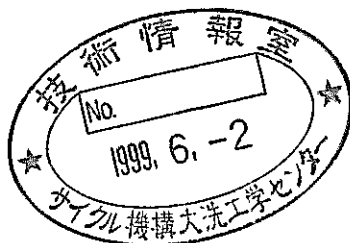


Effects of ligands on the solubility of tin

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配位子の影響を考慮した Sn の溶解度

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要旨

¹²⁶Sn は半減期 1×10^5 [y] の β^- 放出核種であり、高レベル放射性廃棄物の地層処分性能評価研究において重要となる核種の一つである。処分環境条件における Sn の挙動を把握する上で重要となる熱力学データは少なく、処分環境条件における溶解度評価下において溶解度データが取られた例は、高 pH 領域を除いては報告されていない。本研究では、溶解度評価において重要となる配位子 (OH^- , Cl^- および SO_4^{2-}) 濃度と溶解度との関係を調べることを目的とし、Na- ClO_4 -Cl- SO_4 水溶液系およびベントナイト平衡液系における非晶質のスズ酸化物(IV) (錫酸, $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ または $\text{SnO}_2(\text{am})$) の溶解度を測定した。

Na ClO_4 系における溶解度データは、pH 6 ~ 11 の範囲で pH 依存性を示し、それにより Sn(IV) の加水分解定数が求められた (Amaya, 1997)。また、Na- ClO_4 -Cl- SO_4 系においては、 Cl^- , SO_4^{2-} 濃度を変化させても溶解度データが変わらなかったことから、Sn(IV) の塩化物錯体や硫酸塩錯体が加水分解種よりも支配的にはなり得ないことを示した。一方、ベントナイト平衡液系での溶解度データは、ベントナイトを用いなかった他の実験よりも高い溶解度を示した。

実験結果は、以下を示唆する。

処分環境条件の下では、

- (1) Sn(IV) の液相化学種として、加水分解種、塩化物錯体および硫酸塩錯体以外の化学種が支配的に存在する可能性がある。
- (2) $\text{SnO}_2(\text{am})$ 以外の固相が、溶解度制限固相として存在する可能性がある。

本報告書は、1994 年から 1997 年にわたり、動燃事業団から日揮株式会社への委託により実施された研究成果の一部をとりまとめたものである。

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Effects of ligands on the solubility of tin

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Abstract

Solubilities of amorphous stannic oxide, $\text{SnO}_2(\text{am})$ in $\text{Na-ClO}_4\text{-Cl-SO}_4$ aqueous systems were measured to quantitatively investigate the influences of the ligands OH^- , Cl^- and SO_4^{2-} on solubilities. They were also measured in bentonite equilibrated solutions to discuss the behavior of tin under a repository condition of a high-level radioactive waste. The solubility data in sodium perchlorate media in the range of pH from 6 to 11 showed pH dependency, and the hydrolysis constants of tin (IV) were determined (Amaya, et al., 1997). No significant changes in solubilities with the variation in Cl^- , SO_4^{2-} concentrations were observed in $\text{Na-ClO}_4\text{-Cl-SO}_4$ aqueous systems, so this indicates that chloride and sulfate species were less effective than hydroxide complexes. On the other hand, solubilities in bentonite equilibrated solutions were higher than solubilities of other experiments in simple systems.

These results suggest that (1) other complexes of tin except hydroxide, chloride or sulfate complexes of tin (IV) may dominantly exist in aqueous phase, (2) solid phase other than $\text{SnO}_2(\text{am})$ may limit the solubility of tin under repository conditions.

Introduction

^{126}Sn in high level radioactive waste (HLW) is one of the important radionuclides because of its long half time of 10^5 [y], therefore, the migration behavior of ^{126}Sn in the deep geological repository should be well understood. While solubility is an important parameter for the safety assessment, tin solubilities with the wide range from 10^5 to 10^{11} [mol/l] were adopted in the current HLW performance analyses (Vieno, 1995). The difference in solubility was caused by differences in the thermodynamic data for tin solid and/or tin aqueous species adopted in the performance analysis. Furthermore, there were few available data based on experimental measurements. In this work, we studied the behavior of tin (IV) hydrolysis and complexation with Cl^- and SO_4^{2-} as they are major ligands in geological environments.

Experimental

Solubility measurements were carried out in Argon atmosphere (O_2 and CO_2 partial pressure < 1 ppm, 5 ~ 29 °C) using teflon vessels. The details of experimental procedures are described in our previous report (Amaya, et al., 1997). The over-saturation experiments were conducted in NaClO_4 media, bentonite equilibrated media, and $\text{Na-ClO}_4\text{-Cl-SO}_4$ media to investigate the influence of pH, Eh, co-existing ions on

the solubilities of Sn. In the under-saturation experiments, crystalline SnO₂(cr) and amorphous SnO₂(am) were used as initial solid phases.

Materials

All reagents used in the experiments were special grade. Pure water was degassed for 12 hrs and NaOH solution was prepared by using sodium metal and pure water in the glovebox under an Ar atmosphere.

The standard solution of ¹¹³Sn (in 6N-HCl, LMRI) and SnCl₄ (KANTO CHEMICAL CO.) were used to prepare Sn stock solutions for over-saturation experiments.

Another Cl⁻ free alkaline stock solution was also prepared by precipitation of amorphous SnO₂ from acidic chloride solution including SnCl₄ followed by dissolution of washed SnO₂ in NaOH solution.

Crystalline SnO₂ (RARE METAL INC., 99.9%, particle size 74μm) was once washed with pure water (Amaya, 1997), then was used for under-saturation experiments.

Amorphous SnO₂(am) used for under-saturation experiment was obtained as a product precipitated through the over-saturation experiment.

Bentonite equilibrated solution was prepared with Japanese commercial bentonite Knigel V1(KUNIMINE INDUSTRIES CO.). All bentonite particles were removed by means of ultrafiltration method with 10,000 Molecular-Weight-Cut-Off (MWCO) filter before solubility experiments.

Conditions of over-saturation experiment

In the over-saturation experiments, Sn stock solution including ¹¹³Sn (in 6N-HCl) and stable SnCl₄ solution was spiked into the following solutions:

1. 0.1M-NaClO₄ solution
2. Bentonite equilibrated solutions:
 - Bentonite and 0.01M-NaCl,
 - Bentonite and 0.1M-Na₂SO₄ with reducing reagent,
 - Bentonite and 0.4M-NaCl with reducing reagent.

The 0.1M-Na₂SO₄ and 0.4M-NaCl were used to simulate a kind of reference porewater composition in highly compacted bentonite surrounded by deep geological environment.

3. 0.1M-Na₂SO₄, 0.01M-Na₂SO₄ with 0.4M-NaClO₄, and 0.001M-Na₂SO₄ with 0.4M-NaClO₄,
4. 0.4M-NaCl, 0.04M-NaCl with 0.4M-NaClO₄, and 0.004M-NaCl with 0.4M-NaClO₄,

The details of experimental conditions are shown in Table 1-6 together with the results.

Conditions of under-saturation experiment

In the under-saturation experiments, SnO₂(cr) was contacted with the 0.01M -NaClO₄ solution. To perform the under-saturation experiments using SnO₂(am), the precipitates which formed in the process of the over-saturation experiments at pH5, pH 6 and pH8 were successively used as initial solid phases.

The details of experimental conditions are shown in Table1 and Table2 together with the results.

Analytical Methods

After the test periods of 1, 3 and 6 months, a small aliquot of the solution was filtered through 10,000 MWCO filter; prior to filtration, the filter was twice rinsed with the same samples by filtration. The pH and Eh of filtrates were measured by using pH meter(HORIBA B-112) and Eh meter(HORIBA D-14).

Concentrations of Sn in filtrates were calculated by the following equation :

$$\text{Sn(mol/l)} = (\text{radioactive concentration of } ^{113}\text{Sn}) / (\text{specific radioactivity of } ^{113}\text{Sn})$$

The radioactivities of ^{113}Sn were determined by the detection of the daughter nuclide, $^{113\text{m}}\text{In}$ ($E_{\gamma}=0.391\text{MeV}$), using the well type NaI scintillation analyzer (Aloka ARC-300) after the radiation equilibrium of ^{113}Sn - $^{113\text{m}}\text{In}$ was reached. For the experiment with $\text{SnO}_2(\text{cr})$, concentrations of stable Sn were measured by ICP-MS(YOKOKAWA PMS-200).

Results and Discussion

1. Solubility in NaClO_4 media

1-1. Over-saturation experiment (Amaya, et al., 1997)

Solubilities in 0.1M- NaClO_4 media determined for the over-saturation experiment had reached to steady states after 1 month and showed a dependency of pH (Table1, Fig.1: open triangles). The solid phases precipitated from solutions in the over-saturated states were determined as hydrated $\text{SnO}_2(\text{am})$ by XRD analysis and TG-DTA. Solubility limits by these amorphous solid phases were found to be constant through 6 months. Amaya, et al.(1997) derived the hydrolysis constants of Sn(IV) at ionic strength $I = 0.1$ by curve fitting calculation using least square method from the solubility data of the over-saturation experiment, and the result is shown in Fig.1. The hydrolysis constants were corrected to $I = 0$ using the Davies equation as follows :

Reaction		I = 0.1 (this study*)	I = 0 (this study*)
$\text{SnO}_2(\text{am}) + 2\text{H}_2\text{O} = \text{Sn}(\text{OH})_4(\text{aq})$	$\log K(\text{am-4}) =$	-7.46	-7.46
$\text{Sn}(\text{OH})_4(\text{aq}) + \text{H}_2\text{O} = \text{Sn}(\text{OH})_5^- + \text{H}^+$	$\log K(4-5) =$	-7.75	-7.97
$\text{Sn}(\text{OH})_4(\text{aq}) + 2\text{H}_2\text{O} = \text{Sn}(\text{OH})_6^{2-} + 2\text{H}^+$	$\log K(4-6) =$	-17.74	-18.38

* We found that Amaya, et al.(1997) made simple mistakes in calculation of logK. These values have been corrected by this study.

1-2. Additional over-saturation experiment and under-saturation experiment using $\text{SnO}_2(\text{am})$

The additional data at pH5, 7, 9, and 10 in 0.1M- NaClO_4 media were obtained (Table2; the left column, Fig.1: solid squares). Furthermore, the samples with precipitates at pH5, pH 6 and pH8 were successively

TABLE-1 Experimental Conditions and Results

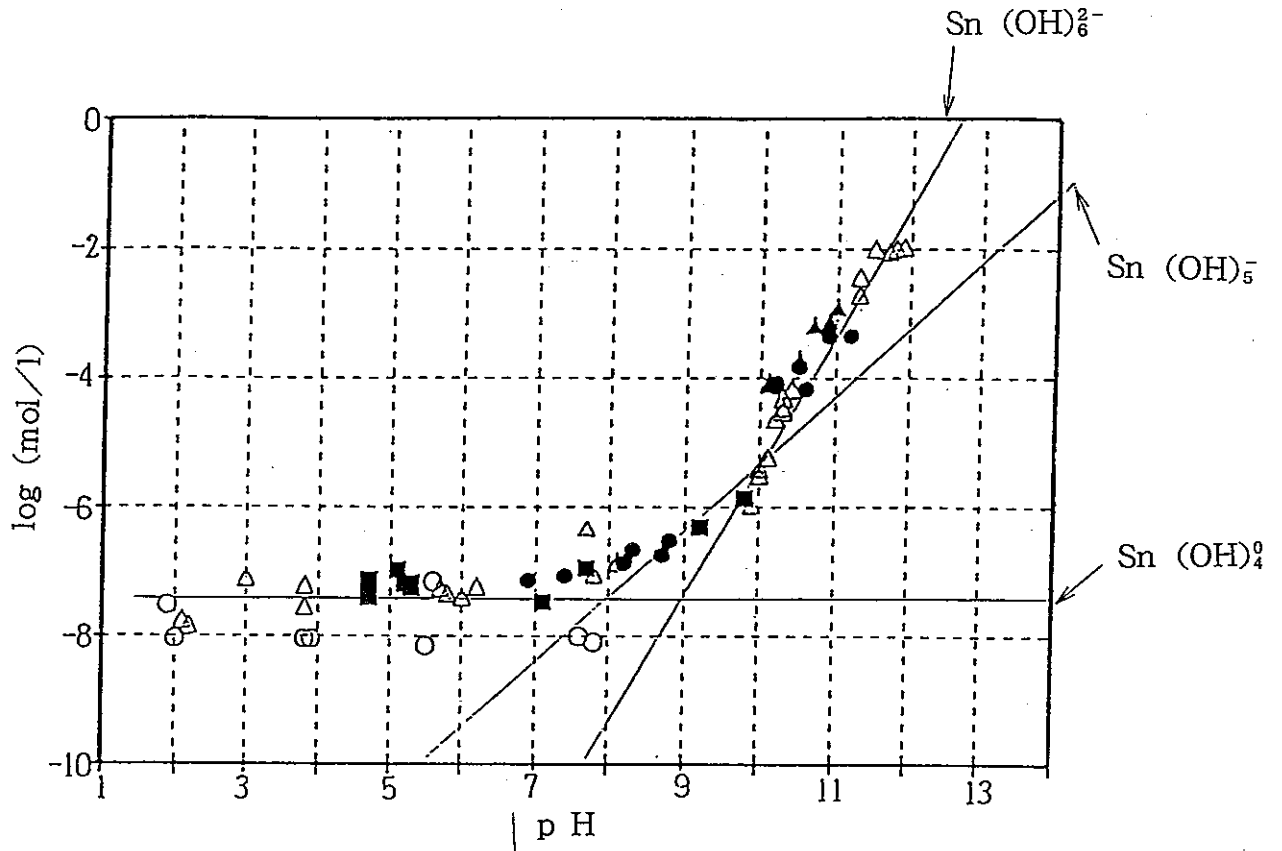
Solution	Reducing agent	Period	Starting materials, Initial Sn con. (mol/l)	Ionic strength	pH	Eh(mV)	Sn con. (mol/l)	XRD
0.01M-NaClO ₄	NON- REDUCING	1 months	SnO ₂ (α) UNDER-SAT.	0.01-0.02	2.1	401	2E-07	SnO ₂ (α) (yellow)
					2.1	422	2E-06	
					3.9	368	6E-08	
					3.9	371	8E-08	
					5.4	358	3E-07	
					5.5	346	7E-06	
					7.6	330	1E-08	
					7.7	279	9E-09	
		3 months	SnO ₂ (α) UNDER-SAT.	0.01-0.02	1.9	396	3E-08	SnO ₂ (α) (yellow)
					2.0	391	9E-09	
					3.8	376	9E-09	
					3.9	385	9E-09	
					5.5	345	7E-09	
					5.6	343	7E-08	
0.1M-NaClO ₄	NON- REDUCING	1 weeks	1E-04	0.10-0.11	2.2	344	(1.2±0.1)E-07	amorphous (white) TG-DTA SnO ₂ • (1-2) H ₂ O
					2.2	356	(5.8±1.1)E-08	
					2.9	313	(5.4±1.1)E-08	
					3.0	329	(1.5±0.1)E-06	
					4.0	318	(1.0±0.1)E-06	
					4.3	307	(8.5±1.2)E-08	
					5.8	273	(1.8±0.1)E-06	
					5.9	277	(1.9±0.1)E-06	
					8.0	255	(1.6±0.1)E-06	
					8.1	272	(1.1±0.1)E-05	
					10.2	255	(3.7±0.1)E-05	
					10.4	228	(7.1±0.1)E-05	
					11.2	197	(9.0±0.1)E-05	
					11.3	193	(9.3±0.1)E-05	
0.1M-NaClO ₄	NON- REDUCING	1 months	1E-04	0.10-0.11	2.1	374	(1.8±1.3)E-08	amorphous (white) TG-DTA SnO ₂ • (1-2) H ₂ O
					2.2	371	(1.5±1.3)E-08	
					3.0	338	(7.9±1.3)E-08	
					3.0	335	(8.4±1.3)E-08	
					3.8	324	(6.2±1.3)E-08	
					3.8	307	(2.9±1.3)E-08	
					5.7	240	(5.6±1.2)E-08	
					6.2	241	(5.9±1.3)E-08	
					7.8	226	(9.1±1.3)E-08	
					7.7	227	(4.7±1.3)E-07	
					10.0	210	(4.1±0.2)E-06	
					10.1	199	(6.1±0.2)E-06	
					10.8	189	(9.7±0.1)E-05	
					10.9	186	(9.6±0.1)E-05	
11.7	159	(9.6±0.1)E-05						
11.8	129	(9.4±0.1)E-05						

TABLE-1 Experimental Conditions and Results (cont.)

Solution	Reducing agent	Period	Starting materials, Initial Sn con. (mol/l)	I.S.	pH	Eh(mV)	Sn con. (mol/l)	XRD
0.1M-NaClO ₄	NON- REDUCING	3 months	1.0E-04	0.12	10.3	242	(3.60±0.02)E-05	no data
					10.4	232	(6.90±0.04)E-05	
		6 months	9.9E-05	0.11	10.2	300	(2.35±0.02)E-05	
					10.2	306	(2.52±0.02)E-05	
		9 months	9.9E-09	0.11	9.9	254	(1.11±0.04)E-06	
					10.0	294	(3.25±0.05)E-06	
		6 months	9.4E-05	0.22	5.8	268	(4.7±0.2)E-08	
					6.0	273	(4.1±0.1)E-08	
			9.4E-05	0.22	8.1	266	(1.50±0.02)E-07	
					8.1	270	(1.36±0.02)E-07	
			9.9E-05	0.11	10.3	275	(5.10±0.04)E-05	
					10.3	295	(3.18±0.03)E-05	
			1.4E-02 1.5E-02	0.37 0.41	11.3	243	(3.71±0.05)E-03	
					11.3	225	(1.94±0.03)E-03	
			1.5E-02	0.43 0.45	11.5	213	(1.02±0.01)E-02	
					11.7	219	(9.1±0.1)E-03	
0.44 0.45	11.8	186		(1.02±0.01)E-02				
	11.9	179		(1.10±0.02)E-02				
1.0E-01	2.2 2.0	12.5	159	(9.27±0.05)E-02				
		12.6	107	(9.64±0.06)E-02				
	2.2	13.0	53	(9.42±0.05)E-02				
		13.0	83	(9.46±0.05)E-02				
2.0	13.5	-48	(9.56±0.05)E-02					
	13.5	-13	(9.68±0.06)E-02					

TABLE-2 Experimental Conditions and Results
(0.1M-NaClO₄ Solution, Non-Reducing)

OVER-SATURATION EXPERIMENT					UNDER-SATURATION EXPERIMENT				
Period	Initial Sn con. (mol/l)	I.S.	pH	Sn con. (mol/l)	Period	I.S.	pH	Sn con. (mol/l)	XRD
1 months precipitates ↓ under-sat. test	1.4E-04	0.11	5.2	(5.5±0.3)E-08	3 months	0.11	6.9	(7.3±0.1)E-08	no data
			4.7	(4.1±0.3)E-08			7.4	(8.5±0.1)E-08	
	4.7	(7.4±0.4)E-08	0.12	8.2			(1.4±0.4)E-07		
			5.1	(10.6±0.4)E-08			8.3	(2.2±0.4)E-07	
	1.1E-04	0.12	5.2	(6.5±0.4)E-08			0.12	8.7	(1.8±0.1)E-07
			5.3	(6.7±0.4)E-08			8.8	(3.1±0.1)E-07	
3 months	1.1E-04	0.21	7.1	(3.4±0.2)E-08	/				
			7.7	(1.14±0.03)E-07					
			9.8	(1.38±0.01)E-06					
			9.2	(4.96±0.07)E-07					
1 months precipitates ↓ under-sat. test	1.8E-02	0.18	4.7	no data	3 months	0.21	10.2	(8.7±0.1)E-05	no data
			4.7				10.2	(7.3±0.1)E-05	
	5.1	0.21	10.5				(1.51±0.03)E-04		
			5.1				10.6	(7.0±0.2)E-05	
	1.3E-02	0.20	5.0	no data			10.9	(4.60±0.05)E-04	
		0.28	5.0				11.2	(4.50±0.04)E-04	
	1.3E-02	0.26	5.0						
		0.25	5.0						
30 min. precipitates ↓ under-sat. test	1.0E-01	no calc.	5	no data	3 months	0.11	10.1	9.1E-05	amorphous (white)
							10.1	8.1E-05	
							10.5	2.0E-04	
							10.7	6.7E-04	
6 months precipitates ↓ under-sat. test	9.4E-05	no calc.	5.8	TABLE-2	3 months	no calc.	9.6	(6.4±0.1)E-07	no data
			6.0				9.9	(1.15±0.01)E-06	
			8.1				9.7	(1.660±0.02)E-06	
			8.1				9.7	(1.71±0.02)E-06	



- [data from table1: under-saturation experiment using $\text{SnO}_2(\text{cr})$, 0.01M- NaClO_4 , 3 months]
- △ [data from table1: over-saturation experiment, 0.1M- NaClO_4 , 1 month and 6 months, $\text{SnO}_2(\text{am})$ precipitated]
- [data from table2: over-saturation experiment, 0.1M- NaClO_4 , 1 month and 3 months, $\text{SnO}_2(\text{am})$ precipitated]
- ▲ [data from table2: under-saturation experiment using $\text{SnO}_2(\text{am})$, 0.1M- NaClO_4 , 3 months]

Fig. 1 Sn concentrations measured in NaClO_4 media

used for the under-saturation experiments using $\text{SnO}_2(\text{am})$ (Table2, the right column: 3 months, in the range of pH from 7 to 11). These data shown in Table 2 showed very good reproducibility and they supported the thermodynamic data derived from Table1 very well (Fig.1: solid circles and solid triangles).

1-3. Under-saturation experiment using $\text{SnO}_2(\text{cr})$ (Amaya, et al., 1997)

Solubilities of $\text{SnO}_2(\text{cr})$ had reached to steady states after 1 month (Table1), however they didn't agree with solubilities determined for the over-saturation experiments (Fig.1: open circles and open triangles).

2. Solubility in bentonite equilibrated solutions

In the bentonite and 0.01M-NaCl equilibrated solutions, measured solubilities at pH 6 and pH 9 (Table3, Fig.2: solid triangles) were higher about two orders of magnitude than data in perchlorate solutions. Solubilities in the bentonite and 0.1M- Na_2SO_4 equilibrated solutions, and the bentonite and 0.4M-NaCl equilibrated solutions, at pH 9.2~9.7 under strongly reducing conditions (Table3, Fig.2: solid circles) agreed with solubilities in the bentonite and 0.01M-NaCl system at pH 6 and 9. The chemical compositions of the bentonite equilibrated solutions were analyzed (Table4).

The comparison of solubilities and chemical compositions is summarized in Table 5. For data at pH 6 and 9, in spite of the variation in concentration of chloride, sulfate and calcium and redox potentials of three bentonite solutions, similar solubilities were measured in these bentonite equilibrated systems.

These results suggest that (1) these ligands had no influence on the behavior of tin solubility, (2) there were no significant change in the solubility of tin (IV) even under strongly reducing conditions.

3. Solubility in chloride and sulfate media

To confirm the effect of chloride and sulfate on Sn solubility accurately, solubility measurements in various concentrations of these ligands were carried out. No change in the solubility was observed in the range of concentrations up to 0.1M of sulfate, up to 0.4M of chloride (Table6, Fig. 3 and 4). These solubilities were all in good agreement with data in perchlorate media. This result supports the assumption that the ligands chloride and sulfate have no influence on the behavior of tin solubility.

Conclusion

Solubilities of amorphous tin dioxide $\text{SnO}_2(\text{am})$, which was stable in an Ar atmosphere were determined in perchlorate media and the hydrolysis constants were determined. However, based on the experimental fact that solubilities only in the bentonite solutions were higher than data in simple media not contacted with bentonite, we can conclude as follows: other complexes of tin except hydroxide, chloride or sulfate complexes of tin (IV) may dominantly exist in aqueous phase, or solubility limiting solid phase other than $\text{SnO}_2(\text{am})$ may form in the bentonite equilibrated system under a repository condition.

TABLE-3 Experimental Conditions and Results
(Bentonite equilibrated solution)

Solution	Reducing agent	Period	Starting materials, Initial Sn con. (mol/l)	I.S.	pH	Eh(mV)	Sn con. (mol/l)	XRD
0.01M-NaCl Bentonite equilibrated	NON- REDUCING	43.days	1.0E-04	0.13	5.9 5.5	292 304	(2.61±0.02)E-06 (2.26±0.02)E-06	no data
			1.0E-04	0.13	8.8 8.8	265 260	(3.79±0.03)E-06 (3.05±0.02)E-06	
			1.0E-01	0.13 0.12	11.1 11.0	222 215	(4.7±0.1)E-03 (3.3±0.1)E-03	
0.1M-Na ₂ SO ₄ Bentonite equilibrated	3E-03M-Na ₂ S ₂ O ₄	3 months	8.5E-03	0.38	9.5	-543	(1.5±0.4)E-06	
			8.4E-03	0.37	9.2	-556	(2.0±0.5)E-06	
0.4M-NaCl Bentonite equilibrated	3E-03M-Na ₂ S ₂ O ₄	3 months	8.4E-03	0.48	9.7	-570	(1.6±0.5)E-06	
			8.1E-03		9.6	-586	(1.7±0.5)E-06	

TABLE-4 Analysis for Bentonite Equilibrated Solutions
(Ultrafiltered, MWCO 10,000)

Solution Elements	0.01M-NaCl Bentonite (10,000 ml/g)			0.1M-Na ₂ SO ₄ + 0.003M-Na ₂ S ₂ O ₄ Bentonite (100 ml/g)*	0.4M-NaCl + 0.003M-Na ₂ S ₂ O ₄ Bentonite (100 ml/g)*
Fe (ppm)	0.1	0.15	<0.1	0.8	0.2
Si (ppm)	1.48	3.39	0.37	14.4	2.4
Al (ppm)	0.44	1.24	<0.1	4.3	1.4
Mg (ppm)	0.53	0.54	0.10	4.1	3.7
Ca (ppm)	1.87	1.62	1.45	53.8	54.5
K (ppm)	0.37	0.41	0.36	6.1	7.6
SO ₄ ²⁻ (ppm)	0.23	0.31	0.34	9310	76.7
Cl ⁻ (mol/l)**	6.8E-02	6.7E-02	4.6E-01	n.a.	4.0E-01
TOC (ppm)	0.13	0.86	0.79	5.2	4.9
pH	6.1	8.9	10.9	8.1	7.9
Conductivity (mS/cm)	1.13	1.14	1.29	16.3	> 40***
Eh (mV)	312	315	240	-421	-337

* Cl-free Sn stock solution was used; pH was adjusted using HClO₄

** calculated by adding all amounts of spiked HCl and Sn stock solution

*** out of range of detector

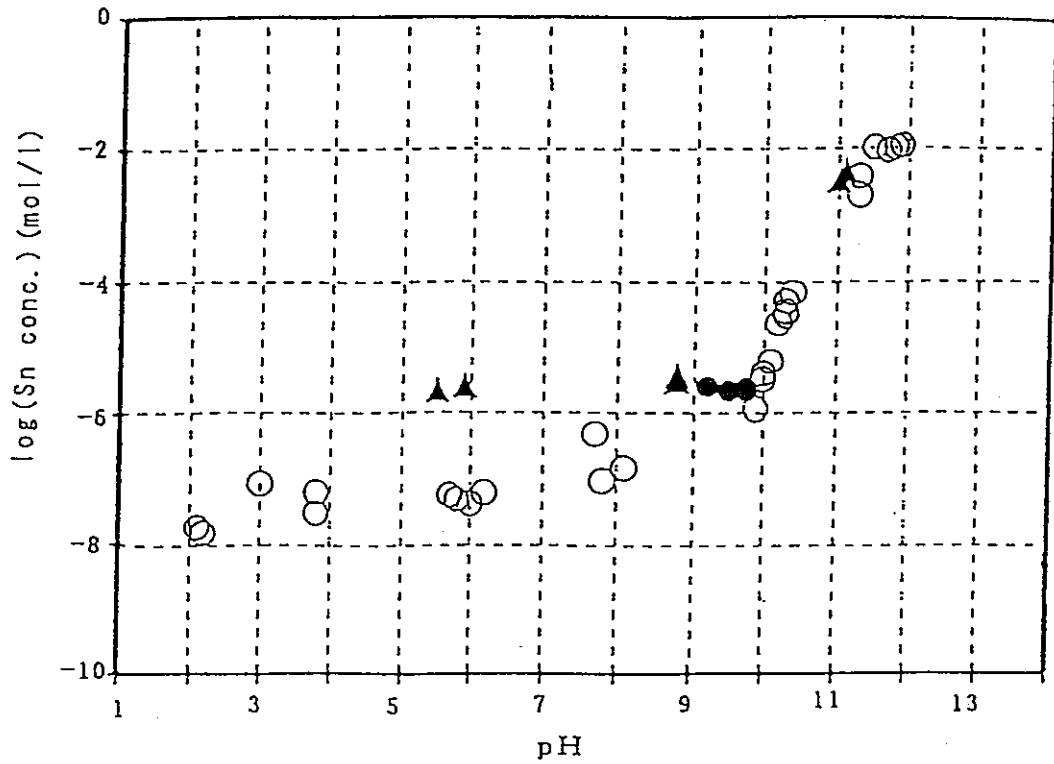
TABLE-5 Difference in Chemical Composition between 0.1M-NaClO₄ and Bentonite Equilibrated Solution

	0.1M-NaClO ₄				Bentonite equilibrated solution				
					0.01M-NaCl			0.003M-Na ₂ S ₂ O ₄	
								+ 0.1M-Na ₂ SO ₄	+ 0.4M-NaCl
Ca (ppm)	n.a.	n.a.	n.a.	n.a.	1.87	1.62	1.45	53.8	54.5
SO ₄ ²⁻ (ppm)	n.a.	n.a.	n.a.	n.a.	0.23	0.31	0.34	9310	76.7
Cl ⁻ (mol/l)**	5.5E-02	5.5E-02	6.4E-02	1.2E-01	6.8E-02	6.7E-02	4.6E-01	n.a.	4.0E-01
TOC (ppm)	n.a.	n.a.	n.a.	n.a.	0.13	0.86	0.79	5.2	4.9
pH	5.8-6.0	8.1	10.2-10.3	11.3	5.5-5.9	8.8	11.0-11.1	9.2-9.5	9.6-9.7
Eh (mV)	268-273	266-270	275-306	243-225	292-304	260-265	215-222	-543 - -556	-570 - -586
Sn (mol/l)	(4.1-4.7) E-08	(1.4-1.5) E-07	(2.4-5.1) E-05	(1.9-3.7) E-03	(2.3-2.6) E-06	(3.8-3.1) E-06	(3.3-4.7) E-03	(1.2-2.0) E-06	(1.6-1.7) E-06

* Cl-free Sn stock solution is used; pH is adjusted using HClO₄
 ** calculated by adding all amounts of spiked HCl and Sn stock solution

TABLE-6 Experimental Conditions and Results (Test for the Effect of Ligands {SO₄²⁻ and Cl⁻} on Solubility, Non-Reducing)

Solution	Reducing agent	Period	Starting materials, Initial Sn con. (mol/l)		LS.	pH	Eh	Sn con. (mol/l)	XRD
0.1M-Na ₂ SO ₄	NON-REDUCING	3 months	1.1E-04 Coexisting [Cl ⁻]; 0.06M (Spiked Sn solution in 6M-HCl)		0.43	8.0	no data	(9.1±0.2)E-08	no data
0.01M-Na ₂ SO ₄ + 0.4M-NaClO ₄					0.56	8.0		(6.6±0.2)E-08	
0.001M-Na ₂ SO ₄ + 0.4M-NaClO ₄					0.53	7.7		(3.7±0.2)E-08	
0.4M-NaCl	NON-REDUCING	3 months	1.1E-04	Coexisting [Cl ⁻]; 0.46M	0.53	8.0	(3.6±0.2)E-08	no data	
0.04M-NaCl + 0.4M-NaClO ₄				Coexisting [Cl ⁻]; 0.1M	0.57	7.8	(5.7±0.2)E-08		
0.004M-NaCl + 0.4M-NaClO ₄				Coexisting [Cl ⁻]; 0.06M	0.54	8.0	(9.1±0.2)E-08		
0.4M-NaClO ₄	NON-REDUCING	3 months	1.1E-04 Coexisting [Cl ⁻]; 0.06M		0.53	7.7	(14.0±0.2)E-08	no data	
						8.2	(7.5±0.2)E-08		
							(13.0±0.2)E-08		
							(14.5±0.2)E-08		
							(11.7±0.2)E-08		



- [data from table1: over-saturation experiment, 0.1M-NaClO₄, 1 month and 6 months, SnO₂(am) precipitated]
- ▲ [data from table3: over-saturation experiment, 0.01M-NaCl and bentonite equilibrated solution, 1 month]
- [data from table3: over-saturation experiment, ((0.1M-NaSO₄ or 0.4M-NaCl) and 0.003M-Na₂S₂O₄) and bentonite equilibrated solution, strongly reducing condition, 3 months]

Fig. 2 Sn concentrations measured in bentonite equilibrated solution

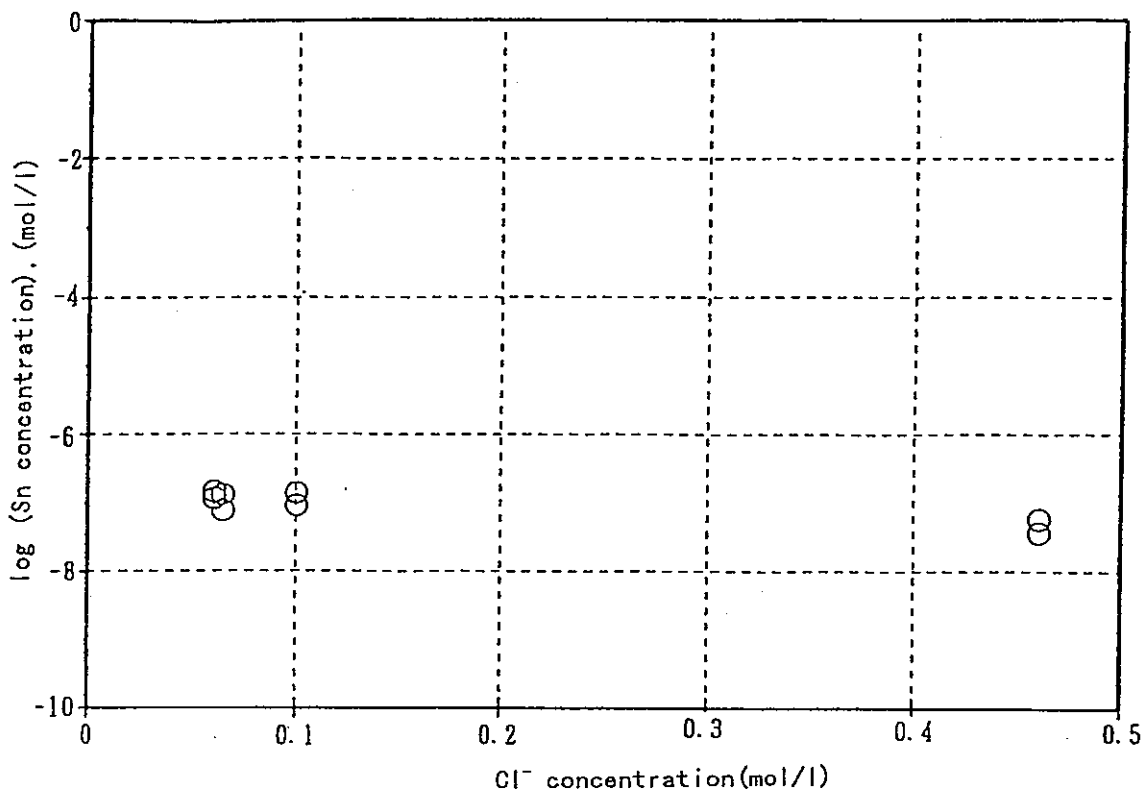


Fig. 3 Effect of Cl⁻ on Sn concentration

ionic strength(I) : 0.53~0.57
pH : 7.6~8.2
temperature : 23±3°C

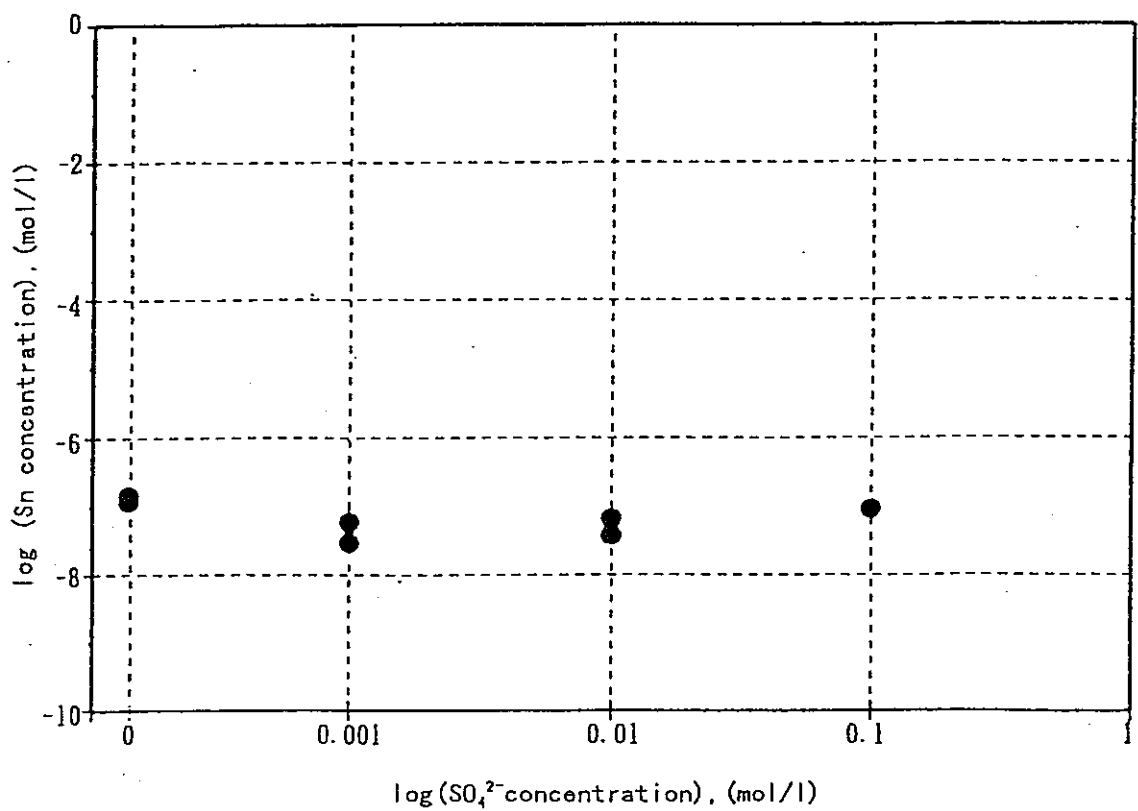


Fig. 4 Effect of SO₄²⁻ on Sn concentration

ionic strength(I) : 0.43~0.57
pH : 7.6~8.2
temperature : 23±3°C

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Reference

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