

NAGRA-JNC QUALITY  
and Migration Workshop

March, 2001

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## **NAGRA-JNC QUALITY and Migration Workshop**

Haruo SATO\*, Akira KITAMURA\*, Satoru SUZUKI\*

### **ABSTRACT**

The NAGRA-JNC QUALITY and Migration Workshop was held at the ENTRY (Engineering Scale Test and Research Facility), Tokai Works, JNC on March 5, 2001. The workshop was held participating totally about 20 persons, including participants from NAGRA (National Cooperative for the Disposal of Radioactive Waste), Moniter Science LLC and JNC. The aim of this workshop is to take review of the QUALITY and to discuss future direction of radionuclide migration researches. Technical tours of the ENTRY and QUALITY (Quantitative Assessment Radionuclide Migration Experimental Facility) were also carried out to accelerate understanding of these facilities. This report summarized transparencies introduced current status of the QUALITY and 5 research activities which were obtained so far in the QUALITY.

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## NAGRA-JNC クオリティ及び核種移行に関する ワークショップ

(会議報告)

佐藤治夫\*, 北村暁\*, 鈴木覚\*

### 要 旨

平成13年3月5日、スイス NAGRA (スイス放射性廃棄物管理共同組合) - JNC 間でクオリティ及び核種移行に関するワークショップを地層処分基盤研究施設 (エントリー) において開催した。ワークショップには、NAGRA から3人、Monitor Science LLC から1人及びJNCからの参加者を含めて約20人が出席した。このワークショップの狙いは地層処分放射化学研究施設 (クオリティ) のレビューを行うとともに、放射性核種の移行に関する研究の今後の方向性について議論することである。当日は、より理解を深めるため、エントリー及びクオリティの見学も実施した。本報告書は、ワークショップの内、主としてクオリティにおける最近の動向及びクオリティにおいてこれまでに得られた5件の研究成果について紹介するとともに議論に用いた OHP をまとめたものである。

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## 1. Introduction of QUALITY, Overview of Research Activities in QUALITY and QUALITY Tour

Current status of research and development on geochemistry and nuclide migration studies in the QUALITY was briefly introduced as background information by Dr. H. Sato. The QUALITY tour was then held. JNC staffs in charge of the QUALITY, Messrs. T. Ashida, K. Iijima and S. Miyamoto, Drs. H. Sato and A. Kitamura, and Ms. S. Tobitsuka guided the tour and explained outline of each study in front of each atmosphere-controlled glove-box or analytical instruments in the QUALITY.

## 2. Status of QUALITY Project

Five research activities obtained so far in the QUALITY were introduced by main experts and then discussed by turns. The outlines of discussion and comments with respect to each study are described as follows.

### 2.1 Discussion and Comments to QUALITY Project

#### (1) The Effect of Carbonate on Np(IV) Solubility (presented by Dr. A. Kitamura)

Concerning solubility of Np(IV) under carbonate conditions, there was a question how analysis to determine equilibrium constants was carried out.

To this question, Dr. Kitamura answered that the equilibrium constants were determined by a least squares fitting to solubility plots obtained in this study.

#### (2) Speciation Analysis Study by Laser-Induced Photoacoustic Spectroscopy (presented by Dr. A. Kitamura)

Concerning speciation analysis study by Laser-Induced Photoacoustic Spectroscopy (LPAS), there was no particular comment or discussion.

#### (3) The Effect of Ionic Strength on Diffusion of Cs in Compacted Smectite (presented by Dr. H. Sato)

Concerning this study, ① purification of smectite, ② comparison of obtained apparent diffusivities ( $D_a$ ) with those for Kunigel-V1, ③ dependency of smectite partial density on  $D_a$  and ④ validity of distribution coefficient ( $K_d$ ) used in the H-12 report, were mainly discussed.

Particularly, concerning ① purification of smectite, Dr. Sato answered that commercial bentonites including impurities which were soluble, were possible to take place buffering action to porewater by contacting with the porewater and that were consequently possible to change ionic strength. He also answered to the question of ② that  $D_a$  values obtained in this work were approximately the same as those obtained for Kunigel-V1. In addition, he also answered to the question of ③ that obtained  $D_a$  values were well correlative with smectite partial density. For ④ validity of  $K_d$  used in the H-12 report, it was commented that validity of  $K_d$  used in the H-12 report was not confirmed, but conservativity of  $K_d$  was confirmed in this work, and he also agreed that.

#### (4) Se Diffusion in Compacted Bentonite under Reducing Conditions (presented by Dr. H. Sato)

Concerning this study, ① relationship between solubility of Se and used tracer concentration, ② importance of Se for dose evaluation, ③ the change of solution contacting with bentonite, ④ redox condition in the porewater of bentonite and ⑤ redox velocity of Se were discussed.

For ① the relationship between solubility of Se and tracer concentration, Dr. Sato answered that used tracer included a lot of carrier and that the concentration of carrier determined almost whole concentration of tracer. In addition, he also answered that there was a strong possibility that tracer pipetted at the surface of bentonite precipitated. Concerning ② importance of Se, he answered that Se was important for dose evaluation in safety assessment, because Se diffusion was fast due to a little sorption onto bentonite. Concerning ③ the change of solution contacting with bentonite during the saturation and diffusion experiment, it was commented that correlation between the change in chemical composition of solution and diffusion should have been investigated. Concerning ④ redox condition in the porewater of bentonite, he introduced a through-diffusion experiment of sodium dithionate ( $\text{Na}_2\text{S}_2\text{O}_4$ ) through a piece of compacted bentonite at a dry density of  $1.8 \text{ Mg/m}^3$ , previously he had carried out a through-diffusion experiment to obtain redox potential conductivity in compacted bentonite. The redox potential of solution in the opposite side of cell against reservoir cell, in which  $\text{Na}_2\text{S}_2\text{O}_4$  was added, gradually began to lower after being added and perfectly reached the same redox potential level after 3 days. Based on this, he explained that redox potential could be conducted in the porewater of compacted bentonite in 3 days at least. For ⑤ the redox velocity of Se, he answered that although he did not check in this work, he compared with Da values obtained under anaerobic conditions. Also for oxidation state of Se leached out from vitrified waste was discussed and it was commented that Se probably took IV and VI as just leached out.

#### (5) The Effect of Ionic Strength on Effective Diffusivities of $\text{Sr}^{2+}$ and $\text{I}^-$ in Compacted Smectite (presented by Dr. S. Suzuki)

Concerning salinity dependencies of effective diffusivities ( $D_e$ ) for  $\text{Sr}^{2+}$  and  $\text{I}^-$  in smectite, consistency of  $K_d$ , particularly, consistency of  $K_d$  values by batch tests and  $K_d$  values obtained from through-diffusion tests were discussed. Generally,  $K_d$  of Sr decreases with increasing ionic strength, but reverse tendency was found in this work. Drs. Suzuki and Sato answered that no consistency between  $K_d$  values obtained by the time-lag method and those by batch method was found and that this problem was under consideration.

### 3. Acknowledgements

This workshop was organized in cooperation of Messrs. M. Shiotsuki and M. Shiozaki of Head Quarter. The authors would hereby like to thank them. Mr. M. Yui, who is a group leader of Barrier Performance Group is also acknowledged for helpful suggestion in programming of the agenda. Furthermore, Messrs. K. Iijima, T. Ashida and S. Miyamoto and Ms. S. Tobitsuka of Radiochemistry Group are also thanked for presenting each study in the QUALITY.

## Proposed Agenda of QUALITY & Migration Workshop on March 5, 2001

Participants: Nagra: 3 persons  
Monitor Science LLC: 1 person  
JNC-Tokai: 12 persons  
JNC-HQ: 1 person

Place: ENTRY meeting room (301 or 302)

(Proposed Agenda)

**March 5, Monday, 2001**

- |   |             |
|---|-------------|
| 1. Introduction for the WS (JNC / Nagra)  | 09:30-09:45 |
| 2. Overview of JNC Research Activities in the Future (JNC)  | 09:45-10:00 |
| 3. Difficulties Encountered for Radionuclides Migration Analysis in H12 PA (JNC)                                      | 10:00-10:30 |
| Coffee Break  | 10:30-10:50 |
| 4. Introduction of QUALITY, Overview of Research Activities in QUALITY and QUALITY Tour (JNC)                         | 10:50-12:00 |
| Lunch   | 12:00-13:15 |
| 5. Status of QUALITY Project (JNC)  | 13:15-14:30 |
| -The Effect of Carbonate on Np(IV) Solubility   | 13:15-13:30 |
| -Speciation Analysis Study by Laser-Induced Photoacoustic Spectroscopy  | 13:30-13:45 |
| -The Effect of Ionic Strength on Diffusion of Cs in Compacted Smectite  | 13:45-14:00 |
| -Se Diffusion in Compacted Bentonite under Reducing Conditions  | 14:00-14:15 |
| -The Effect of Ionic Strength on Effective Diffusivities of Sr <sup>2+</sup> and I <sup>-</sup> in Compacted Smectite | 14:15-14:30 |
| 6. Status of TRU Waste (JNC)  | 14:30-15:00 |
| Coffee Break  | 15:00-15:20 |



7. Future Direction of Radionuclide Migration Researches (Discussion)

- Confidence Building
- Understanding the Migration Behavior/Long-term
- Colloid/Organics/Microbes Effects
- Cementitious Effects
- Linkage Between Lab. Studies and URL Studies
- Database Development
- Input to HLW/TRU
- Regulatory/Implementation
- Future Collaboration Items

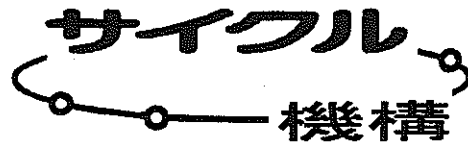
15:20-17:00

# Current Status of Research & Development on Geochemistry and Nuclide Migration Studies in the QUALITY

**QUALITY: Quantitative Assessment Radionuclide  
Migration Experimental Facility**

**Nagra-JNC QUALITY & Migration Workshop  
on March 5, 2001  
Haruo SATO**

*Japan Nuclear Cycle  
Development Institute*



QUALITY Project

## Outline of the QUALITY

### Outline of the facility

- a research facility for obtaining basic data concerning the chemical properties and migration behaviour of radionuclides using radioisotopes (RI) under atmospheric-controlled conditions.
- The construction of the QUALITY started on January 22, 1998 and completed at the end of July, 1999.  
Hot operation started on August 18, 1999.
- Main specification
  - Structure: reinforced concrete
  - Number of stories: one under and two above ground
  - Base area: 1200m<sup>2</sup>
  - Total floor area: 3600m<sup>2</sup>
  - All area of the 1st floor is used as laboratories and analysis room

## Equipments for research and development

- Atmospheric-controlled glove-box: 12 (total)
  - (N<sub>2</sub> atmosphere/O<sub>2</sub> concentration < 1ppm/CO<sub>2</sub> free)
  - CO<sub>2</sub> concentration controllable GB: 3 (10-1000ppm)
  - Ar usable GB: 1
- Air type GB: 9 (experiments under air/analysis/waste liquid treatment)
- Hood: 7 (pretreatment/analysis)

## QUALITY Project

### Permitted nuclides (26 nuclides, 107.16GBq/year)

- Group 1: <sup>208</sup>Po, <sup>226</sup>Ra, <sup>227</sup>Ac, <sup>231</sup>Pa, <sup>237</sup>Np, <sup>241</sup>Am, <sup>243</sup>Am, <sup>245</sup>Cm, <sup>244</sup>Cm
- Group 2: <sup>36</sup>Cl, <sup>63</sup>Ni, <sup>75</sup>Se, <sup>79</sup>Se, <sup>95</sup>Zr, <sup>95</sup>Nb, <sup>107</sup>Pd, <sup>113</sup>Sn, <sup>125</sup>Sb, <sup>129</sup>I, <sup>137</sup>Cs, <sup>151</sup>Sm, <sup>207</sup>Bi, <sup>210</sup>Pb, <sup>99</sup>Tc
- Group 4: <sup>3</sup>H, <sup>14</sup>C

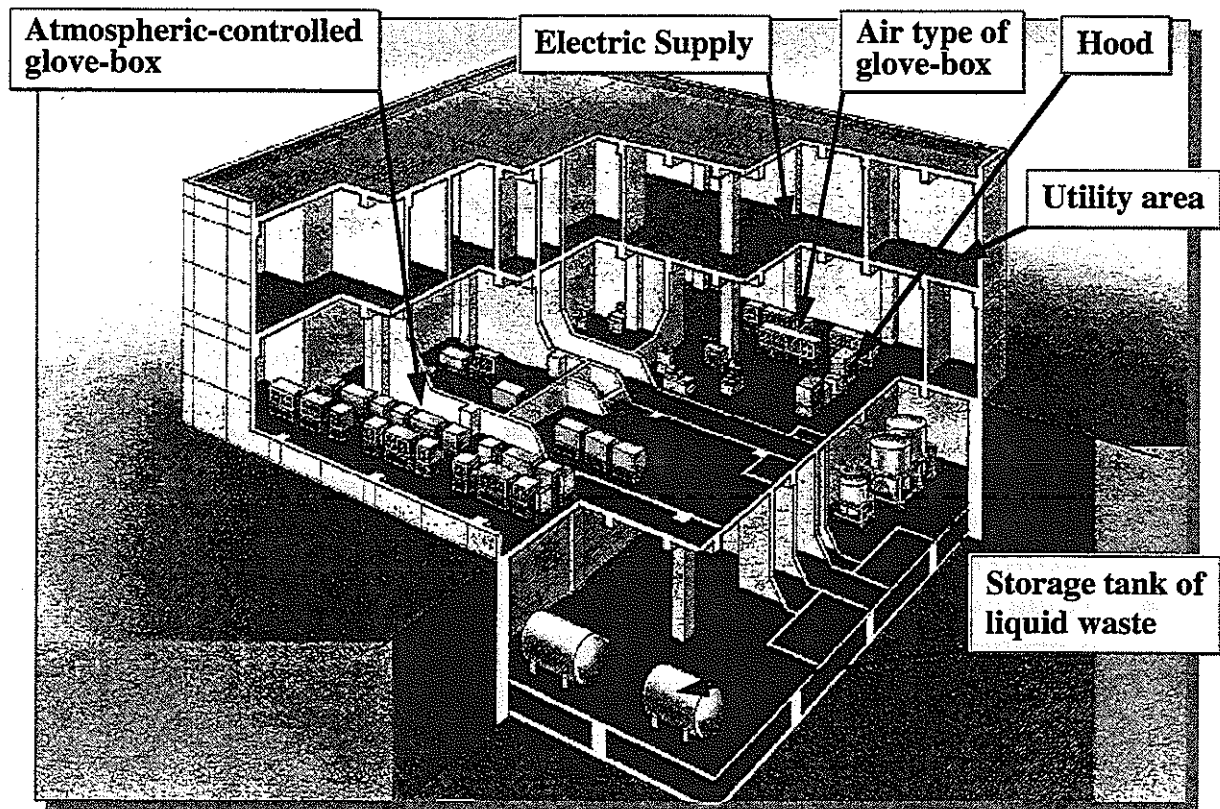
### Nuclides being held in the QUALITY

- To date, <sup>226</sup>Ra, <sup>237</sup>Np, <sup>244</sup>Cm, <sup>75</sup>Se, <sup>137</sup>Cs and <sup>210</sup>Pb were transferred into the QUALITY.
- To date, we have carried out experiments for solubility, sorption and diffusion using 7 atmospheric-controlled glove-boxes (4 boxes: for α nuclide (<sup>237</sup>Np, <sup>244</sup>Cm), 1 box: for βγ nuclide (<sup>210</sup>Pb, <sup>75</sup>Se), 2 boxes: for preliminary tests) and 1 air glove-box (<sup>137</sup>Cs).

### Recent topic for the QUALITY

- About 1,300 data for solubility, sorption and diffusion obtained in the QUALITY were reflected in the second progress report (H-12 report).

## Cross Sectional View of the QUALITY



## Analytical Instruments in the QUALITY

### Surface Analysis

- Analysis in Atmospheric-controlled GB: wet-X Ray Diffractometer (XRD), Fourier Transform Infrared Spectroscopy (FT-IR)
- Analysis in Air: wet-Scanning Electron Microscope (SEM), Electron Probe Micro Analyzer (EPMA)

### Solution Analysis

- Analysis in Atmospheric-controlled GB: Laser Particle Size Distribution Analyzer, Laser-Induced Speciation Analyzer with Laser-Induced Photoacoustic Spectroscopy (LPAS) and Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS), FT-IR, Absorption Spectrophotometer
- Analysis in Air: Gas Chromatography Mass Spectrometer (GC-MS), IC, TOC, ICP-AES, ICP-MS, AAS

### Radiation Counter

- Analysis in Air: Ge-semiconductor  $\gamma$  spectrometer, Si-semiconductor  $\alpha$  spectrometer, Liquid Scintillation Counter,  $2\pi$  Gasflow Counter, ZnS  $\alpha$  Scintillation Counter, GM Counter

## Present Work in the QUALITY Study on Solubility

### ■ Study on Np(IV) Solubility

- Effect of Carbonate (partly finished)
  - measurements of Np(IV) as a function of pH(8.5~12.5) and carbonate concentration(0.001~0.1M) at ionic strengths of 0.5 and 1.0(NaClO<sub>4</sub>) under reducing conditions
  - check of the valency of Np by solvent extraction
  - discussion on a possibility of hydroxo-carbonate complexes and determination of the stability constants
- Effect of Humic Acid(HA)(on going)
  - measurements of Np(IV) as a function of HA concentration (~1000ppm)
  - furthermore evaluation of Np(IV) in the system added carbonate

### ■ Evaluation of Solubility Product of NpO<sub>2</sub>(am)

- (in preliminary tests)(A.Kitamura)
- measurement of solubility product of NpO<sub>2</sub>(am)

QUALITY Project

## Study on Sorption and Diffusion

### ■ Study on Sorption of Cs, Pb and Cm on Rocks and Bentonite (finished)

- batch sorption tests of <sup>137</sup>Cs (under air), <sup>210</sup>Pb (under anaerobic) and <sup>244</sup>Cm (under anaerobic) on bentonite and rocks (granodiorite, tuff, basalt, mudstone, sandstone) at ionic strengths of 0.01 and 0.1 (NaCl)
- evaluation in validity of K<sub>d</sub> values used in the H-12 report

### ■ Study on Effect of Carbonate on Np(IV) Sorption on Smectite (under data analysis)

- batch sorption tests of <sup>237</sup>Np (under reducing conditions) on smectite as a function of carbonate concentration (0.04~0.15M, NaHCO<sub>3</sub>) at an ionic strength of 1.0 (NaCl)
- check of the valency of Np by solvent extraction
- desorption tests by 1M KCl and HCl and discussion of sorption behaviour

- **Study on Effect of Ionic Strength on Diffusion Behaviour of Cs in Compacted Smectite**
  - **In-diffusion Experiments(finished)**
    - measurements of  $D_a$  of  $^{137}\text{Cs}$  as a function of ionic strength(0.01, 0.1, 0.5, 5) and dry density(0.8, 1.4, 1.8Mg/m<sup>3</sup>)
    - evaluation in the effect of ionic strength on  $D_a$  and furthermore evaluation in validity of  $K_d$  used in the H-12 report
  - **Through-diffusion Experiments(on going)**
    - measurements of  $D_e$  of  $^{137}\text{Cs}$  as a function of ionic strength(0.01, 0.1, 0.5, 5) at a dry density of 1.4Mg/m<sup>3</sup>
    - discussion on diffusion mechanism in compacted system
- **Study on Diffusion of Nuclides in Compacted Bentonite/Smectite**
  - **In-diffusion Experiments of Pb(partly finished)**
    - measurements of  $D_a$  of  $^{210}\text{Pb}$  in bentonite as a function of dry density (0.8, 1.4, 1.6, 1.8Mg/m<sup>3</sup>), silica sand content(0, 30, 50wt%) and temperature(22.5, 60°C) under anaerobic conditions
    - measurements of background of  $^{210}\text{Pb}$  in bentonite

## QUALITY Project

- **In-diffusion Experiments of Se(-II)(just finished)**
  - measurements of  $D_a$  of  $^{75}\text{Se}$  in bentonite as a function of silica sand content(0, 30, 50wt%) and temperature(22.5, 60°C) under reducing conditions
  - measurements of background of  $^{75}\text{Se}$  in bentonite
- **In-diffusion Experiments of Np(IV)(in immersion)**
  - measurements of  $D_a$  of  $^{237}\text{Np}$  in bentonite as a function of dry density (0.8, 1.4, 1.6, 1.8Mg/m<sup>3</sup>) under reducing conditions
  - are to be performed as a link in the chain of collabration work with Kyusyu University
- **Through-diffusion Experiments of Sr<sup>2+</sup> and I<sup>-</sup>(partly finished, ENTRY/QUALITY)**
  - measurements of  $D_e$  of Sr<sup>2+</sup> and I<sup>-</sup> in smectite as a function of ionic strength(0.01~ 0.5) at a dry density of 0.9Mg/m<sup>3</sup>
  - measurements of basal space of smectite by XRD as a function of ionic strength

## **Study on Analytical Technology**

- **Study on speciation by Laser-Induced Photoacoustic Spectroscopy (partly finished)**
  - preliminary measurements for speciation by LPAS using Nd solutions with different concentrations
  - consideration of a possibility of Np speciation by LPAS

# *Solubility of Np(IV) under Carbonate Conditions*

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## *Introduction*

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- *Under reducing and carbonate conditions, the major aqueous species of neptunium are expected to be  $\text{Np}(\text{OH})_4^0$  and/or  $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$  in weak alkaline solutions.*
- *The previously reported thermodynamic data are insufficient to elucidate the solubility, hydrolysis and carbonate complexation of Np(IV).*



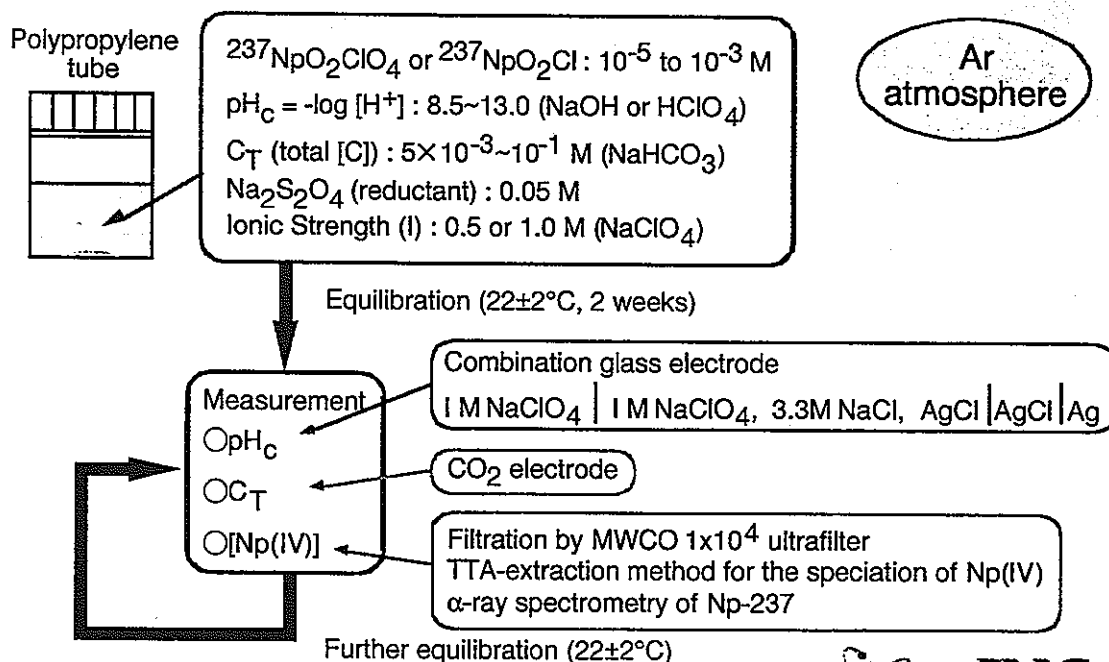


## Objectives

- Solubility measurement of Np(IV) under reducing and carbonate conditions in alkaline solutions
- Determination of the equilibrium constants of aqueous species of Np(IV) from the obtained solubility data
  - Including ionic strength corrections
- Comparison of the present equilibrium constants with the literature values



## Experimental Procedure for Np(IV) Solubility



## Obtained Solubility Curves of Np(IV) (I=0.5M)

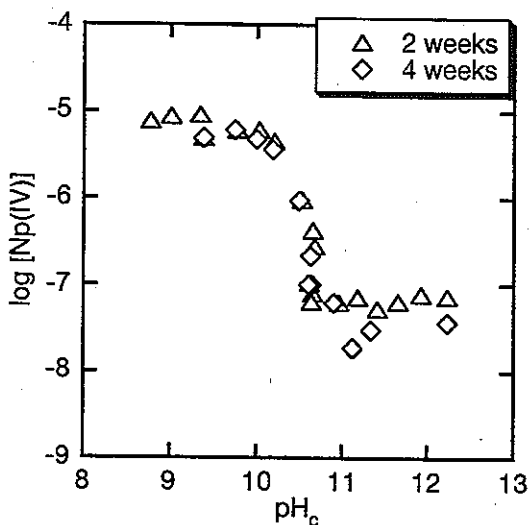


Fig. Solubility of Np(IV) as a function of  $pH_c$ .  
(I = 0.5 M,  $C_T = 0.1M$ )

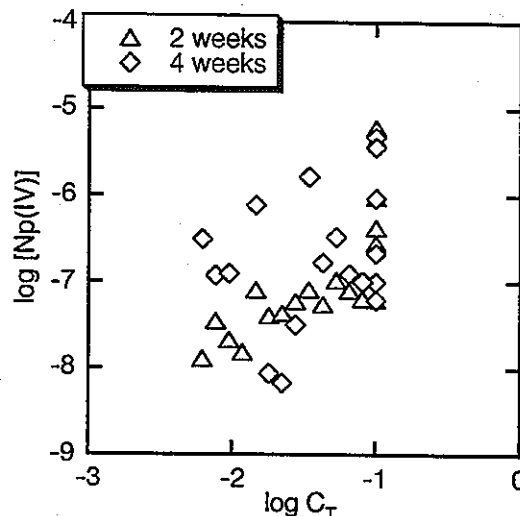
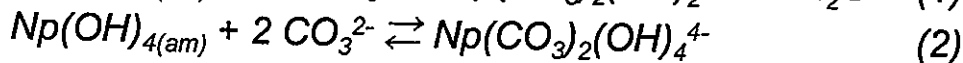
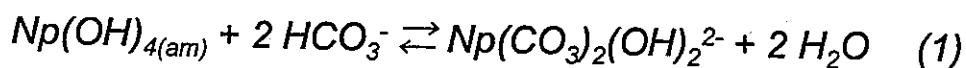


Fig. Solubility of Np(IV) as a function of  $C_T$ .  
(I = 0.5 M,  $pH_c: 10-11$ )



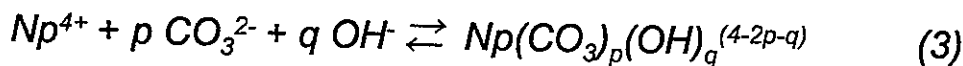
## Analytical Methods

Two carbonatohydroxo complexes of Np(IV) are expected to be major contributions in the present experimental conditions.



The apparent equilibrium constants ( $K'$ ) at I = 0.5 and 1.0 M are determined by a least-squares fitting analysis.

Cf. Stability constant ( $\beta$ ) is defined as the equilibrium constant of the following reaction



## Analytical Results of Np(IV) ( $I=0.5M$ )

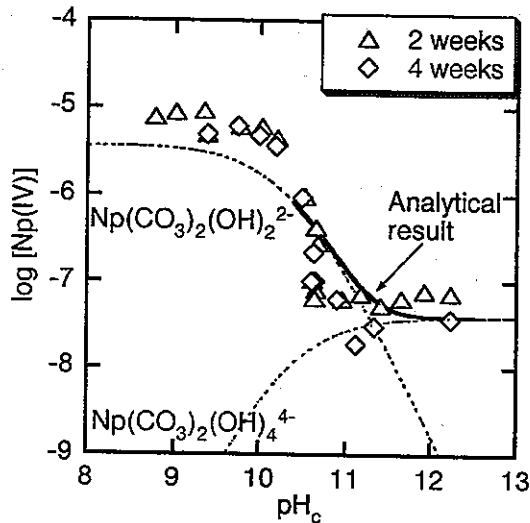


Fig. Solubility of Np(IV) as a function of  $pH_c$ . ( $I=0.5 M, C_T=0.1M$ )

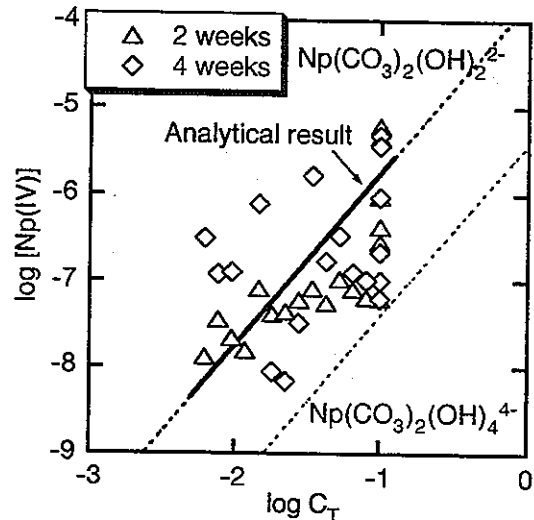


Fig. Solubility of Np(IV) as a function of  $C_T$ . ( $I=0.5 M, pH_c: 10-11$ )



## Ionic Strength Correction by "SIT" method

- The activity constant of ion  $j$  ( $\gamma_j$ ) is expressed as

$$\log \gamma_j = -z_j^2 D + \sum \epsilon(j,k, I_m) m_k \quad (4)$$

- The equilibrium constant of  $Np(CO_3)_2(OH)_2^{2-}$  at standard state ( $K^0$ ) is written as

$$\log K^0 = \log K' - 2D + \Delta \epsilon I_m \quad (5)$$

- Thus, a linear relationship between  $I_m$  and  $\log K-2D$  is found, and the  $\log K^0$  is determined from the intercept.

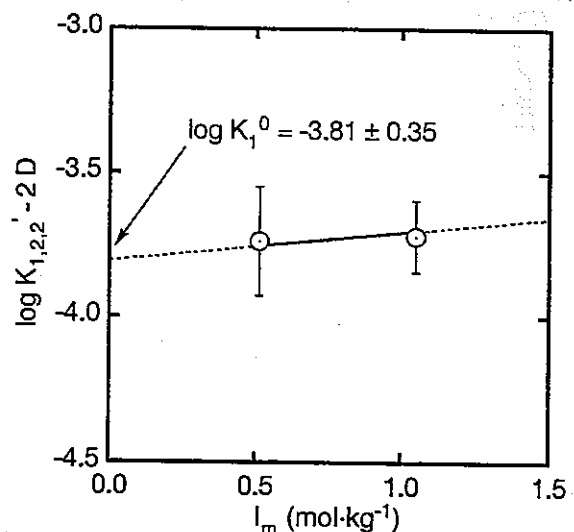


Fig. Calculations of the equilibrium constants extrapolated to  $I_m = 0 \text{ mol}\cdot\text{kg}^{-1}$  according to SIT



## Determined Equilibrium Constants

Table Summary for the logarithm of apparent equilibrium constants ( $\log K'$ ) and equilibrium constants extrapolated to  $I = 0$  M ( $\log K^0$ )

Species	$\log K$		$\log K^0$
	$I = 0.5$ M	$I = 1.0$ M	
$\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$	$-3.30 \pm 0.08$	$-3.31 \pm 0.12$	$-3.81 \pm 0.35$
$\text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$	$-5.41 \pm 0.26$	$-5.43 \pm 0.37$	$-6.82 \pm 1.03$

Comparison of  $\log K$  and  $\log \beta$  of  $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$  with the Literature Values



element	$I$ (M)	$\log K$	$\log \beta$	ref.
Np	0	$-3.81 \pm 0.35$	$43.35 \pm 0.35$	present
	0	-4.44	43.17	Rai(1999)
	0.3	$-0.35 \pm 0.33$	$45.69 \pm 0.44$	Pratopo(1990)
U	0	-4.8	41.33	Rai(1998)
	var.	$>-2.44$	$>41.7$	Pratopo(1990)
Pu	0	-4.78	44.76	Rai(1999)
	0.1	$-2.7 \pm 0.5$	$44.2 \pm 0.6$	Yamaguchi(1994)

\*Using  $\log K_{sp}^0 = \log [\text{Np}^{4+}] + 4 \log [\text{OH}^-]$   
 $= -54.5 \pm 0.3$  (Rai et al.(1987))



## Comparison of $\log K$ and $\log \beta$ of $Np(CO_3)_2(OH)_4^{4-}$ with the Literature Values

element	I (M)	$\log K$	$\log \beta$	ref.
Np	0	$-6.82 \pm 1.03$	$47.48 \pm 1.07$	present
	0.3	$-1.43 \pm 0.33$	$53.07 \pm 0.44$	Pratopo(1990)
Pu	0.1	$-4.98 \pm 0.31$	$49.72 \pm 0.48$	Yamaguchi(1994)
$AnCO_3(OH)_4^{2-}$				
Np	var.		$53.08 \pm 0.01$	Moskvin(1971)
	0.5		$49.20 \pm 0.50$	Eriksen(1993)

\*Using  $\log K_{sp}^0 = \log [Np^{4+}] + 4 \log [OH^-] = -54.5 \pm 0.3$   
(Rai et al.(1987))



## Conclusions

- Solubility of Np(IV) was measured under reducing and carbonate conditions in basic solutions.
- The obtained solubility curves were interpreted by considering the two carbonatohydroxo complexes of  $Np(CO_3)_2(OH)_2^{2-}$  and  $Np(CO_3)_2(OH)_4^{4-}$ .
- The apparent equilibrium constants were determined and the equilibrium constants at standard state were extrapolated.
- The obtained  $\log K^0 = -3.81 \pm 0.35$  for  $Np(CO_3)_2(OH)_2^{2-}$  was found to be similar to the recent literature value by Rai et al., and  $\log K^0 = -6.82 \pm 1.03$  for  $Np(CO_3)_2(OH)_4^{4-}$  was first determined.



# *Measurement of Aqueous Neodymium Solutions by Laser-Induced Photoacoustic Spectroscopy (LPAS):*

## *A Preliminary Study for Speciation of Aqueous Neptunium(IV) Species*

**AKIRA KITAMURA**

Waste Isolation Research Division,  
TOKAI WORKS, JNC



### *Introduction*

- Spectroscopic method is one of the major technique for the speciation of aqueous species. Laser-Induced Photoacoustic Spectroscopy (LPAS) is one of the powerful method for the direct speciation of actinides in natural aquatic systems.
- The operation of the instrument is very difficult, thus a preliminary test operation without using radionuclides is required.

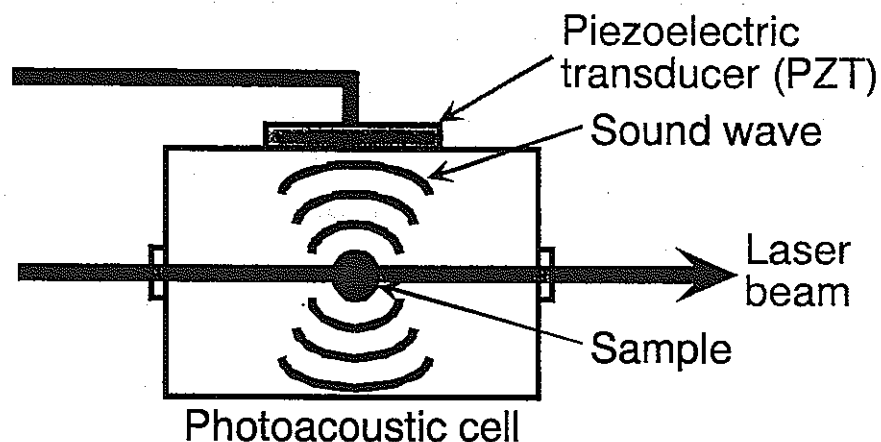


## Objectives

- *Measurement of photoacoustic signals of Nd(III)*
  - Nd(III) has many absorption maxima in the ultraviolet, visible and infrared regions.
- *Drawing photoacoustic spectra of Nd(III) and investigation of their detection limit*
- *Consideration of the speciation of Np(IV) in carbonate solutions*



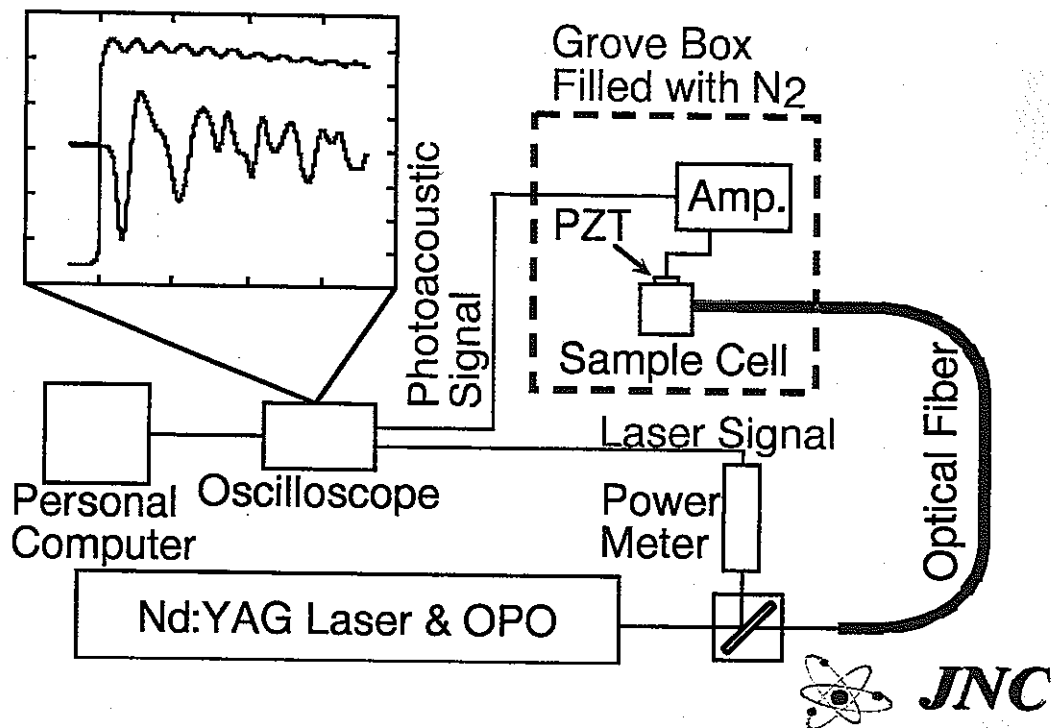
## Schematic of Photoacoustic Detection



- *Heat energy accompanied with radiationless transition can be converted to sound wave.*
- *The intensity of the sound wave is proportional to the energy of a light source, molar extinction coefficient of the species.*

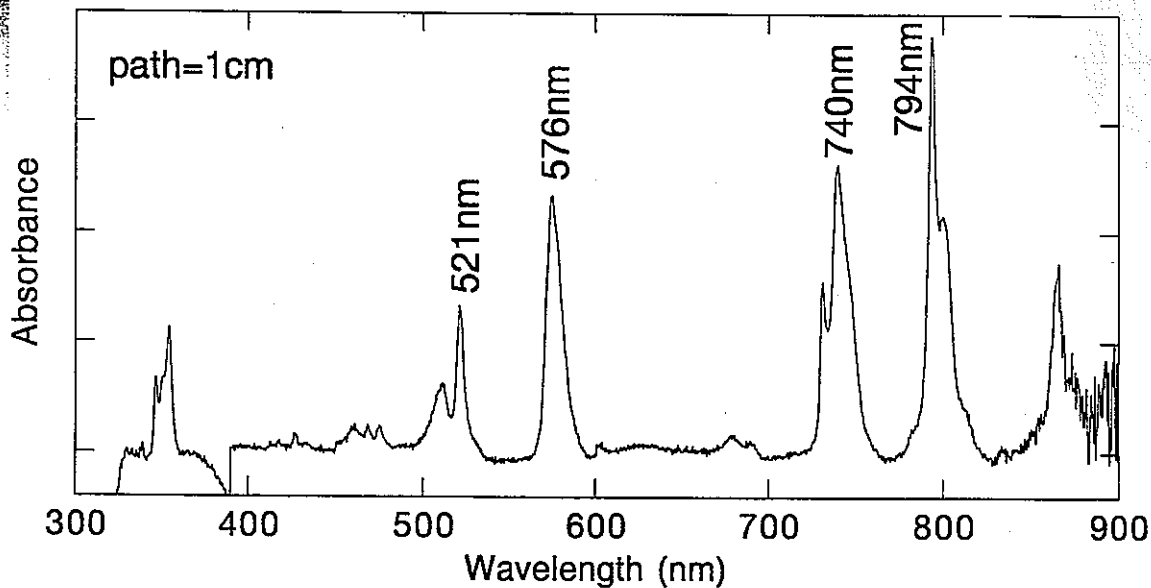


## Instruments of LPAS System



## Absorption Spectrum of Nd(III)

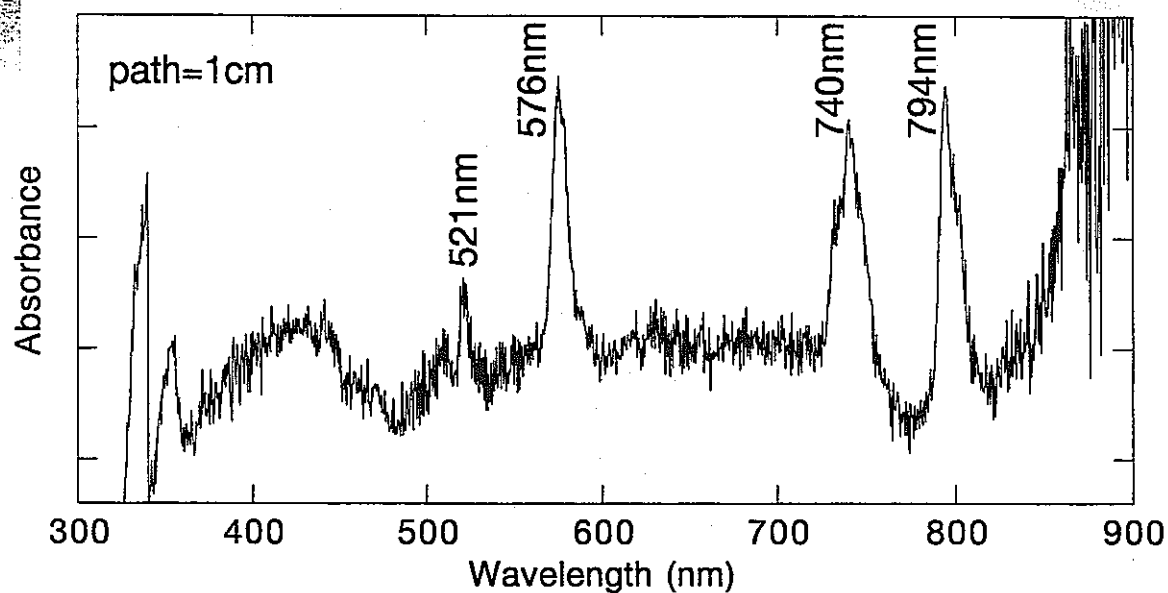
([Nd<sup>3+</sup>] = 2 × 10<sup>-3</sup> M)





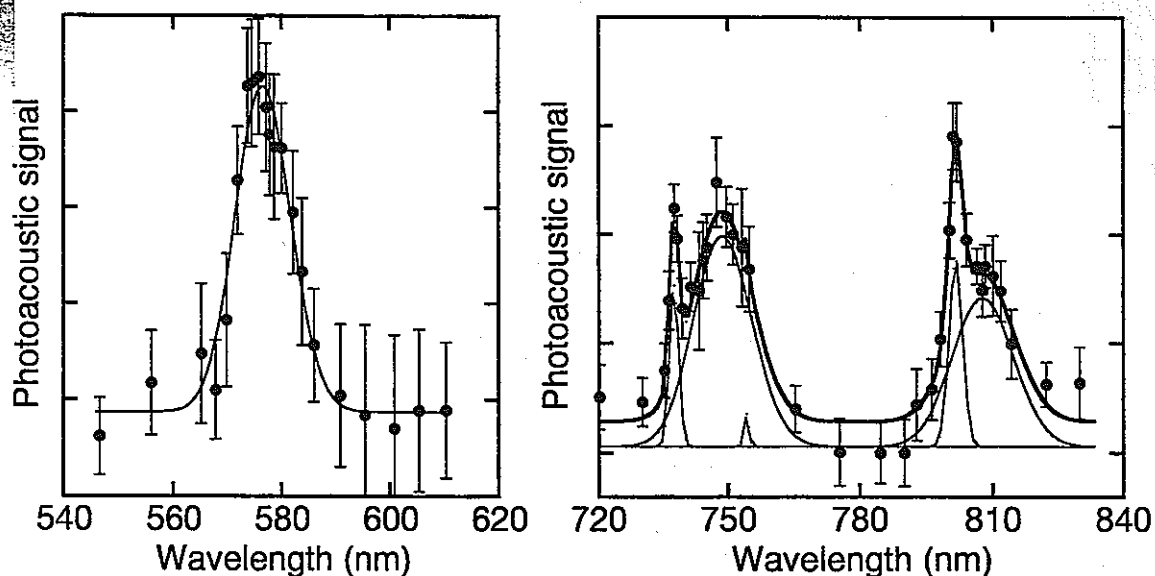
## Absorption Spectrum of Nd(III)

( $[Nd^{3+}] = 2 \times 10^{-4} M$ )

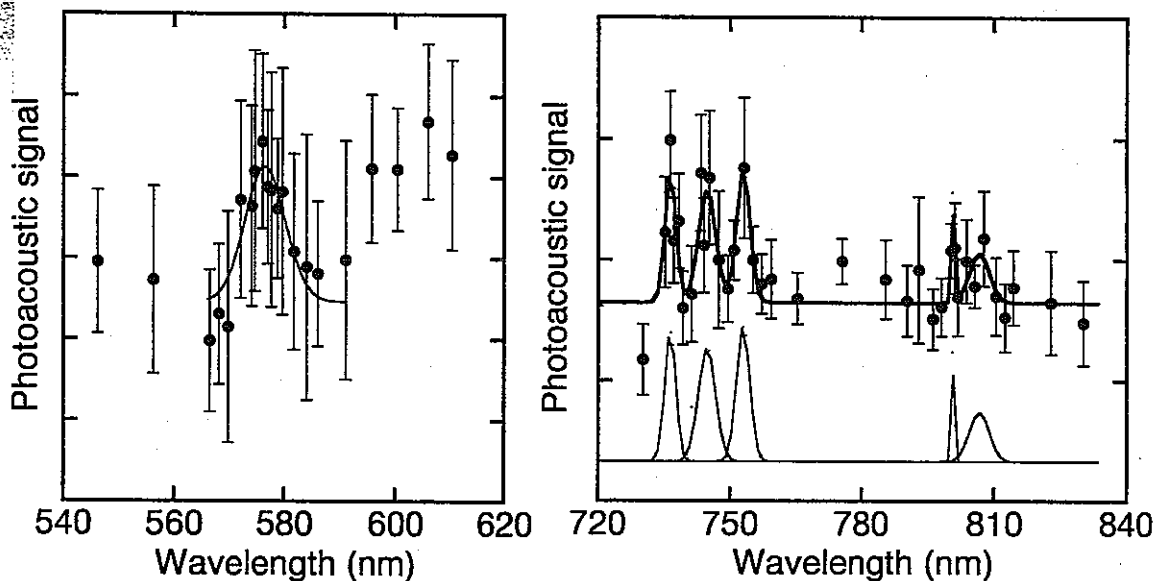


## Photoacoustic Spectra of Nd<sup>3+</sup>

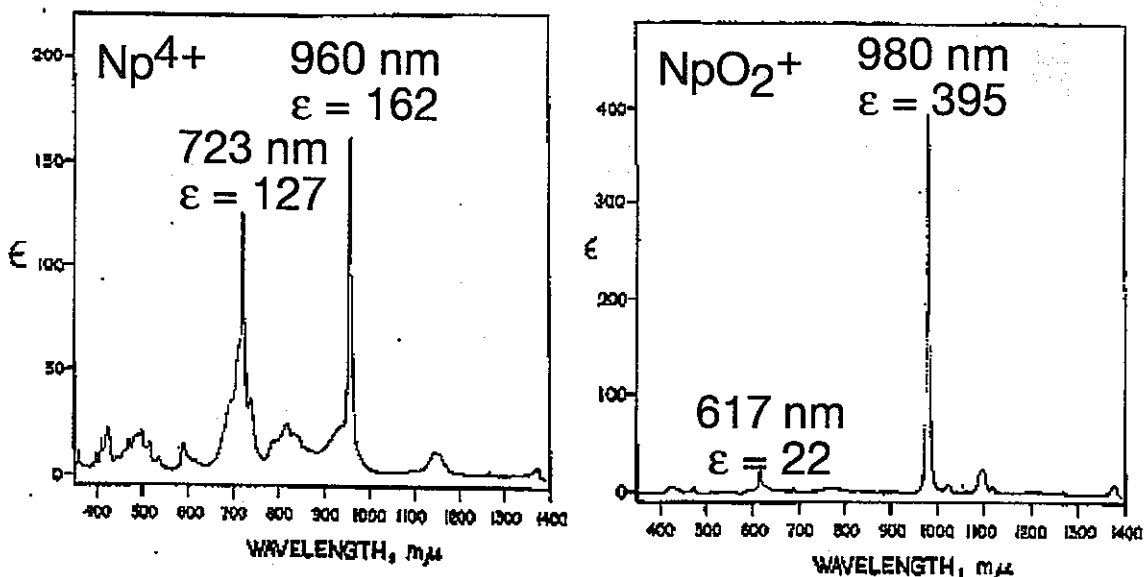
( $[Nd^{3+}] = 2 \times 10^{-4} M$ )



## Photoacoustic Spectra of $Nd^{3+}$ ( $[Nd^{3+}] = 2 \times 10^{-5} M$ )



## Absorption Spectra of $Np(IV, V)$ (arranged from Hagan and Cleveland(1968))



## Expected Detection Limits for the speciation of Np(IV,V)

species	wavelength (nm)	$\epsilon$	measured concn. (M)	expected concn. (M)
Nd(III)	576	7.20	$2 \times 10^{-5}$	
	740	7.27	$2 \times 10^{-5}$	
	794	12.5	$2 \times 10^{-5}$	
Np(IV)	723	127		$1 \times 10^{-6}$
Np(V)	617	22		$6 \times 10^{-6}$

## Solubility of Np(IV) under Carbonate Conditions ( $I=0.5M$ )

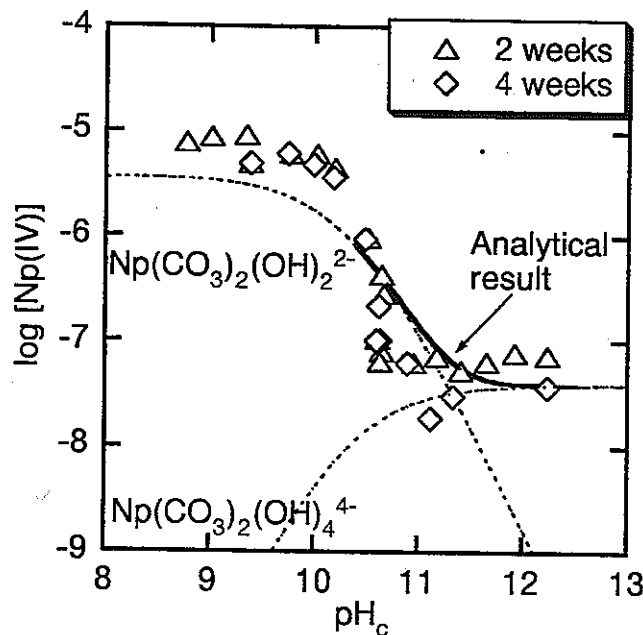


Fig. Solubility of Np(IV) as a function of pH<sub>c</sub>.  
( $I = 0.5 M, C_T = 0.1M$ )



## *Conclusions*

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- *The LPAS spectra of Nd<sup>3+</sup> were measured at [Nd<sup>3+</sup>] of  $2 \times 10^{-5}$  and  $2 \times 10^{-4}$  M.*
  - *The detection limit was expected to be approximately 10 times lower than that by absorption spectroscopy.*
- *The LPAS spectra of Np(V) at  $6 \times 10^{-6}$  M and that of Np(IV) at  $1 \times 10^{-6}$  M were expected to be determined.*
  - *The results show that the LPAS spectrum of carbonatohydroxo complex of Np(IV) can be determined.*



# Current Status of Research & Development on Geochemistry and Nuclide Migration Studies in the QUALITY

-The Effect of Ionic Strength on Apparent Diffusion  
Coefficient of Cs in Compacted Smectite-

Nagra-JNC QUALITY & Migration Workshop  
on March 5, 2001  
Haruo SATO

*Japan Nuclear Cycle  
Development Institute*



QUALITY Project -Cs diffusion in bentonite

## Background of the Study

- Kd values on bentonite for saline groundwater systems were determined based on an ionic strength dependence of Kd values obtained by batch method in the H-12 report. However, the effect of ionic strength on Kd in compacted system is unclear, because few data have been reported.

## Objectives

- Accumulation of diffusivity data as a function of ionic strength particularly, focused on ion exchangeable nuclides such as Cs.
- Validity evaluation of Kd values of Cs on bentonite used in the H-12 report (particularly the effect of ionic strength).

## Outline of the Study

- Implementation of non-steady state diffusion experiments as a function of smectite density and ionic strength by in-diffusion method under aerobic conditions.
- Discussion of diffusion and retardation mechanism of Cs in compacted system.

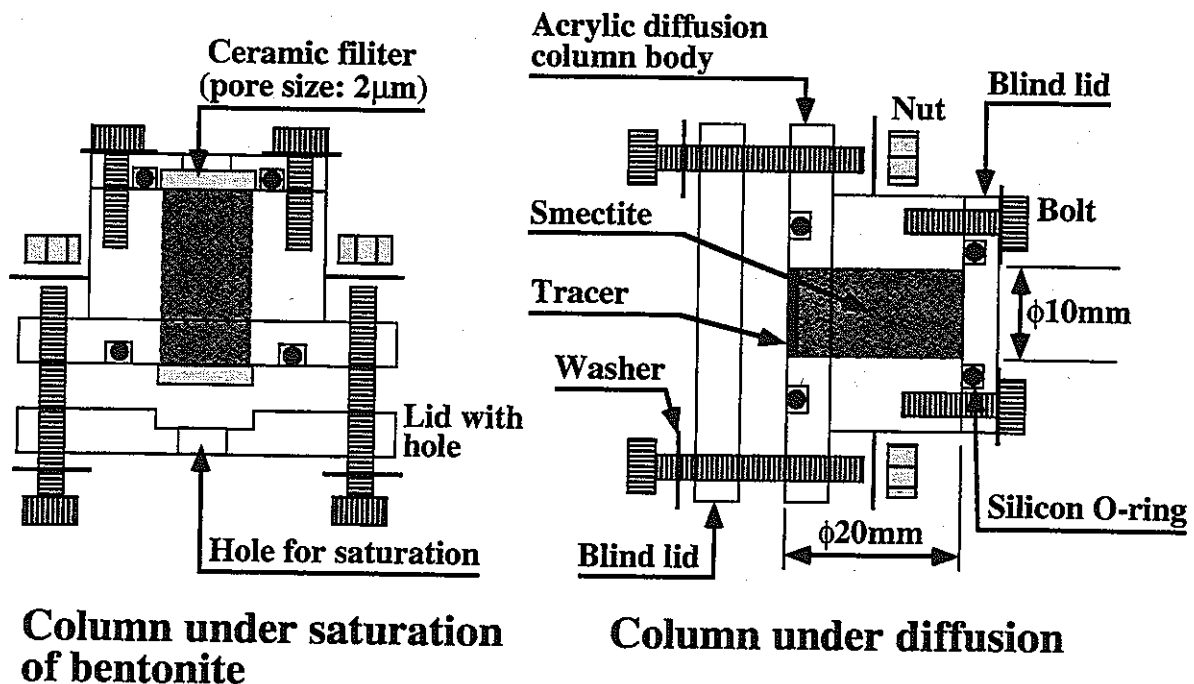
## Diffusion Experiment

### Experimental Condition for Cs Diffusion in Smectite

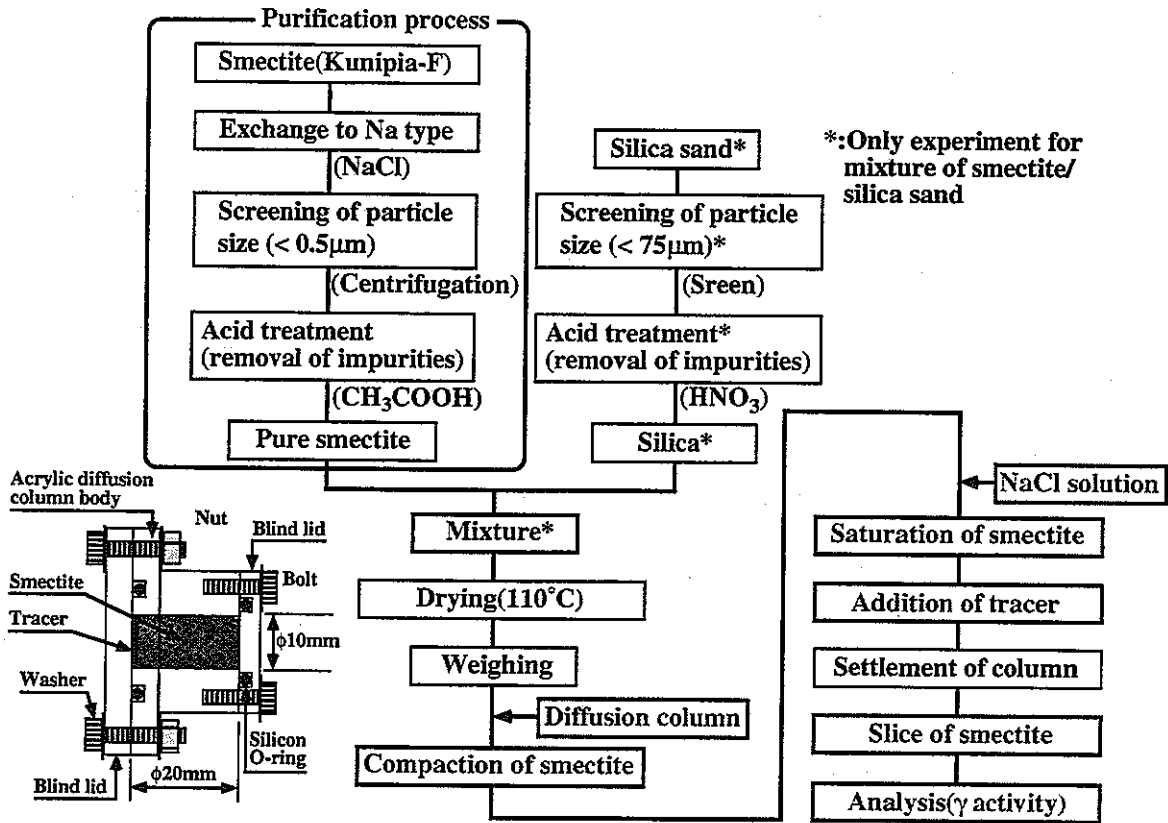
Method	In-diffusion method(one way diffusion)
Solid	Smectite(purified)(0.8, 1.4, 1.8Mg/m <sup>3</sup> ), mixture of smectite/silica sand(1:1)(only 1.4Mg/m <sup>3</sup> )
Dry density	0.8, 1.4, 1.8Mg/m <sup>3</sup> (sample size: $\phi$ 10mmx20mm)
Saturated sol.	0.01, 0.1, 0.5, 5M(only 1.4Mg/m <sup>3</sup> )-NaCl
Tracer sol. (carrier conc.)	<sup>137</sup> Cs(170MBq/L(3.8E-7M),1M-HCl) $\Rightarrow$ neutralization (2.7E-5M)
Introduced tracer quantity	20 $\mu$ L/sample(3.4kBq/sample)
pH	7(pH of solution contacted with smectite)
Temperature	Room temperature(22 $\pm$ 0.2 $^{\circ}$ C)
Atmosphere	Aerobic
Diffusing time	12~67days
Analysis	Ge semiconductor $\gamma$ spectrometer
Producibility	n=2

## Diffusion Experiment

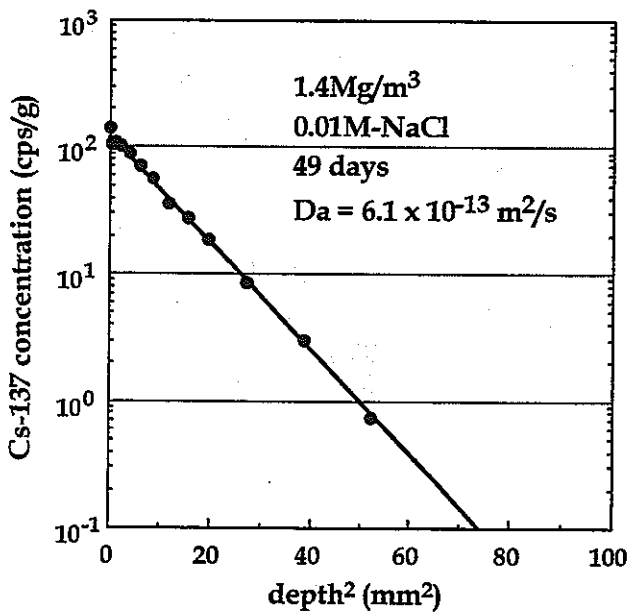
### Sectional view of a diffusion column



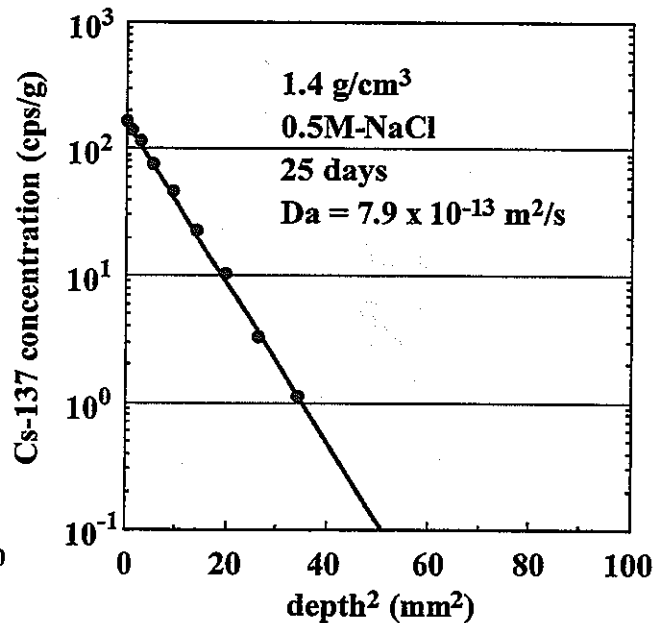
### Experimental Procedure for Cs Diffusion



### Examples of Concentration Profiles of $^{137}\text{Cs}$ in Smectite (A least squares fitting curves)



Concentration profiles of  $^{137}\text{Cs}$  in compacted smectite at 1.4Mg/m<sup>3</sup> for 0.01M NaCl system (after 49days)



Concentration profiles of  $^{137}\text{Cs}$  in compacted smectite at 1.4Mg/m<sup>3</sup> for 0.5M NaCl system (after 25days)

### Calculations of Apparent Diffusivity

Diffusion equation for one-dimensional non-steady state

$$\frac{\partial C}{\partial t} = \left(\frac{De}{\alpha}\right) \frac{\partial^2 C}{\partial x^2} = Da \frac{\partial^2 C}{\partial x^2}$$

Analytical solution for an instantaneous planar source

Initial condition

$$C=0, t=0, X \neq 0$$

Boundary condition

$$C=0, t>0, |X|=\infty$$

$$C = \frac{M}{2\sqrt{\pi Da}} \exp\left(-\frac{x^2}{4Dat}\right)$$

Logarithm of above equation

$$\ln C = \ln\left(\frac{M}{2\sqrt{\pi Da}}\right) - \frac{x^2}{4Dat}$$

Where C: concentration of the tracer in bentonite

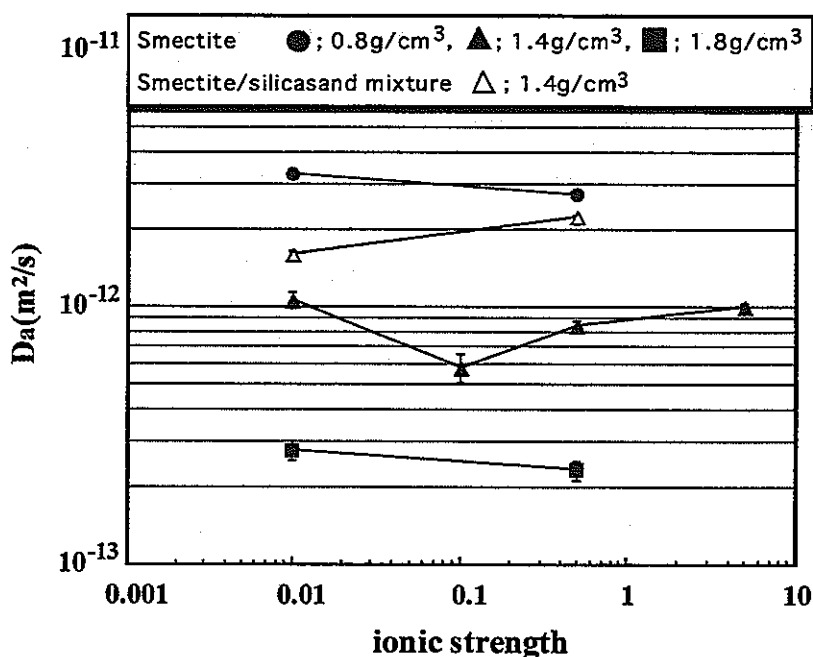
t: diffusing time De: effective diffusivity

α: rock capacity factor x: distance from source

M: total amount of tracer added per unit area

Da: apparent diffusivity

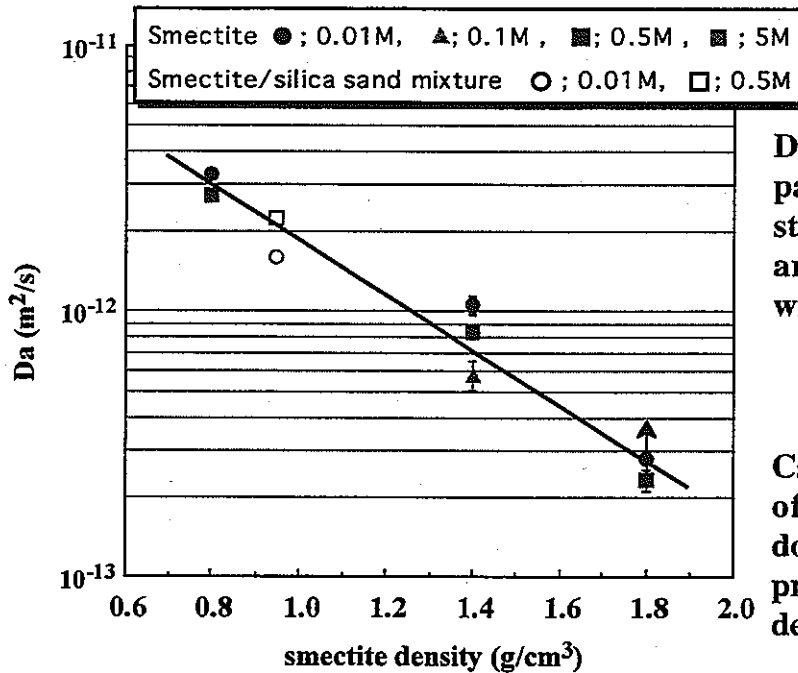
### Ionic Strength Dependences for Da of <sup>137</sup>Cs in Smectite



- No significant effect of ionic strength on Da is found.
- The change of Da on ionic strength is not simple and the tendency is different depending on region of ionic strength (for 1.4Mg/m³).
- Da for the system with silica sand shows a different tendency from those for the system without silica sand.



## Normalization by Smectite Density for Da of <sup>137</sup>Cs in Compacted Smectite



Da is well correlative with smectite partial density even though ionic strength and silica sand content are different, and Da decreases with increasing smectite density.



Cs predominantly diffuses in part of smectite and Cs diffusion is dominantly controlled by smectite properties such as smectite partial density.

### Conclusions

- The Da values of Cs were in the order of E-13 to E-12 m²/s in a smectite density range of 0.8 to 1.8 Mg/m³ and showed a tendency to decrease with increasing density, but no significant effect of ionic strength on Da was found.
- The obtained Da values were well correlative with smectite density. Based on this, Cs diffusion is dominantly controlled by smectite properties.
- The conservativity of Kd values of Cs on bentonite for saline groundwater systems used in the H-12 report was confirmed.

### Future Work

- Implementation of steady state diffusion experiments as a function of ionic strength by through-diffusion method (now on going in the QUALITY).
- Detailed discussion for diffusion and retardation mechanism of Cs in compacted system and modeling, considering the change in micropore structure of smectite by ionic strength.

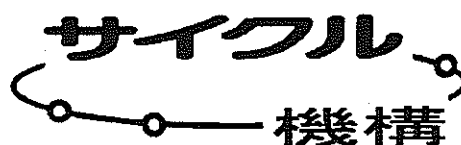
# Current Status of Research & Development on Geochemistry and Nuclide Migration Studies in the QUALITY

-The Effect of Silica Sand Content and Temperature  
on Apparent Diffusion Coefficient of Se in  
Compacted Bentonite under Reducing Conditions-

Nagra-JNC QUALITY & Migration Workshop  
on March 5, 2001

Haruo SATO

*Japan Nuclear Cycle  
Development Institute*



## Background of the Study

### ■ Importance of Se in Safety Assessment

- redox sensitive and chemical species changes depending on redox condition
- low sorptive on bentonite because Se is predicted to form anionic species in the porewater( $\text{HSe}^-$ )
- important for dose equivalent evaluation in safety assessment
- long half-life( $^{79}\text{Se}:\beta^-$ ;  $T_{1/2}=1.13\text{E}6\text{y}$ )
- diffusion data obtained in the system controlled redox condition is quite limited

### ■ Treatment of Retardation of Se in H-12 Report

- $K_d$  on bentonite was determined to be 0 based on  $D_a$  obtained under reducing conditions and  $D_e(\text{I}^-$  as analogue of  $\text{HSe}^-$ )

### ■ Diffusion Data for Se Reported to Date

- although a density dependence of  $D_a$  was reported, quantitative data concerning retardation property and information are short

## Objectives

### ■ Improvement of Reliability of Safety Assessment and Database Development

- to accumulate basic data by obtaining  $D_a$  of Se in bentonite under reducing conditions and to make clear diffusion behaviour

### ■ Follow-up of H-12 Report

- to quantitatively evaluate retardation of Se in compacted bentonite

## Outline of the Study

### ■ Diffusion Experiment

- implementation of in-diffusion experiments using  $^{75}\text{Se}$  as a function of silica sand content and temperature

### ■ Measurement of BG

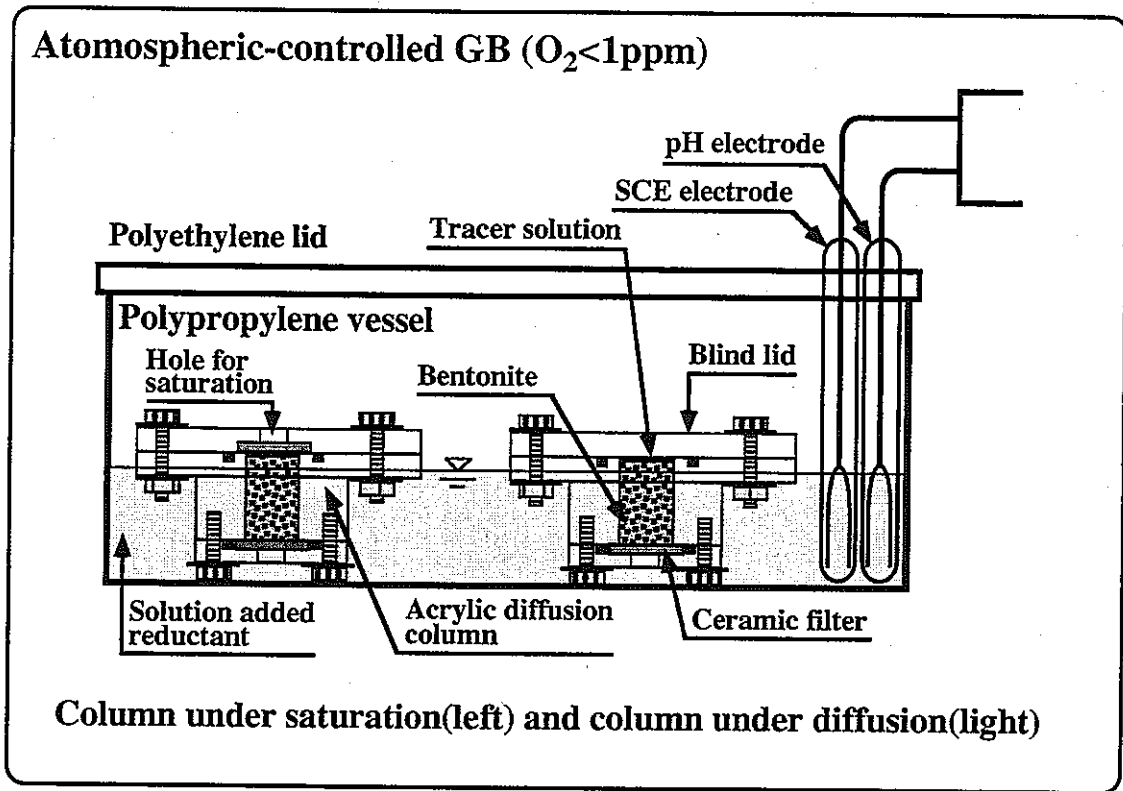
- measurement of background of  $^{75}\text{Se}$  in bentonite

## Diffusion Experiment

### Experimental Condition for Se Diffusion in Bentonite

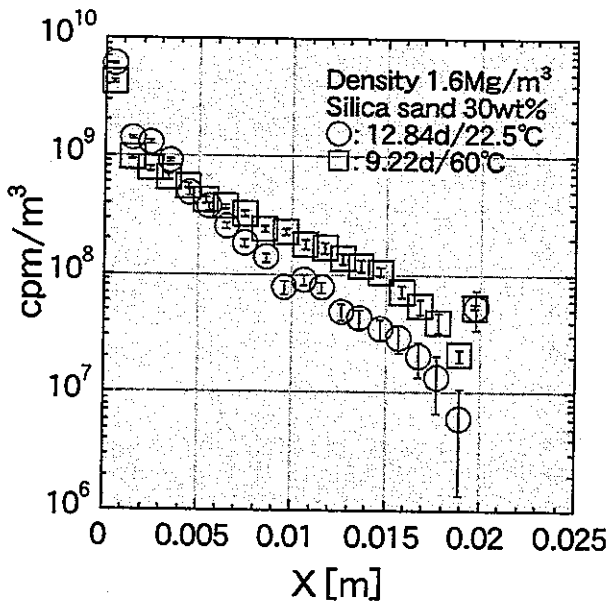
Method	In-diffusion method(one way diffusion)
Solid	Kunigel-V1®(Na-smectite 46-49wt%)
Silica sand content	0, 30, 50wt% (particle size:1-5, 0.1-1mm(mixed with 1:1)
Dry density	1.6Mg/m <sup>3</sup> (sample size: φ20mmx20mm)
Saturated sol.	Degassed distilled water+reductant([NaS <sub>2</sub> O <sub>4</sub> ]=5.2E-3M)
Tracer sol. (carrier conc.)	$^{75}\text{Se}$ (Na <sub>2</sub> SeO <sub>3</sub> solution, 2.63MBq/5ml(1.31E-8M)) 50ppm-Se(6.33E-4M)
Introduced tracer quantity	50μL/sample(21.96kBq/sample)
pH	6.5-7.5(pH of solution contacted with bentonite)
Temperature	Room temperature(22±0.2°C), 60±0.1°C(oven)
Atmosphere	N <sub>2</sub> atmosphere(O <sub>2</sub> < 1ppm)
Diffusing time	1-14days
Producibility	n=2

### Set-up for Se Diffusion Experiment



### Results and Discussion

An example of concentration profile of  $^{75}Se$  in bentonite



### Calculation of Da

Fickian 2nd law considered decay

$$\frac{\partial C}{\partial t} = Da \frac{\partial^2 C}{\partial x^2} - \lambda C$$

Initial and boundary conditions

$$C=0, t=0, |X| \neq 0$$

$$C=C_0, t>0, X=0$$

$$C=0, t>0, |X|=\infty$$

$$C = \frac{C_0}{2} \left\{ \exp\left(|X|\sqrt{\frac{\lambda}{Da}}\right) \operatorname{erfc}\left(\frac{|X|}{2\sqrt{Da \cdot t}} + \sqrt{\lambda t}\right) + \exp\left(-|X|\sqrt{\frac{\lambda}{Da}}\right) \operatorname{erfc}\left(\frac{|X|}{2\sqrt{Da \cdot t}} - \sqrt{\lambda t}\right) \right\}$$

C: concentration t:time

$C_0$ : boundary concentration

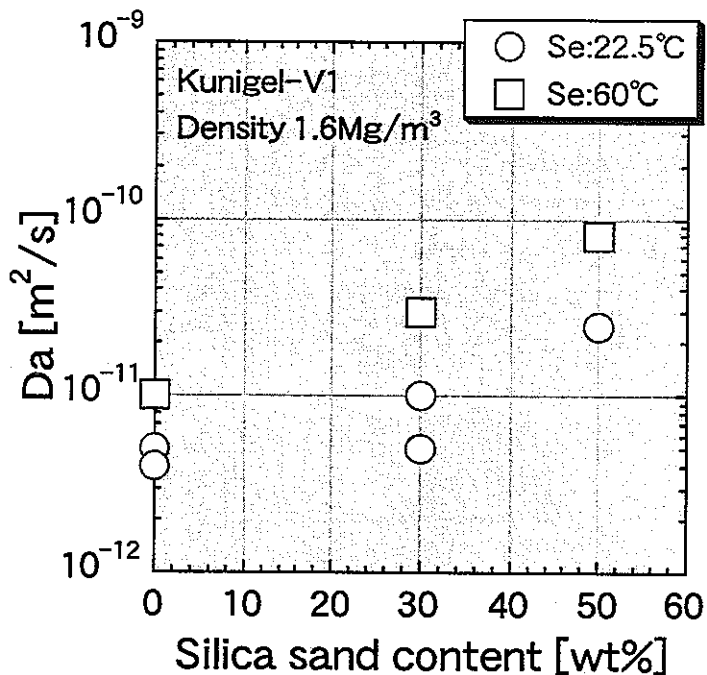
X: distance

Da: apparent diffusion coefficient

$\lambda$ : decay constant

## Results and Discussion

### Effect of Silica Sand Content and Temperature on Da of <sup>75</sup>Se



- Da values for both temperatures show a tendency to increase with increasing silica sand content in bentonite.
- Da shows a tendency to increase with increasing temperature.
- Increasing rate of Da for the increase of temperature is approximately constant, unconcerned with silica sand content.

## Results and Discussion

### Normalization by Smectite Density for Da of <sup>75</sup>Se in Bentonite

Equation for smectite density

$$\rho_{dm} = \frac{(1-f_s) \cdot f_m \cdot \rho_d}{1 - \left\{ \frac{(1-f_s)(1-f_m)}{\rho_{im}} + \frac{f_s}{\rho_s} \right\} \rho_d}$$

$\rho_{dm}$ : smectite density

$\rho_d$ : bentonite density

$\rho_{im}$ : pure density of impurity (2.7Mg/m<sup>3</sup>)

$\rho_s$ : pure density of silica sand (2.7Mg/m<sup>3</sup>)

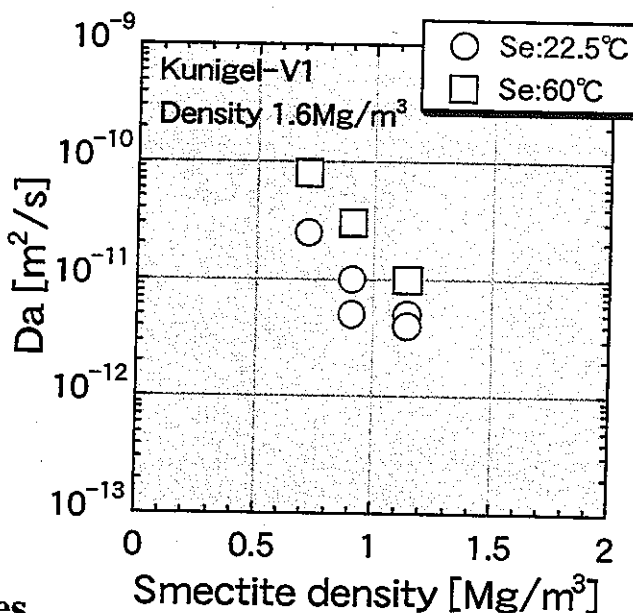
$f_s$ : silica sand content

$f_m$ : smectite content

- Da is well correlative with smectite partial density.

➔ Se diffusion is predominantly controlled by smectite properties

Smectite density dependency for Da of <sup>75</sup>Se



## **Conclusions**

- **The Da values of Se in bentonite were obtained as a function of silica sand content and temperature at a bentonite density of 1.6 Mg/m<sup>3</sup> under reducing conditions.**
- **The obtained Da values increased with increasing silica sand content and temperature.**
- **The obtained Da values were well correlative with smectite density. This indicates that Se diffusion is dominantly controlled by the properties in part of smctite(now is under discussion).**
- **The conservativity of Kd values of Se on bentonite for saline groundwater systems used in the H-12 report was confirmed.**

# Effects of Salinity on Diffusivities of $\text{Sr}^{2+}$ and $\text{I}^-$ Ions in Compacted Na-Bentonite

Satoru SUZUKI, Haruo SATO

Postdoctoral Fellow

Japan Nuclear Cycle Development Institute

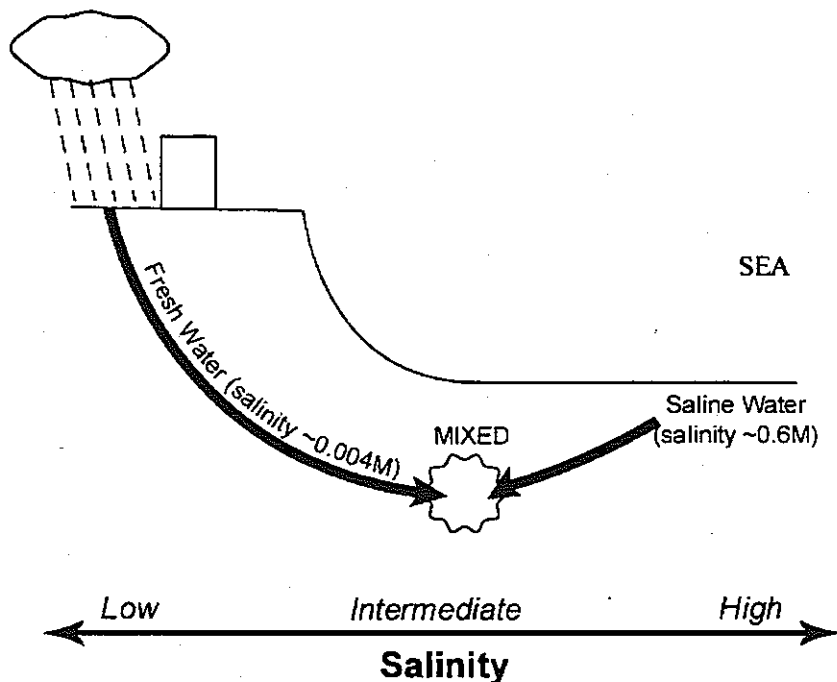
## Factor affecting the diffusivities in the buffer materials

Geological Environments	Engineering Conditions
Groundwater chemistry	Mineral Composition
pH	Silica-sand content
REDOX condition	Smectite type
Salinity	
Temperature & Pressure	Dry density

focus on

**Effects of Salinity on Diffusivities of Ions in the Bentonite**

### Considering a case of the HLW repository near sea / under sea floor



### Previous works reported effects of salinity on $D_e$ of ions

For cations (Sr, Cs) : decrease with increasing salinity

For anions (Cl and I) : increase with increasing salinity

These behaviors were explained by the hypothesis of  
the surface diffusion of sorbed cations  
the anion exclusion due to the negative charge of clay surface

### Problems:

- (1) There were a few works about this phenomena.
- (2) Data were accumulated under the limited conditions of the MX-80 bentonite at dry density of ca.  $1.8 \text{ Mg/m}^3$  only a few saline-condition



**Aims:**

- Confirming the phenomena of the salinity effect on De at low dry density
- Understanding the mechanism

The through-diffusion experiments have been conducted under conditions of

Diffusants:  $\text{Sr}^{2+}$ ,  $\text{I}^-$  ions (inactive) and HDO

Bentonite: Purified Na-bentonite (Na-montmorillonite > 99wt%)  
 at dry density of  $0.9 \text{ Mg/m}^3$

Salinity (NaCl): 0.01, 0.05, 0.1, 0.3, 0.5 M

**Results**

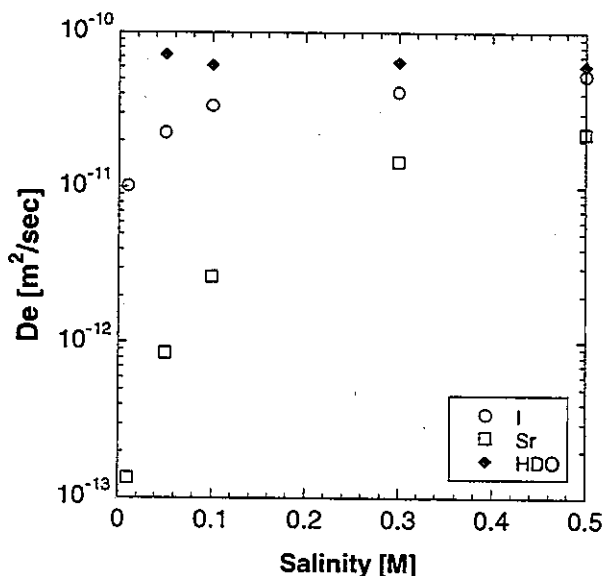


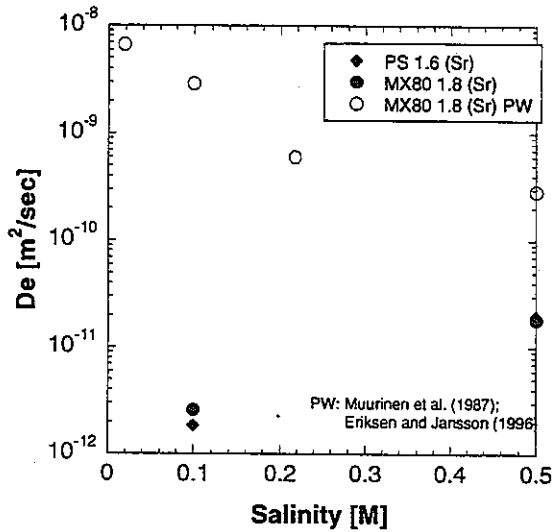
Fig. . Effective diffusion coefficients,  $D_e$  of  $\text{I}^-$ ,  $\text{Sr}^{2+}$  and HDO were plotted as a function of salinity.

$D_e$  of  $\text{Sr}^{2+}$  and  $\text{I}^-$  ions increased with increasing salinity.

Effects of salinity were more significant for Sr ion than for I one at low-saline conditions.

Those of HDO were independent with salinity.

In order to confirm their data, additional T-D experiments were performed for the MX80 bentonite at  $\rho_{dry} = 1.8 \text{ Mg/m}^3$



De of  $\text{Sr}^{2+}$  also increased with increasing salinity.

Data of the other works are correct?

**Need to confirm the effects of salinity on De of cation**

### On going & Future studies

For confirming the phenomena

- (1) To continue data accumulation of De of  $\text{Sr}^{2+}$ ,  $\text{I}^-$  ions and HDO as a function of salinity and dry density
- (2) Data accumulation of De of the other nuclides (i.e. transition metals) The similar tendency has been obtained for De of  $\text{Cs}^+$  ion.

For the better understandings of the mechanism

- (3) Study of microstructural development with respect to salinity and dry density
- (4) Interactions of the diffusants and smectite