PNC ZJ1281 97-004

COMMERCIAL PROPRIETARY

Study Both for Migration in Heterogeneous Permeability／Sorption Field and for Behavior of FP Migration in Near-Field

－Behavior of FP Migration in Near-Field－

(summary)

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Study Both for Migration in Heterogeneous Permeability/Sorption Field and for Behavior of FP Migration in Near-Field.

Vol. II Behavior of FP Migration in Near-Field

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Abstract

It is very important to explain the sorption mechanisms of relevant radionuclides, for the performance assessment of geological disposal and for the technical development of engineering barrier system.

In the previous studies 1993-1996, these tests were carried out to understand sorption mechanism of Sn;

- solubility tests
- sorption tests onto bentonite, pure montmorillonite, α-FeO(OH)
- extraction tests from these minerals
- sorption tests onto tuff

As a next step, these tests were carried out regarding Sn in this study;

- diffusion tests(in-diffusion)
- tests for effect of Sn concentration and ionic strength on sorption
- sorption tests onto granite
- tests for effect of coexistent ions on solubility

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* Work performed by JGC corporation under contract with Power Reactor and Nuclear Fuel Development Corporation

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APPENDIX Under-Saturated Solubility Test of Amorphous Sn

TABLES

FIGURES

1. Introduction

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

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

In 1993, sorption mechanism onto α-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, experimental study and analysis on bentonite was carried out.

In 1996, solubility test in reducing condition and sorption test onto tuff were carried out.

In 1997, as a new step, experimental study for effect of Sn concentration and ionic strength on sorption and sorption test onto granite were carried out.

2. Items of study

(1)Diffusion Test of Sn within Bentonite using In-Diffusion Method

Da has been acquired by diffusion test of Sn within the bentonite of dried density 0.4g/cm^3, by using In-Diffusion method.
In addition, an analysis has been performed on the diffusion behavior of Sn within the compacted bentonite of dried density 1.8g/cm^3.

(2)Test for Influence of Sn Concentration and Ionic Strength upon Sn Sorption and Modeling of Adsorption Behavior

In the purpose of constructing an analytical model and acquiring data to be used for confirmation of the model,adsorption data have been acquired with parameters of ionic strength and Sn concentration.
Suitable modeling of the adsorption onto bentonite has been studied ,basing on results of Sn adsorption test acquired through former study.

(3)Sn Sorption Test onto Rock

Distribution coefficient has been acquired through tests of sorption onto granite.

(4)Test for Influence of Coexisting Ions upon Sn Solubility

While solubility tests up to the end of 1995 have been performed under non reducing condition, those of 1996 have been performed under reducing condition. Studies performed in 1997 are performed as complementing tests on Sn solubility, following to the test results acquired up to the end of 1996.

3.Diffusion Test of Sn within Bentonite using In-Diffusion Method

3.1 Test Condition

Dried density of sample bentonite was 0.4g/m^3 and diffusion period was6,9,12 months. Number of samples was 6 (2 samples for 3 periods).

3.2 Test Method

3.2.1 Spread Sn solution

As boundary condition, it was assumed that Sn concentration of column surface was constant in spite of diffusion. Data of spread Sn solution was shown in Table 3-1.

3.2.2 Test Procedure

The column apparatus used in this test is shown in Fig.3-1.

Dried bentonite was filled in the column and saturated with deaerated water for 4 months. After the saturation of water, Sn solution containing ^{113}Sn was spread onto the surface of bentonite, and the Sn spread sides of two bentonite columns were connected to assemble the column system, and in-diffusion tests were carried out in room temperature. After diffusion period, each 0.2mm thickness of bentonite was sliced and Sn concentration of each slice was calculated.

This test was carried out within Ar-base glove box(Ar:99.999%, O_2<1ppm, CO_2< 1ppm).

3.2.3 Analytical Method

Sn concentration in unit weight C_w(mol/g) was calculated using following formula.

$$C_w = \frac{\varepsilon R_f C_0}{\rho'} \operatorname{erfc} \frac{\chi}{2(D_a t)^{1/2}} \qquad \cdots (3-1)$$

ε : porosity[−]
R_f : retardation coefficient
C_0 : Sn concentration on spread surface(mol/l)
ρ' : apparent density of saturated bentonite(g/cm^3)
D_a : apparent diffusion coefficient(m^2/sec)
χ : diffusion distance(m)
t : elapsed time(sec)

Apparent diffusion coefficient(D_a) was obtained by fitting formula(3-1) to diffusion profile.

3.3 Results

Diffusion profiles were shown in Fig.3-2~Fig.3-7. The rapid decrease of Sn concentration from surface to 0.2cm was interpreted as infiltration of Sn solution and the profile from 0.2cm was interpreted as Sn diffusion. According to the assumption that diffusion phenomena started from 0.2cm point, apparent diffusion coefficients were calculated by fitting of formula (3-1).

Obtained apparent diffusion coefficients for each periods were, 4×10^{-13}m^2/s(6 months), 3×10^{-13}m^2/s(9months), 2×10^{-13}m^2/s(12months), respectively. Change of values due to change of periods was within the range of error.

3.4 Discussion

Calculated Kd from apparent diffusion coefficient(4×10^{-13}m^2/s) was 10^1~10^2ml/g. However, Kd value obtained by batch test in 1995 study was 10^5ml/g at around pH9, and larger than calculated value from diffusion test by 3 order. It was considered that eluted component from bentonite might influence.

3.5 Diffusion Analysis

Sn diffusion profiles within bentonite(dried density 0.4g/cm^3(this study) and 1.8g/cm^3) were analyzed using the same method in 'Study for sorption mechanism of radioactive nuclides in deep underground condition (Ⅲ)'.

Analysis conditions were as follows. Based upon solubility experiments in the previous work, both neutral and negative species were assumed as aqueous species of Sn(Ⅳ).

·Dried Density	0.4, 1.8 [g/cm^3]
·Kd	10, 100, 1000, 10000 [ml/g]
·Diffusion Period	6, 9, 12 [months]

·Effective Diffusion coefficients

	(neutral species)	(negative species)
(ρ=0.4g/cm^3)	1.83E-09 [m^2/s]	1.20E-10 [m^2/s]
(ρ=1.8g/cm^3)	7.60E-11 [m^2/s]	9.30E-12 [m^2/s]

Diffusion profiles of negative species with Kd=10, 100, which are relevant to experimental conditions of diffusion test, were shown in Fig.3-8 and Fig.3-9. From these figures, it was suggested that the difference of diffusion profile within bentonite of two dried density became explicit as Kd increased.

3.6 Conclusion

①Obtained apparent diffusion coefficients were $2\sim4\times10^{-13}$m^2/s.

②No significant changes ware observed due to diffusion period change(6, 9, 12 months) in diffusion profile.

③The possibility that pH value of bentonite pore water was below 10.6 was suggested.

④It was suggested that eluted component from bentonite decreased sorption/desorption property of Sn onto bentonite.

⑤Results of analysis showed that difference of diffusion behavior due to dried density became explicit as Kd increased.

Table 3-1 Spread Sn Solution

		data
spread Sn solution	Sn Concentration (mol/l)	5.0×10^{-2}
	pH	pH13[*1]
	Specific Activity (Bq/mol)	1.5×10^{11}
	Total Activity(Bq) (Activity of each sample)	1.4×10^{6} (2.3×10^{5})
Spread Sn Quantity of each Sample(mol)		1.5×10^{-6}
Spread Quantity of each Sample (μ l)		31 [*2]

*1 estimated value

*2 Spread Sn quantity(μ l/sample) $= \dfrac{\text{spiked Sn quantity(mol/sample)}}{\text{Sn concentration(mol/l)}}$

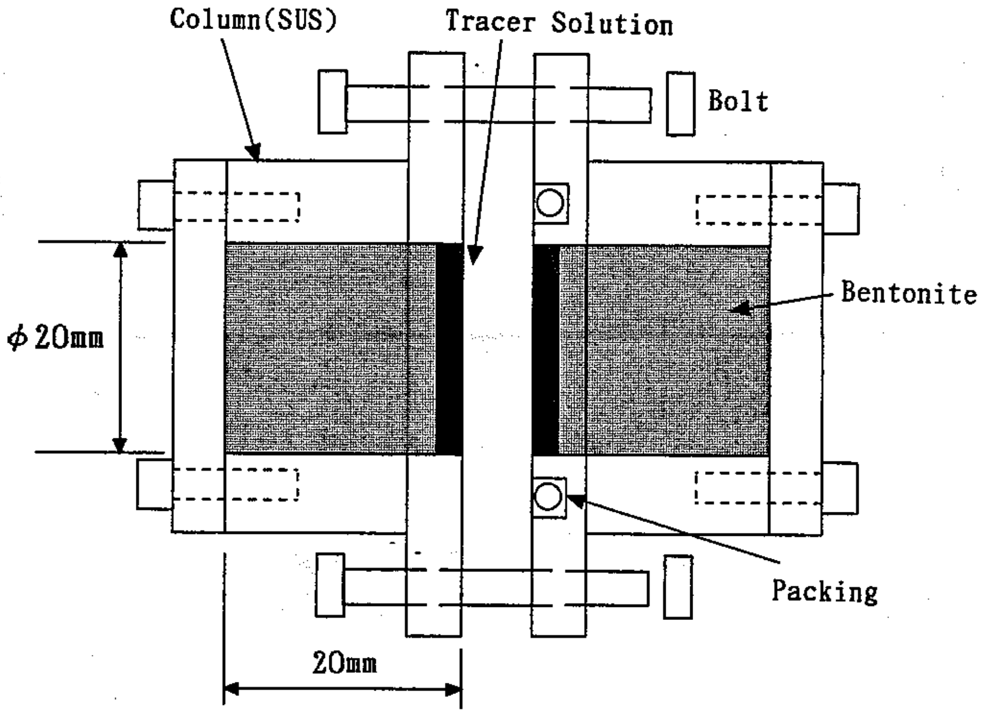


Fig. 3-1 Column Apparatus for Diffusion Test

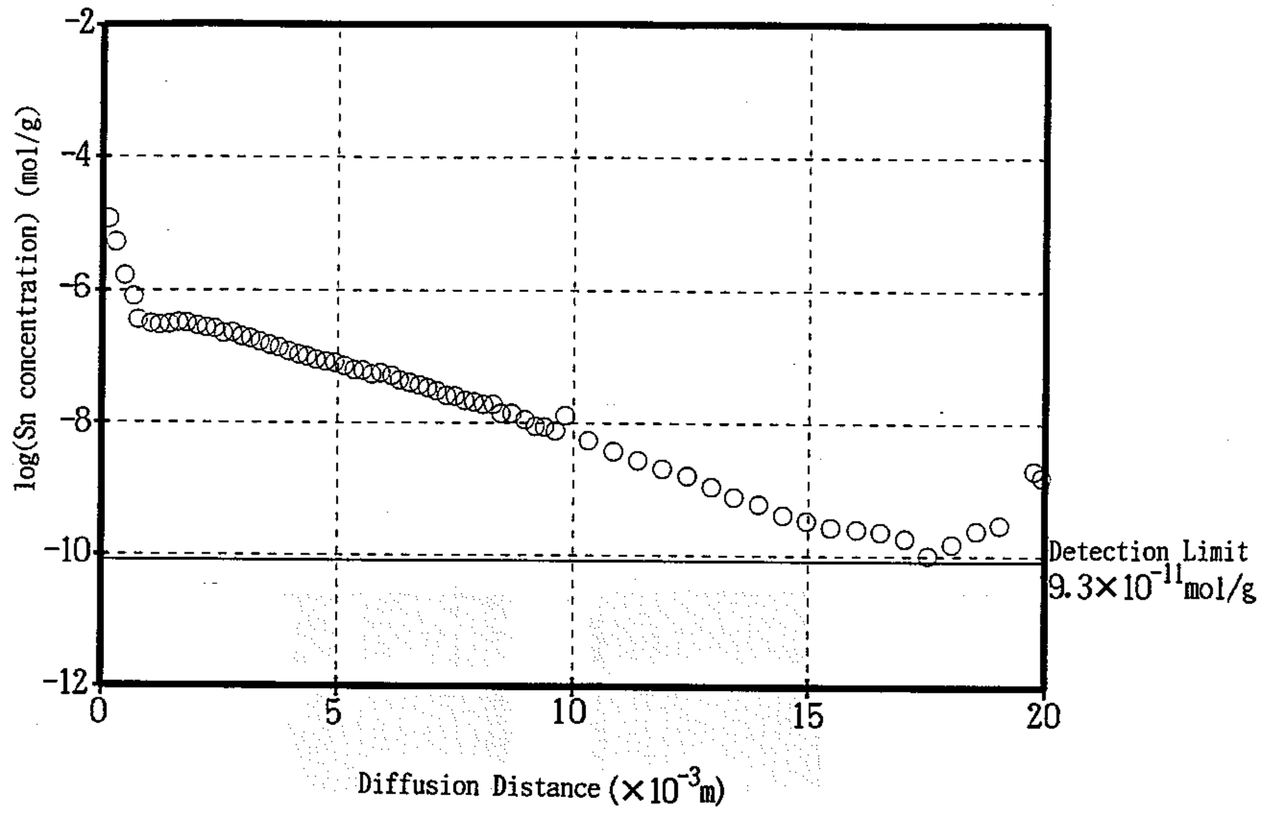


Fig. 3-2 Diffusion Profile(sample 6M-1)
(diffusion period=6months)

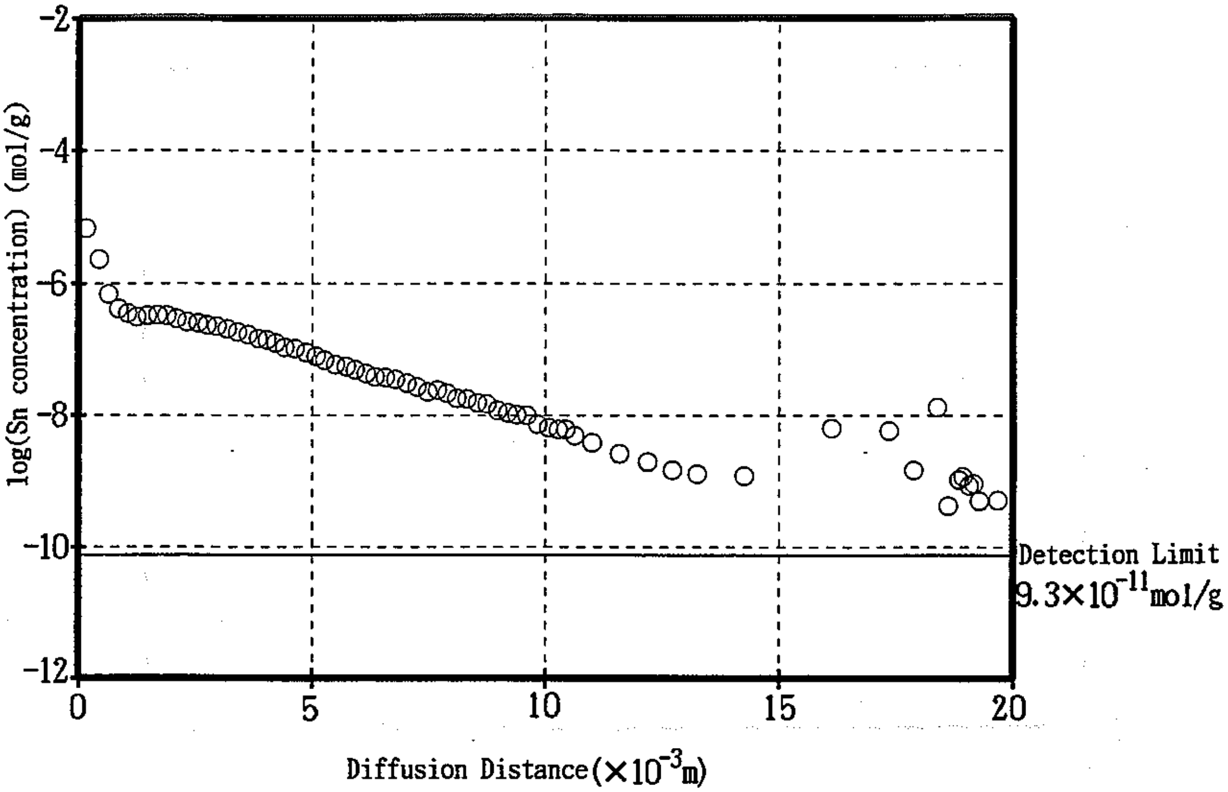


Fig. 3-3 Diffusion Profile(sample 6M-2)
(diffusion period=6months)

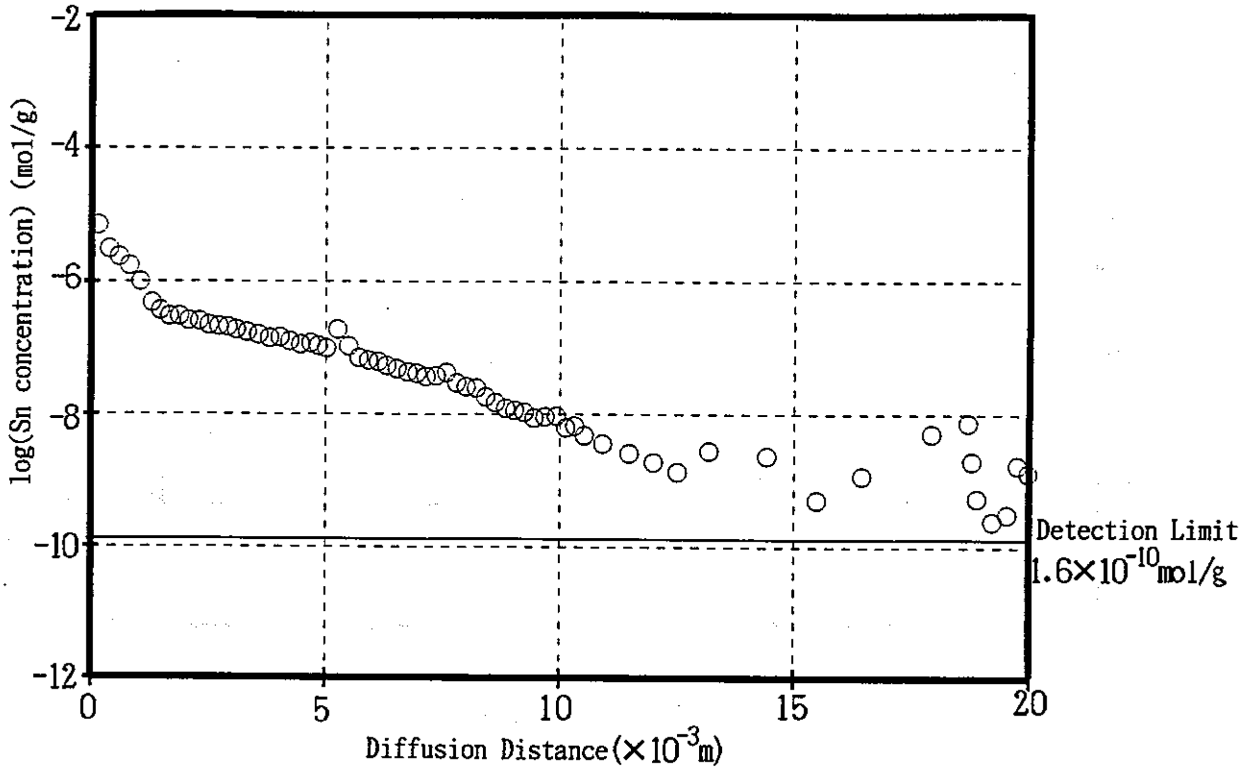


Fig. 3-4 Diffusion Profile(sample 9M-1)
(diffusion period=9months)

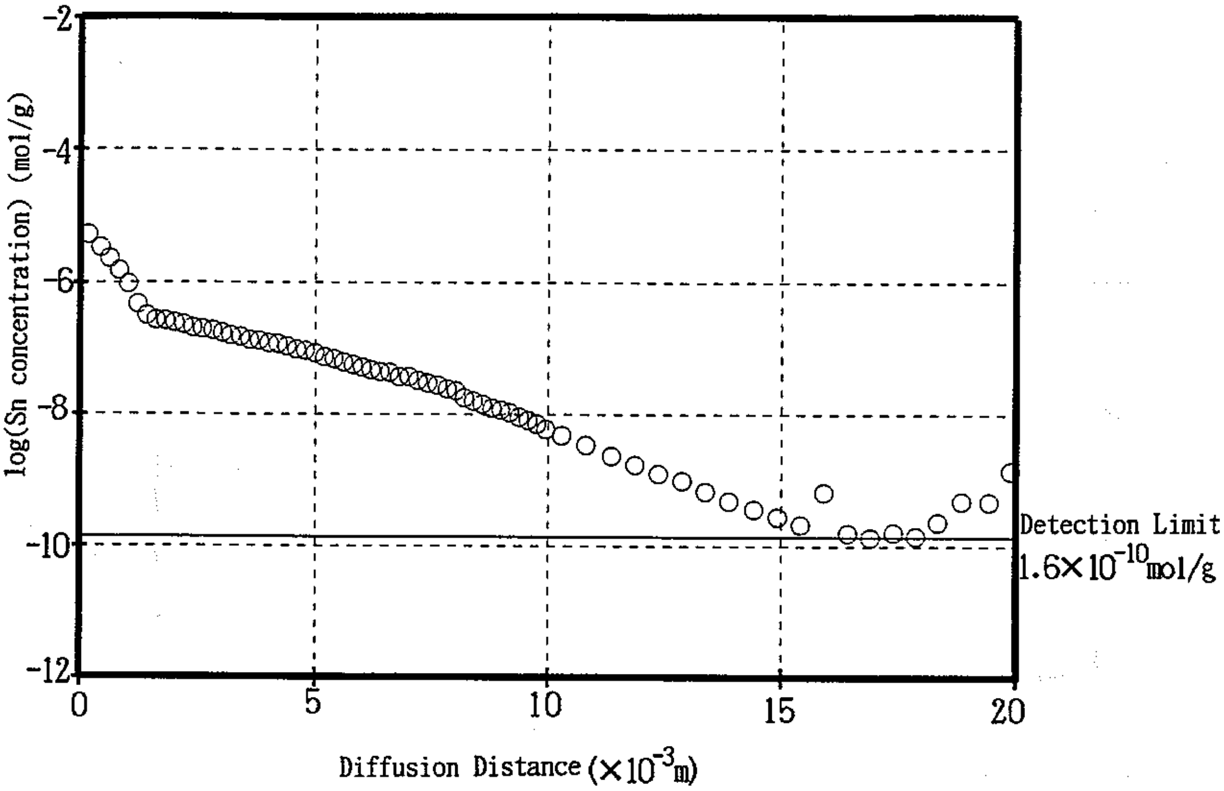


Fig. 3-5 Diffusion Profile(sample 9M-2)
(diffusion period=9months)

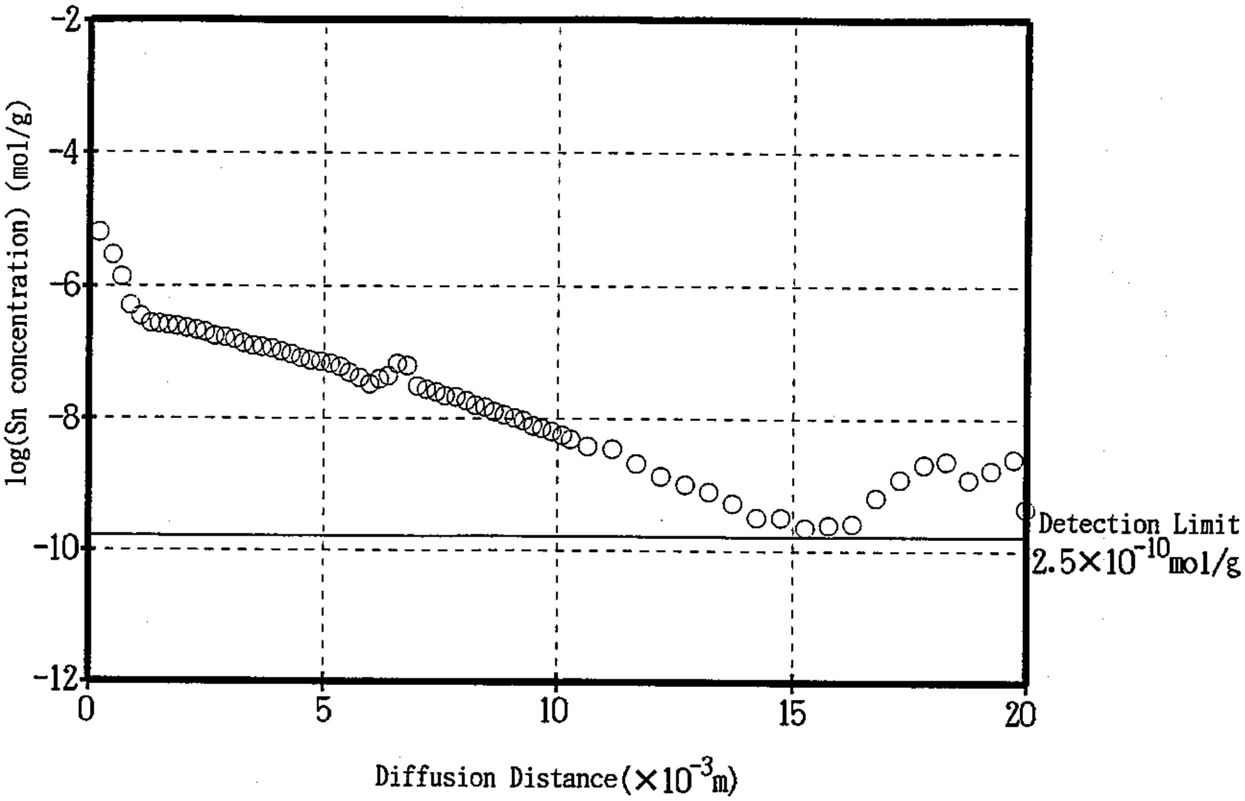


Fig. 3-6 Diffusion Profile(sample 12M-1)
(diffusion period=12months)

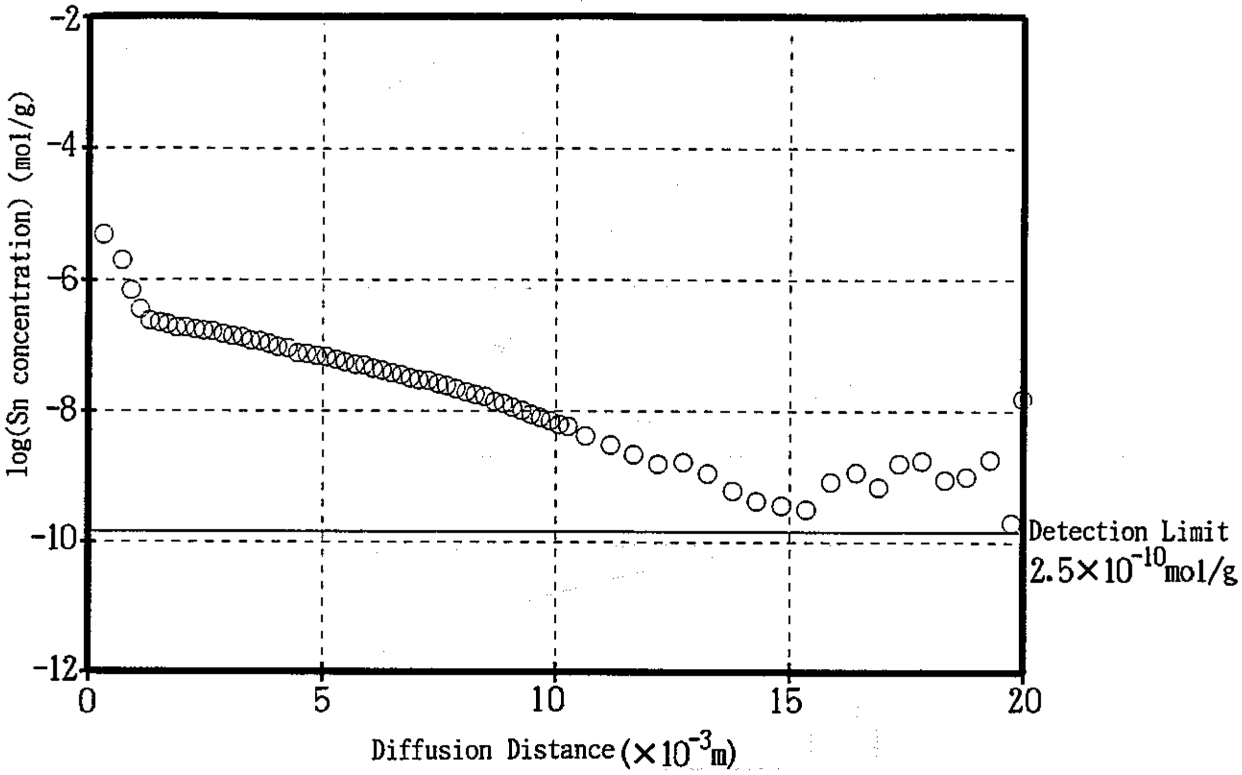
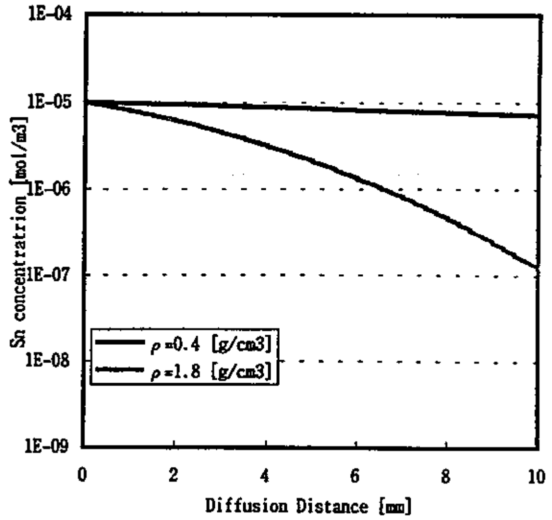
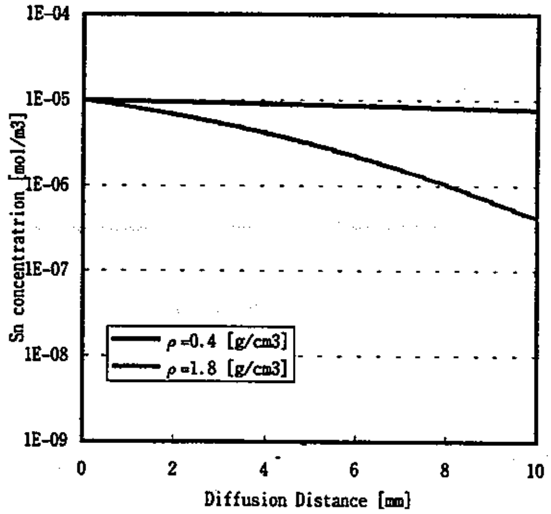


Fig. 3-7 Diffusion Profile(sample 12M-2)
(diffusion period=12months)

Kd = 10mL/g、6months



Kd = 10mL/g、9months



Kd = 10mL/g、12months

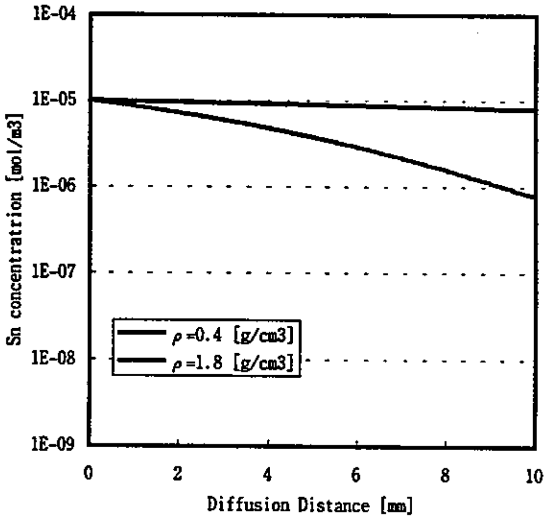
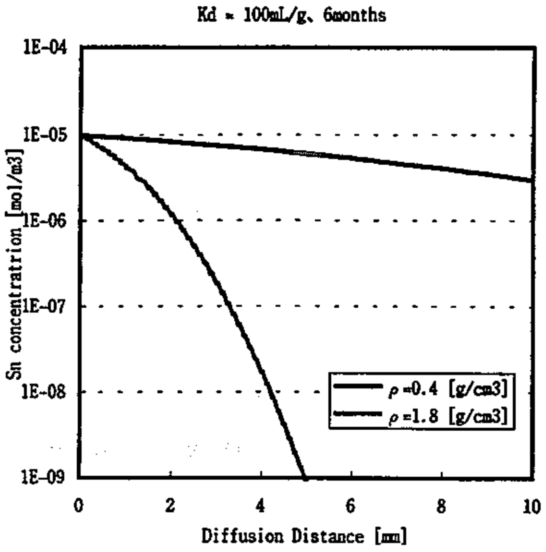
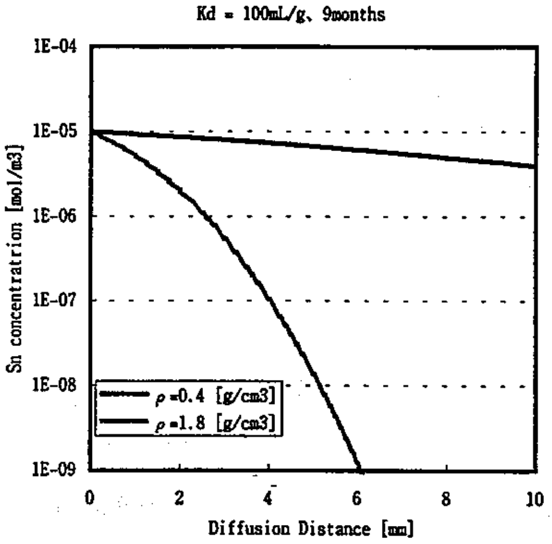


Fig.3-8 Diffusion Profile (negative species, Kd=10mL/g)





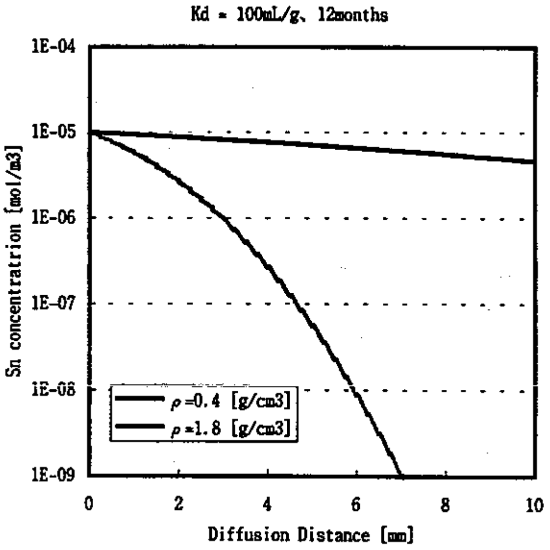


Fig.3-9 Diffusion Distance (negative species, Kd=100mL/g)

4. Test for Influence of Sn Concentration and Ionic Strength upon Sn Sorption and Modelling of Sorption Behavior

4.1 Test Condition

Test condition is shown in Table 4-1. Following to sorption test onto bentonite carried out in 1995, sorption tests were carried out in order to compare the sorption behavior when following conditions were changed.

①reducing and non-reducing environment(comparison of Condition1 and Condition2)

②ionic strength(equilibrated solution of 0.1M NaCl and 0.01M NaCl, comparison of Condition2 and Condition4)

③Sn concentration(~1×10^{-6}mol/l and 7×10^{-9}mol/l, comparison of Condition3 and Condition4)

This test was carried out within Ar base glove box(Ar:99.999%, O_2<1ppm, CO_2<1ppm).

4.2 Test Method

4.2.1 Test Procedure

(1)Conditioning of bentonite-equilibrated solution

Bentonite was contacted to 0.1M NaCl or 0.01M NaCl solution at a liquid/solid ratio 10000ml/g using deaerated water. In case of reducing condition, 1M $Na_2S_2O_4$ was spiked into solution and Eh was adjusted to below -300mV.

In order to adjust pH, HCl and NaOH was spiked into solution and immersed 1month in room temperature. After 1month, solution was filtered using 10000MWCO filter and the filtrate was used as bentonite-equilibrated solution.

(2)Sorption test procedure

10mg of bentonite was mixed into 100ml of bentonite-equilibrated solution and immersed for 1month. Then Sn stock solution containing ^{113}Sn was spiked into solution in order to adjust Sn concentration and pH was adjusted using HCl and NaOH. In case of reducing condition, $Na_2S_2O_4$ was spiked in order to adjust Eh below -300mV.

4.2.2 Calculation of distribution coefficients

Distribution coefficients(Kd) of bentonite were calculated using following formula.

$$Kd = \frac{(C_0 - C_1)}{C_1} \times \frac{V}{M} \quad [ml/g]$$

Kd:Distribution coefficient(ml/g)
M:Dried weight of bentonite(g)
V:Volume of bentonite-equilibrated solution(ml)
C_0:Initial radioactive concentration in solution(cpm/ml)
C_1:Radioactive concentration in solution after solid-liquid separation(cpm/ml)

4.3 Results

Kd values of bentonite(containing 1995 study) were shown in Table 4-2. pH dependence of Kd was shown in Fig.4-1.

(1)Comparison of environment(reducing and non-reducing)

In Table 4-2, Kd values of Condition1 and Condition2 were compared. Under both reducing and non-reducing environment, Kd values were almost the same and pH dependence of Kd was similar. No significant difference of Kd due to difference of environment was detected.

(2)Comparison of ionic strength(0.1M NaCl and 0.01M NaCl)

In Table 4-2, Kd values of Condition2 and Condition4 were compared. At pH6, Kd of 0.1M NaCl was larger by 1 order. At pH9, Kd of both 0.1M NaCl and 0.01M NaCl were almost the same. At pH11, Kd of 0.1M NaCl was smaller, however, the value was almost the same of Condition3(0.01M NaCl). Thus, it was not considered to be the effect of ionic strength.

(3)Comparison of Sn concentration

In Table 4-2, Kd values of Condition3 and Condition4 were compared. Kd value of Condition3(higher Sn concentration) was a little smaller. However, Kd value of Condition3 was the same to that of Condition1 and Condition2 in which Sn concentrations were the same to that of Condition4. Thus, no significant change of Kd due to difference of Sn concentration was detected.

4.4 Conclusion

About sorption behavior of Sn onto bentonite,

①No significant difference of Kd values were detected under reducing and non-reducing condition.

②At low pH(pH6), Kd value was larger when ionic strength was larger.

4.5 Sorption Modelling

Modelling of Sn(Ⅳ) sorption onto FeOOH, montmorillonite and bentonite was attempted based on the sorption test results onto those solids.

For FeOOH, surface complexation onto solid surface was regarded as sorption process. For montmorillonite, surface complexation onto two edge site was regarded as sorption process. For bentonite, as a first step, sorption onto bentonite was interpreted as combination of that onto montmorillonite and FeOOH, assuming that sorption onto 50% of montmorillonite and that onto a few % of FeOOH.

All analysis were carried out with both Diffuse Layer Model(DLM) and Triple Layer Model(TLM). For all solids, these sorptive species of Sn(Ⅳ) was assumed,

$$SOH + Sn^{4+} + 4H_2O = SOH\text{-}Sn(OH)_4 + 4H^+$$

$$SOH + Sn^{4+} + 5H_2O = SOH_2\text{-}Sn(OH)_5 + 4H^+$$

SOH : sorption site on solid surface

Results were shown in Fig.4-2(DLM) and Fig.4-3(TLM). From this analysis, following conclusions were suggested.

·Sn(Ⅳ) sorption onto FeOOH was well explained by surface complexation with FeOOH surface.

·Sn(Ⅳ) sorption onto montmorillonite was could be explained by surface complexation with edge site of montmorillonite. However, further discussion should be necessary, regarding characteristics of montmorillonite surface and modification of modelling approach consistent with them.

- It was suggested that other sorption site(not FeOOH) than montmorillonite contributed within Sn(Ⅳ) sorption onto bentonite.

Table 4-1 Test Condition

	Test Condition			1995 Test Condition (reference)
	Condition1	Condition2	Condition3	Condition4
Solid Phase	Bentonite (Kunigel V1)			Bentonite (Kunigel V1)
Liquid Phase	0.1M NaCl equilibrated solution	0.1M NaCl equilibrated solution	0.01M NaCl equilibrated solution	0.01M NaCl equilibrated solution
Liquid/Solid Ratio	10000ml/g			10000ml/g
Spiked Sn Concentration (6M HCl)	9×10^{-9}mol/l	9×10^{-9}mol/l	1×10^{-6}mol/l	7×10^{-9}mol/l
pH	6、9、11	6、9、11	11	6、9、11
Environment	Reducing Environment	Non-Reducing Environment	Non-Reducing Environment	Non-Reducing Environment
Immersion Period	1 month			2 months
Reproducibility	2			2
Number of Samples	6	6	2	6

Table 4-2 Summary of Kd for Bentonite

		1997 Study							1995 Study		
		Condition1			Condition2			Condition3	Condition4		
Liquid Phase		0.1M NaCl + Bentonite-equilibrated Solution						0.01M NaCl + Bentonite-equilibrated solution	0.01M NaCl + Bentonite-equilibrated solution		
Environment		Reducing Environment			Non-Reducing Environment				Non-Reducing Environment		
Ionic Strength		~0.12			~0.11			~0.03	~0.03		
Spiked Sn Concentration		9×10^{-9}			9×10^{-9}			1×10^{-8}	$\sim7\times10^{-9}$		
pH		6	9	11	6	9	11	11	6	9	11
Kd (ml/g)	Reproducibility 1	7×10^{5}	1×10^{6}	7×10^{3}	2×10^{6}	2×10^{5}	9×10^{3}	7×10^{3}	4×10^{5}	2×10^{5}	3×10^{4}
	2	1×10^{6}	1×10^{5}	1×10^{4}	3×10^{6}	3×10^{5}	6×10^{3}	7×10^{3}	3×10^{5}	1×10^{5}	3×10^{4}

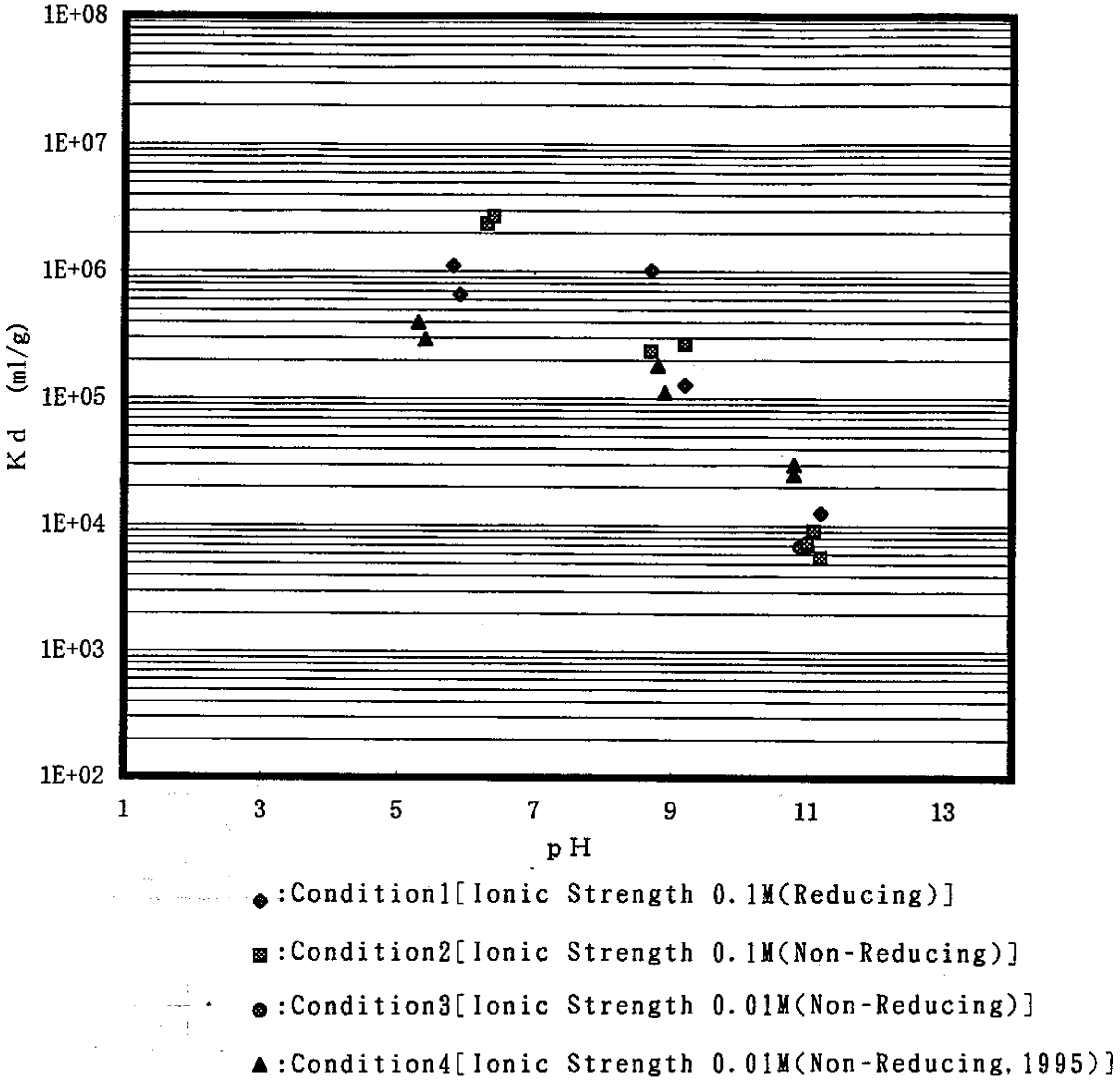


Fig.4-1 pH Dependence of Kd

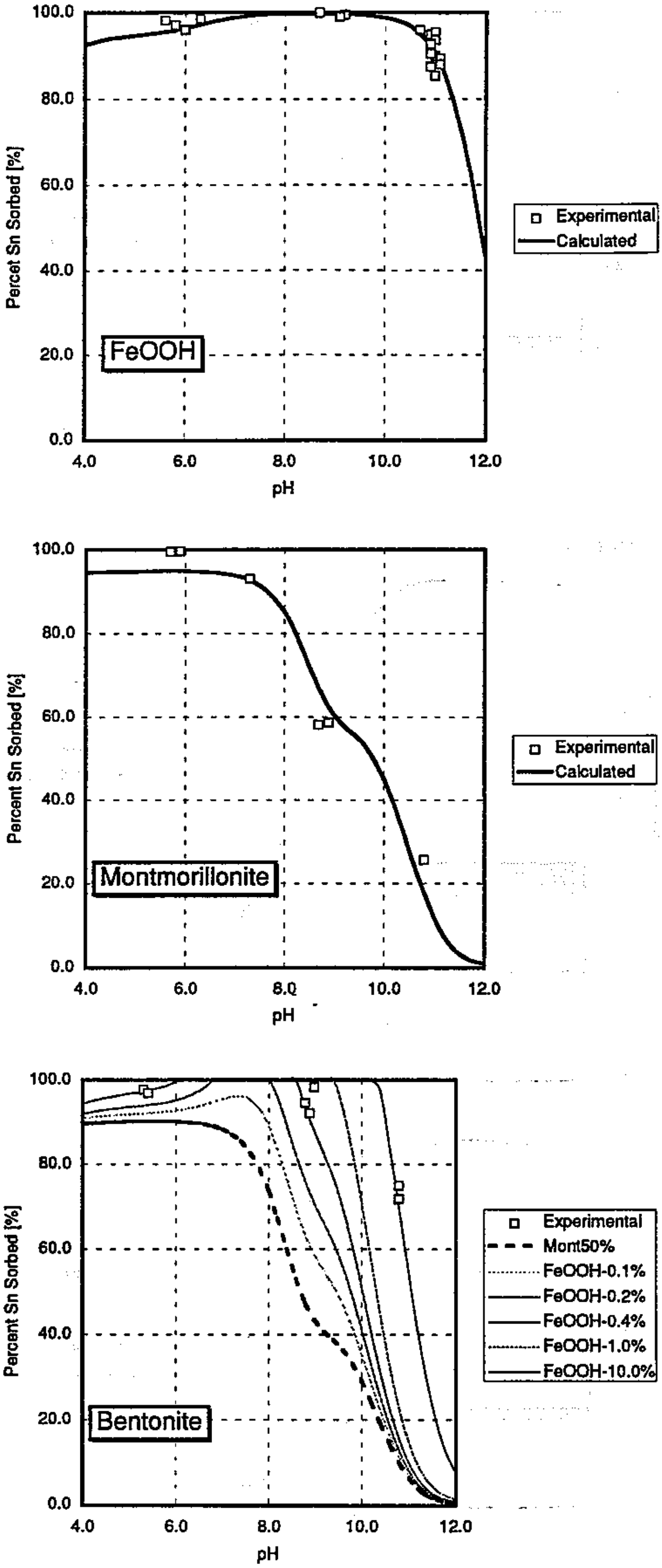


Fig. 4-2 Sn Adsorption onto Solids (DLM)

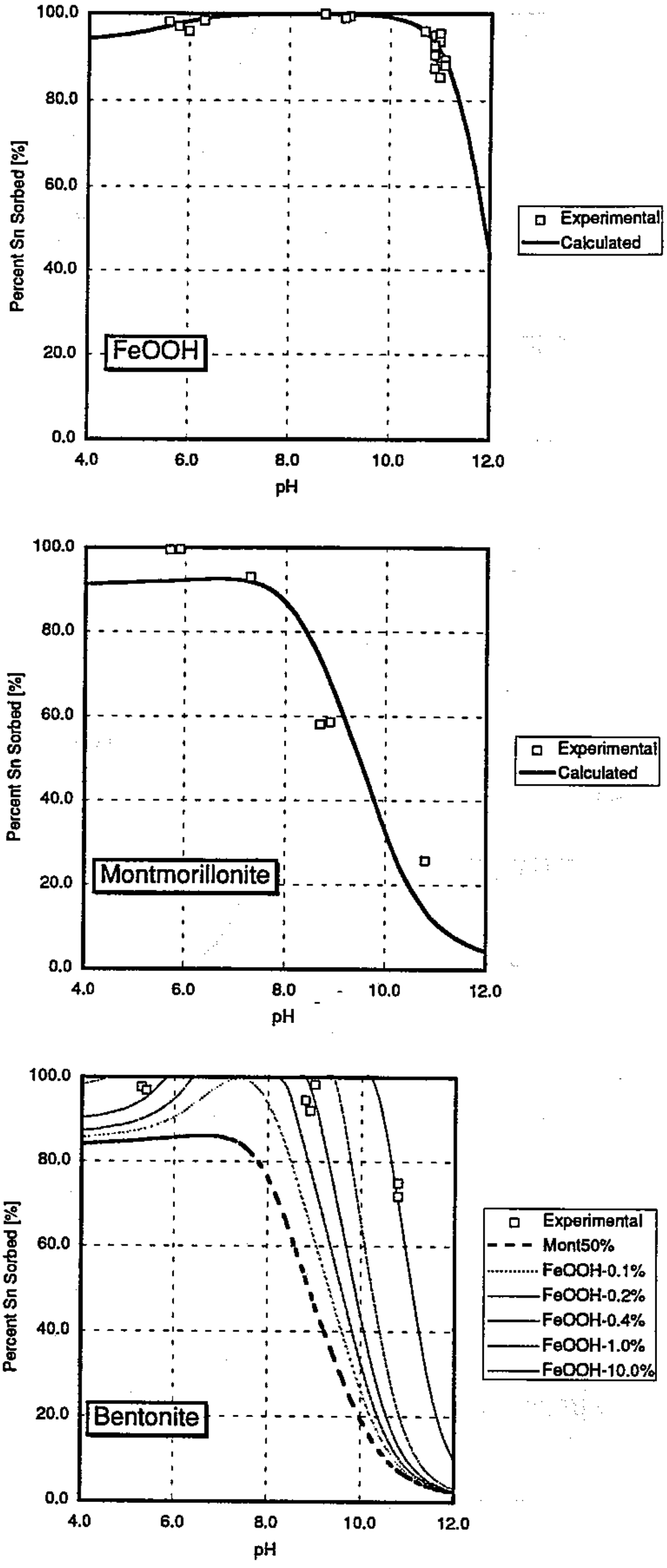


Fig. 4-3 Sn Adsorption onto Solids (TLM)

5. Sn Sorption Test onto Rock

5.1 Test Condition

Test condition was shown in Table 5-1. The rock used in this test was granite.

5.2 Test Method

5.2.1 Test Procedure

(1) Conditioning of granite-equilibrated solution

Granite was contacted to 0.1M NaCl solution at a liquid/solid ratio 10000ml/g using deaerated water. 1M $Na_2S_2O_4$ solution was spiked into this solution and Eh was adjusted to below -300mV. pH of the solution was adjusted using HCl and NaOH. After 1month immersion, the solution was filtered using 10000MWCO filter and the filtrate was used as granite-equilibrated solution.

(2) Sorption test procedure

10mg of granite was mixed into 100ml of granite-equilibrated solution, and immersed for 1month in room temperature. Then Sn stock solution containing ^{113}Sn was spiked into solution in order to adjust Sn concentration and Eh was measured to confirm that Eh value was below -300mV. pH was adjusted using HCl and NaOH.

All procedures until solid-liquid separation were carried out within low-oxygen glove box.

5.2.2 Calculation of distribution coefficients

Distribution coefficients(Kd) of rock was calculated using following formula.

$$Kd = \frac{(C_0 - C_1)}{C_1} \times \frac{V}{M} \quad [ml/g]$$

Kd: Distribution coefficient(ml/g)

M : Dried weight of rock(g)

V : Volume of rock-equilibrated solution(ml)

C_0: Initial radioactive concentration in solution(cpm/ml)

C_1: Radioactive concentration in solution after solid-liquid separation(cpm/ml)

5.3 Results

Table 5-2 shows test results. Obtained Kd showed the tendency to fall as pH rose.

5.4 Discussion

pH dependence of Kd was shown in Fig.5-1 with 1995 and 1996 test results and 1997 bentonite test. Kd of granite falls as pH value rises, similar to α-FeO(OH), pure montmorillonite and bentonite.

5.5 Conclusion

①In sorption test onto granite, following Kd values were obtained.

	pH6	pH9	pH11
Kd (ml/g)	$3\sim4\times10^5$	1×10^4	$1\sim2\times10^3$

②Obtained Kd fall as pH rose.

Table 5-1 Test Condition

	Test Condition
Solid Phase	Granite
Liquid Phase	0.1M NaCl Solution (Equilibrated Solution)
Liquid/Solid Ratio	10000ml/g
Spiked Sn Concentration	Below Solubility ($7 \sim 9 \times 10^{-9}$mol/l)
pH	6、9、11
Environment	Reducing Environment
Immersion Period	1 month
Reproducibility	2
Number of Samples	6

Table 5-2 Test Results

Test Conditions									Test Results			
pH	Reproducibility	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	Adjusted Eh (for SHE)	Final pH	Final Eh (for SHE)	Sn concentration (mol/l) (Radioactive conc. cpm/ml)	K d (ml/g)
6	1	35	9.2×10^{-9} (6375±27)	11	99	9000	6.0	-400	6.3	-413	$(3.03\pm0.07)\times10^{-10}$ (211±5)	2.6×10^{5}
6	2		9.1×10^{-9} (6324±27)	11	99	9000	6.0	-343	6.3	-387	$(1.83\pm0.06)\times10^{-10}$ (127±4)	4.4×10^{5}
9	1	35	9.2×10^{-9} (6375±27)	11	99	9000	9.0	-533	9.2	-499	$(4.49\pm0.05)\times10^{-9}$ (3127±29)	9.3×10^{3}
9	2		8.6×10^{-9} (6018±26)	10	99	9900	9.3	-492	9.3	-535	$(4.07\pm0.05)\times10^{-9}$ (2834±28)	1.1×10^{4}
11	1	35	8.3×10^{-9} (5763±24)	10	99	9900	11.0	-585	11.3	-600	$(7.26\pm0.07)\times10^{-9}$ (5054±43)	1.4×10^{3}
11	2		7.5×10^{-9} (5202±22)	10	99	9900	11.0	-605	11.2	-632	$(6.20\pm0.07)\times10^{-9}$ (4312±39)	2.0×10^{3}

*1 Radioactive concentration:Corrected on 1, March, 1996

*2 Temperature:25±3℃

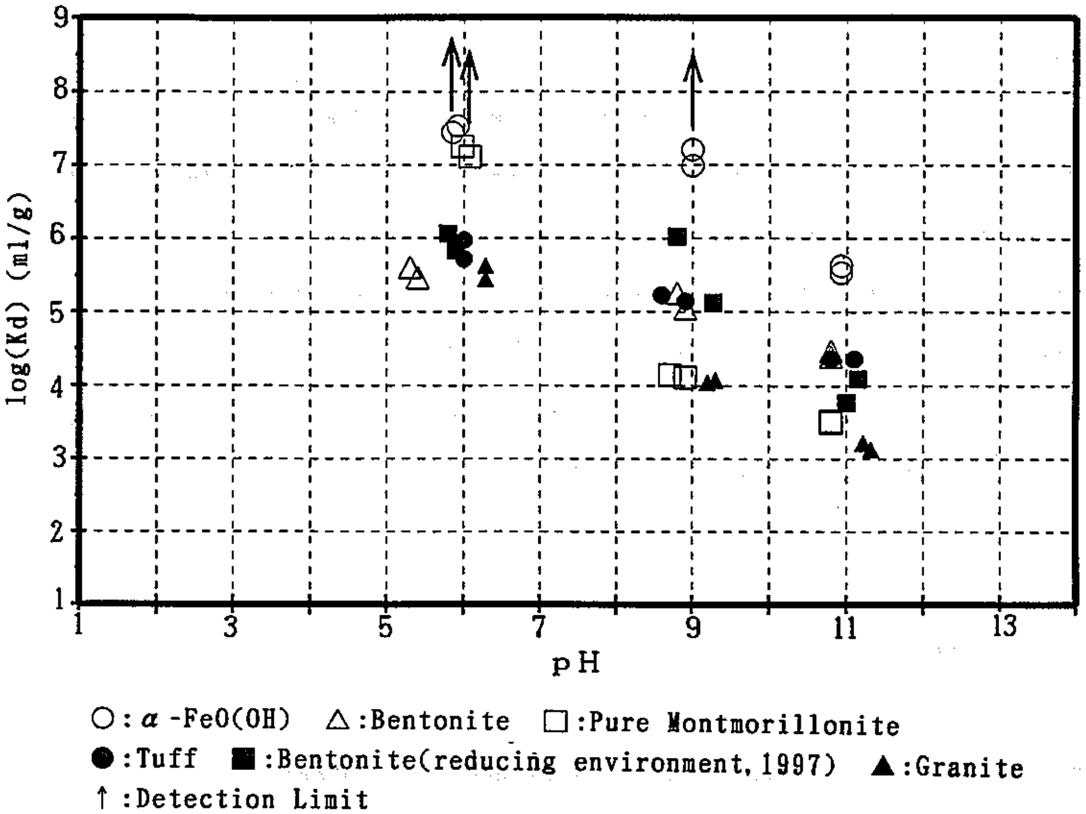


Fig. 5-1 pH Dependence of Kd

6. Test for Influence of Coexisting Ions upon Sn Solubility

6.1 Test Condition

In order to investigate the influence of coexisting ions(SO_4^{2-}, Cl^-) upon Sn solubility(over-saturated condition), solubility tests containing various concentration of those ions were carried out. Test condition is shown in Table 6-1.

6.2 Test Method

Sn stock solution containing ^{113}Sn was spiked into 50ml of Na_2SO_4 or NaCl solution, and initial Sn concentration was adjusted to 1.1×10^{-4}mol/l. The pH of solution was adjusted to pH8 using NaOH, and immersed for 3months in room temperature. After 3months, solution was filtered using 10000MWCO filter, and Sn concentration of filtrate was calculated.

All procedures until solid-liquid separation were carried out within low-oxygen glove box(Ar base: O_2<1ppm, CO_2<1ppm).

6.3 Results

Table 6-2 shows test results.

(1)Influence of SO_4^{2-}

Fig.6-1 shows the influence of SO_4^{2-} ions upon Sn concentration.
No significant change of Sn concentration was shown although SO_4^{2-} concentration changed from 0.001M to 0.1M, in comparison with blank test result(0.4M $NaClO_4$).

(2)Influence of Cl^-

Fig.6-2 shows the influence of Cl^- ions upon Sn concentration.
No significant change of Sn concentration was shown although Cl^- concentration changed from 0.004M to 0.4M, in comparison with blank test result(0.4M $NaClO_4$).

6.4 Discussion

In 1996 study, Sn solubility tests which used rain water originated and seawater originated solution were carried out, and Sn concentration of both solutions were almost the same, then it was suggested that influence of $SO_4{}^{2-}$ or Cl^- was little. The results of this test are in accordance with the result of 1996 test, and it was confirmed that no influence of $SO_4{}^{2-}$ and Cl^- upon Sn concentration existed.

6.5 Conclusion

No influence of coexisting ions($SO_4{}^{2-}$,Cl^-) upon Sn concentration under the condition of pH8, ionic strength 0.4～0.6, over-saturated condition was detected.

Table 6-1 Test Condition

	Test Condition(Over-Saturated Condition)						
Solution	Influence of SO_4^{2-}			Influence of Cl^-			Blank
	0.1M Na_2SO_4	0.01M Na_2SO_4 +0.4M $NaClO_4$	0.001M Na_2SO_4 +0.4M $NaClO_4$	0.4M NaCl	0.04M NaCl +0.4M $NaClO_4$	0.004M NaCl +0.4M $NaClO_4$	0.4M $NaClO_4$
Spiked Sn concentration	1.1×10^{-4}mol/l (6M HCl Solution)						
pH	pH 8						
Environment	Non-reducing Environment						
Immersion Period	3 months						
Reproducibility	2						
Number of Samples	14						

Table 6-2 Test Results

Test Conditions					Results	
Solution	Reproduci-bility	Initial Sn conc. (mol/l) (Radioactive conc. cpm/ml)*1	Immersion Period	Initial pH	Final pH	Sn conc. (mol/l) (Radioactive conc. cpm/ml)
0.1M Na_2SO_4	1	1.1×10^{-4} (48802±263)	3months	8.0	8.0	(9.1±0.2)E-8 (38.8±0.8)
	2	1.1×10^{-4} (47341±255)	3months	8.0	8.0	(9.2±0.2)E-8 (39.7±0.8)
0.01M Na_2SO_4 +0.4M $NaClO_4$	1	1.1×10^{-4} (48051±259)	3months	7.9	8.0	(6.6±0.2)E-8 (28.2±0.7)
	2	1.1×10^{-4} (48259±260)	3months	7.8	7.7	(3.7±0.2)E-8 (16.1±0.6)
0.001M Na_2SO_4 +0.4M $NaClO_4$	1	1.1×10^{-4} (47693±257)	3months	8.0	7.7	(5.9±0.2)E-8 (25.2±0.7)
	2	1.1×10^{-4} (47078±253)	3months	8.1	7.9	(3.0±0.1)E-8 (12.7±0.6)
0.4M NaCl	1	1.1×10^{-4} (47926±258)	3months	7.9	8.0	(3.6±0.2)E-8 (15.5±0.7)
	2	1.1×10^{-4} (48416±261)	3months	7.8	7.7	(5.7±0.2)E-8 (24.4±0.7)
0.04M NaCl +0.4M $NaClO_4$	1	1.1×10^{-4} (47487±256)	3months	7.6	7.8	(9.1±0.2)E-8 (38.8±0.8)
	2	1.1×10^{-4} (47206±254)	3months	8.0	8.0	(14.0±0.2)E-8 (59.8±0.9)
0.004M NaCl +0.4M $NaClO_4$	1	1.1×10^{-4} (47484±256)	3months	8.1	8.0	(7.5±0.2)E-8 (32.3±0.8)
	2	1.1×10^{-4} (46959±253)	3months	8.0	8.2	(13.0±0.2)E-8 (55.9±0.9)
0.4M $NaClO_4$	1	1.1×10^{-4} (46714±251)	3months	7.7	7.7	(14.5±0.2)E-8 (62.3±0.9)
	2	1.1×10^{-4} (47269±254)	3months	8.2	8.2	(11.7±0.2)E-8 (50.0±0.9)

*1 Radioactive concentration:Corrected on 1, August, 1996
*2 Temperature: 23 ± 3℃

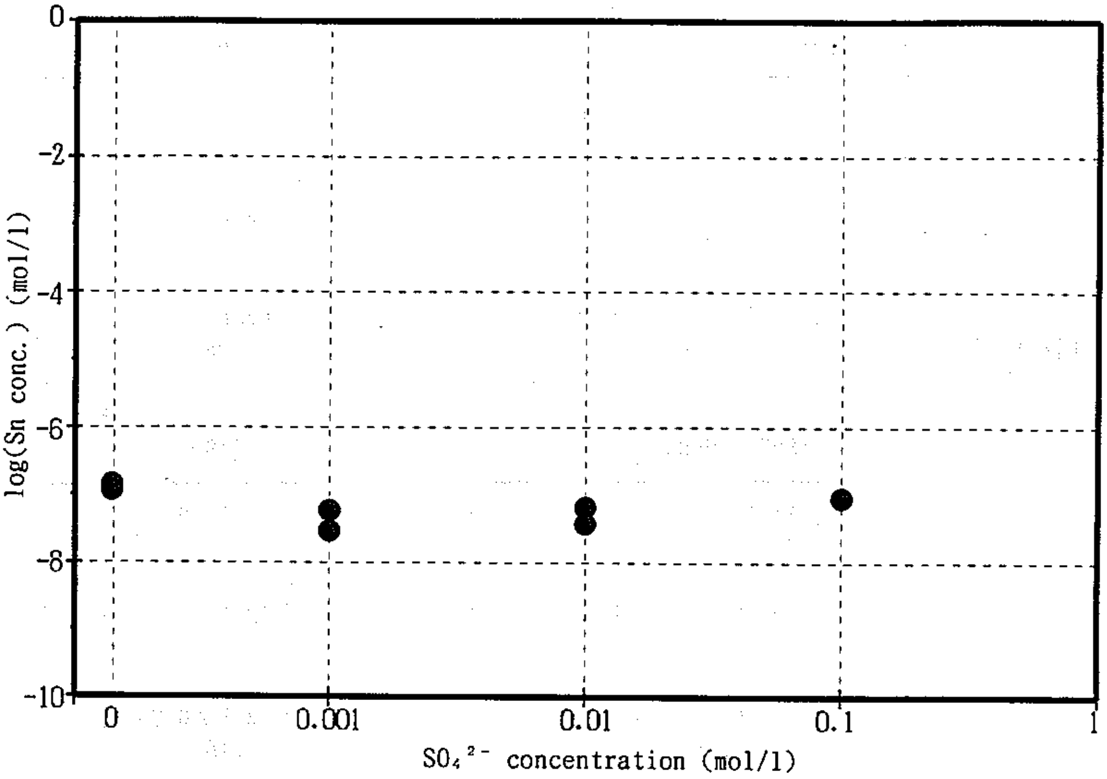


Fig. 6-1 Influence of SO_4^{2-} upon Sn Concentration

Ionic Strength(I): 0.43～0.57
pH: 7.6～8.2
Temperature: 23 ± 3 ℃

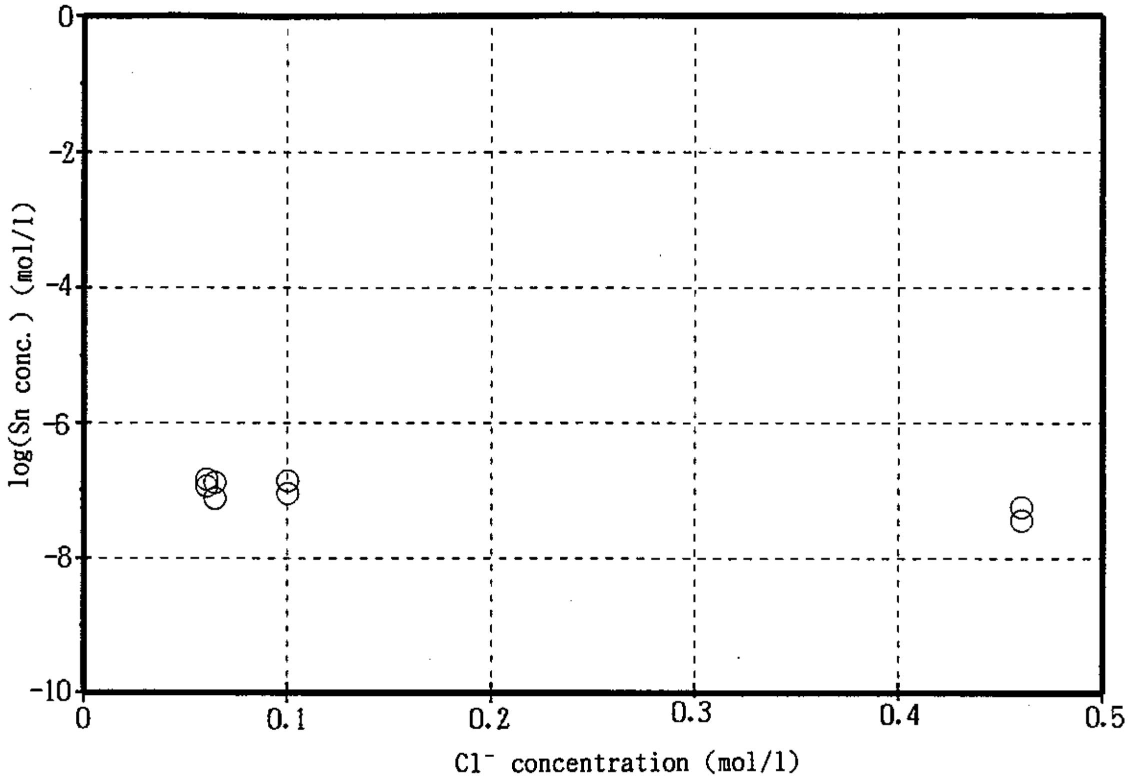


Fig. 6-2 Influence of Cl^- upon Sn Concentration

Ionic Strength(I):0.53~0.57
p H:7.6~8.2
Temperature: 23 ± 3 ℃

APPENDIX

Under-Saturated Solubility Test of Amorphous Sn

Under-Saturated Solubility Test of Amorphous Sn

1. Test Condition

Test conditions are shown in Table A-1 and Table A-2. Under Condition1,3 and 4, under-saturated solubility tests of amorphous Sn were carried out. Under Condition2, over-saturated solubility test was carried out.

2. Test Method

(1) RI Test

Sn stock solution was mixed into 50ml of 0.1M $NaClO_4$ solution which was conditioned using deaerated water. pH of solution was adjusted using NaOH and $HClO_4$ after conditioning of Sn concentration. Following procedures were carried out according to each condition as follows.

①Under-saturated solubility tests(Condition1, Condition3)

After 1 month, the solution was percolated using filter and Sn concentration of filtrate was calculated. Then, pH of solution was adjusted and the condition was made under-saturated, and left for 3 months. After 3 months, solution was percolated and Sn concentration of filtrate was calculated.

②Over-saturated solubility test(Condition2)

After 3 months, solution was percolated using filter, and Sn concentration of filtrate was calculated.

(2) Cold Test

①Under-saturated solubility test(Condition4)

780mg of amorphous Sn solid was mixed into 50ml of 0.1M $NaClO_4$ solution which was conditioned using deaerated water and immersed 3 months after adjustment of pH using NaOH and $HclO_4$. Precipitation was analyzed by XRD.

Both (1) and (2), all procedures until solid-liquid separation were carried out within low-oxygen glove box(Ar base: O_2<1ppm, CO_2<1ppm)

3.Results

Results of solubility tests were shown in Table A-3.

3.1 RI Tests(Condition1, Condition2, Condition3)

①Over-saturated solubility tests(Condition1, Condition2)

Under Condition1, Sn concentration was $4\sim7\times10^{-8}$mol/l(pH~5). Under Condition2, Sn concentrations were 3×10^{-8}mol/l(pH7) and 5×10^{-7}mol/l(pH9).

②Under-saturated solubility tests(Condition1, Condition3)

Under Condition1, Sn concentrations were 8×10^{-8}mol/l(pH7), 2×10^{-7}mol/l(pH8) and 3×10^{-7}mol/l(pH9), respectively. Under Condition3, Sn concentrations were 8×10^{-5}mol/l(pH10), 1×10^{-4}mol/l(pH10.5) and 5×10^{-4}mol/l(pH11), respectively.

3.2 Cold Test(Condition4)

①Under-saturated solubility test

Under Condition4, Sn concentrations were 8.1×10^{-5}mol/l(pH10.1), 2×10^{-4}mol/l(pH10.5), 6.7×10^{-4}mol/l(pH10.7), 8.1×10^{-4}mol/l(pH10.9) and 1.3×10^{-3}mol/l(pH11), respectively. Fig.A-1 shows Sn concentrations of each pH value. Fig.A-1 shows that results of cold solubility tests were almost the same value of RI tests.

②XRD analysis of solid phase

XRD pattern of Sn solid (after test) showed no explicit peak and suggested that it was amorphous Sn.

4.Discussion

①Over-saturated condition and Under-saturated condition

Result of 1997 study(this study) was shown in Fig.A-1 with results of 1994 and 1995 study. Sn concentrations of each pH values obtained in 1997 study were almost the same value of results of 1994 and 1995 study, and it was suggested that 1997 data were in accord with solubility curve obtained by over-saturated solubility tests.

②Solubility curve

Fig.A-1 suggests that solubility curve is consist of following 3 lines.

①pH2～pH8

②pH8～pH10

③pH10～pH11.5

It suggests that $Sn(OH)_4{}^0$ at range of below pH8, $Sn(OH)_5{}^-$ at range of pH8～pH10 and $Sn(OH)_6{}^{2-}$ at range of over pH10 are the principal species.

5.Conclusion

①In this study, solubilities of under-saturated condition and over-saturated condition were almost the same value (at the same pH).

②Solubility obtained in this study was that of amorphous Sn.

③At range of pH2～pH11.5, it was suggested that solubility curve consist of 3 species existed.

④Solid phase used in under-saturated solubility test(cold test) was amorphous Sn and crystallization was not detected after 3 months immersion.

Table A-1 Test Condition (1)

		R I Test		
		Condition 1 (Over-Saturated ↓ Under-Saturated)	Condition 2 Over-Saturated	Condition 3 (Over-Saturated ↓ Under-Saturated)
Over-Saturated	Spiked RI	$SnCl_4$ 6M HCl Solution		$SnCl_4$ 6M HCl Solution
	Sn Concentration	10^{-4} M		10^{-2} M
	pH Adjuster	$HClO_4$, NaOH		$HClO_4$, NaOH
	Solution	0.1M $NaClO_4$		0.1M $NaClO_4$
	Immersion Period	1 month	3 months	1 month
	pH Condition	pH5, pH5, pH5	pH7, pH9	pH5, pH5, pH5
Under-Saturated	pH Condition	pH7, pH8, pH9		pH10, pH10.5, pH11
	pH Adjuster	($HClO_4$), NaOH		($HClO_4$), NaOH
	Immersion Period	3 months		3 months
Cl^- Concentration		6×10^{-3}mol/l		6×10^{-2}mol/l
Reproducibility		2		
Number of Samples		12	4	6

Table A-2 Test Condition (2)

		Condition 4 (Under-Saturated)
Under-Saturated	Sn Solid	Amorphous Sn
	Sn Concentration	10^{-1} M
	pH Adjuster	$HClO_4$, NaOH
	Solution	0.1M $NaClO_4$
	Immersion Period	3 months
	pH Condition	pH10, pH10.5, pH11
Cl^- Concentration		6×10^{-3} mol/l
Reproducibility		2
Number of Samples		6

Table A-3 Results of Solubility Tests

	Test Conditions			Over-Saturated Condition				Under-Saturated Condition			
•	pH	Reproducibility	Initial Sn conc. (mol/l) (Radioactive conc. cpm/ml)*1	Immersion period	Initial pH	Final pH	Sn conc. (mol/l) (Radioactive conc. cpm/ml)	Immersion period	Initial pH	Final pH	Sn conc. (mol/l) (Radioactive conc. cpm/ml)
Condition1	5	1	1.4E-4 (15399±85)	1month	5.2	5.3	(5.5±0.3)E-8 (7.7±1)	3months	7.1	6.9	(7.3±0.1)E-8 (3.4±1)
		2	1.4E-4 (15740±87)	1month	4.7	4.7	(4.1±0.3)E-8 (5.6±1)	3months	6.9	7.4	(8.5±0.1)E-8 (4.0±1)
		3	1.4E-4 (15902±88)	1month	4.7	4.7	(7.4±0.4)E-8 (10.4±1)	3months	7.9	8.2	(1.4±0.4)E-7 (20±2)
		4	1.4E-4 (15537±86)	1month	5.1	5.1	(10.6±0.4)E-8 (14.8±1)	3months	8.1	8.3	(2.2±0.4)E-7 (31±2)
		5	1.1E-4 (12474±69)	1month	4.9	5.2	(6.5±0.4)E-8 (7.4±1)	3months	8.9	8.7	(1.8±0.1)E-7 (21±1)
		6	1.1E-4 (12307±68)	1month	5.0	5.3	(6.7±0.4)E-8 (7.5±1)	3months	9.0	8.8	(3.1±0.1)E-7 (35±1)
Condition2	7	1	1.1E-4 (159036±875)	3months	6.9	7.1	(3.4±0.2)E-8 (47.0±3.0)				
		2	1.1E-4 (155400±855)	3months	7.4	7.7	(1.14±0.03)E-7 (158.7±4.6)				
	9	1	1.1E-4 (157727±868)	3months	9.2	9.8	(1.38±0.01)E-6 (1932.3±14.8)				
		2	1.1E-4 (156680±862)	3months	8.8	9.2	(4.96±0.07)E-7 (692.3±9.1)				
Condition3	10	1	1.8E-2 (15098±82)	1month	4.7			3months	10.0	10.2	(8.7±0.1)E-5 (74±1)
		2	1.8E-2 (15427±84)	1month	4.7			3months	10.0	10.2	(7.3±0.1)E-5 (62±1)
	10.5	1	1.3E-2 (90722±383)	1month	5.1			3months	10.4	10.5	(1.51±0.03)E-4 (1053±19)
		2	1.3E-2 (87854±371)	1month	5.1			3months	10.4	10.6	(7.0±0.2)E-5 (487±15)
	11	1	1.3E-2 (89357±378)	1month	5.0			3months	11.0	10.9	(4.6±0.05)E-4 (3185±28)
		2	1.3E-2 (88103±372)	1month	5.0			3months	11.0	11.2	(4.5±0.04)E-4 (3147±28)
Condition4 *2	10	1	1.0E-1					3months	10.1	10.1	9.1E-5
		2	1.0E-1					3months	10.1	10.1	8.1E-5
	10.5	1	1.0E-1					3months	10.4	10.5	2.0E-4
		2	1.0E-1					3months	10.5	10.7	6.7E-4
	11	1	1.0E-1					3months	11.0	11.0	1.3E-3
		2	1.0E-1					3months	10.9	10.9	8.1E-4

＊1 Radioactive concentration:Corrected on 1, August, 1996

＊2 Cold Test

＊3 Temperature: 25 ± 3 ℃

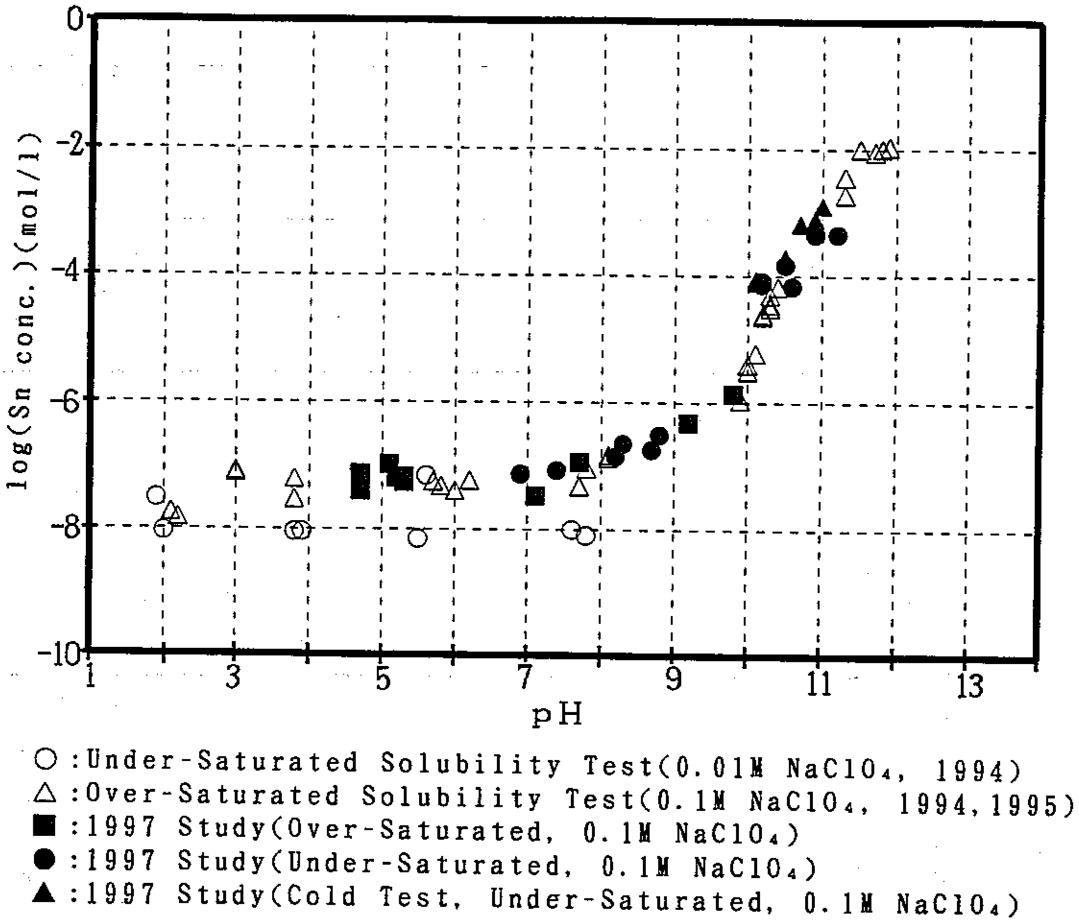


Fig.A-1 Results of Solubility Tests

Temperature:25± 3℃