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# Study for sorption mechanism of radioactive nuclides in deep underground condition (III)

## summary

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March 1995

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## 1. Introduction

It is very important for the safety assessment of HLW disposal to elucidate the sorption mechanism of radionuclides onto the engineered barriers. However, the variety of deep geological environment and the long study period make the complete elucidation very difficult.

This study had started in 1993 to elucidate the sorption mechanism of Sn on which less knowledge had gathered so far.

In 1993, sorption mechanism onto  $\alpha$ -FeO(OH) was investigated by experimental study and analysis.

In 1994, solubility test, prediction of dominant aqueous species and sequential extraction test were carried out.

In 1995, as a new step, experimental study and analysis on bentonite was carried out.



## 2. Items of study

### (1) Prediction of Sn aqueous species and acquisition of thermodynamic data

In order to predict Sn aqueous species and obtain the thermodynamic data, over-saturated solubility tests are carried out.

### (2) Acquisition of Sn distribution coefficients onto bentonite, pure montmorillonite and $\alpha$ -FeO(OH)

In order to obtain the distribution coefficients and confirm the pH dependence of those coefficients, Sn sorption tests are carried out.

### (3) Estimation of dominant Sn sorption mechanism in bentonite

- Equilibrium constants on surface complex formation reaction are obtained in the Sn sorption behavior onto  $\alpha$ -FeO(OH), according to results of sorption tests in (2).

- Dominant Sn sorption mechanism in bentonite are estimated taking account of sorption behavior onto bentonite, pure montmorillonite and  $\alpha$ -FeO(OH).

### (4) Acquisition of apparent diffusion coefficient in compacted bentonite.

In order to obtain the apparent diffusion coefficient, Sn diffusion test into compacted bentonite by In-Diffusion Method is carried out.

### 3. Prediction of Sn aqueous species and acquisition of thermodynamic data

In order to simulate deep geological environment, these tests were carried out in a atmosphere-controlled glove box in which argon gas were used (Ar:99.999%, O<sub>2</sub>:<1ppm, CO<sub>2</sub>:<1ppm).

#### 3.1 Test condition

##### (1) 0.1M NaClO<sub>4</sub> solution

Test conditions for over-saturated solubility tests used 0.1M NaClO<sub>4</sub> solution are shown in Table3-1. For pH10 solution, Sn concentrations were measured at immersion period 3, 6, 9 months respectively, and confirmed the precipitation equilibrium was established. For other pH samples, immersion periods were 6 months.

##### (2) Bentonite-equilibrated solution

Test conditions for over-saturated solubility tests used bentonite-equilibrated solution are shown in Table3-1. This bentonite was supplied by PNC.

#### 3.2 Test method

##### (1) 0.1M NaClO<sub>4</sub> solution

Sn stock solution containing <sup>113</sup>Sn were spiked into 0.1M NaClO<sub>4</sub> solution in order to establish the over-saturated state (total 50ml). HClO<sub>4</sub> and NaOH were employed for pH adjustment. After immersion, 2 ml solution was filtrated 3 times and radioactivity was measured. Sn concentration was calculated from measured radioactivity and that of stock solution.

(2) Bentonite-equilibrated solution

Sn stock solution containing  $^{113}\text{Sn}$  were spiked into bentonite-equilibrated solution (0.01M  $\text{NaClO}_4$  solution) in order to establish the over-saturated state (total 50ml).  $\text{HClO}_4$  and  $\text{NaOH}$  were used to pH adjustment. After immersion, 2 ml solution was filtrated 3 times and radioactivity was measured. Sn concentration was calculated from measured radioactivity and that of stock solution.

(3) Measurement of radioactivity

① Method

Sample was left as it was for over 1 day, which is long enough to establish the radioactive equilibrium state  $^{113}\text{Sn}-^{113\text{m}}\text{In}$  ( $^{113\text{m}}\text{In}$ : half-life period 1.7h). Radioactivity was measured by counting that of  $^{113\text{m}}\text{In}$  ( $\gamma$ -ray energy: 0.392 Mev, emission ratio: 64%).

② Correction for counting errors

Correction for counting errors is required because the radioactivity count is very small.

$$\sigma = \sqrt{N}$$

N : total radioactivity counting

$\sqrt{N}$  : counting error

$\sigma$  : standard deviation

Therefore, the counting rate in measurement for t minutes involves the following counting errors.

$$\frac{N}{t} \pm \frac{\sqrt{N}}{t}$$

In addition, the following statistical technique used generally was adopted for the error calculation.

$$(A \pm \sigma_A) + (B \pm \sigma_B) = (A + B) \pm (\sigma_A^2 + \sigma_B^2)^{1/2}$$

$$(A \pm \sigma_A) - (B \pm \sigma_B) = (A - B) \pm (\sigma_A^2 + \sigma_B^2)^{1/2}$$

$$(A \pm \sigma_A) \times (B \pm \sigma_B) = (A \times B) \pm (A \times B) \left[ \left( \frac{\sigma_A}{A} \right)^2 + \left( \frac{\sigma_B}{B} \right)^2 \right]^{1/2}$$

$$(A \pm \sigma_A) / (B \pm \sigma_B) = (A / B) \pm (A / B) \left[ \left( \frac{\sigma_A}{A} \right)^2 + \left( \frac{\sigma_B}{B} \right)^2 \right]^{1/2}$$

$\sigma_A, \sigma_B$  : standard deviation of A, B

### ③ Detection limit

Detection limit  $n_{DL}$ (cpm) was calculated by following equation.

$$n_{DL} = \frac{3}{2} \left[ \frac{3}{t_s} + \left[ \left( \frac{3}{t_s} \right)^2 + 4 n_b \left( \frac{1}{t_s} + \frac{1}{t_b} \right) \right]^{1/2} \right]$$

$n_b$  : background counting ratio

$t_s$  : sample counting time(minutes)

$t_b$  : background counting time(minutes)

## 3.3 Result

### (1) 0.1M NaClO<sub>4</sub> solution

Sn concentration at each pH are shown in Table3-2. Within the range of pH12.5~13.5, no precipitation was found at the end of test period. It might suggest that over-saturated condition was not established.

### (2) Bentonite-equilibrated solution

Sn concentration at each pH are shown in Table3-3. At pH6 and pH9, Sn concentration in liquid phase was nearly constant  $2 \sim 3 \times 10^{-6}$ M, however, at pH11,  $3 \sim 4 \times 10^{-8}$ M.

## 3.4 Discussion

### (1) 0.1M NaClO<sub>4</sub> solution

Under-saturated solubility data(1993) and over-saturated solubility data are shown in Fig.3-1. Within the range of pH2~6, Sn concentration in liquid phase was nearly constant about  $5 \times 10^{-8}$ M. Within the range of pH10~12, Sn concentration increases with pH. Over pH12, solubility exceeded

the concentration of initial spike, that means the concentration in liquid phase reached the same value of spike.

Within the range of pH2~8, over-saturated solubility data is 5~10times higher than under-saturated data. Generally, solid-liquid equilibrium for crystalline phase requires longer period, so that it might be a reason of higher solubility at over-saturated experiment.

It is suggested that, over-saturated solubility data is that of amorphous Sn, i.e. quasi-equilibrium of amorphous precipitation and Sn in liquid phase.

## (2) Bentonite-equilibrated solution

Over-saturated solubility data employed 0.1M NaClO<sub>4</sub> solution and bentonite equilibrated solution are shown in Fig.3-2.

At pH11, both data are nearly the same value, however, at pH6 and pH9, the difference between them is clear. Immersion period of bentonite-equilibrated solution is about 1 month and is shorter than that of 0.1M NaClO<sub>4</sub> solution(6 months). Generally, at the neutral pH, solid-liquid equilibrium requires longer period. The result at neutral pH suggests that longer period over 42 days might be necessary for equilibrium.

For reference, pH vs. Eh in solubility tests are shown in Fig.3-3.

### 3.5 Analysis

#### (1) Experimental Results Employed for Analysis

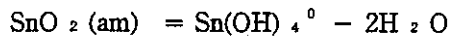
Experimental results used to identify thermodynamic data are summarized in Table 3-4. These results were obtained under these conditions :

- oversaturated equilibrium (including this work and previous work)
- amorphous  $\text{SnO}_2 \cdot 2\text{H}_2\text{O}$  as solubility limiting phase
- pH = 2 - 13, approximately
- 3 or 6 months
- 0.1M  $\text{NaClO}_4$

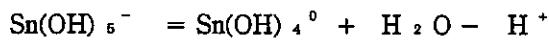
Results whose pH is beyond 12.5, are excluded for analysis because no precipitation were observed under such pH condition.

#### (2) Speciation of Sn

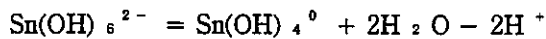
It was observed regarding Sn solubility experiments that the higher the pH, the higher the solubility. This could be explained that negative charged hydrolysis products became dominant aqueous species at higher pH. These reactions can be assumed :



$$K_{\text{am}} = \{ \text{Sn}(\text{OH})_4^0 \}$$



$$K_5 = \frac{\{ \text{Sn}(\text{OH})_5^- \} \{ \text{H}^+ \}}{\{ \text{Sn}(\text{OH})_4^0 \}}$$



$$K_6 = \frac{\{ \text{Sn}(\text{OH})_6^{2-} \} \{ \text{H}^+ \}^2}{\{ \text{Sn}(\text{OH})_4^0 \}}$$

Hence,

$$\log \{ \text{Sn}(\text{OH})_4^0 \} = \log K_{\text{am}}$$

$$\log\{\text{Sn(OH)}_4^0\} = \log K_{am} + \log K_5 + \text{pH}$$

$$\log\{\text{Sn(OH)}_6^{2-}\} = \log K_{am} + \log K_6 + 2\text{pH}$$

Fig.3- 4 shows how experimental results of Sn solubility could be appropriately fitted using these 3 lines in  $\log[\text{Sn}]\text{-pH}$  plot. With regard to speciation of Sn, these could be suggested :

- $\text{Sn(OH)}_4^0$  are dominant, pH below 8
- $\text{Sn(OH)}_5^-$  are dominant, pH from 8 to 10
- $\text{Sn(OH)}_6^{2-}$  are dominant, pH above 10

### (3) Thermodynamic data of Sn

As a result of fitting of Fig.3- 4, some thermodynamic data of Sn can be predicted. Using Davies approximation for correction of activity coefficient, these are derived :

	I = 0.1	I = 0
$\log K_{am}$ :	- 7.46	- 7.46
$\log K_5$ :	- 7.86	- 7.65
$\log K_6$ :	- 17.95	- 17.31

### 3.6 Conclusion

Experimental results of this work showed that solubility of Sn are much higher than ever estimated by other researchers especially at higher pH.

-  $2 \times 10^{-8}$  or  $3 \times 10^{-8}$  mol/L (TVO-92, PNC/H-3, SKB-91)

-  $5 \times 10^{-8}$  mol/L (pH=7),  $5 \times 10^{-5}$  mol/L (pH=10.5) (obtained in this work)

Higher solubility of Sn were observed at pH = 6 in bentonite pore water than in NaClO<sub>4</sub> solution. Longer period might be necessary to establish equilibrium.

Increase of Sn solubility at higher pH could be explained assuming both Sn(OH)<sub>6</sub><sup>-</sup> and Sn(OH)<sub>6</sub><sup>2-</sup> exist in such solution.

These thermodynamic data are obtained correcting activity coefficient :

$$\log K_{am} = \log [\text{Sn(OH)}_4^0] = -7.46$$

$$\log K_5 = \log \frac{[\text{Sn(OH)}_6^-] [\text{H}^+]}{[\text{Sn(OH)}_4^0]} = -7.65$$

$$\log K_6 = \log \frac{[\text{Sn(OH)}_6^{2-}] [\text{H}^+]^2}{[\text{Sn(OH)}_4^0]} = -17.31$$



Table 3-1 Conditions of over-saturated solubility test.

solution	0.1M NaClO <sub>4</sub> solution	bentonite-equilibrated solution (0.01M NaCl solution)
initial Sn concentration	pH6 ~pH10.5 → 10 <sup>-4</sup> M pH11 ~pH12 → 10 <sup>-2</sup> M pH12.5 ~pH13.5 → 10 <sup>-1</sup> M	
pH	10 points (6, 8, 10, 10.5, 11, 11.5, 12, 12.5, 13, 13.5)	3 points (6, 9, 11)
immersion period	①pH10 → 3 points (3, 6, 9 months) ②others → 1 point (6 months)	1 point (43 days)
reproducibility	2	
number of samples	24	6

Table 3-2 Results of over-saturated solubility tests(0.1M NaClO<sub>4</sub> solution)

conditions				results				note <sup>3</sup>
pH	reproducibility	initial Sn conc. (mol/l) (radioactive conc. cpm/ml) <sup>1</sup>	period (months)	initial pH	final pH	Eh (vs. S. H. E) (mV)	Sn conc. (mol/l) (radioactive conc. cpm/ml)	
6	1	$9.4 \times 10^{-5}$ (113658±308)	6	6.0	5.8	268	$(4.7 \pm 0.2) E-8$ (57±2)	
	2	$9.4 \times 10^{-5}$ (113695±308)	6	6.2	6.0	273	$(4.1 \pm 0.1) E-8$ (49±2)	
8	1	$9.4 \times 10^{-5}$ (113349±307)	6	7.8	8.1	266	$(1.50 \pm 0.02) E-7$ (181±3)	
	2	$9.4 \times 10^{-5}$ (113300±307)	6	7.9	8.1	270	$(1.36 \pm 0.02) E-7$ (164±2)	
10	1	$1.0 \times 10^{-4}$	3	10.0	10.4	232	$(6.90 \pm 0.04) E-5$ (5734±24)	
	2	(8361±27)	3	10.0	10.3	242	$(3.60 \pm 0.02) E-5$ (3039±16)	
10	1	$9.9 \times 10^{-5}$ (8320±27)	6	10.1	10.2	300	$(2.35 \pm 0.02) E-5$ (1970±12)	
	2	$9.9 \times 10^{-5}$ (8315±27)	6	10.0	10.2	306	$(2.52 \pm 0.02) E-5$ (2111±13)	
10.5	1	$9.9 \times 10^{-5}$ (8228±27)	6	10.4	10.3	275	$(5.10 \pm 0.04) E-5$ (4230±32)	
	2	$9.9 \times 10^{-5}$ (8226±27)	6	10.5	10.3	295	$(3.18 \pm 0.03) E-5$ (2638±25)	
11	1	$1.4 \times 10^{-2}$ (6626±70)	6	11.2	11.3	243	$(3.71 \pm 0.05) E-3$ (1764±17)	
	2	$1.5 \times 10^{-2}$ (7072±75)	6	11.2	11.3	225	$(1.94 \pm 0.03) E-3$ (924±13)	
11.5	1	$1.5 \times 10^{-2}$ (7047±74)	6	11.5	11.5	213	$(1.02 \pm 0.01) E-2$ (4888±49)	
	2	$1.5 \times 10^{-2}$ (7019±74)	6	11.5	11.7	219	$(9.1 \pm 0.1) E-3$ (4348±46)	
12	1	$1.5 \times 10^{-2}$ (7048±74)	6	12.0	11.8	186	$(1.02 \pm 0.01) E-2$ (4873±49)	
	2	$1.5 \times 10^{-2}$ (7019±74)	6	12.1	11.9	179	$(1.10 \pm 0.02) E-2$ (5240±51)	
12.5	1	$1.0 \times 10^{-1}$ (42880±123)	6	12.5	12.5	159	$(9.27 \pm 0.05) E-2$ (39744±204)	*
	2	$1.0 \times 10^{-1}$ (42801±122)	6	12.5	12.6	107	$(9.64 \pm 0.06) E-2$ (41274±206)	*
13	1	$1.0 \times 10^{-1}$ (45447±129)	6	13.0	13.0	53	$(9.42 \pm 0.05) E-2$ (39861±340)	*
	2	$1.0 \times 10^{-1}$ (45447±129)	6	13.0	13.0	83	$(9.46 \pm 0.05) E-2$ (42810±211)	*
13.5	1	$1.0 \times 10^{-1}$ (51837±148)	6	13.5	13.5	-48	$(9.56 \pm 0.05) E-2$ (49537±225)	*
	2	$1.0 \times 10^{-1}$ (51745±147)	6	13.5	13.5	-13	$(9.68 \pm 0.05) E-2$ (50075±232)	*

\*1 radioactive concentration : decay corrected on 28, September, 1994.

\*2 temperature :  $25 \pm 2$  °C (room temperature)

\*3 \*: initial Sn concentration is greater than  $1.5 \times 10^{-2}$  mol/l and no precipitation was observed.

Table 3-3 Results of over-saturated solubility tests  
(bentonite-equilibrated solution)

conditions				results		
pH	reproducibility	initial Sn conc. (mol/l) (radioactive conc. cpm/ml)	initial pH	final pH	Eh (vs. S. H. E) (mV)	Sn conc. (mol/l) (radioactive conc. <sup>*1</sup> cpm/ml)
6	1	$1.0 \times 10^{-4}$ (30261 ± 175)	5.9	5.9	292	$(2.61 \pm 0.02) E-6$ (709 ± 4)
	2	$1.0 \times 10^{-4}$ (30646 ± 177)	5.5	5.5	304	$(2.26 \pm 0.02) E-6$ (614 ± 4)
9	1	$1.0 \times 10^{-4}$ (30591 ± 177)	8.9	8.8	265	$(3.79 \pm 0.03) E-6$ (1030 ± 5)
	2	$1.0 \times 10^{-4}$ (30371 ± 175)	8.9	8.8	260	$(3.05 \pm 0.02) E-6$ (829 ± 5)
11	1	$1.0 \times 10^{-1}$ (2066 ± 15)	11.1	11.1	222	$(4.7 \pm 0.1) E-3$ (87 ± 2)
	2	$1.0 \times 10^{-1}$ (2072 ± 15)	11.0	11.0	215	$(3.3 \pm 0.1) E-3$ (62 ± 2)

\*1 radioactive concentration : decay corrected on 28, September, 1994.

\*2 temperature :  $20 \pm 2$  °C (room temperature)

Table 3-4 Solubility data employed for analysis.

this study		previous study	
pH (final)	solubility [mo/L]	pH (final)	solubility [mo/L]
5.8	4.7E-08	2.1	1.8E-08
6.0	4.1E-08	2.2	1.5E-08
8.1	1.5E-07	3.0	7.9E-08
8.1	1.4E-07	3.0	8.4E-08
10.4	6.9E-05	3.8	6.2E-08
10.3	3.6E-05	3.8	2.9E-08
10.2	2.4E-05	5.7	5.5E-08
10.2	2.5E-05	6.2	5.9E-08
10.3	5.1E-05	7.8	9.1E-08
10.3	3.2E-05	7.7	4.6E-07
11.3	3.7E-03	10.0	4.0E-06
11.3	1.9E-03	10.1	6.1E-06
11.5	1.0E-02	10.8	9.7E-05
11.7	9.1E-03	10.9	9.6E-05
11.8	1.0E-02	-	-
11.9	1.1E-02	-	-

(note)

including under-saturated solubility test data.

solvent : 0.01M NaClO<sub>4</sub> solution.

immersion period : 3 or 6 months.

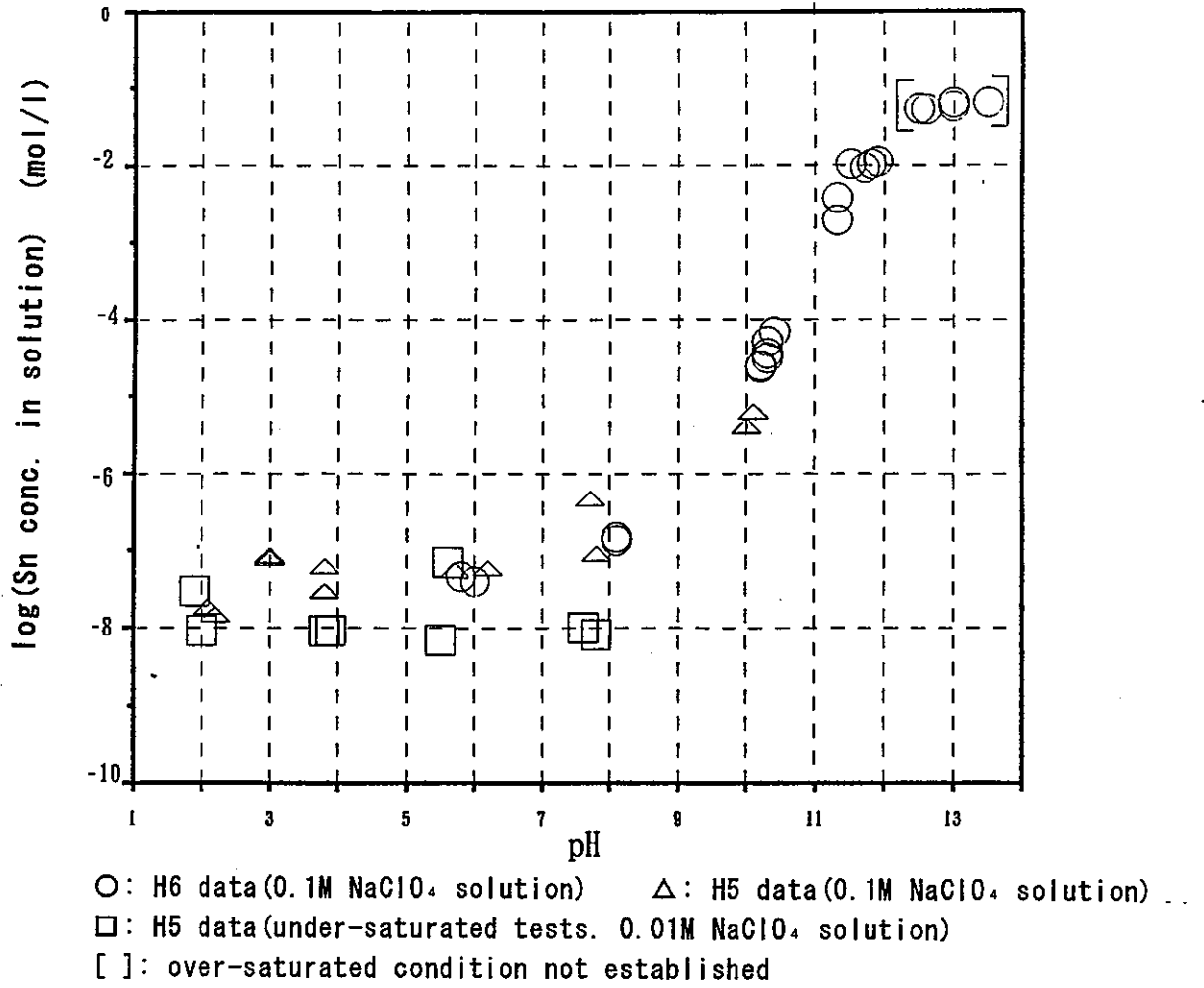


Fig. 3-1 Results of over-saturated and under-saturated solubility tests. (temperature:  $23 \pm 4^\circ\text{C}$ )

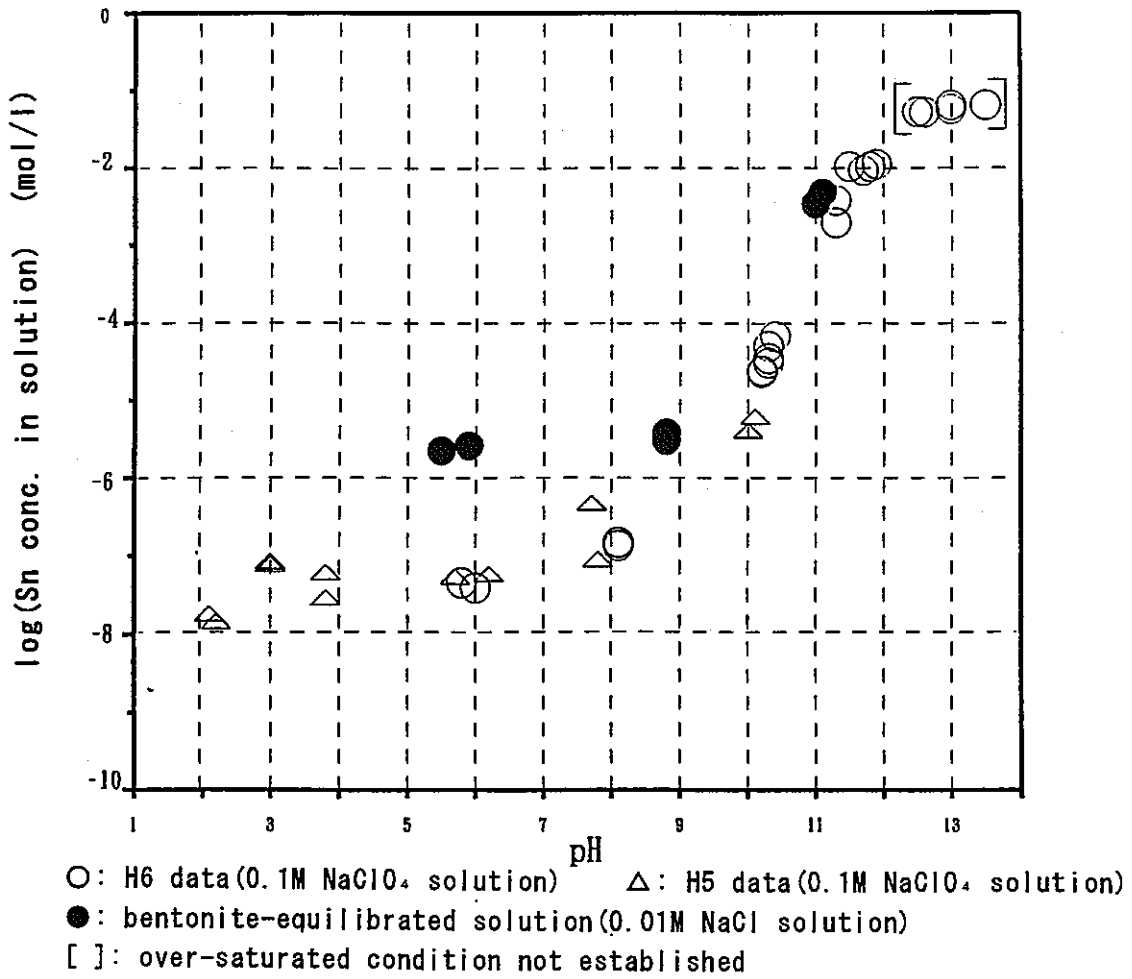


Fig. 3-2 Sn concentration in NaClO<sub>4</sub> solution and bentonite-equilibrated solution. (temperature: 23 ± 3°C)

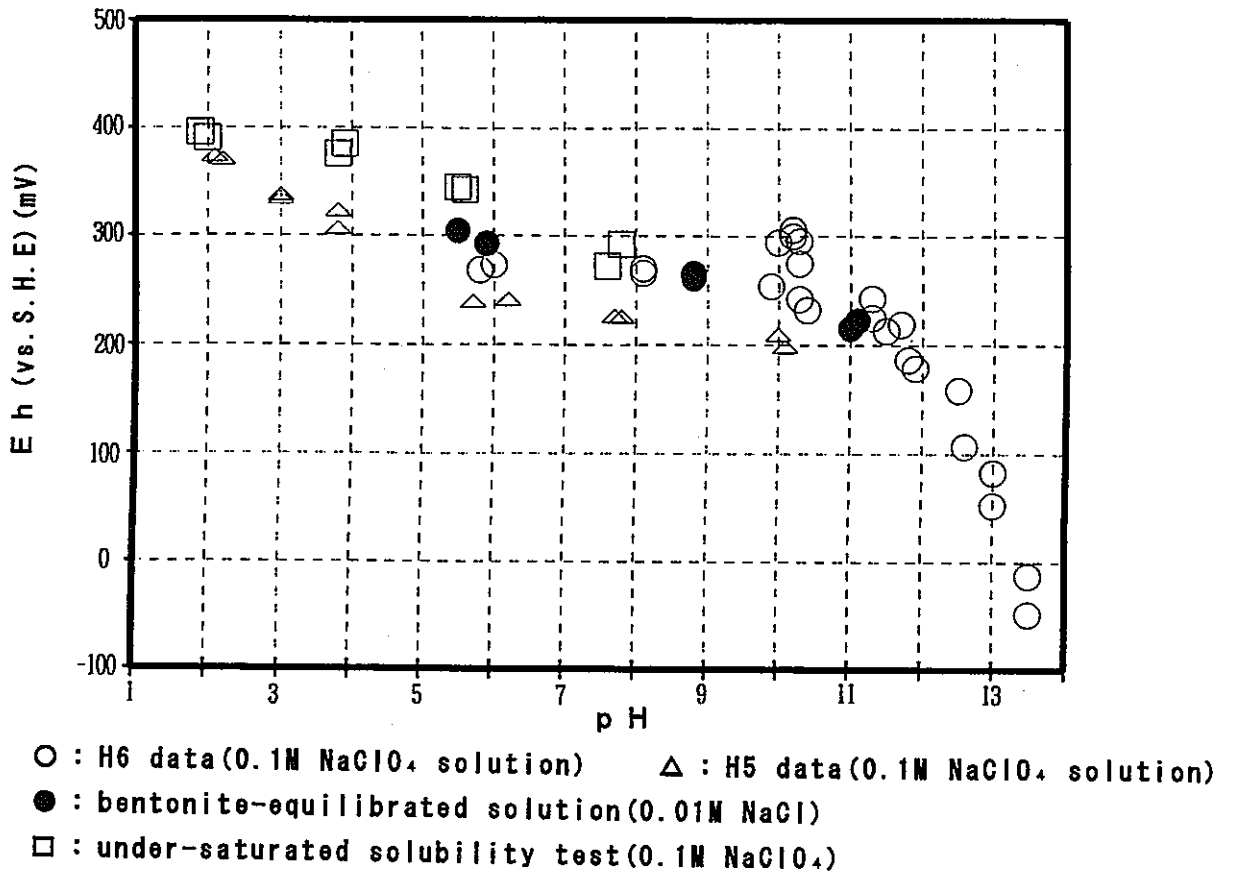


Fig.3-3 pH vs. Eh in solubility tests

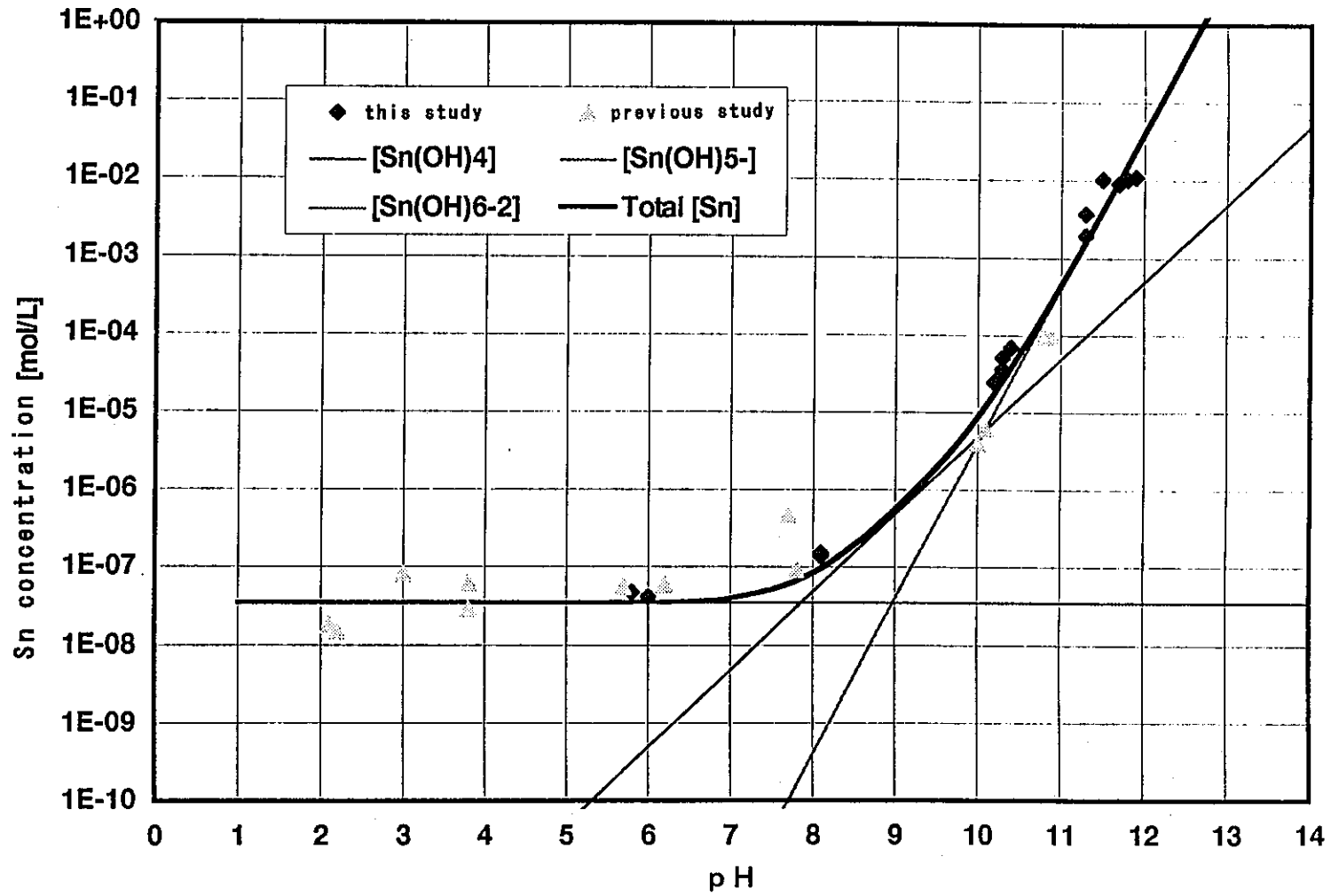


Fig.3-4 Sn solubility curve.



#### 4. Acquisition of Sn distribution coefficients onto bentonite, pure montmorillonite and $\alpha$ -FeO(OH)

##### 4.1 Sorption test

In order to obtain the distribution coefficients, sorption tests onto  $\alpha$ -FeO(OH), bentonite and pure montmorillonite were carried out. In order to simulate deep geological environment, these tests were carried out in a atmosphere-controlled glove box in which argon gas were used (Ar:99.999%, O<sub>2</sub>:<1ppm, CO<sub>2</sub>:<1ppm).

##### 4.1.1 Test condition

Test conditions are shown in Table4-1. Sequential spike method was employed for  $\alpha$ -FeO(OH), batch method was employed for bentonite and pure montmorillonite. However, in test for pure montmorillonite at pH6, Sn was not detected in liquid phase after immersion for 2 months, following sequential spike method was employed.

##### 4.1.2 Method

###### (1) $\alpha$ -FeO(OH)

$\alpha$ -FeO(OH) equilibrated solution (0.01M NaClO<sub>4</sub>) and  $\alpha$ -FeO(OH) was mixed and Sn stock solution containing <sup>113</sup>Sn were spiked into them. HClO<sub>4</sub> and NaOH were employed to pH adjustment.

After immersion, 2 ml solution was filtrated 3 times and radioactivity was measured.

Distribution coefficient was calculated from following scheme.

###### ① Distribution coefficient

$$K_d = C_s / C$$

$K_d$  : distribution coefficient (ml/g)

$C_s$  : Sn concentration in solid phase (mol/g)

$C$  : Sn concentration in liquid phase (mol/ml)

② Sn concentration in solid phase

$$C_s = \frac{\Sigma (R_n - C_n V_n)}{M}$$

$C_s$  : Sn concentration in solid phase (mol/g)

$R_n$  : spiked Sn quantity +  $C_{n-1} V_{n-1}$

$C_n$  : Sn concentration in liquid phase equilibrated after n-th spike (mol/l)

$V_n$  : (liquid phase volume at (n-1)th spike)+(spiked volume(n times))  
+(pH adjustment solution volume)-(sampled volume)

$M$  : solid phase weight (0.013g)

(2) Bentonite and pure montmorillonite

Equilibrated solution of each solid phase(0.01M NaClO<sub>4</sub>) and each solid phase was mixed and Sn stock solution containing <sup>113</sup>Sn were spiked into them. HClO<sub>4</sub> and NaOH were employed for pH adjustment.

After immersion, 2 ml solution was filtrated 3 times and radioactivity was measured.

Distribution coefficient was calculated from following scheme.

$$K_d = \frac{V}{M} \times \frac{C_0 - C}{C}$$

$K_d$  : distribution coefficient (ml/g)

$M$  : solid phase weight (g)

$V$  : liquid phase volume (ml)

$C_0$  : initial radioactive concentration in liquid phase (cpm/ml)

$C$  : radioactive concentration in liquid phase after solid-liquid separation (cpm/ml)

#### 4.1.3 Result

##### (1) $\alpha$ -FeO(OH)

Results of sorption tests onto  $\alpha$ -FeO(OH) are shown in Table 4-2~4-4.

It is not clear that sorption equilibrium was established. Assuming established, distribution coefficients are  $2 \times 10^6$  ml/g,  $3 \sim 6 \times 10^6$  ml/g,  $5 \sim 7 \times 10^5$  ml/g at pH6, pH9, pH11 respectively.

##### (2) Bentonite

Results of sorption tests onto bentonite are shown in Table 4-5.

Distribution coefficients were  $1 \sim 4 \times 10^5$  ml/g,  $3 \times 10^4$  ml/g at pH6, pH9 respectively.

##### (3) Pure montmorillonite

Results of sorption tests onto pure montmorillonite are shown in Table 4-6 and Table 4-7. At pH9 and pH11, Sn in liquid phase was detected. Distribution coefficients were  $1 \times 10^4$  ml/g,  $3 \times 10^3$  ml/g at pH9, pH11 respectively.

At pH6, sorption equilibrium state had not established yet. Assuming established, distribution coefficient is over  $3 \times 10^6$  ml/g.

#### 4.1.4 Discussion

##### (1) Behavior of sorption onto each solid phase

In order to compare the Sn sorption behavior onto  $\alpha$ -FeO(OH), bentonite and pure montmorillonite, relation between distribution coefficient and pH was investigated. The result is shown in Fig. 4-1.

At pH9 and pH11, the value of distribution coefficient of  $\alpha$ -FeO(OH) is the highest and that of pure montmorillonite is the lowest. This tendency suggests that bentonite could be regarded as mixture of  $\alpha$ -FeO(OH) and montmorillonite from sorption point of view. At pH6, bentonite is less sorptive than  $\alpha$ -FeO(OH) and pure montmorillonite. Particularly, sorption onto pure montmorillonite increased with pH decrease from alkali to neutral.

It is suggested that, because of the abundant impurities in bentonite, this tendency was not observed in bentonite test.

(2)pH dependence of sorption

PZC(empirical value) of  $\alpha$ -FeO(OH) and pure montmorillonite(depend on ionic strength) are obtained pH8.4 and pH6.1 respectively. Sn aqueous species could be regarded as  $\text{Sn(OH)}_5^-$  and  $\text{Sn(OH)}_6^{2-}$  from solubility test within the region of  $\text{pH} > 9$ . Obtained distribution coefficients are large, and that it is suggested that main mechanism of sorption could be surface complexation reaction.

4.1.5 Conclusion

①Distribution coefficients onto  $\alpha$ -FeO(OH), bentonite and pure montmorillonite were obtained.

	pH6	pH9	pH11
$\alpha$ -FeO(OH)	$2 \times 10^6$	$3 \sim 6 \times 10^6$	$5 \sim 7 \times 10^5$
bentonite	$3 \sim 4 \times 10^5$	$1 \sim 2 \times 10^5$	$3 \times 10^4$
pure montmorillonite	$> 2 \times 10^7$	$1 \times 10^4$	$3 \times 10^3$

②High sorption onto each solid phase could not be fully explained by electrostatic attraction alone. It is suggested that surface complexation or others could occur.

## 4.2 Sequential extraction test

### 4.2.1 Test condition

Conditions of sequential extraction tests are shown in Table4-8.

Solid phase were bentonite and montmorillonite and liquid phase were equilibrated solution of each solid phase. Extraction conditions and objective effects are shown in Table4-9.

### 4.2.2 Method

#### (1)Conditioning of Sn sorbed solid phase

Equilibrated solutions of each solid phase(0.01M NaCl) and each solid phase were mixed and Sn stock solution containing  $^{113}\text{Sn}$  was spiked into them. HCl and NaOH were employed for pH adjustment.

After immersion, bentonite was collected using  $0.45\mu\text{m}$  microfilter, and  $\alpha\text{-FeO(OH)}$  was collected using centrifuge.

#### (2)Extraction method

Conditions and effects of sequential extraction test are shown in Table4-9.

Sn ratio of each fraction were calculated by following scheme.

$$\text{Sn ratio(\%)} = \frac{\text{radioactivity of each fraction(after extraction)}}{\text{total radioactivity(before extraction)}}$$

### 4.2.3 Result

#### (1)Bentonite

Results of test for  $\alpha\text{-FeO(OH)}$ (including previous study for  $\alpha\text{-FeO(OH)}$ ) are shown in Fig.4-10.

Sn ratio of each fractions were, NaCl:below 1%, NaOH:28~34%, TAO reagent: 46~50%, Coffin reagent:about1%, remainder:18~19%, respectively.

(2) Pure montmorillonite

Results of test for pure montmorillonite (including previous study for  $\alpha$ -FeO(OH)) are shown in Fig. 4-10.

Sn ratio of each fractions were, NaCl: below 1%, NaOH: 62~64%, TAO reagent: 16~22%, Coffin reagent: below 1%, remainder: 14~18%, respectively.

#### 4.2.4 Discussion

(1) Comparison of  $\alpha$ -FeO(OH), bentonite and pure montmorillonite

Sorption states onto  $\alpha$ -FeO(OH) (previous study), bentonite and pure montmorillonite are shown in Table 4-10 and Fig. 4-2.

For pure montmorillonite, ratio of reversible adsorption was large and for  $\alpha$ -FeO(OH) ratio of adsorption onto amorphous phase was large. For bentonite (containing both minerals), ratio of reversible adsorption and adsorption onto amorphous phase were large.

(2) Sn sorption state

According to Fig. 4-2 and Table 4-10, following discussion would be made.

Assuming that ratio of reversible component could be regarded as (P1+P2) (Table 4-10),  $\alpha$ -FeO(OH): 10%, bentonite: 30%, pure montmorillonite: 65%, respectively.

Ratio of component adsorbed onto amorphous phase (weak adsorption) were,  $\alpha$ -FeO(OH): 60%, bentonite: 50%, pure montmorillonite: 20%, respectively.

For strong adsorption, remainder must be taken into account. Remainder could be regarded as precipitation of extracted Sn by Coffin reagent and particularly-strong connected Sn onto solid phase. Assuming that adsorbed component onto crystalline phase and remainder could be regarded as strongly adsorbed component, the ratio were,  $\alpha$ -FeO(OH): 30%, bentonite: 20%, pure montmorillonite: 15%, respectively.

The above results are shown in Table 4-11.

#### 4.2.5 Conclusion

① Sn adsorption onto each solid phase was estimated.

	$\alpha$ -FeO(OH)	bentonite	pure montmorillonite
reversible adsorption	10%	30%	65%
weak adsorption	60%	50%	20%
strong adsorption	30%	20%	15%

② For pure montmorillonite, ratio of reversible adsorption was large and for  $\alpha$ -FeO(OH) ratio of adsorption onto amorphous phase was large. For bentonite(containing both minerals), ratio of reversible adsorption and adsorption onto amorphous phase were large.

③ Although some issues which need more comprehensive discussion still remain, sequential extraction test could be regarded as an effective method in order to investigate the adsorption state.

Table 4-1 Conditions of sorption tests.

	sorption tests.		
	$\alpha$ -FeO(OH)	bentonite	pure montmorillonite
test methods	sequential spike method (max 12times)	batch method	batch method / sequential spike method (pH6 only)
liquid-solid ratio (ml/g)	4 0 0 0 0	1 0 0 0 0	1 0 0 0 0
solid phase weight	1 0 mg	1 0 mg	1 0 mg
liquid phase weight (equilibrated)	4 0 0	1 0 0	1 0 0
pH	3 points (6, 9, 11)	3 points (6, 9, 11)	3 points (6, 9, 11)
immersion period	1 week x number of spikes	2 months	2 months
reproducibility	2	2	2
number of samples	6	6	6



Table 4-2 Results of sorption test onto  $\alpha$ -FeO(OH) (1)

conditions									results				
pH	reproducibility	R I spikes	immersion period (days)	initial Sn conc. (mol/l) (radioactive conc. cpm/ml)	solid phase weight M(mg)	liquid phase volume V(ml)	liquid-solid ratio V/M	adjusted pH	final pH	elapsed time from spikes (days)	Sn in solid A (mol/g)	Sn in liquid B (mol/ml) *1 (radioactive conc. cpm/ml)	K d (ml/g) A/B
6	1	1	17	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)	10	400	40000	5.9	5.9	16	3E-7	<4E-14 (<5)	>7E6
		2	24	$7.3 \times 10^{-9}$ (1088 $\pm$ 10)				6.4	6.0	6	6E-7	<4E-14 (<6)	>1E7
		3	42	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.3	6.0	12	9E-7	<4E-14 (<6)	>1E7
		4	70	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.2	5.9	10	1E-6	<5E-14 (<7)	>2E7
		5	80	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.0	6.0	9	2E-6	<5E-14 (<7)	>2E7
		6	97	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.0	5.8	5	2E-6	<5E-14 (<8)	>3E7
		7	118	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.2	6.2	7	2E-6	<6E-14 (<9)	>3E7
		8	130	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				5.7	5.7	8	2E-6	<7E-14 (<10)	>4E7
		9	138	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.1	6.0	5	2.5E-6	2.7E-12 (408 $\pm$ 6)	9E5
		159	6.3	11					2.6E-6	1.1E-12 (168 $\pm$ 5)	2E6		
6	2	1	17	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)	13	400	30800	6.1	5.8	16	3E-7	<4E-14 (<5)	>7E6
		2	24	$7.3 \times 10^{-9}$ (1056 $\pm$ 10)				6.2	6.1	6	6E-7	<4E-14 (<6)	>1E7
		3	42	$7.3 \times 10^{-9}$ (1088 $\pm$ 10)				6.1	5.6	12	9E-7	<4E-14 (<6)	>1E7
		4	70	$7.3 \times 10^{-9}$ (1088 $\pm$ 10)				6.0	5.4	10	2E-6	<5E-14 (<7)	>2E7
		5	80	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.0	5.8	9	2E-6	<5E-14 (<7)	>2E7
		6	97	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.0	5.9	5	2E-6	<5E-14 (<8)	>3E7
		7	118	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				6.0	6.0	7	2E-6	<6E-14 (<9)	>3E7
		8	130	$7.3 \times 10^{-9}$ (1088 $\pm$ 10)				6.1	6.0	8	2E-6	<7E-14 (<10)	>4E7
		9	138	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				5.9	5.8	5	2.5E-6	2.5E-12 (368 $\pm$ 6)	1E6
		159	5.6	11					2.5E-6	1.6E-12 (232 $\pm$ 6)	2E6		

\*1 radioactive concentration : decay corrected on 28. September, 1994.

\*2 temperature : 25  $\pm$  3 °C (room temperature)

Table 4-3 Results of sorption test onto  $\alpha$ -FeO(OH) (2)

conditions									results				
pH	reproducibility	R I spikes	immersion period (days)	initial Sn conc. (mol/l) (radioactive conc. cpm/ml)	solid phase weight M (mg)	liquid phase volume V (ml)	liquid-solid ratio V/M	adjusted pH	final pH	elapsed time from spikes (days)	Sn in solid A (mol/g)	Sn in liquid B (mol/ml) *1 (radioactive conc. cpm/ml)	K d (ml/g) A/B
9	1	1	17	$7.3 \times 10^{-9}$ (1078 ± 10)	10	400	40000	8.9	8.5	16	2.9E-7	6.5E-14 (10 ± 1)	4E6
		2	24	$7.3 \times 10^{-9}$ (1088 ± 10)				9.0	9.0	6	5.8E-7	1.0E-13 (13 ± 1)	6E6
			35	8.8					11	5.8E-7	6.3E-14 (9 ± 2)	9E6	
		3	42	$7.3 \times 10^{-9}$ (1078 ± 10)				9.1	8.9	6	8.6E-7	2.1E-13 (31 ± 2)	4E6
			80	9.1					38	9E-7	<5E-14 (<7)	>2E7	
		4	97	$7.3 \times 10^{-9}$ (1088 ± 10)				8.9	8.7	5	1E-6	<5E-14 (<8)	>2E7
		5	118	$7.3 \times 10^{-9}$ (1078 ± 10)				8.9	8.7	17	2E-6	<6E-14 (<9)	>3E7
		6	130	$7.3 \times 10^{-9}$ (1078 ± 10)				9.0	8.4	8	2E-6	<7E-14 (<10)	>3E7
7	138	$7.3 \times 10^{-9}$ (1078 ± 10)	8.9	8.7	5	2.0E-6	1.4E-13 (21 ± 4)	1E7					
8	164	$7.3 \times 10^{-9}$ (1072 ± 10)	9.1	9.2	9	2.3E-6	4.1E-13 (58 ± 5)	6E6					
9	2	1	17	$7.3 \times 10^{-9}$ (1053 ± 10)	11	400	36400	9.0	9.0	16	3E-7	<4E-14 (<5)	>7E6
		2	24	$7.3 \times 10^{-9}$ (1088 ± 10)				9.4	9.3	6	5.3E-7	5.3E-14 (7 ± 1)	1E7
			35	9.3					11	6E-7	<4E-14 (<6)	>1E7	
		3	42	$7.3 \times 10^{-9}$ (1078 ± 10)				9.2	8.9	6	9E-7	<5E-14 (<7)	>2E6
		4	97	$7.3 \times 10^{-9}$ (1078 ± 10)				8.9	8.8	43	1E-6	<5E-14 (<8)	>2E7
		5	118	$7.3 \times 10^{-9}$ (1078 ± 10)				9.1	8.9	17	2E-6	<6E-14 (<9)	>3E7
		6	130	$7.3 \times 10^{-9}$ (1078 ± 10)				9.1	8.5	8	2E-6	<7E-14 (<10)	>3E7
		7	138	$7.3 \times 10^{-9}$ (1078 ± 10)				8.9	8.7	5	2.0E-6	8.2E-14 (12 ± 4)	2E7
8	164	$7.3 \times 10^{-9}$ (1073 ± 10)	9.1	9.1	9	2.2E-6	6.8E-13 (96 ± 5)	3E6					

\*1 radioactive concentration : decay corrected on 28, September, 1994.

\*2 temperature :  $25 \pm 3$  °C (room temperature)

Table 4-4 Results of sorption test onto  $\alpha$ -FeO(OH) (3)

conditions									results				
pH	reproducibility	R I spikes	immersion period (days)	initial Sn conc. (mol/l) (radioactive conc. cpm/ml)	solid phase weight M (mg)	liquid phase volume V (ml)	liquid-solid ratio V/M	adjusted pH	final pH	elapsed time from spikes (days)	Sn in solid A (mol/g)	Sn in liquid B (mol/ml) *1 (radioactive conc. cpm/ml)	K d (ml/g) A/B
11	1	1	17	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)	11	400	36400	11.1	11.1	16	2.4E-7	7.9E-13 (117 $\pm$ 2)	3E5
		2	24	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				11.0	11.0	6	3.6E-7	1.7E-12 (235 $\pm$ 2)	2E5
			35						11.0	11	4.5E-7	1.4E-12 (189 $\pm$ 3)	3E5
			80						11.0	45	4.6E-7	8.0E-13 (111 $\pm$ 3)	6E5
		3	116	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				10.9	10.9	6	6.3E-7	2.5E-12 (340 $\pm$ 5)	3E5
		4	138	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				10.9	10.7	7	8.2E-7	9.7E-13 (145 $\pm$ 5)	8E5
		5	164	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				10.9	10.9	13	9.4E-7	1.4E-12 (200 $\pm$ 6)	7E5
11	2	1	17	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)	10	400	40000	11.1	11.1	16	2.6E-7	7.8E-13 (115 $\pm$ 2)	3E5
		2	24	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				11.0	11.1	6	4.7E-7	1.6E-12 (226 $\pm$ 2)	3E5
			35						10.9	11	4.9E-7	1.3E-12 (173 $\pm$ 3)	4E5
			80						11.0	45	5.1E-7	6.3E-13 (87 $\pm$ 3)	8E5
		3	116	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				11.1	11.0	6	7.5E-7	1.3E-12 (177 $\pm$ 4)	6E5
		4	138	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				10.9	10.9	7	9.2E-7	1.8E-12 (264 $\pm$ 6)	5E5
		5	164	$7.3 \times 10^{-9}$ (1078 $\pm$ 10)				10.9	10.9	13	1.0E-6	2.0E-12 (301 $\pm$ 6)	5E5

\*1 radioactive concentration : decay corrected on 28, September, 1994.

\*2 temperature : 25  $\pm$  3 °C (room temperature)

Table 4-5 Results of sorption test onto bentonite.

conditions							results			
pH	reproducibility	liquid-solid ratio V/M	initial Sn concentration (mol/l) (radioactive concentration: cpm/ml)	solid phase weight M(mg)	liquid phase volume V(ml)	adjusted pH	immersion period (days)	final pH	Sn concentration in liquid (mol/l)	K d (ml/g)
6	1	9100	7 E-9 (1031±10)	11	100	5.6	60	5.3	(1.6±0.2) E-10 (25±2)	(4.0±0.4) E 5
	2	9100		11		5.8		5.4	(2.2±0.2) E-10 (34±2)	(2.9±0.2) E 5
9	1	10000	7 E-9 (1022±10)	10	100	9.1	60	8.8	(3.8±0.2) E-10 (59±2)	(1.82±0.09) E 5
	2	9100	7 E-9 (1005±9)	11		9.1		8.9	(5.6±0.2) E-10 (86±2)	(1.10±0.04) E 5
*2 10	1	10000	7 E-9 (1022±10)	5	50	9.6	56	9.0	(1.2±0.05) E-10 (18±1)	(5.6±0.2) E 5
11	1	10000	7 E-9 (1031±10)	10	100	11.0	60	10.8	(1.75±0.03) E-9 (169±3)	(0.30±0.01) E 5
	2	10000	7 E-9 (1005±9)	10		11.0		10.8	(1.97±0.04) E-9 (304±3)	(0.25±0.01) E 5

\*1 temperature : 22 ± 2 °C (room temperature)

\*2 result of preliminary test.

Table 4-6 Results of sorption test onto montmorillonite.

conditions							results			
pH	reproducibility	liquid-solid ratio V/M	initial Sn concentration (mol/l) (radioactive concentration:cpm/ml)	solid phase weight M(mg)	liquid phase volume V(ml)	adjusted pH	immersion period (days)	final pH	Sn concentration in liquid (mol/l)	K d (ml/g)
*2 7	1	10000	7 E-9 (1022±10)	5	50	7.5	56	7.3	(4.9±0.2) E-10 (71±1)	(13.4±0.5) E 4
9	1	10000	7 E-9 (1031±10)	10	100	9.2	60	8.7	(2.94±0.04) E-9 (453±3)	(1.38±0.03) E 4
	2	9100	7 E-9 (1005±10)	11		8.8		8.9	(2.90±0.04) E-9 (447±3)	(1.28±0.03) E 4
11	1	9100	7 E-9 (1022±10)	11	100	11.0	60	10.8	(5.2±0.1) E-9 (804±4)	(0.31±0.02) E 4
	2	10000	7 E-9 (1022±10)	10		11.1		10.8	(5.2±0.1) E-9 (808±4)	(0.33±0.03) E 4

\*1 temperature : 25 ± 3 °C (room temperature)

\*2 result of preliminary test.

Table 4-7 Results of sorption test onto montmorillonite. (sequential spike method)

conditions									results				
pH	reproducibility	R I spikes	immersion period (days)	initial Sn conc. (mol/l) (radioactive conc. cpm/ml)	solid phase weight M (mg)	liquid phase volume V (ml)	liquid -solid ratio V/M	adjusted pH	final pH	elapsed time from spikes (days)	Sn in solid A (mol/g)	Sn in liquid B (mol/ml) *1 (radioactive conc. cpm/ml)	K d (ml/g) A/B
6	1	1	60	$7.3 \times 10^{-9}$ (1005±9)	11	100	9100	6.0	6.2	60	3E-7	<5E-14 (<7)	>6E6
		2	88	$7.3 \times 10^{-9}$ (1005±9)				6.0	5.7	7	6E-7	<6E-14 (<8)	>1E7
		3	98	$7.3 \times 10^{-9}$ (914±8)				5.9	5.8	7	9E-7	<6E-14 (<9)	>1E7
		4	109	$7.3 \times 10^{-9}$ (1005±9)				6.1	5.9	7	1E-6	<7E-14 (<10)	>2E7
		5	118	$7.3 \times 10^{-9}$ (1005±9)				6.2	6.2	7	2E-6	<7E-14 (<10)	>2E7
		6	135	$7.3 \times 10^{-9}$ (1005±9)				5.9	5.8	6	3E-6	<8E-14 (<11)	>2E7
6	2	1	60	$7.3 \times 10^{-9}$ (1005±9)	11	100	9100	5.9	5.7	60	3E-7	<5E-14 (<7)	>6E6
		2	88	$7.3 \times 10^{-9}$ (1005±9)				6.1	5.9	7	6E-7	<6E-14 (<8)	>1E7
		3	98	$7.3 \times 10^{-9}$ (1005±9)				5.8	6.3	7	9E-7	<6E-14 (<9)	>1E7
		4	109	$7.3 \times 10^{-9}$ (1096±10)				5.8	5.8	7	1E-6	<7E-14 (<10)	>2E7
		5	118	$7.3 \times 10^{-9}$ (1096±10)				5.9	5.7	7	1.4E-6	8.3E-13 (122±5)	2E6
		6	130	$7.3 \times 10^{-9}$ (1096±10)				5.7	5.7	18	1E-6	<7E-14 (<11)	>2E7
6	141	$7.3 \times 10^{-9}$ (1005±9)	5.9	5.9	7	1.7E-6	6.7E-13 (99±5)	3E6					

\*1 radioactive concentration : decay corrected on 28, September, 1994.

\*2 temperature :  $25 \pm 3^\circ\text{C}$  (room temperature)

Table 4-8 Conditions of sequential extraction tests.

solid phase		bentonite / pure montmorillonite
sample condition	liquid phase	bentonite-equilibrated 0.01M NaCl/ montmorillonite-equilibrated 0.01M NaCl (liquid-solid ratio:500ml/g)
	pH	10
	Sn conc.	below solubility (initial conc. $7.3 \times 10^{-9} M$ )
	immersion period	1 month
extracting reagents and numbers of trials		①1M NaCl × 3 ②0.1M NaOH × 3 ③TAO reagent × 3 ④Coffin reagent × 3
reproducibility		2
number of samples		4

Table 4-9 Conditions and effects of sequential extraction tests.

fraction No.	extraction method	solid/liquid ratio	temperature	extraction time	expected extraction effect
1	1M NaCl	1/20	room temperature	1 hour ×3	adsorbed Sn by ion exchanges onto solid surface
2	0.1M NaOH	"	"	1 hour ×3	precipitated Sn after extraction by NaCl
3	TAO reagent at pH3 in dark 0.2M (COONH <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O 0.2M (COOH) <sub>2</sub> ·2H <sub>2</sub> O	"	"	2 hours ×3	soluble Sn adsorbed onto amorphous phase
4	Coffin reagent in solution 40ml 0.175M sodium citrate (Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·2H <sub>2</sub> O) 0.025M citric acid 5% (V/V) sodium hydrosulfite (Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> )	"	"	3 hours ×3	soluble Sn adsorbed onto crystalline phase
5	remainder in fractions 1~4 above	—	—	—	insoluble Sn adsorbed onto crystalline phase or precipitated Sn in fractions 3, 4



Table 4-10 Results of sequential extraction tests.

conditions				results					
solid phase	reproducibility	solid weight (g)	radioactive conc. (cpm) (Sn mol)	exchangable component (P1)%	alkaline hydrate (P2)%	amorphous oxide (P3)%	crystalline oxide (P4)%	remainder (R5)%	total P1+P2+P3+R3
*1 $\alpha$ -FeO (OH)	1	0.096	4753±28 ( $4.9 \times 10^{-11}$ )	- *2	13.0±0.1	62.5±0.4	2.8±0.1	24.9±0.2	103.2±0.5
	2	0.100	4680±27 ( $4.9 \times 10^{-11}$ )	-	12.8±0.1	60.9±0.3	3.0±0.1	26.9±0.2	103.6±0.4
bentonite	1	0.040	20279±152 ( $1.5 \times 10^{-10}$ )	1.2±0.5	34.1±0.2	45.6±0.3	1.4±0.0	17.5±1.0	99.9±1.0
	2	0.042	21513±156 ( $1.5 \times 10^{-10}$ )	1.5±0.7	28.1±0.2	50.0±0.3	1.4±0.1	19.5±0.9	100.5±1.0
montmorillonite	1	0.010	4022±40 ( $3.5 \times 10^{-11}$ )	0.4±0.1	64.4±0.4	16.5±0.3	0.3±0.2	14.5±1.0	96.1±1.2
	2	0.010	4059±40 ( $3.5 \times 10^{-11}$ )	0.7±0.1	62.4±0.5	21.5±0.3	0.5±0.1	17.9±1.3	103.0±1.3

\* 1 : from PNC ZJ1281 94-002 p.84

\* 2 : not sampled.

Table 4-11 Adsorption form for each solid phase.

adsorption form	$\alpha\text{-FeO(OH)}$	bentonite	pure montmorillonite
reversible adsorption	10%	30%	65%
weak adsorption	60%	50%	20%
strong adsorption	30%	20%	15%

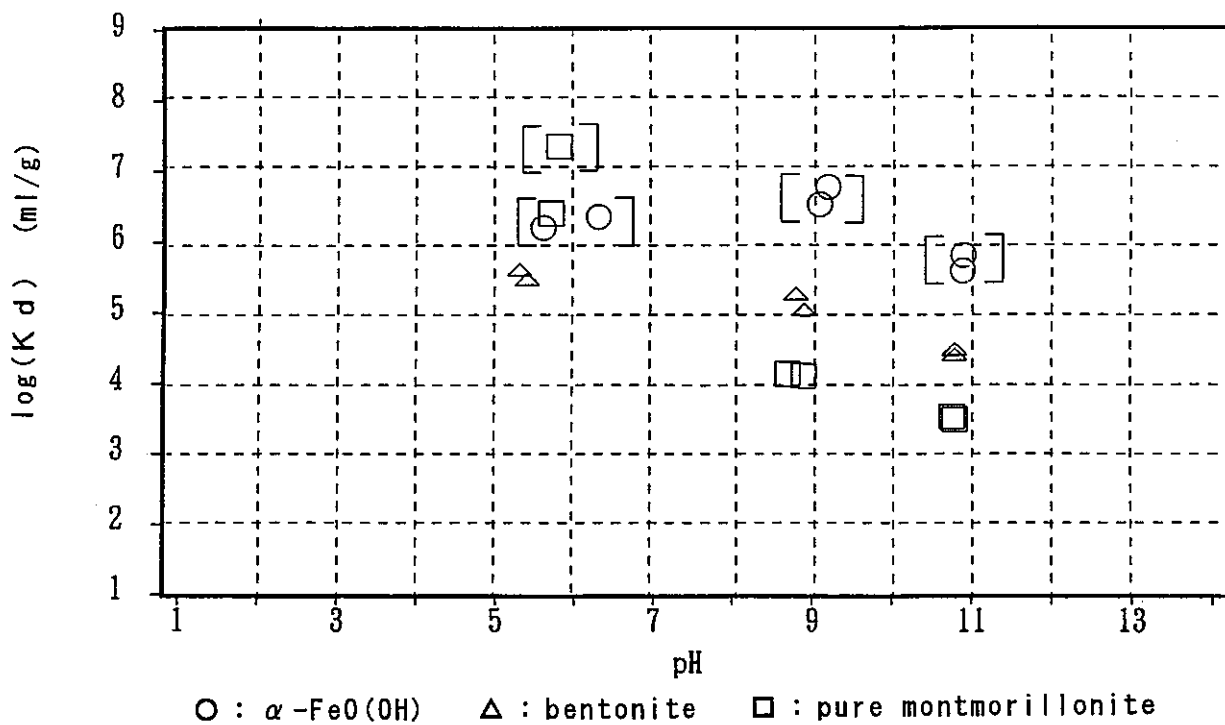


Fig. 4-1 pH dependence of distribution coefficients.

\*1 [ ] test ongoing.

\*2 temperature :  $23 \pm 4^\circ\text{C}$  (room temperature)

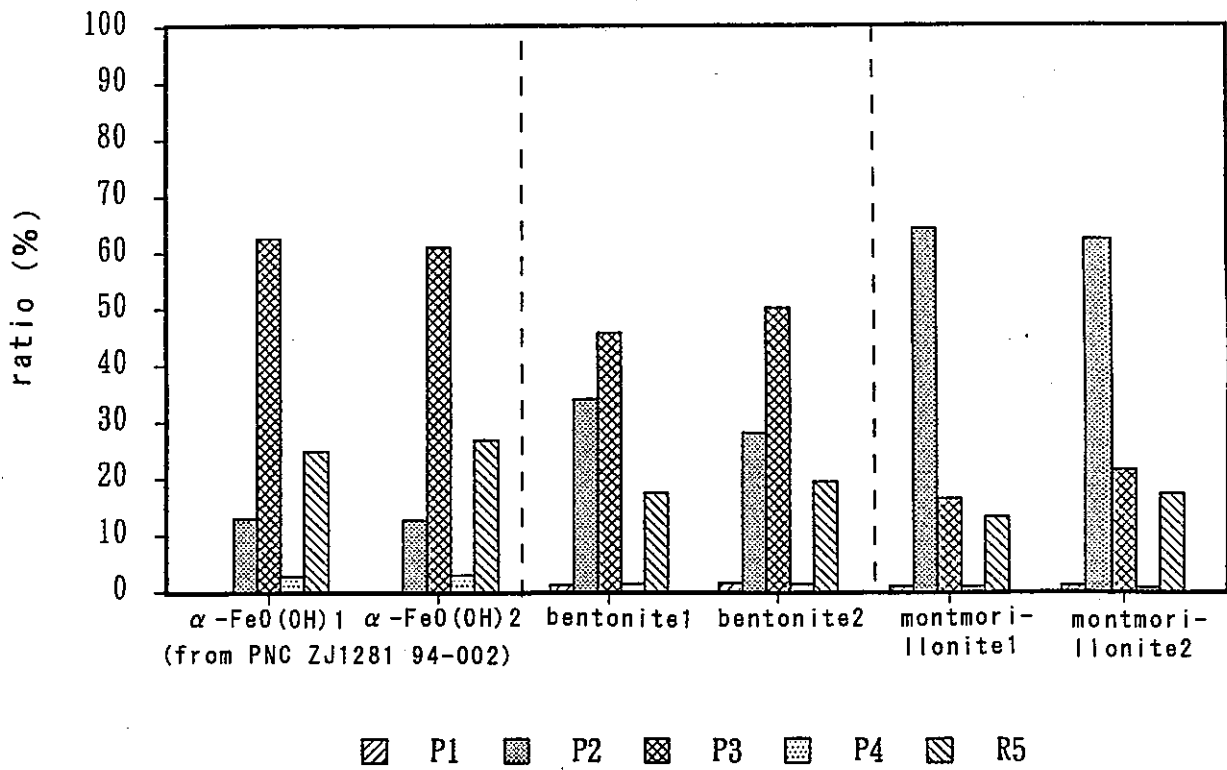


Fig.4-2 Sn ratio of each fractions in sequential extraction tests.

- P1 : 1M NaCl (exchangeable component:  $\alpha$ -FeO(OH) not sampled)
- P2 : 0.1M NaOH (soluble component of alkaline hydrate)
- P3 : TAO reagent (adsorbed onto amorphous oxide)
- P4 : Coffin reagent (adsorbed onto crystalline oxide)
- R5 : remainder

## 5. Mechanisms of Sn Sorption onto Bentonite

Based upon preliminary consideration for both batch sorption experiments and sequential extraction, these are suggested with regard to mechanisms of Sn sorption onto FeOOH, montmorillonite and bentonite :

- There is less possibility that ion exchange occurs for Sn sorption.
  
- It is suggested that reversible sorption of surface complexation and any irreversible sorption occur simultaneously.
  
- Understanding pH dependence of Sn sorption, solid surface evolution might be major cause for sorption onto FeOOH, otherwise Sn speciation might be for montmorillonite.
  
- With regard to pH dependence of Sn sorption, bentonite has intermediate tendency between FeOOH and montmorillonite. Sn sorption onto bentonite might be modelled integrating sorption models both for FeOOH and montmorillonite.

## 6. Apparent Diffusion Coefficient in Compacted Bentonite

### 6.1 Preliminary Analysis to Predict Diffusion of Sn in Bentonite

In this section, preliminary analysis are carried out for Sn diffusion in bentonite in order to estimate how far Sn will transport in bentonite and how long experiment should be continued in realistic point of view.

Sn transport by diffusion in 1-D semi infinite media can be analytically solved under some initial and boundary conditions to predict Sn concentration in it. Fig.6-1 and Fig.6-2 show Sn distribution in bentonite pore water and onto bentonite after a year, using analytical solution. In this case, linear isotherm sorption are assumed any period and any point.

In order to carry out realistic experiments in this work, these conditions are required :

- experiment period should be within a year.
- Detectable amount of Sn should be distributed beyond 2mm.

Fig.6-3 and Fig.6-4 are maps which show feasibility of experiment. It is clear that diffusion experiment is easily feasible for neutral species, otherwise less feasible for negative species. Therefore it is suggested that dry density of bentonite should be as low as possible so that high  $D_e$  could be expected and hence Sn would diffuse faster.

## 6.2 Test condition

Sn diffusion test into compacted bentonite using In-Diffusion method was carried out. Test samples were kept in a atmosphere-controlled glove box in which argon gas were used(Ar:99.999%, O<sub>2</sub>:<1ppm, CO<sub>2</sub>:<1ppm).

Dry density of used bentonite was 0.4g/cm<sup>3</sup>, diffusion periods were 6, 9, 12 months. For each periods, number of sample was 1 and in order to confirm the test reliance, tests of same condition was carried out for 2 samples.

## 6.3 Method

### (1)Conditioning of spread Sn solution

Condition of spread Sn solution is shown in Table6-1. The quantity of spread solution was 25~50ml.

### (2)Procedure

Column instrument for this test is shown in Fig.6-5.

This column was stuffed with dried bentonite(at 110°C for 24h) and immersed for 3 weeks in order to make bentonite saturated. After saturation, Sn solution containing <sup>113</sup>Sn(53 μ l) was spread using micropipet. After diffusion period, bentonite will be sliced(0.5mm thick) and measured the radioactivity, and Sn concentration will be calculated. The test is ongoing at present.

Table 6-1 Conditioning of spread Sn solution.

		objective	result
parameters	spiked Sn concentration in one sample (mol/l)	$4 \times 10^{-2}$	$2.0 \times 10^{-2}$
	pH	12	13*
	radioactive concentration (cpm/mol) (1. March, 1995)	$3.3 \times 10^{12}$	$1.4 \times 10^{12}$
total radioactivity in original RI solution (cpm) (radioactivity in one sample) (1. March, 1995)		$2 \times 10^7$  $(3.3 \times 10^6)$	
added Sn quantity in one sample (mol)		$1 \times 10^{-6}$	$1.1 \times 10^{-6}$
spread Sn quantity in one sample ( $\mu$ l)		25	53

\* estimated value



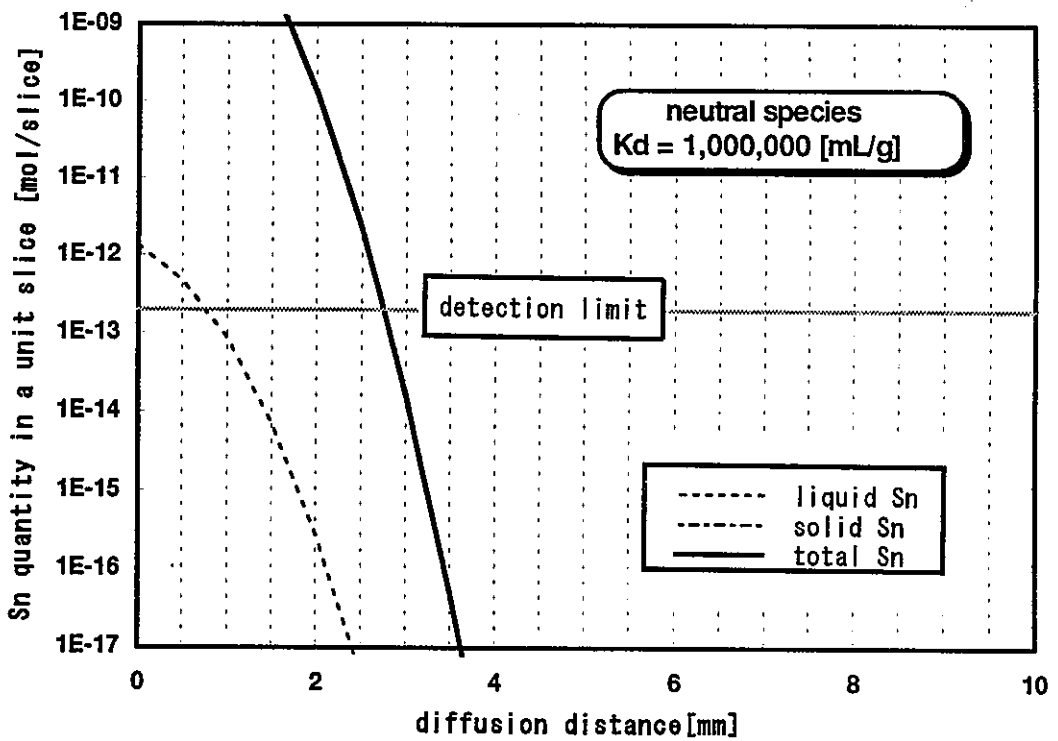
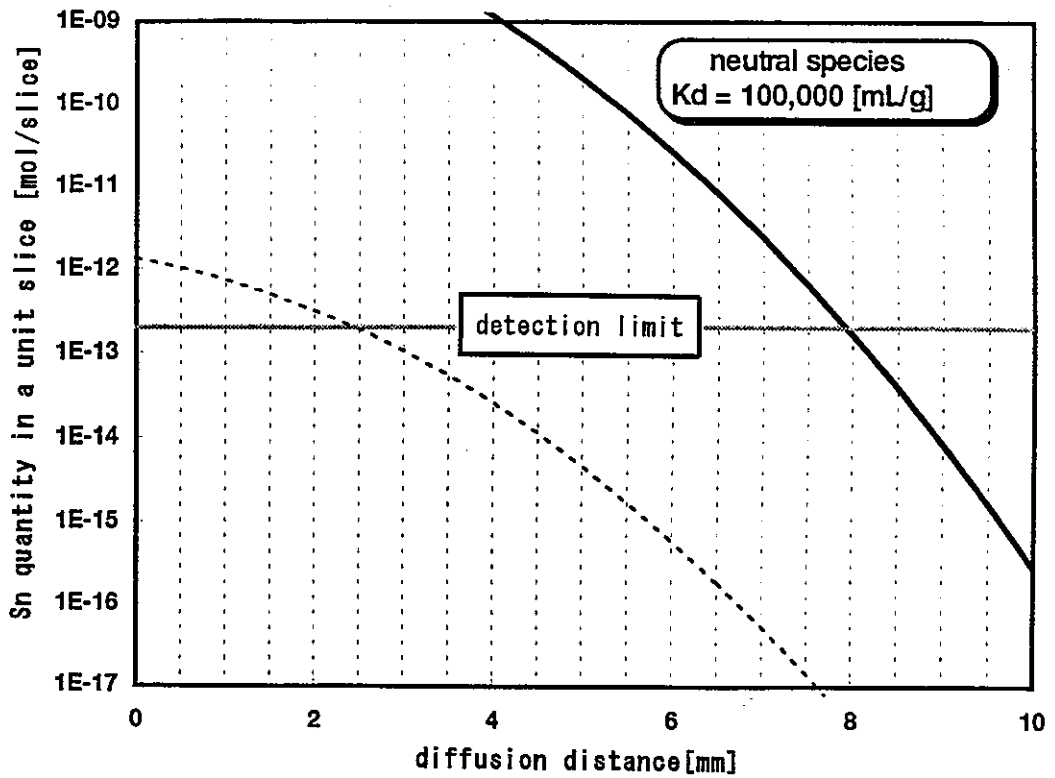


Fig.6-1 Prediction of Sn distribution after 1 year. (neutral species)  
(dry density 0.4[g/cm<sup>3</sup>], effective diffusion coefficient 5.8E-2[m<sup>2</sup>/y])

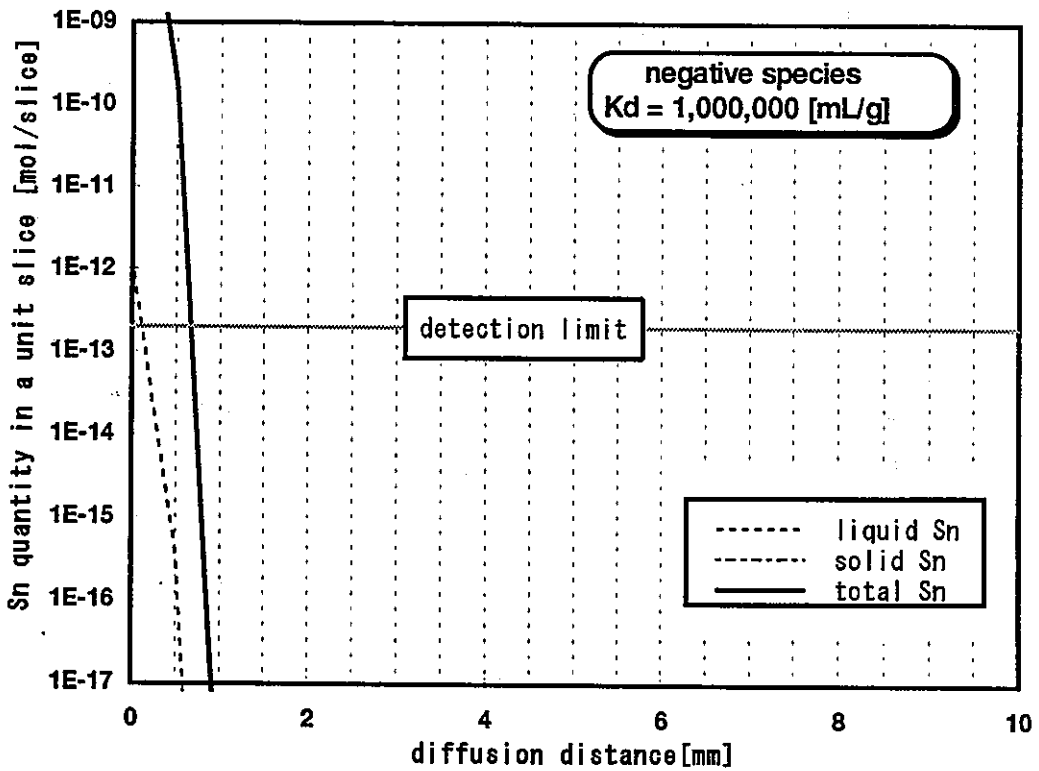
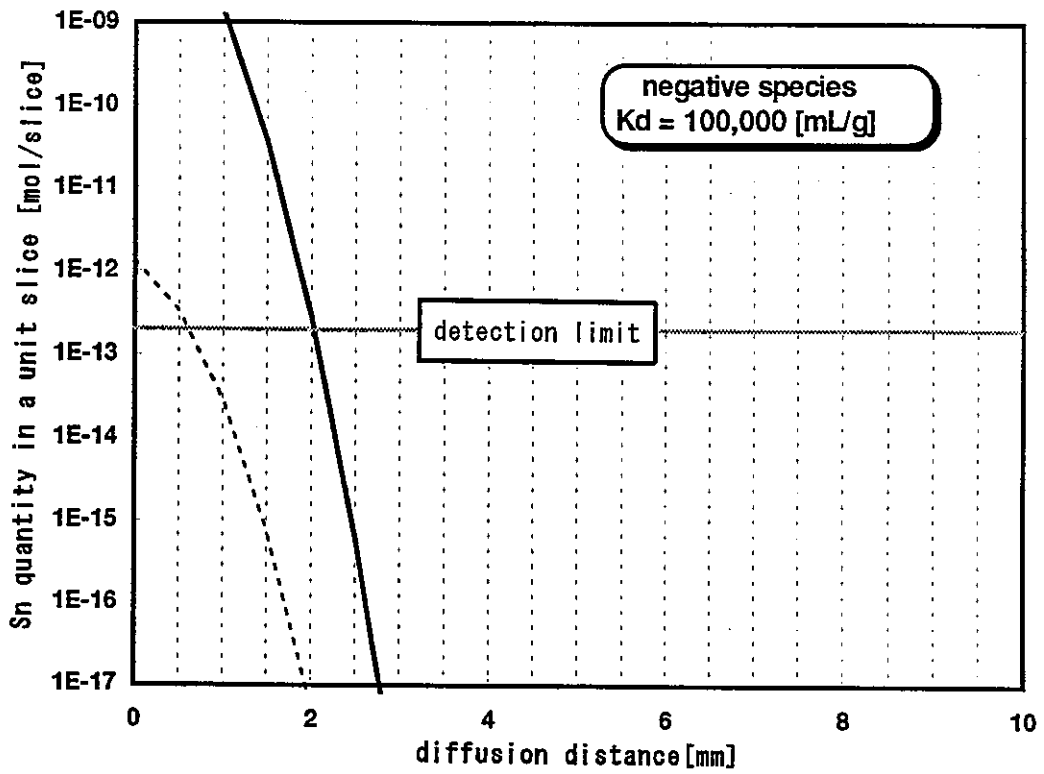


Fig. 6-2 Prediction of Sn distribution after 1 year. (negative species)  
(dry density 0.4[g/cm<sup>3</sup>], effective diffusion coefficient 3.8E-3[m<sup>2</sup>/y])

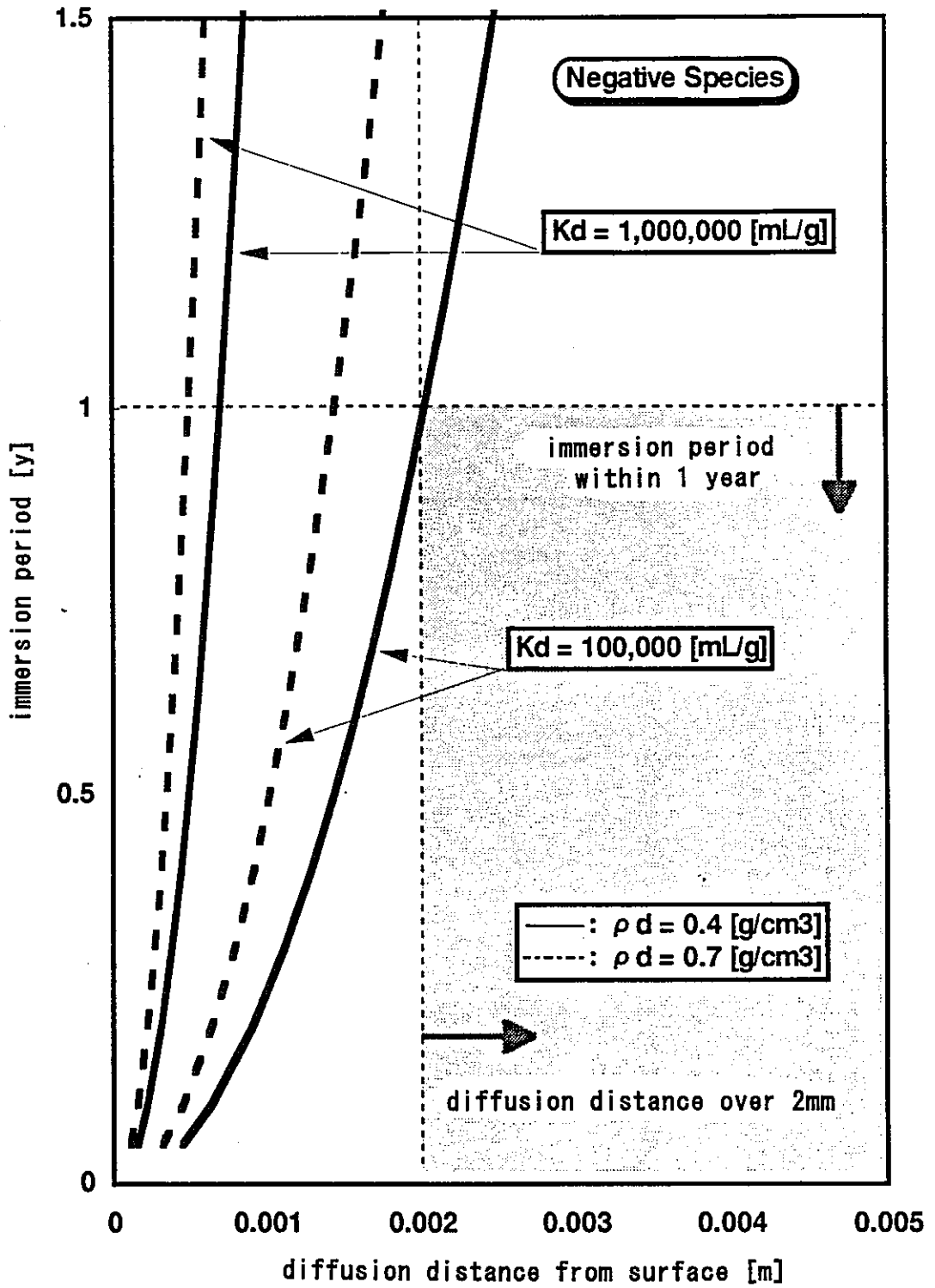


Fig. 6-3 Detection limit map(negative species)

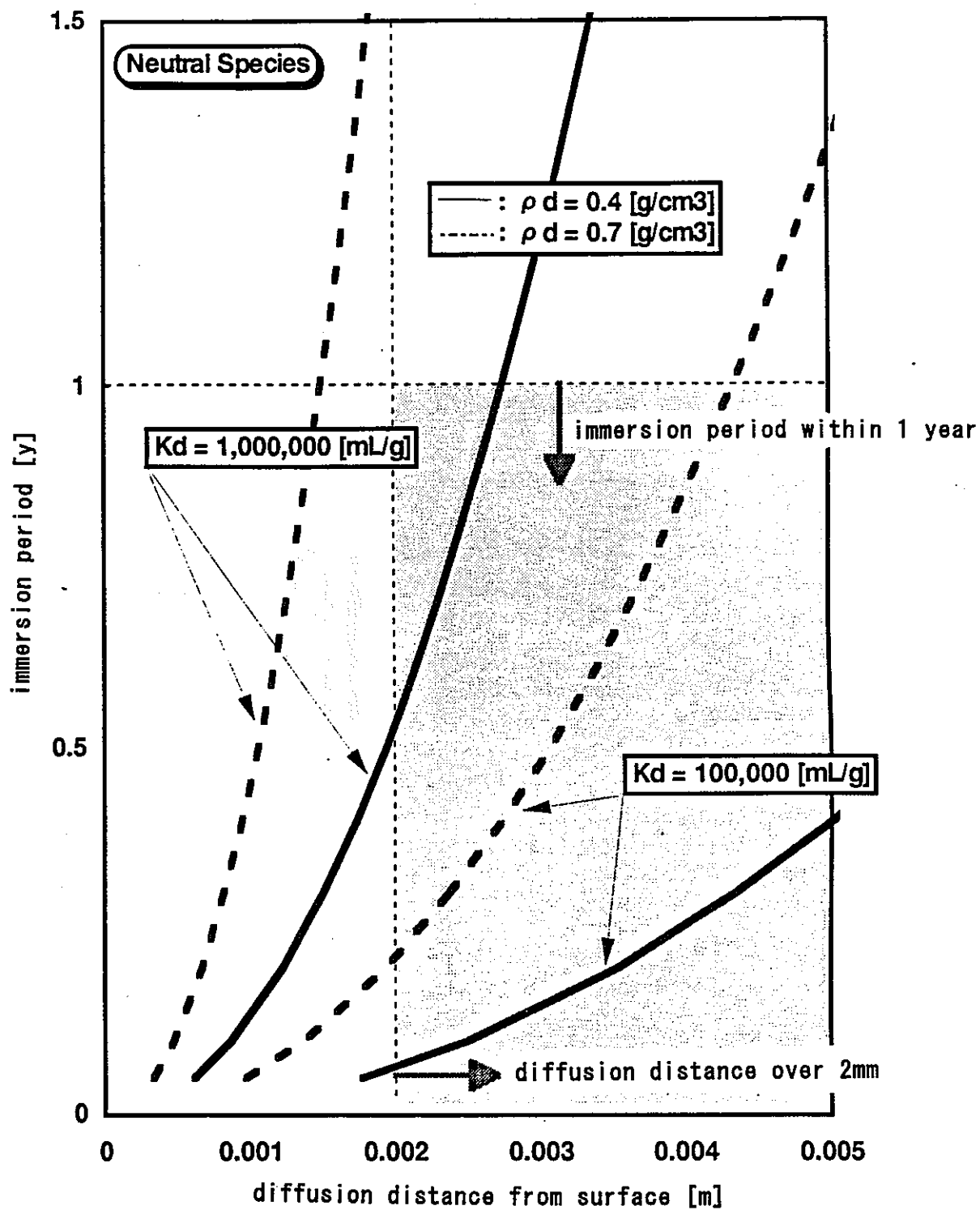


Fig. 6-4 Detection limit map (neutral species)

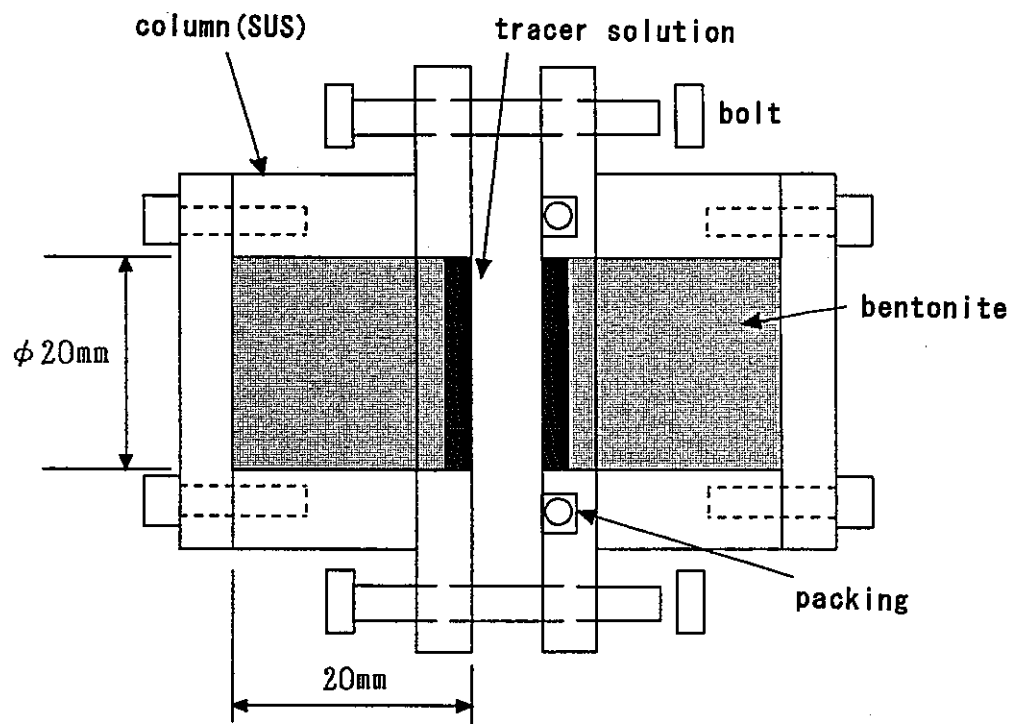


Fig. 6-5 Column instrument for diffusion test.

## 7. Conclusion

(1) Prediction of Sn aqueous species and acquisition of thermodynamic data

① Solubility of Sn

- 0.1M NaClO<sub>4</sub> solution :  $5 \times 10^{-8}$  mol/l (pH7)  $\sim$   $5 \times 10^{-5}$  mol/l (pH10.5)
- bentonite-equilibrated solution : Immersion period was not long enough, solubility data at pH6 was large.

② Increase of solubility in high pH range suggests the presence of Sn(OH)<sub>6</sub><sup>-</sup> and Sn(OH)<sub>6</sub><sup>2-</sup>.

③ As thermodynamic data, following values were obtained.

$$\log K_{a,m} = \log [\text{Sn(OH)}_4^0] = -7.46$$

$$\log K_5 = \log \frac{[\text{Sn(OH)}_6^-][\text{H}^+]}{[\text{Sn(OH)}_4^0]} = -7.65$$

$$\log K_6 = \log \frac{[\text{Sn(OH)}_6^{2-}][\text{H}^+]^2}{[\text{Sn(OH)}_4^0]} = -17.31$$

(I = 0)

(2) Acquisition of Sn distribution coefficients onto bentonite, pure montmorillonite and  $\alpha$ -FeO(OH)

	pH6	pH9	pH11
$\alpha$ -FeO(OH)	$2 \times 10^6$	$3 \sim 6 \times 10^6$	$5 \sim 7 \times 10^5$
bentonite	$3 \sim 4 \times 10^5$	$1 \sim 2 \times 10^5$	$3 \times 10^4$
pure montmorillonite	$> 2 \times 10^7$	$1 \times 10^4$	$3 \times 10^3$

- It is suggested that adsorption reaction could be a surface complex reaction or others.

(3) Sequential extraction test

Sn adsorption onto each solid phase was estimated.

	$\alpha$ -FeO(OH)	bentonite	pure montmorillonite
reversible adsorption	10%	30%	65%
weak adsorption	60%	50%	20%
strong adsorption	30%	20%	15%

(4) Estimation of dominant Sn sorption mechanism in bentonite.

- ① Sorption mechanism could not be regarded as ion exchange reaction.
- ② It is suggested that sorption mechanism could be regarded as surface complex formation and some irreversible reactions.
- ③ pH dependence of sorption onto montmorillonite is different from that of  $\alpha$ -FeO(OH), therefore sorption mechanisms of them could be different.

(5) Acquisition of apparent diffusion coefficient in compacted bentonite.

Test is ongoing at present.