Thalhamer, T. (2017). Spatial and temporal characteristics of elevated temperatures in municipal solid waste landfills. *Waste Management*, 59, 286–301. <https://doi.org/10.1016/j.wasman.2016.10.052>
- Jones R. (2010). Environmental contamination associated with a marine landfill ('seafill') beside a coral reef. *Marine pollution bulletin*, 60(11): 1993–2006. <https://doi.org/10.1016/j.marpolbul.2010.07.028>
- McBride, M. B. (1994). Environmental chemistry of soils. In *Suparyanto dan Rosad (2015)*. Oxford university press.
- Mo, J., Flores, G., Inui, T., & Katsumi, T. (2020). Hydraulic and sorption performances of soil amended with calcium-magnesium composite powder against natural arsenic contamination. *Soils and Foundations*, 60(5), 1084–1096. <https://doi.org/10.1016/j.sandf.2020.05.007>
- Takai, A., Inui, T., & Katsumi, T. (2016). Evaluating the hydraulic barrier performance of soil-bentonite cutoff walls using the piezocone penetration test. *Soils and Foundations*, 56(2), 277–290. <https://doi.org/10.1016/j.sandf.2016.02.010>
- Tveit, T. M., Savola, T., Gebremedhin, A., & Fogelholm, C. J. (2009). Multi-period MINLP model for optimising operation and structural changes to CHP plants in district heating networks with long-term thermal storage. *Energy Conversion and Management*, 50(3), 639–647. <https://doi.org/10.1016/j.enconman.2008.10.010>

CHAPTER 6

Conclusions and future research needed

6.1 Conclusions

This dissertation discusses the temperature effects on hydraulic and buffering performances of soil-bentonite mixture (SB) made by bentonite powder (B) and decomposed granite soil (S), which is a barrier material. The experimental works including the batch test to evaluate the basic properties of materials and column type hydraulic conductivity test to evaluate the barrier performances of SB by emulating in-situ conditions. The conclusions from Chapter 2 to Chapter 5 are summarized as follows:

In Chapter 2, the temperature effects to the adsorption behaviors of SB were studied. Adsorptions of B, S, and SB against Ca^{2+} were evaluated by operating batch tests in 200 mL natural CaCl_2 solutions with different initial Ca^{2+} molarities (0.5 to $1000 \text{ mmol}\cdot\text{L}^{-1}$) and with different constant temperature conditions (20°C to 50°C), respectively. The equilibrium amounts of adsorption and desorption were characterized by ordinary ads/des amounts (Q_e) and modified ads/des amounts (q_e) where the latter considered the volume change of bulk solution and is more correct in principle.

The kinetics of Ca^{2+} adsorption and Na^+ desorption by bentonite were observed to occur rapidly in batch system. The ads/des amounts instantaneously reached considerable values, and showed characteristics of stabilization after several hours. The tests were operated with a longest period of 72 h of oscillation, with no significant differences in Ca^{2+} adsorption and Na^+ desorption amounts compared to the 24 h. The 24 h oscillation was approximately sufficient to achieve the equilibrium for Ca^{2+} adsorption and Na^+ desorption.

The free swell test was carried out to assess the unit volumes of interlamellar space of bentonite in aqueous system (V_{in}/m_s). The V_{in}/m_s was defined as the difference between the free swell volume and particle volume of unit mass bentonite. The V_{in}/m_s was found can be empirically fitted by exponential model as a function of equilibrium Ca^{2+} bulk molarity (c_t).

When characterizing adsorption isotherms, Q_e were lower than q_e and the differences increased significantly as the increased of c_t . When characterizing exchange isotherms, $-Q_e$ were higher than $-q_e$ while the differences between Q_e and q_e were relatively insignificant. Test results indicated that the Q_e underestimated the adsorption amounts, and overestimated the desorption amounts of bentonite. Except for very dilute bulk solution, the volume change of bulk solution in batch system contains bentonite should not be ignored.

The Ca^{2+} adsorption (q_e) isotherms showed characteristics of decreasing at about $10 \text{ mol}\cdot\text{L}^{-1}$ of c_t , which were attributed to the rapidly decreasing of V_{in}/m_s . When c_t exceeded $100 \text{ mol}\cdot\text{L}^{-1}$,

the adsorption isotherms were observed increased linearly as the c_t increased, q_e exceeded 2 mmol·g⁻¹ at approximate 1000 mmol·L⁻¹ of c_t . The Na⁺ exchange ($-q_e$) isotherms showed characteristics of initial values of approximately 0.4 mmol·g⁻¹, and continuously slight increasing as the c_t increased. At approximate 1000 mmol·L⁻¹ of c_t , $-q_e$ reached 0.7 mmol·g⁻¹. The adsorption/exchange isotherms of bentonite and SB shared same characteristics. The q_e of SB were approximately equal to the q_e of B multiplied by the bentonite mass ratio of SB at various temperatures. Bentonite can fully utilize its adsorption capability as SB regardless of the temperature changes.

The temperature effects to Ca²⁺ adsorption (q_e) isotherms were relatively insignificant when c_t were lower than 50 mmol·L⁻¹, and were significantly observed when c_t were higher than 100 mmol·L⁻¹, where q_e decreased as the temperature increased, exhibited characteristics of exothermal. On contrast, the temperature effects to Na⁺ exchange ($-q_e$) isotherms were more significantly observed when c_t were lower than 50 mmol·L⁻¹, where $-q_e$ increased as the temperature increased, exhibited characteristics of endothermal.

The Ca²⁺ adsorbed amount can be characterized by the molarity of Ca²⁺ in the internal space (c_{in}), which is calculated from q_e and V_{in}/m_s . The c_{in} increased monotonically as the c_t increased and c_{in} were always higher than c_t . Suggesting the nature of bentonite to attract Ca²⁺ in bulk solutions remained unchanged. The observed c_{in} exhibited approximately linear correlations with c_t in a wide range.

The Ca²⁺ adsorption by bentonite is the consequences of ion exchange and direct adsorption processes. The standard thermodynamic parameters of the direct adsorption process were calculated by analyzing the relation between c_{in} and c_t . The direct adsorption was found to be an exothermal reaction with $\Delta H^0 = -6.49$ kJ·mol⁻¹, which is different with the reported ΔH^0 of ion exchange reaction in sign. The sign of the equivalent ΔH^0 of Ca²⁺ been adsorbed depends on the proportions of the two reactions. Which explained the results that adsorption showed more significant exothermic characteristics when q_e were relatively high, with direct adsorption fractions ($q(dir)$) significantly higher than ion exchange fractions ($q(exc)$). The endothermic or exothermic nature of the equivalent reaction for Ca²⁺ adsorption can be determined using a diagram showing relations between Na⁺ desorbed amount and Ca²⁺ adsorbed amount.

In Chapter 3, the temperature effects to the hydraulic performance of SB were evaluated by operating falling-head hydraulic conductivity tests at constant temperatures of 20°C, 40°C, and 60°C with modified flexible-wall permeameter. The SB barriers were emulated by consolidated SB specimens with 20 mm initial height and 1.46 to 1.47 Mg·m⁻³ initial dry densities. The hydraulic performance was characterized by hydraulic conductivity (k) and intrinsic permeability (K).

The equilibrium k were observed increase with increased temperature when permeated with 0.1M (Set 1) and 1M CaCl₂ (Set 2). Equilibrium k were 2.7×10^{-10} and 5.7×10^{-10} m·s⁻¹ on average at 20°C and 60°C in Set 1. Equilibrium k were 1.1×10^{-10} , 1.7×10^{-10} , and 2.3×10^{-10} m·s⁻¹ on average at 20°C, 40°C, and 60°C, respectively, in Set 2. The temperature dependencies of equilibrium k of Set 1 and Set 2 were found consistent with the estimation calculated with permeant densities and viscosities at corresponding temperatures. The K was calculated by

eliminate the fluid density and viscosity from equilibrium k . The K did not show significant temperature dependencies, which were 2.6×10^{-18} and $1.5 \times 10^{-17} \text{ m}^2$ on averages in Set 1 and Set 2, respectively. Indicating that the changes of equilibrium k in different temperatures were predominantly attributed to the changes of fluid viscosity and density.

The prehydrated SB specimens exhibited good chemical compatibility. The increases of the K when permeated with 1M CaCl_2 were less than one magnitude compared to the cases permeated with distilled water. The temperature effects on the chemical compatibilities gained from prehydration were insignificant. The chemical compatibility of prehydrated SB barrier is unlikely to be significantly affected by a temperature change of temperature from 20°C to 60°C during practical functioning. Temporary changes of k were observed in profiles of k among with time and PVF. The temporary changes were characterized by the differences between initial k and equilibrium k , where initial k were determined as the first 5 values obtained in the test. The initial k increased as temperature rose, with temperature having a more significant impact on the initial k than on the equilibrium k .

In Chapter 4, the temperature effects to the buffering performance of SB were evaluated by operating column test at 20°C , 40°C , 60°C with modified flexible-wall permeameter and permeated with 0.1M (Set 1) and 1M (Set 2) CaCl_2 . The buffering performance was characterized by Ca^{2+} sorbed amount (q_{sorb}).

The temperature dependencies on the molarities and cumulative amounts of ionic compositions in effluent samples exhibited consistent profiles over time or PVF in Set 1, but exhibited significant variations in Set 2. The variations observed in Set 2 were attributed to the more significant changes in hydraulic conductivity (changes in Set 1 were same but insignificant) that flow rates were faster at higher temperatures. When Ca^{2+} molarity was relatively low (Set 1), the temperature effects to the buffering performance were largely dependent on the temperature dependencies of physical-chemical interactions between SB and permeant; When Ca^{2+} molarity was very high (Set 2), the temperature effects to the buffering performance were predominantly dependent on the temperature dependency of SB's hydraulic performance if considering practical implications.

The profiles of q_{sorb} were showed rapid initial increases and then gradually slowed down. The temperature dependency of q_{sorb} was obtained by comparing the last q_{sorb} at the last collected effluent samples. In Set 1, the last q_{sorb} were 0.072 and 0.052 $\text{mmol}\cdot\text{g}^{-1}$ on average at 20°C and 60°C , respectively. Suggesting the buffering performance of SB against Ca^{2+} decreased as the temperature increased when permeated with 0.1M CaCl_2 ; In Set 2, the last q_{sorb} were 0.60, 0.59, and 0.67 $\text{mmol}\cdot\text{g}^{-1}$ on average at 20°C , 40°C , and 60°C , respectively. Suggesting that the buffering performance of SB against Ca^{2+} did not significantly decrease but even slightly increased as temperature increased when permeated with 1M CaCl_2 .

The breakthrough curves of Ca^{2+} observed in column test were analytically expressed with coefficients of retardation (R) and dispersive (D) derived from the Advection-dispersion equation (ADE). The R were obtained by linear fitting the profiles of q_{sorb} among with Ca^{2+} molarity in effluent sample. The D were obtained by fitting the experimental curves to the analytical solution of ADE at position of effluent after the R were obtained. The values of R

were 2.36 and 1.98 at 20°C and 60°C in Set 1, and were 2.13, 2.43, and 2.70 at 20°C, 40°C, and 60°C, respectively in Set 2. The values of D ($\text{m}^2\cdot\text{s}^{-1}$) were 6.96×10^{-12} and 2.79×10^{-11} at 20°C and 60°C in Set 1, and were 7.67×10^{-11} , 1.16×10^{-10} , and 2.40×10^{-10} at 20°C, 40°C, and 60°C, respectively in Set 2.

The different temperature dependencies in profiles of q_{sorb} over PVF in Set 1 and Set 2 can be explained with an assumption that most of the immobilized Ca^{2+} were sorbed onto the outer-surface space of montmorillonite, named as external sorption and the fraction was symbolled as $q(\text{ext})$. The external sorption was inferred to has a nature of endotherm ($\Delta H^0(\text{ext}) > 0$), and the external sorption increased the entropy of the system ($\Delta S^0(\text{ext}) > 0$). The external sorption possibly, indicated from test results, inhibited the processes of ion exchange and direct adsorption in the interlamellar space of montmorillonite by physically constraining the particles within the interlamellar space, preventing their movement outward. The q_{sorb} was assumed to consist of three fractions: $q(\text{exc})$, $q(\text{dir})$, and $q(\text{ext})$, which varied with q_e containing $q(\text{exc})$ and $q(\text{dir})$. The $q(\text{ext})$ significantly increased the values of q_{sorb} in column test compare to q_e in batch test under the same bulk Ca^{2+} molarity. However, the equilibriums of q_{sorb} in column tests and the equilibriums adsorption amounts (q_e) in batch tests are likely to share same equilibrium curves in a diagram of the relations between Ca^{2+} sorbed amount and Na^+ desorbed amount.

In Chapter 5, interpretations of experimental results were discussed in consideration with practical implications. To mitigate the inhibitory effects of (ad)sorption caused by exothermic reaction at high temperatures and to take advantage of the endothermal characteristics of ion exchange reaction, a suggestion was made to implement Na^+ pretreatment during mixing or prehydration procedures of SB preparation. In terms of application scenarios, low-contaminated and high-contaminated scenarios were discussed and corresponding improvement suggestions were given. Also, the effects of accidental factors like dynamic temperature conditions and seismic stability were discussed.

6.2 Further researches needed

This dissertation attempted to clarify the temperature effects on hydraulic and buffering performances of SB. While there have been some minor achievements, several new problems have also emerged and required further researches.

- (1) In interpreting some experimental results, especially in the discussions of Chapter 4, the observed phenomenon was explained through theoretical deduction, where solid evidence was not provided.
- (2) The hydraulic and buffering performances of SB barriers under dynamic temperature conditions are still lacking comprehensive understanding.
- (3) Some minor components in solutions were not considered in this dissertation (e.g. complexes of CaCl^+ and ClO_4^-), whether and how they affect the obtained results required verifications.
- (4) This research only targeted on Ca^{2+} ion, whether the behaviors of SB against other divalent metal ions are consistent with the obtained results has not been experimentally confirmed.

APPENDIX A

Chi-square test for variable correlations

Introduction

The Chi-square test is a statistical method used to determine if there is a significant association between two categorical variables. It is widely used in hypothesis testing to compare observed data with data we would expect to obtain according to a specific hypothesis. The Chi-square test of goodness-of-fit is introduced in appendix A.

Steps:

1. Compute the Chi-square Statistic (χ^2).

The χ^2 is calculated as follows:

$$\chi^2 = \sum \frac{(O_i - E_i)^2}{E_i} \quad (\text{ex.1})$$

where O_i is the observed value; E_i is the expected value, which refers to the fitted value.

2. Determine the degrees of freedom.

The degrees of freedom is calculated as follows:

$$df = [\text{Number of values}] - [\text{Number of control parameters}] \quad (\text{ex.2})$$

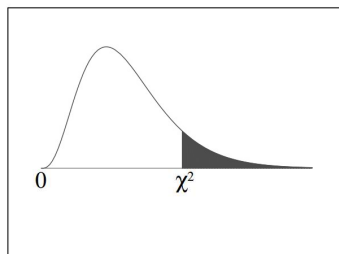
where df is the degrees of freedom; The control parameters refer to the parameters in fitting function (e.g. $y = ax^2 + bx + c$ has three control parameters a , b , and c).

3. Find the critical value in Chi-square distribution table.

Figure ex.1 shows the Chi-square distribution table, the critical values of χ^2 is given. Compare the calculated χ^2 to the critical value from the Chi-square distribution table at the correspond df , the significance level (α) of the fitting can be determined. Basically, the smaller the value of χ^2 , the higher the significance level will be.

The significance level is conforming to the Pearson distribution of probability. Numerically, on the right-tail table, the values of significance level (α) and the probability of correlation (p -value) are equal. Therefore, for a given df , if the calculated χ^2 is lower than the critical values at a column, then the α as well as the p -value of the fitting is higher than the value of that column.

Chi-Square Distribution Table



The shaded area is equal to α for $\chi^2 = \chi^2_{\alpha}$.

df	$\chi^2_{.995}$	$\chi^2_{.990}$	$\chi^2_{.975}$	$\chi^2_{.950}$	$\chi^2_{.900}$	$\chi^2_{.100}$	$\chi^2_{.050}$	$\chi^2_{.025}$	$\chi^2_{.010}$	$\chi^2_{.005}$
1	0.000	0.000	0.001	0.004	0.016	2.706	3.841	5.024	6.635	7.879
2	0.010	0.020	0.051	0.103	0.211	4.605	5.991	7.378	9.210	10.597
3	0.072	0.115	0.216	0.352	0.584	6.251	7.815	9.348	11.345	12.838
4	0.207	0.297	0.484	0.711	1.064	7.779	9.488	11.143	13.277	14.860
5	0.412	0.554	0.831	1.145	1.610	9.236	11.070	12.833	15.086	16.750
6	0.676	0.872	1.237	1.635	2.204	10.645	12.592	14.449	16.812	18.548
7	0.989	1.239	1.690	2.167	2.833	12.017	14.067	16.013	18.475	20.278
8	1.344	1.646	2.180	2.733	3.490	13.362	15.507	17.535	20.090	21.955
9	1.735	2.088	2.700	3.325	4.168	14.684	16.919	19.023	21.666	23.589
10	2.156	2.558	3.247	3.940	4.865	15.987	18.307	20.483	23.209	25.188
11	2.603	3.053	3.816	4.575	5.578	17.275	19.675	21.920	24.725	26.757
12	3.074	3.571	4.404	5.226	6.304	18.549	21.026	23.337	26.217	28.300
13	3.565	4.107	5.009	5.892	7.042	19.812	22.362	24.736	27.688	29.819
14	4.075	4.660	5.629	6.571	7.790	21.064	23.685	26.119	29.141	31.319
15	4.601	5.229	6.262	7.261	8.547	22.307	24.996	27.488	30.578	32.801
16	5.142	5.812	6.908	7.962	9.312	23.542	26.296	28.845	32.000	34.267
17	5.697	6.408	7.564	8.672	10.085	24.769	27.587	30.191	33.409	35.718
18	6.265	7.015	8.231	9.390	10.865	25.989	28.869	31.526	34.805	37.156
19	6.844	7.633	8.907	10.117	11.651	27.204	30.144	32.852	36.191	38.582
20	7.434	8.260	9.591	10.851	12.443	28.412	31.410	34.170	37.566	39.997
21	8.034	8.897	10.283	11.591	13.240	29.615	32.671	35.479	38.932	41.401
22	8.643	9.542	10.982	12.338	14.041	30.813	33.924	36.781	40.289	42.796
23	9.260	10.196	11.689	13.091	14.848	32.007	35.172	38.076	41.638	44.181
24	9.886	10.856	12.401	13.848	15.659	33.196	36.415	39.364	42.980	45.559
25	10.520	11.524	13.120	14.611	16.473	34.382	37.652	40.646	44.314	46.928
26	11.160	12.198	13.844	15.379	17.292	35.563	38.885	41.923	45.642	48.290
27	11.808	12.879	14.573	16.151	18.114	36.741	40.113	43.195	46.963	49.645
28	12.461	13.565	15.308	16.928	18.939	37.916	41.337	44.461	48.278	50.993
29	13.121	14.256	16.047	17.708	19.768	39.087	42.557	45.722	49.588	52.336
30	13.787	14.953	16.791	18.493	20.599	40.256	43.773	46.979	50.892	53.672
40	20.707	22.164	24.433	26.509	29.051	51.805	55.758	59.342	63.691	66.766
50	27.991	29.707	32.357	34.764	37.689	63.167	67.505	71.420	76.154	79.490
60	35.534	37.485	40.482	43.188	46.459	74.397	79.082	83.298	88.379	91.952
70	43.275	45.442	48.758	51.739	55.329	85.527	90.531	95.023	100.425	104.215
80	51.172	53.540	57.153	60.391	64.278	96.578	101.879	106.629	112.329	116.321
90	59.196	61.754	65.647	69.126	73.291	107.565	113.145	118.136	124.116	128.299
100	67.328	70.065	74.222	77.929	82.358	118.498	124.342	129.561	135.807	140.169

Figure ex.1 Chi-square distribution table
<https://www.math.arizona.edu/~jwatkins/chi-square-table.pdf>.

APPENDIX B

Attempts in calculating modified adsorption isotherm (q_e) from ordinary adsorption isotherm (Q_e)

Theoretical deduction

Following the Subsection 2.5.3. The similarity in mathematical descriptions of the adsorption isotherms of q_e and Q_e suggests the possibility that q_e could be calculated from the Q_e directly, which do not require, or do not require many, independent free swell test to be carried out to find the values of V_{in}/m_s . As a supplementary of the doctoral dissertation, the feasibility to obtain q_e from Q_e is discussed in this part.

Re-giving the analytical form of the adsorption isotherms of q_e and Q_e as follows:

$$q_e = [(K_{11} \cdot c + K_{12}) \cdot e^{-c/i^*}] + [K_{21} \cdot c + K_{22}] - q_0 \quad (\text{ex.3})$$

$$Q_e = [(K_{11}^* \cdot c + K_{12}) \cdot e^{-c/i^*}] + [K_{21}^* \cdot c + K_{22}] - q_0 \quad (\text{ex.4})$$

The similarity between adsorption isotherms of q_e and Q_e can be characterized by the differences in parameters of their mathematical descriptions:

$$K_{ij} = \begin{bmatrix} K_{11} & K_{12} \\ K_{21} & K_{22} \end{bmatrix} = [i]_{2 \times 1} \cdot [j]_{1 \times 2} = \begin{bmatrix} i_1 j_1 & i_1 j_2 \\ i_2 j_1 & i_2 j_2 \end{bmatrix} \quad (\text{ex.5})$$

$$K_{ij}^* = \begin{bmatrix} K_{11}^* & K_{12} \\ K_{21}^* & K_{22} \end{bmatrix} = [i]_{2 \times 1} \cdot \left\{ [j]_{1 \times 2} + \begin{bmatrix} -1 \\ 0 \end{bmatrix} \right\} = \begin{bmatrix} i_1 j_1^* & i_1 j_2 \\ i_2 j_1^* & i_2 j_2 \end{bmatrix} \quad (\text{ex.6})$$

$$j_1 = j_1^* + 1 \quad (\text{ex.7})$$

The K_{ij}^* is obtained on the profile of adsorption isotherm of Q_e . Naturally, an assertion can be state as below.

Assertion: *if K_{ij} can be derived from K_{ij}^* , then q_e can be derived from Q_e by calculations without any results of free swell test.*

The **premise** of the **Assertion** can be test by the determinants of Matrix K_{ij} and K_{ij}^* , which are calculated as below:

$$\det(K_{ij}^*) = \det(K_{ij}) = i_1 j_1 \cdot i_2 j_2 - i_1 j_2 \cdot i_2 j_1 = 0 \quad (\text{ex.8})$$

The zero of the determinants indicated that there is no inverse Matrix for K_{ij}^* and K_{ij} , hence the individuals of i_n and j_n cannot be solved from K_{ij}^* and K_{ij} . That is, **K_{ij} cannot be derived from**

K_{ij}^* , and q_e cannot be derived from Q_e without any additional information. Therefore, additional information refer to the individual values of i_n and j_n or their relations is needed. For a second-order matrix K_{ij}^* , only a small amount of the additional information is sufficient to solve the individuals of i_n and j_n^* .

Consequently, a theorem can be deducted as follows.

Theorem B: *If knowing K_{ij}^* and any single individual value of i_n or j_n^* , then K_{ij} can be derived from K_{ij}^* , and then q_e can be derived from Q_e by transferring.*

Proof. The key to transfer the K_{ij}^* into the K_{ij} is the value of j_1^* , which can be calculated by K_{ij}^* plus any single individual value of i_n or j_n^* as below:

$$j_1^* = \frac{K_{11}^*}{i_1} = \frac{K_{21}^*}{i_2} = j_2 \cdot \frac{K_{11}^*}{K_{21}} = j_2 \cdot \frac{K_{12}}{K_{22}} \quad (\text{ex.9})$$

Thus, **Theorem B** is proof.

Application of theorem B

A readily obtainable individual value of i_n or j_n^* is the i_2 . Figure ex.2 shows the profile of the empirical model for V_{in}/m_s used in this dissertation. Apparently, i_2 is the convergence value of the function and should have the physical meaning of, for example, the minimum volume of interlamellar space of unit mass bentonite.

In principle, the value of V_{in}/m_s will converge as the molarity of bulk Ca^{2+} , as well as other cations, increases. As summarized in Table 2–7, the empirical fitted models for molarity of $\text{Ca}^{2+} \geq 100 \text{ mmol} \cdot \text{L}^{-1}$ showed convergence value of $2.09 \times 10^{-3} \text{ L} \cdot \text{g}^{-1}$, which is very close to the experimental value when molarity of $\text{Ca}^{2+} = 1000 \text{ mmol} \cdot \text{L}^{-1}$. Notably, the convergence values of fitted model when concentration were relatively low failed to represent the physical meaning of i_2 , they are available only in their domains.

Since this part only discusses the feasibility of this method rather than the accuracy of the parameters, let the i_2 to be assumed as $2 \times 10^{-3} \text{ L} \cdot \text{g}^{-1}$. Taking the Ca^{2+} adsorption isotherm of bentonite at 20°C as an example, let the parameter of index $i^* = 17.92$, same as the index in fitted curve of 20°C in Table 2–7.

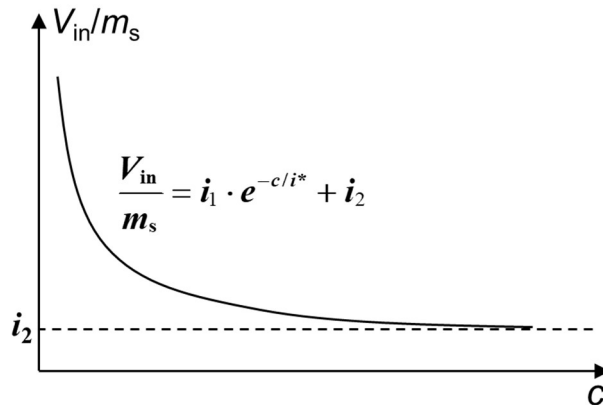
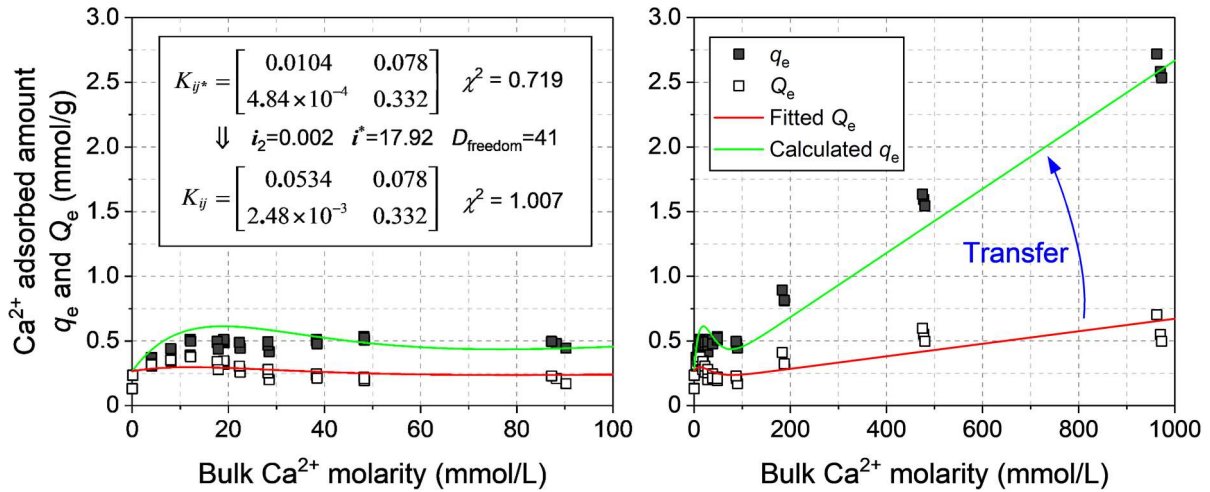


Figure ex.2 Profile of V_{in}/m_s among with c .

Figure ex.3 Transferring Q_e into q_e with the value of i_2 .

The profiles of Ca^{2+} adsorption isotherms are shown in Figure ex.3, where the plots are experimental values obtained in Chapter 2, curves in red are the fitted Q_e and curves in blue are q_e calculated with the fitted Q_e plus the single value of i_2 . The correlations between the experimental data and the fitted Q_e curve and the calculated q_e curve are tested with Chi-squared method, the significance levels exceeding 0.99. The consistency observed between the profiles of curves and plots indicated the accuracy of the adsorption isotherm model, and the feasibility of obtaining q_e by transferring the Q_e isotherm.

Imperfection of calculated q_e are also been observed in Figure ex.3. When molarity of bulk Ca^{2+} is lower than $30 \text{ mmol} \cdot \text{L}^{-1}$, the q_e curve overestimated the values of q_e while the Q_e curve was slightly below the plots of Q_e . This difference amplified the peak of q_e profile at low concentrations, which is highly dependent on the value of K_{11} . Therefore, additional correction to K_{11} may be required in order to obtain the more accurate q_e isotherm.

Another obstacle to the application of transferring Q_e into q_e is the selection of exponential parameter i^* , which determined the timing of the convergence of e^{-c/i^*} , and also the values and positions of peak and trough of q_e isotherm. Although the value of i^* can be given with process of fitting, the common algorithms (e.g. Levenberg-Marquardt algorithm) do not fit exponential parameters very well, especially when there are many other non-exponential parameters. Hence, method like hyperparameter tuning might be needed to obtain the accurate i^* numerically. Or, the value of i^* should be given from its physical meaning, which is still unclear up to this point. Perhaps the physical meaning of i^* can be suggested from the exponential parameter in thermodynamics (e.g. E/RT).

Lastly, the flow charts of sequences obtaining q_e and the raw data used in Appendix B are shown in Figure ex.4 and Figure ex.5.

Long Name	A(X)	B(Y)	C(Y)
Units	Ca	Qe	qe
Comments	mmol/L	mmol/g	mmol/g
F(X)=			
1	0.0165	0.13398	0.13421
2	0.01651	0.13219	0.13242
3	0.01433	0.13103	0.13123
4	0.12893	0.23291	0.23469
5	0.13213	0.23329	0.23511
6	0.13663	0.2352	0.23709
7	4.03108	0.32383	0.37329
8	4.09448	0.30643	0.35657
9	4.05255	0.31765	0.36734
10	19.1582	0.32004	0.48618
11	19.0991	0.33402	0.49982
12	19.05105	0.3463	0.51182
13	8.05	0.35053	0.43909
14	8.1	0.34182	0.43082
15	8.025	0.35248	0.44082
16	12.072	0.39141	0.51198
17	12.12	0.38089	0.50181
18	12.168	0.37671	0.49798
19	17.7	0.33069	0.48826
20	17.675	0.34045	0.49787
21	17.9	0.27851	0.43727
22	22.4	0.28037	0.46457
23	22.475	0.25931	0.44392
24	22.3	0.30585	0.48951
25	28.5	0.2	0.41576
26	28.25	0.25333	0.46763
27	28.25	0.28	0.4945
28	38.375	0.23333	0.49766
29	38.325	0.24667	0.51076
30	38.45	0.21333	0.47803
31	48.3	0.19333	0.50697
32	48.2	0.22	0.53313
33	48.25	0.20946	0.52284
34	88.25	0.20958	0.47969
35	90.25	0.16966	0.44484
36	87.25	0.22886	0.49643
37	187.75	0.31873	0.81067
38	187.5	0.32338	0.81482
39	183.25	0.41082	0.89367
40	477.5	0.5511	1.59257
41	475	0.59821	1.63489
42	480	0.49801	1.54427
43	970	0.55055	2.58228
44	972.5	0.49751	2.53441
45	962.5	0.70281	2.71903

Figure ex.5 Raw data

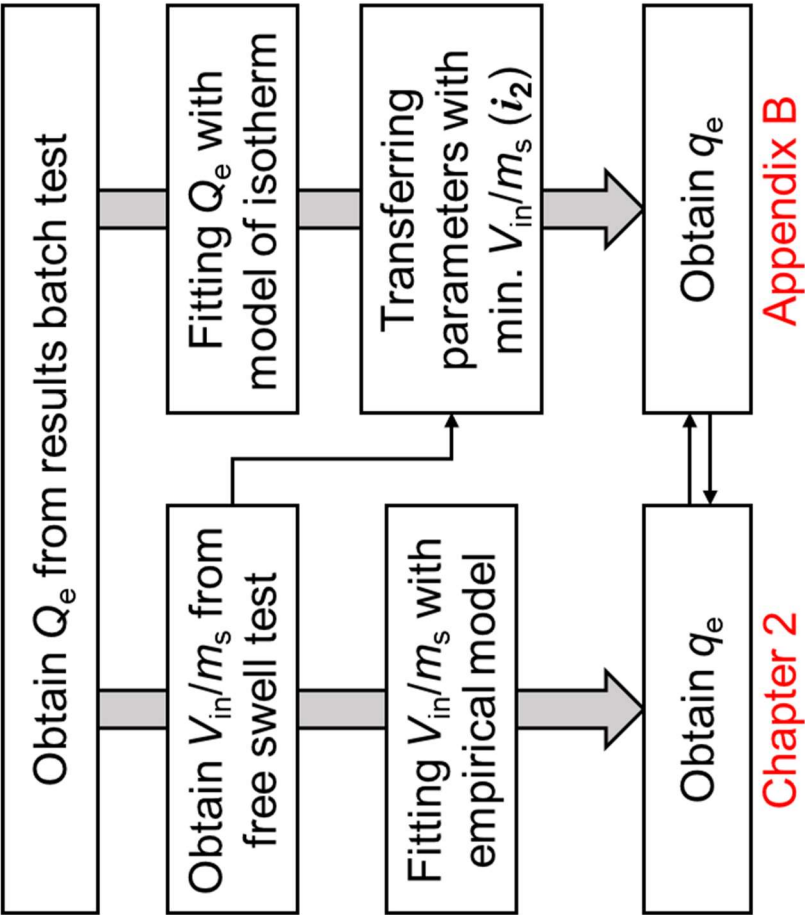


Figure ex.4 Flow charts of sequences obtaining q_e

APPENDIX C

Vishnu, the god of Hinduism

Nature of the Vishnu

Following the page 1. Vishnu also known as Narayana and Hari, one of the principal deities of Hinduism, is revered as the preserver and protector of the universe. He is the supreme being within Vaishnavism, one of the major traditions within contemporary Hinduismⁱ.

Vishnu is commonly depicted with four arms, each holding a symbolic object. These represent his omnipresence and omnipotence. His skin is often blue, symbolizing his infinite nature like the sky and the ocean; He wears a crown that signifies his supreme authority and divinity; His body is adorned with various jewels, enhancing his divine appearance. The well-known image of Avatar in James Cameron's movie was inspired on the iconography of Vishnu, the word "Avatar" also comes from ancient Hinduism.

Vishnu in *Bhagavad-Gita*

The motto of Vishnu cited by J. Robert Oppenheimer originated from the *Vishvarupa Darshana-Yoga*, the eleventh of the eighteen Chapters of the Hindu scripture *Bhagavad-Gita*ⁱⁱ. The story unfolds as dialogues between Prince Arjuna and his chariot driver Krishna, who is the incarnation of Vishnu.

At the time, Prince Arjuna is forced to participate in a war that would require him to fight his own relatives. After surveying the armies in the center of the battlefield, Prince Arjuna sits within his chariot and sets aside his bow and arrows, and fell into despair. The Prince exclaims to Krishna that he would rather be slain by the enemy unopposed and unarmed than fighting against his teachers and family members.

Krishna encourages Arjuna and explains that the soul is eternal and cannot be killed, only the body is perishable; He advises Arjuna to conquer the inner enemies of desire and anger by practicing self-control and discipline; Krishna then teaches him the Dharma, the higher philosophy that will enable him to carry out his duties as a warrior irrespective of his personal concerns.

Arjuna is still hesitant, to seeking further counsel, Arjuna asks Krishna to reveal his universal form. It is this moment that entered Oppenheimer's mind. Krishna manifests as a divine and terrifying being with multi-arms, mouths, eyes (Figure ex.6) and says the famous motto: "Now I am become Death, the destroyer of worlds".

ⁱ Vishnu, Wikipedia.

ⁱⁱ Prabhupada A. C. B. S., & Swami B. (1972). *Bhagavad-Gita as it is*.



Figure ex.6 Statue of the true form Vishnu revealed to Prince Arjuna.
(Metropolitan Museum of Art, NY)

Arjuna is deeply shocked, he realized that his consciousness was meaningless in front of the cosmic order; He realized that although he is the Prince of human, he is just a soldier of Gods; He realized the inevitability to fulfill his duty of fighting and to believe Vishnu could save his soul permanently.

It can be indicated that J. Robert Oppenheimer had the same feeling as Arjuna when he seeing the explosion of atomic bomb test. He realized that the creation of the atomic bomb is an inevitable development of human civilization, he is nothing but a soldier in this grand process. He might feel the burden of became Death had been released, one way or another.

Afterword

In *Bhagavad-Gita*, Vishnu becomes the salvation of Prince Arjuna. In real world, back to July 6, 1945, who is the Vishnu, the chariot driver, and the salvation of J. Robert Oppenheimer? Anyway, what makes the author think most is why a top physicist became so sensitive and emotional at the moment.

The work of modern scientific researchers is to operate reasoning to approaching the ultimate objective, which required highly rational thinking. Naturally, Oppenheimer should have possessed one of the most excellent and practiced rational mind in his era. He could have expressed his guiltiness and hollowness in a more rational way, like a physicist, rather than crying and searching for salvation in religion tale. Nevertheless, the reason Oppenheimer bring out the story in *Bhagavad-Gita* is quite rational, considering its unspoken meaning.

The sensibility of J. Robert Oppenheimer reminds the author the opinion Immanuel Kant put in his *Critique of Pure Reason* that it is impossible to entirely segregate rational knowledge from sensory knowledge by reasoning, even if philosophers and scientists try their best to peel off, that is, any judgment inherently possesses subjective attributes. Maybe, sometimes, there is only a fine line between extreme rationality and extreme sensibility, also.