



HOKKAIDO UNIVERSITY

Title	Evaluation of bentonite/hyperalkaline-fluids interaction in compacted system by X-ray computed tomography
Author(s)	中林, 亮
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第11467号
Issue Date	2014-03-25
DOI	https://doi.org/10.14943/doctoral.k11467
Doc URL	https://hdl.handle.net/2115/55463
Type	doctoral thesis
File Information	Ryo_Nakabayashi.pdf



学位論文

**Evaluation of bentonite/hyperalkaline-fluids
interaction in compacted system
by X-ray computed tomography**
(X 線 CT による圧縮ベントナイト -
高アルカリ間隙水相互作用の評価)

北海道大学大学院工学院
環境循環システム専攻

学籍番号：26115047

氏名：中林 亮

主任指導教員名：佐藤 努

学位論文内容の要旨

博士専攻分野の名称 博士（工学）

氏名 中林 亮

学位論文題名

Evaluation of bentonite/hyperalkaline-fluids interaction in compacted system by X-ray
computed tomography

(X 線 CT による圧縮ベントナイト - 高アルカリ間隙水相互作用の評価)

放射性廃棄物の地層処分では、処分場からの放射性核種の移行を抑制する目的から、様々な材料から構成される人工バリア材の設置が検討されている。その中でも、膨潤性粘土鉱物であるモンモリロナイトを主成分とするベントナイトには高い止水性や核種などの低い拡散性が期待されている。一方、廃棄体定置領域の充填や支保、グラウト等に大量のセメント系材料も利用される。これらセメント系材料は地下水と反応することで高アルカリ性間隙水が生成し、セメントとベントナイトが接する界面ではベントナイトを変質させる可能性がある。このため、地層処分の安全評価では、ベントナイト－高アルカリ間隙水の相互作用を定量的に理解する必要がある。しかし、実際の処分場で使用予定である圧縮ベントナイトでは、実験的に求められてきたモンモリロナイトの溶解速度よりも遅延することが報告されているが、その要因や機構の詳細な解明には至っていない。そこで本研究では、経時変化をトレースするツールとして X 線 CT によるその場観察を取り入れ、地球化学モデリングによる計算結果等を検証するための多数のデータを取得し、ベントナイトと高アルカリ性間隙水の相互作用による変質を支配するパラメータを決定することを目的とした。

本報は 5 章で構成されている。第 1 章は序論であり、研究の背景、目的について示した。第 2 章では、低圧縮ベントナイト試料（乾燥密度 0.3Mg m^{-3} ）に対し、 80°C 下において高アルカリ性間隙水を模擬した 0.3M NaOH 溶液を用いた透水変質実験を実施した。10 日ごとに X 線 CT を用いて内部観察を行い、ベントナイト中の二次鉱物の生成過程の定量的評価を試みた。その結果、二次鉱物の生成過程の経時変化を定量的に評価することに成功し、X 線回折分析結果と併用することにより二次鉱物を方沸石と特定した。また、モデル検証の結果、X 線 CT による鉱物生成の経時変化の定量的なデータは、地球化学モデルの検証に有意なものであることが証明されるとともに、圧縮ベントナイト中のモンモリロナイトの溶解速度が粉末状のモンモリロナイトよりも一桁程度遅く、その要因として反応表面積の制限とモンモリロナイトの溶解度に対する飽和度が大き

く影響する可能性を明らかにした。実際の処分環境では、圧縮による反応表面積の制限や飽和度の影響がより一層大きくなると予想される。

第 3 章では、二次鉱物と同様に、初期鉱物である玉髄が溶解することでベントナイト間隙水中の溶液組成が変化し、モンモリロナイトの溶解に影響を与える可能性があるため、第 2 章と同様に透水変質実験を実施し、入水側を撮影することで初期鉱物であるシリカ鉱物の溶解に着目し X 線 CT 観察を実施した。その結果、付随鉱物である玉髄の溶解過程の経時変化を定量的に評価することに成功した。また、二次鉱物の定量的データ同様に地球化学モデルの検証に有効であることが証明され、さらに圧縮ベントナイト中の玉髄の溶解により、モンモリロナイトの溶解度に対する飽和度が抑制され、結果的にモンモリロナイトの溶解速度が遅延されることが明らかとなった。実際の処分環境では、間隙水の滞留時間が長くなり、間隙水中の溶存シリカ濃度がモンモリロナイトの溶解速度に与える影響は一層大きくなると予想される。

第 4 章では、第 2、3 章で得られた知見を基に、実際の処分システムで施工されるコンクリート/ベントナイト系の相互作用に、モンモリロナイトの溶解速度や玉髄の溶解速度が与える影響について 100,000 年の長期シミュレーションを実施し検討した。その結果、圧縮影響の有無で、少なくともモンモリロナイトの溶解速度に三桁の差が生じることが明らかとなった。また、モンモリロナイトの溶解速度の違いは、特に反応初期（～1,000 年）において解析結果に大きく反映され、反応が進むにつれ溶解速度の違いによる影響は小さくなることが示唆された。このことは短期試験を再現可能とするモデルの重要性を示唆し、X 線 CT 法によって得られる鉱物の溶解・生成の経時変化の定量的データを、新たにモデル検証の手法の一つに取り入れる意義を示している。一方、玉髄の溶解速度の違いによる解析結果への影響は示唆されなかった。これは二次鉱物の種類やその生成速度が支配的であるということが示唆され、実際の処分環境下における二次鉱物種やその生成速度を明らかにすることの重要性が示唆される結果となった。

第 5 章は本研究全体の結論である。X 線 CT 法による微小構造解析はベントナイトの変質過程の経時変化を定量的に評価することに有効であり、取得した定量的データは人工バリア材長期評価モデルを構築する上で、地球化学モデルの検証に非常に有意なものであることが示唆された。また、圧縮ベントナイト中のモンモリロナイトの溶解速度は圧縮の影響を考慮有り無しで、少なくとも三桁の違いが生じることが明らかとなり、現実的な評価を実施するうえで圧縮の影響を考慮することが非常に重要であることが明らかとなった。今後、NaOH 以外の様々なセメント間隙模擬水（KOH や $\text{Ca}(\text{OH})_2$ ）とベントナイトの相互作用による変質過程に対し本試験と同様な知見の積み上げが必要不可欠である。本

研究で開発した X 線 CT 法による微小構造解析法を分析手法の一つとして取り入れることで、地球化学モデルの検証や圧縮ベントナイト中のモンモリロナイトの溶解速度を検証することが可能となり、得られた知見を総括することによって人工バリア材の性能をより現実的かつ合理的に評価すること可能となるであろう。

Abstract

Long-term performance of engineered barriers has been evaluated by geochemical modeling and a number of key parameters (e.g., dissolution rate and the reactive surface area of montmorillonite, formation rate of secondary minerals, dissolution rate of accessory minerals) that significantly affect the model results have been proposed. These key parameters have been determined by experimental studies, which are commonly conducted for short periods only. The results of the experimental studies are then extrapolated for longer-term prediction to validate the models. To make such extrapolations it is essential to have quantitative information of the evolution of mineral phases as a function of time. One difficulty in obtaining such quantitative information during interactions between bentonite and hyperalkaline-fluid stems from the employment of destructive mineralogical analyses (X-ray diffraction and other methods of analysis), which cannot track the alteration processes at exactly the same locations. Therefore, the development of a non-destructive mineralogical analysis method would be helpful to determine the parameters governing the alteration of bentonite. In this paper, a microstructural method of analysis by micro-focus X-ray CT was developed to track the alteration processes involved in bentonite/hyperalkaline-fluid interactions as a function of time. The dissolution of montmorillonite in compacted bentonite was considered to clarify the effect of compaction using the quantitative data on the dissolution/precipitation of minerals obtained by the microstructural method. Based on these data, the effect of the dissolution rate of montmorillonite in compacted bentonite was considered in order to model the long-term performance of bentonite buffer materials.

An advective alteration experiment through compacted bentonite specimens with a dry density of 0.3 Mg m^{-3} was conducted using hyperalkaline fluids to observe the formation and dissolution processes of secondary and accessory minerals, respectively, in bentonite by X-ray CT. The secondary mineral and the dissolved mineral were identified as analcime and chalcedony, respectively from XRD and SEM data. Furthermore, the volume of formed analcime and dissolved chalcedony were quantified as a function of time. The geochemical transport model became consistent with the

experimental results when the reactive surface area in the rate equation for montmorillonite dissolution was reduced and the effect of the Gibbs free energy with respect to the montmorillonite was considered. Thus, this suggests that the actual dissolution rate of compacted montmorillonite is lower than that of powdered montmorillonite. On the other hand, the presence of silica minerals in bentonite significantly affects the dissolution rate of montmorillonite in compacted bentonite. Therefore, it is important to consider the dissolution behavior of silica minerals to sufficiently evaluate the long-term performance of bentonite as a component of engineered barriers for radioactive waste disposal. Based on the obtained information, the sensitivity analyses of the models were conducted to consider the effects of key factors such as the reactive surface area of montmorillonite, the departure from equilibrium and dissolution of silica minerals on the evaluation of the long-term performance of the bentonite buffer material. These simulations indicated that the dissolution rates of montmorillonite with and without consideration of the effects of compaction differed by three orders of magnitude. Furthermore, these also indicated that the reaction between bentonite and concrete was controlled by the dissolution of montmorillonite in the short-term (~1,000 years), suggesting that geochemical models should be sufficiently validated to simulate the short-term experiments for the evaluation of the long-term performance of the bentonite buffer materials. On the other hand, there is no difference between the results of the simulations with and without consideration of the effects of the surface area of chalcedony, suggesting that the accessory silica minerals such as chalcedony do not affect the long-term results. The types of secondary minerals and kinetic data for the formation of secondary minerals are necessary to evaluate the long-term performance of bentonite barriers by modeling.

As described above, a microstructural method of analysis by micro-focus X-ray CT developed in this study is applicable to evaluate the performance of bentonite buffer materials. Moreover, it is necessary to consider the effect of surface area of montmorillonite and ΔG_r in order to create reasonable and realistic evaluations of the performance of the bentonite barrier.

Table of contents

Abstract.....	iv
List of Table.....	ix
List of Figure	x
 Chapter 1 General introduction	 1
1.1 Background.....	1
1.2 Evaluation of the long-term performance of engineered barriers by geochemical modeling.....	2
1.3 Dissolution rate of montmorillonite in compacted bentonite at hyperalkaline condition.....	3
1.4 Effect of formation and dissolution of minerals in bentonite on dissolution rate of montmorillonite.....	4
1.5 Investigation of X-ray CT studies for the geological materials	5
1.5.1 Previous works on the X-ray computed tomography studies of geologic materials and bentonite.....	6
1.6 Objectives and structure of this paper.....	8
 Chapter 2 Microstructural analysis by X-ray computed tomography and geochemical modeling of the dissolution and precipitation minerals in compacted bentonite in hyperalkaline conditions.....	 15
2.1 Introduction.....	15
2.2 Material and method	16
2.2.1 Experimental.....	16
2.2.2 Imaging processes	17
2.3 Modeling approach	19
2.3.1 Thermodynamic and kinetic database	19
2.3.4 Input data	24
2.4 Results and discussion	24
2.4.1 Advective alteration experiments	24
2.4.2 Observations by X-ray CT.....	25
2.4.3 Modeling.....	28
2.5 Near future issues for X-ray CT analysis.....	32
2.6 Conclusion	33

Chapter 3 Quantitative analysis for dissolution of silica minerals in the compacted bentonite at hyperalkaline conditions by X-ray computed tomography and geochemical modeling	61
3.1 Introduction.....	61
3.2 Material and methods.....	61
3.2.1 Experimental.....	61
3.2.2 X-ray CT observation and imaging processes	62
3.2.3 Modeling approach	63
3.3 Results and discussion	64
3.3.1 Advective alteration experiments	64
3.3.2 Observations by X-ray CT.....	65
3.3.3 Modeling.....	66
3.4 Effect of dissolution of silica minerals on dissolution of montmorillonite.....	68
3.5 Conclusion	69
Chapter 4 Long-term evaluation for the performance of bentonite buffer materials under hyperalkaline environment	83
4.1 Introduction.....	83
4.2 Modeling approach	84
4.2.1 Characteristic of the materials	84
4.2.2 Kinetic	85
4.2.3 Ion exchange.....	85
4.2.4 Sensitivity analysis	86
4.3 Results.....	87
4.4 Discussion.....	88
4.4.1 Effect of the dissolution of montmorillonite on the long-term prediction of the performance of bentonite buffer	88
4.4.2 Effect of the dissolution of silica minerals on the long-term evaluation of the performance of the bentonite buffer	89
4.5 Conclusion	90
Chapter 5 General conclusion	103
References	106
Acknowledgement.....	116

Appendix I	Phreeqc input file of Sato-Oda model modified with specific surface area of montmorillonite ($7 \times 0.2 \text{ m}^2\text{g}^{-1}$) in Chapter 2	118
Appendix II	Phreeqc input file of Sato-Oda model modified with specific surface area of montmorillonite ($7 \times 0.12 \text{ m}^2\text{g}^{-1}$) in Chapter 3	123
Appendix III	Phreeqc input file in Case 4 of Chapter 4	129

List of Table

Table 1 - 1	Volumetric percentages of the constituent minerals in the bentonite (Ito et al., 1993).	11
Table 2 - 1	Scanning and imaging conditions in the X-ray CT analysis.	35
Table 2 - 2	Thermodynamic constants (25°C) and molar volumes of minerals considered in the simulations.	35
Table 2 - 3	Kinetic parameters of montmorillonite for Eq. (2 - 7).	36
Table 2 - 4	Kinetics parameters for Eq. 2-9 at 25°C.....	37
Table 2 - 5	Initial pore solution chemistry in bentonite.....	38
Table 3 - 1	Scanning and imaging conditions in the X-ray CT analysis.	70
Table 3 - 2	Kinetics parameters for Eq. 2-9 at 25°C (including Analcime).	71
Table 4 - 1	Mineralogical composition of concrete (Elakneswaran et al., 2009). ..	92
Table 4 - 2	Ground water composition at 25°C (JNC, 2000).	92
Table 4 - 3	Thermodynamic constants (25°C) and molar volume of minerals considered in simulations (Blanc et al., 2009).....	93
Table 4 - 4	Kinetic parameters of montmorillonite for Eq. (2-7).	94
Table 4 - 5	Values of the equilibrium constants for the ion-exchange reactions. .	94
Table 4 - 6	Summary of the parameter values used for each Case.	94

List of Figure

Fig. 1 - 1	Cross-section view of disposal tunnel in a TRU waste repository facility (NUMO 2011).	12
Fig. 1 - 2	Idealized structure of montmorillonite.....	13
Fig. 1 - 3	Predicted evolution of the pH within the near-field of the proposed UK ILW repository with an average cement content of 185 kg m^{-3} (Atkinson 1985).	14
Fig. 2 - 1	Effect of the degree of saturation on montmorillonite dissolution rate (Sato-TST and Sato-Oda equation).	39
Fig. 2 - 2	Schematic diagram of one-dimensional react and transport model for the permeability experiment in bentonite.	40
Fig. 2 - 3	X-ray diffraction patterns of the bentonite in different sections of the column after 180 days. Peak assignments: A = Analcime; M = Na-Montmorillonite; Q = Quartz; Ch = Chalcedony.....	41
Fig. 2 - 4	SEM images of secondary analcime in the 12-15 mm section. Scale bars are (a, b, and d) $10 \text{ }\mu\text{m}$, and (c) $5 \text{ }\mu\text{m}$. The crystals of analcime observed are single crystals (a), aggregates on the surface of the montmorillonite (b), and aggregates on the surface of plagioclase (c and d).	42
Fig. 2 - 5	CT images of bentonites with different densities. The center of the image where the brightness is high (coloring is lighter) is bentonite and the lower brightness (darker) area around the bentonite is the acrylic column. Scale bars = 10 mm	43
Fig. 2 - 6	CT images of the bentonite column sample (0.3 Mg m^{-3} of dry density) at different durations of the advective experiment. Scale bars = 1 mm	44
Fig. 2 - 7	CT images of the trimmed ROI (region of interest) of the red rectangles in Fig. 2 - 6.	45
Fig. 2 - 8	Accumulated histogram of the 8-bit voxel brightness of a ROI. In this study, the volumetric fraction of the hydrated montmorillonite is 0.94 and that of accessory and secondary minerals are 0.06. The threshold value between the hydrated montmorillonite and accessory/secondary minerals was given by the brightness at 0.94 of the accumulated frequency.....	46
Fig. 2 - 9	Binary CT images of the trimmed ROI (region of interest) in the red rectangles in Fig. 2-5. White dots are secondary minerals, accessory minerals, and an error component. The volumes of the white dot clusters increase (inside the red dashed circles) with time, and indicate the formation of secondary	

minerals.	47
Fig. 2 - 10 Volume of the secondary mineral calculated based on the CT image analysis at different experiment durations.	48
Fig. 2 - 11 Experimental and calculated concentrations of silica and aluminum in output solution using Sato-TST model.	49
Fig. 2 - 12 Experimental and calculated concentrations of silica. Thermodynamic data of chalcedony and amorphous silica was involved in the simulation.	50
Fig. 2 - 13 Calculated and measured pH changes of the output solution. (a): Sato-TST model, (b): Sato-Oda model.	51
Fig. 2 - 14 Calculated and measured concentration of silica and aluminum in the output solution. (a): Sato-TST model, (b): Sato-Oda model.	52
Fig. 2 - 15 Calculated mineralogical distributions in bentonite as a function of distance. (a): Sato-TST model, (b): Sato-Oda model.	53
Fig. 2 - 16 Calculated volume of analcime in the 12 – 15 mm section. (a): Sato-TST model, (b): Sato-Oda model.	54
Fig. 2 - 17 Calculated and measured pH changes of the output solution. (a): Sato-TST model modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite, (b): Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.	55
Fig. 2 - 18 Calculated and measured concentration of silica and aluminum in the output solution. (a): Sato-TST model modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite, (b): Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.	56
Fig. 2 - 19 Calculated mineralogical distributions in bentonite as a function of distance. (a): Sato-TST model modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite, (b): Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.	57
Fig. 2 - 20 Calculated volume of analcime in the 12 – 15 mm section. (a): Sato-TST model modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite, (b): Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.	58
Fig. 2 - 21 Effect of the degree of saturation on montmorillonite dissolution rate (Sato-TST equation modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite and Sato-Oda equation modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite).	59
Fig. 2 - 22 Calculated the Gibbs free energy with respect to montmorillonite in	

the 0-2 mm section in Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.....	60
Fig. 3 - 1 Imaging processing of real image: (a) real image, (b) quantized image, (c) class separation in image (Yamanaka et al., 2011).....	72
Fig. 3 - 2 Histogram of brightness in Fig. 3-1c. t_1 and t_2 are boundary of brightness between class 1 and 3, class 2 and 3, respectively (Yamanaka et al., 2011).....	73
Fig. 3 - 3 pH change of the output solution (a), hydraulic conductivity change of bentonite (b) and the concentrations of dissolved silica and aluminum in the output solution (c).....	74
Fig. 3 - 4 X-ray diffraction patterns of the bentonite in different sections of the column after 360 days using oriented sample treated with ethylene glycol on glass (a) and oriented sample on glass (b). Peak assignments: A = Analcime; M = Na-Montmorillonite; Q = Quartz; Ch = Chalcedony; C = Calcite; P = Plagioclase.	75
Fig. 3 - 5 CT images of the bentonite column sample (0.3 Mg m^{-3} of dry density) at different durations of the advective experiment. Scale bars = 1 mm.	76
Fig. 3 - 6 CT images of the trimmed ROI (region of interest) of the black rectangle in Fig. 3-5 (left) and histogram of brightness in the rectangle of (a) and (b) (right).	77
Fig. 3 - 7 Binary CT images of the trimmed ROI (region of interest) in the black rectangle in Fig. 3-5. White dots are accessory minerals including minor amounts of secondary mineral. The volumes of the white dot clusters decrease with time, and indicate the dissolution of accessory minerals. Volume of the secondary mineral calculated based on the CT image analysis at different experiment durations.	78
Fig. 3 - 8 Residual volume percentage of the accessory minerals calculated based on the CT image analysis at different experiment durations.	79
Fig. 3 - 9 Calculated results plotted vs. time or distance using the geochemical model. Eq. (2-7) was used as the rate law for Na-montmorillonite dissolution/precipitation with $7 \times 0.12 \text{ m}^2 \text{ g}^{-1}$ of specific surface area and Eq. (2-9) was used as the rate law for quartz, chalcedony, albite, and analcime with 0.07×0.5 , 0.03×0.06 , 0.24×0.2 , and $0.03 \times 0.1 \text{ m}^2 \text{ g}^{-1}$, respectively and the dissolution/precipitation of calcite, dolomite, pyrite, and brucite were modeled based on thermodynamic considerations in the simulations. The kinetic parameters of accessory minerals are shown in Table 3-2. pH changes of the	

output solution is shown in (a), and the concentrations of dissolved silica and aluminum in the output solution is shown in (b). the calculated mineralogical distributions in bentonite as a function of distance is shown in (c) and the residual volume percentage of accessory minerals in the 0 – 2 mm section is shown in (d).....	80
Fig. 3 - 10 Effect of the degree of saturation on montmorillonite dissolution rate (Sato-Oda equation modified with $7 \times 0.12 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite).....	81
Fig. 3 - 11 Calculated distribution of the Gibbs energy (ΔG_r) of the dissolution reaction of montmorillonite and the concentration of dissolved silica in porewater of bentonite at 60 days (a) and 360 days (b).....	82
Fig. 4 - 1 Schematic diagram of one-dimensional reaction and transport model for the concrete/bentonite system.....	95
Fig. 4 - 2 Calculated mineralogical distributions in concrete/bentonite system as a function of distance. (a): Case 1 (after 100,000 years), (b) Case 2 (after 100,000 years), (c): Case 3 (after 100,000 years), (d) at 0 year.	96
Fig. 4 - 3 Calculated distribution of residual volume percentages of the montmorillonite (a) and the chalcedony (b) in Case 1, 2 and 3.....	97
Fig. 4 - 4 Calculated mineralogical distributions in concrete/bentonite system as a function of distance. (a): Case 2 (after 100,000 years), (b): Case 4 (after 100,000 years).	98
Fig. 4 - 5 Calculated distribution of residual volume percentages of the montmorillonite (a) and the chalcedony (b) in Case 2 and 4.....	99
Fig. 4 - 6 Effect of the degree of saturation on montmorillonite dissolution rate using Sato-TST equation, Sato-Oda equation and Sato-Oda equation modified with the surface area of montmorillonite.....	100
Fig. 4 - 7 Calculated distribution of the Gibbs free energy (ΔG_r) of the dissolution reaction of montmorillonite in Case 1, 2 and 3 after 1,000 years (a) and 100,000 years (b).	101
Fig. 4 - 8 Calculated distribution of the Gibbs free energy (ΔG_r) of the dissolution reaction of chalcedony (a) and montmorillonite (b) in Case 2 and 4 after 100,000 years.....	102

Chapter 1 General introduction

1.1 Background

The concept for the geologic disposal of transuranic wastes involves the use of an engineered barrier, consisting of a bentonite buffer and cementitious materials for structural support, to prevent the migration of radioactive nuclides from the radioactive wastes into the surrounding environment (Fig. 1 - 1). The bentonite buffer is made up mainly of smectite-type swelling clays. However, since bentonite is a natural material, it includes both clay (illite, kaolinite, and chlorite) and non-clay (quartz, cristobalite, feldspar, mica, carbonates, sulfates, sulfides) accessory minerals. In Japan, the bentonite Kunigel V1 (70%, silica sand: 30%, dry density: 1.6 Mg m^{-3}) is considered as the buffer material component of the Japanese engineered barrier concept to constrain the migration of radioactive nuclides due to favorable properties such as swelling and low permeability provided by its smectite content (JNC and FEPC, 2005). The mineralogical composition of Kunigel V1 is shown in Table 1 - 1. The smectite content of Kunigel V1 is dioctahedral and is dominated by montmorillonite. Montmorillonite has two tetrahedral sheets sandwiching one octahedral sheet (2:1 structure shown in Fig. 1 - 2) and belongs to the smectite group, a group of minerals having a layered structure. It contains exchangeable cations and water molecules between its layers. The cations between the layers of montmorillonite in Kunigel V1 are Na^+ , Ca^{2+} , Mg^{2+} , and K^+ . In this study, Na-type montmorillonite, whose interlayer cations consist mostly of Na^+ (Ito et al., 1993), is used. The properties of bentonite such as swelling depend on the type of interlayer cations of smectite. However, since the assessment period for the safety and stability of a conceptual geologic disposal system for radioactive waste is greater than a few thousand years, there is a possibility that those expected favorable properties could be affected by the alteration of bentonite depending on the environment in which they are exposed during this period.

Saturation of cementitious materials with groundwater will occur in the post-closure period of disposal, producing hyperalkaline pore fluids with pH in the range of 10-13.5 (Berner, 1992). The relatively low solubility of cement and slow groundwater flow rates

will result in prolonged hyperalkaline conditions in the disposal environment. Laboratory and modeling studies (e. g. Atkinson, 1985; Atkinson et al., 1987; Berner, 1992) suggest that, depending on groundwater flow rate and composition, pore fluids will be dominated by readily leachable K and Na hydroxides (present in trace amounts in the cement) for at least 1000 years after repository closure (pH = 13-13.5) shown in Fig. 1 - 3. These will be followed by Ca leachates, having a pH of ~12.5 (buffered by portlandite [$\text{Ca}(\text{OH})_2$] solubility), which will decrease to pH 10-11 (buffered by calcium silicate hydrate gel) for a time period in the order of 100,000 years after repository closure, depending on local hydraulic and hydrochemical conditions. These pore fluids have the potential to migrate and react chemically with other engineered barrier components such as bentonite, which is present in some repository concepts (JNC, 2000). They also have the potential to migrate from the repository according to local groundwater flow conditions and react with the host rock (e.g. Steefel and Lichtner, 1994).

With regard to the performance of bentonite, these reactions may affect its capacity to act as a physical and chemical barrier to the migration of radionuclides released from the repository after the degradation of the waste packages. Potential deleterious reactions include the loss of swelling capacity, an increase in porosity and a decrease in sorption capacity (e. g. Savage, 1997). Therefore, the effects of these chemical reactions need to be investigated for the purposes of assessing the safety of the repository design.

1.2 Evaluation of the long-term performance of engineered barriers by geochemical modeling

Long-term interactions between bentonite and hyperalkaline fluids have been evaluated by reactive transport models (Savage et al., 2002; Gaucher et al., 2004; Vieillard et al., 2004; Fernández et al., 2009; Watson et al., 2009), and a number of key parameters (e.g., dissolution rate and the reactive surface area of montmorillonite, and formation rate of secondary minerals) that significantly affect the model results have been proposed (Oda et al., 2004, Takase et al., 2004). These key parameters have been determined by experimental studies, which are commonly conducted for short periods

only (Cama et al., 2000; Sato et al., 2004; Sánchez et al., 2006; Yamaguchi et al., 2007; Marty et al., 2011; Oda et al., 2012). The results of the experimental studies are then extrapolated for long-term prediction to validate the models. To make such extrapolations it is essential to have quantitative information of the evolution of mineral phases as a function of time. One difficulty in obtaining such quantitative information during interactions between bentonite and hyperalkaline-fluid stems from the employment of destructive mineralogical analyses (X-ray diffraction and other methods of analysis), which cannot track the alteration processes at exactly the same locations. Therefore, the development of a non-destructive mineralogical analysis would be helpful to determine the parameters governing the alteration of bentonite.

1.3 Dissolution rate of montmorillonite in compacted bentonite at hyperalkaline condition

Bentonite/hyperalkaline-fluid interactions are an important issue in performance assessments of radioactive waste disposal designs. In particular, the dissolution rate of montmorillonite is important to provide long-term estimates of the geochemical changes in the bentonite buffer. These geochemical changes have been investigated based on the dissolution rate of montmorillonite under such hyperalkaline conditions (Bauer and Berger, 1998; Cama et al., 2000; Sato et al., 2004; Bauer et al., 2006; Rozalen et al., 2009; Oda et al., 2012). The dissolution rate of montmorillonite was obtained from batch and flow-through experiments under high fluid/solid weight ratio conditions. These studies have contributed to the development of kinetic models for smectite dissolution.

It is well-known that mineral dissolution rates depend on several kinetic parameters. Generally, the effects that physical and chemical parameters exert on mineral weathering rates (temperature, pH, ionic strength, catalysis/inhibition by aqueous species and solution saturation state) are incorporated in a general form of mineral dissolution rate law that is expressed as (Lasaga et al., 1994; Lasaga, 1998):

$$Rate = k_0 \cdot e^{\frac{-E_a}{RT}} \cdot a_{H^+}^{n_{H^+}} \cdot A_{min} \cdot g(I) \cdot \prod_i a_i^{n_i} \cdot f(\Delta G_r) \quad (1-1)$$

where r is the overall rate of reaction in mol s^{-1} , k_0 is a constant ($\text{mol m}^{-2} \text{s}^{-1}$), A_{min} is the reactive surface area of the mineral (m^2), E_a is the activation energy of the overall reaction (J mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), a_i and a_{H^+} are the activities in solution of species i and H^+ , respectively, n_i (>0) and n_{H^+} are the orders of the reaction with respect to these species, $g(I)$ describes the dependence of the rate on ionic strength, and ΔG_r is the Gibbs energy of the overall reaction (J mol^{-1}). The term $\prod_i a_i^{n_i}$ incorporates possible catalytic or inhibitory effects on the overall rate, whereas $a_{\text{H}^+}^{n_{\text{H}^+}}$ describes the pH dependency of the dissolution/precipitation reactions. The last term $f(\Delta G_r)$ accounts for the variation of the rate with deviation from equilibrium.

Some of important factors affecting montmorillonite dissolution rate, such as pH of reactive fluid, temperature and deviation from equilibrium on smectite dissolution rate, have been identified (Cama et al., 2000; Sato et al., 2004; Rozalen et al., 2009). However, the experimental conditions in such studies were completely different from the conditions in actual radioactive waste disposal systems. Dissolution experiments for the compacted bentonite have also been reported (Nakayama et al., 2004; Fernandez et al., 2006; Sanchez et al., 2006; Yamaguchi et al., 2007). These studies showed that the dissolution rate of compacted bentonite was different from that obtained from batch and flow-through experiments. However, the different reasons for the disparity between the published dissolution rates of powdered and compacted montmorillonite have not yet been clarified in detail. The dissolution rate of montmorillonite in compacted bentonite is necessary to underpin predictive reactive transport models to provide long-term estimates of the likely geochemical changes in the bentonite buffer.

1.4 Effect of formation and dissolution of minerals in bentonite on dissolution rate of montmorillonite

As described above, bentonite contains both clay (illite, kaolinite, and chlorite) and non-clay (quartz, chalcedony, cristobalite, feldspar, mica, carbonate, sulfate, and sulfide) accessory minerals. These minerals will have varying stabilities under alkaline

conditions, resulting to a varied range of dissolution kinetics. The ions liberated by the dissolutions will, in part, be “reused” in the formation of new, more stable mineral phases. Therefore, the role of secondary minerals in governing the potential alteration of bentonite by hyperalkaline fluids is principally through their influence on solution chemistry (notably pH) and the associated effects on the rate, and possibly the mechanism, of montmorillonite dissolution (e.g. Oda et al., 2004; Vieillard et al., 2004).

In particular, the dissolution of silica minerals in bentonite may affect the dissolution of montmorillonite by promoting changes in pore water chemistry and saturation states. The bentonite “Kunigel V1”, which is considered for use radioactive waste disposal barriers in Japan, actually contains a large amount (~50%) of accessory silica minerals, such as chalcedony and quartz. Dissolution of the silica minerals may inhibit the dissolution of montmorillonite in the bentonite by increasing the silica concentration and hence the saturation state with respect to montmorillonite in the pore water. Therefore, the effects of the dissolution of accessory minerals and the formation of secondary minerals on dissolution of the montmorillonite are extremely important for the long-term safety assessments of engineered barriers performance.

1.5 Investigation of X-ray CT studies for the geological materials

One potential analytical method that can be used to observe the alteration processes in bentonite, such as the dissolution of accessory minerals and precipitation of secondary minerals, as function of time is X-ray computed tomography (CT), a powerful non-destructive tool that can be used to study the micro- and inner-structure of materials, and which is able to conduct measurements on one sample at different positions and times. X-ray CT is a radiological imaging system first developed by Hounsfield (1973). It was originally developed for medical use, but geological applications have been performed since the 1980s. Nakashima (2000) compiled the literature on the application of X-ray CT to geologic research (e.g. Wellington and Vinegar, 1987; Raynaud et al., 1989; Colletta et al., 1991; Inazaki et al., 1995; Nakashima et al., 1997; Ohtani et al., 1997; Nakashima et al., 1998). These studies have clearly demonstrated the power of CT compared to classical petrography in geologic

research. However, one disadvantage of classical medical CT is that its resolution is too low (lowest order of magnitude: $60\ \mu\text{m} \times 60\ \mu\text{m} \times 1\ \text{mm}$) for detailed geologic research such as reservoir appraisal. Recent developments in the field of microfocus computed tomography (μCT) overcame much of this problem. These instruments are based on the same principle as medical CT scanners, but obtain much better resolutions (presently as low as $5\ \mu\text{m} \times 5\ \mu\text{m} \times 5\ \mu\text{m}$). In next chapter, microfocus X-ray studies of geologic materials since 2000 were reviewed, and the possibility of applying the X-ray CT observation technique to the present study is discussed.

1.5.1 Previous works on the X-ray computed tomography studies of geologic materials and bentonite

Generally, X-ray CT analysis of geologic materials has been performed to characterize their inner structures. Van Geet et al. (2000) demonstrated the inner structure observation of sedimentary rocks such as dolomite, limestone, and sandstone and introduced an optimizing technique for quantitative analysis. They mentioned that the X-ray attenuation data can be translated into quantitative physical parameters such as density of the materials. Unfortunately, microfocus X-ray CT is not free of artifacts (Joseph, 1981). As the physical cause of those artifacts is known, some techniques to diminish or minimize these artifacts have been carried out to increase the accuracy of quantitative measurements. Ring artifacts are caused by inhomogeneities of the detector and are minimized by randomly moving the object and with it the field of the detector used. Other artifacts are due to the presence of very dense inclusions in the object. These can create a secondary radiation that augments the noise and creates star artifacts. Filters such as aluminum and copper are placed in front of the detector to help reduce secondary radiation and suppress, to a major extent, the star artifact. The most serious artifact is beam hardening. Beam hardening is more pronounced in dense materials, such as reservoir rocks, than in light materials such as coal or human tissue. Some software packages are available to correct for beam hardening. However, these are not always optimal solutions, at least for industrial research applications, since a prior knowledge of the object characteristics is necessary. Van Geet et al. (2001) also

demonstrated the visualization and quantification of coal macerals within three dimensions in the sample by using the microfocus X-ray CT and SEM-EDX based on the optimizing technique for quantitative analysis in Van Geet et al. (2000).

In the case of bentonite, since the properties of the buffer material are closely related to the microstructure of the bentonite, the study of the microstructure is also a key issue for the safety assessment of geologic disposal systems (e.g., to inhibit ground water flow and also to retard the migration of radionuclides in the region between the waste forms and the surrounding host rock). Kozaki et al. (2001) reported the results of the application of microfocus X-ray CT to compacted bentonite and the internal microstructures of dry and wet bentonite samples. They confirmed that the three-dimensional images with high resolution (pixel size of 8 μ m) could be obtained by microfocus X-ray CT. In addition, such microstructures can easily be evaluated quantitatively if the image data are analyzed with computer graphics. Furthermore, it can be expected that this method can also be applied to wet bentonite samples and to the evaluation of internal microstructures such as pores, which are closely related to mass transport in bentonite. Tomioka et al. (2010) reported the observation of compacted bentonite samples before and after water saturation by using a newly developed microfocus X-ray CT having a high spatial resolution (about 0.8 μ m under ideal conditions). They developed the computer code which could determine grain boundaries of montmorillonite in the CT images by using appropriate discrimination levels, and provide information on size and shape of montmorillonite grains.

In the study of geologic materials, X-ray CT has been used to obtain the diffusion coefficient and diffusion paths within the materials. Nakashima (2000) conducted the I⁻ diffusion experiments in two typical porous media (synthesized saponite and rhyolitic lava) saturated with water at room temperature to show that X-ray CT was a reliable new technique for the measurement of the heavy-ion diffusion. In their study, a commercially available CT system was applied successfully to the diffusion measurement of iodine in porous media. Medical CT was used to observe the centimeter-scale diffusion in the experiments, and they mentioned that the measurement of the micrometer-scale diffusion would also be possible if industrial high-resolution CT is used. Van Geet et al. (2005) demonstrated the possible use of microfocus X-ray CT

for the characterization of the hydration properties of a mixture of bentonite powder and pellets. The mixture used in the study has a dry density of 1.36 Mg/m^3 . The resulting data showed the progressive decrease of the dry density of the pellets, the preferential suction of the pellets and final homogenization at complete saturation. Kawaragi et al. (2009) conducted the permeability tests and micro X-ray CT observations of Wyoming bentonite to describe the relationship between microstructure and permeability of the bentonite used as a barrier material. Compacted bentonite-quartz sand mixtures (CBMs) and raw bentonite ores were used in the study. The X-ray CT observations of CBMs showed that vacant pores and bentonite-water complexes of the CBMs before and after water permeation are distinguishable in X-ray CT images, and that the differences in the microstructure of the CBMs depend on the mixing conditions and sample preparation. Permeability tests and X-ray CT observations of the bentonite ore samples showed that the permeability and the microstructure are independent of the sedimentary texture shown in the ore samples. Furthermore, X-ray CT observations of saturated ore samples showed self-sealing of micro-cracks with bentonite-water complexes.

As reviewed above, these recent studies on geologic materials characterization has shown X-ray CT to be a very powerful tool to study microstructure and hydro-osmotic phenomena, and X-ray CT has been widely used to evaluate the internal structure and swelling properties of bentonite as well as to provide information on diffusion coefficients and diffusion paths. However, few studies have focused on the alteration process such as the dissolution/precipitation of minerals in geologic materials as a function of time. Recently, Fukuda et al. (2012) investigated the sealing of a crack in high-strength and ultra-low-permeability concrete (HSULPC) using microfocus X-ray CT. The sealing by precipitation occurred. They evaluated temporal changes of the sealing deposits in the crack quantitatively. However, they did not discuss the availability of quantitative data obtained by image processing to validate the geochemical model to simulate the experimental results.

1.6 Objectives and structure of this paper

The objective of this paper is to develop a microstructural method of analysis by

X-ray CT to track the alteration processes involved in bentonite/hyperalkaline-fluid interactions as a function of time and to use these data to validate a geochemical model of the alteration process. Using this method, quantitative data on the dissolution of accessory minerals and secondary mineral precipitation will be derived. The dissolution of montmorillonite in compacted bentonite will then be considered to clarify the effect of compaction.

This paper consists of 5 chapters. This chapter presents the background and objectives of the study.

Chapter 2 presents the development of a microstructural method of analysis by X-ray CT to track the alteration process, especially the precipitation of secondary minerals, involved in bentonite/hyperalkaline-fluid interactions as a function of time. An advective alteration experiment using reference “Kunigel V1” bentonite (dry density = 0.3 Mg m^{-3}) was performed using 0.3M NaOH solutions at 80 °C (pH = 13.5 at 25 °C) for 180 days. X-ray CT images were recorded for a chosen area positioned at 12 – 15 mm from the input side of the column every 10 days. A Mathematica program was used to quantify the volume of minerals in the CT images. Based on the quantitative data obtained by image processing, a geochemical model to simulate the experimental result was verified and the dissolution rate of montmorillonite in compacted bentonite was considered to clarify the effect of compaction.

Chapter 3 investigates the effect of the dissolution of accessory minerals such as silica minerals on the dissolution rate of montmorillonite. As in Chapter 2, a microstructural method of analysis by X-ray CT was conducted to observe the dissolution process of accessory minerals in bentonite as a function of time. A similar advective alteration experiment using reference “Kunigel V1” bentonite (dry density = 0.3 Mg m^{-3}) 0.3M NaOH solutions was performed, this time at 70 °C (pH = 13.5 at 25 °C) for 360 days and X-ray CT images were also recorded for an area 0 – 2 mm from the input side of the column every 10 days. Image processing using a Mathematica program, was also used to quantify the volume of minerals in the CT images. Based on the quantitative data obtained by image processing, a geochemical model to simulate the experimental result was verified and the effect of dissolved silica on the dissolution of montmorillonite in a compacted bentonite was clarified.

Chapter 4 presents the modeling of the long-term performance of bentonite in hyperalkaline conditions based on the new knowledge obtained from the previous chapters.

Chapter 5 concludes the paper. It summarizes the previous chapters and presents a consolidated discussion on the long-term stability of the buffer material in engineered barriers affected by the interaction between hyperalkaline fluids and bentonite.

Table 1 - 1 Volumetric percentages of the constituent minerals in the bentonite (Ito et al., 1993).

Minerals	Density (Mg m ⁻³)	wt%	Volume%
Na-montmorillonite	2.73	48.0	47.2
Quartz	2.65	0.6	0.6
Chalcedony	2.62	38.0	38.9
Albite	2.75	4.7	4.6
Calcite	2.71	2.4	2.4
Dolomite	3.02	2.4	2.1
Analcime	2.26	3.3	3.9
Pyrite	5.02	0.6	0.3

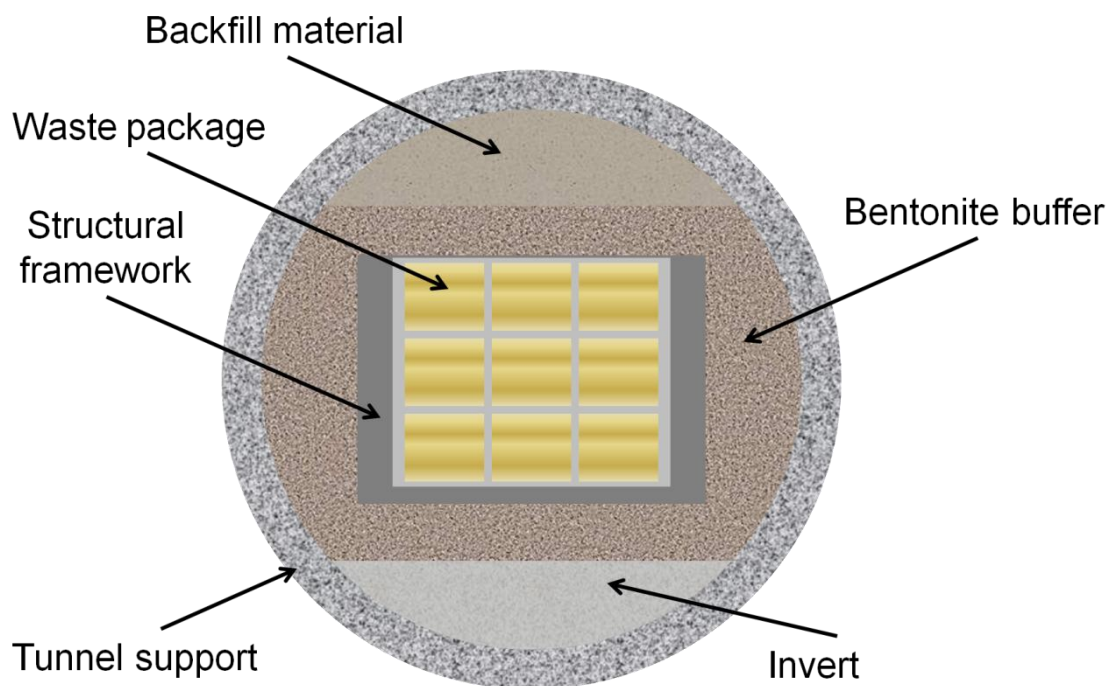
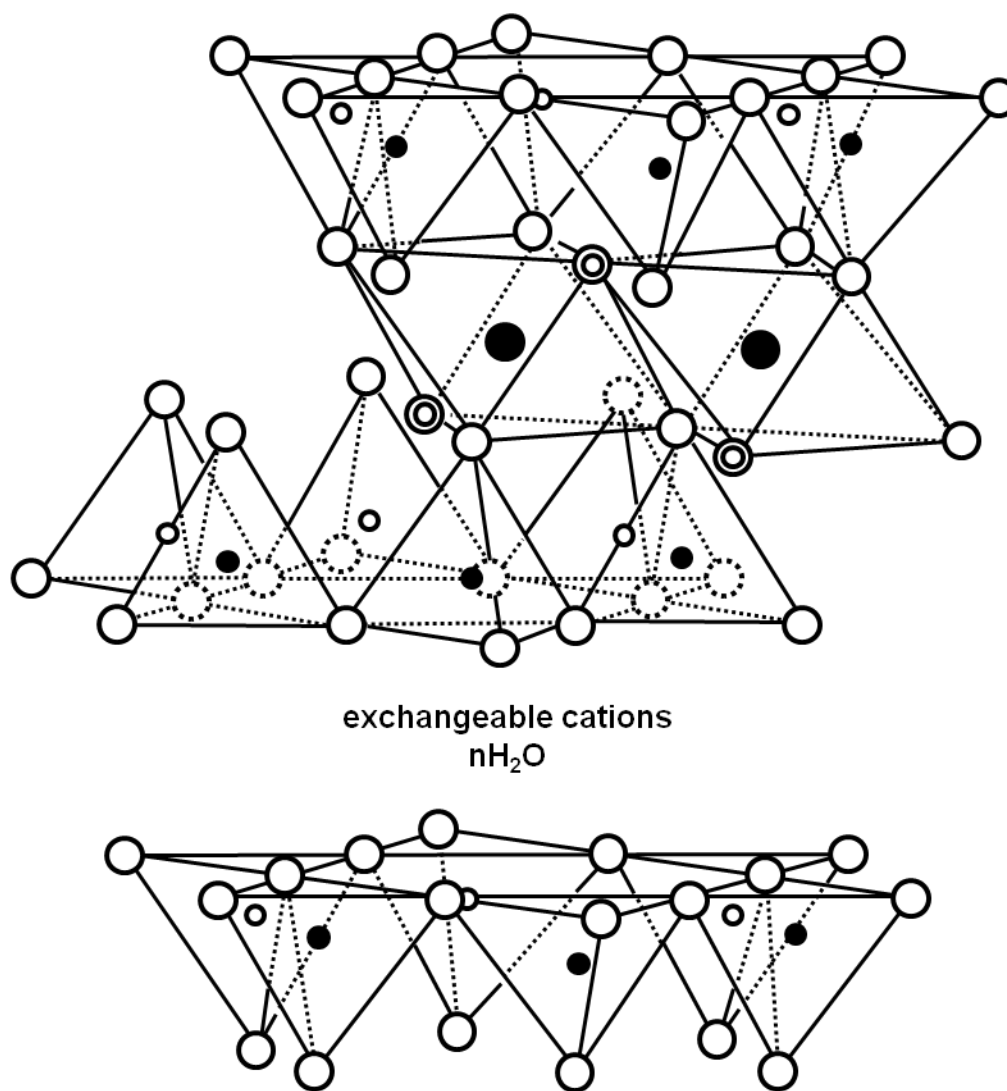


Fig. 1 - 1 Cross-section view of disposal tunnel in a TRU waste repository facility (NUMO 2011).



Key:

- oxygen ⊙ hydroxyl ● aluminum, iron, magnesium
- ● silicon, occasionally aluminum

Fig. 1 - 2 Idealized structure of montmorillonite.

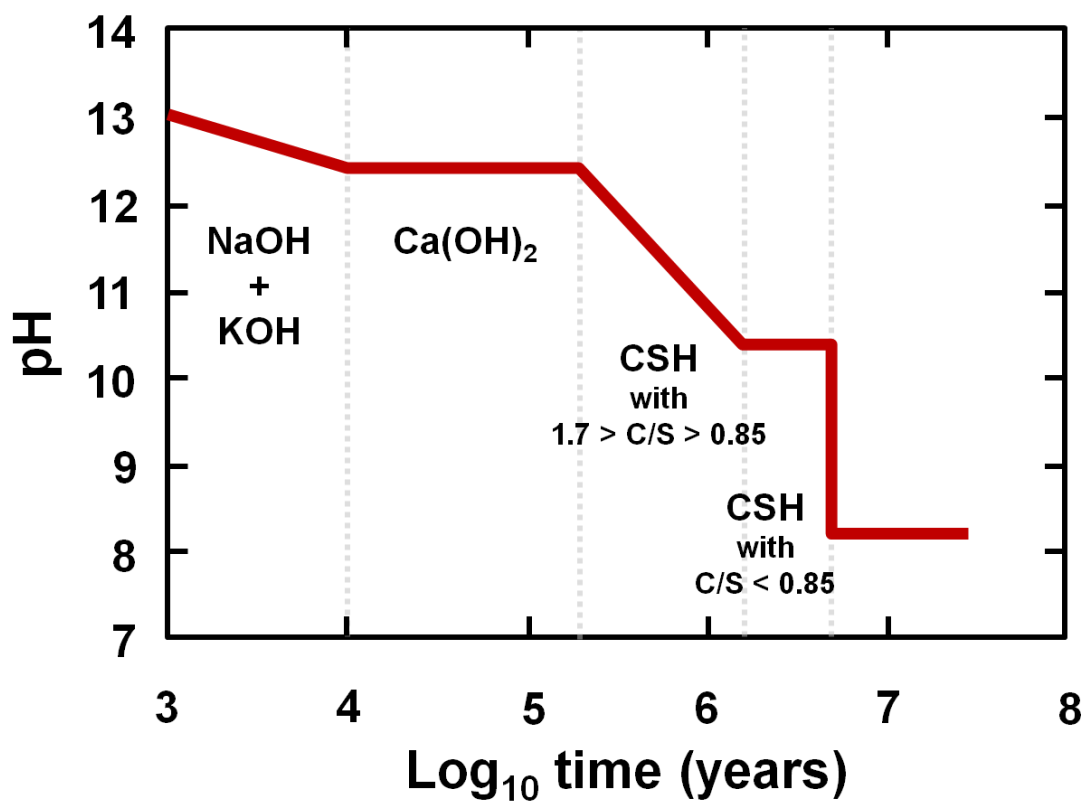


Fig. 1 - 3 Predicted evolution of the pH within the near-field of the proposed UK ILW repository with an average cement content of 185 kg m^{-3} (Atkinson 1985).

Chapter 2 Microstructural analysis by X-ray computed tomography and geochemical modeling of the dissolution and precipitation minerals in compacted bentonite in hyperalkaline conditions

2.1 Introduction

Engineering barriers in geological repositories of radioactive waste are commonly composed of a bentonite buffer and cementitious materials which function to constrain radionuclide migration. However, hyperalkaline environments induced by the cementitious materials interacting with groundwater may be predicted to alter montmorillonite (the main constituent of bentonite buffer materials) and deteriorate the physical and chemical properties of the buffer. Because of this, a detailed understanding of the bentonite/hyperalkaline-fluid interactions is an important issue in performance assessments of radioactive waste disposal designs.

Long-term interactions between bentonite and hyperalkaline fluids have been evaluated by reactive transport models (Savage et al., 2002; Gaucher et al., 2004; Vieillard et al., 2004; Fernández et al., 2009; Watson et al., 2009), and a number of key parameters (e.g., dissolution rate and the reactive surface area of montmorillonite) that significantly affect the model results have been proposed (Oda et al., 2004, Takase et al., 2004). These key parameters have been determined by experimental studies, which are commonly conducted for short periods only (Cama et al., 2000; Sato et al., 2004; Sánchez et al., 2006; Yamaguchi et al., 2007; Marty et al., 2011; Oda et al., 2012). The results of the experimental studies are then extrapolated for long-term prediction to validate the models. To make such extrapolations it is essential to have quantitative information of the evolution of mineral phases as a function of time. One difficulty in obtaining such quantitative information during interactions between bentonite and hyperalkaline-fluid stems from the employment of destructive mineralogical analyses (X-ray diffraction and other methods of analysis), which cannot track the alteration processes at exactly the same locations. Therefore, the development of a non-destructive mineralogical analysis would be helpful to determine the parameters governing the alteration of bentonite.

One candidate for such an analysis is X-ray computed tomography (CT), a powerful non-destructive tool that can be used to study the micro- and inner-structure of materials, and which is able to conduct measurements on one sample at different positions and times. Further, three dimensional imaging using X-ray CT can quantify details of the surface area and the volume of pore clusters (Nakashima and Kamiya, 2007). This suggests that X-ray CT offers the potential to follow the alteration process in bentonite/hyperalkaline-fluid interactions as a function of time. Several reports have been published on X-ray CT observations of geological samples (Nakashima et al., 2004; Van Geet et al., 2005; Devore et al., 2006) and also of bentonite buffer materials (Kozaki et al., 2001; Liu et al., 2003; Tomioka et al., 2008; Kawaragi et al., 2009), focused on observations of the inner structure and mass transfer in the materials. However, there has been no study of the dissolution of buffer minerals or of the formation of secondary minerals at buffer interfaces as a function of time. The objective of the current study is to develop a microstructural method of analysis by X-ray CT to track the alteration process involved in bentonite/hyperalkaline-fluid interactions as a function of time and to use these data to underpin a geochemical model of the alteration process. Using this method, quantitative data on the dissolution of accessory minerals and secondary mineral precipitation will be derived. The dissolution of montmorillonite in compacted bentonite will then be considered to clarify the effect of compaction.

2.2 Material and method

2.2.1 Experimental

Japanese reference bentonite (“Kunigel V1” from the Tsukinuno Mine, Yamagata, Japan) was used in the experiments, the mineralogical composition of Kunigel V1 bentonite is shown in Table 1 - 1 (Ito et al., 1993). An acrylic column ($\phi = 20\text{mm}$, $h = 30\text{mm}$) was used for advective alteration experiments as it is able to transmit X-rays. The advective experiment was performed at 80 °C for 180 days using bentonite with a dry density of 0.3 Mg m^{-3} , lower than the dry density of the bentonite ($\sim 1.6 \text{ Mg m}^{-3}$) considered for use in radioactive disposal barriers in Japan (JAEA and FEPC, 2007). A 0.3 M (pH 13.5 at 25°C) NaOH solution simulating cement pore water of early leaching

of alkaline hydroxides was passed through the bentonite specimen at a flow pressure of 0.03 MPa.

In the advective alteration experiment, the effluent was collected and the permeability coefficient and pH were measured periodically (pH meter, WM-22, TOADKK). The concentration of dissolved aluminum in the effluent was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu), and the dissolved silica concentrations were determined with molybdenum-blue spectrometry by ultraviolet visible absorption spectroscopy (UV-VIS, V-550, JASCO). The inner structure of the bentonite specimens was observed every 10 days by the micro-focus X-ray CT (TOSCANER 31300 μC^3 , TOSHIBA IT Solutions) at Hokkaido University. A 3mm thick section of the bentonite at the 12–15 mm position from the input side (dry density 0.3 Mg/m^3) was observed by X-ray CT. The scanning and imaging conditions for the 0.3 Mg/m^3 dry density bentonite specimen are shown in Table 2 - 1.

After completion of the experiments, the reacting solid was analyzed by X-ray diffractometry (XRD, Rint2000, Rigaku operating at 40 kV and 30 mA with a $1^\circ/\text{min}$ scanning rate, 0.5° divergence, 0.5° scattering, and 0.15 mm receiving slits) with the preferred orientation method to determine the mineral phases. The bentonite specimen was divided into seven sections for XRD analysis from the input side: 0–3 mm, 3–6 mm, 6–9 mm, 9–12 mm, 12–15mm, 15–27mm, and 27–30mm. For the observations by scanning electron microscope (SEM, SSX-550, Shimadzu), the sample at 12–15mm, which is the section that was also observed by X-ray CT, was mounted on carbon stubs and coated with platinum.

2.2.2 Imaging processes

A Mathematica based program developed by Nakashima and Kamiya (2007) was used to quantify the volume of minerals in the CT images. The program used the Itrimming.nb and Clabel.nb subroutines to evaluate the volume of minerals in the CT images. The functioning of these programs will be explained in the following sections.

2.2.2.1 Descriptions of the Mathematica programs

All programs developed in the present study are of the note book type and are for the Mathematica version 5.2 or later. It should be noted that although there are some 2-D illustrations below for simplicity and pedagogical purposes, all the programs are for the 3-D image analysis. Thus, users should prepare 3-D 8-bit (not 16-bit) CT images as a set of contiguous 2-D slices. The dimensions of the voxel (a volume element) of each image should be cubic. If they are not cubic Clabel.nb cannot calculate the correct surface area value of each pore cluster and Rwalk.nb cannot calculate the correct value of the mean-square displacement of random walkers. The programs, user manuals, and an example of 3-D CT images of a rhyolitic lava sample are available at <http://www.jstage.jst.go.jp/browse/jnst/44/9/> and <http://staff.aist.go.jp/nakashima.yoshito/progeng.htm>. The programs are outlined briefly below and summarized in Table 1. For further information, such as details about data preparation and program execution, readers should refer to the “readme” text file available at the URLs above.

2.2.2.2 Itrimming.nb

The function of the Itrimming.nb program is to trim the raw CT images and to export the trimmed rectangular images in TIFF, BMP, Comma-Separated Values (CSV), or Tab-Separated Values (TSV) format. This program should be run before using Clabel.nb and Rwalk.nb to extract a 3-D rectangular region of interest (ROI) from a set of the raw CT images. Both pore connectivity analysis (i.e., cluster-labeling analysis) and random walk simulations will be performed on the extracted 3-D rectangular image system.

2.2.2.3 Clabel.nb

Clabel.nb is cluster-labeling program. Pore clusters are connected pore voxels and cluster labeling refers to the examination of the 3-D pore connectivity in order to export a 3-D image set of the labeled pore clusters (Stauffer and Aharony, 1994). All pore voxels in the porous media are colored cluster by cluster and are assigned to one of the

pore clusters by this processing. Some pores in the porous media are three-dimensionally connected to form a single large percolation cluster responsible for the macroscopic transport of materials; other pores are isolated and do not contribute to macroscopic diffusion and the Darcy flow. The Clabel.nb program allows us to characterize such pore clusters.

2.3 Modeling approach

The geochemical reactive transport code PHREEQC (Parkhurst and Appelo, 1999) was used to simulate the advective alteration experiment for bentonite with dry density of 0.3 Mg m^{-3} . The analysis also used the thermodynamic database Thermoddem obtained from <http://thermoddem.brgm.fr> (Blanc et al., 2012). Only advective transport mechanisms were taken into account in this model because the experiments were conducted with a flow velocity that is sufficiently rapid to disregard diffusion mechanisms. Cation exchange properties were not included due to the high concentration of sodium ions in the reacting solution.

2.3.1 Thermodynamic and kinetic database

The mineral composition of the bentonite (Kunigel V1) used in this study is shown in Table 1 - 1. The thermodynamic properties of these minerals and aqueous species are collected from Thermoddem. In this model, the thermodynamic data of amorphous silica was used instead of that of chalcedony. It will be discussed in detail in Chapter 2.4.3.1.

The rate equations ($\text{mol dm}^{-3} \text{ s}^{-1}$) for the dissolution of all minerals considered in this study based on Eq. (1-1), described by (Lasaga, 1981, 1984; Nagy and Lasaga, 1992; Lasaga et al., 1994):

$$\text{Rate} = k(T) \cdot (a_H)^n \cdot A_{min} \cdot f(\Delta G_r) \quad (2-1)$$

where $k(T)$ is the temperature dependent rate constant ($\text{mol m}^2 \text{ s}^{-1}$), $(a_H)^n$ is the

proton activity raised to the power n , which is a value experimentally determined, A_{min} is the reactive surface area of mineral ($\text{m}^2 \text{ dm}^{-3}$), ΔG_r is the deviation from the Gibbs free energy (J mol^{-1}), p and q are power term, which are value experimentally determined, R is molar gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K).

The ΔG_r function in Eq. (2-1) is readily obtained when the overall mechanism consists of a single elementary reaction (Lasaga, 1981). In this case, the relation can be derived from transition state theory (TST), and is given by (Aagaard and Helgeson, 1982; Lasaga et al., 1994):

$$f(\Delta G_r) = 1 - \exp\left(\frac{\Delta G_r}{\sigma RT}\right) \quad (2-2)$$

where σ is a coefficient that is not necessarily equal to one. ΔG_r is given by:

$$\Delta G_r = RT \ln\left(\frac{IAP}{K_{eq}}\right) \quad (2-3)$$

where IAP and K_{eq} are the ion activity product and the equilibrium constant of the dissolution reaction, respectively. However, the shape of the ΔG_r function for overall reactions is difficult to predict *a priori*. Although laboratory dissolution rates of minerals such as quartz (Berger et al., 1994) and anorthite (Oelkers and Schott, 1995) are well approximated with kinetic laws based on Eq. (2-2), such formulations cannot be applied to clay dissolution without caution (Schott and Oelkers, 1995). The effect that ΔG_r exerts on clay dissolution rate leads to computed dissolution rates that are overestimated by several orders of magnitude at near-equilibrium conditions. This result could in part explain the existing discrepancies between laboratory and field mineral dissolution rates (e.g., Velbel, 1993). Several authors (Cama et al., 2000; Metz et al., 2005; Sato et al., 2007) have shown that smectite dissolution rate is a non-linear function of the Gibbs free energy. Dissolution rate of smectite measured sufficiently far from equilibrium becomes independent of the Gibbs free energy (ΔG_r). As equilibrium is approached, the dissolution rate decreases sharply over a small range of ΔG_r . When close-to-equilibrium conditions are achieved, the dissolution rate is approximately

linear with a small slope and rate is slow. Based on the study of Nagy and Lasaga (1992) on gibbsite dissolution kinetics, Cama et al. (2000) and Sato et al. (2007) proposed for the ΔG_r -smectite rate dependence a fully non linear rate law in which the rate is not a linear function of the Gibbs energy even very close to equilibrium:

$$f(\Delta G_r) = 1 - \exp\left(p \cdot \left(\frac{\Delta G_r}{\sigma RT}\right)^q\right) \quad (2-4)$$

where p and q are fitting coefficients. Consequently, the rate equations ($\text{mol dm}^{-3} \text{ s}^{-1}$) for the dissolution of all minerals considered in this study based on Eq. (2-1 and 2-4),

$$\text{Rate} = k(T) \cdot (a_H)^n \cdot A_{\min} \cdot \left[1 - \exp\left(p \cdot \left(\frac{\Delta G_r}{\sigma RT}\right)^q\right)\right] \quad (2-5)$$

2.3.2 Montmorillonite

The dissolution rate of montmorillonite is a key research issue in the performance assessment of radioactive waste disposal systems (Cama and Ayora, 1998). In particular, the pH dependence and the temperature dependent rate constant, Eq. (2-5), are fundamental to accurately model the changes in a nuclear waste repository via a coupled reaction transport model (Cama and Ayora, 1998).

Typically, the dissolution rate of montmorillonite is obtained from batch or flow-through experiments, which are high liquid/solid ratio systems (far-from-equilibrium). As noted in Eq. (2-5), pH and temperature of the reactive solution affects montmorillonite dissolution. Therefore, the effect of pH and temperature on dissolution rate of montmorillonite was estimated and a proton (hydroxyl) -promoted dissolution model of montmorillonite was proposed by Huertas et al. (2001), Sato et al. (2004), Kuwahara et al. (2006), Sanchez et al. (2006), Yamaguchi et al. (2007), and Rozalen et al. (2009). It is known that the dissolution of montmorillonite begins from the edge surfaces of the particles, which contain the silanol and alminol groups, suggesting that dissolution occurs in two sites. However, these proton (hydroxyl) -promoted models do not specify which sites are affected by dissolution. Thus, to quantitatively evaluate the dissolution of montmorillonite in a wide

range of pH, a two-site dissolution model must be considered. Sato et al. (2004) proposed the following twin-site model:

$$Rate = k(T) \cdot (a_{H^+})^n = 4.74 \cdot 10^{-6} \cdot e^{-39.6/RT} \cdot \frac{177 \cdot e^{20.4/RT} \cdot a_{OH^-}}{1 + 177 \cdot e^{20.4/RT} \cdot a_{OH^-}} + 1.70 \cdot e^{-69.7/RT} \cdot \frac{0.0297 \cdot e^{23.5/RT} \cdot a_{OH^-}}{1 + 0.0297 \cdot e^{23.5/RT} \cdot a_{OH^-}} \quad (2-6)$$

where a_{OH^-} is the hydroxyl activity. The dissolution mechanism can be interpreted in terms of surface complexation theory and the first and second reaction sites in the above equation are Si site and Al site, respectively.

The last term in Eq. (2.5), $f(\Delta G_r)$ for an elementary reaction is based on the Transition State Theory (TST; Lasaga, 1998), when p and $q = 1$. TST for overall reactions is difficult to predict *a priori*. However, the experimental observations lead to fully nonlinear rate laws, i.e., rate laws in which the rate is not a linear function of the Gibbs free energy even very close to equilibrium. The montmorillonite dissolution experiments of Cama et al. (2000) in a flow-through reactor at 80°C and pH 8.8 focused on elucidating the dependence dissolution rate on the solution saturation state. However, the pH in actual radioactive waste disposal conditions is expected to be around 12 to 13.5. Oda et al. (2012), on the other hand, studied montmorillonite dissolution in a flow-through reactor at 70°C and pH 12.1 and observed a stronger ΔG_r effect on montmorillonite dissolution than in moderately alkaline solution. Thus, montmorillonite dissolution varied more significantly depending on the system's deviation from equilibrium in hyperalkaline condition compared to moderately alkaline condition. Furthermore, they formulated the dissolution rate of montmorillonite by compiling the experimental data obtained from Cama et al. (2000) and Oda et al. (2012).

Incorporating these equations, the general rate law (Eq. 2-5 and 2-6) will give two equations, Sato-TST and Sato-Oda equation, gives;

$$Rate = \left(4.74 \cdot 10^{-6} \cdot e^{-39.6/RT} \cdot \frac{177 \cdot e^{20.4/RT} \cdot a_{OH^-}}{1 + 177 \cdot e^{20.4/RT} \cdot a_{OH^-}} + 1.70 \cdot e^{-69.7/RT} \cdot \frac{0.0297 \cdot e^{23.5/RT} \cdot a_{OH^-}}{1 + 0.0297 \cdot e^{23.5/RT} \cdot a_{OH^-}} \right) \cdot$$

$$A_{min} \cdot \left[1 - \exp \left(p \cdot \left(\frac{\Delta G_r}{\sigma RT} \right)^q \right) \right] \quad (2-7)$$

where σ is constant. For the TST equations, $\sigma = 1$ was used, while Oda for the equation, $\sigma = 2$. This is due to the overall dissolution reaction of montmorillonite being described using O_{20} stoichiometry by Sato et al. (2004), while O_{10} stoichiometry was used by Oda et al. (2012). Thus, the rate equation from Oda et al. (2012) had to be modified to the same unit in the present paper by dividing a function of the Gibbs free energy by two due to the Oda equation being described by an O_{10} stoichiometry. Fig. 2 - 1 shows the dissolution rate of montmorillonite vs. ΔG_r of overall reaction calculated from Sato-TST and Sato-Oda equation at pH 12.1 and 70 °C. The dissolution rate increases as Gibbs free energy decreases (Fig. 2 - 1). In this study, the appropriate equation for dissolution rate of montmorillonite will be considered to simulate the experimental results.

2.3.3 Accessory minerals

Except for the montmorillonite, the kinetic rate constant $k(T)$ in Eq. (2-5) only considers the well-studied mechanisms in pure H_2O (neutral pH). Dissolution and precipitation of minerals are often catalyzed by H^+ (acid mechanism) and OH^- (base mechanism). For many minerals, the kinetic rate constant $k(T)$ includes each of these three mechanisms (Lasaga et al., 1994; Palandri and Kharaka, 2004), gives

$$Rate = k(T) \cdot (a_{H^+})^n = k_{25}^{nu} \exp \left[\frac{-E_a^{nu}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{nu} + k_{25}^H \exp \left[\frac{-E_a^H}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{nH} + k_{25}^{OH} \exp \left[\frac{-E_a^{OH}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{nOH} \quad (2-8)$$

where superscripts or subscripts nu , H , and OH indicate neutral, acid and base mechanisms, respectively; a is the activity of the species; and n is power term (constant). The following equation was used for dissolution of accessory mineral in this study based on Eq. (2-5 and 2-6):

$$Rate = \left(k_{25}^{nu} \exp \left[\frac{-E_a^{nu}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{nu} + k_{25}^H \exp \left[\frac{-E_a^H}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{nH} + k_{25}^{OH} \exp \left[\frac{-E_a^{OH}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_H^{nOH} \right) \cdot A_{min} \cdot \left[1 - \exp \left(\frac{\Delta G_r}{RT} \right) \right] \quad (2-9)$$

2.3.4 Input data

The conceptual design of the reactive transport in the column shown in Fig. 2 - 2 to simulate the advective alteration experiment for bentonite with dry density of 0.3 Mg/m³ (dry density of 0.3 Mg m⁻³ for short-term experiment was performed to observe the alteration process of bentonite by X-ray CT). The thermodynamic properties of minerals considered in this simulation are tabulated in Table 2 - 2. The dissolution of montmorillonite, quartz, chalcedony, and albite were modeled based on available kinetic data while analcime, calcite, and dolomite were modeled based on thermodynamic considerations. The kinetic equation of the montmorillonite considers three equation, Sato-TST, Sato-Cama and Sato-Oda equation, Eq. (2-7). The kinetic parameters of montmorillonite are shown in Table 2 - 3. The kinetic equation of the albite, chalcedony and quartz follows Eq. (2-9) and their kinetic parameters shown in Table 2 - 4 were compiled from the literature. The porosity of the bentonite is about 0.89. The pore in the bentonite with dry density of 0.3 Mg m⁻³ is filled deionized water before the advective alteration experiment, and the pore water composition (Table 2 - 5) are calculated by equilibrated deionized water with the bentonite. 0.3 M NaOH solution was passed through the bentonite. Initial and final boundary conditions are set to the constant and flux, respectively. The simulation was carried out for a period of 180 days at 80 °C.

2.4 Results and discussion

2.4.1 Advective alteration experiments

The permeability coefficient of bentonite with a dry density (0.3 Mg m⁻³) was measured in advective alteration experiments. The values of the coefficient ranged from 2.47×10⁻¹⁰ m s⁻¹ to 4.41×10⁻¹⁰ m s⁻¹ throughout the experiments. The pH (25°C) of the

output solution decreased from 13.5 to 9 during the initial 20 days of the experiment due to the buffering capacity of the montmorillonite and dissolved silica components including $\text{H}_2\text{SiO}_4^{2-}$, and increased to around 13.0 from 20 to 100 days, after 100 days did not change further. The dissolved silica concentration in the effluent increased gradually until 50 days due to dissolution of chalcedony, then decreased from 50 to 100 days, and after 100 days maintained a constant value, the graph of the concentrations of silica and aluminum in the output solution will be discussed further in Chapter 2.4.3. The dissolved aluminum concentrations maintained constant values until 100 days, due to the potential effect of silicon inhibition on the montmorillonite dissolution rate (Cama et al., 2000).

The XRD patterns show that there is no peak of analcime near the input side (0 to 6 mm), and that analcime peaks appear in the sections beyond 6 mm from the input side (Fig. 2 - 3). The absence of analcime near the input side is likely due to the dissolution of previously formed analcime. The XRD patterns also show no changes in the peak intensity and shift at 7.1° for the basal (001) reflection of the montmorillonite, suggesting that no directly observable changes took place in the montmorillonite. Fig. 2 - 4 shows SEM images of the secondary analcime in the section observed with X-ray CT. Analcime occurs as spherical single crystals, as aggregates on the surface of montmorillonite, and as aggregates on the surface of plagioclase, and have sizes of about 5, 30, and $30\mu\text{m}$, respectively. These morphologies are similar to those of the analcime reported by Sánchez et al. (2006).

2.4.2 Observations by X-ray CT

The sensitivity of the brightness in the CT images to the dry density of bentonite was examined before the advective experiment. Three different dry densities (0.1, 0.2, and 0.3 Mg m^{-3}) of compacted bentonite specimens were prepared, and placed in a vacuum vessel in deionized water for 1 month for hydration. The CT images of the bentonite specimens with different dry densities showed clear differences in the brightness (Fig. 2 - 5). The dry densities of bentonite correspond to dry densities of the montmorillonite of 1.028, 1.059, and 1.093 Mg m^{-3} , respectively. These results suggest that dissolution of

montmorillonite can be determined based on the changes in the brightness of the CT images of bentonite with a dry density of 0.3 Mg m^{-3} when significant volumes of the montmorillonite had dissolved.

The advective experiment was conducted using bentonite with a dry density of 0.3 Mg m^{-3} and the compacted bentonite specimen had been maintained in a vacuum vessel in deionized water for 1 month prior to the experiment. Fig. 2 - 6 shows CT images of the bentonite sample at different time points during the advective experiment, and indicates the presence of high density particles (lighter colored dots in the CT images, accessory and secondary minerals), as well as lower density particles (darker colored dots in the CT images, hydrated montmorillonite) in the bentonite. Dissolution of the montmorillonite was not observed in the 12–15 mm section during the experiment, based on the CT images (Fig. 2 - 6), as the brightness of the montmorillonite grains did not change significantly. This is consistent with the XRD results that there were no changes in the peak intensity or shift at 7.1° for the basal (001) reflection of the montmorillonite as observed before and after the experiments (Fig. 2 - 3). Lighter colored dots appear and increase in size as the experiment progressed (red rectangles in Fig. 2 - 6). This is attributed to the formation of secondary low density minerals. The XRD analysis showed that analcime was the only mineral formed at the section observed by X-ray CT (Fig. 2 - 3). However, discrimination of secondary minerals from the accessory minerals is difficult based on only the brightness in the CT images. To enable a better discrimination and quantification, a methodology using the volumes of secondary mineral in the CT images was developed.

Firstly, images of trimmed ROI (regions of interest) were generated from the CT images by Itrimming.nb (Nakashima and Kamiya, 2007). For example, the red rectangles in Fig. 2 - 6 were selected and trimmed and the results are shown in Fig. 2 - 7. Secondly, Clabel.nb was used to calculate the volume of accessory and secondary minerals in the trimmed ROI. The Clabel.nb program requires the determination of a threshold value of the brightness that distinguishes between hydrated montmorillonite and accessory minerals (secondary minerals) in the ROI. Here, the threshold value was determined based on an accumulated histogram of the 8-bit voxel brightness of an ROI (Fig. 2 - 8). Assuming that the numerical ratio of bright pixels to all the pixels is

identical to the theoretical volumetric fraction of hydrated montmorillonite, η , the threshold value is given by the brightness at η of the accumulated frequency. The η value is calculated by the following equation:

$$\eta = 1 - \left(\frac{\rho_d - \rho_a}{\rho_s - \rho_a} \right) \cdot \theta \quad (2-10)$$

where ρ_d is the dry density of the specimen (the packing density in the dry condition; here 0.3 Mg m^{-3}), ρ_s is the density of the specimen (2.73 Mg m^{-3}), ρ_a is the density of air ($\sim 0 \text{ Mg m}^{-3}$), and θ is the volumetric percentage of montmorillonite (47.2 volume% given in Table 1). The η value calculated in this manner was 0.94. This value is the sum of 0.89 for the porosity of the specimen and 0.05 for the volumetric percentage of non-hydrated montmorillonite, and indicates the volumetric percentage of the hydrated montmorillonite due to the swelling capacity of the montmorillonite.

The ROIs were converted to binary images using the threshold values obtained above and introduced into Clabel.nb (Fig. 2 - 8). Clabel.nb provides the volumes of white dot clusters in the binarized ROIs, and because the white dot clusters include both secondary and accessory minerals, it is necessary to discriminate between these for the quantification of the volume of secondary minerals. Here, it was assumed that no secondary mineral had formed in bentonite at 10 days, and that the volume of secondary mineral was larger than that of the accessory minerals initially present at 10 days. For example, because the volume of the largest accessory minerals at 10 days was $7.46 \times 10^5 \mu\text{m}^3$ in the ROI shown in Fig. 2 - 9, the formation of secondary minerals were considered only when the volume of white dots exceeded this value, such as those in the red circles from 100 days. It must be noted that the white dots in the red circles at 60 days were not considered as secondary minerals because the volumes were smaller than $7.46 \times 10^5 \mu\text{m}^3$.

The ROIs were selected to cover all the secondary minerals found in the CT images and avoid accessory minerals as much as possible. The analysis described above was performed for every ROI at each time point in the experiment. The volume of analcime formed in the whole of the section (300 mm^3) at each time point was quantified based on the assumption that the ratio of the total volume of the analcime to the volume

observed by X-ray CT (58.9 mm^3) can be extrapolated to the whole section. The volume of analcime formed vs. time shows that significant analcime formation started after 60 days, and that the volume converged gradually to a constant value after ~ 150 days (Fig. 2 - 10).

2.4.3 Modeling

2.4.3.1 Sato – TST and Sato-Oda model

The volume of secondary mineral formed as a function of time in the sections observed by X-ray CT analysis were used to validate a geochemical model simulating the experimental results using PHREEQC code.

Firstly, Sato-TST equation (Eq. 2-7, using $p = 1$, $q = 1$, and $\sigma = 1$) was used to simulate the experimental results. Fig. 2 - 11 shows the simulated and experimental concentrations of dissolved Si and Al in effluent solutions with time in Sato-TST equation. It can be seen that the simulated pattern and maximum concentration of dissolved Si differed from the experimental results from 0 to 150 days. The maximum concentration of dissolved Si is due to thermodynamic data of chalcedony. The maximum concentration of Si in the effluent was fitted to the experimental result by considering the thermodynamic data of amorphous silica instead of that of chalcedony (Fig. 2 - 12). On the other hand, the calculated morphology of the curve describing the concentration of dissolved silica in output solution is due to the kinetic data of chalcedony. White and Brantley (2003) show that rate of feldspar dissolution in laboratory experiments was 10^2 to 10^5 times faster than in natural conditions. Furthermore, Zhu (2005) shows that the dissolution rate of natural feldspar is 10^5 times slower than the rate determined in the laboratory experiment under similar conditions. The estimated dissolution rates of feldspar decrease in the order powder < block < field (Yokoyama and Banfield, 2002). In addition, the differences in mineral surface areas between estimations and/or measurements have been proposed as one of the possible causes of the discrepancy between laboratory and field rates (White and Peterson, 1990). Therefore, the reactive surface area of chalcedony was varied to obtain a dissolution rate of the chalcedony that is compatible with the experimental results here. It is inferred

that the reactive surface area of other accessory minerals such as (Quartz and Albite) also need to be reduced in addition to chalcedony. Therefore Eq. (2-9) was used as the rate law for quartz, chalcedony, and albite with 0.07×0.02 , 0.03×0.02 , and $0.24 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area, respectively in the following models.

Sato-TST equation (Eq. 2-7, using $p = 1$, $q = 1$, and $\sigma = 1$) and Sato-Oda equation (Eq. 2-7, using $p = 2.75 \times 10^{-5}$, $q = 3$, and $\sigma = 2$) were used to simulate the experimental results. Fig. 2 - 13 shows the simulated and experimental pH in effluent with time in Sato-TST and Sato-Oda model, and Fig. 2 - 14 shows the simulated concentrations of dissolved Si and Al in effluent with time in Sato-TST and Sato-Oda model. These simulated results using Sato-Oda equation agree well with experimental results. On the other hand, the simulated mineralogical distribution in the bentonite of dry density of 0.3 Mg m^{-3} after 180 days (Fig. 2 - 15) and the simulated volume of the secondary formed analcime at the section observed by X-ray CT with time (Fig. 2 - 16) were inconsistent with the results obtained from the XRD and X-ray CT analysis, respectively (Fig. 2 - 3 and Fig. 2 - 10). It can be seen that the distribution of analcime in the bentonite is different from XRD result (Fig. 2 - 3): simulated result shows the formation of analcime from 0mm in Sato-TST model (Fig. 2 - 15a), or 2mm in Sato-Oda model (Fig. 2 - 15b and d) while XRD gives from 6mm. The simulation using Sato-TST equation predicts the formation of analcime from 0 days (Fig. 2 - 16a) while the microstructural analytical method shows that analcime formation begins after 60 days (Fig. 2 - 10). While the volume of analcime converges to a constant value after ~150 days based on the X-ray CT results (Fig. 2 - 10), it did not reach a constant value in the calculations in Sato-Oda model (Fig. 2 - 16b and c).

This leads to that the differences in the dissolution rates obtained from compacted (low liquid/solid ratio) and powdered (high liquid/solid ratio) montmorillonite need to be considered as well as the accessory minerals such as quartz, chalcedony, and albite. Nakayama et al. (2004) conducted diffusion experiments with compacted sand-bentonite mixtures (dry density is 1.6 Mg m^{-3}) to estimate the dissolution rate of the montmorillonite with 0.1M NaOH solution, and compared the dissolution rate with data obtained from batch dissolution experiments of smectite in hyperalkaline solutions at 35°C and 80°C (Bauer and Berger, 1998). Nakayama et al. (2004) concluded that the

dissolution rates of montmorillonite obtained for compacted sand-bentonite mixtures was one order of magnitude lower than those in the batch dissolution experiments. Further, differences in mineral surface areas of the estimations and measurements have been proposed to account for the discrepancies between dissolution rates determined in the laboratory and field (White and Peterson, 1990). Recently, Satoh et al. (2013) measured the dissolution rate of compacted montmorillonite at hyperalkaline pH and 70 °C under pressures ranging from 0.04 to 10.00 MPa (dry density of 1.0 to 1.7 Mg m⁻³) using *in situ* vertical scanning interferometry (VSI) and *ex situ* atomic force microscopy (AFM) measurements. They revealed the limitation of reactive surface area of montmorillonite under compaction system. Therefore the dissolution rate of the montmorillonite in compacted bentonite is fixed by changing the surface area of montmorillonite in powder bentonite.

2.4.3.2 Sato-TST and Sato-Oda model modified with specific surface area of montmorillonite and accessory minerals.

The Sato-TST model is modified by multiplying the montmorillonite surface area (7 m² g⁻¹) by a factor of 0.01 and those of other minerals by a factor of 0.02 (hereafter referred to as modified Sato-TST equation), and the Sato-Oda model is modified by multiplying the montmorillonite surface area (7 m² g⁻¹) by a factor of 0.2 and those of other minerals by a factor of 0.02 (hereafter referred to as modified Sato-Oda equation).

Using the modified dissolution rate of the montmorillonite, the simulated pH (Fig. 2 - 17), and concentrations of dissolved Si and Al in the effluent (Fig. 2 - 18) and the simulated mineralogical distribution in the bentonite at 180 days (Fig. 2 - 19) agree well with the experimental results (Fig. 2 - 3). Fig. 2 - 20 shows the simulated volume of the secondary formed analcime at the section observed by X-ray CT with time in modified Sato-TST and Sato-Oda, respectively. The calculated curve showing the temporal changes in the volume of analcime formation (Fig. 2 - 20a) in modified Sato-TST model was inconsistent with the result obtained from the X-ray CT analysis (Fig. 2 - 10). The simulation using Sato-TST equation predicts the formation of analcime from 0 days as well as in modified Sato-TST model. On the other hand, it can be seen that the

formation pattern/tendency of the analcime in modified Sato-Oda model (Fig. 2 - 20b and c) becomes similar to the experimental results (Fig. 2 - 10) which show the formation of analcime from 50 days.

The above results suggest that the dissolution rate of montmorillonite in compacted bentonite not only depends on the effect of surface area of montmorillonite but also on the departure from equilibrium. It has been reported that several factors influence the dissolution rate of montmorillonite. The accessible surface area of minerals in a compacted system should be lower than that of powders usually studied in the laboratory. However, differences in the overall rates of reaction measured in laboratory and field settings are due to a variety of factors as surface area, departure from equilibrium, inhibition or catalysis (Maher et al., 2006) Therefore, the dissolution rate of montmorillonite in compacted bentonite needs to be considered to simulate the experiments in this study, especially for surface area of montmorillonite and departure from equilibrium. Therefore, the simulation results in modified Sato-Oda equation are consistent with the experimental results compared with that in modified Sato-TST equation. Satoh et al. (2013) empirically formulated the relationship between the effective specific surface area of montmorillonite and dry density of bentonite. The effective specific surface area of montmorillonite at a dry density of 0.3 Mg m^{-3} is extrapolated by using this relationship and a value of $7 \times 0.14 \text{ m}^2 \text{ g}^{-1}$ for the effective specific surface area of montmorillonite can be obtained. This value is consistent with the Sato-Oda modified with surface area of montmorillonite ($7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$).

2.4.3.3 Differences between Sato-TST and Sato-Oda model modified with specific surface area of montmorillonite.

The differences between modified Sato-TST and Sato-Oda equation can be attributed to the dependence of dissolution rate on ΔG_r . Fig. 2 - 21 shows the dissolution rate of montmorillonite vs. ΔG_r of overall reaction calculated from modified Sato-TST and Sato-Oda equation modified with surface area of montmorillonite at pH 12.1 and 70 °C. Compared with Fig. 2 - 1, the dissolution rates of montmorillonite in both modified Sato-TST and Sato-Oda equations decrease due to limiting the specific surface area of

montmorillonite. Especially, a straight line for Sato-TST equation and a curve line for Sato-Oda equation cross around -90 kJ mol^{-1} of ΔG_r as shown in Fig. 2 - 21. From the simulation results (Fig. 2 - 22), ΔG_r with respect to montmorillonite in bentonite pore solution ranges from around -110 to -50 kJ mol^{-1} during this advective experiment, suggesting that the dissolution rates of montmorillonite obtained from the modified Sato-TST and Sato-Oda equation differ by just one order of magnitude during this advective experiment. Thus, there is no significant difference between the simulation results such as the pH (Fig. 2 - 17), concentrations of dissolved Si and Al in the effluent (Fig. 2 - 18), and the mineralogical distribution in the bentonite at 180 days (Fig. 2 - 19) between the Sato-TST and Sato-Oda models. However, the simulated formation pattern/tendency of the analcime is different between modified Sato-TST and Sato-Oda model, indicating that the ΔG_r exerts a stronger influence on the formation pattern/tendency of minerals than other factors such as the pH, and concentrations of dissolved Si and Al in the effluent. Thus the use of X-ray CT can make it possible to obtain the critical data to validate the geochemical model.

In actual radioactive disposal barrier systems, the use of a compacted bentonite with higher dry density such as 1.6 Mg m^{-3} has been considered. In this case, the pore water in the bentonite may approach near saturation with respect to montmorillonite. Satoh et al. (2013) showed that the effective surface area of montmorillonite is a function of pressure. These observed rates for compacted montmorillonite (with dry density from 1.0 to 1.7 Mg m^{-3}) are two-orders of magnitude slower ($2.63 \times 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$) than dissolution rates obtained for the powdered state. Additionally, the dissolution rate of montmorillonite from the Sato-Oda equation significantly decreases near equilibrium as shown in Fig. 2 - 21. These data suggest that the effects of montmorillonite surface area and ΔG_r on the dissolution of montmorillonite will become more apparent in actual disposal systems. Therefore, the dissolution rate of compacted montmorillonite must be used in predicting the long-term performance of barrier systems realistically.

2.5 Near future issues for X-ray CT analysis

As a result of sensitivity analysis for factors such as the reactive surface area of

montmorillonite and ΔG_r on dissolution rate of montmorillonite, it can be considered that the actual reactive surface area of montmorillonite in compacted bentonite (dry density is 0.3 Mg m^{-3}) is one to two orders smaller than that in powder bentonite, and the actual dissolution rate of montmorillonite in compacted bentonite is influenced by the effect of departure from equilibrium.

However, the simulated volume of analcime was not quantitatively validated by the experimental data since the volume of analcime obtained in the experiments is lower than that obtained by the simulations. This may be explained by the spatial resolution of the X-ray CT used in this study, $4 \mu\text{m}$, the size of secondary analcime particles smaller than $4 \mu\text{m}$ cannot be observed in the CT images, and as single crystal sizes are smaller than $5 \mu\text{m}$, the image analysis would not detect analcime particles smaller than $5 \mu\text{m}$. The ROI in this study was manually selected to include the smallest possible amount of accessory minerals and the results were extrapolated to whole sections. As a result, the visual identification of the formed secondary minerals employed here may not have included all of the secondary minerals and the extrapolated volume may have differed from the actual amounts of formed secondary minerals, leading to inaccuracies in the experimentally determined amounts of analcime. Future investigation with more detailed observations of the dissolution process of accessory minerals by X-ray CT measurements near the input side of the specimen will be necessary to validate the model more sufficiently.

2.6 Conclusion

An advective alteration experiment of compacted bentonite specimens with a dry density of 0.3 Mg m^{-3} (under low fluid/solid weight ratio conditions) was conducted with hyperalkaline-fluid to observe the alteration process in bentonite by X-ray CT. There were no significant differences in the brightness of the CT images for montmorillonite. This can be explained by the dissolution rate of compacted montmorillonite (low liquid/solid ratio) being lower than that of powdered (high liquid/solid ratio) montmorillonite. The formation of secondary minerals in bentonite was confirmed by both XRD and X-ray CT. The type of secondary minerals was

identified as analcime by XRD. The dissolution of montmorillonite was likely affected by the formation of the secondary mineral, analcime. Based on a CT image analysis, the amount of formed analcime was quantified as a function of time in the experiment.

The geochemical transport model with the Sato-TST and Sato-Oda equation does not simulate the experimental results well. This may be attributed to the differences in the dissolution rate of compacted and powdered montmorillonite. In this study, the dissolution rate of compacted montmorillonite was varied by reducing the reactive surface area of the powdered montmorillonite. As a result, the concentration of dissolved Si and Al in output solution and the mineralogical distribution in bentonite was replicated, while the formation pattern/tendency of analcime was not replicated by modified Sato-TST model. It suggests that the dissolution rate of montmorillonite in compacted bentonite is not only affected by the surface area of montmorillonite but also by departure from equilibrium. Geochemical transport model with modified Sato-Oda equation validated the formation pattern of secondary mineral and the concentration of Al and Si. Therefore, it can be considered that the actual dissolution rate of the montmorillonite in compacted bentonite is one or two orders lower than that of the montmorillonite in powder bentonite and it is influenced by the effect of departure from equilibrium as determined from the microstructural analytical method by X-ray CT. Thus the dissolution rate of compacted montmorillonite must be used in predicting the long-term performance of barrier systems.

The results demonstrate that a microstructural analytical method based on X-ray CT can be used to validate models for an accurate prediction of the performance of engineering barriers. However, not all of the modeling results were validated by the X-ray CT data in this study, and further experimental details and modeling studies are necessary.

Table 2 - 1 Scanning and imaging conditions in the X-ray CT analysis.

Scanning mode	Cone-beam
Tube voltage	70 kV
Tube current	60 mA
Slice thickness	0.020 mm
Slice pitch	0.020 mm
Cross-sectional area	19.6 mm ²
The number of slices	150
Spatial resolution	1024×1024
Pixel size	0.004 mm

Table 2 - 2 Thermodynamic constants (25°C) and molar volumes of minerals considered in the simulations.

Minerals	Structural formula	Log K	Molar volume (cm ³ mol ⁻¹)
Na-Montmorillonite	Na _{0.66} Mg _{0.66} Al _{3.34} Si ₈ O ₂₀ (OH) ₄	2.64	262.48
Quartz	SiO ₂	-3.74	22.69
Chalcedony	SiO ₂	-2.70	22.68
Albite	NaAlSi ₃ O ₈	4.14	100.43
Calcite	CaCO ₃	1.85	36.93
Dolomite	CaMg(CO ₃) ₂	3.53	64.37
Analcime	Na _{0.99} Al _{0.99} Si _{2.01} O ₆ ·H ₂ O	6.64	96.68
Pyrite	FeS ₂	-23.6	23.94
Brucite	Mg(OH) ₂	17.11	24.63

Table 2 - 3 Kinetic parameters of montmorillonite for Eq. (2 - 7).

	TST	Cama ^[1]	Oda ^[2]
p	1	-6.00×10^{-10}	2.75×10^{-5}
q	1	6	3
σ	1	1	2

[1] Cama et al. (2000)

[2] Oda et al. (2012)

Table 2 - 4 Kinetics parameters for Eq. 2-9 at 25°C.

Minerals	Quartz ^[1]	Albite ^[2]	Chalcedony ^[3]
Specific surface area (m ² g ⁻¹)	0.07	0.24	0.03
Log k ^{nu} (mol m ⁻² s ⁻¹)	-12.03	-12.1	-12.5
E _a ^{nu} (kJ mol ⁻¹)	76.7	61.1	87.1
Nnu	-	-	-0.52
Log k ^H (mol m ⁻² s ⁻¹)	-	-9.47	-
E _a ^H (kJ mol ⁻¹)	-	64.3	-
nH	-	0.335	-
Log k ^{OH} (mol m ⁻² s ⁻¹)	-8.56	-9.38	-
E _a ^{OH} (kJ mol ⁻¹)	80	60.6	-
nOH	0.339		-

The kinetic constants are determined with data from:

[1] Schwartzentruber et al. (1987); Bennett et al. (1988); Knauss and Wolery (1988);

Blum et al. (1990); Brady and Walther (1990); Casey et al. (1990); Dove and Crerar

(1990); Bennett (1991); House and Orr (1992); Dove (1994); Dove (1999); Icenhower

and Dove (2000); Bickmore et al. (2006)

[2] Chou and Wollast (1984); Chou and Wollast (1985); Burch et al. (1993); Hellmann

(1994); Knauss and Copenhaver, (1995); Alekseyev et al. (1997); Hellmann and

Tisserand (2006)

[3] Savage et al. (2002)

Table 2 - 5 Initial pore solution chemistry in bentonite.

Chemical composition	
pH	8.59
Pe	-3.06
Element	Total concentration (mol kg ⁻¹ w)
Al	2.89×10 ⁻⁴
C	2.23×10 ⁻⁴
Ca	1.73×10 ⁻⁴
Mg	5.03×10 ⁻⁵
Na	2.59×10 ⁻⁴
Si	5.25×10 ⁻⁴

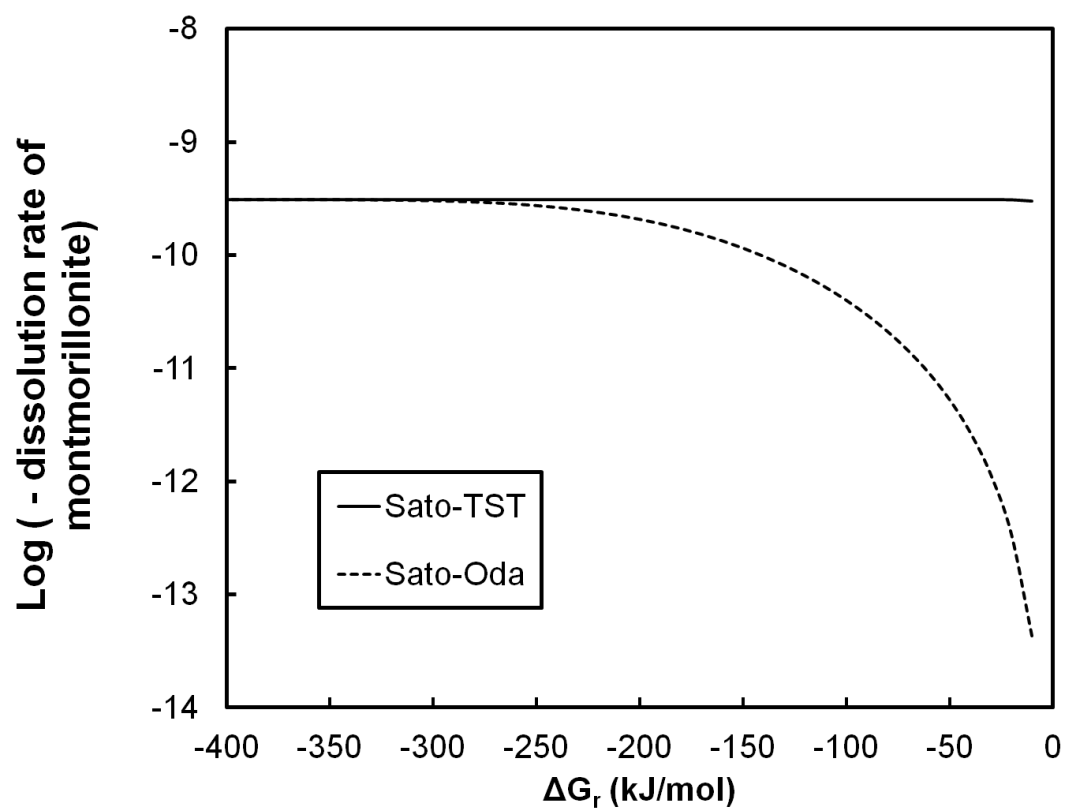


Fig. 2 - 1 Effect of the degree of saturation on montmorillonite dissolution rate (Sato-TST and Sato-Oda equation).

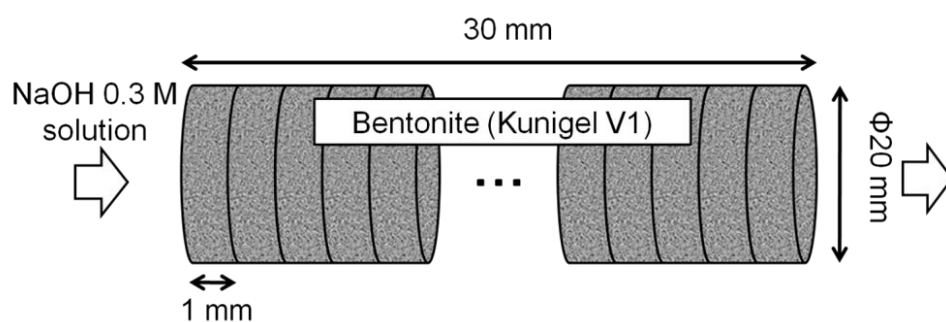


Fig. 2 - 2 Schematic diagram of one-dimensional react and transport model for the permeability experiment in bentonite.

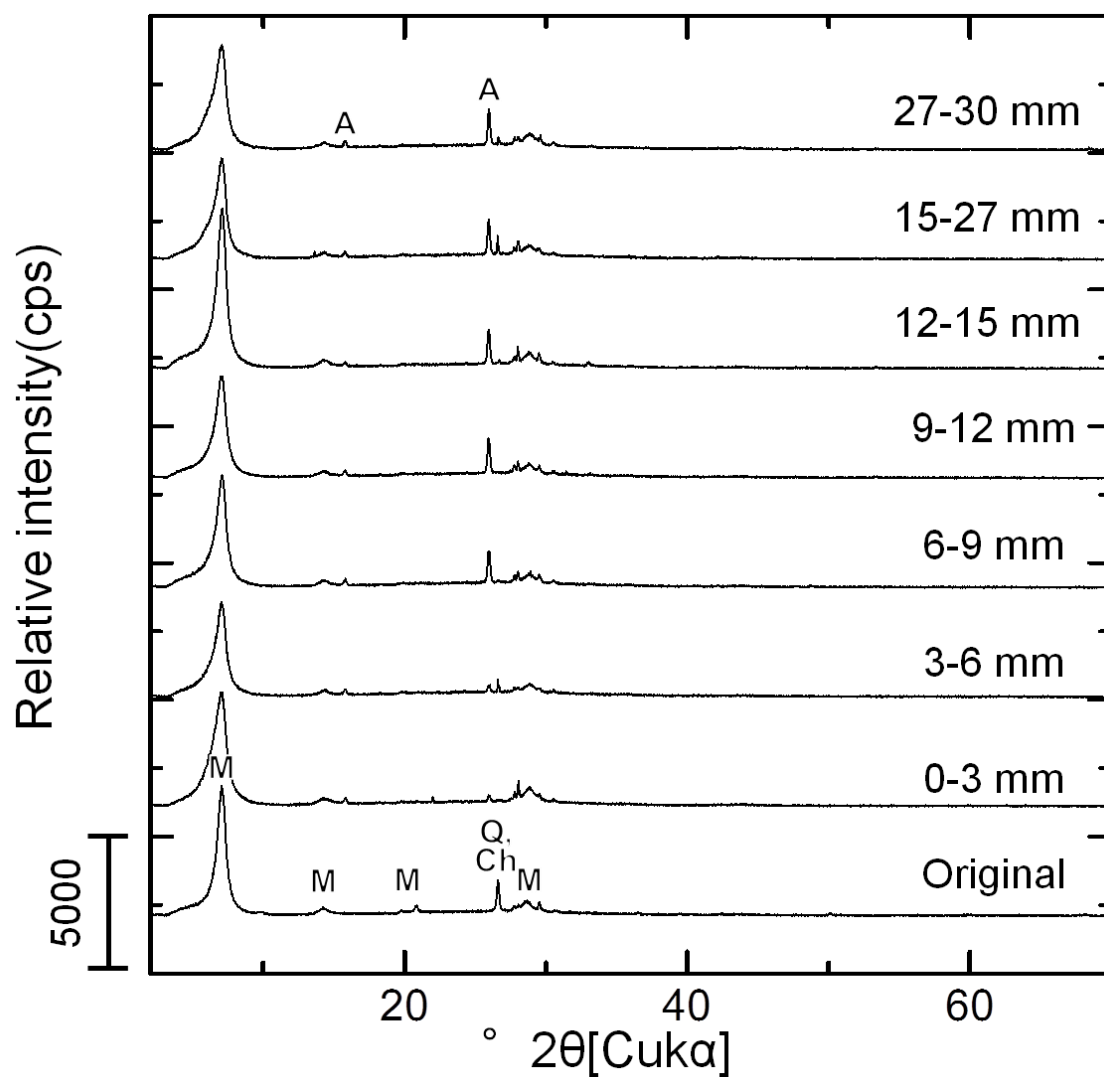


Fig. 2 - 3 X-ray diffraction patterns of the bentonite in different sections of the column after 180 days. Peak assignments: A = Analcime; M = Na-Montmorillonite; Q = Quartz; Ch = Chalcedony.

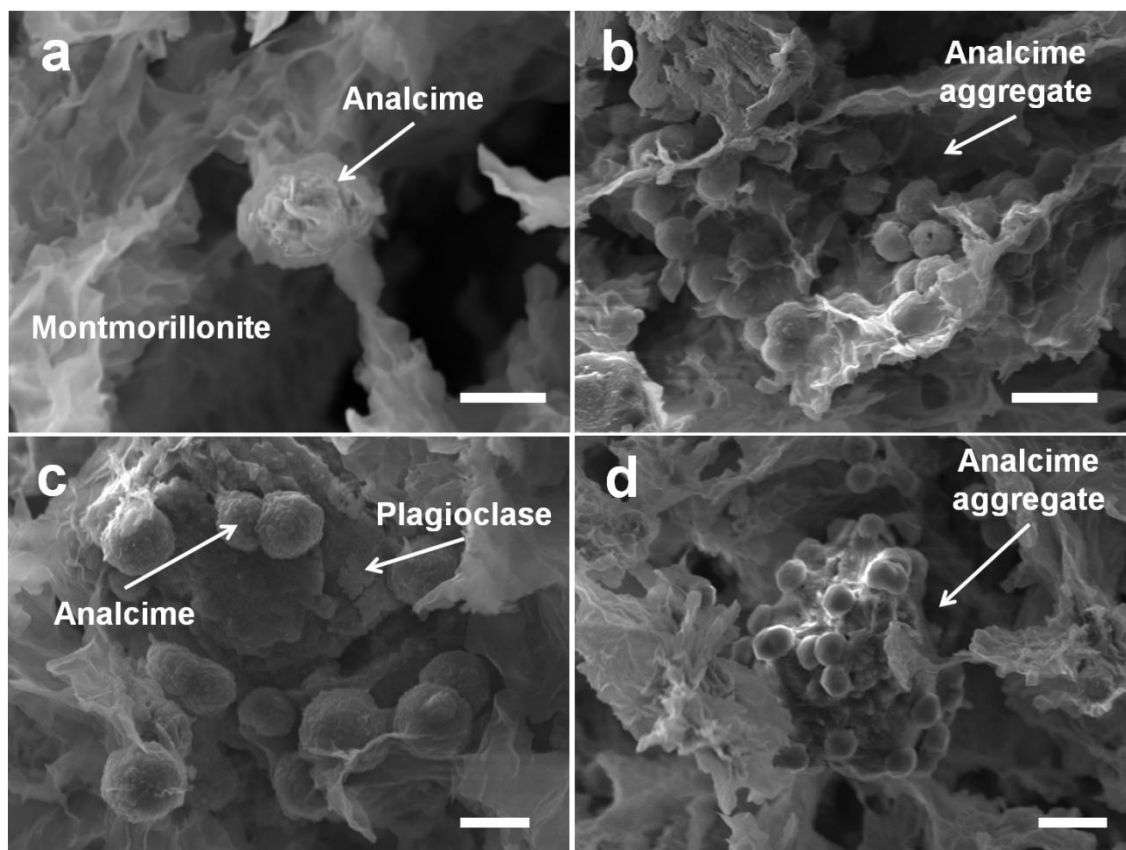


Fig. 2 - 4 SEM images of secondary analcime in the 12-15 mm section. Scale bars are (a, b, and d) 10 μm , and (c) 5 μm . The crystals of analcime observed are single crystals (a), aggregates on the surface of the montmorillonite (b), and aggregates on the surface of plagioclase (c and d).

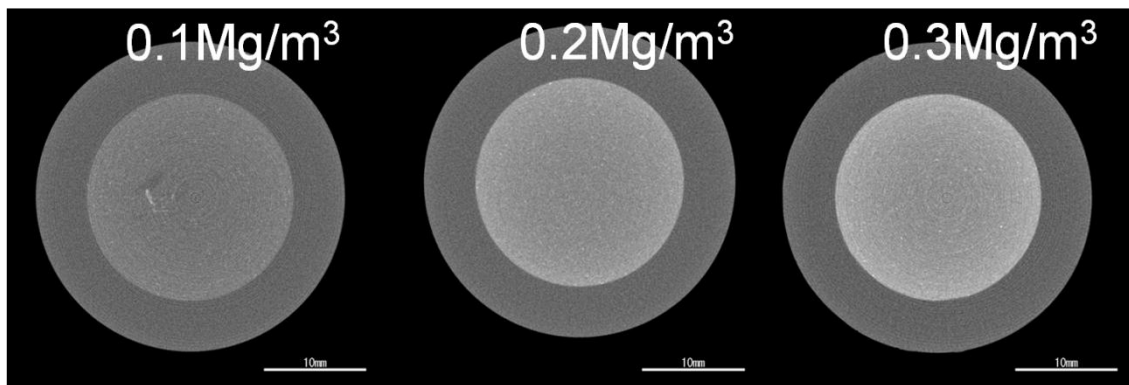


Fig. 2 - 5 CT images of bentonites with different densities. The center of the image where the brightness is high (coloring is lighter) is bentonite and the lower brightness (darker) area around the bentonite is the acrylic column. Scale bars = 10 mm.

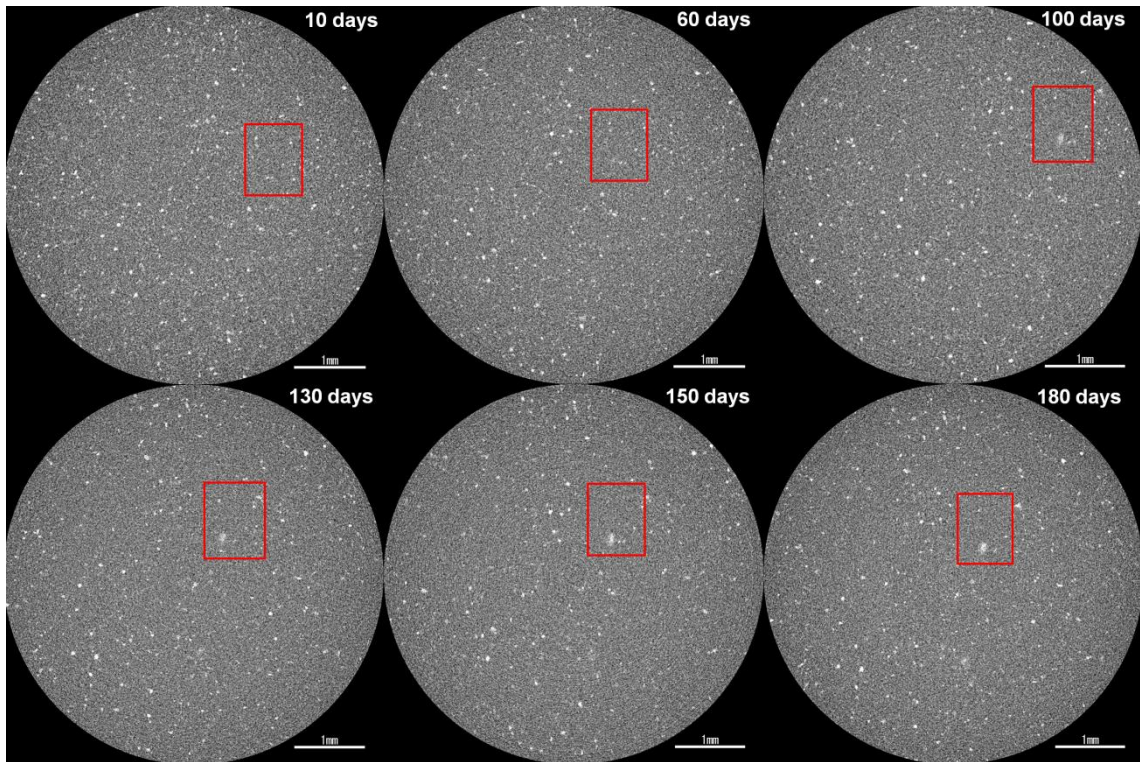


Fig. 2 - 6 CT images of the bentonite column sample (0.3 Mg m^{-3} of dry density) at different durations of the advective experiment. Scale bars = 1 mm.

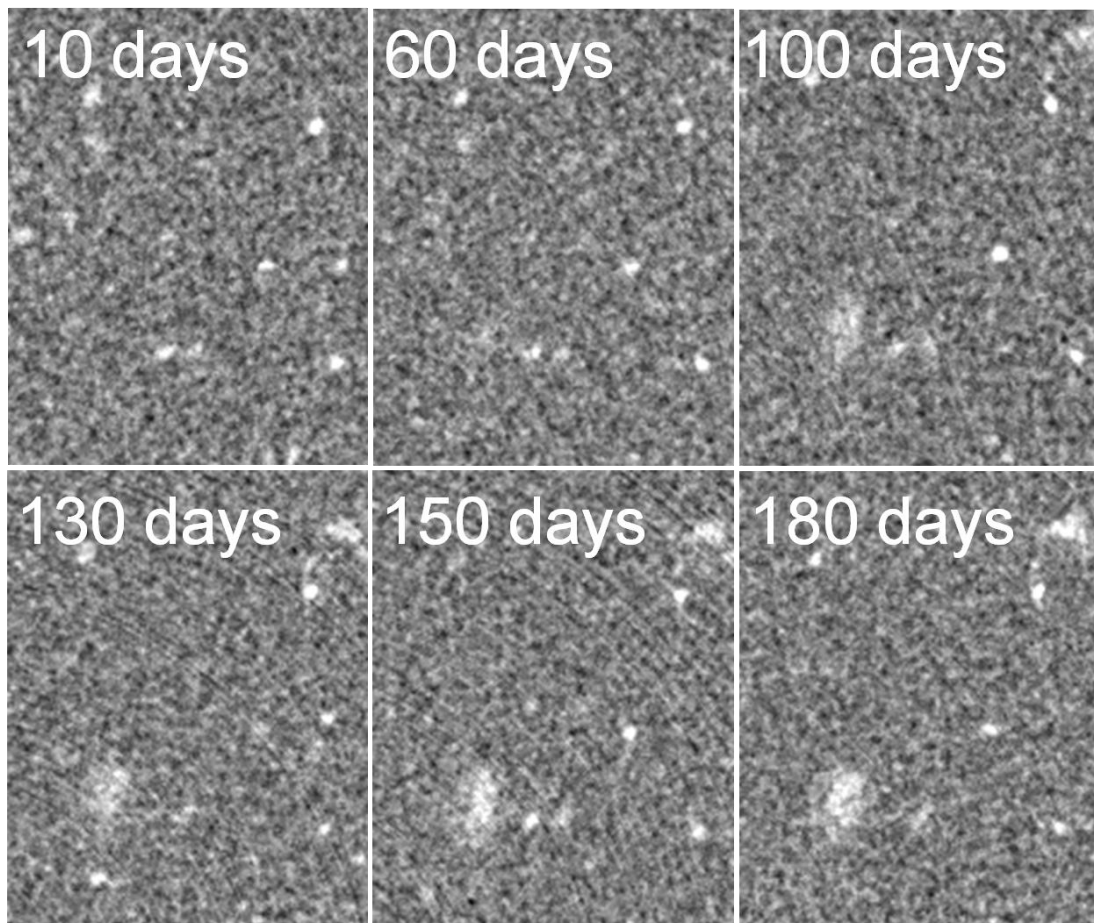


Fig. 2 - 7 CT images of the trimmed ROI (region of interest) of the red rectangles in Fig. 2 - 6.

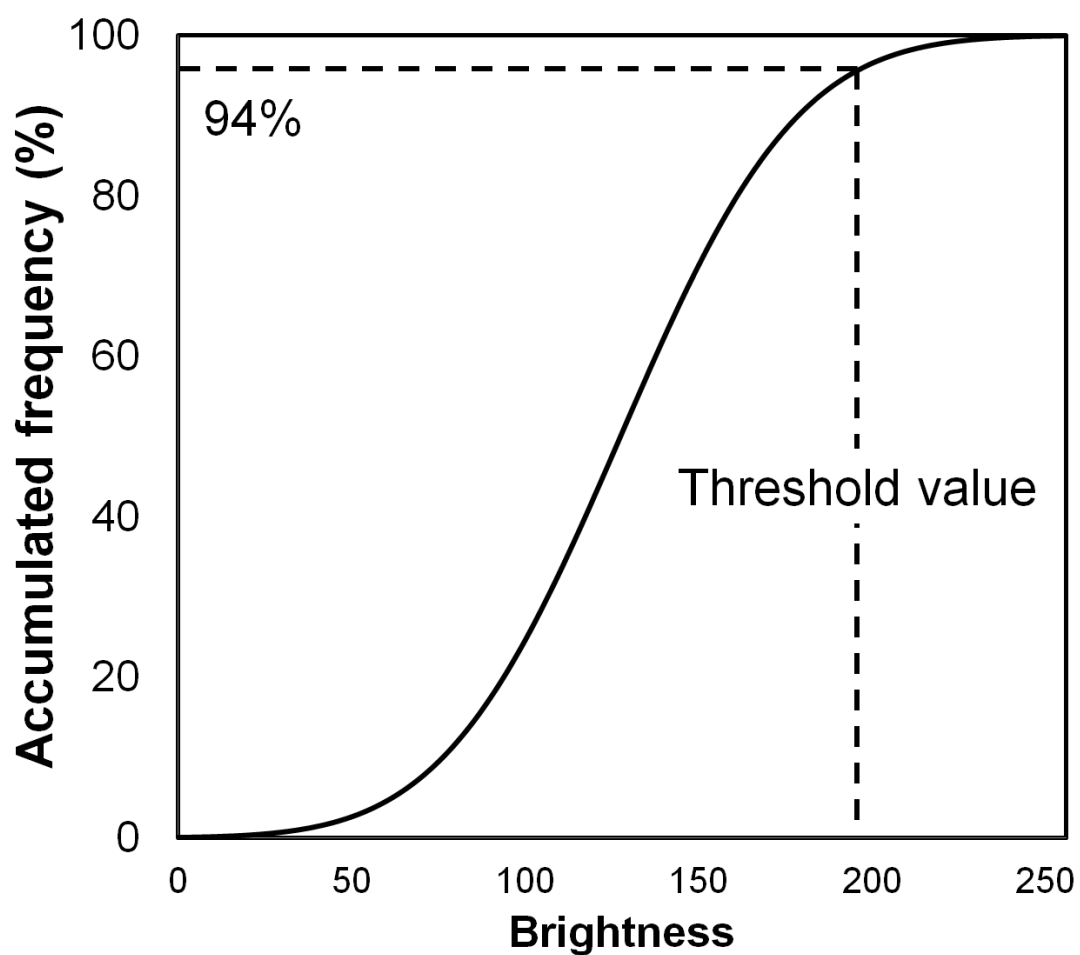


Fig. 2 - 8 Accumulated histogram of the 8-bit voxel brightness of a ROI. In this study, the volumetric fraction of the hydrated montmorillonite is 0.94 and that of accessory and secondary minerals are 0.06. The threshold value between the hydrated montmorillonite and accessory/secondary minerals was given by the brightness at 0.94 of the accumulated frequency.

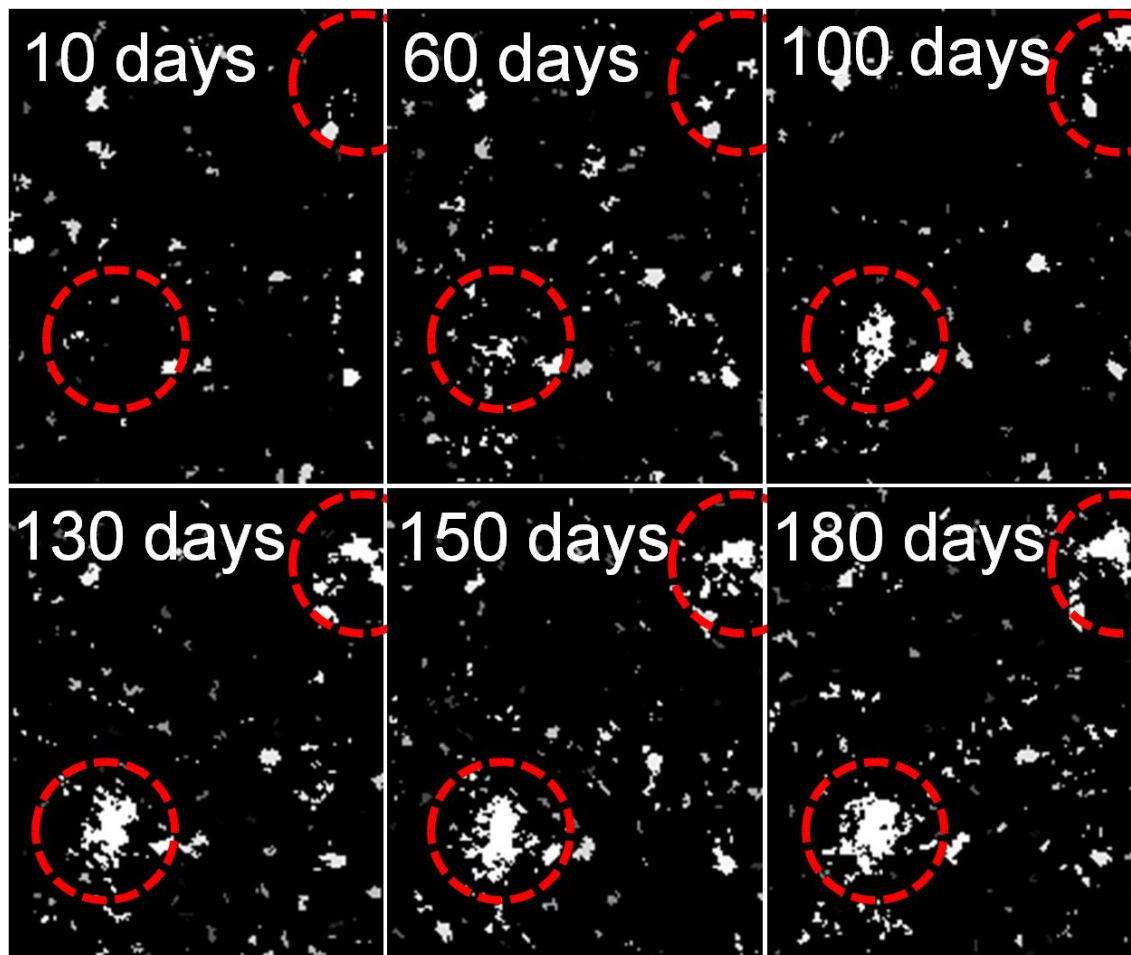


Fig. 2 - 9 Binary CT images of the trimmed ROI (region of interest) in the red rectangles in Fig. 2-5. White dots are secondary minerals, accessory minerals, and an error component. The volumes of the white dot clusters increase (inside the red dashed circles) with time, and indicate the formation of secondary minerals.

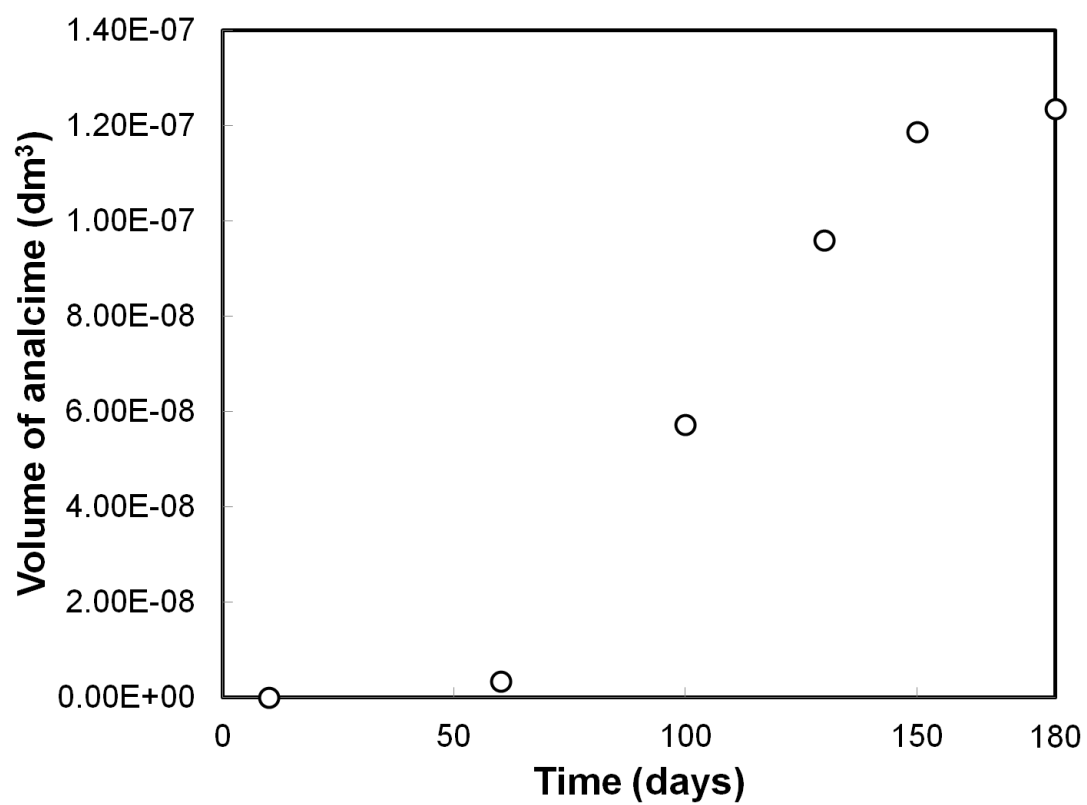


Fig. 2 - 10 Volume of the secondary mineral calculated based on the CT image analysis at different experiment durations.

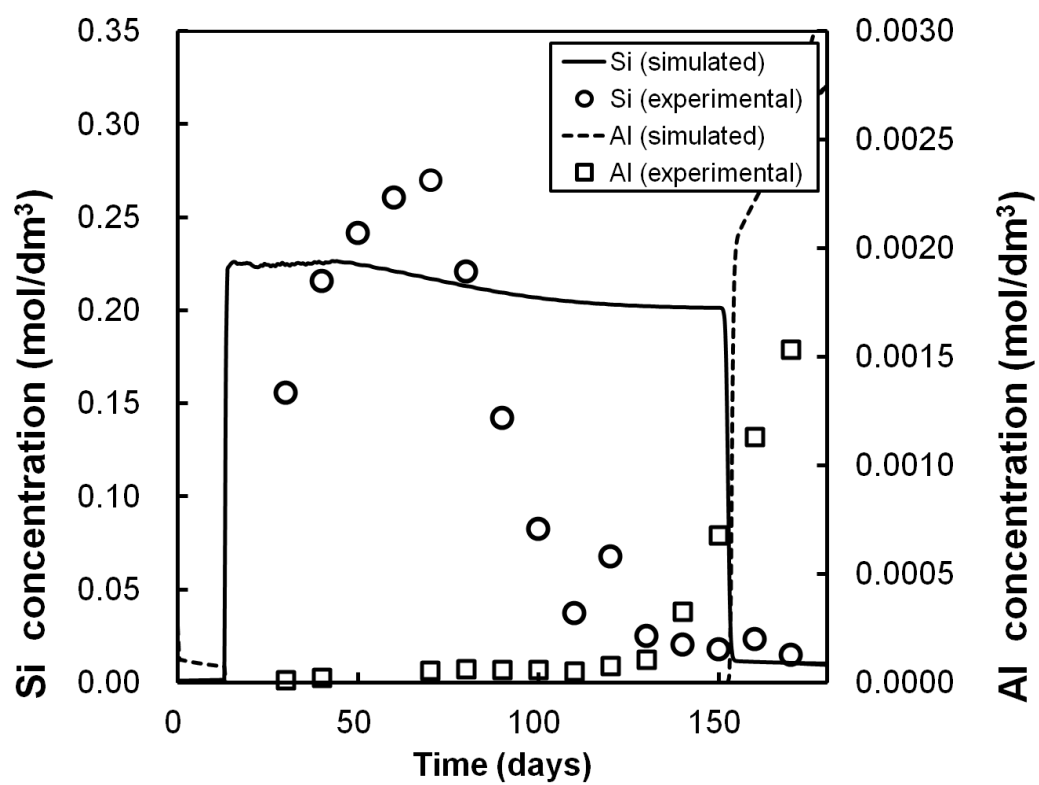


Fig. 2 - 11 Experimental and calculated concentrations of silica and aluminum in output solution using Sato-TST model.

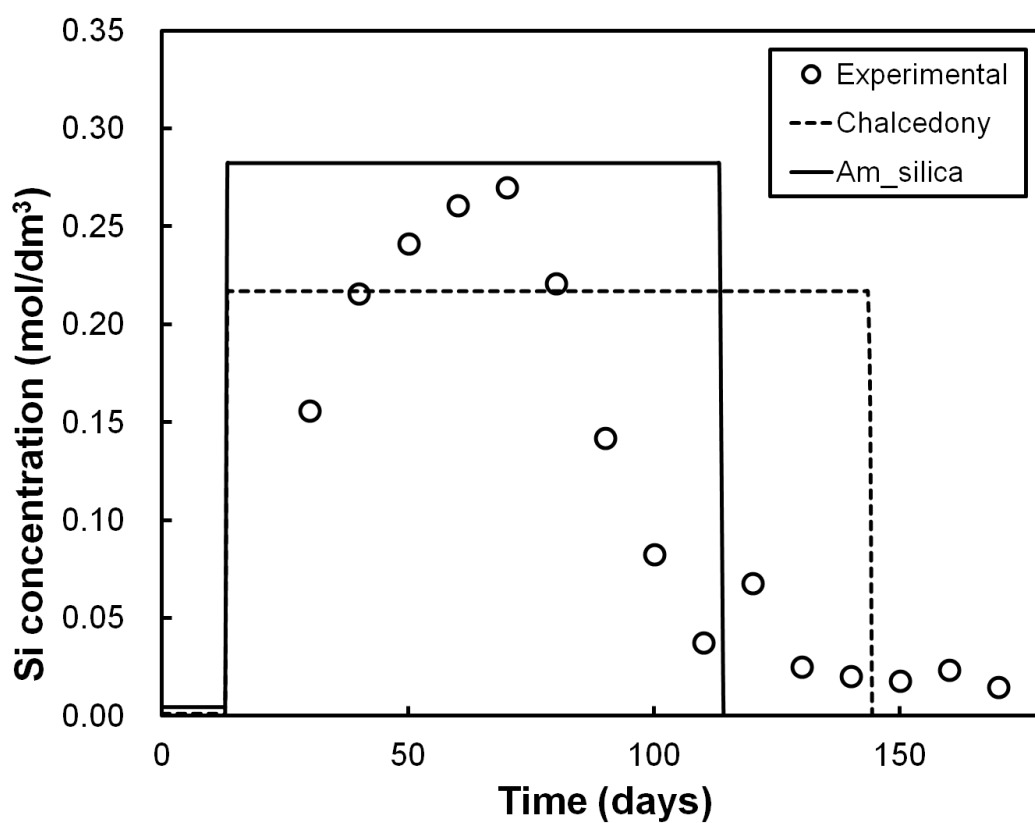


Fig. 2 - 12 Experimental and calculated concentrations of silica. Thermodynamic data of chalcedony and amorphous silica was involved in the simulation.

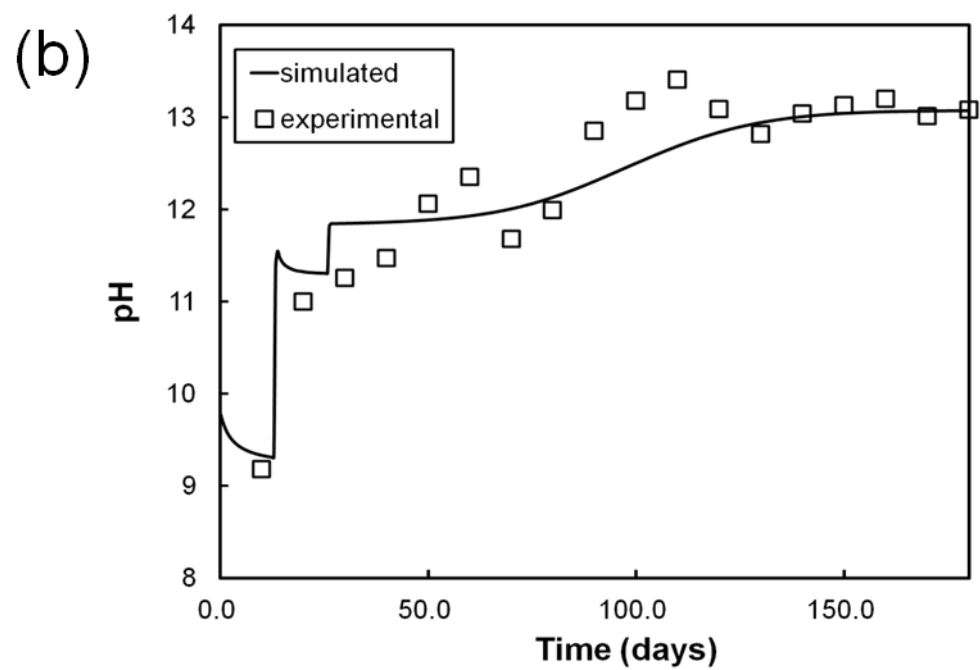
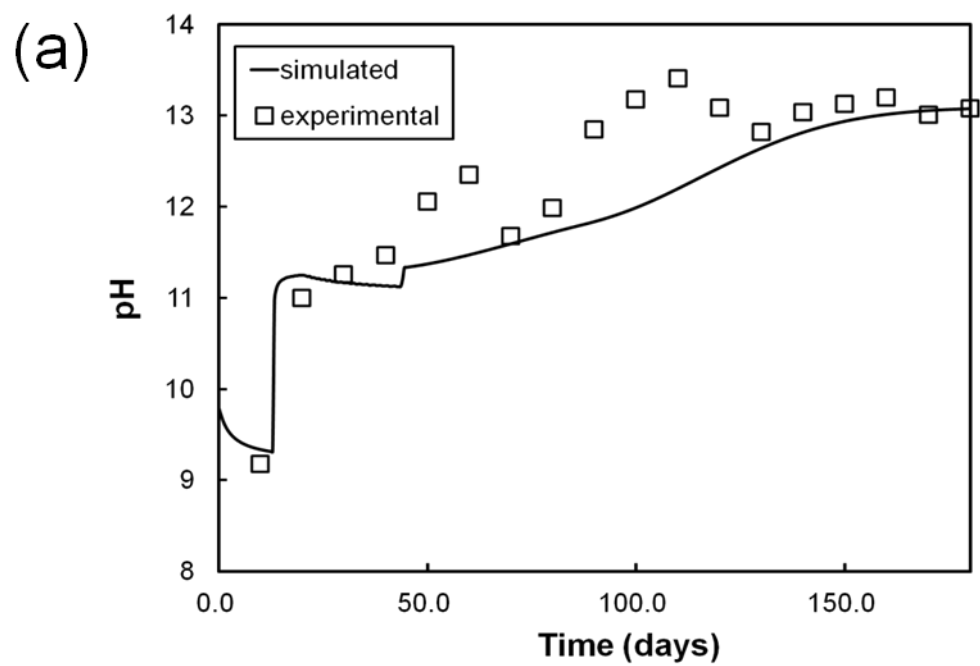


Fig. 2 - 13 Calculated and measured pH changes of the output solution. (a): Sato-TST model, (b): Sato-Oda model.

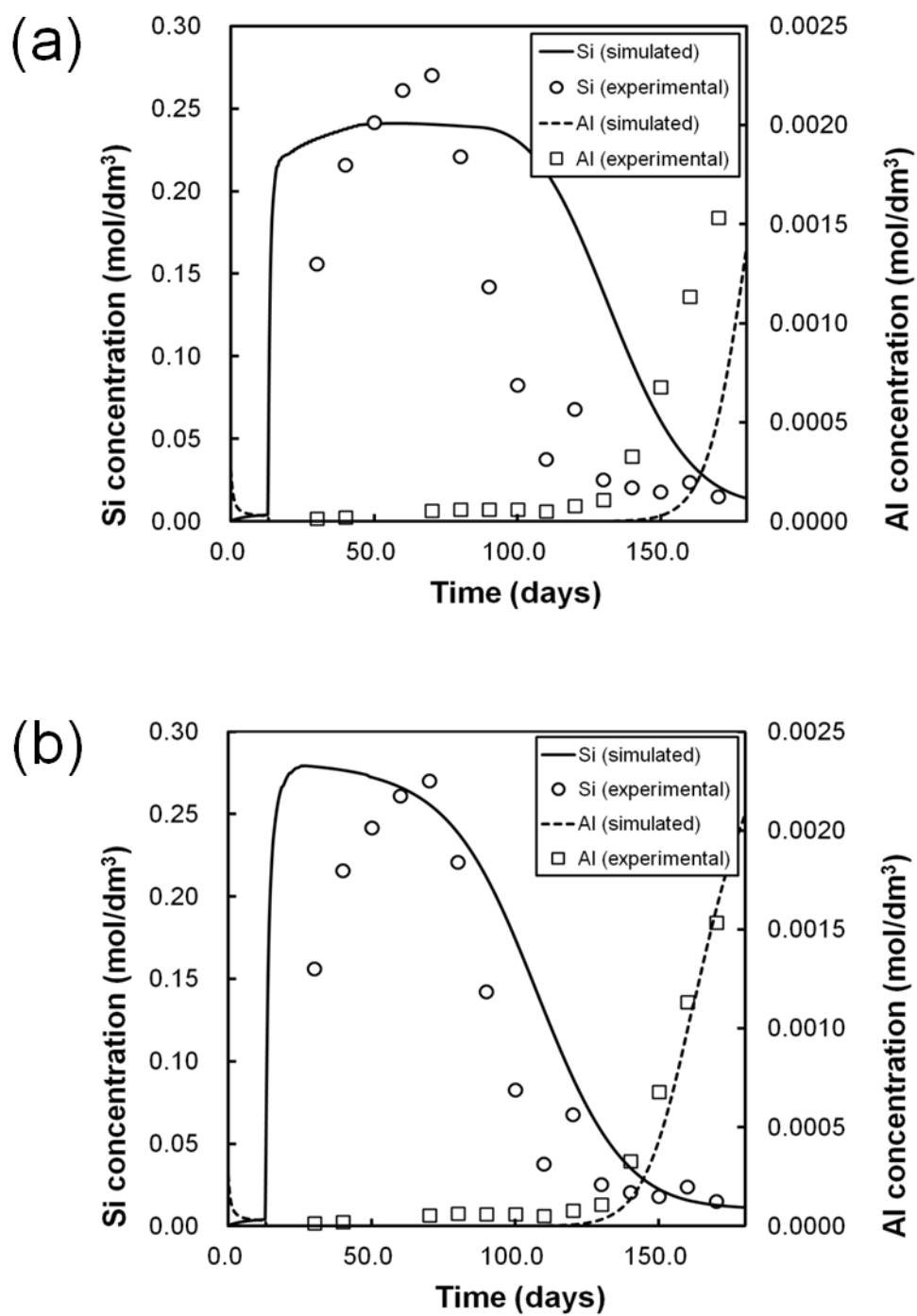


Fig. 2 - 14 Calculated and measured concentration of silica and aluminum in the output solution. (a): Sato-TST model, (b): Sato-Oda model.

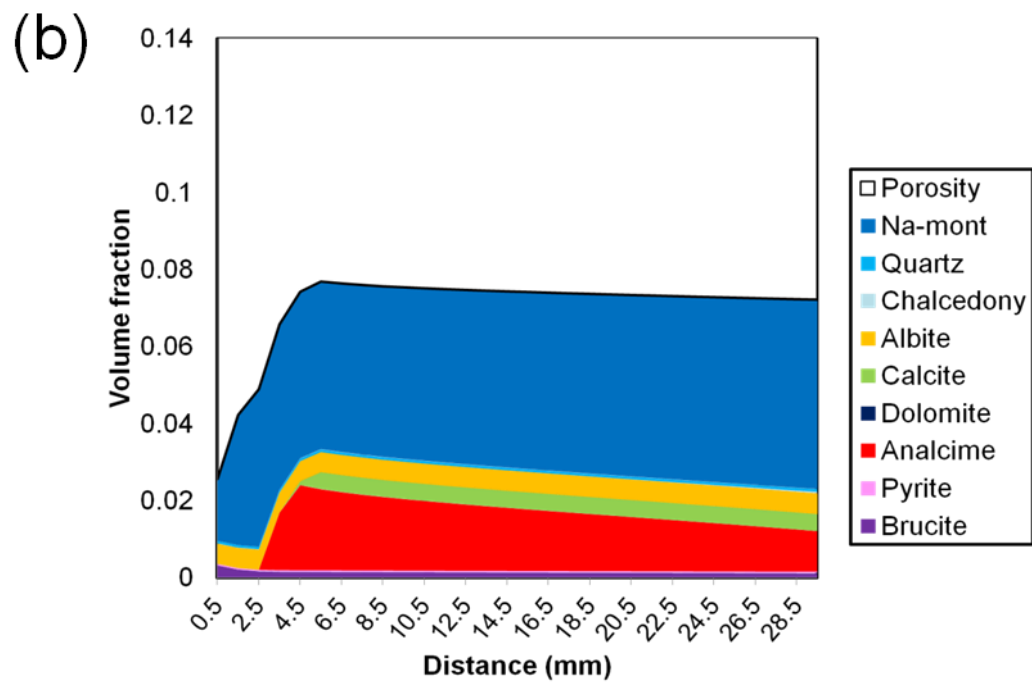
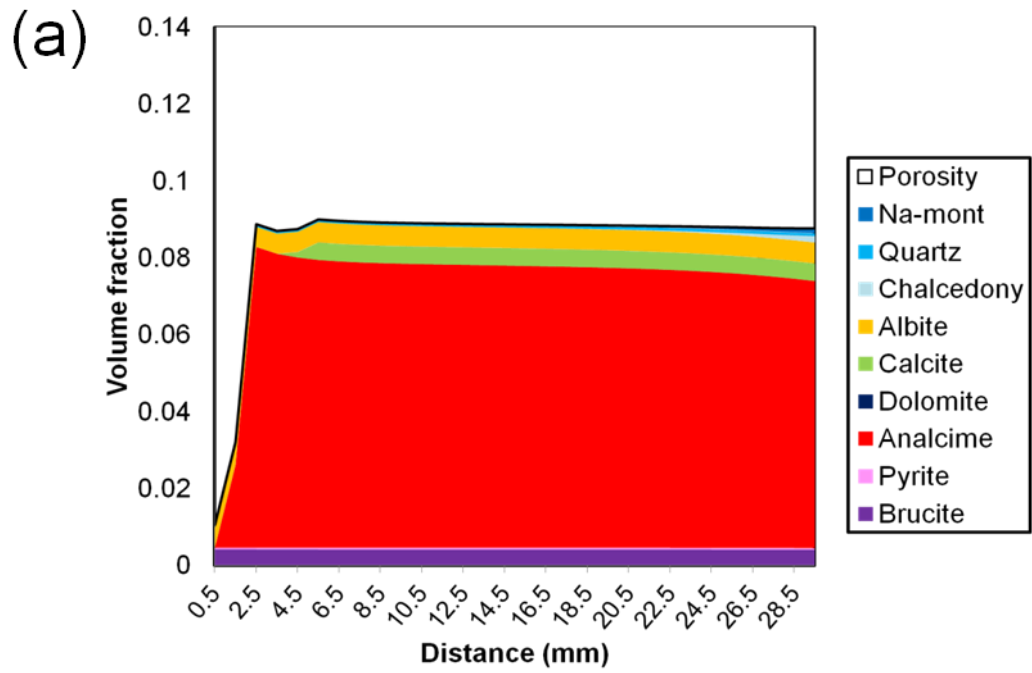


Fig. 2 - 15 Calculated mineralogical distributions in bentonite as a function of distance. (a): Sato-TST model, (b): Sato-Oda model.

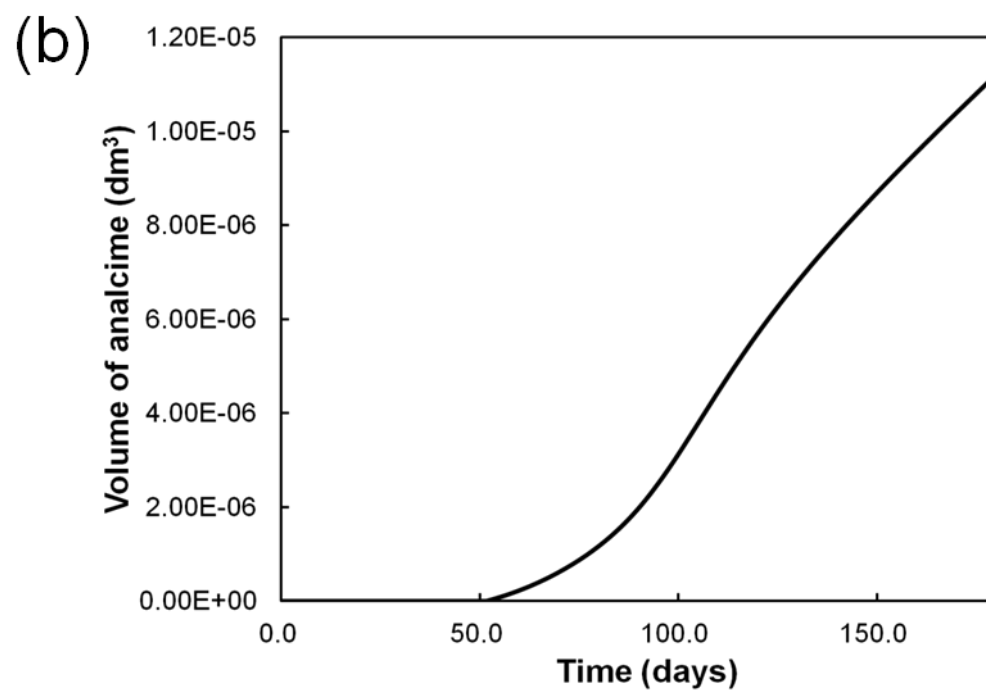
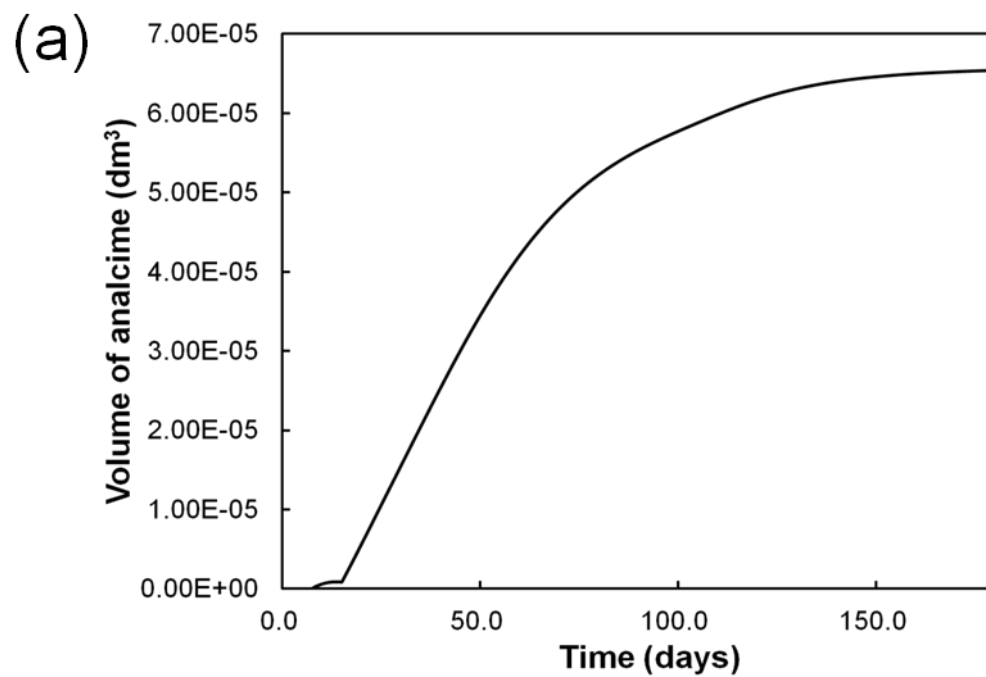


Fig. 2 - 16 Calculated volume of analcime in the 12 – 15 mm section. (a): Sato-TST model, (b): Sato-Oda model.

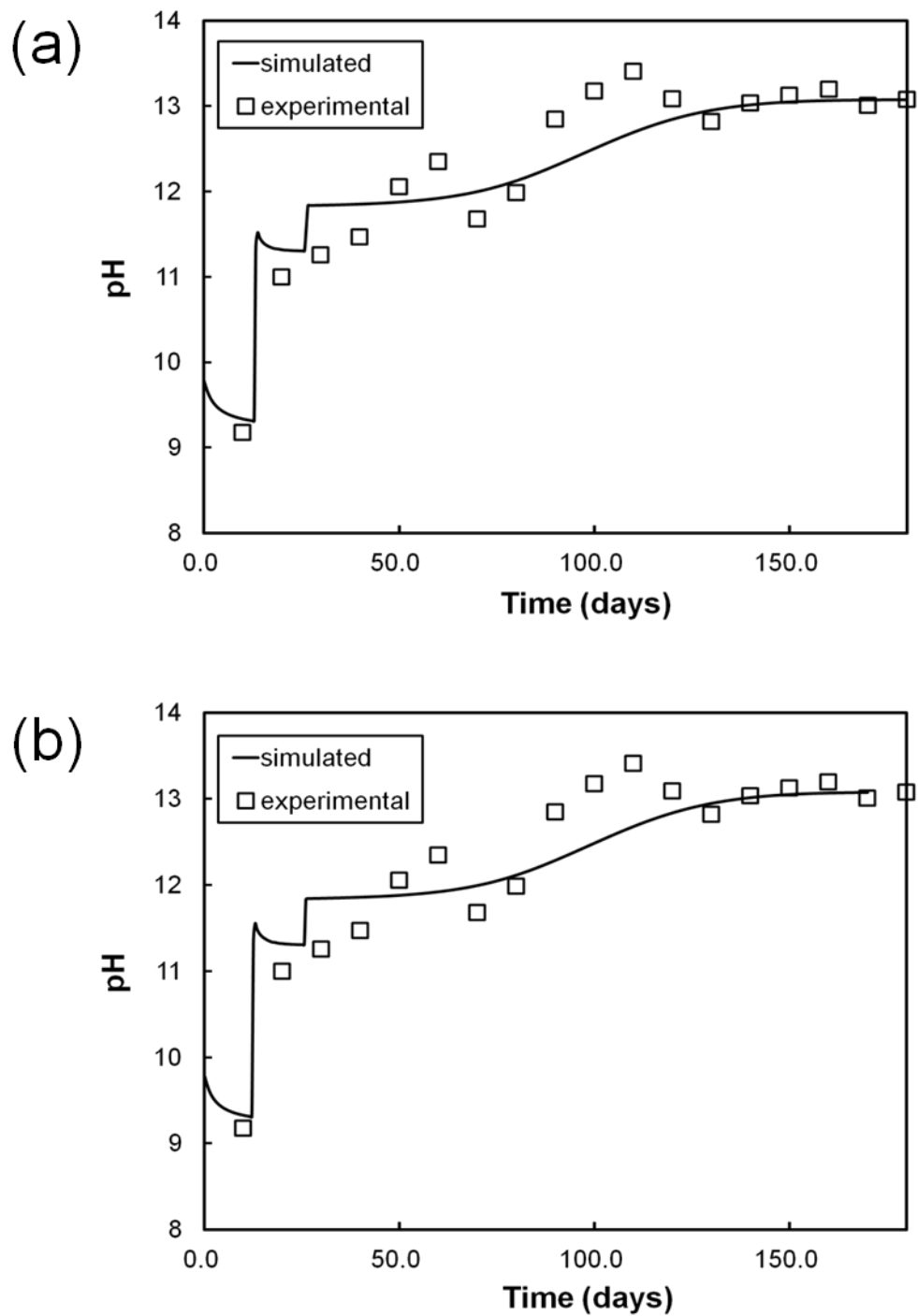


Fig. 2 - 17 Calculated and measured pH changes of the output solution. (a): Sato-TST model modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite, (b): Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.

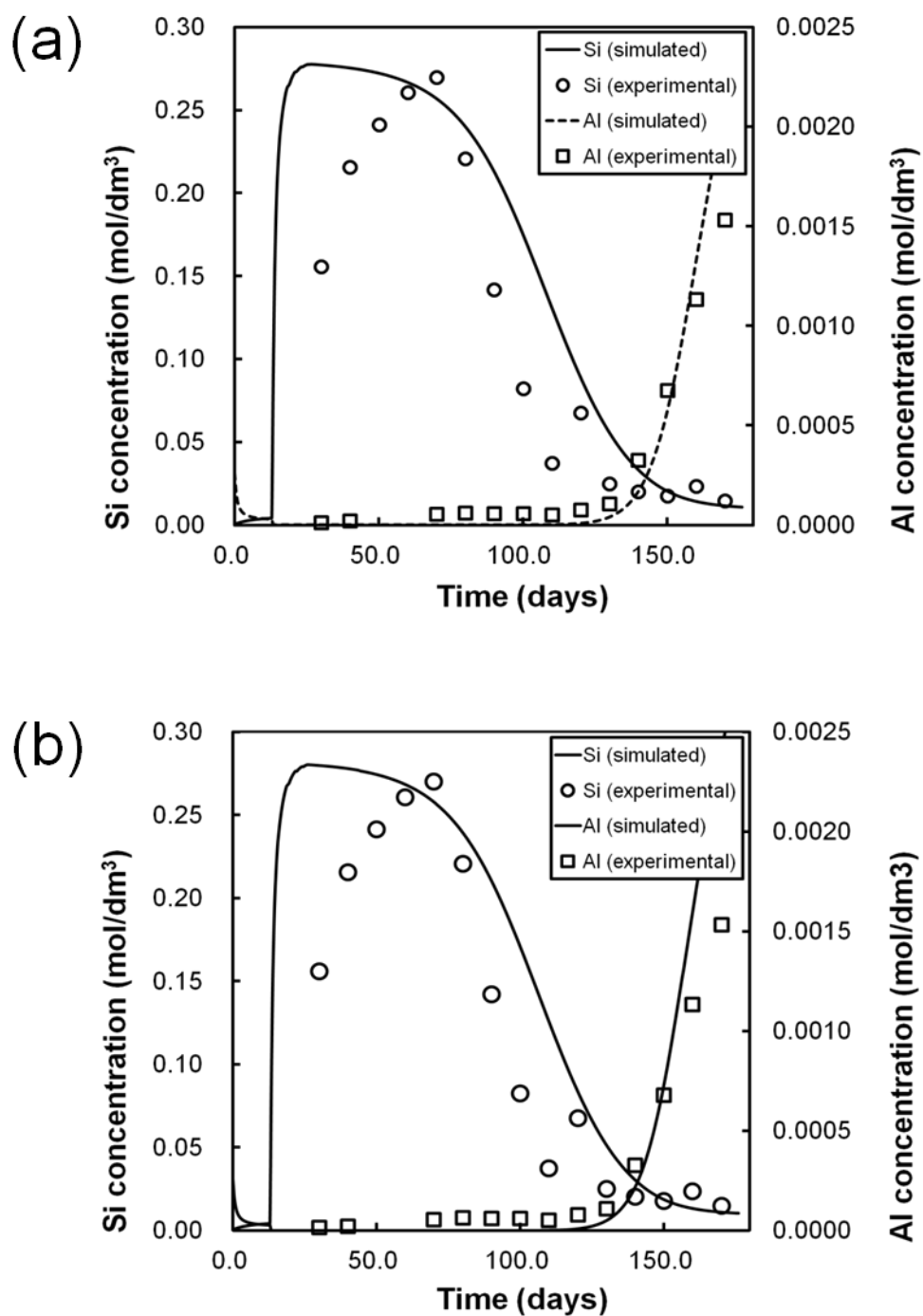


Fig. 2 - 18 Calculated and measured concentration of silica and aluminum in the output solution. (a): Sato-TST model modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite, (b): Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.

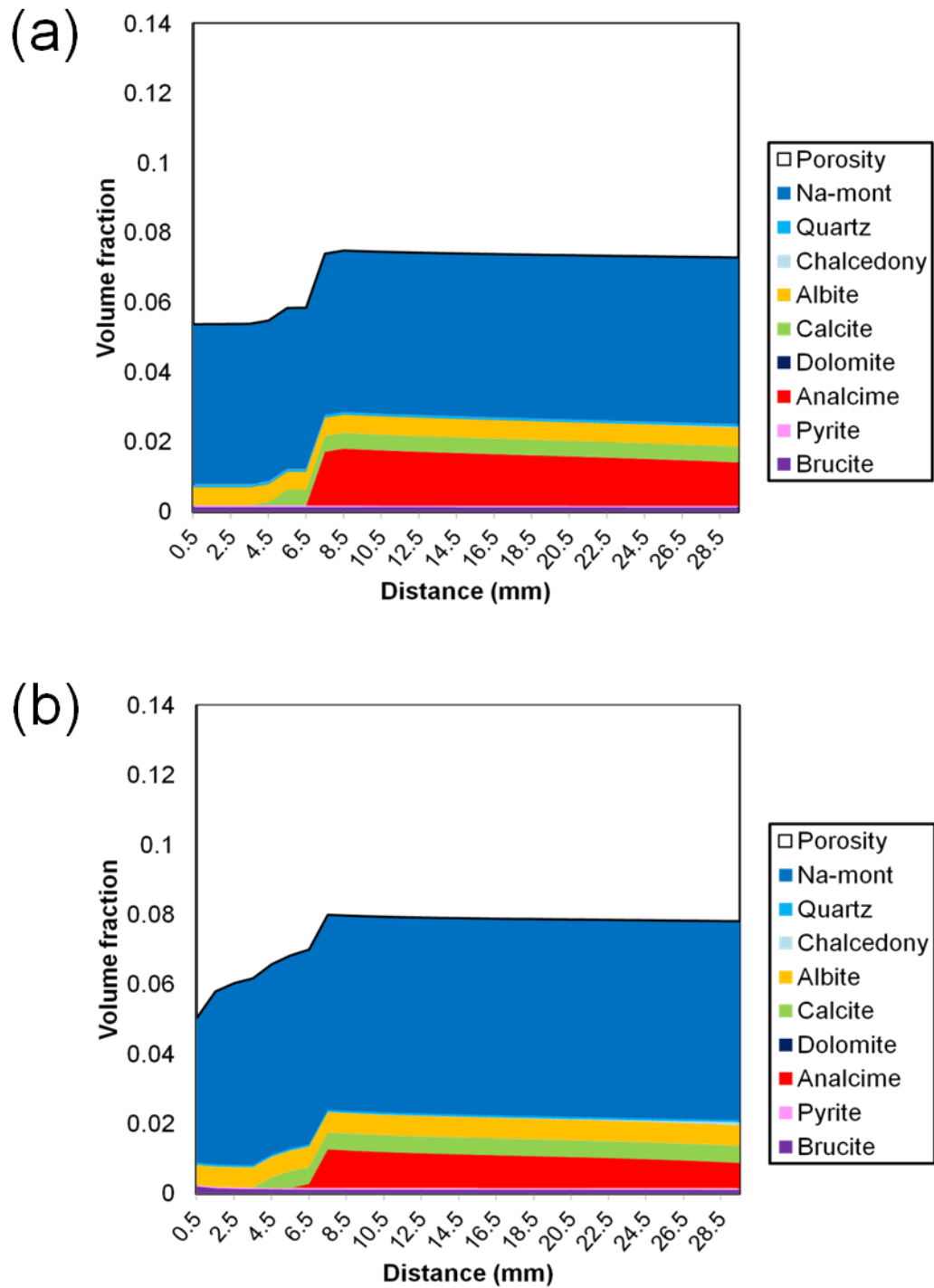


Fig. 2 - 19 Calculated mineralogical distributions in bentonite as a function of distance. (a): Sato-TST model modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite, (b): Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite

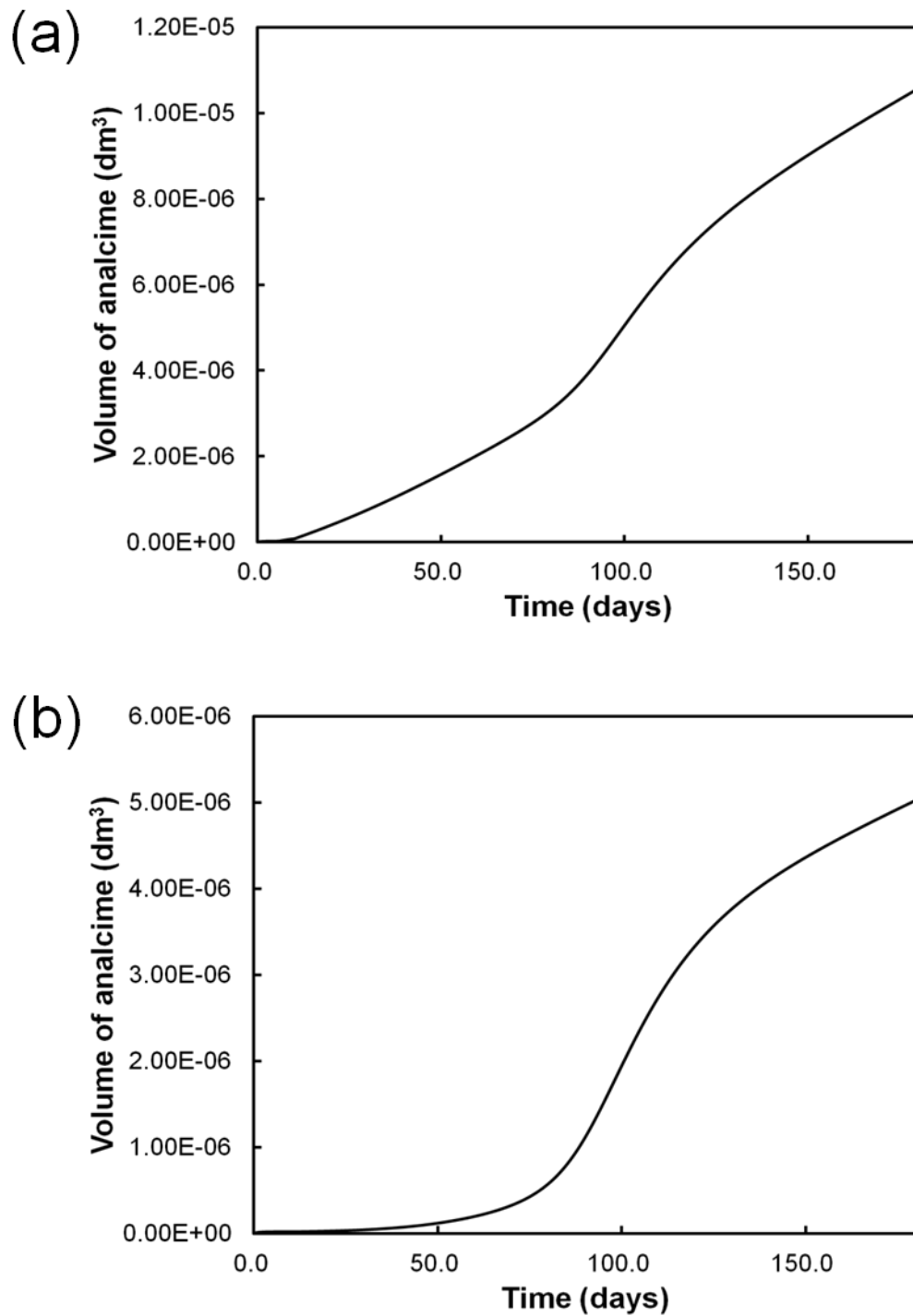


Fig. 2 - 20 Calculated volume of analcime in the 12 – 15 mm section. (a): Sato-TST model modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite, (b): Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.

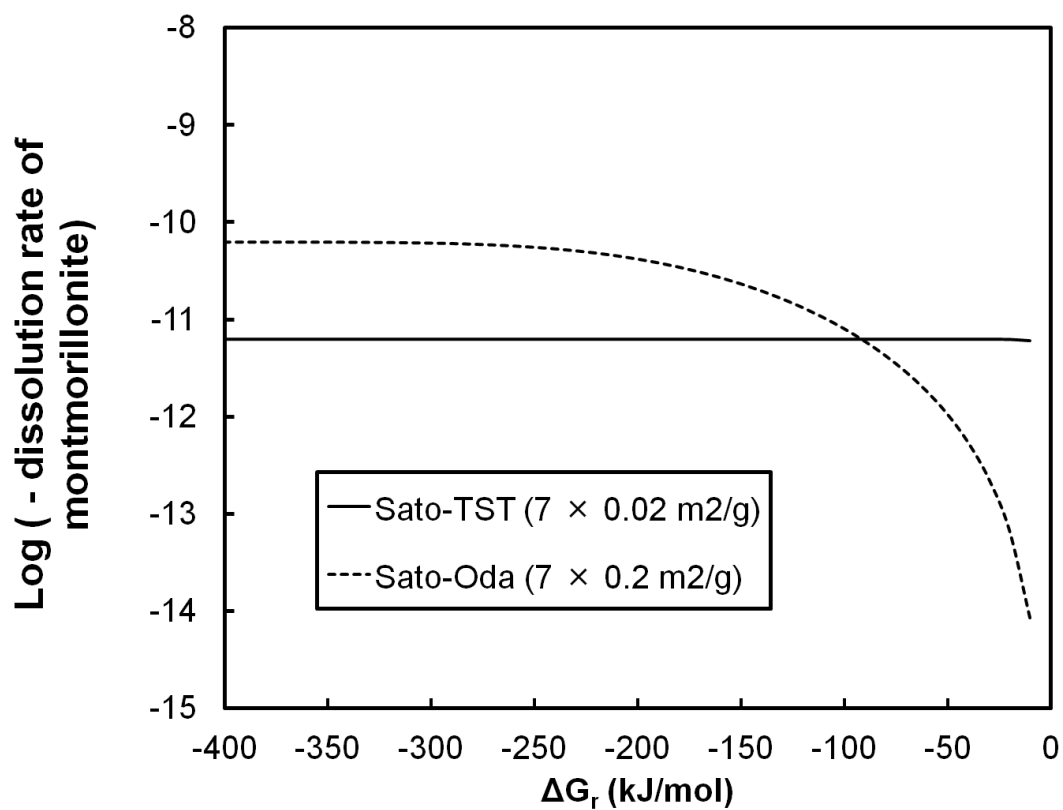


Fig. 2 - 21 Effect of the degree of saturation on montmorillonite dissolution rate (Sato-TST equation modified with $7 \times 0.02 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite and Sato-Oda equation modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite).

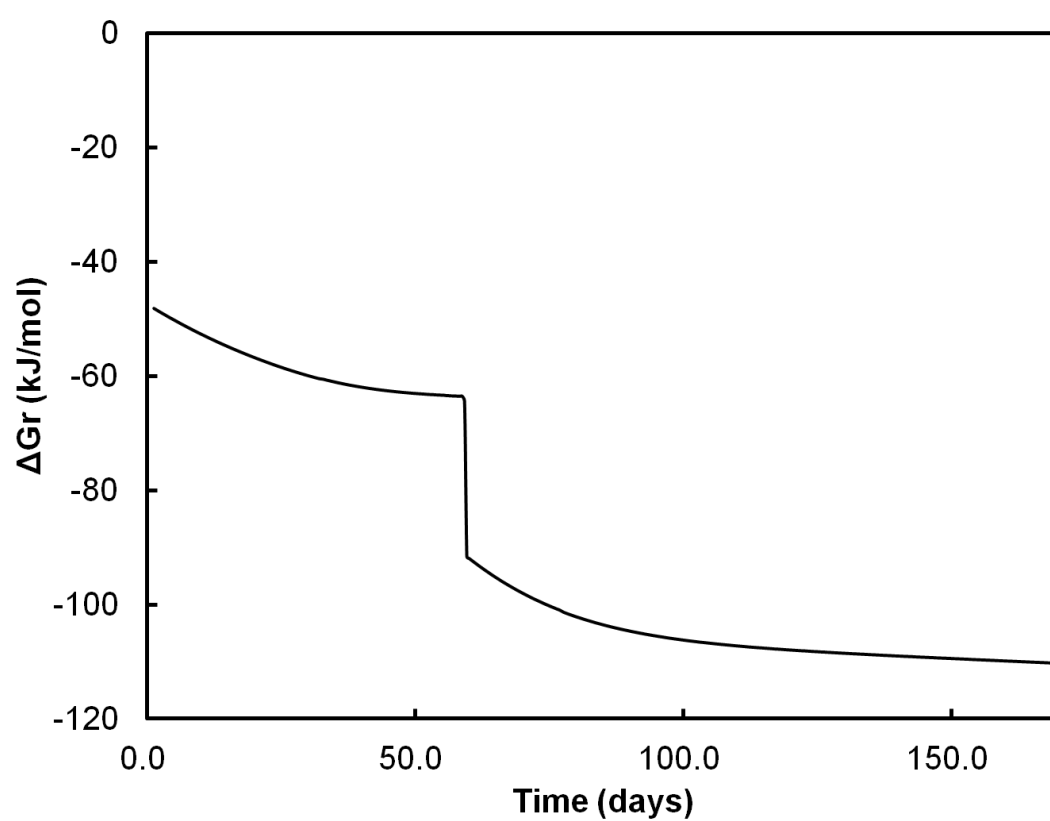


Fig. 2 - 22 Calculated the Gibbs free energy with respect to montmorillonite in the 0-2 mm section in Sato-Oda model modified with $7 \times 0.2 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite.

Chapter 3 Quantitative analysis for dissolution of silica minerals in the compacted bentonite at hyperalkaline conditions by X-ray computed tomography and geochemical modeling

3.1 Introduction

Chapter 2 shows that a microstructural analytical method for quantitative evaluation of the formation of secondary minerals as a function of time was developed. The formation of secondary minerals significantly affects the dissolution of montmorillonite in bentonite (Oda et al., 2004, Takase et al., 2004). On the other hand, the dissolution of silica minerals in bentonite also affect the dissolution of montmorillonite in bentonite as well as formation of secondary minerals by initiating changes in pore water chemistry including the saturation state. The bentonite “Kunigel V1”, which is considered to be used in radioactive disposal barriers in Japan, actually contains a large amount (~50 %) of accessory silica minerals, such as chalcedony and quartz. Dissolution of the silica minerals may inhibit the dissolution of montmorillonite in the bentonite by increasing the silica concentration and hence the saturation state with respect to montmorillonite in the pore water. Therefore, the objectives of this study are to examine the dissolution kinetics of the silica minerals and the effect of dissolved silica on the dissolution of montmorillonite in a compacted bentonite using X-ray computed tomography (CT) and geochemical modeling.

3.2 Material and methods

3.2.1 Experimental

The Japanese reference bentonite (“Kunigel V1” from the Tsukinuno Mine, Yamagata, Japan) was used in the experiments, and the mineralogical composition of Kunigel V1 was shown in Table 1 - 1 (Ito et al., 1993). An acrylic column ($\phi = 20\text{mm}$, $h = 30\text{mm}$) was used for advective alteration experiments as it is able to transmit X-rays. The advective experiment was performed at 70 °C for 360 days using bentonite with a dry density of 0.3 Mg m^{-3} , lower than the dry density of bentonite ($\sim 1.6 \text{ Mg m}^{-3}$) considered for use in radioactive disposal barriers in Japan (JAEA and FEPC, 2007). A 0.3 M

NaOH solution (pH 13.5 at 25°C), a representative cement pore water of early leaching of alkaline hydroxides was passed through the bentonite specimen with flow pressure of 0.03 MPa.

In the advective alteration experiment, the effluent was collected and the permeability coefficient and pH were measured periodically (pH meter, WM-22, TOADKK). The concentration of dissolved aluminum in the effluent was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu), and the dissolved silica concentrations were determined with molybdenum-blue spectrometry by ultraviolet visible absorption spectroscopy (UV-VIS, V-550, JASCO).

After completion of the experiments, the reacting solid was analyzed by X-ray diffractometry (XRD, Rint2000, Rigaku operating at 40 kV and 30 mA with a 1°/min scanning rate, 1.0°divergence, 1.0°scattering, and 0.3 mm receiving slits) with the preferred orientation method to identify the mineral phases using oriented sample on glass and to confirm the dissolution of montmorillonite using oriented sample treated with ethylene glycol on glass. The bentonite specimen was divided into seven sections for XRD analysis from the input side: 0–1 mm, 1–2 mm, 2–3 mm, 3–6 mm, 6–9 mm, 9–12 mm, 12–15 mm, 15–18 mm, 18–21 mm, 21–24mm, 24–27mm, 27–28 mm, 28–29 mm, and 29–30mm.

3.2.2 X-ray CT observation and imaging processes

The inner structure of the bentonite specimens was observed every 10 days by the micro-focus X-ray CT (TOSCANER 31300 μC^3 , TOSHIBA IT Solutions) at Hokkaido University. A 2 mm thick section of the bentonite at the 0–2 mm position from the input side (dry density 0.3 Mg m^{-3}) was observed by X-ray CT. The scanning and imaging conditions for the 0.3 Mg m^{-3} dry density bentonite specimen are shown in Table 3 - 1.

As well as in Chapter 2, a Mathematica based program developed by Nakashima and Kamiya (2007) was used to quantify the volume of minerals in the CT images. The program used the Itrimming.nb and Clabel.nb subroutines to evaluate the volume of minerals in the CT images. The functioning of these programs was explained in Chapter 2.

In this chapter, the volume of dissolved minerals was estimated based on a maximum

likelihood thresholding method considering the effect of mixels (Kato et al., 2008; Yamanaka et al., 2011). The real image including phase 1 and 2 shown in Fig. 3 - 1a was transformed to a quantized image shown in Fig. 3 - 1b. If a voxel includes both phases, the brightness of this voxel takes an intermediate brightness between these two phases. Such a voxel is called a “mixel” shown in Fig. 3 - 1c (Kitamoto and Takagi, 1999). Based on this, a maximum likelihood thresholding method considering the effect of mixels was used to set an appropriate threshold value of brightness between hydrated montmorillonite and accessory minerals. Fig. 3 - 2 shows that the histogram of brightness in Fig. 3 - 1c. t1 and t2 are boundary of brightness between class1 and 3, class 2 and 3, respectively. In this chapter, t2 was used to binarize the CT images obtained for discrimination between the hydrated montmorillonite and accessory minerals because the binarization of CT image using the t1 as threshold value was not successful, which overestimated the volume of accessory minerals visually.

3.2.3 Modeling approach

The geochemical modeling approach used in this chapter is similar to the one used in Chapter 2. The geochemical model used in Chapter 2 considered analcime formation based on thermodynamic data. However, analcime formation was considered based on kinetic data to simulate the experimental results in this chapter.

The one dimensional geochemical reactive transport code PHREEQC (Parkhurst and Appelo, 1999) was used to simulate the advective alteration experiment for bentonite with dry density of 0.3 Mg m^{-3} . The analysis also used the thermodynamic database Thermoddem obtained from <http://thermoddem.brgm.fr> (Blanc et al., 2012). The thermodynamic properties of the minerals considered in this simulation are tabulated in Table 2 - 2. Only advective transport mechanisms were taken into account in this model because the experiments were conducted with a flow velocity that is sufficiently rapid to disregard diffusion mechanisms. Cation exchange properties were not included due to the high concentration of sodium ions in the reacting solution.

The dissolution/precipitation of montmorillonite, quartz, chalcedony, albite, and analcime were modeled based on available kinetic data while calcite, dolomite, and pyrite were modeled based on thermodynamic considerations. The rate equations (mol

$\text{dm}^{-3} \text{s}^{-1}$) for the dissolution of montmorillonite considered in this work are described by Eq. (2-7). The rate equations ($\text{mol dm}^{-3} \text{s}^{-1}$) for the other minerals are as described by Eq. (2-9). The kinetics parameters of quartz, albite, and chalcedony were as reported in the literature (Table 3 - 2).

3.3 Results and discussion

3.3.1 Advective alteration experiments

The pH (25°C) of the output solution decreased from 13.5 to 10.5 during the initial 20 days of the experiment due to the buffering capacity of the montmorillonite and dissolved silica components including $\text{H}_2\text{SiO}_4^{2-}$, increased to around 13.0 from 20 to 100 days, and remained approximately the same beyond 100 days (Fig. 3 - 3a). The permeability coefficient of bentonite with a dry density (0.3Mg m^{-3}) was measured in advective alteration experiments. The values of the coefficient ranged from $9.67 \times 10^{-11} \text{ m s}^{-1}$ to $5.20 \times 10^{-10} \text{ m s}^{-1}$ throughout the experiments (Fig. 3 - 3b). The dissolved silica concentration in the effluent increased gradually until 80 days due to dissolution of chalcedony, then decreased from 80 to 200 days, and after 200 days maintained a constant value (Fig. 3 - 3c). The dissolved aluminum concentrations maintained constant values until 200 days, due to the potential effect of silicon inhibition on the montmorillonite dissolution rate (Cama et al., 2000). The dissolved aluminum in the effluent increased gradually until 260 days, and after 260 days maintained a constant value.

XRD patterns of the bentonite in different sections of the column after 360 days using oriented samples treated with ethylene glycol on glass show that the peak intensity at 7.1° for the basal (001) reflection of the montmorillonite decreased near the input side (0 to 3 mm), suggesting that small amounts of montmorillonite were dissolved due to reaction with the fresh solution (Fig. 3 - 4a). Concerning the precipitation/dissolution of minerals, XRD patterns of the bentonite in different sections of the column after 360 days using oriented sample on glass show that the analcime peaks appear in the whole sections, and quartz or chalcedony peaks disappear in the whole sections (Fig. 3 - 4b). The bentonite specimen used in this experiment includes quartz and chalcedony with weight percentages of 0.6 and 38.0, respectively. Quartz is thermodynamically more

stable than chalcedony. Therefore, it was inferred that the decrease of peak intensity was due to dissolution of chalcedony.

3.3.2 Observations by X-ray CT

The advective experiment was conducted using bentonite with a dry density of 0.3 Mg m^{-3} and the compacted bentonite specimen had been maintained in a vacuum vessel in deionized water for 1 month prior to the experiment. Fig. 3 - 5 shows CT images of the bentonite sample at different time points during the advective experiment, and indicates the presence of high density particles (lighter colored dots in the CT images, accessory and secondary minerals), as well as lower density particles (darker colored dots in the CT images, hydrated montmorillonite) in the bentonite. Lighter colored dots disappeared as the experiment progressed (Fig. 3 - 5). This is attributed to the dissolution of accessory minerals. The XRD analysis showed that chalcedony was dissolved at the section observed by X-ray CT after 360 days (Fig. 3 - 4b). However, discrimination of accessory minerals from the secondary minerals is difficult to determine based on only the brightness in the CT images. Therefore, in this chapter, the volume of dissolved minerals including a small amount of secondary minerals was quantified by image processing, which will be explained next.

Firstly, as in the image processing in Chapter 2, images of trimmed ROI (regions of interest) were generated from the CT images by Itrimming.nb (Nakashima and Kamiya, 2007). For example, the black squares in Fig. 3 - 5 were selected and trimmed. Secondly, Clabel.nb was used to calculate the volume of accessory and secondary minerals in the trimmed ROI. The Clabel.nb program requires the determination of a threshold value t_2 of the brightness shown in Fig. 3 - 2 that distinguishes between hydrated montmorillonite and accessory minerals in the ROI. Here, the threshold value was determined based on a maximum likelihood thresholding method considering the effect of mixels (Fig. 3 - 6). This determination method needs to obtain a histogram with two peaks which is called “bimodal” in ROI. For example, the dashed square (a) including two phases (white dots and gray dots) in Fig. 3 - 6 was selected and the histogram (a) with one peak was obtained. It is due to the volume percentage of the hydrated montmorillonite in the dashed square (a) of Fig. 3 - 6 being more dominant than that of

accessory minerals. On the other hand, the solid square (b) including two phases (white dots and gray dots) in Fig. 3 - 6 was selected and the histogram (b) with two peaks was obtained. When the volume percentages of the hydrated montmorillonite and accessory minerals are around 50, respectively, a bimodal histogram was obtained successfully. Therefore, the analysis described above was performed for 100 points in ROI shown in Fig. 3 - 5 and obtained the threshold values t_2 . The averaged t_2 value was used for Clabel.nb to obtain the binary CT images of the trimmed ROI in the black rectangle in Fig. 3 - 5 (Fig. 3 - 7), and to quantify the volume of accessory minerals.

The total volume of white voxels was estimated at different experiment durations from Fig. 3 - 7. The total volume of white voxels at 0 day set to 100 %, and the residual volume percentage of accessory minerals at different experiment durations were calculated (Fig. 3 - 8). The residual volume percentages of accessory minerals vs. time shows that significant accessory minerals started to decrease until ~60 days, and that the residual volume converged gradually to a constant value after ~200days (Fig. 3 - 8). This decrease of the volume of accessory minerals is attributed to dissolution of chalcedony from XRD results (Fig. 3 - 4b). The pattern that indicated the constant values around 20 % after ~200 days is due to remaining primary minerals such as quartz, plagioclase, analcime, calcite, dolomite, and pyrite and also to the formation of small amounts of analcime as a secondary mineral in this specimen.

3.3.3 Modeling

The volume of accessory minerals dissolved as a function of time in the sections observed by X-ray CT analysis were used to validate a geochemical model simulating the experimental results using PHREEQC code. Chapter 2 indicated that the dissolution rate of montmorillonite in compacted systems is slower than that of montmorillonite in powdered system due to the effect of reactive surface area and departure from equilibrium. Therefore, in this chapter, the Sato-Oda equation (Eq. 2-7), modified by reducing the reactive surface area of the powdered montmorillonite, was used to simulate the experimental results. Kinetic equations (Eq. 2-9) for quartz, albite, analcime, and chalcedony were also modified by reducing the surface area and used in addition to that of montmorillonite.

The reactive surface area in the Sato-Oda model (Eq. 2-7) was varied to obtain a dissolution rate of the montmorillonite that is compatible with the experimental results here. The calculations yielded a best fit to the experimental results with the reactive surface area ($7 \text{ m}^2 \text{ g}^{-1}$) multiplied by 0.12. Using the modified dissolution rate of the montmorillonite, the simulated pH and concentrations of dissolved Si and Al in the effluent (Fig. 3 - 9a and Fig. 3 - 9b) agree well with the experimental results. The formation of analcime as a secondary mineral in the bentonite after 360 days was also simulated with the modified Eq. 2-7 (Fig. 3 - 9c) and is predicted to precipitate in the whole section, consistent with the experimental results (Fig. 3 - 4b). The simulated residual volume of accessory minerals agrees well with the experimental results (Fig. 3 - 9d). However, the model simulates the dissolution of dolomite, calcite, and pyrite at 0-2 mm. From XRD results, the peaks of these minerals could not be detected due to the use of small amounts of the sample oriented on glass (Fig. 3 - 4b). Therefore, the mineralogical distribution of dolomite, calcite, and pyrite shown in Fig. 3 - 9c cannot be discussed here. If these minerals were not dissolved at 0-2 mm in this experiment, the residual volume percentage of accessory minerals should increase from 20 to 28 % after 100 days. Therefore, the precipitation/dissolution of calcite, dolomite, and pyrite will have to be modeled based on kinetic data to sufficiently model the experiment.

In this chapter, the section 0-2 mm from input side was observed to exclude the formation of secondary minerals as much as possible, and the residual volume percentage of accessory minerals was quantified accurately. However, another technique of image processing needs to be considered for quantifying the volume change of accessory and secondary minerals more accurately in the near future. For example, an image subtraction technique is appropriate for quantification of accessory and secondary minerals between the CT images before and after the specimen. Before conducting image subtraction, it is necessary to minimize the alignment gap by using the image registration technique (Zitová and Flusser, 2003).

However, due to the bentonite specimen used in this chapter being 0.3 Mg m^{-3} of dry density and thus deformable by alteration and flow pressure, 2D image registration could not be applied in this chapter. Future investigation with more detailed

observations of the dissolution process of accessory minerals by X-ray CT measurements will be necessary to change the experimental conditions such as using the specimen of high dry density for constraining the 3D alignment gap

3.4 Effect of dissolution of silica minerals on dissolution of montmorillonite

The effect of dissolved silica on the dissolution of montmorillonite in compacted bentonite was discussed based on the geochemical transport model consistent with the experimental results. Fig. 3 - 10 shows the dissolution rate of montmorillonite vs. ΔG_r of overall reaction calculated from Sato-Oda equation (Eq. 2-7) at pH 12.1 and 70 °C. The dissolution rate increases as Gibbs free energy decreases (Fig. 3 - 10).

The geochemical transport model simulated the spatial distribution of dissolved silica concentrations and the Gibbs free energy in the bentonite after 60 and 360 days (Fig. 3 - 11). Fig. 3 - 11a shows that the dissolved silica concentration is around 0.3 mol dm^{-3} in the sections beyond 15 mm from the input side due to dissolution of chalcedony supported with the results of solution and XRD analysis (Fig. 3 - 3b and Fig. 3 - 4). In this case, ΔG_r was -15 kJ mol^{-1} 30 mm from the input side, while ΔG_r was -120 kJ mol^{-1} 0 mm from the input side due to the almost complete dissolution of chalcedony near the input side. Here, the dissolution rates of montmorillonite were $-6.13 \times 10^{-15} \text{ mol m}^2 \text{ s}^{-1}$ and $-9.42 \times 10^{-12} \text{ mol m}^2 \text{ s}^{-1}$ when ΔG_r was -15 and -120 kJ mol^{-1} , respectively. There is around three orders difference between the dissolution rate of montmorillonite at 0 and 30 mm from input side. Fig. 3 - 11b shows that the dissolved silica concentrations maintain the constant value in the whole specimen due to the chalcedony being almost dissolved after 360 days, ΔG_r were -150 and -60 kJ mol^{-1} at 0 and 30 mm from input side, respectively. Here, the dissolution rates of montmorillonite were $-1.65 \times 10^{-11} \text{ mol m}^2 \text{ s}^{-1}$ and $-1.30 \times 10^{-12} \text{ mol m}^2 \text{ s}^{-1}$ when ΔG_r was -150 and -60 kJ mol^{-1} , respectively. There is around one orders difference between the dissolution rate of montmorillonite at 0 and 30 mm from input side. This indicates that the presence of silica minerals in bentonite significantly affects the dissolution rate of montmorillonite in compacted bentonite.

The model also indicates that the inhibition of montmorillonite dissolution will not be sustained beyond the experimental duration under the same experimental conditions.

However, a compacted bentonite with higher dry density such as 1.6 Mg m^{-3} , where diffusion is the dominant mass transport mechanism, has been considered for use in actual radioactive disposal barriers in Japan. In the much more compacted bentonite system, dissolution of montmorillonite will be inhibited for a much longer term. Therefore, it is important to consider the dissolution behavior of silica minerals to sufficiently evaluate the long-term performance of bentonite as a component of engineered barriers for radioactive waste disposal.

3.5 Conclusion

An advective alteration experiment of compacted bentonite specimens with a dry density of 0.3 Mg m^{-3} was conducted with hyperalkaline-fluid to observe the dissolution process of accessory minerals in bentonite by X-ray CT. X-ray CT images, which were taken every 10 days, showed that the volume of a light colored material decreased as the interaction between the bentonite and hyperalkaline-fluid progressed during the experiments. This is attributed to the dissolution of accessory silica minerals in the bentonite. XRD analyses of altered bentonite after the experiments identified that the accessory mineral was mainly chalcedony. The kinetic data for dissolution of chalcedony was obtained by developing the methodology to quantify the volume of accessory minerals in the CT images. These results showed that chalcedony was almost completely dissolved in the area close to the fluid input within 80 days. The geochemical transport model consistent with the experimental results indicates that the pore water in the bentonite approached near saturation with respect to montmorillonite due to the dissolution of silica minerals in bentonite, inhibiting the dissolution of montmorillonite in bentonite. In the much more compacted bentonite system, dissolution of montmorillonite will be inhibited for a much longer term. Therefore, it is important to consider the dissolution behavior of silica minerals to sufficiently evaluate the long-term performance of bentonite as a component of engineered barriers for radioactive waste disposal.

Table 3 - 1 Scanning and imaging conditions in the X-ray CT analysis.

Scanning mode	Cone-beam
Tube voltage	90 kV
Tube current	89 mA
Slice thickness	0.01 mm
Slice pitch	0.01 mm
Cross-sectional area	19.6 mm ²
The number of slices	200
Spatial resolution	1024×1024
Pixel size	0.004 mm

Table 3 - 2 Kinetics parameters for Eq. 2-9 at 25°C (including Analcime).

Minerals	Quartz ^[1]	Albite ^[2]	Chalcedony ^[3]	Analcime ^[3]
Specific surface area (m ² g ⁻¹)	0.07	0.24	0.03	0.03
Log k ^{nu} (mol m ⁻² s ⁻¹)	-12.03	-12.1	-12.5*	-14.4*
E _a ^{nu} (kJ mol ⁻¹)	76.7	61.1	-	-
n _{nu}	-	-	-0.6*	-0.6*
Log k ^H (mol m ⁻² s ⁻¹)	-	-9.47	-	-
E _a ^H (kJ mol ⁻¹)	-	64.3	-	-
n _H	-	0.335	-	-
Log k ^{OH} (mol m ⁻² s ⁻¹)	-8.56	-9.38	-	-
E _a ^{OH} (kJ mol ⁻¹)	80	60.6	-	-
n _{OH}	0.339	-	-	-

The kinetic constants are determined with data from:

[1] Schwartzentruber et al. (1987); Bennett et al. (1988); Knauss and Wolery (1988); Blum et al. (1990); Brady and Walther (1990); Casey et al. (1990); Dove and Crerar (1990); Bennett (1991); House and Orr (1992); Dove (1994); Dove (1999); Icenhower and Dove (2000); Bickmore et al. (2006)

[2] Chou and Wollast (1984); Chou and Wollast (1985); Burch et al. (1993); Hellmann (1994); Knauss and Copenhaver, (1995); Alekseyev et al. (1997); Hellmann and Tisserand (2006)

[3] Savage et al. (2002)

* The parameters are obtained at 70 °C

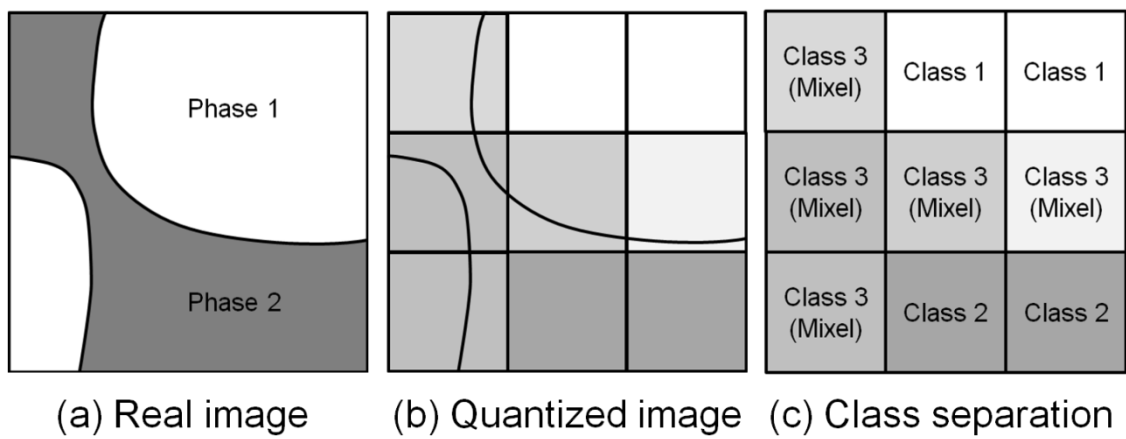


Fig. 3 - 1 Imaging processing of real image: (a) real image, (b) quantized image, (c) class separation in image (Yamanaka et al., 2011).

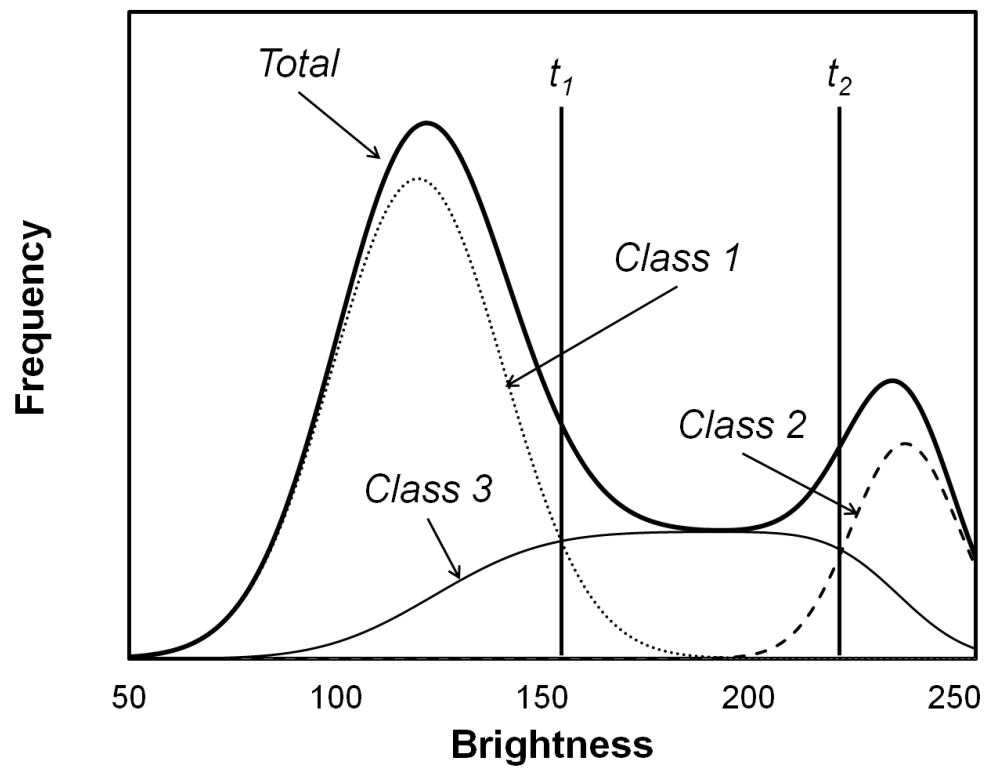


Fig. 3 - 2 Histogram of brightness in Fig. 3-1c. t_1 and t_2 are boundary of brightness between class 1 and 3, class 2 and 3, respectively (Yamanaka et al., 2011).

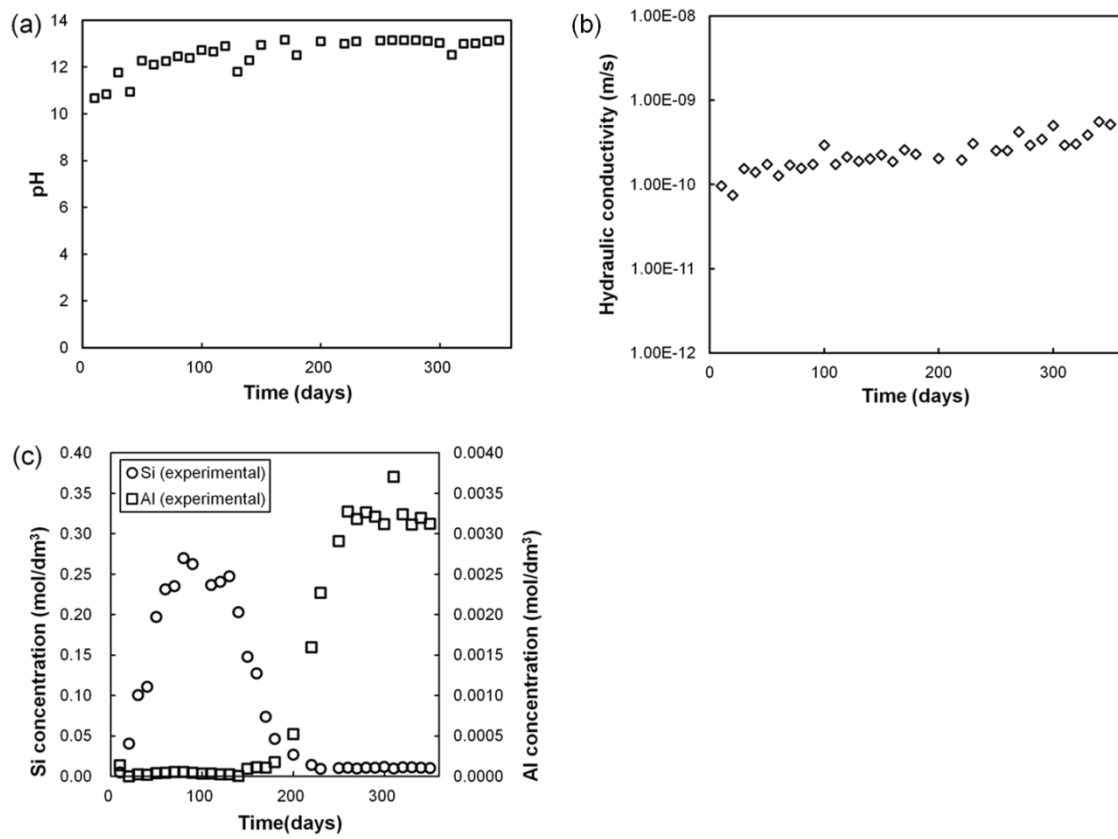


Fig. 3 - 3 pH change of the output solution (a), hydraulic conductivity change of bentonite (b) and the concentrations of dissolved silica and aluminum in the output solution (c).

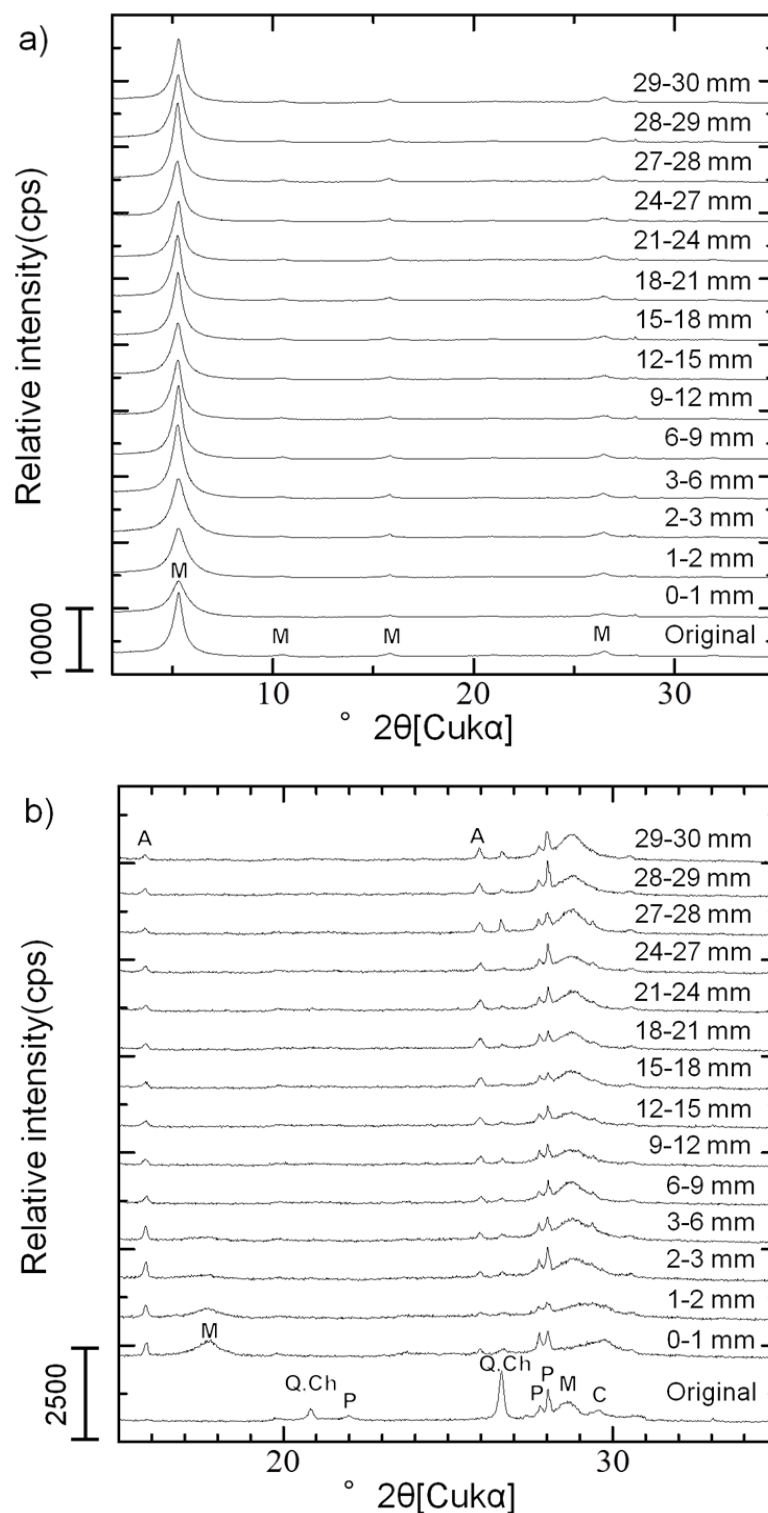


Fig. 3 - 4 X-ray diffraction patterns of the bentonite in different sections of the column after 360 days using oriented sample treated with ethylene glycol on glass (a) and oriented sample on glass (b). Peak assignments: A = Analcime; M = Na-Montmorillonite; Q = Quartz; Ch = Chalcedony; C = Calcite; P = Plagioclase.

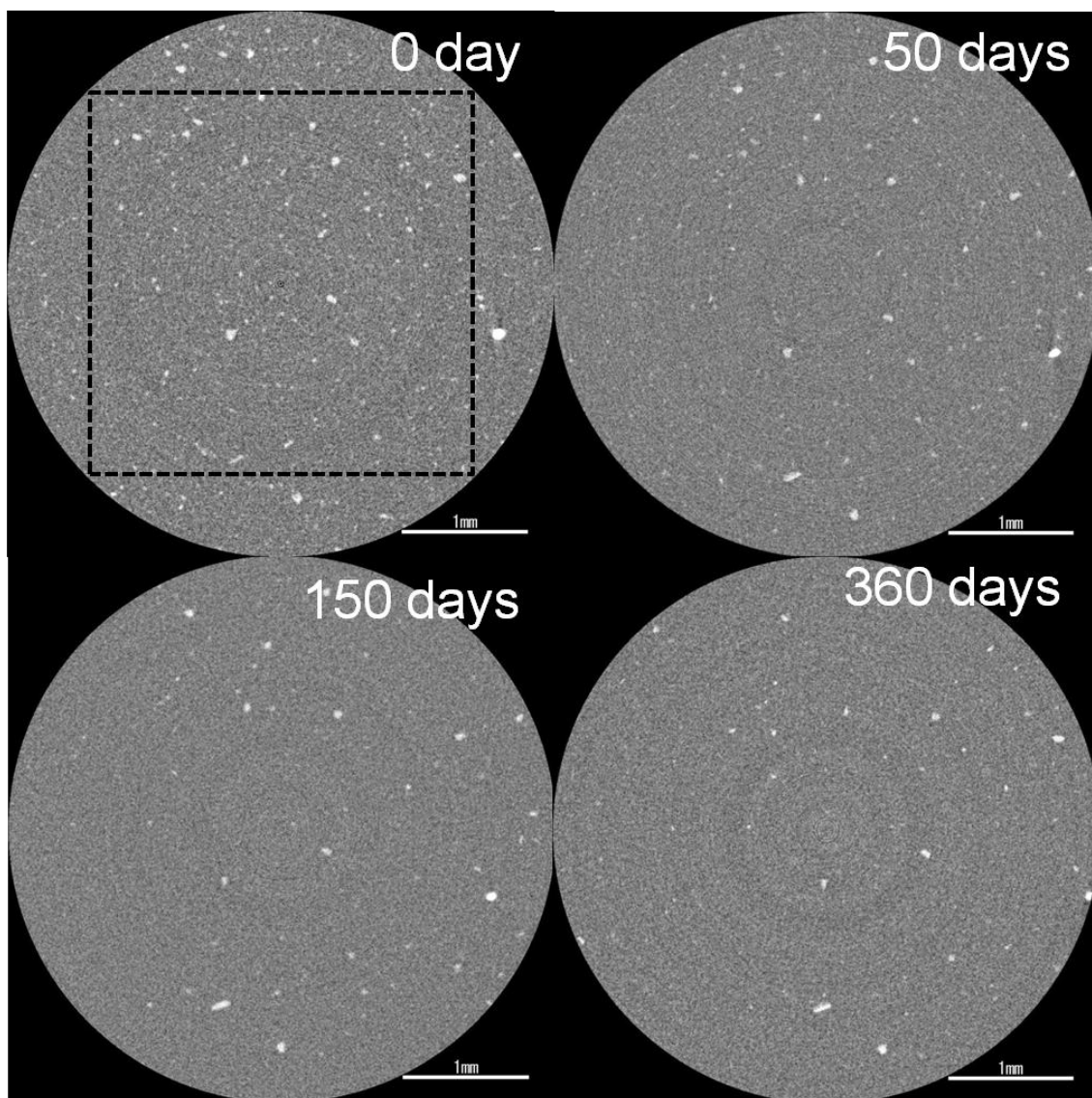


Fig. 3 - 5 CT images of the bentonite column sample (0.3 Mg m^{-3} of dry density) at different durations of the advective experiment. Scale bars = 1 mm.

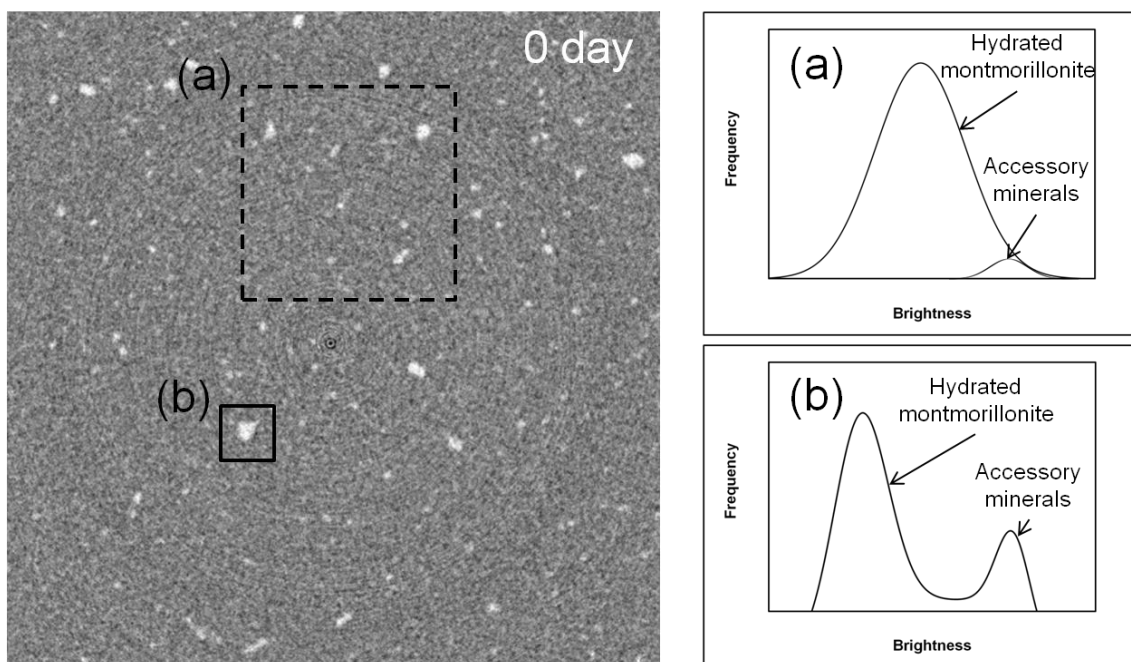


Fig. 3 - 6 CT images of the trimmed ROI (region of interest) of the black rectangle in Fig. 3-5 (left) and histogram of brightness in the rectangle of (a) and (b) (right).

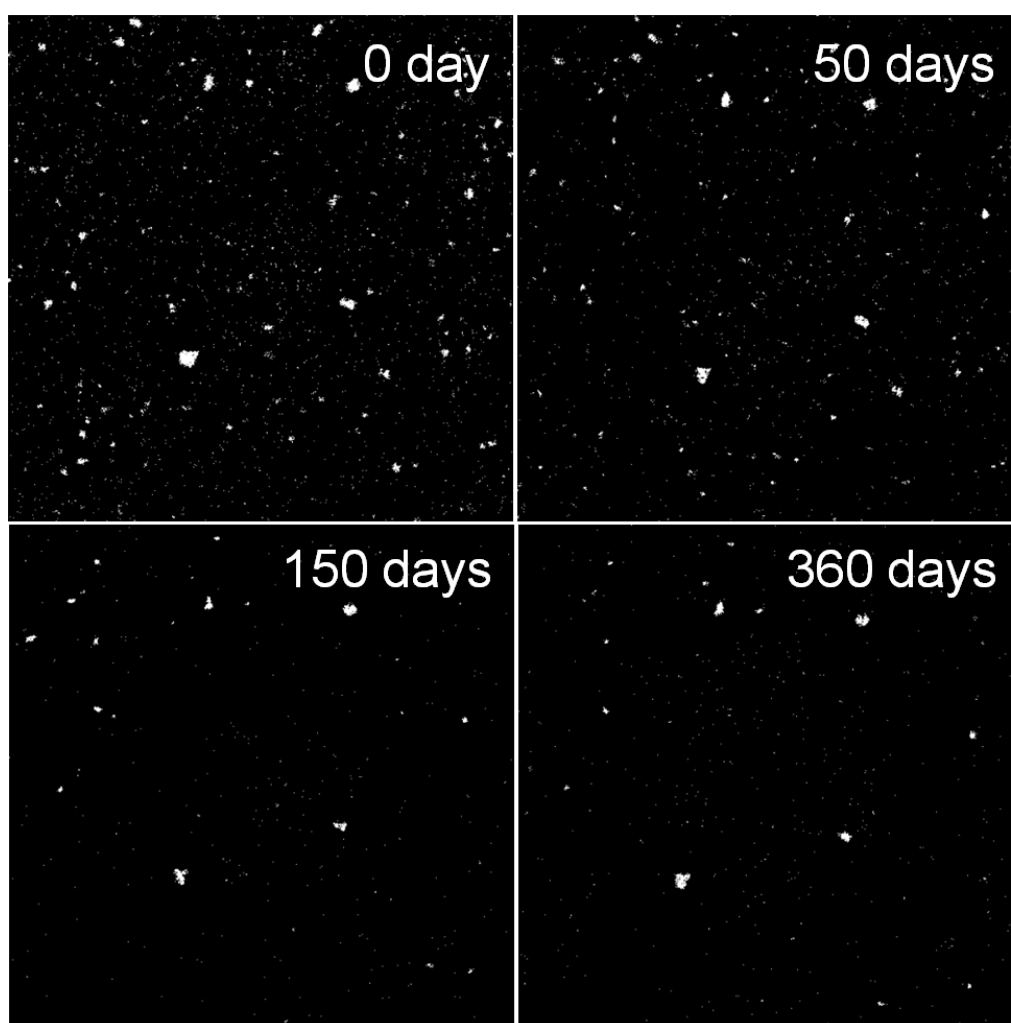


Fig. 3 - 7 Binary CT images of the trimmed ROI (region of interest) in the black rectangle in Fig. 3-5. White dots are accessory minerals including minor amounts of secondary mineral. The volumes of the white dot clusters decrease with time, and indicate the dissolution of accessory minerals. Volume of the secondary mineral calculated based on the CT image analysis at different experiment durations.

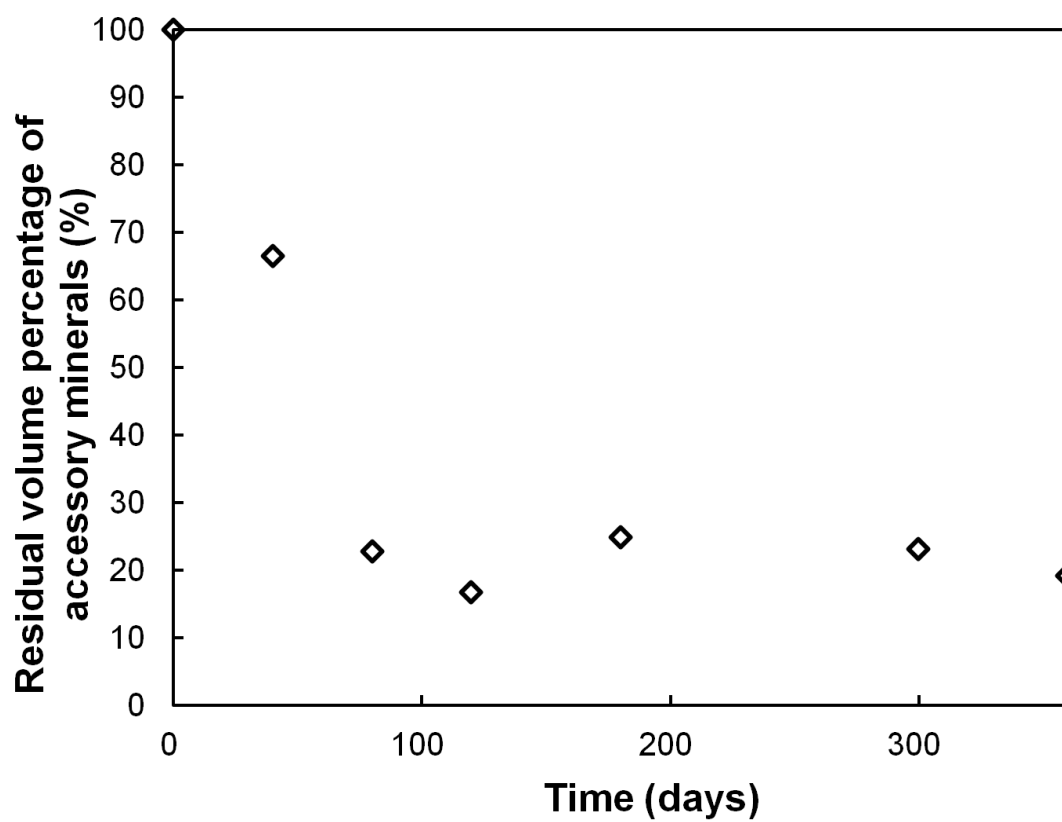


Fig. 3 - 8 Residual volume percentage of the accessory minerals calculated based on the CT image analysis at different experiment durations.

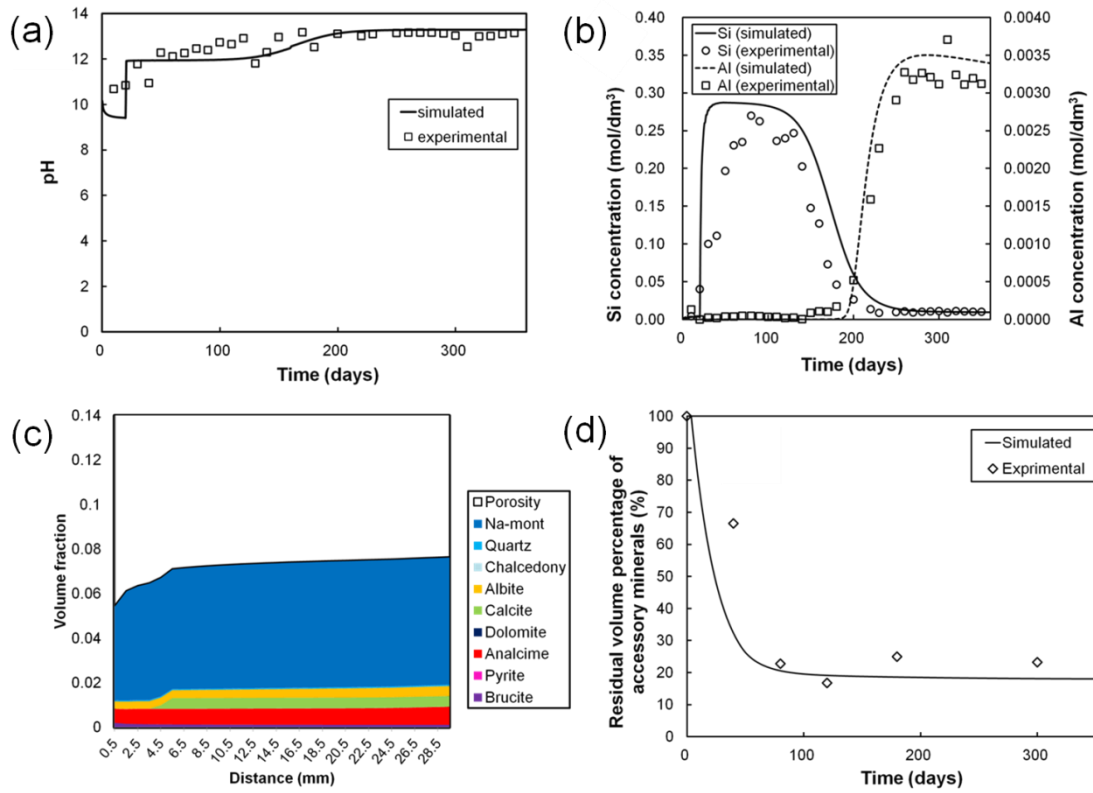


Fig. 3 - 9 Calculated results plotted vs. time or distance using the geochemical model. Eq. (2-7) was used as the rate law for Na-montmorillonite dissolution/precipitation with $7 \times 0.12 \text{ m}^2 \text{ g}^{-1}$ of specific surface area and Eq. (2-9) was used as the rate law for quartz, chalcedony, albite, and analcime with 0.07×0.5 , 0.03×0.06 , 0.24×0.2 , and $0.03 \times 0.1 \text{ m}^2 \text{ g}^{-1}$, respectively and the dissolution/precipitation of calcite, dolomite, pyrite, and brucite were modeled based on thermodynamic considerations in the simulations. The kinetic parameters of accessory minerals are shown in Table 3-2. pH changes of the output solution is shown in (a), and the concentrations of dissolved silica and aluminum in the output solution is shown in (b). the calculated mineralogical distributions in bentonite as a function of distance is shown in (c) and the residual volume percentage of accessory minerals in the 0 – 2 mm section is shown in (d).

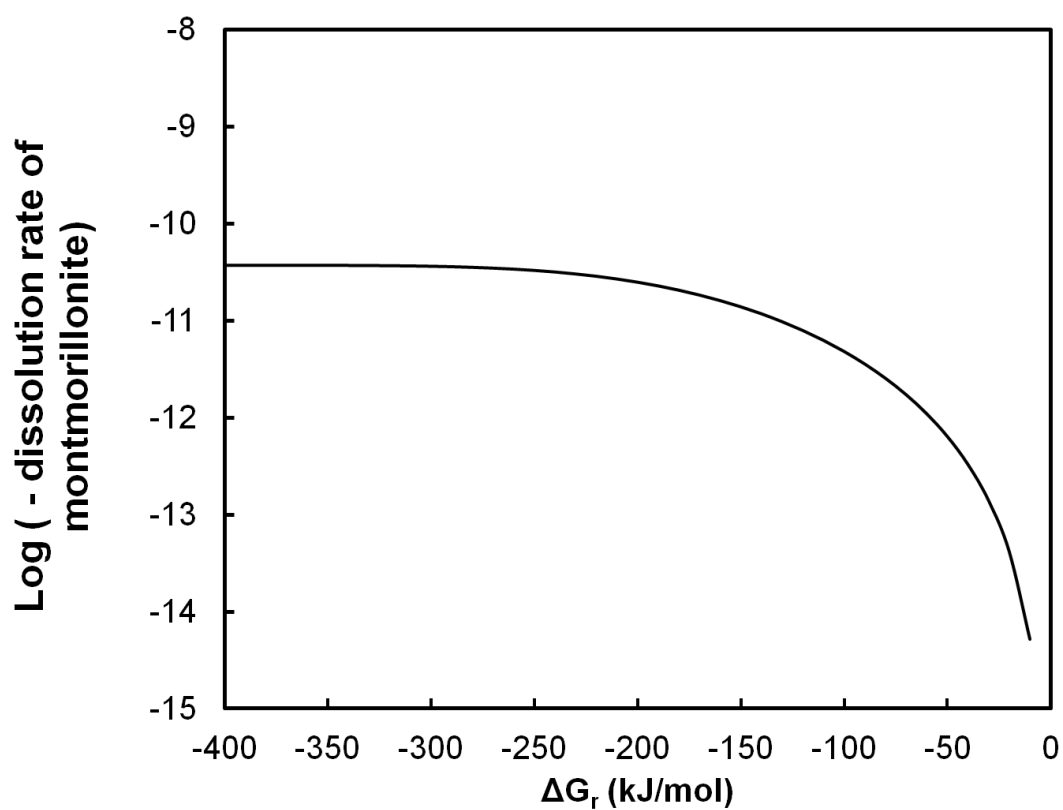


Fig. 3 - 10 Effect of the degree of saturation on montmorillonite dissolution rate (Sato-Oda equation modified with $7 \times 0.12 \text{ m}^2 \text{ g}^{-1}$ of specific surface area of montmorillonite).

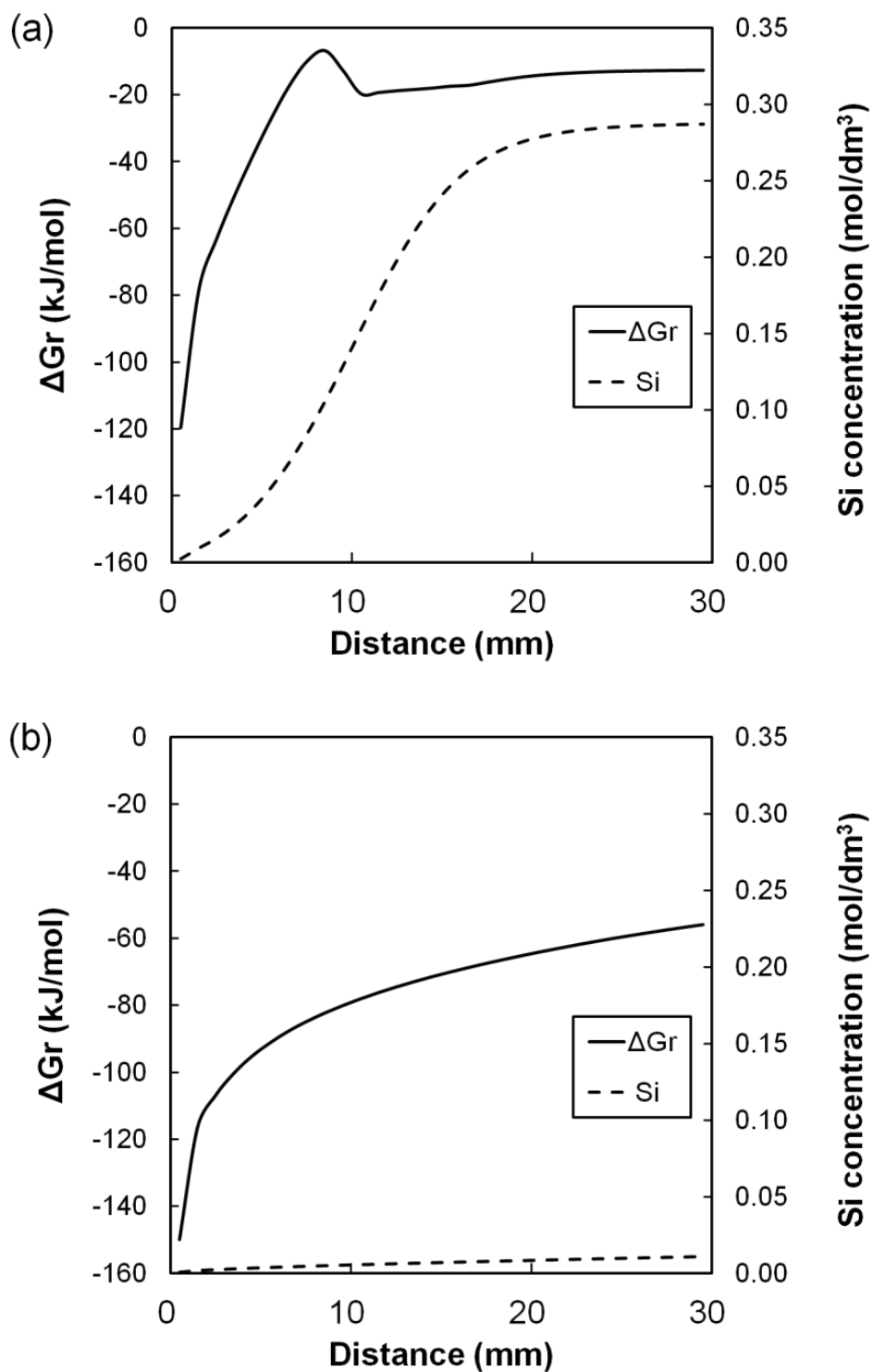


Fig. 3 - 11 Calculated distribution of the Gibbs energy (ΔG_r) of the dissolution reaction of montmorillonite and the concentration of dissolved silica in porewater of bentonite at 60 days (a) and 360 days (b).

Chapter 4 Long-term evaluation for the performance of bentonite buffer materials under hyperalkaline environment

4.1 Introduction

The long-term performance of bentonite as engineered barrier components under hyperalkaline conditions has been evaluated by geochemical modeling (e.g. JNC and FEPC, 2005). However, the results generated in those studies were not realistic. The model used in previous studies has considered a number of key parameters (e.g., dissolution rate and the reactive surface area of montmorillonite) that significantly affect the model results (Oda et al., 2004, Takase et al., 2004). However, these key parameters have been obtained from batch and flow-through experiments under high fluid/solid weight ratio conditions. The experimental conditions in such studies were completely different from the conditions in an actual radioactive waste disposal system.

Chapters 2 and 3 developed a microstructural analysis method using X-ray CT to trace the alteration process between compacted bentonite and hyperalkaline-fluids as a function of time and obtained quantitative data for the dissolution/formation of minerals in the compacted bentonite with time. Furthermore, it can be considered that the actual dissolution rate of the montmorillonite in compacted bentonite is one or two orders lower than that of the montmorillonite in powder bentonite and is influenced by the surface area of montmorillonite and departure from equilibrium. In addition, the presence of silica minerals in compacted bentonite significantly affects the dissolution rate of montmorillonite in compacted bentonite. However, it is unclear how the evaluation of the long-term performance of the compacted bentonite in actual radioactive disposal systems would be influenced by the effect of surface area of montmorillonite, departure from equilibrium, and the presence of silica minerals because these factors were obtained from the short-term experiments using compacted bentonite with a relatively low dry density of 0.3 Mg m^{-3} .

In this chapter, sensitivity analyses for the model was conducted to consider the effect of key factors such as the reactive surface area of montmorillonite, the departure from equilibrium and dissolution of silica minerals on the evaluation of the long-term performance of the compacted bentonite as a buffer material.

4.2 Modeling approach

The geochemical modeling approach in this chapter is similar to Chapters 2 and 3. The one dimensional geochemical reactive transport code PHREEQC (Parkhurst and Appelo, 1999) was used to simulate the alteration process at the interface between cement and bentonite. A concrete in contact with bentonite was considered for the simulations. A one-dimensional non-radial geometry was chosen (Fig. 4 - 1). Therefore, the profile does not strictly represent a waste repository system. This study aims to increase the level of knowledge about the effects of reactive surface area of montmorillonite, ΔG_r with respect to montmorillonite, and the dissolution of silica minerals in compacted bentonite on the evaluation of the long-term performance of the bentonite buffer materials. The initially equilibrated bentonite-solution is assumed to interact in fully hydrated conditions at 25 °C with elements coming from the concrete pore water. The last cell of bentonite far from the concrete/bentonite interface (Fig. 4 - 1) is assumed to have a very large volume. Therefore bentonite pore water may be assimilated to an infinite source whereas the quantity of concrete is limited.

4.2.1 Characteristic of the materials

Physical and chemical properties of concrete and bentonite materials are needed in advance as the input data to the model. In the simulations, ordinary portland cement concrete and Kunigel V1 were considered as the primary materials. The initial amount of minerals in the materials is needed to run the model. The mineralogical composition of the concrete, considered as mature, is given in Table 4 - 1 (Elakneswaran et al., 2009). Aggregates (both fine and coarse) were assumed to be chemically inert and to have no accessible porosity. Thus, the transport of ions through concrete results from the transport process in the cement matrix. The assumed porosity for the concrete is equal to the porosity of hydrated cement paste and is equal to 0.25 (Elakneswaran et al., 2009). The mineral composition of Kunigel V1 bentonite is shown in Table 1 - 1. The porosity of the bentonite is assumed to be 0.4. The pores of the concrete and bentonite are initially filled with ground water, as shown in Table 4 - 2. In this study, the simulation

considered diffusion as the only transport mechanism and assumed an effective diffusion coefficient of $2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for the concrete/bentonite system, which remained constant during the simulation. The Thermoddem database was used as the basis for the thermodynamic properties of aqueous species and mineral phases (Blanc et al., 2007). The thermodynamic properties of minerals considered in the simulation are tabulated in Table 4 - 3. The 20 minerals considered in the simulations were selected based on the author's review of cement/clay interactions.

4.2.2 Kinetic

The dissolution/precipitation of montmorillonite, quartz, chalcedony, albite, and analcime were modeled based on available kinetic data while the other minerals were modeled based on thermodynamic considerations. The Sato-TST model, Sato-Oda model and the Sato-Oda model modified with reactive surface area of montmorillonite were considered in the simulation. The rate equations ($\text{mol dm}^{-3} \text{ s}^{-1}$) for the dissolution of montmorillonite considered in this work are described by Eq. (2-7). For the TST equation, $\sigma = 1$, while for the Oda equation, $\sigma = 2$. p and q are fitting coefficients. The kinetic parameters of montmorillonite are shown in Table 4 - 4. The rate equations ($\text{mol dm}^{-3} \text{ s}^{-1}$) for the other minerals are as described by Eq. (2-9). The kinetic parameters of quartz, albite, and chalcedony as reported in the literature are shown in Table 2 - 4.

4.2.3 Ion exchange

The reaction among cations sorbed on the charged surface and in the solution is called cation exchange. An ion exchange model in Phreeqc considers mass-action equations and mole-balance equations for exchange sites (Appelo et al., 2009). Ion exchange reactions are simulated as ion association reactions in the form of half reactions. The exchange of Ca^{2+} for Na^+ can be written as:



$$K_{Ca/Na} = \frac{[CaX_2]^{0.5}[Na^+]}{[Ca^{2+}]^{0.5}[NaX]} \quad (4-2)$$

Eq. (4-1) is split into two half reactions:



where X⁻ indicates the exchanger surface, and CaX₂ and NaX are exchangeable cations. The use of equivalent fraction of exchangeable cations for activities in Eq. (4-1) is known as the Gaines Thomas convention (Appelo et al., 2009). The main input data to Phreeqc for performing these calculations are the chemical equation for mole balance and mass-action expressions, and the equilibrium constant and its corresponding values at different temperatures. The four equations governing the ion exchange process in the montmorillonite are listed in Table 4 - 5.

4.2.4 Sensitivity analysis

As described in above, a reference case and a number of variations upon this were considered with the aim of identifying factors to which the system is particularly sensitive. A summary of the various cases is given in Table 4 - 6. Case 1 is the base case using the Sato-TST model. Case 2 is based on the Sato-Oda model and Case 3 is based on the Sato-Oda model modified with the reactive surface area of montmorillonite. In these simulations (Case 1, 2, and 3), the effect of key factors such as the reactive surface area of montmorillonite, the departure from equilibrium and dissolution of silica minerals on the evaluation of the long-term performance of the bentonite buffer material was considered. Case 4 is based on Case 2 with the reactive surface area of chalcedony modified to consider the effect of dissolution of silica minerals. The duration of the simulations is 100,000 years.

4.3 Results

Fig. 4 - 2 shows the simulation results of the distribution of solid phases after 100,000 years of pore solution transport through concrete/bentonite barrier system in Case 1, 2 and 3. All simulation results show the precipitation of tobermorite and porosity clogging at the concrete side of the interface between the concrete and bentonite. It is noted that the effective diffusion coefficient for aqueous species in the concrete/bentonite system is constant in the model regardless of the porosity change, and thus the alteration at the interface between concrete and bentonite was not retarded. The tobermorite was formed due to the dissolution of CSH and portlandite. In the bentonite side, clinoptilolite (Ca) and phillipsite (Na) were formed as secondary minerals, with phillipsite (Na) forming in the whole bentonite section and clinoptilolite (Ca) being confined to concrete-bentonite interface. On the other hand, analcime and albite were completely dissolved. The dissolved Na, Si and Al from the analcime and albite were consumed to form clinoptilolite (Ca) and phillipsite (Na).

In Cases 1 and 2, phillipsite (Ca) was formed at the bentonite side of the concrete-bentonite interface (Fig. 4 - 2a and b), while the simulation in Case 3 showed that the volume fraction of tobermorite and calcite at the bentonite side of the concrete-bentonite interface is higher than that in Case 1 and 2 (Fig. 4 - 2c). It is due to the dissolution of montmorillonite at the bentonite side of the concrete-bentonite interface. Fig. 4 - 3a shows the residual volume percentages of montmorillonite in the bentonite side after 100,000 years in Cases 1, 2 and 3. About 0 - 0.35 m from the concrete-bentonite interface, the montmorillonite was completely dissolved in Case 1, and the simulation in Case 2 and 3 indicated that the volume fractions of montmorillonite were from 5 to 65 % and 50 to 68 %, respectively. Fig. 4 - 3b shows the residual volume percentages of chalcedony in the bentonite side after 100,000 years in Cases 1, 2 and 3. At 0.05 m from the concrete-bentonite interface, the chalcedony was completely dissolved in all simulations, and the residual volume percentages of the chalcedony remain at 90 to 95% beyond 0.05 m. There is no difference between Cases 1, 2 and 3 in terms of the amounts of chalcedony dissolved. The formation of phillipsite (Ca) needs to consume not only H_4SiO_4 but also Al^{3+} in the bentonite pore solution. Therefore, the formation of phillipsite (Ca) is due to the dissolution of montmorillonite.

Fig. 4 - 4 shows the simulation results for the distribution of solid phases after 100,000 years of pore solution transport through concrete-bentonite barrier system in Cases 2 and 4. A small amount of phillipsite (Ca) was formed at the bentonite side of concrete-bentonite interface in Case 4. Aside from that, there is no difference between the simulation results in Cases 2 and 4 (Fig. 4 - 4). Fig. 4 - 5a shows the residual volume percentages of montmorillonite in the bentonite side after 100,000 years in Cases 2 and 4. The simulation indicated that the residual volume fractions of montmorillonite ranged from 5 to 65 % at 0 – 0.35 m from the concrete-bentonite interface and from 65 to 80% beyond 0.35 m. There is no difference between Cases 2 and 3 in terms of the amounts of montmorillonite dissolved. Fig. 4 - 5b shows the residual volume percentages of chalcedony in the bentonite side after 100,000 years in Cases 2 and 4. At 0.05 m from the concrete-bentonite interface, the chalcedony was completely dissolved in both cases, while the residual volume percentages of the chalcedony remain at 95 to 98 % beyond 0.05 m. There is no difference between Cases 2 and 4 on the amounts of chalcedony dissolved.

4.4 Discussion

4.4.1 Effect of the dissolution of montmorillonite on the long-term prediction of the performance of bentonite buffer

The residual volume percentage of montmorillonite in Case 3 (modified Sato-Oda model) is higher compared to the simulation results in Cases 1 (Sato-TST model) and 2 (Sato-Oda model). Fig. 4 - 6 shows the dissolution rate ($\text{mol m}^{-2} \text{g}^{-1}$) of montmorillonite considering the effects of the surface area of montmorillonite calculated from Sato-TST, Sato-Oda and modified Sato-Oda equations plotted against the ΔG_r of the overall reaction at pH 12.1 and 25 °C. Fig. 4 - 7 the spatial distribution of the Gibbs free energy with respect to montmorillonite in the bentonite after 1,000 and 100,000 years simulated by the geochemical transport model. From Fig. 4 - 7, ΔG_r ranges from -30 to 0 kJ mol^{-1} during the duration of the simulations. At $\Delta G_r = -30 \text{ kJ mol}^{-1}$, the dissolution rates of montmorillonite are -3.11×10^{-10} , -1.16×10^{-12} and -2.31×10^{-13} in Case 1, 2 and 3, respectively. The difference between Case 1 and 3 spans three orders, suggesting that the effects of the reactive surface area of montmorillonite and ΔG_r with respect to

montmorillonite in compacted bentonite are important to realistically evaluate the long-term performance of the bentonite buffer material.

In Fig. 4 - 7a, ΔG_r were -1.0×10^{-3} , -19.24 and -26.80 kJ mol⁻¹ 0.05 m from the bentonite side of the concrete/bentonite interface in Case 1 (Sato-TST model), Case 2 (Sato-Oda model) and Case 3 (modified Sato-Oda model), respectively after 1,000 years. At these ΔG_r values, the dissolution rates of montmorillonite were -1.09×10^{-12} , -3.40×10^{-13} and -2.31×10^{-13} mol m² g⁻¹, respectively. The montmorillonite dissolution rate varies within the range 8.59×10^{-13} between Cases 1, 2 and 3. After 100,000 years, ΔG_r were -6.47 and -8.64 kJ mol⁻¹ 0.5 m from the concrete-bentonite interface in Case 2 (Sato-Oda model) and Case 3 (modified Sato-Oda model), respectively in Fig. 4 - 7b. In Case 1 (Sato-TST model), the montmorillonite was almost completely dissolved as shown in Fig. 4 - 3a. Here, the dissolution rates of montmorillonite were -9.26×10^{-15} and -4.39×10^{-15} mol m² g⁻¹ when ΔG_r was -6.47 and -8.64 kJ mol⁻¹, respectively. There is a 4.87×10^{-15} mol m² g⁻¹ difference between Case 2 and 3. Comparing the range of dissolution rates of montmorillonite in each case between after 1,000 and 100,000 years, it can be seen that the differences will narrow down as the reaction between bentonite and the hyperalkaline pore solution progresses, suggesting that the effect of the dissolution rate of montmorillonite on the long-term behavior of the bentonite will decrease with time. These simulations indicated that the reaction between bentonite and concrete was controlled by the dissolution of montmorillonite over shorter time spans (~1000 years). In Chapter 2 and 3, it was shown that quantitative data obtained from the X-ray CT method could allow us to sufficiently validate the geochemical model simulating short-term experiments. Therefore, it can also be applied to rigorously validate geochemical models evaluating the long-term performance of bentonite buffer materials.

4.4.2 Effect of the dissolution of silica minerals on the long-term evaluation of the performance of the bentonite buffer

The simulation in Cases 2 and 4 shows almost same results shown in Fig. 4 - 4 and Fig. 4 - 5, suggesting that the primary silica minerals such as chalcedony does not affect the long-term results. It is due to the formation of secondary minerals such as

clinoptilolite and phillipsite, which are composed of Al and Si. The geochemical transport model using Cases 2 and 4 simulated the spatial distribution of the Gibbs free energy with respect to chalcedony and montmorillonite in the bentonite after 100,000 years (Fig. 4 - 8). After 100,000 years, at 0.05 m from the concrete-bentonite interface in both cases, the ΔG_r with respect to chalcedony is about -1.4 kJ mol^{-1} , and then plateaus at 0 kJ mol^{-1} beyond 0.05 m (Fig. 4 - 8a). On the other hand, ΔG_r values with respect to montmorillonite were generally less than those of chalcedony (Fig. 4 - 8b). The framework of montmorillonite is composed of various elements such as Si, Al, Mg, H and O, while that of chalcedony is composed of only Si and O. A large variety of secondary minerals such as phillipsite and clinoptilolite, whose framework consists mainly of Si, Al, H and O, were considered in the simulation. Furthermore, the simulation in this Chapter considered secondary mineral formation based on thermodynamic considerations. Therefore, the formation of secondary minerals needs to significantly consume the dissolved Si and Al in the bentonite pore solution, suggesting that the saturation state with respect to montmorillonite in bentonite pore solution decreases. In Chapter 2, the simulation considered analcime as the only secondary mineral and its formation is based on kinetic data, with the result that the saturation state with respect to montmorillonite did not decrease significantly. Therefore, the types of secondary minerals and kinetic data for their formation are necessary for the evaluation of the long-term performance of bentonite barriers using modeling.

4.5 Conclusion

The sensitivity analyses of the models were conducted to consider the effects of key factors such as the reactive surface area of montmorillonite, the departure from equilibrium and dissolution of silica minerals on the evaluation of the long-term performance of the bentonite buffer material. The one dimensional geochemical reactive transport code PHREEQC was used to simulate the alteration process at the interface between concrete and bentonite. A concrete in contact with bentonite was considered for the simulations and the duration of the simulations is 100,000 years at the maximum. A reference case and a number of variations, such as the reactive surface area of montmorillonite and chalcedony, the departure from equilibrium, were considered with

the aim of identifying factors to which the system is particularly sensitive.

These simulations indicated that the reaction between bentonite and concrete was controlled by the dissolution of montmorillonite in the short-term (~1,000 years). Therefore, the effect of reactive surface area of montmorillonite, ΔG_r with regard to montmorillonite in compacted bentonite are key factors and choosing the dissolution rate model of montmorillonite in compacted bentonite may become important to evaluate the long-term performance of the bentonite buffer material. On the other hand, there is no difference between the simulations with and without considering the effects of the surface area of chalcedony, suggesting that the primary silica minerals such as chalcedony do not affect the long-term results. It is due to the formation of secondary minerals such as clinoptilolite and phillipsite composed of Al and Si. The types of secondary minerals and kinetic data for the formation of secondary minerals are necessary to evaluate the long-term performance of bentonite barriers by modeling.

Table 4 - 1 Mineralogical composition of concrete (Elakneswaran et al., 2009).

Elements	Volume %
C-S-H: 1.6	11.17
Portlandite	3.86
Monosulfoaluminate	0.92
Ettringite	0.45
Aggregates	83.6

Table 4 - 2 Ground water composition at 25°C (JNC, 2000).

Chemical composition	
pH	8.5
Eh (mV)	-281
Element	Concentration (mol/l)
Na	3.6×10^{-3}
K	6.2×10^{-5}
Ca	1.1×10^{-4}
Mg	5.0×10^{-5}
B	2.9×10^{-4}
P	2.9×10^{-6}
F	5.4×10^{-5}
Cl	1.5×10^{-5}
SO ₄	1.1×10^{-4}
NO ₃	2.3×10^{-5}
CO ₃	3.5×10^{-3}
Si	3.4×10^{-4}

Table 4 - 3 Thermodynamic constants (25°C) and molar volume of minerals considered in simulations (Blanc et al., 2009).

Minerals	Structural formula	Log K	Molar volume (cm ³ mol ⁻¹)
Na-Montmorillonite	Na _{0.66} Mg _{0.66} Al _{3.34} Si ₈ O ₂₀ (OH) ₄	2.64	262.48
Chalcedony	SiO ₂	-2.70	22.68
Quartz	SiO ₂	-3.74	22.69
Albite	NaAlSi ₃ O ₈	4.14	100.43
Analcime	Na _{0.99} Al _{0.99} Si _{2.01} O ₆ ·H ₂ O	6.64	96.68
Clinoptilolite (Na)	Na _{1.1} (Si _{4.9} Al _{1.1})O ₁₂ ·3.5H ₂ O	-0.14	214.78
Clinoptilolite (K)	K _{1.1} (Si _{4.9} Al _{1.1})O ₁₂ ·2.7H ₂ O	-1.17	210.73
Clinoptilolite (Ca)	Ca _{0.55} (Si _{4.9} Al _{1.1})O ₁₂ ·3.9H ₂ O	-2.11	209.66
Illite (Mg)	K _{0.85} Mg _{0.25} Al _{2.35} Si _{3.4} O ₁₀ (OH) ₂	10.26	140.25
Phillipsite (Na)	NaAlSi ₃ O ₈ ·3H ₂ O	1.45	149.69
Phillipsite (K)	KAlSi ₃ O ₈ ·3H ₂ O	0.04	148.97
Phillipsite (Ca)	Ca _{0.5} AlSi ₃ O ₈ ·3H ₂ O	2.32	151.15
Tobermorite (11A)	Ca ₅ Si ₆ H ₁₁ O _{22.5}	65.58	286.19
Pyrite	FeS ₂	-23.59	23.94
Dolomite	CaMg(CO ₃) ₂	3.53	64.37
Calcite	CaCO ₃	1.85	36.93
Portlandite	Ca(OH) ₂	22.81	33.06
CSH (1.6)	Ca _{1.60} SiO _{3.6} ·2.58H ₂ O	28.00	84.68
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O	57.01	710.32
Monosulfoaluminate	Ca ₄ Al ₂ SO ₁₀ ·12H ₂ O	73.09	311.26

Table 4 - 4 Kinetic parameters of montmorillonite for Eq. (2-7).

	TST	Oda ^[1]
p	1	2.75×10^{-5}
q	1	3
σ	1	2

[1] Oda et al. (2012)

Table 4 - 5 Values of the equilibrium constants for the ion-exchange reactions.

Equation	Log K
$X^- = X^-$	0
$X^- + Na^+ = XNa$	0
$2X^- + Ca^{2+} = X_2Ca$	0.69
$X^- + K^+ = XK$	0.42
$2X^- + Mg^{2+} = X_2Mg$	0.67

Data from JNC (2000)

Table 4 - 6 Summary of the parameter values used for each Case.

Case	Rate equation for montmorillonite	Montmorillonite surface area ($m^2 g^{-1}$)	Chalcedony surface area ($m^2 g^{-1}$)
1	Sato-TST	7	0.03
2	Sato-Oda	7	0.03
3	Sato-Oda	7×0.2	0.03
4	Sato-Oda	7	0.03×0.02

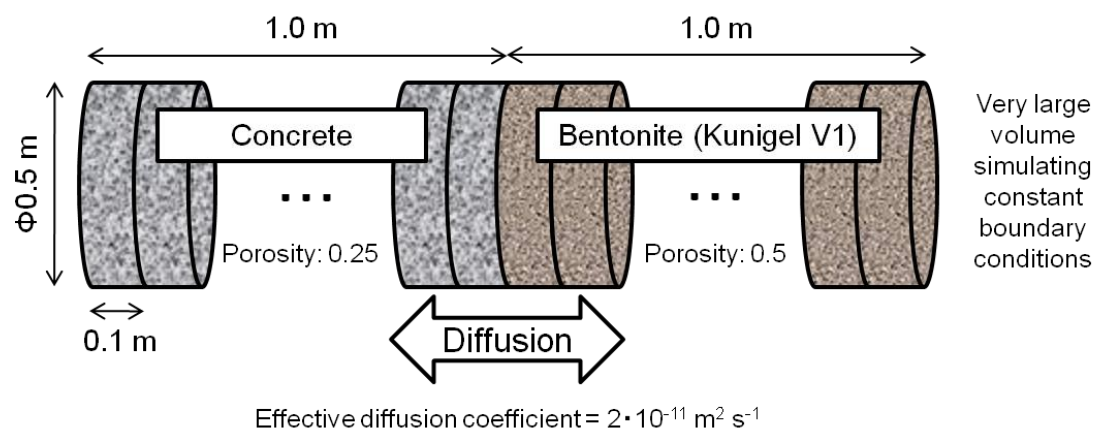


Fig. 4 - 1 Schematic diagram of one-dimensional reaction and transport model for the concrete/bentonite system.

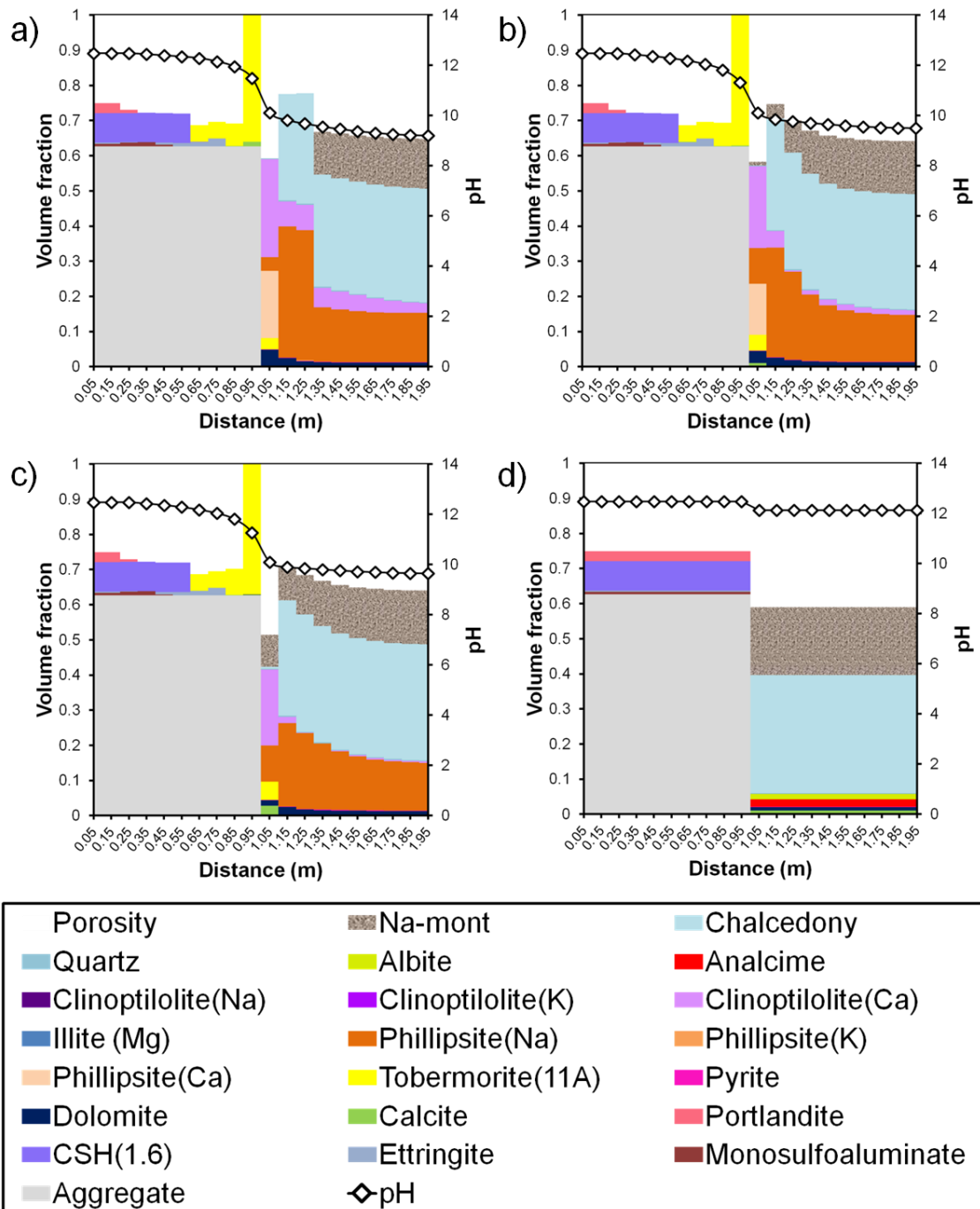


Fig. 4 - 2 Calculated mineralogical distributions in concrete/bentonite system as a function of distance. (a): Case 1 (after 100,000 years), (b) Case 2 (after 100,000 years), (c): Case 3 (after 100,000 years), (d) at 0 year.

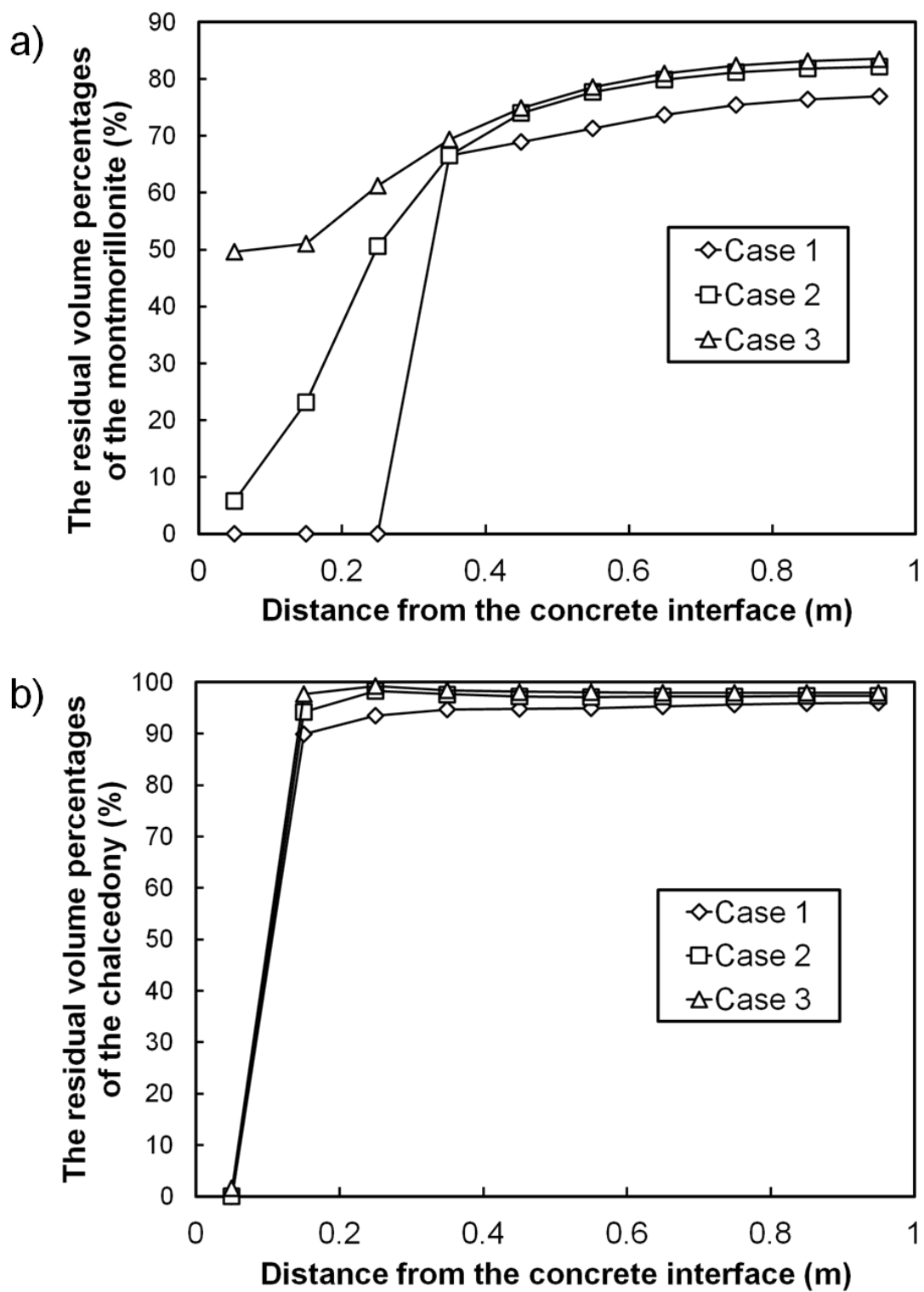


Fig. 4 - 3 Calculated distribution of residual volume percentages of the montmorillonite (a) and the chalcedony (b) in Case 1, 2 and 3.

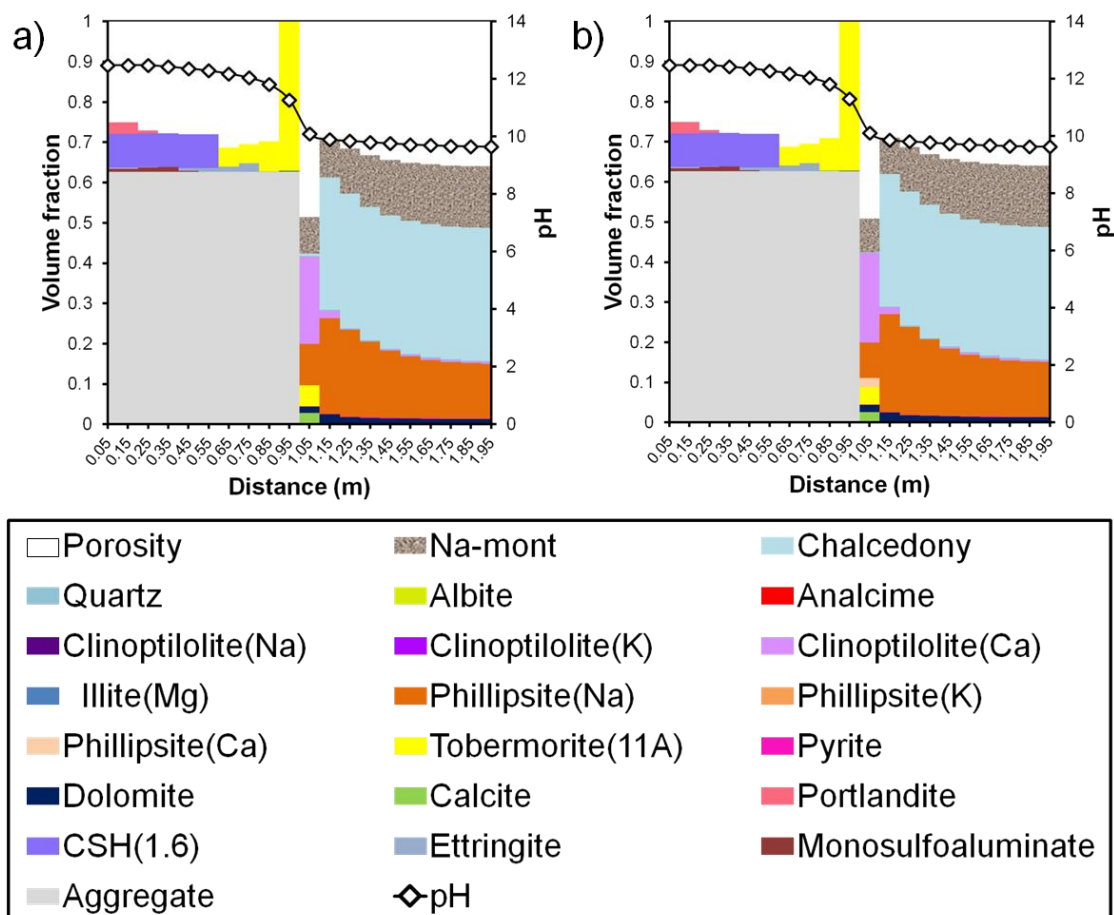


Fig. 4 - 4 Calculated mineralogical distributions in concrete/bentonite system as a function of distance. (a): Case 2 (after 100,000 years), (b): Case 4 (after 100,000 years).

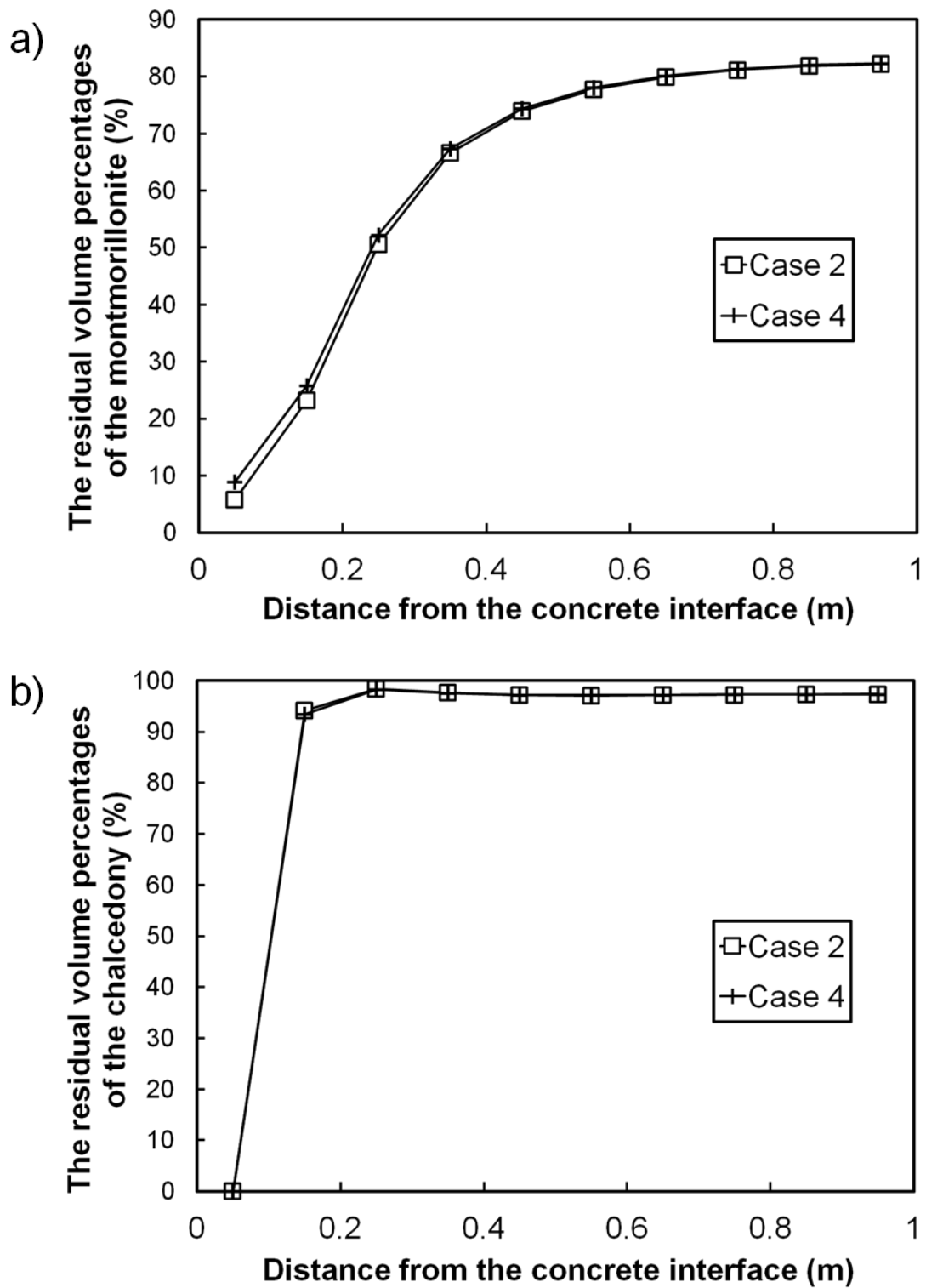


Fig. 4 - 5 Calculated distribution of residual volume percentages of the montmorillonite (a) and the chalcedony (b) in Case 2 and 4.

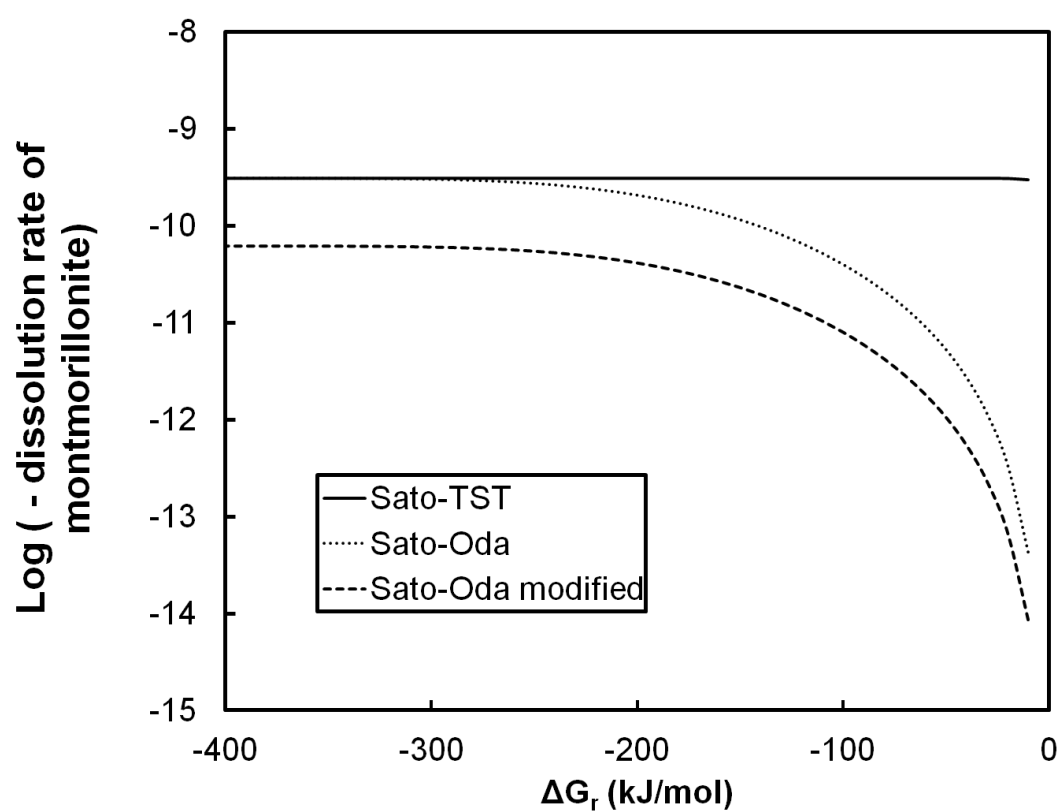


Fig. 4 - 6 Effect of the degree of saturation on montmorillonite dissolution rate using Sato-TST equation, Sato-Oda equation and Sato-Oda equation modified with the surface area of montmorillonite.

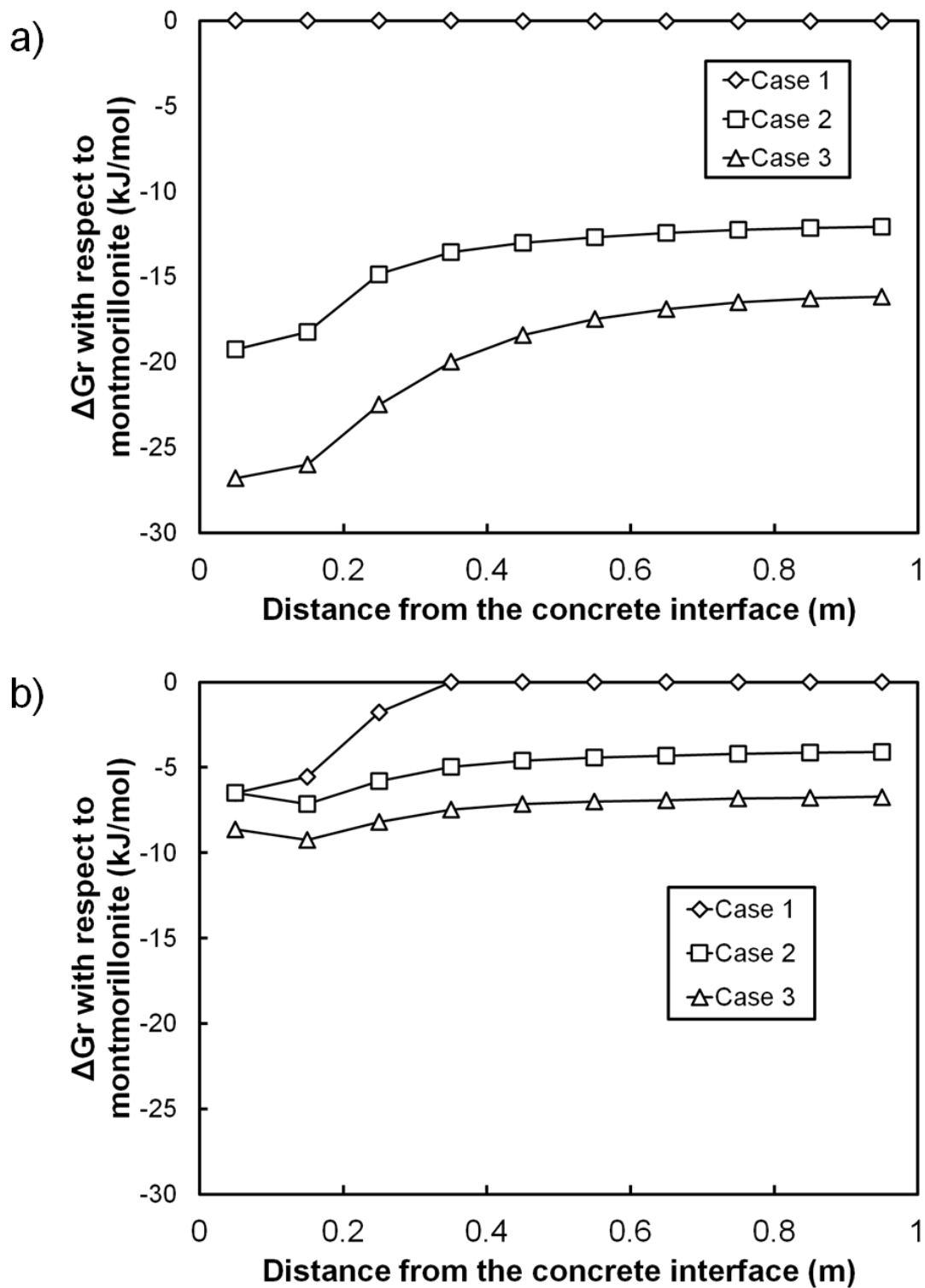


Fig. 4 - 7 Calculated distribution of the Gibbs free energy (ΔG_r) of the dissolution reaction of montmorillonite in Case 1, 2 and 3 after 1,000 years (a) and 100,000 years (b).

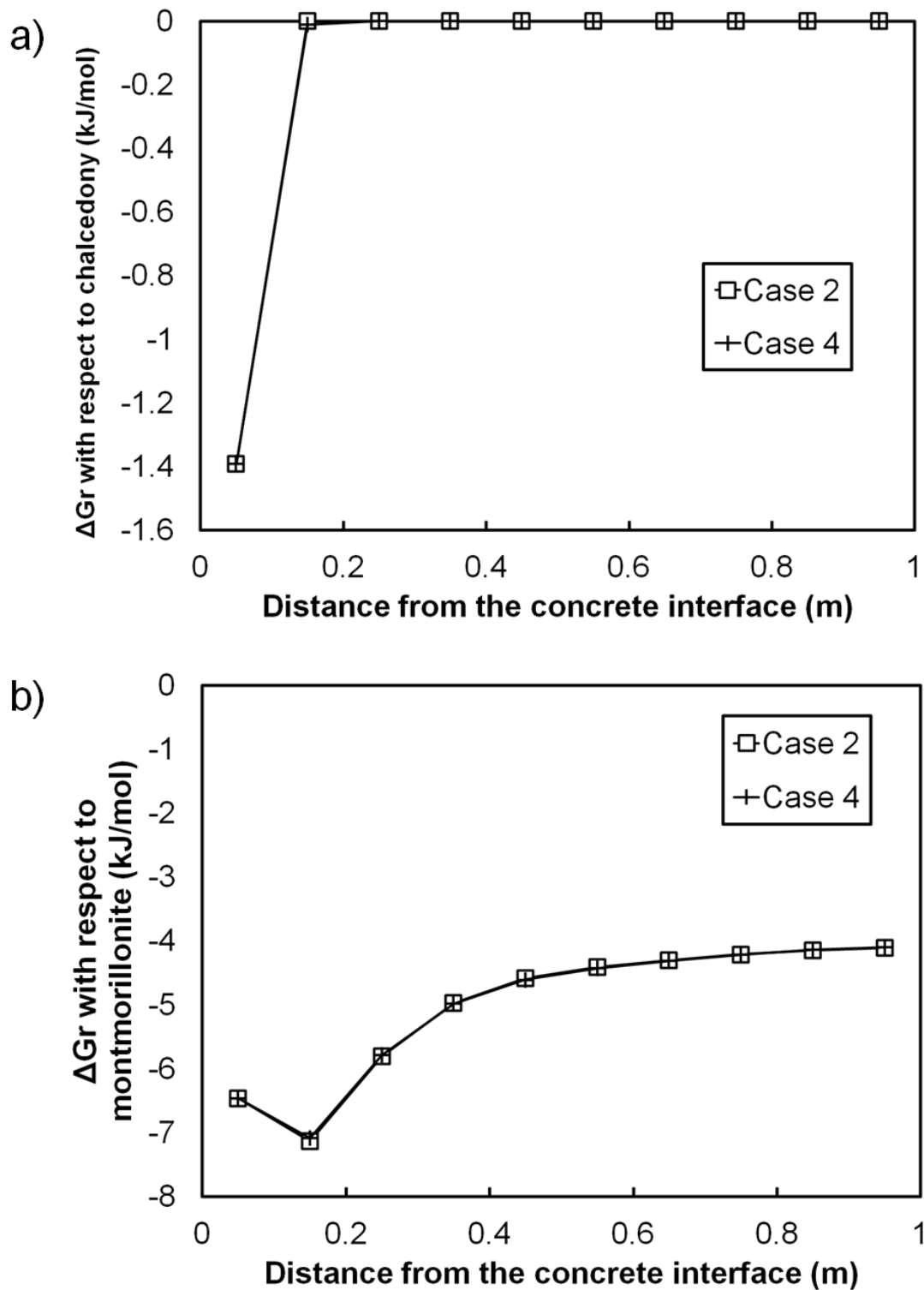


Fig. 4 - 8 Calculated distribution of the Gibbs free energy (ΔG_r) of the dissolution reaction of chalcedony (a) and montmorillonite (b) in Case 2 and 4 after 100,000 years.

Chapter 5 General conclusion

In this paper, a microstructural method of analysis by micro-focus X-ray CT was developed to track the alteration processes involved in bentonite/hyperalkaline-fluid interactions as a function of time. The dissolution of montmorillonite in compacted bentonite was then considered to clarify the effect of compaction. Based on these data, the dissolution rate of montmorillonite in compacted bentonite was considered in order to model the long-term performance of bentonite buffer materials.

First, microfocus X-ray CT studies for geologic materials since 2000 were reviewed, and the possibility of whether X-ray CT can be applied or not to the present study was discussed. As a result, it is inferred that the use of microfocus X-ray CT will enable the tracking of the alteration processes involved in bentonite/hyperalkaline-fluid interactions as a function of time. Observation of these processes will provide the necessary quantitative data to validate the geochemical model simulating the experimental results.

An advective alteration experiment of compacted bentonite specimens with a dry density of 0.3 Mg m^{-3} was conducted with hyperalkaline-fluid to observe the formation and dissolution processes of secondary and accessory minerals, respectively, in bentonite by X-ray CT. In bentonite/hyperalkaline-fluid interactions, the formation of a secondary mineral in the bentonite was observed in the CT images. The secondary mineral was identified as analcime by the XRD data. By developing a methodology that discriminates analcime from montmorillonite and other accessory minerals in the CT images, the volume of analcime formed was quantified as a function of time. The geochemical transport model became consistent with the experimental results when the reactive surface area in the rate equation for the montmorillonite dissolution was reduced and the effect of departure from equilibrium was considered. Consequently, it can be considered that the actual dissolution rate of the montmorillonite in compacted bentonite is one or two orders lower than that of the montmorillonite in powder bentonite and it is influenced by the effect of departure from equilibrium as determined from the microstructural analytical method by X-ray CT. Thus the dissolution rate of compacted montmorillonite must be used in predicting the long-term performance of

barrier systems. On the other hand, dissolution of the silica minerals may inhibit the dissolution of montmorillonite in the bentonite by increasing the silica concentration and hence the saturation state with respect to montmorillonite in the pore water. Therefore, the kinetic data for the dissolution of chalcedony was obtained by developing the methodology to quantify the volume of accessory minerals in the CT images. The geochemical transport model consistent with the experimental results indicates that the pore water in the bentonite approached near saturation with respect to montmorillonite due to the dissolution of silica minerals in bentonite, inhibiting the dissolution of montmorillonite in bentonite. In the much more compacted bentonite system, dissolution of montmorillonite will be inhibited for a much longer term. Therefore, it is important to consider the dissolution behavior of silica minerals to sufficiently evaluate the long-term performance of bentonite as a component of engineered barriers for radioactive waste disposal.

Based on the above data, the sensitivity analyses of the models were conducted to investigate the effects of key factors such as the reactive surface area of montmorillonite, the departure from equilibrium and the dissolution of silica minerals on the long-term performance of the bentonite buffer material. These simulations indicated that the reaction between bentonite and concrete was controlled by the dissolution of montmorillonite in the short-term (~1000 years). Therefore, the reactive surface area of montmorillonite and the ΔG_r with respect to montmorillonite in compacted bentonite are the key factors that must be considered. In addition, choosing the appropriate dissolution rate model of montmorillonite in compacted bentonite may become important to evaluate the long-term performance of the bentonite buffer material. On the other hand, the simulation results for chalcedony do not show a difference between case that considers the effect of surface area and the case that does not, suggesting that the primary silica minerals such as chalcedony do not affect the long-term results. This is due to the formation of secondary minerals such as clinoptilolite and phillipsite that control the concentrations of Al and Si. The types of secondary minerals and kinetic data for the formation of secondary minerals are necessary parameters in evaluating the long-term performance of bentonite barriers by modeling.

As described above, a microstructural method of analysis by micro-focus X-ray CT

developed in this study is applicable to evaluate the performance of bentonite buffer materials. Furthermore, in order to create reasonable and realistic evaluations of the bentonite barriers it is necessary to consider the effects of surface area of montmorillonite and ΔG_r . However, this study focused only on the interaction between bentonite and a hyperalkaline fluid composed only of Na-OH. In the future, advective or diffusion alteration experiments in the K-OH system, Ca-OH system and cement/bentonite system will also need to be studied using micro-focus X-ray CT in order to derive quantitative data on the formation of secondary minerals and porosity changes in the sample as a function of time, over a wider range of conditions. These quantitative data will allow us to sufficiently evaluate the long-term performance of bentonite buffer materials.

References

- Aagaard, P., Helgeson, H. C., 1982. Thermodynamic and kinetics constraints on reaction rates among minerals and aqueous solutions; I, theoretical considerations." *American Journal of Science* 282, 237-285
- Atkinson, A., 1985. The time dependence of pH within a repository for radioactive waste disposal. United Kingdom Atomic Energy Research Establishment Report AERE-R11777, United Kingdom Atomic Energy Research Establishment, Harwell, UK
- Atkinson, A., Everitt, N. M., Guppy, R., 1987. Evolution of pH in a radwaste repository. Experimental simulation of cement leaching. United Kingdom Atomic Energy Research Establishment Report AERE-R12594, United Kingdom Atomic Energy Research Establishment, Harwell, UK
- Alekseyev, V. A., Medvedeva, L. S., Prisyagina, N. I., Meshalkin, S. S., Balabin, A. I., 1997. Change in the dissolution rates of alkali feldspars as a result of secondary mineral precipitation and approach to equilibrium. *Geochimica et Cosmochimica Acta* 61, 1125-1142
- Appelo, C. A. J., Postma, D., 2009. *Geochemistry, ground water and pollution*: CRC Press Taylor and Francis Group
- Bauer, A., Berger, G., 1998. Kaolinite and smectite dissolution rate in high molar KOH solutions at 35 °C and 80 °C. *Applied Geochemistry* 13, 905-916
- Bauer, A., Lanson, B., Ferrage, E., Emmerich, K., Taubald, H., Schild, D., Velde, B., 2006. The fate of smectite in KOH solutions. *American Mineralogist* 91, 1313-1322
- Bennett, P. C., 1991. Quartz dissolution in organic-rich aqueous systems. *Geochimica et Cosmochimica Acta* 55, 1781-1797
- Bennett, P. C., Melcer, M. E., Siegel, D. I., Hassett, J. P., 1988. The dissolution of quartz in dilute aqueous-solutions of organic-acids at 25°C. *Geochimica et Cosmochimica Acta* 52, 1521-1530
- Berger, G., Cadore, E., Schott, J., Dove, P. M., 1994. Dissolution rate of quartz in lead and sodium electrolyte solutions between 25 and 300°C: effect of the nature of

- surface complexes and reaction affinity. *Geochimica Et Cosmochimica Acta* 58, 541-551
- Berner, U. R., 1992, Evolution of pore water chemistry during degradation of cement in a radioactive waste repository environment. *Waste Management* 12, 201-219
- Bickmore, B. R., Nagy, K. L., Gray, A. K., Brinkerhoff, A. R., 2006. The effect of Al(OH)(4)(-) on the dissolution rate of quartz. *Geochimica et Cosmochimica Acta* 70, 290-305
- Blanc, Ph., Lassin. A., Piantone, P., Azaroual, M., Jacquemet, N., Fabbri, A., Gaucher, E. C., 2012. Thermoddem: A geochemical database focused on low temperature water/rock interactions and waste materials. *Applied Geochemistry* 27, 2107-2116
- Blum, A. E., Yund, R. A., Lasaga, A. C., 1990. The effect of dislocation density on the dissolution rate of quartz. *Geochimica et Cosmochimica Acta* 54, 283-297
- Brady, P. V., Walther, J. V., 1990. Kinetics of quartz dissolution at low-temperatures. *Chemical Geology* 82, 253-264
- Burch, T. E., Nagy, K. L., Lasaga, A. C., 1993. Free-energy dependence of albite dissolution Kinetics at 80°C and pH 8.8. *Chemical Geology* 105, 137-162
- Cama, J., Ayora, C., 1998. Modeling the dissolution behaviour of a clayey barrier. *Mineralog. Mag* 62A part1, 271-272
- Cama, J., Ganor, J., Ayora, C., Lasaga, C. A., 2000. Smectite dissolution kinetics at 80 °C and pH 8.8. *Geochimica et Cosmochimica Acta* 64, 2701-2717
- Casey, W. H., Lasaga, A. C., Gibbs, G. V., 1990. Mechanisms of Silica dissolution as Inferred from the kinetic isotope effect. *Geochimica et Cosmochimica Acta* 54, 3369-3378
- Chou, L., Wollast, R., 1984. Study of the weathering of albite at room-temperature and pressure with a fluidized-bed reactor. *Geochimica et Cosmochimica Acta* 48, 2205-2217
- Chou, L., Wollast, R., 1985. Steady-state kinetics and dissolution mechanisms of albite. *American Journal of Science* 285, 963-993
- Colletta, B., Letouzey, J., Pinedo, R., Ballard, J. F., Bale, P., 1991. Computerized X-ray tomography analysis of sandbox models - examples of thin-skinned thrust

- systems. *Geology* 19, 1063-1067
- Dove, P. M., 1994. The dissolution kinetics of quartz in sodium-chloride solutions at 25°C to 300°C. *American Journal of Science* 294, 665-712
- Dove, P. M., 1999. The dissolution kinetics of quartz in aqueous mixed cation solutions. *Geochimica et Cosmochimica Acta* 63, 3715-3727
- Dove, P. M., Crerar, D. A., 1990. Kinetics of quartz dissolution in electrolyte-solutions using a hydrothermal mixed flow reactor. *Geochimica et Cosmochimica Acta* 54, 955-969
- Devore, M. L., Kenrick, P., Pigg, K. B., Ketcham, R. A., 2006. Utility of high resolution x-ray computed tomography (HRXCT) for paleobotanical studies: An example using London Clay fruits and seeds. *American Journal of Botany* 93, 1848-1851
- Elakneswaran, Y., Nawa, T., Kurumisawa, K., 2009. Electrokinetic potential of hydrated cement in relation to adsorption of chlorides. *Cement and Concrete Research* 39, 340-344
- Elakneswaran, Y., Nawa, T., Sato, T., Nakabayashi, R., Yoneda, T., 2011. Integrated thermodynamic modeling approach for predicting long-term performance of concrete/bentonite engineered barrier systems in a geological repository for radioactive waste disposal. *Internet Journal of Society for Social Management*, Serial No. SMS11-5786, 1-10
- Fernández, R., Cuevas, J., Sánchez, L., R. de la Villa, V., Leguey, S., 2006. Reactivity of the cement-bentonite interface with alkaline solutions using transport cells. *Applied Geochemistry* 21, 977-992
- Fernández, R., Cuevas, J., Mäder, U. K., 2009. Modelling concrete interaction with a bentonite barrier. *European Journal of Mineralogy* 21, 177-191
- Fukuda, D., Nara, Y., Kobayashi, Y., Maruyama, M., Koketsu, M., Hayashi, D., Ogawa, H., Kaneko, K., 2012. Investigation of self-sealing in high-strength and ultra-low-permeability concrete in water using micro-focus X-ray CT. *Cement and Concrete Research* 42, 1494-1500
- Gaucher, E. C., Blanc, P., Matray, J. M., Michau, N., 2004. Modeling diffusion of an alkaline plume in a clay barrier. *Applied Geochemistry* 19, 1505-1515
- Hellmann, R., 1994. The albite-water system: Part I. The kinetics of dissolution as a

- function of pH at 100, 200, and 300°C. *Geochimica et Cosmochimica Acta* 58, 595-611
- Hellmann, R., Tisserand, D., 2006. Dissolution kinetics as a function of the Gibbs free energy of reaction: An experimental study based on albite feldspar. *Geochimica et Cosmochimica Acta* 70, 364-383
- Hounsfield, G. N., 1973. Computerized transverse axial scanning (tomography): Part 1. Description of system. *British Journal of Radiology* 46, 1016-1022
- House, W. A., Orr, D. R., 1992. Investigation of the pH-dependence of the kinetics of quartz dissolution at 25°C. *Journal of the Chemical Society-Faraday Transactions* 88, 233-241
- Huertas, F. J., Caballero, E., de Cisneros, C. J., Huertas, F., Linares, J., 2001. Kinetics of montmorillonite dissolution in granitic solutions. *Applied Geochemistry* 16, 397-407
- Icenhower, J. P., Dove, P. M., 2000. The dissolution kinetics of amorphous silica into sodium chloride solutions: Effects of temperature and ionic strength. *Geochimica et Cosmochimica Acta* 64, 4193-4203
- Inazaki, T., Inouchi, Y., Nakano, T., 1995. Use of medical X-ray CT scanner for nondestructive and quantitative analysis of lake sediments. *Bulletin of the Geological Survey of Japan* 46, 629-642 (in Japanese with English abstract)
- Ito, M., Okamoto, M., Shibata, M., Sasaki, Y., Danhara, T., Suzuki, K., Watanabe, T., 1993. Mineral Composition Analysis of Bentonite. PNC TN 8430 93-003: Power Reactor and Nuclear Fuel Develop, Corporation, Tokyo (in Japanese)
- JAEA, FEPC, 2007. Second progress report on research and development for TRU waste disposal in Japan –repository design, safety assessment and means of implementation in the generic phase. Japan Atomic Energy Agency and Federation of Electric Power Companies of Japan, JAEA-Review 2007-010, FEPC TRU-TR2-2007-01
- JNC, 2000. Progress report on disposal concept for TRU waste in Japan. Japan Nuclear Cycle Development Institute Report JNC TY1400 2000-02
- Joseph, P. M., 1981. Artifacts in computed tomography, in *Radiology of the Skull and Brain: Technical Aspects of Computed Tomography*, In: Newton, T. H., Potts, T.

- G. (Eds.), vol. 5. CV Mosby Company, Mosby, St. Louis, pp. 3956-3992."(1981)
- Kawaragi, C., Yoneda, T., Sato, T., Kaneko, K., 2009. Microstructure of saturated bentonites characterized by X-ray CT observations. *Engineering Geology* 106, 51-57
- Kitamoto, A., Takagi, T., 1999. Image classification using probabilistic models that reflect the internal structure of mixels. *Pattern Analysis and Applications* 2, 31-43
- Knauss, K. G., Wolery, T. J., 1988. The dissolution kinetics of quartz as a function of pH and time at 70°C. *Geochimica et Cosmochimica Acta* 52, 43-53
- Knauss, K. G., Copenhaver, S. A., 1955. The effect of malonate on the dissolution kinetics of albite, quartz, and microcline as a function of pH at 70°C. *Applied Geochemistry* 10, 17-33
- Kozaki, T., Suzuki, S., Kozai, N., Sato, S., Ohashi, H., 2001. Observation of microstructures of compacted bentonite by microfocus X-ray computerized tomography (micro-CT). *Journal of Nuclear Science and Technology* 38, 697-699
- Kuwahara, Y., 2006. In-situ AFM study of smectite dissolution under alkaline conditions at room temperature. *American Mineralogist* 91, 1142-1149
- Lasaga, A. C., 1981. Transition state theory. *Reviews in Mineralogy and Geochemistry* 8, 135-168
- Lasaga, A. C., 1998. *Kinetic Theory in the Earth Sciences*. Princeton University Press, Princeton
- Lasaga, A. C., Soler, J. M., Ganor, J., Burch, T. E., Nagy, K. L., 1994. Chemical-weathering rate laws and global geochemical cycles. *Geochimica et Cosmochimica Acta* 58, 2361-2386
- Liu, J., Kozaki, T., Horiuchi, Y., Sato, S., 2003. Microstructure of montmorillonite/silica sand mixture and its effects on the diffusion of strontium ions. *Applied Clay Science* 23, 89-95
- Maher, K., Steefel, C. I., DePaolo, D. J., Viani, B. E., 2006. The mineral dissolution rate conundrum: Insights from reactive transport modeling of U isotopes and pore

- fluid chemistry in marine sediments. *Geochimica Et Cosmochimica Acta* 70, 337-363
- Marty, N. C. M., Cama, J., Sato, T., Chino, D., Villi  ras, F., Razafitianamaharavo, A., Brendl  , J., Giffaut, E., Soler, J. M., Gaucher, E. C., Tournassat, C., 2011. Dissolution kinetics of synthetic Na-smectite. An integrated experimental approach. *Geochimica et Cosmochimica Acta* 75, 5849-5864
- Metz, V., Amram, K., Ganor, J., 2005. Stoichiometry of smectite dissolution reaction." *Geochimica Et Cosmochimica Acta* 69, 1755-1772
- Nagy, K. L., Lasaga, A. C., 1992. Dissolution and precipitation kinetics of gibbsite at 80  C and pH 3: the dependency on solution saturation state." *Geochimica Et Cosmochimica Acta* 56, 3093-3111
- Nakashima, Y., 2000. The use of X-ray CT to measure diffusion coefficients of heavy ions in water-saturated porous media. *Engineering Geology* 56, 11-17
- Nakashima, Y., Hirai, H., Koishikawa, A., Ohtani, T., 1997. Three-dimensional imaging of arrays of fluid inclusions in fluorite by high-resolution X-ray CT. *Neues Jahrbuch Fur Mineralogie-Monatshefte*, 559-568
- Nakashima, Y., Kamiya, S., 2007. Mathematica programs for the analysis of three-dimensional pore connectivity and anisotropic tortuosity of porous rocks using X-ray computed tomography image data. *Journal of Nuclear Science and Technology* 44, 1233-1247
- Nakashima, Y., Nakano, T., Nakamura, K., Uesugi, K., Tsuchiyama, A., Ikeda, S., 2004. Three-dimensional diffusion of non-sorbing species in porous sandstone: computer simulation based on X-ray microtomography using synchrotron. *Journal of Contaminant Hydrology* 74, 253-264
- Nakashima, Y., Nakashima, S., Gross, D., Weiss, K., Yamauchi, K., 1998. NMR imaging of H-1 in hydrous minerals. *Geothermics* 27, 43-53
- Nakayama, S., Sakamoto, Y., Yamaguchi, T., Akai, M., Tanaka, T., Sato, T., Iida, Y., 2004. Dissolution of montmorillonite in compacted bentonite by highly alkaline aqueous solutions and diffusivity of hydroxide ions. *Applied Clay Science* 27, 53-65
- NUMO, 2011. Technical and safety related to the disposal of low-level radioactive

- waste in geological disposal. NUMO-TR-10-03
- Oelkers, E. H., Schott, J., 1995. Experimental study of anorthite dissolution and the relative mechanism of feldspar hydrolysis. *Geochimica Et Cosmochimica Acta* 59, 5039-5053
- Oda, C., Honda, A., Savage, D., 2004. An analysis of cement-bentonite interaction and evolution of pore water chemistry. Pp. A3-74A3-79 in: *Proceedings of the International Workshop on Bentonite-Cement Interaction in the Repository Environment* (R. Metcalfe and C. Walker, editors). Nuclear Waste Management Organisation of Japan, Tokyo.
- Oda, C., Walker, C., Chino, D., Ichige, S., Honda, A., Sato, T., Yoneda, T., 2012. Na-montmorillonite dissolution and analcime precipitation kinetics as a function of the Gibbs free energy of reaction at 70 °C in 0.3 M NaOH solution. *Applied Clay Science*, submitted.
- Ohtani, T., Nakashima, Y., Muraoka, H., 1997. Three-dimensional imaging of miarolitic cavities in the Kakkonda granite using X-ray CT. *Journal of the Geothermal Research Society of Japan* 19, 209-216 (in Japanese with English abstract)
- Palandri, J. L., Kharaka, Y. K., 2004. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. U. S. Geological Survey Water-Resources Investigations Report, 04-1068
- Parkhurst, D. L., Appelo, C. A. J., 1999. User's guide to PHREEQC (version 2)-a computer program for speciation, batch-reaction, one-dimesnional transport, and inverse geochemical calculations. USGS Water-resour. Inv. Rep., 99-4259
- Raynaud, S., Fabre, D., Mazerolle, F., Geraud, Y., Latiere, H. J., 1989. Analysis of the internal structure of rocks and characterization of mechanical deformation by a non-destructive method - X-ray tomodensitometry. *Tectonophysics* 159, 149-159
- Rozalen, M., Brady, P. V., Huertas, F. J., 2009. Surface chemistry of K-montmorillonite: Ionic strength, temperature dependence and dissolution kinetics. *Journal of Colloid and Interface Science* 333, 474-484
- Sánchez, L., Cuevas, J., Ramírez, S., De León, D. R., Fernández, R., Dela Villa, R. V.

- and Leguey, S., 2006. Reaction kinetics of FEBEX bentonite in hyperalkaline conditions resembling the cement-bentonite interface. *Applied Clay Science* 33, 125-141
- Sato, T., Kuroda, M., Tsutsui, M., Fukushi, K., Tanaka, T., Nakayama, S., 2004. Dissolution mechanism and kinetics of smectite under alkaline conditions. *Proceedings of the international workshop on bentonite-cement interaction in repository environments*, NUMO-TR-04-05
- Satoh, H., Ishii, T., Owada, H., 2013. Dissolution of compacted montmorillonite at hyperalkaline pH and 70 °C: *in situ* VSI and *ex situ* AFM measurements. *Clay Minerals* 48, 285-294
- Savage, D., 1997. Review of the potential effects of alkaline plume migration from a cementitious repository for radioactive waste. Implications for performance assessment. UK Environment Agency Technical Report: P60
- Savage, D., Noy, D., Mihara, M., 2002. Modelling the interaction of bentonite with hyperalkaline fluids. *Applied Geochemistry* 17, 207-223
- Schwartzentruber, J., Fürst, W., Renon, H., 1987. Dissolution of quartz into dilute alkaline-solutions at 90°C – a kinetic-study. *Geochimica et Cosmochimica Acta* 51, 1867-1874
- Schott, J., Oelkers, E. H., 1995. Dissolution and crystallization rates of silicate minerals as a function of chemical affinity. *Pure and Applied Chemistry* 67, 903-910
- Stauffer, D., Aharony, A., 1994. *Introduction to Percolation Theory*, Revised 2nd Edition. Taylor & Francis, London, 192
- Steefel, C. I., Lichtner, P. C., 1994. Diffusion and reaction in rock matrix bordering a hyperalkalinefluid-filled fracture. *Geochimica Et Cosmochimica Acta* 58, 3595-3612
- Takase, H., 2004. Discussion on PA model development for bentonite barriers affected by chemical interaction with concrete: do we have enough evidence to support bentonite stability? *Proceedings of the International Workshop on Bentonite-Cement Interaction in Repository Environments*, Posiva Working Report 2004-25, Posiva Oy, Olkiluoto, Finland.
- Tomioka, S., Kozaki, T., Takamatsu, H., Noda, N., Nisiyama, S., Kozai, N., Suzuki, S.,

- Sato, S., 2008. Analysis of microstructural images of dry and water-saturated compacted bentonite samples observed with X-ray micro CT. *Applied Clay Science* 47, 65-71
- Vigil de la Villa, R., Cuevas, J., Ramírez, S., Leguey, S., 2001. Zeolite formation during the alkaline reaction of bentonite. *European Journal of Mineralogy* 13, 635-644
- Vieillard, P., Ramírez, S., Bouchet, A., Cassagnabère, A., Meunier, A., Jacquot, E., 2004. Alteration of the Callov-Oxfordian clay from Meuse-Haute Marne Underground Laboratory (France) by alkaline solution: II. Modelling of mineral reactions. *Applied Geochemistry* 19, 1699-1709
- Van Geet, M., Swennen, R., Wevers, M., 2000. Quantitative analysis of reservoir rocks by microfocus X-ray computerised tomography. *Sedimentary Geology* 132, 25-36
- Van Geet, M., Swennen, R., David, P., 2001, Quantitative coal characterisation by means of microfocus X-ray computer tomography, colour image analysis and back-scattered scanning electron microscopy. *International Journal of Coal Geology* 46, 11-25
- Van Geet, M., Volckaert, G., Roels, S., 2005. The use of microfocus X-ray computed tomography in characterising the hydration of a clay pellet/powder mixture. *Applied Clay Science* 29, 73-87
- Velbel, M. A., 1993. Constancy of silicate-mineral weathering-rate ratios between natural and experimental weathering: implications for hydrologic control of differences in absolute rates. *Chemical Geology* 105, 89-99
- Watson, C., Hane, K., Savage, D., Benbow, S., Cuevas, J., Fernandez, R., 2009. Reaction and diffusion of cementitious water in bentonite: Results of 'blind' modelling. *Applied Clay Science* 45, 54-69
- Wellington, S. L., Vinegar, H. J., 1987. X-ray computerized tomography. *Journal of Petroleum Technology* 39, 885-898
- White, A. F., Brantley, S. L., 2003. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? *Chemical Geology* 202, 479-506
- White, A. F., Peterson, M. L., 1990. Role of reactive-surface-area characterization in

- geochemical kinetic-models. *Acs Symposium Series* 416, 461-475
- Yamaguchi, T., Sakamoto, Y., Akai, Takazawa, M., Iida, Y., Tanaka, T., Nakayama, S., 2007. Experimental and modeling study on long-term alteration of compacted bentonite with alkaline groundwater. *Physics and Chemistry of the Earth* 32, 298-310.
- Yokoyama, T., Banfield, J. F., 2002. Direct determinations of the rates of rhyolite dissolution and clay formation over 52,000 years and comparison with laboratory measurements. *Geochimica Et Cosmochimica Acta* 66, 2665-2681
- Yokoyama, S., Kuroda, M., Sato, T., 2005. Atomic force microscopy study of montmorillonite dissolution under highly alkaline conditions. *Clays and Clay Minerals* 53, 147-154
- Zhu, C., 2005. In situ feldspar dissolution rates in an aquifer. *Geochimica Et Cosmochimica Acta* 69, 1435-1453
- Zitova, B., Flusser, J., 2003. Image registration methods: a survey. *Image and Vision Computing* 21, 977-1000

Acknowledgement

I would particularly like to thank Professor Dr. Tsutomu Sato, the author's supervisor, Professor Dr. Tetsuro Yoneda and Associate Professor Dr Tsubasa Otake (Laboratory of Environmental Geology, Hokkaido University) for their long-term encouragement and under the direction of this studies and their comment and suggestion for the editing this thesis.

I also has a deep sense of appreciation to Professor Dr. Katsuhiko Kaneko, Associate Professor Dr. Satoru Kawasaki and Assistant Professor Dr. Masaji Kato (Laboratory of Terrestrial Engineering, Hokkaido University) for supplying the machine time of X-ray CT and helpful discussion. I thank Assistant Professor Dr. Yoshitaka Nara (Laboratory of Earth Crust Engineering, Kyoto University) and Dr. Daisuke Fukuda (Laboratory of Rock Mechanics, Hokkaido University) for experimental help and helpful advices with regard to X-ray CT study.

I am also thankful Dr. Chie Oda (Geological Isolation Research and Development Directorate, JAEA) for helpful advices during my studies. I would like to thanks for Dr. Eric Gaucher, Dr. Claret Francis, Dr. Christophe Tournassat, Dr. Philip Blanc, Dr. Nicolas Marty (BRGM, France) and Elakneswaran Yogarajah (Laboratory of Concrete, Tokyo University) for helpful discussion for Phreeqc. Their advice, suggestion and encouragement are very strong support to progress for this study. I am grateful to the following people.

And I want to express my thanks to the present and former members of our laboratory; Dr. Keizo Suzuki, Dr. Kenichi Ito, Dr. Shuji Tamamura, Dr. Yoshitaka Nara, Dr. Kazuya Morimoto, Dr. Chie Kawaragi, Mrs. Keiko Ota, Dr. Einstine Opiso, Dr. Pich Bunchoeun, Dr. Liu Xiaoji, Mr. Shinya Gamo, Mr. Hideki Takayama, Mr. Atsushi Asai, Mr. Keishiro Ishida, Mr. Yukinobu Kimura, Mr. Shotaro Anraku, Mr. Daisuke Chino, Ms. Kaori Hiroyama, Mr. Hiroshi Mokko, Mr. Shunsuke Ota, Mr. Hiroki Okamoto, Mr Kohhei Tani, Mr. Tomoya Bando, Mr. Masato Mikami, Mr. Kenta Fujita, Ms. Shimeno Aoi, Ms. Megumi Hatayama, Mr. Shohei Hara, Mr. Jun Hoshino, Mr. Tatsuya Kijima, Mr. Toru Nishiuchi, Mr. Takato Nishita, Mr. Hajime Hasegawa, Mr Isamu Matsubara, Mr. Akira Matsumoto, Mr. Francisco Paul Clarence Magdael, Ms. Mai Ueda, Ms.

Haruko Okahashi, Ms Syafina Binti Mohd Ghazi, Mr. Yasumoto Tsukada, Mr. Yasutaka Yamane, Mr. Tadashi Kasahara, Mr. Takashi Sanbuichi, Mr. Ryohei Suzuki, Mr. Naoki Fukuhara, Mrs. Yoshie Hoshi a and Mrs Ami Sato (Hokkaido University)

Finally, I would like to thanks my father and mother for kind support for my study activities.

Appendix I Phreeqc input file of Sato-Oda model modified with specific surface area of montmorillonite ($7 \times 0.2 \text{ m}^2\text{g}^{-1}$) in Chapter 2

PRINT

-user_print true
-reset false
-selected_output true
-status true

SELECTED_OUTPUT

-file Chapter 2.csv
-reset false
-distance true
-time true
-water true
-pH true
-pe true
-temperature true
-ionic_strength true
-totals Na K Ca Mg C S Fe Al Cl Si
-equilibrium_phases Pyrite Analcime Dolomite Calcite Gibbsite Brucite
-saturation_indices Na-mont
-kinetics Anorthite Albite Chalcedony Quartz Na-mont

PHASES

Na-mont #O20unit 80degree

$\text{Na}_{0.66}\text{Mg}_{0.66}\text{Al}_{3.34}\text{Si}_8\text{O}_{20}(\text{OH})_4 + 12\text{H}^+ + 8\text{H}_2\text{O} = 3.34\text{Al}^{+++} + 0.66\text{Mg}^{++} + 0.66\text{Na}^+ + 8\text{H}_4\text{SiO}_4$
log_k -4.677984505

Chalcedony #Instead of amorphous silica

$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$

log_k -2.700

-delta_H 13.616 kJ/mol # References :00gun/arn

-analytic 1.4680170e+01 3.9464550e-03 -1.0348495e+03 -6.0255500e+00
-1.5862750e+04

RATES

Na-mont

```

-start
1 moles = 0
10 if (m <= 0) or (SR("Na-mont")>1) then goto 2000
20 R = 8.31
30 Rk = 8.31E-3
25 si_mna=(SI("Na-mont"))
50 if(si_mna = 0) then goto 2000
60 A = 177*exp(20.37/(Rk*TK))*ACT("OH-")
70 B = 0.0297*exp(23.53/(Rk*TK))*ACT("OH-")
80                                     Sato =
4.74e-6*exp(-39.57/(Rk*TK))*A/(1+A)+1.7*exp(-69.67/(Rk*TK))*B/(1+B)
85 Oda = 1-exp(2.56e-5*(0.5*(si_mna)*LOG(10))^3)
90 rf = Oda * Sato
100 if(si_mna > 0 ) then goto 1000
110 moles = rf * 7 * 367.0214*2 * M * TIME *0.2
120 goto 2000
1000 moles = -1.0 * rf * 7 * 367.0214*2 * M * TIME *0.2
2000 SAVE moles
-end

```

Chalcedony # instead of Quartz_alpha, chalcedony

warning dissolution only

```

-start
10 mole = 0
20 If (m <= 0) or (SR("Chalcedony") > 1) Then GoTo 120
30 S = 0.03 # average BET; suggested value in m2/g
40 Mm = 60.1 # molar mass in g/mol
50
70 k = 10^(-12.12477265) * ACT("H+")^(-0.62567)
100 rate = S * m * Mm * k * ((1 - SR("Chalcedony") ^ theta) ^ eta)*0.02
110 mole = rate * Time
120 Save mole
-end

```

Albite

warning dissolution only

-start

10 mole = 0

20 If (m <= 0) or (SR("Albite") > 1) Then GoTo 130

30 S = 0.24 # average BET; suggested value in m2/g

40 Mm = 262.2 # molar mass in g/mol

50 knu = 0.000000000000019 * exp((-61100 / 8.314) * ((1 / TK) - (1 / 298.15)))

60 k1 = 0.000000000000815 * exp((-64300 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("H+") ^ 0.335)

70 k2 = 0.000000000001 * exp((-60600 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("OH-") ^ 0.317)

80 k = knu + k1 + k2

90 theta = 1#0.48 # default value

100 eta = 1#100 # default value

theta = 0.48 and eta = 100 at pH 8.8 & 80 – C (extracted from 93bur/nag)

theta = 0.18 and eta = 5 at pH 9.2 & 150 – C (extracted from 06hel/tis)

theta = 0.76 and eta = 90 at pH 8.8 & 300 – C & 88 bars (extracted from 97ale/med)

110 rate = S * m * Mm * k * ((1 - SR("Albite")) ^ theta) ^ eta * 0.02

120 mole = rate * Time

130 Save mole

-end

Quartz

warning dissolution only

-start

10 mole = 0

20 If (m <= 0) or (SR("Quartz") > 1) Then GoTo 120

30 S = 0.07 # average BET; suggested value in m2/g

40 Mm = 60.1 # molar mass in g/mol

50 knu = 6.42E-14 * exp((-76700 / 8.314) * ((1 / TK) - (1 / 298.15)))

60 k1 = 0.00000000000192 * exp((-80000 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("OH-") ^ 0.339)

70 k = knu + k1

80 theta = 1 # default value

```

90 eta = 1 # default value
100 rate = S * m * Mm * k * ((1 - SR("Quartz")) ^ theta) ^ eta) * 0.02
110 mole = rate * Time
120 Save mole
-end

```

```

INCREMENTAL_REACTIONS true

```

```

#####
###      Input solution      ###
#####

```

```

Solution 0
-temp 80
REACTION 0
NaOH 1
0.3
Save solution 0
End

```

```

#####
###      bentonite phase      ###
#####

```

```

Solution 1-30
-temp 80

```

```

Equilibrium_phases 1-30
Calcite      0    0.081
Dolomite     0    0.044
Analcime     0    0.047
Pyrite       0    0.017
Brucite      0    0

```

```

Kinetics 1-30
Na-mont

```

-formula $\text{Na}_{0.66}\text{Mg}_{0.66}\text{Al}_{3.34}\text{Si}_8\text{O}_{20}(\text{OH})_4$
-cvoid true
-m0 0.22

Albite
-formula $\text{NaAlSi}_3\text{O}_8$
-m0 0.060

Chalcedony
-formula SiO_2
-m0 2.124

Quartz
-formula SiO_2
-m0 0.034

Save solution 1-30
END

Solution 31
-temp 80
END

TRANSPORT
-cells 30
-lengths 0.001
-dispersivities 1
-shifts 429
-flow_direction forward
-time_step 362598
-boundary_conditions constant flux s
-diffusion_coefficient 0 s
-punch_cells 1-30
-punch_frequency 1#

Appendix II Phreeqc input file of Sato-Oda model modified with specific surface area of montmorillonite ($7 \times 0.12 \text{ m}^2\text{g}^{-1}$) in Chapter 3

PRINT

-user_print true
-reset true
-selected_output true
-status true

SELECTED_OUTPUT

-file Chapter 3.csv
-reset false
-distance true
-time true
-water true
-pH true
-pe true
-temperature true
-ionic_strength true
-totals Na K Ca Mg C S Fe Al Cl Si
-equilibrium_phases Pyrite Dolomite Calcite Gibbsite Brucite
-kinetics Analcime Anorhite Albite Chalcedony Quartz Na-mont

PHASES

Na-mont #O20unit 70degree

$\text{Na}_{0.66}\text{Mg}_{0.66}\text{Al}_{3.34}\text{Si}_8\text{O}_{20}(\text{OH})_4 + 12\text{H}^+ + 8\text{H}_2\text{O} = 3.34\text{Al}^{+++} + 0.66\text{Mg}^{++} + 0.66\text{Na}^+ + 8\text{H}_4\text{SiO}_4$
log_k -3.52192655

Chalcedony #Instead of amorphous silica

$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$

log_k -2.700

-delta_H 13.616 kJ/mol # References :00gun/arn

-analytic 1.4680170e+01 3.9464550e-03 -1.0348495e+03 -6.0255500e+00
-1.5862750e+04

RATES

Na-mont

```

-start
1 moles = 0
10 if (m <= 0) or (SR("Na-mont")>1) then goto 2000
20 R = 8.31          # J/mol/K
30 Rk = 8.31E-3 # kJ/mol/k
25 si_mna=(SI("Na-mont"))
50 if(si_mna = 0) then goto 2000
60 A = 177*exp(20.37/(Rk*TK))*ACT("OH-")
70 B = 0.0297*exp(23.53/(Rk*TK))*ACT("OH-")
80                                     Sato =
4.74e-6*exp(-39.57/(Rk*TK))*A/(1+A)+1.7*exp(-69.67/(Rk*TK))*B/(1+B)
85 Oda = 1-exp(2.75e-5*(0.5*(si_mna)*LOG(10))^3)
90 rf = Oda * Sato
100 if(si_mna > 0 ) then goto 1000
110 moles = rf * 7 * 367.0214*2 * M * TIME *0.12
120 goto 2000
1000 moles = -1.0 * rf * 7 * 367.0214*2 * M * TIME *0.12
2000 SAVE moles
-end

```

Chalcedony # instead of Quartz_alpha, chalcedony

warning dissolution only

```

-start
10 mole = 0
20 If (m <= 0) or (SR("Chalcedony") > 1) Then GoTo 120
30 S = 0.03 # average BET; suggested value in m2/g
40 Mm = 60.1 # molar mass in g/mol
70 k = 10^(-12.5) * ACT("H+")^(-0.6)
100 rate = S * m * Mm * k * ((1 - SR("Chalcedony") ^ theta) ^ eta)* 0.06#0.04#*
0.0155
110 mole = rate * Time
120 Save mole
-end

```

Albite

warning dissolution only

-start

10 mole = 0

20 If (m <= 0) or (SR("Albite") > 1) Then GoTo 130

30 S = 0.24 # average BET; suggested value in m²/g

40 Mm = 262.2 # molar mass in g/mol

50 knu = 0.000000000000019 * exp((-61100 / 8.314) * ((1 / TK) - (1 / 298.15)))

60 k1 = 0.00000000000815 * exp((-64300 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("H+") ^ 0.335)

70 k2 = 0.00000000001 * exp((-60600 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("OH-") ^ 0.317)

80 k = knu + k1 + k2

90 theta = 1

100 eta = 1

110 rate = S * m * Mm * k * ((1 - SR("Albite")) ^ theta) ^ eta * 0.2

120 mole = rate * Time

130 Save mole

-end

Quartz

warning dissolution only

-start

10 mole = 0

20 If (m <= 0) or (SR("Quartz") > 1) Then GoTo 120

30 S = 0.07 # average BET; suggested value in m²/g

40 Mm = 60.1 # molar mass in g/mol

50 knu = 6.42E-14 * exp((-76700 / 8.314) * ((1 / TK) - (1 / 298.15)))

60 k1 = 0.0000000000192 * exp((-80000 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("OH-") ^ 0.339)

70 k = knu + k1

80 theta = 1

90 eta = 1

100 rate = S * m * Mm * k * ((1 - SR("Quartz")) ^ theta) ^ eta * 0.5

110 mole = rate * Time

120 Save mole

-end

Analcime

-start

1 moles = 0

10 if (m < 0) then goto 2000# or (SR("Analcime")>1) then goto 2000

20 R = 8.31 # J/mol/K

30 Rk = 8.31E-3 # kJ/mol/k

35 n = -0.6416

40 k = 1.616E-17

45 Am = 0.05 # m²/g

60 si_mna=(SI("Analcime"))

90 rf = k * ACT("H+") ^ n * (SR("Analcime")-1)

100 if(si_mna < 0) then goto 1000

110 moles = -1.0 * rf * Am * 222 * M * TIME

120 goto 2000

1000 moles = 1.0 * rf * Am * 222 * M * TIME

2000 SAVE moles

-end

INCREMENTAL_REACTIONS true

#####

Input solution

#####

Solution 0

-temp 70

REACTION 0

NaOH 1

0.3

Save solution 0

End

#####

```
###      bentonite phase      ###
#####
```

```
Solution 1-30
-temp 70
```

```
Equilibrium_phases 1-30
Calcite          0    0.081
Dolomite         0    0.044
Pyrite           0    0.017
Brucite          0     0
```

```
Kinetics 1-30
Na-mont
-formula Na0.66Mg0.66Al3.34Si8O20(OH)4
-cvode true
-m0  0.22
```

```
Albite
-formula NaAlSi3O8
-m0  0.060
```

```
Chalcedony
-formula SiO2
-m0 2.124
```

```
Quartz
-formula SiO2
-m0  0.034
```

```
Analcime
-formula Na0.99Al0.99Si2.01O6:H2O
-m0  0.047
```

```
Save solution 1-30
END
```

Solution 31

-temp 70

END

TRANSPORT

-cells 30

-lengths 0.001

-dispersivities 0

-shifts 527

-flow_direction forward

-time_step 58995.19844

-boundary_conditions constant flux

-diffusion_coefficient 0

-punch_cells 1-30

-punch_frequency 1

Appendix III Phreeqc input file in Case 4 of Chapter 4

PRINT

-user_print true
-reset true
-selected_output true
-status true

SELECTED_OUTPUT

-file Chapter 4.csv
-reset false
-distance true
-time true
-water true
-pH true
-pe true
-temperature true
-ionic_strength true
-totals Na K Ca Mg Sr Fe Fe(2) Fe(3) Cl S(6) S(-2) C(4) Si Al N(5)
-molalities H2 CO3-2 HCO3- CO2 Ca+2 Fe+2 Fe+3 Mg+2 Na+ Cl- NO3- XNa X2Ca
XK X2Mg
-equilibrium_phases Monosulfoaluminate Ettringite CSH(1.6) Portlandite Calcite
Dolomite Pyrite Tobermorite(11A) Phillipsite(Ca) Phillipsite(K) Phillipsite(Na)
Illite(Mg) Saponite(Ca) Saponite(K) Saponite(Mg) Saponite(Na) Clinoptilolite(Ca)
Clinoptilolite(K) Clinoptilolite(Na) Analcime #Albite Quartz Chalcedony Na-mont
-saturation_indices Na-mont
-kinetics Albite Quartz Chalcedony Na-mont

PHASES

Na-mont #O20unit 70degree

$$\text{Na}_{0.66}\text{Mg}_{0.66}\text{Al}_{3.34}\text{Si}_8\text{O}_{20}(\text{OH})_4 + 12\text{H}^+ + 8\text{H}_2\text{O} = 3.34\text{Al}^{+++} +$$
$$0.66\text{Mg}^{++} + 0.66\text{Na}^+ + 8\text{H}_4\text{SiO}_4$$

log_k 2.64 #-3.52192655

Chalcedony #Instead of amorphous silica

$$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$$

log_k -2.700
 -delta_H 13.616 kJ/mol # References :00gun/arn
 -analytic 1.4680170e+01 3.9464550e-03 -1.0348495e+03 -6.0255500e+00
 -1.5862750e+04

Albite

$\text{NaAlSi}_3\text{O}_8 + 4\text{H}^+ + 4\text{H}_2\text{O} = 1\text{Al}^{+++} + 1\text{Na}^+ + 3\text{H}_4\text{SiO}_4$
 log_k 2.741
 -delta_H -82.813 kJ/mol # References :06bla/pia
 -analytic -6.8971151e+02 -1.1421168e-01 3.8929472e+04 2.4929217e+02
 -1.8599180e+06

Quartz

$\text{SiO}_2 + 2\text{H}_2\text{O} = 1\text{H}_4\text{SiO}_4$
 log_k -3.740
 -delta_H 21.166 kJ/mol # References :82ric/bot
 -analytic -2.0340816e+01 -3.6232532e-03 -2.7341036e+02 7.6290847e+00
 -2.4835911e+04

Exchange_master_species

X X-

Exchange_species

X- = X-

log_k 0

X- + Na+ = XNa

log_k 0

2X- + Ca+2 = X2Ca

log_k 0.69

X- + K+ = XK

log_k 0.42

2X- + Mg+2 = X2Mg

RATES

Na-mont

-start

```

1 moles = 0
10 if (m <= 0) or (SR("Na-mont")>1) then goto 2000
20 R = 8.31          # J/mol/K
30 Rk = 8.31E-3 # kJ/mol/k
25 si_mna=(SI("Na-mont"))
50 if(si_mna = 0) then goto 2000
# dG/RT=LN (SR)=SI*LN10
60 A = 177*exp(20.37/(Rk*TK))*ACT("OH-")
70 B = 0.0297*exp(23.53/(Rk*TK))*ACT("OH-")
80                                     Sato =
4.74e-6*exp(-39.57/(Rk*TK))*A/(1+A)+1.7*exp(-69.67/(Rk*TK))*B/(1+B)
85 Oda = 1-exp(2.75e-5*(0.5*(si_mna)*LOG(10))^3)
# 86 if(Cama > 1.67e-3) then goto 90
# 87 Cama = 1.67e-3
90 rf = Oda * Sato
100 if(si_mna > 0 ) then goto 1000
# 100 if(si_mna > 0 ) then goto 2000
110 moles = rf * 7 * 367.0214*2 * M * TIME
120 goto 2000
1000 moles = -1.0 * rf * 7 * 367.0214*2 * M * TIME
2000 SAVE moles
-end

```

Chalcedony

```

# warning dissolution only
-start
10 mole = 0
20 If (m <= 0) or (SR("Chalcedony") > 1) Then GoTo 120
30 S = 0.03 # average BET; suggested value in m2/g
40 Mm = 60.1 # molar mass in g/mol
70 k = 10^(-14.5) * ACT("H+")^(-0.52)
80 theta = 1
90 eta = 1
100 rate = S * m * Mm * k * ((1 - SR("Chalcedony")) ^ theta) ^ eta) *0.02
110 mole = rate * Time
120 Save mole

```

-end

Albite

warning dissolution only

-start

10 mole = 0

20 If (m <= 0) or (SR("Albite") > 1) Then GoTo 130

30 S = 0.24 # average BET; suggested value in m²/g

40 Mm = 262.2 # molar mass in g/mol

50 knu = 0.00000000000019 * exp((-61100 / 8.314) * ((1 / TK) - (1 / 298.15)))

60 k1 = 0.00000000000815 * exp((-64300 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("H+") ^ 0.335)

70 k2 = 0.000000000001 * exp((-60600 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("OH-") ^ 0.317)

80 k = knu + k1 + k2

90 theta = 1

100 eta = 1

110 rate = S * m * Mm * k * ((1 - SR("Albite")) ^ theta) ^ eta

120 mole = rate * Time

130 Save mole

-end

Quartz

warning dissolution only

-start

10 mole = 0

20 If (m <= 0) or (SR("Quartz") > 1) Then GoTo 120

30 S = 0.07 # average BET; suggested value in m²/g

40 Mm = 60.1 # molar mass in g/mol

50 knu = 6.42E-14 * exp((-76700 / 8.314) * ((1 / TK) - (1 / 298.15)))

60 k1 = 0.0000000000192 * exp((-80000 / 8.314) * ((1 / TK) - (1 / 298.15))) *
(ACT("OH-") ^ 0.339)

70 k = knu + k1

80 theta = 1

90 eta = 1

100 rate = S * m * Mm * k * ((1 - SR("Quartz")) ^ theta) ^ eta

110 mole = rate * Time

120 Save mole

-end

Analcime

-start

1 moles = 0

10 if (m < 0) then goto 2000# or (SR("Analcime")>1) then goto 2000

20 R = 8.31 # J/mol/K

30 Rk = 8.31E-3 # kJ/mol/k

35 n = -0.6416

40 k = 1.616E-17

45 Am = 0.05#0.03#0.005#0.001 #0.5 # m2/g

60 si_mna=(SI("Analcime"))

90 rf = k * ACT("H+") ^ n * (SR("Analcime")-1)

100 if(si_mna < 0) then goto 1000

110 moles = -1.0 * rf * Am * 222 * M * TIME

120 goto 2000

1000 moles = 1.0 * rf * Am * 222 * M * TIME

2000 SAVE moles

-end

INCREMENTAL_REACTIONS true

#####

Concrete phase

#####

Solution 1-10

pH 8.46

pe -4.76

-temperature 25

-water 4.908738521

-units mol/L

Na 3.55E-03

K 6.15E-05

Ca	1.09E-04	
Mg	5.00E-05	
B	2.93E-04	
P	2.86E-06	
F	5.40E-05	
Cl	1.46E-05	
S(6)	1.11E-04	as SO4--
N(5)	2.30E-05	as NO3-
C(4)	3.54E-03	as HCO3-
Si	3.39E-04	

EQUILIBRIUM_PHASES 1-10

primary minerals

#Aggregates	0	-
Monosulfoaluminate	0	0.435266925
Ettringite	0	0.093293121
CSH(1.6)	0	19.42510957
Portlandite	0	17.19602858

#Secondary minerals

Tobermorite(11A)	0	0
Phillipsite(Ca)	0	0
Phillipsite(K)	0	0
Phillipsite(Na)	0	0
Illite(Mg)	0	0
Clinoptilolite(Ca)	0	0
Clinoptilolite(K)	0	0
Clinoptilolite(Na)	0	0
Microcline	0	0
Calcite	0	0
Dolomite	0	0
Pyrite	0	0
#Quartz	0	0
#Chalcedony	0	0
#Albite	0	0
Analcime	0	0
#Na-mont	0	0

```
#KINETICS 1-10
#Na-mont
#-formula Na0.66Mg0.66Al3.34Si8O20(OH)4
#-cvoid true
#-m0 0.0000000000000001
```

```
#Albite
#-formula NaAlSi3O8
#-m0 0.0000000000000001
```

```
#Chalcedony
#-formula SiO2
#-m0 0.0000000000000001
```

```
#Quartz
#-formula SiO2
#-m0 0.0000000000000001
```

```
#Analcime
#-formula Na0.99Al0.99Si2.01O6:H2O
#-m0 0.0000000000000001
```

```
Save solution 1-10
END
```

```
#####
####      Bentonite phase      #####
#####
```

```
Solution 11-20 # bentonite
pH      8.46
pe -4.76
-temperature 25
-water 8.138494309
-units mol/L
```

Na	0.003551	
K	0.0000615	
Ca	0.000109	
Mg	0.00005	
B	0.000293	
P	0.00000286	
F	0.000054	
Cl	0.0000146	
S(6)	0.000111	as SO4--
N(5)	0.000023	as NO3-
C(4)	0.00354	as HCO3-
Si	0.000339	

Exchange 11-20

XNa 11.30345037

X2Ca 0.814772055

XK 0.126229193

X2Mg 0.073010613

EQUILIBRIUM_PHASES 11-20

primary mineral

Calcite 0 5.272603055

Dolomite 0 2.862188535

Pyrite 0 1.099557429

#Quartz 0 3.136365378

#Chalcedony 0 198.6364739

#Albite 0 5.631382712

Analcime 0 4.352332392

#Na-mont 0 20.54447512

secondary minerals

Tobermorite(11A) 0 0

Phillipsite(Ca) 0 0

Phillipsite(K) 0 0

Phillipsite(Na) 0 0

Illite(Mg) 0 0

Clinoptilolite(Ca) 0 0

Clinoptilolite(K)	0	
Clinoptilolite(Na)	0	0
Microcline	0	0
Monosulfoaluminate	0	0
Ettringite	0	0
CSH(1.6)	0	0
Portlandite	0	0

KINETICS 11-20

Na-mont

-formula $\text{Na}_{0.66}\text{Mg}_{0.66}\text{Al}_{3.34}\text{Si}_8\text{O}_{20}(\text{OH})_4$

-cvsd true

-m0 14.38113258

Albite

-formula $\text{NaAlSi}_3\text{O}_8$

-cvsd true

-m0 3.941967899

Chalcedony

-formula SiO_2

-cvsd true

-m0 295.8638007

Quartz

-formula SiO_2

-cvsd true

-m0 2.195455765

#Analcime

#-formula $\text{Na}_{0.99}\text{Al}_{0.99}\text{Si}_{2.01}\text{O}_6\text{:H}_2\text{O}$

#-cvsd true

#-m0 3.046632674

Save solution 11-20

END

Transport

-cells 20
-lengths 0.1
-dispersivities 0
-shifts 63072
-flow_direction diffusion
-time_step 50000000
-boundary_conditions constant closed
-diffusion_coefficient 2.0E-11
-punch_cells 1-20
-punch_frequency 10
-print_cells 1-20
-print_frequency 10