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Proceedings of the International Information Exchange Meeting on Diffusion Phenomena in Bentonite and Rock

-Aiming at the Safety Assessment of the Geological Disposal-July 18, 2006 Horonobe Underground Research Center Horonobe-cho, Teshio-gun, Hokkaido, Japan

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Proceedings of the International Information Exchange Meeting on Diffusion Phenomena in Bentonite and Rock –Aiming at the Safety Assessment of the Geological Disposal– July 18, 2006 Horonobe Underground Research Center Horonobe-cho, Teshio-gun, Hokkaido, Japan

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The international information exchange meeting on diffusion phenomena in bentonite and rock was held at Horonobe Underground Research Center on 18th July, 2006. This meeting was hosted by Japan Atomic Energy Agency (JAEA) and supported by Hokkaido University and Radioactive Waste Management Funding and Research Center (RWMC).

Totally 18 scientists who are specialists of diffusion participated from Finland (VTT) and Japan (7 research organizations) in the meeting. 6 presentations were made on recent research activities and outputs on diffusion phenomena in bentonite and rock. The following is the 6 topics reported in the meeting;

- (1) Consistency in the description of diffusion in compacted bentonite (VTT, Finland),
- (2) Experimental approaches to the understanding of diffusion behavior of radionuclides in bentonite (Hokkaido University),
- (3) Assessment of data uncertainty on the diffusion coefficients for nuclides in engineered and natural barriers (JAEA Tokai)
- (4) Sorption and diffusion of Cs and HTO in compacted bentonite saturated with saline water at high temperatures (IRI),
- (5) The effects of aqueous composition on diffusion coefficient in bentonite (Mitsubishi Materials Corp.), and
- (6) Activation energies of diffusion for I and Cs in compacted smectite (JAEA Horonobe).

The presented papers and documents are compiled in the proceedings.

Keywords: Diffusion, Radionuclide, Bentonite, Compacted Bentonite, Rock, Geological Disposal, Safety Assessment

This is a proceedings compiled papers and documents in the meeting "International Information Exchange Meeting on Diffusion Phenomena in Bentonite and Rock".

⁺ Sedimentary Environment Engineering Group

ベントナイト及び岩石中に於ける拡散現象に関する情報交換会 ー地層処分の安全評価を目指してー 論文集 2006 年 7 月 18 日 北海道天塩郡幌延町 幌延深地層研究センター

日本原子力研究開発機構 地層処分研究開発部門 幌延深地層研究ユニット 佐藤 治夫⁺、畑中 耕一郎⁺

(2008年1月9日受理)

2006年7月18日、幌延深地層研究センターに於いて、「ベントナイト及び岩石中に於ける拡 散現象に関する情報交換会 一地層処分の安全評価を目指して一」が、日本原子力研究開発機構 の主催、北海道大学及び原子力環境整備促進・資金管理センターの後援により開催された。

フィンランドと日本から8研究機関、総勢18人の研究者が参加し、ベントナイト及び岩石中の核種の拡散現象に関する最新の研究成果について6件の発表が行われると共に、それらについて活発な議論が展開された。以下に、情報交換会で報告された6件のトピックス(含む所属) を示す。

- (1) 圧縮ベントナイト中の拡散の記述に於ける整合性(フィンランドVTT技術研究センター)
- (2) 圧縮ベントナイト中の放射性核種の拡散挙動に関する実験的手法(北海道大学)
- (3) 人工バリア及び天然バリア中での核種の拡散係数データの不確実性の評価(原子力機構 安全研究センター)
- (4) 海水条件での圧縮ベントナイト中のCs及びHTOの収着及び拡散に及ぼす温度の影響(産業創造研究所)
- (5) ベントナイト中の拡散係数に及ぼす液性の影響(三菱マテリアル)
- (6) 圧縮スメクタイト中の I 及び Cs の拡散の活性化エネルギー(原子力機構地層処分研究開 発部門)

本報告書は、情報交換会に於ける発表資料及び論文を取りまとめたものである。

本報告書は、「ベントナイト及び岩石中に於ける拡散現象に関する情報交換会 -地層処分の安 全評価を目指して-」に於いて報告された論文と資料をプロシーディングスとして取りまとめ たものである。

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1. Consistency in the Description of Diffusion in Compacted Bentonite

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A macro-level diffusion model, which aims to provide a unifying framework for explaining the experimentally observed co-ion exclusion and greatly controversial counter-ion surface diffusion in a consistent fashion, is presented. It is explained in detail why a term accounting for the non-zero mobility of the counter-ion surface excess is required in the mathematical form of the macroscopic diffusion flux. The prerequisites for the consistency of the model and the problems associated with the interpretation of diffusion in such complex pore geometries as in compacted smectite clays are discussed.

Keywords: bentonite, smectite, diffusion, model, geological disposal, radioactive waste

1. Background

For the needs of safety assessment (SA) of nuclear waste disposal, quantities such as the apparent diffusivity, D_a , and effective diffusivity, D_e , are believed to persist. However, at present, there is no generally accepted macroscopic model for tracer diffusion in compacted bentonite that could be stated as a consistent one. In particular, the surface diffusivity, D_s , has retained its controversial character over the years. There are some indications of increased D_e for cations, but this should be corroborated with further experiments. A major obstacle for obtaining D_e 's, and therefore, direct information on D_s , for cations is the inherently long experimental time needed to attain steady state. Here, an attempt to shed light on these quantities is made in the form of a revised diffusion model.

2. Revised diffusion model and discussion

The repulsion of co-ions is known to give rise to a local deficit (negative surface excess) of co-ions in the environment of the clay particle in comparison with the equilibrium solution. This deficit has also been termed negative adsorption or co-ion exclusion, which can occur only for species in the diffuse-ion swarm. It follows that electric double layers form on clay particle surfaces, which was taken as the basis of the revised diffusion model development.

The model geometry was chosen as an array of tortuous parallel planar surfaces with a uniform charge density. A trace amount of a diffusing solute was assumed to be dispersed in a viscous quiescent solvent in the domain, $0 \Omega y \Omega 2d$, bounded a solid plane wall at $y \mid 0$ and $y \mid 2d$. The diffusion process occurs under the influence of a concentration gradient maintained parallel to the bounding planar wall in the *x*-direction. Further, the solid phase is in equilibrium with the fluid phase, and local chemical equilibrium prevails along the diffusion path, that is, the time required to attain equilibrium over the pore cross-section is much shorter than the characteristic time of diffusion. These assumptions ensure the validity of Henry's law and, consequently, the applicability of a linear adsorption isotherm, that the only driving force for diffusion is the concentration gradient in the *x*-direction, and that the diffusion coefficient is a function of *y* alone, i.e., $D \mid D(y)$. Due to plane symmetry, it suffices to consider the domain, $0 \Omega y \Omega d$.

The following (standard) definitions were made:

- pore diffusion coefficient, $D_{\rm p} \mid \vartheta^{41} \mid_{\rm b}^{\rm l} D(\bullet) d\bullet \quad (E \Sigma 0)$, (1)
- effective diffusion coefficient, $D_{\rm e} \mid \lambda D_{\rm p}$, (2)
- reduced surface excess, $\mathbf{B} \mid \int_{0}^{1} (e^{4E(\bullet)} 41) \mathrm{d} \bullet$, (3)
- capacity factor, $\zeta \mid \lambda(1+B)$, (4)

• apparent diffusion coefficient, $D_a \mid \zeta^{-1} D_e$, (5)

where • is the reduced distance (y/d), ϑ is the pore tortuosity, λ is the porosity, and $E(\bullet)$ is the reduced solute-pore wall interaction energy. Accordingly, adsorption was conceived in a general sense as enrichment (positive adsorption) or depletion (negative adsorption) of one or more components in an interfacial layer. Consequently, the distribution coefficient, K_d , which describes solute partition between the adsorbed and free phases, was defined in terms of the surface excess, B, as

•
$$K_{\rm d} \mid \lambda B / [(1 4 \lambda) \psi],$$

.

(10)

where ψ is the specific density of the medium.

Rearranging terms in the equations for the diffusion flux and continuity, it can be shown that D_e and D_a call for redefinition according to,

- $D_{\mathfrak{P}} D_{\mathfrak{e}}(12 \varsigma B)$, (7)
- $D_a^{\mathfrak{N}} D_a \vartheta^{41} (12 \zeta B),$ (8)

respectively. The apostrophe is used to indicate a revised quantity. The term, ζB , which can be regarded as mobile adsorption, gives rise to surface diffusion, or more properly termed, *surface excess diffusion*. Writing the revised apparent diffusivity in Eqn. 8 in terms of the pore diffusivity, D_p ,

 $D_{a} \mathcal{N} D_{p} \mid \vartheta^{41}(12 \,\varsigma B) / (12 \,B)$,

shows that the apparent diffusivity is proportional to the mobile fraction of the capacity factor.

Substituting Eqn. 4 in Eqn. 6 yields $\zeta \mid \lambda + (1 - \lambda)\psi K_d$, in accord with the conventional macroscopic theory. Similarly, the revised effective diffusivity in Eqn. 7 can be recast in the following form,

 $D_{e} \mathcal{N} D_{e} 2 (14 \lambda) \psi K_{d} D_{s},$

where the surface diffusivity, D_s (| ζD_p), is shown to have clear physical significance.

Theoretical model calculations for $(1+\zeta B)/(1+B)$, assuming a form of $E(\bullet)$ that takes into consideration the hydration of ions as well as dielectric saturation, were carried out for Na⁺, Cs⁺, Sr²⁺ and Cl⁻ ions as a function of the half-distance separation between pore walls. The results indicated virtually no ionic-strength dependence for a given ion below 0.01 mol/l. A likely reason for the mismatch found between theoretical and experimental results for cations is that, in reality, their surface excess contains a component that is due to specific adsorption. For Na⁺, Cs⁺ and Sr²⁺, ~20%, >90% and ~80% of specific uptake, respectively, is needed in the model to explain the experimental results. These figures for Cs⁺ and Sr²⁺ are reasonably close to those suggested in the literature: up to 95% ¹⁾ and 85–90% ²⁾, respectively. On the other hand, the model deviation for Cl⁻ from experimental results is likely attributable to a longer diffusion path Cl⁻ has to take in comparison to water and cations. This is reflected in an increased tortuosity, which in the present case was calculated to be up to 1.7 times that for water.

3. Conclusions

It was shown that it is possible to obtain a consistent macroscopic diffusion model based on an integrated molecular-level description. It is also possible to retain porosity as a purely volumetric notion, which means that there is no need to introduce derived quantities, such as 'co-ion porosity'. Negative adsorption (co-ion exclusion) was incorporated in the diffusion model in a strictly non-empirical fashion.

From the viewpoint of SA, it is not crucial to recognize the most plausible micro-level diffusion model in great detail. Rather, it is of importance to acknowledge the presence of a term that is indicative of surface diffusion (ζB) in the revised macro-level diffusion coefficients, D_a ' and D_e '.

Acknowledgements

The author (JL) would like to thank Dr. H. Sato of Horonobe Underground Research Unit, JAEA, Japan, and Prof. T. Kozaki of Hokkaido University, Sapporo, Japan, for the cordial invitation to the Horonobe Information Exchange Meeting.

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WITH REBURCH REPARENCE OF MULTICE Model geometry and assumptions (2/3) • the solutes are dispersed in a viscous quiescent solvent in the finite interlayer domain, $0 \Omega y \Omega 2d$, bounded by a solid plane wall at $y \mid 0$ and $y \mid 2d$, • a trace amount of a diffusing substance is concerned, • the solid phase is in equilibrium with the fluid phase, and • local adsorption equilibrium prevails along the diffusion path, that is, the time required to attain equilibrium in an infinitesimal element, dx, across the domain, $0 \Omega y \Omega 2d$, is much shorter than the characteristic time of diffusion.

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Model geometry and assumptions (3/3)

- the validity of Henry's law and, consequently, the applicability of a linear adsorption isotherm,
- that the only driving force for diffusion is the concentration
- gradient, *G*, in the *x*-direction, and
- that the diffusion coefficient is a function of y alone, i.e., $D \mid D(y)$.

Due to plane symmetry, it suffices to consider the domain, 0 $\Omega y \Omega d$. Hereafter, the reduced distance, • (| ydd), is used in the analysis.

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2. Experimental Approaches to Understanding of Diffusion Behavior of Radionuclides in Bentonite

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The diffusion behavior of radionuclides in bentonite is an important issue to be studied for the safety assessment of the geological disposal of high-level radioactive waste. In this study, the apparent diffusion coefficients were determined for some radionuclides under different diffusion conditions such as diffusion temperature and salinity of solution used for water-saturation of the bentonite, and then the diffusion behaviors of the radionuclides were discussed in terms of the microstructure of the water-saturated, compacted bentonite observed by XRD and X-ray micro-CT methods.

Keywords: geological disposal, radioactive waste, bentonite, diffusion, activation energy, basal spacing, X-ray micro-CT

1. Introduction

Compacted bentonite is the most promising buffer material for geological disposal of high-level radioactive waste. An important function of the compacted bentonite is to retard the transport of radionuclides from waste forms to the surrounding host rock after degradation of an overpack¹⁾. Due to the low hydraulic conductivity of the bentonite, the radioactive transport is considered to be governed by diffusion. Therefore, it is essential to clarify diffusion behavior of radionuclides in compacted bentonite in repository, where relatively higher temperature and groundwater with high salinity are expected. However, the effects of salinity and diffusion coefficients were determined for some radionuclides under different diffusion temperature and salinity. Microstructure of the water-saturated, compacted bentonite was also observed by XRD and X-ray micro-CT methods. From the results of these experimental approaches, diffusion mechanism of radionuclides in compacted bentonite is discussed.

2. Experimental

The bentonite used in this study is homoionized montmorillonite, which is prepared from Kunipia-F(a product of the Kunimine Industries Co. Ltd.) by contacting the sample with 1M NaCl or CaCl₂ solutions. The compacted bentonite samples used for diffusion, XRD, and X-ray micro-CT experiments were saturated with distilled water or NaCl solutions of 0.01 to 0.5M.

The apparent diffusion coefficients of radionuclides in the bentonite were determined by one-dimensional, non-steady diffusion experiments under the conditions of different parameters, such as dry density of bentonite, salinity, temperature, Na/Ca ratio of exchangeable cations in bentonite. Detail procedures of the homoionization, compaction, water-saturation, and diffusion experiments were described elsewhere².

The basal spacing of the compacted bentonite in the water-saturated state was determined from XRD profiles measured from 3 to 8 degrees of 2 θ . A flat diffraction plane was obtained by sectioning the sample soon after it was removed from a water saturation cell³).

Microstructures of the compacted bentonite both in the dry and water-saturated states were observed with the microfocus X-ray computerized tomograph system (X-ray micro-CT). The system used in this study is a SkyScan-1172(Skyscan, Belgium). The bentonite sample was compacted into a sample holder (glassy carbon tube, 5 mm in internal diameter and 10 mm in height) together with glass beads (around 0.1 mm in diameter) to obtain a dry density of 1.0 Mg m⁻³ for bentonite. Water-saturated bentonite samples were prepared by contacting the samples with

distilled water through sintered stainless steel filters. The microstructure of the bentonite in the tube was directly observed with X-ray micro-CT. The sample examined while being rotated 360 degrees in 0.10-degree steps. Data acquisition time was about 15 h for each sample. The detectable spatial resolution of the CT image was about 2 μ m.

3. Results and Discussion

3.1 Microstructure of bentonite

The microstructure of compacted bentonite in the dry state observed with X-ray micro-CT system is shown in Figure 1. Bright dapples and circles in a dark big ring, which correspond respectively to the montmorillonite particles and glass beads in the sample holder, were clearly identified. It is likely that major particles at the inner area have different orientations from the outer; large portion of particles at the inner area orient toward horizontal direction, whereas those at the outer area toward vertical direction. This is probably due to physical contact of the montmorillonite particles with the wall of sample holder at the outer area during the compaction. Figure 2 shows the microstructure of compacted bentonite in the water-saturated state observed with X-ray micro-CT. Only glass beads and the sample holder could be identified in the figure; the image of montmorillonite particles, which were composed from tactoids, wholly changed into montmorillonite gel or smaller particles than the spatial resolution of the micro-CT system during their water-saturation.

Figure 3 shows the basal spacing of water-saturated, compacted bentonite determined by XRD method³). The basal spacing of 1.88 nm was observed at the dry densities from 1.0 to 1.5 Mg m⁻³, while the basal spacing of 1.56 nm was observed at the dry densities from 1.4 to 1.8 Mg m⁻³. On the other hand, neither of the diffraction peaks could be obtained at dry densities below 1.0 Mg m⁻³. The basal spacings of 1.88 and 1.56 nm correspond to a three-water-layer and a two-water-layer hydrate states of the interlayer (interlamellar) spaces of the montmorillonite, respectively⁴). Then, it can be said that well-arranged montmorillonite tactoids, which can be detected by XRD method, could form at the dry densities of 1.0 Mg m⁻³ and above. However, such morphological formation could not be found in the X-ray micro-CT observation at least at the dry density of 1.0 Mg m⁻³. Figure 4 shows XRD profiles of the compacted bentonite saturated with NaCl solutions of different concentration⁵). The dry density of the samples in this measurement was 1.0 Mg m⁻³. It should be noted that two-water-layer hydrate state appeared at the salinities of 0.1 M and above. This means that relatively high salinity solution of 0.1 M and above can remove water molecules from the montmorillonite interlayers, resulting in the shrinkages of the interlayers.



Fig. 1 X-ray micro CT image for the compacted montmorillonite at dry density of 1.0 Mgm⁻³ before water-saturation.

Fig. 2 X-ray micro CT image for the compacted montmorillonite at dry density of 1.0 Mgm^{-3} after water-saturation.





Fig. 3 Basal spacing of water-saturated, compacted montmorillonite as a function of dry density.

Fig. 4 Basal spacing of water-saturated, compacted montmorillonite as a function of salinity.

3.2 Diffusion of radionuclides in bentonite

Apparent diffusion coefficients of several radionuclides in water-saturated, compacted bentonite were determined under different conditions of diffusion temperatures, dry densities, kind of exchangeable cation, and salinities. The activation energies for radionuclide diffusion, which is one of the promising parameters to clarify the diffusion mechanism, were calculated from the temperature dependences of the apparent diffusion coefficients.

Figure 5 indicates the activation energy for the apparent self-diffusion of sodium ions as a function of dry density of the bentonite²⁾. The activation energies of 18.4 and 13 kJ mol⁻¹ were reported for the sodium diffusion in free water⁶⁾ and on the montmorillonite surface⁷⁾, respectively. However, at least three different values of the activation energy were found in this study; about 18 kJ

mol⁻¹ at dry densities from 0.7 to 0.9 Mg m⁻³, 14.1 kJ mol⁻¹ at dry densities from 0.7 to 0.9 Mg m⁻³, 14.1 kJ mol⁻¹ at dry densities of 1.0 Mg m⁻³, and about 24 kJ mol⁻¹ at dry densities of 1.7 and 1.8 Mg m⁻³. This suggests that the diffusion behavior of sodium ion in compacted montmorillonite cannot be explained only by a single process, such as the pore water diffusion⁸; the predominant diffusion process varied with an increase in dry density. Similar dry density dependences of the activation energy were found for the apparent diffusion of radionuclides, as shown in Fig. 6 ⁹⁻¹³.

Effect of exchangeable cations on the diffusivity was studied for cesium ions in the mixture of Na- and Ca-type montmorillonite. Figure 7 shows the activation energy for cesium diffusion as a function of ionic fraction of Ca^{2+} of the mixture¹⁴⁾. The activation energy increased from 34 kJ mol⁻¹ to 49 kJ mol⁻¹ as the ionic fraction increased from zero (corresponding to Na-type montmorillonite) to 1.0 (corresponding to Ca-type montmorillonite). This result suggests that the interlayer, where most exchangeable cations are located, is the essential pathway for Cs⁺ diffusion.



Fig. 5 Activation energy for apparent self-diffusion of sodium ions in the compacted montmorillonite as a function of dry density.





Fig. 6 Activation energies for apparent diffusion of several radionuclides in the compacted montmorillonite as a function of dry density.

Fig. 7 Activation energy for cesium diffusion in the compacted montmorillonite at dry density of 1.0 Mgm⁻³ as a function of ionic equivalent fraction of Ca^{2+} ions.

The salinity of pore water was considered to be another parameter that can change the activation energy. Figure 8 indicates the activation energies for apparent diffusivities of sodium and chlorine ions in compacted Na-montmorillonite at the dry density of 1.0 Mg m⁻³ as a function of salinity⁵⁾. At least three different values of the activation energy were obtained for sodium diffusion, whereas almost constant values for chlorine diffusion. As indicated in Fig. 4, high salinity solution can change the microstructure of montmorillonite; shrinkage of montmorillonite particles due to the alteration of the interlayers from three-water-layer hydrate state into two-water-layer hydrate state. In addition, it can be readily supposed that the increase of salinity can change the distribution of ions in the montmorillonite; e.g. it could cause the re-distribution of sodium ions in the pore water, resulting in the decrease of the thickness of electrical double layer which could form in solution adjacent to the montmorillonite surfaces. By considering these changes in the montmorillonite sample, the alteration of the activation energy for the sodium diffusion can be

explained by the shifts of the predominant diffusion process from the external surface diffusion into the pore water diffusion via the interlayer diffusion. However, the reasonable explanation cannot be made for the activation energy for chloride diffusion (about 14 kJ mol⁻¹), which is lower than that in free water(17.4 kJ mol⁻¹,⁶).

4. Conclusions

Microstructure of the compacted montmorillonite was observed by X-ray micro-CT method. Different orientations of the montmorillonite particles were identified between the inner and the outer areas of the sample at its dry state. On the other hand, decreases of the basal spacing of montmorillonite due to the increase of the dry density or the salinity were found in the XRD measurements. The activation energies for the



Fig. 8 Activation energies for Na^+ and Cl^- ions in the compacted montmorillonite at dry density of 1.0 Mgm⁻³ as a function of salinity.

apparent diffusion also varied with the dry density of the montmorillonite, kind of exchangeable cations, and the salinity. These changes in the activation energy cannot be explained only by the simple diffusion model, such as the pore water diffusion model. The diffusion model including the shifts of the predominant diffusion process could be applicable in some case. However, there are still uncertainties in the diffusion process of radionuclides in the compacted montmorillonite.

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X-ray micro CT measurement

- Montmorillonite particles (75-150µm) in dry state were clearly identified.
- In dry state, different orientations of montmorillonite particles between inner and outer areas of the sample were found.
- After water-saturation, no image of the montmorillonite particles(at least > a few ten µm) was obtained.

















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3. Assessment of Data Uncertainty on the Diffusion Coefficients for

Nuclides in Engineered and Natural Barriers

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In order to perform probabilistic safety assessment of the geological disposal, the data uncertainty on diffusion coefficient in bentonite and rock samples was examined based on the published data. As the result, it was confirmed that the montmorillonite-gel density in bentonite was one of important factors for systematically evaluating the data uncertainties on diffusion coefficients for radionuclide elements and that the effective diffusion coefficients in rock depended on the porosity and pH.

Keywords : probabilistic safety assessment, data uncertainty, diffusion coefficient, bentonite, rock

1. Introduction

In long-term safety assessment of geological disposal for radioactive wastes, there are various uncertainties caused by the space-time expanse of the disposal system, generally classified into scenario, model and data uncertainties. In order to evaluate the safety with reliability, it is important to clarify the factor and influence of the data uncertainty quantitatively. Deterministic and probabilistic safety assessment code systems have being developed, to deal with the problems of the various uncertainties in the Japan Atomic Energy Agency. In this study, the database on the diffusion coefficient for radionuclide elements, which was one of nuclide-transport parameters in bentonite and rocks, was developed through the document investigation and experiments. From the data uncertainty and estimate the variable range of the diffusion coefficient data.

2. Database on Diffusion Coefficients in Engineered Barrier

At first, the data on diffusion coefficients in bentonite were collected with bibliographic database, INIS, NUCLEAN and JST. It was thought that the data uncertainties in the collected diffusion coefficients were caused by experimental errors and the difference of the important factors making a great influence on diffusion coefficient in bentonite. For experimental errors, it was confirmed that the data, which were provided by same experimenter under same condition, were within $10 \%^{1}$. Based on the result, we assumed that the most of data uncertainties on the diffusion coefficients were due to the difference of the important factors which was variable under the disposal environment condition. As the important factors, conformation of nuclides, density, composition, ionic strength, temperature, etc. were considered. As is well known, it is assumed that the diffusion for nuclide in compacted bentonite is explained by Pore-Water diffusion model. In this case, the diffusion coefficient is treated as a function of the porosity. So it was thought that the density was particularly important influence factor under the condition that pore diffusion becomes dominant, because density is close to the porosity. Liu²) reported that in an in-diffusion experiment that changed the ratio of silica sand to montmorillonite, good dependence was shown in provided apparent diffusion coefficients of HTO and Na⁺ for montmorillonite-gel density. The montmorillonite-gel density can be expressed by following equation.

$$\psi_{mont} \mid \frac{f \psi}{14 \frac{(14 f) \psi}{\psi_{others}}}$$

Where ρ_{mont} is montmorillonite-gel density, ρ_{others} density of other minerals, ρ total dry density, f weight fraction of montmorillonite. Figure 1 showed the apparent diffusion coefficients for

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cations, anions, and HTO in bentonite as the function of effective-clay density and montmorillonite-gel density. From these figures, the negative correlation of apparent diffusion coefficients for the both densities was noticed. Furthermore it was confirmed that the variable range of diffusion coefficients for montmorillonite-gel density decreased than for effective-clay density. Therefore it was suggested that the montmorillonite-gel density in bentonite was one of important factors.



Fig.1 The apparent diffusion coefficients in bentnite as the function of effective-clay density and montmorillonite-gel density

3. Database on Diffusion Coefficients in Natural Barrier

In the same way as the engineering barrier, the data on diffusion coefficients in crystalline and sedimentary rocks were collected. Generally it is assumed that the diffusion coefficient in rock is connected with porosity. And the chemical composition of pore water, which might have influence on the chemical form of nuclide and the electrostatic interaction with rock and nuclide, is thought to affect the diffusion. Therefore the diffusion coefficients for rocks were examined with attention to the porosity and pH. Figure 2 shows the effective diffusion coefficients for cations and anions in crystalline rock as the function of porosity. This figure indicated the positive correlation of effective diffusion coefficients for the porosity. Then it was confirmed that the effective diffusion coefficients of Cl which had large variable range at same porosity depended on pH.



4. Conclusion

In this study, in order to perform probabilistic safety assessment of the geological disposal, the variable range of data and the influence factors on the diffusion coefficients in bentonite and rock samples were examined. As for engineered barrier, it was confirmed that the evaluation of the diffusion coefficients in bentonite by montmorillonite-gel density tended to decrease the variable range. And as for natural barrier, it was confirmed that the effective diffusion coefficients in rock tended to depend on the porosity and pH.

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18 July 2006 International Information Exchange Meeting on Diffusion Phenomenon in Bentonite and Rock –Aiming at the Safety Assessment of the Geological Disposal

Assessment of Data Uncertainty on the Diffusion Coefficients for Nuclides in Engineered and Natural Barriers

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performed under the contract with Japanese Ministry of Economy,Trade and Industry











	Effective diffusion coefficient	Apparent diffusion coefficient
Typical cations (Cs, Sr, Ra etc.)	51	488
Typical anions (C, Cl, I, Se etc.)	185	414
Other elements (Tc, U, Eu, Co, Ni <i>etc.</i>)	32	480
Neuter molecules (HTO, HDO, H ₂ O)	88	158
Total	356	1, 540
Keywords : Bentor diffusi	nite, Kunigel, Kunip on coefficient, diffus	ia, MX-80 <i>etc.</i> ion constant, diffusiv























Conclusion

Database on nuclide-transport parameter : diffusion coefficient Estimate of reliable variable range by considering influence factors

Engineered Barrier

It was confirmed that the evaluation of the diffusion coefficients in bentonite by montmorillonite:gel density tend to decrease the variable range. And positive correlation of diffusion coefficients for ionic strength was also confirmed.

Natural Barrier

By the examination that paid attention to porosity and pH, it was confirmed that the effective diffusion coefficients in rock tended to depend on those factors.

It was suggested that density (or porosity) and chemical composition of pore water (ionic strength, pH, etc.) were the influence factors on diffusion coefficients in engineered and natural barriers.

Future works

We will carry out the following works for the purpose of contribution to safety analysis.

- 1. We find the correlation between influence factors and diffusion coefficient, and formulate the relations.
- 2. We get the range of assessment parameters from that of influence factors in the disposal environment.
- 3. About elements of which the number of data are not enough for 1 and 2 above, we have to make fundamental data for future database expansion.

4. Sorption and Diffusion of Cs and HTO in Compacted Bentonite Saturated with Saline Water at High Temperatures

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Abstract

The temperature dependence of the diffusion and sorption of Cs and HTO was investigated in compacted bentonite saturated with saline water. The activation energies of the Cs diffusion were 21.4 \pm 2.8 kJ/mol and 45.1 \pm 2.9 kJ/mol determined by D_e and D_a . This difference was due to the temperature dependence of the distribution coefficient K_d of Cs.

Introduction

In Japanese geological environment, a candidate place of repository may be located in fresh and/or saline ground water, and a ground temperature is will be 60°C in the most conservative case¹⁾. The present study reported the sorption and diffusion of Cs and HTO in compacted bentonite saturated with saline water at temperatures of 30 to 60°C.

Experimental procedure

Kunigel V1 bentonite which is a standard material for Japanese engineered barrier was mixed with 30 wt.% of silica sand (up to a few millimeters in diameter), and then compacted to



Fig. 1 Typical fitting results of the break through curve of TD.

a dry density of 1.6 Mg/m³. After saturation with the simulated sea water for 1 month, three different diffusion experiments: the in-diffusion $(ID)^{2}$, the through-diffusion $(TD)^{3}$ and the reservoir-depletion $(RD)^{3, 4}$ were performed at elevated temperatures of 30, 40, 50 and 60°C. The details of these experiments were described elsewhere. To determine K_d and D_e (or D_a), the break through curve for TD and the depletion curve for RD were analyzed based on Fick's second law with the appropriate initial and boundary conditions (Fig. 1).

Rsults and Discussion

The effective diffusion coefficient D_e increased from 3.2×10^{-10} to 8.0×10^{-10} m^2/s for Cs, while 1.9×10^{-10} to 3.6×10^{-10} m^2/s for HTO with increasing (Table 1). temperature Assuming type equation Arrhenius for the temperature dependence of D_{e} , the activation energy for diffusion was determined to be 15.8±0.9 and 21.4±2.8 kJ/mol for Cs and HTO, respectively (Fig.2). While K_d for Cs decreased from 0.024 to 0.053 m^3/kg with increasing temperature, and the apparent energy for sorption was -22.7±2.3 kJ/mol (Fig. 2).



Fig. 2 Arrhenius plots of De, Da and Kd.

T

$$D_a$$
 was expressed by D_e and K_d as follows

$$D_{a} \mid D_{a}^{0} \exp \left[\frac{R}{TM} \frac{Q_{Da}}{RT} \right] \mid \frac{D_{e}}{\kappa^{2} \ \psi K_{d}} \mid \frac{D_{e}^{0} \exp \left[\frac{M}{TM} \frac{Q_{De}}{RT} \right]}{\kappa^{2} \ \psi K_{d}^{0} \exp \left[\frac{R}{TM} \frac{E_{Kd}}{RT} \right]} - \frac{D_{e}^{0}}{\psi K_{d}^{0}} \exp \left[\frac{R}{TM} \frac{Q_{De} 4 E_{Kd}}{RT} \right]$$

where $D_a^{\ 0}$, $D_e^{\ 0}$ and $K_d^{\ 0}$ are the empirical constant for D_a , D_e and K_d , Q_{Da} and Q_{De} are activation energies for diffusion calculated by using D_a and D_e , respectively, E_{Kd} is the apparent energy for the temperature dependence of K_d , κ and ψ are porosity and dry density, respectively. Because $\kappa(0.4)$ is negligibly smaller than ψK_d (34), Table 1 D_e , D_a and K_d determined by ID, RD, and TD.

 Q_{Da} was estimated to be Q_{De} - E_{Kd} = 44.1 kJ/mol which was in good accordance with that directly determined by D_a obtained by RD (45.1±2.9 kJ/mol). The relationship among Q_{Da} , Q_{De} and E_{Kd} was thus experimentally confirmed. The activation energy for diffusion (D_e) may be influenced by change in the properties of pore water in compacted bentonite. Their values were, however, equivalent to those in aqueous solution (15 to 20 kJ/mol).

T [°C]	$D_a \left[imes 10^{-11} \text{ m}^2/\text{s} ight]$	$D_e \left[imes 10^{-10} \mathrm{m^{2/s}} ight]$	K_d [m ³ /kg]
30	$0.55 {\pm} 0.01$ (ID)	3.2 ± 0.1 (TD)	0.053 (RD)
	0.43 (RD)	3.3 ± 0.1 (TD)	
		3.9 ± 0.1 (TD)	
		3.3 ± 0.1 (TD)	
40	0.91±0.01 (ID)	4.3±0.1 (TD)	0.052 (RD)
	0.62 (RD)	5.5 ± 0.1 (TD)	
50	1.4±0.1 (ID)	5.9 ± 0.1 (TD)	0.029 (RD)
	1.2 (RD)	6.6±0.1 (TD)	
60	2.3±0.1 (ID)	7.2 ± 0.1 (TD)	0.024 (RD)
	2.3 ± 0.1 (ID)	8.0±0.1 (TD)	
	3.2 ± 0.1 (TD)	7.6 ± 0.1 (TD)	
	2.5 ± 0.1 (TD)	8.0 ± 0.1 (TD)	
	2.2 (RD)		

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 HSe^{-} any

Others

 C_{S^+} Species

> $\mathbf{C}^{\mathbf{s}}$ $\mathbf{s}^{\mathbf{e}}$

Elements

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		K	Č,		
	Method	[m ₃	i/kg]	D_{e}^{-10-10}	P_{10-10}^{a}
		Compacted	Batch	[s/_m 01 ~]	[s/_m 01 ~]
ОТП	UT.		•	2.8 ± 0.1	I
OTH	1 1		ı	3.0 ± 0.1	ŗ
	ſ	-	I	I	0.23 ± 0.01
		1	ı	ı	0.19 ± 0.01
	Ê	0.020 ± 0.001	1	7.2 ± 0.1	0.32 ± 0.01
		0.014 ± 0.001	ı	8.0 ± 0.1	0.25 ± 0.01
¹³⁷ Cs		0.022 ± 0.001	1	7.3 ± 0.1	1
	3	0.021 ± 0.001	ı	6.8 ± 0.1	ı
			0.026 ± 0.002		
	Batch		0.025 ± 0.002		
		,	0.022 ± 0.002	,	ı

A:FF.) ţ 7 ς 4 ć Pore water chemistry of compacted bentonite (H12 report)

	Fresh	water	Saline	water
	Ground water	Pore water	Ground water	Pore water
Hq	8.5	8.0	8.4	7.8
Eh	-281	-276	-303	-309
Ionic strength [mol/dm ³]	5.5×10^{-3}	2.4 × 10 ⁻²	7.0×10^{-1}	6.7×10^{-1}
	4.4 ti	imes	Approx	. same
In saline wat between pore	er system, ion e water and gr	iic-strength is ound water.	approximatel	y the same

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 D_{e}, D_{a} and K_{d} were in good accordance among the different methods.

5. The Effect of Aqueous Composition on Diffusion Coefficient in Bentonite

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The diffusion coefficients (De) in bentonite were measured to understand and quantify the influence of groundwater chemistry such as ionic strength and to quantify the alteration of smectite mineralogical transformations.

Keywords: sub-surface disposal, LLW, bentonite, diffusion

1. Introduction

In Japan, confinement of radionuclides and open land use are required, for the radioactive waste disposal, after the end of control period. To achieve this requirement, even sub-surface disposal for LLW is built in more than 10m depth, and barrier system of bentonite and cementitious material is constructed to minimize the release of radionuclides and to minimize the groundwater inflow through the repository. Rock cavern type disposal which is to contain long-lived radionuclide such as C-14, is required to prove the confinement performance longer period. This system has two engineered barriers.

- Low hydraulic conductive bentonite/sand layer to keep diffusive dominant condition in the repository.
- Low diffusive cementitious material layer with small pore size to minimize the nuclide release from the waste package.

Therefore radionuclides might diffuse from a waste package through the bentonite / sand layer. It is important to measure the diffusion coefficients for performance assessment of sub-surface disposal for Low Level Waste. The objectives of this work are to understand and quantify the influence of groundwater chemistry such as ionic strength and to quantify the alteration of smectite mineralogical transformations affect for De in bentonite.

2. Experimental

2.1 The effect of aqueous composition on De

The experimental conditions are shown in Table 1. The exchange of interlayer cations in smectite will occur for interaction between bentonite and cementitious materials, therefore Ca type bentonite was used in this work. The different salinity of solution was used in the range from 0 from 1.0M CaCl₂ and 0.01M NaCl. Tracer was tritiated water (HTO), Cl-36 as anion spiecies, and three forms of organic C-14 (sodium acetic acid, formaldehyde and ethanol). C-14 is one of the most critical nuclides from the point of view of the sub-surface disposal. C-14 is released from the dissolution of metal waste, which has variety of lower organic forms (carboxylic acid, aldehyde and alcohol) and inorganic carbonate. Organic forms may change by a microbial activity through geological layer. However this microbial affects are the

most important for the behavior of C-14 but is not sufficiently understood. So in this work, three type of organic were used for tracers. The diffusion experiments were carried out at room temperature. To avoid generation of calcium carbonate, only the experiments for CaCl₂ solution were carried out under anaerobic <u>condition</u>.

Table 1	Exmerimental	conditions

Bentonite	Ca-bentonite
	- dry density : 1.4 Mg/m3
Solution	0~1.0M CaCl2 solution, 0.01M NaCl solution
Tracer	HTO, C1-36
	C-14(sodium acetic acid, formaldehyde, ethanol)
Temperature	Room temperature
Atmosphere	anaerobic (CaCl2), aerobic (NaCl)

2.2 The effect of alteration of bentonite material on De

The experimental conditions are shown in Table 2. Two different materials were used as the simulated alteration of bentonite sample. Analcime was used as alteration mineral of smectite, which was

prepared by the hydrothermal treatment of smectite (kunipia F). Spherical glass beads had particle diameters of 0.4mm. Bentonite (Kunigel V1) and the simulated materials were homogeneously mixed to be a certain bentonite content. Bentonite contents were in the range from 20 to 80 wt.% at dry density of the mixture 1.4 Mg/m^3 .

Table 2 Exmerimental conditions

Bentonite	Na-bentonite (Kunigel V1)
	- dry density : 1.4 Mg/m3
	- bentonite content 20-80wt%
	- alteration material : analcime or glass beads
Solution	Deionized water
Tracer	НТО
Temperature	Room temperature
Atmosphere	anaerobic

3. Results and Discussion

3.1 The effect of aqueous composition on De

Figure 1 shows De as a function of salinity. De of HTO remains constant, approximately 2×10^{-10} m^2/s , at Salinity and salt type have no effect on De. Furthermore the measured De for Ca bentonite is in excellent agreement with that for Na bentonite, which was shown as a function of porosity and smectite fraction in TRU2 report of JNC. De of C-14 (formaldehyde, Ethanol) is smaller than that of HTO and remains constant, approximately 1×10^{-10} m²/s, which are not dependent on the salt concentration. On the

other hand, that of acetic acid increases in the range from 0.1M to 1.0M. However for acetic acid, we haven't been able to measure the appropriate data because of the experimental conditions weren't controlled, specifically the tracer concentration didn't keep constant.

De of HTO, C-14(formaldehyde, ethanol) in Neutral aqueous species have little effect on salinity. De of Cl-36 in anion aqueous species increased with increasing salt concentration. So, it will require the aqueous composition such as ionic strength to set appropriate diffusion data for PA.



3.2 The effect of alteration of bentonite material on De

Figure 2 shows De of HTO as a function of content of alteration materials. De increased with increasing content of alteration material. However, only a factor of two increased in the range from 20 to 80wt%. The effect of a kind of alteration material on De was not significant. Therefore it was considered that analcime was inert for diffusion as well as glass beads. The De in the simulated alteration sample of bentonite were estimated by the same method for the sand-mixed bentonite^{(1,2}. When the alteration of smectite into zeolite (analcime) will occur, the estimation of De will be applicable in the same method for that of the sand-bentonite mixture.



Fig. 2 De as a function of alteration material (Na-bentonite, 1.4Mg/m³)

4. Conclusions

From these experiments, the results are shown as follows:

- De of HTO, C-14(formaldehyde, ethanol) in Neutral aqueous species have little effect on salinity. De of Cl-36, C-14(acetic acid) in anion aqueous species increased with increasing salinity. So, it will require the aqueous composition such as ionic strength to set appropriate diffusion data for PA.
- De increased with increasing content of alteration material. However, only a factor of two increased in the range from 20wt% to 80wt%. The effect of a kind of alteration material on De is not significant. Therefore it was considered that analcime was inert for diffusion as well as glass beads. When the alteration of smectite into zeolite (analcime) will occur, the estimation of De will be applicable for the same method for that of the sand-bentonite mixture.

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6. Activation Energies of Diffusion for I and Cs in Compacted Smectite

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The apparent diffusivities (D_a) for Γ and Cs^+ ions in the directions parallel and perpendicular to the orientation of smectite particles were measured as a function of smectite's dry density, salinity and temperature. The diffusion pathways of both ions in the compacted smectite were discussed based on the anisotropies and the effect of salinity in the D_a and activation energies ($\div E_a$) for both ions. Obtained results indicated that Γ ions predominantly diffuse in external pores and Cs^+ ions diffuse in all pores. The $\div E_a$ values for Γ ions were at similar levels as that for the ionic diffusivity in free water (D°) of Γ ions at low dry density and increased with increasing dry density. In contrast, the $\div E_a$ values for Cs^+ ions were clearly high than that for the D° of Cs^+ ions were considered to be due to the combined effects of the ion exchange enthalpy between Cs^+ and Na^+ ions in smectite and the lowering in the activity of porewater.

Keywords: geological disposal, radioactive waste, bentonite, smectite, diffusion, iodine, cesium, activation energy

1. Introduction

In the safety assessment (SA) of the geological disposal for a high-level radioactive waste, the role as a barrier function of the bentonite buffer is important to restrict the release of radionuclides (RN) from repository. Particularly, because the diffusion properties of RNs in bentonite directly control the release of RNs from the bentonite buffer, it is regarded as one of the important characteristics in the SA.

It is well known from conventional studies that the retardation in the diffusion process of RNs in bentonite is affected by various physico-chemical properties such as porosity, bentonite's dry density, sorption properties, exchangeable cations in interlayer, porewater chemistry, additives to bentonite (*e.g.*, silica sand), bentonite grain size, temperature etc. In recent studies, the author has reported that clay particles oriented in the direction perpendicular to the direction of compaction for a bentonite with high smectite content, such as Kunipia-F which is almost 100wt% smectite ¹⁾ and that the effective diffusivities (D_e) of HTO and HDO are different between directions parallel and perpendicular to the orientation of the smectite particles ^{1,2)}. Suzuki et al. ²⁾ have indicated in previous study that the nature of porewater near the solid-liquid interface differs from that of free water because $\div E_a$ values for the D_e values of HDO in compacted smectite were slightly higher than $\div E_a$ of the D^o for HDO. The author and Miyamoto ³⁾ also have discussed the nature of porewater in compacted bentonite by calculating the relative partial molar activation energies for hydroselenide ions (HSe⁻) and indicated the same possibility as Suzuki et al. ²⁾

In this study, the anisotropies and the effect of salinity in the D_a and $\div E_a$ values for Γ and Cs^+ ions in compacted Na-smectite are discussed.

2. Experimental

Na-smectite, of which the exchangeable cations were exchanged with Na⁺ ions, was used in this study. The Na-smectite was prepared by exchanging with Na⁺ ions for a Na-bentonite, Kunipia-F (Kunimine Industries Co. Ltd.), of which the smectite content is over 99wt.% and by removing soluble salts.

The diffusion experiments were carried out by the in-diffusion method. Table 1 shows the experimental conditions. The smectite powder was filled into a sample holder for compaction so as to

obtain desired dry densities and was compacted. After the compaction, the smectite block was transferred to an acrylic sample holder. The diffusion experiments in the direction perpendicular to the orientation of smectite particles were performed without changing the sample direction. In contrast the diffusion experiments in the direction parallel to the orientation of smectite particles were performed by rotating the smectite block by 90° in angle after being compacted. The smectite in the sample holder was saturated.

Item	Method / Condition
Method	In-diffusion method (one side back-to-back)
Bentonite	Na-smectite (Kunipia-F exchanged for interlayer cations by Na ⁺ ions)
Dry density	1.0, 1.4 Mg/m ³ (sample: cube of 15 mm)
Diffusion direction	Direction parallel / perpendicular to the orientation of smectite particles
Saturated solution	NaCl ([NaCl]=0.01, 0.51 M)
Saturated period	54-150d (saturated with distilled water for a month before saturation by
	NaCl)
Tracer solution	CsI ([CsI]=1.5E-2 M)
Spiked tracer quantity	50 σL/sample
Temperature	295-333 K (295, 303, 310, 313, 323, 333 K)
Atmosphere	Aerobic condition
Diffusion period	6h-11d (depending on dry density and temperature)
Recovery of tracer	Desorption by KCl ([KCl]=0.5-1 M)
Analysis	Cs: High Resolution ICP-MS / I: ICP-AES

3. Results and Discussion

3.1 Apparent diffusion coefficient (D_a)

The D_a values for Γ ions decreased with increasing dry density, similarly to the trends reported so far ⁴⁾, and showed a tendency to be higher in the direction parallel than in the direction perpendicular to the orientation of smectite particles over the range of dry density and salinity. The D_a values generally increased with increasing salinity, but those for diffusion in the direction parallel decreased with increasing salinity only at low dry density over the range of temperature. The surface of smectite sheet is negatively charged and its interlayer space depends on dry density and salinity. The interlayer space is also quite narrow being 2 or 3 water layers. Because of this, anions such as Γ ions are generally regarded to be restricted to diffuse in compacted bentonite by ion exclusion. Considering what is occurring in the pores of the compacted smectite, the interlayer space of smectite decreases with increasing dry density and salinity, and external pore space and electrostatic effect from smectite surface strongly depend on the interlayer space.

Assuming that Γ ions diffuse in interlayer and external pores, tortuosity increases with increasing dry density, but it should not depend on salinity ⁵⁾. However, the D_a values of Γ ions clearly depend on salinity, dry density and diffusion direction. Therefore, the trends of the D_a values of Γ ions on salinity can not be well explained. Assuming that Γ ions predominantly diffuse in external pores, tortuosity in the direction parallel to the orientation of smectite particles depends on dry density and salinity. This is because smectite sheets and stacks or aggregates are coagulating by the decrease in electrostatic repulsion with increasing salinity, and in this case, part of the external porewater is converted to interlayer water by coagulation. Considering that Γ ions can scarcely or not diffuse in such ultra-narrow interlayer, Γ ions can not help taking a roundabout route. Therefore, the D_a values of Γ ions are considered to have increased with increasing salinity.

The D_a values for Cs^+ ions also decreased with increasing dry density, similarly to the trends reported so far ⁴⁾, and increased with increasing salinity in all conditions. Since Cs^+ ions sorb onto smectite by ion exchange, it is clear that Cs^+ ions can diffuse in the interlayer of smectite. Therefore,

tortuosity increases with increasing dry density, but it should not depend on salinity. The trends of the D_a values for Cs^+ ions on dry density and salinity can be interpreted to be the combined results of the change in tortuosity with changing dry density and the change in sorption by competing with Na⁺ ions with changing salinity.

3.2 Activation energy (+E_a)

Figures 1 and 2 show dependencies of the $\div E_a$ values for I^- and Cs^+ ions on dry density, respectively. Average $\div E_a$ of I^- ions, 15.67±0.37 kJ/mol at a low dry density of 1.0 Mg/m^3 , increased with increasing dry density and was 24.29±1.31 kJ/mol at a high dry density of 1.4 Mg/m³. Neither anisotropy nor effect of salinity was found. External pore space and the degree of electrostatic effect from smectite surface depend on dry density and salinity. Furthermore, since both of interlayer space and external pore space and liquid-solid ratio decrease with increasing dry density, correlatively the thermodynamic properties of porewater such as activity (a_{H2O}) are also considered to change, because some studies have been reported that a_{H2O} of water near the surface of montmorillonite is lower than that of free water⁸⁾. The interlayer space of smectite is 3 water layers at a low dry density of 1.0 Mg/m³ and a mixture of 2 and 3 water layers at a high dry density of 1.4 Mg/m³. Therefore, the reason that the \div E_a of I^{-} ions increased with increasing dry density might be because electrostatic repulsion from smectite surface correlatively increased by the decrease in external pore space with increasing dry density and a_{H2O} of porewater lowered with increasing dry density.

Average $\div E_a$ of Cs⁺ ions, 24.66±0.96 kJ/mol at a low dry density of 1.0 Mg/m³ over the range of salinity, increased with increasing dry density and was 35.20±0.83



Fig. 1 A dependency of $\div E_a$ values for Γ ions in smectite on dry density together with $\div E_a$ data of $C\Gamma$ ions in Na-montmorillonite ⁶.



Fig. 2 A dependency of $\div E_a$ values for Cs⁺ ions in smectite on dry density together with $\div E_a$ data of Cs⁺ ions in Na-montmorillonite ⁷).

kJ/mol at a high dry density of 1.4 Mg/m³. No anisotropic effect was found in the $\div E_a$ values. Where, the $\div E_a$ of Cs⁺ ions also include enthalpy for sorption (K_d) onto smectite. Since Cs⁺ ions sorb onto smectite by ion exchange with Na⁺ ions, the $\div E_a$ values of Cs⁺ ions can be thought to include both effects of the ion exchange enthalpy (\div H^o) between Cs⁺ and Na⁺ ions in the interlayer of smectite and $\div E_a$ for the diffusion of Cs⁺ ions in the porewater of smectite ($\div E_p$).

Assuming that the $\div E_p$ for Cs⁺ ions is equivalent to $\div E_a$ of its D^o, the relationship between $\div E_a$ and $\div H^o$ can be approximately derived as follows;

$$\div E_a \mid \div E_p 4 \div H^o$$
,

(1)

where $\div E_p$ is the $\div E_a$ of D^o and $\div H^o$ is the ion exchange enthalpy.

The \div H^o between Cs⁺ and Na⁺ ions in a Na-smectite (Chambers montmorillonite) is reported to be -11.10 kJ/mol ⁹⁾, and therefore \div E_a for the D_a of Cs⁺ ions in compacted smectite is estimated to be 27.57 kJ/mol. This is relatively consistent with \div E_a values obtained at low dry density. In contrast, \div E_a values at high dry density are clearly high.

As described in $\div E_a$ for the diffusion of Γ ions, a_{H2O} of porewater in compacted montmorillonite is lower than that of free water. Therefore, such high $\div E_a$ values for Cs^+ ions at high dry density are considered to be due to the combined effects of $\div H^o$ and the lowering in a_{H2O} of porewater.

4. Conclusions

The D_a and $\div E_a$ values of Γ and Cs^+ ions in the directions parallel and perpendicular to the orientation of smectite particles were obtained as a function of the smectite's dry density and salinity. The results are summarized as below.

 Γ ions predominantly diffuse in external pores, and the D_a values are considered to have changed by the changes in tortuosity and electrostatic repulsion with changing dry density and salinity. The $\div E_a$ values are considered to have changed by the changes in external pore space and electrostatic repulsion from smectite surface and a_{H2O} of porewater with changing dry density and salinity.

On the other hand, Cs^+ ions diffuse in both of interlayer and external pores, and the D_a values are considered to have changed by the change in tortuosity with changing dry density and the change in sorption with changing salinity. The $\div E_a$ values are considered to be due to the effect of $\div H^o$ between Cs^+ and Na^+ ions in the interlayer of smectite at low dry density, and to be due to the combined effects of the $\div H^o$ and the lowering in a_{H2O} of porewater at high dry density.

Acknowledgement

The author would like to thank Mr. S. Kibe of PESCO Co. Ltd. for supporting the analyses of I and Cs by ICP-AES and HR ICP-MS, respectively.

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International Information Exchange Meeting, 18 July, 2006

Activation Energies of Diffusion for I and Cs in Compacted Smectite

International Information Exchange Meeting on Diffusion Phenomena in Bentonite and Rock –Aiming at the Safety Assessment of the Geological Disposal, 18 July, 2006, Horonobe Underground Research Center, Japan

Haruo SATO Residence at Horonobe Underground Research Center Japan Atomic Energy Agency (JAEA)

Presentation Outline

- Concept of Multi-barrier System in HLW Disposal
- Background and Objective
- Anisotropy in Diffusive Pathway in Compacted Bentonite
- Diffusion Experiments (1- and Cs*)
- In-diffusion method
- Results and Discussion
 - · Examples of penetration curves
 - Apparent diffusion coefficients (D_a)
 - · Arrhenius plots for D,
 - Activation energies (ΔE_n) of diffusion
 - · Diffusion mechanisms of ions in smectite
- Conclusions









Item	Method / Condition
Method	In-diffusion method (one side back-to-back)
Bentonite	Na-smectite (Kunipia-F [®] exchanged for interlayer cations by Na ⁺)
Dry density	1.0, 1.4 Mg/m3 (sample: cube of 15 mm)
Diffusion direction	Direction parallel / perpendicular to the orientation of smectite particles
Saturated solution	NaCl ([NaCl]=0.01, 0.51 M)
Saturated period	54-150 d (saturated with distilled water for a month before saturation by NaCl)
Tracer solution	CsI ([CsI]=1.5E-2 M)
Spiked tracer quantity	50 oL/sample
Temperature	295-333 K (22-60 °C): 295, 303, 310, 313, 323, 333 K)
Atmosphere	Aerobic condition
Diffusion period	6h-11 d (depending on dry density and temp.)
Recovery of tracer	Desorption by KCl ([KCl]=0.5-1 M)
Analysis	Cs: High Resolution ICP-MS / I: ICP-AES















Conclusions

- \blacksquare Discuss the anisotropies and the effect of salinity in the diffusion and $\div E_{a}s$ for I^- and Cs^+ ions in compacted smectite.
- □ Considering the effects of dry density, salinity and diffusion direction to the orientation of clay particles on the D_as and +E_as for both ions, interlayer aperture, external pore aperture and electrostatic effect from smectite surface, diffusive pathway when charged ions diffuse in compacted smectite depends on the charge of the diffusion species. Namely,
- □ I⁻ predominantly diffuses in external pores, and the D_as change by the changes in tortuosity and electrostatic repulsion with changing dry density and salinity. The +E_as increase by the increase in electrostatic repulsion and the lowering in a_{H20} with increasing dry density.
- $\hfill\Box\ensuremath{\mathsf{Cs}^*}\xspace$ decrease in both of interlayer and external pores, and the D_as decrease by the increase in tortuosity with increasing dry density and increase by the decrease in K_d with increasing salinity. The $+E_as$ are mainly due to the effect of $+H^o$ at low dry density and the combined effects of $+H^o$ and the lowering in a_{H2O} at high dry density.

Findings through This Study

- $\square What \div E_a is controlled by ?$
- Changes in micropore structure (interlayer aperture, external pore aperture) and activity of porewater with changing dry density and salinity.
- □ In actual repository condition, how much of $+E_a$ in compacted bentonite should be used ?
- ➡ Precisely +E_a depends on species, but pure bentonite will not be used for repository. If the reference case in the H-12 report (Kunigel-V1, dry density 1.6 Mg/m³, silica sand content 30wt.%: 0.9 Mg/m³ in smectite (montmorillonite) partial density) is assumed, +E_a for diffusion in free water is valid.

Future Study

- \square Measurements of D_as and $\div E_as$ for both ions in the interlayer of smectite (2 water-layer).
- $\label{eq:measurements} \square \mbox{ Measurements of the change in a_{H2O} in compacted bentonite (smectite) and quantitative discussion of the effect of the change in a_{H2O} on diffusion.}$

Acknowledgements

The authors would like to thank all participants to this meeting and presenters. The authors would especially like to thank assistant prof. Tamotsu KOZAKI of Hokkaido University for advising and supporting in many points for the sake of holding this meeting. Additionally, Radioactive Waste Management Funding and Research Center is also appreciated for financial support for this meeting.

Finally, the authors thank all staffs of Horonobe Underground Research Unit and Horonobe Underground Research Center who prepared for meeting place.

Appendix 1

Programme and Schedule

International Information Exchange Meeting on Diffusion Phenomena in Bentonite and Rock –Aiming at the Safety Assessment of the Geological Disposal

Programme

Date: July 18'06, 13:15-17:30 Place: 3rd Meeting Room (2F), Horonobe Underground Research Center (Presentation time includes discussion) Host: Japan Atomic Energy Agency

Supporter's Organizations:

Hokkaido University Radioactive Waste Management Funding and Research Center (RWMC)

Chairperson (JAEA Horonobe·Haruo SATO)

13:15-13:20 (5min) Self-introduction (All participants)

1. 13:20-14:00 (40min) Consistency in the Description of Diffusion in Compacted Bentonite

(VTT·Jarmo LEHIKOINEN)

- 14:00-14:40 (40min)
 Experimental Approaches to the Understanding of Diffusion Behavior of Radionuclides in Bentonite
 - (Hokkaido Univ.·Tamotsu KOZAKI)
- 14:40-15:20 (40min)
 Assessment of Data Uncertainty on the Diffusion Coefficients for Nuclides in Engineered and Natural Barriers

(JAEA Tokai, Nucl. Safety Res. Center Takuma SAWAGUCHI)

Break (20min)

 15:40-16:20 (40min) Sorption and Diffusion of Cs, HTO, Cl in Compacted Bentonite Saturated with Saline Water and CaCl₂ Solution –The Effects of Temperature and Experimental Methods

(IRI-Satoru SUZUKI)

 16:20-17:00 (40min) The Effect of Aqueous Composition on Diffusion Coefficient in Bentonite

(Mitsubishi Materials Corp. Toshiyuki NAKAZAWA)

 17:00-17:30 (30min) Activation Energies of Diffusion for I and Cs in Compacted Smectite

(JAEA Horonobe Haruo SATO)

Move to banquet place (by JAEA car)18:30-21:30Banquat (Hotel Hokuto-so)

Appendix 2

Participant List

Participant List

(Honorific title abbreviation, changeable this)

- 1. VTT, Finland Jarmo LEHIKOINEN^{1,2}
- Division of Energy and Environmental Systems, Graduate School of Engineering, Hokkaido University Seichi SATO
- Division of Energy and Environmental Systems, Graduate School of Engineering, Hokkaido University Tamotsu KOZAKI²
- Division of Energy and Environmental Systems, Graduate School of Engineering, Hokkaido University, Graduate student (M2) Masaaki GORAI
- Division of Energy and Environmental Systems, Graduate School of Engineering, Hokkaido University, Graduate student (M2) Chikanori MIWATA
- Division of Energy and Environmental Systems, Graduate School of Engineering, Hokkaido University, Graduate student (M1) Shingo TANAKA
- Nuclear Chemistry and Chemical Engineering Center, Kashiwa Laboratory, Institute of Research and Innovation (IRI) Satoru SUZUKI²
- Nuclear Chemistry and Chemical Engineering Center, Kashiwa Laboratory, Institute of Research and Innovation (IRI) Yoshimi SEIDA
- 9. Nuclear Chemistry and Chemical Engineering Center, Kashiwa Laboratory, Institute of Research and Innovation (IRI) Hiroaki TAKAHASHI
- 10. Energy Project and Technology Center,

Mitsubishi Materials Corporation (MMTL) Hiroyasu KATO

- 11. Mitsubishi Materials Corporation (MMTL) Toshiyuki NAKAZAWA²
- Radioactive Waste Disposal Business Division, Japan Nuclear Fuel Limited (JNFL) Tomofumi SHIMIZU
- Radioactive Waste Disposal Business Division, Japan Nuclear Fuel Limited (JNFL) Yoshihiro MIYAUCHI
- 14. Industry Project Division, JGC Corporation (JGC) Wataru KOBAYASHI
- Civil Engineering Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI) Tomohiro HIGASHIHARA
- Geological Isolation Research Unit, Geological Isolation Research and Development Directorate, Japan Atomic Energy Agency (JAEA) Takamitsu ISHIDERA
- 17. Nuclear Safety Research Center, Japan Atomic Energy Agency (JAEA) Takuma SAWAGUCHI²
- Horonobe Underground Research Unit, Geological Isolation Research and Development Directorate, Japan Atomic Energy Agency (JAEA) Haruo SATO ^{2,3}
- 1 Lecturer in the lecturing meeting
- 2 Speaker in the international information exchange meeting

3 Secretariat of the international information exchange meeting

表1. SI 基本単位						
	SI 基本ì	单位				
蓝个里	名称	記号				
長さ	メートル	m				
質 量	キログラム	kg				
時 間	秒	s				
電 流	アンペア	А				
熱力学温度	ケルビン	Κ				
物質量	モル	mol				
光 度	カンデラ	cd				

	表 2.	불	吉本 里(立る	r用いて表されるSI組立里	豆の例
和古書					SI 基本単位	
	彩日	<u>. v</u> .	里		名称	記号
面				積	平方メートル	m ²
体				積	立法メートル	m ³
速	さ	,	速	度	メートル毎秒	m/s
加		速		度	メートル毎秒毎秒	m/s^2
波				数	毎メートル	m^{-1}
密	度,	質	量 密	度	キログラム毎立方メートル	kg/m ³
面	積		密	度	キログラム毎平方メートル	kg/m^2
比		体		積	立方メートル毎キログラム	m ³ /kg
電	流		密	度	アンペア毎平方メートル	A/m^2
磁	界	Ф	強	さ	アンペア毎メートル	A/m
量	濃 度	(a)	, 濃	度	モル毎立方メートル	mol/m ³
質	量		濃	度	キログラム毎立法メートル	kg/m ³
輝				度	カンデラ毎平方メートル	cd/m^2
屈	折		率	(b)	(数字の) 1	1
比	诱	磁	率	(b)	(数字の) 1	1

(a) 量濃度(amount concentration)は臨床化学の分野では物質濃度 (substance concentration)ともよばれる。
 (b) これらは無次元量あるいは次元1をもつ量であるが、そのこと を表す単位記号である数字の1は通常は表記しない。

表3. 固有の名称と記号で表されるSI組立単位

		51 租立单位				
組立量		名称	記号	他のSI単位による 表し方	SI基本単位による 表し方	
平面	角	ラジアン ^(b)	rad	1 ^(b)	m/m	
立体	角	ステラジアン ^(b)	$sr^{(c)}$	1 (b)	m^{2/m^2}	
周波	数	ヘルツ ^(d)	Hz	-	s ⁻¹	
力		ニュートン	Ν		m kg s ⁻²	
压力, 応	5 力	パスカル	Pa	N/m^2	$m^{-1}kg s^{-2}$	
エネルギー,仕事	,熱量	ジュール	J	N m	$m^2 kg s^2$	
仕事率,工率,	放射束	ワット	W	J/s	$m^2 kg s^{-3}$	
電 荷 , 電	気 量	クーロン	С		s A	
電位差(電圧),	起電力	ボルト	V	W/A	$m^2 kg s^3 A^1$	
静 電 容	量	ファラド	F	C/V	${ m m}^{-2}{ m kg}^{-1}{ m s}^{4}{ m A}^{2}$	
電 気 抵	抗	オーム	Ω	V/A	$m^2 kg s^3 A^2$	
コンダクタ	ンス	ジーメンス	s	A/V	${ m m}^{-2}{ m kg}^{-1}{ m s}^{3}{ m A}^{2}$	
磁	束	ウエーバ	Wb	Vs	$m^2 kg s^2 A^1$	
磁 束 密	度	テスラ	Т	Wb/m ²	$kg s^2 A^1$	
インダクタ	ンス	ヘンリー	Η	Wb/A	$m^2 kg s^2 A^2$	
セルシウス	温度	セルシウス度 ^(e)	°C		K	
光	束	ルーメン	lm	cd sr ^(c)	cd	
照	度	ルクス	lx	lm/m^2	m ⁻² cd	
放射性核種の放射	能(f)	ベクレル ^(d)	Bq		s ⁻¹	
吸収線量,比エネルギ	一分与,	グレイ	Gv	J/kg	$m^2 s^{-2}$	
カーマ			Зy	0,115	m 5	
線量当量,周辺線量当: 件線量当量 個人線量:	量, 方向 当量	シーベルト ^(g)	Sv	J/kg	$m^2 s^{-2}$	
酸素活		カタール	kat		s ¹ mol	

衣4. 単位の中に固有の名称と記方を含む51組を単位	表4.	単位の中	に固有の	名称と	記号を含る	かSI組立単	位の
----------------------------	-----	------	------	-----	-------	--------	----

	S	I 組立単位	
組立量	名称	記号	SI 基本単位による 表し方
粘。	モ パスカル秒	Pa s	m ⁻¹ kg s ⁻¹
カのモーメン	ニュートンメートル	N m	$m^2 kg s^2$
表 面 張 力	コニュートン毎メートル	N/m	kg s ⁻²
角 速 月	夏 ラジアン毎秒	rad/s	$m m^{-1} s^{-1} = s^{-1}$
角 加 速 月	ミ ラジアン毎秒毎秒	rad/s^2	$m m^{-1} s^{-2} = s^{-2}$
熱流密度,放射照風	『 ワット毎平方メートル	W/m^2	kg s ⁻³
熱容量、エントロピー	- ジュール毎ケルビン	J/K	$m^2 kg s^{-2} K^{-1}$
比熱容量, 比エントロピー	- ジュール毎キログラム毎ケルビン	J/(kg K)	$m^{2} s^{-2} K^{-1}$
比エネルギー	- ジュール毎キログラム	J/kg	$m^{2} s^{-2}$
熱 伝 導 🔤	『ワット毎メートル毎ケルビン	W/(m K)	$\mathrm{m~kg~s^{-3}~K^{-1}}$
体積エネルギー	- ジュール毎立方メートル	J/m ³	m^{-1} kg s ⁻²
電界の強さ	ボルト毎メートル	V/m	m kg s ³ A ¹
電 荷 密 月	夏 クーロン毎立方メートル	C/m ³	m ⁻³ sA
表 面 電 荷	f クーロン毎平方メートル	C/m^2	m^{-2} sA
電 束 密 度 , 電 気 変 伯	z クーロン毎平方メートル	C/m ²	m ⁻² sA
誘 電 🔤	『ファラド毎メートル	F/m	$m^{-3} kg^{-1} s^4 A^2$
透磁 🔤	ミ ヘンリー毎メートル	H/m	$m \text{ kg s}^2 \text{ A}^2$
モルエネルギー	- ジュール毎モル	J/mol	$m^2 kg s^2 mol^1$
モルエントロピー,モル熱容量	ジュール毎モル毎ケルビン	J/(mol K)	$m^{2} kg s^{2} K^{1} mol^{1}$
照射線量 (X線及びγ線)	クーロン毎キログラム	C/kg	kg ⁻¹ sA
吸収線量 3	ビグレイ毎秒	Gy/s	$m^{2} s^{-3}$
放射 强 月	モ ワット毎ステラジアン	W/sr	$m^4 m^{-2} kg s^{-3} = m^2 kg s^{-3}$
放射輝 月	F ワット毎平方メートル毎ステラジアン	$W/(m^2 sr)$	$m^2 m^2 kg s^3 = kg s^3$
酵素活性濃厚	ミ カタール毎立方メートル	kat/m ³	$m^{-3} s^{-1} mol$

表 5. SI 接頭語							
乗数	接頭語	接頭語 記号 乗数		接頭語	記号		
10^{24}	Э 9	Y	10^{-1}	デシ	d		
10^{21}	ゼタ	Z	10^{-2}	センチ	с		
10^{18}	エクサ	Е	10^{-3}	ミリ	m		
10^{15}	ペタ	Р	10^{-6}	マイクロ	μ		
10^{12}	テラ	Т	10^{-9}	ナノ	n		
10^{9}	ギガ	G	10^{-12}	ピョ	р		
10^{6}	メガ	М	10^{-15}	フェムト	f		
10^3	キロ	k	10^{-18}	アト	а		
10^2	ヘクト	h	10^{-21}	ゼプト	z		
10^{1}	デ カ	da	10^{-24}	ヨクト	у		

表6. SIに属さないが、SIと併用される単位

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20 - 1 - NAT - 7		
名称	記号	SI 単位による値
分	min	1 min=60s
時	h	1h =60 min=3600 s
日	d	1 d=24 h=86 400 s
度	٥	1°=(п/180) rad
分	,	1'=(1/60)°=(п/10800) rad
秒	"	1"=(1/60)'=(п/648000) rad
ヘクタール	ha	$1ha=1hm^{2}=10^{4}m^{2}$
リットル	L, 1	$1L=11=1dm^{3}=10^{3}cm^{3}=10^{-3}m^{3}$
トン	t	$1t=10^3 \text{ kg}$

表7. SIに属さないが、SIと併用される単位で、SI単位で

表される数値が実験的に得られるもの						
名称	記号	SI 単位で表される数値				
電子ボルト	eV	1eV=1.602 176 53(14)×10 ⁻¹⁹ J				
ダルトン	Da	1Da=1.660 538 86(28)×10 ⁻²⁷ kg				
統一原子質量単位	u	1u=1 Da				
天 文 単 位	ua	1ua=1.495 978 706 91(6)×10 ¹¹ m				

	表8.SIに属さないが、SIと併用されるその他の単位						
	名称		記号	SI 単位で表される数値			
バ	-	ル	bar	1 bar=0.1MPa=100kPa=10 ⁵ Pa			
水銀	柱ミリメー	トル	mmHg	1mmHg=133.322Pa			
オン	グストロー	- 4	Å	1 Å=0.1nm=100pm=10 ⁻¹⁰ m			
海		里	М	1 M=1852m			
バ	-	\sim	b	$1 \text{ b}=100 \text{ fm}^2=(10^{-12} \text{ cm})2=10^{-28} \text{m}^2$			
1	ツ	ŀ	kn	1 kn=(1852/3600)m/s			
ネ	-	パ	Np	の形法しの粉結めな眼球は			
~		N	В	31単位との数値的な関係は、 対数量の定義に依存。			
デ	ジベ	N	dB -				

	表9. 固有の名称をもつCGS組立単位							
	名称		記号	SI 単位で表される数値				
Ŧ	IV	グ	erg	1 erg=10 ⁻⁷ J				
ダ	イ	\sim	dyn	1 dyn=10 ⁻⁵ N				
ポ	T	ズ	Р	1 P=1 dyn s cm ⁻² =0.1Pa s				
ス	トーク	ス	St	$1 \text{ St} = 1 \text{ cm}^2 \text{ s}^{-1} = 10^{-4} \text{m}^2 \text{ s}^{-1}$				
ス	チル	ブ	$^{\mathrm{sb}}$	$1 \text{ sb} = 1 \text{ cd} \text{ cm}^{-2} = 10^4 \text{ cd} \text{ m}^{-2}$				
フ	オ	ŀ	$_{\rm ph}$	$1 \text{ ph}=1 \text{cd sr cm}^{-2} 10^4 \text{lx}$				
ガ		N	Gal	$1 \text{ Gal} = 1 \text{ cm s}^{-2} = 10^{-2} \text{ ms}^{-2}$				
7	クスウェ	N	Mx	$1 \text{ Mx} = 1 \text{ G cm}^2 = 10^{-8} \text{Wb}$				
ガ	ウ	ス	G	$1 \text{ G} = 1 \text{Mx cm}^{-2} = 10^{-4} \text{T}$				
エノ	レステッド((c)	Oe	$1 \text{ Oe} \triangleq (10^3/4\pi) \text{A m}^{-1}$				

(c) 3元系のCGS単位系とSIでは直接比較できないため、等号「 ▲ 」 は対応関係を示すものである。

			表	ŧ10.	SIに 属	属さないその他の単位の例
	:	名利	尓		記号	SI 単位で表される数値
キ	ユ		IJ	ĺ	Ci	1 Ci=3.7×10 ¹⁰ Bq
$\boldsymbol{\nu}$	\sim	ŀ	ゲ	\sim	R	$1 \text{ R} = 2.58 \times 10^{-4} \text{C/kg}$
ラ				ド	rad	1 rad=1cGy=10 ⁻² Gy
$\boldsymbol{\nu}$				Д	rem	$1 \text{ rem}=1 \text{ cSv}=10^{-2} \text{Sv}$
ガ		$\boldsymbol{\mathcal{V}}$		7	γ	1 γ =1 nT=10-9T
フ	I		\mathcal{N}	1		1フェルミ=1 fm=10-15m
メー	- トル	系	カラ	ット		1メートル系カラット=200 mg=2×10-4kg
F				N	Torr	1 Torr = (101 325/760) Pa
標	準	大	気	圧	atm	1 atm = 101 325 Pa
力			IJ	_	cal	1cal=4.1858J(「15℃」カロリー), 4.1868J (「IT」カロリー) 4.184J(「熱化学」カロリー)
3	ク			ン	u	$1 \mu = 1 \mu m = 10^{-6} m$