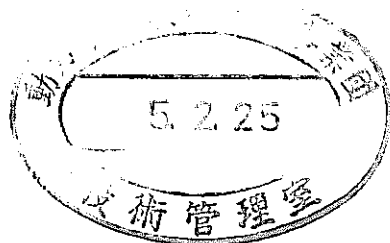


Executive Summary

A Study on the Migration of Iodine Species of Various
Chemical Forms in Geological Media (IV)



February, 1992

Institute of Research and Innovation

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A Study on the Migration of Iodine Species of
Various Chemical Forms in Geological Media (IV)

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Abstract

The present study have been carried out to establish the final disposal methods for the wastes containing radioactive iodines. From the previous studies, it was clarified that the iodine species exist as I^- ions in the ground water and that anions such as I^- ions are little adsorbed on the natural minerals. Hence, three kinds of adsorbents, i. e., cinnabar, montmorillonites containing Ag-thiourea complex, and inorganic ion exchangers, were examined as the artificial barrier materials. Furthermore, the hydrophobic iodine adsorbents were studied from the viewpoint of leaching-resistant. The results are summarized as follows :

1. Adsorption mechanism of cinnabar

① The adsorption of I^- ions on the cinnabar was not affected by an increase in temperature and the coexistent ions. These results suggest that the adsorption of I^- ions on cinnabar takes place through mechanism except for the ion exchange.

② The amount of I^- ions adsorbed on the cinnabar was found to be around 10^{-5} mol/g, which is extremely smaller than that of HgS contained in the cinnabar. The I^- ions were found to not react with HgS reagents. These results suggest that the adsorption of I^- ions on the cinnabar is due to the formation of Hg_2I_2 by the reaction with Hg(I).

③ The distribution ratio for I^- ions less than 10^{-6} M was found to be about 10^4 even in the solutions containing various ions such as ground water.

2. Adsorption mechanism of montmorillonite containing Ag-thiourea complexes

① From the elemental analyses and IR measurements, it was confirmed that the Ag-thiourea complex used for preparing the adsorbent is $Ag(tu)^{3+}$ (tu = thiourea), where tu coordinates to Ag ions through S element.

② It was supposed that the adsorption of I^- ions on the adsorbents is attributed to the interaction between I^- ions and Ag-thiourea complexes or the hydrolysis species of Ag^+ in the montmorillonite.

3. Adsorptivity of inorganic ion exchangers

Various hydrotalcite-type exchangers were prepared and their adsorptivities were examined. Compounds of Mg/Bi types were found to have high adsorptivity in solutions without containing coexistent ions.

4. Wettability of hydrophobic iodine adsorbent containing AgI (HIA)

The contact angles of HIA were measured by powder method. The wettability of HIA was found to be very low. However, it was observed that AgI species are eluted from the surface contacting with water.

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PNC Liaison : Waste Technology Development Division, Geological Isolation Technology Section, Noriaki Sasaki

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1. Introduction

Literature survey and experimental studies for the chemical forms of iodine under various conditions and adsorption materials for I^- ions have been carried out to confirm the final disposal methods for radioactive iodine. It was clarified that iodine exists as I^- ion in ground water and that I^- ions are not adsorbed on minerals except for cinnabar and materials containing Ag^+ ions. Solubility of AgI , which is formed in the fixation materials for radioactive iodine, was found to increase by a factor of about 10^4 depending on the disposal conditions.

Hence, in order to develop the reasonable disposal method for radioactive iodine, the studies on adsorption mechanism and stability of the adsorptive materials for I^- were carried out in more detail.

2. Stability of Cinnabar and Its Adsorption Mechanism of I^- Ions

From the previous studies, it was clarified that cinnabar can adsorb I^- ions efficiently and suggested that the adsorptivity is due to the formation of Hg_2I_2 . Here, more detail studies for adsorption of I^- ions on cinnabar was carried out.

2.1 Chemical Composition of Cinnabar

2.1.1 Sample Preparation

Cinnabar (Spain, Almaden) was crushed with a stainless steel mortar and further finely crushed with a stainless steel ball mill, followed by sieving with standard sieves ($<74 \mu m$).

2.1.2 XRD Analysis

The results show that main component of cinnabar is SiO_2 (content : about 77%) and second component is HgS (content : about 27%).

2.1.3 X-ray Fluorescence Analysis

Table 2-1 shows the results of qualitative total elemental analyses and suggests that 19 elements are contained in cinnabar. From the results in Table 2-1, it was found that the main components are SiO_2 (content : 77%) and HgS (content : 18%) and that the elements forming insoluble iodide compounds are not contained in cinnabar.

Table 2-1 Results of Qualitative Analyses in Cinnabar by X-ray Fluorescence Analysis

No.	elements	spectrum	intensity (kcps)	content (%)
1	O	O $K\alpha$	7.2708	47.4990
2	Si	Si $K\alpha$	297.4437	31.5088
3	Hg	Hg $L\alpha_1$	435.8227	13.1114
4	S	S $K\alpha$	55.4764	5.2675
5	Al	Al $K\alpha$	9.2083	0.8672
6	Fe	Fe $K\alpha$	17.5854	0.8579
7	K	K $K\alpha$	0.9831	0.2464
8	Cr	Cr $K\alpha$	1.9233	0.2028
9	Ti	Ti $K\alpha$	0.3450	0.1085
10	Ni	Ni $K\alpha$	3.1358	0.0878
11	V	V $K\alpha$	0.4730	0.0847
12	Mg	Mg $K\alpha$	0.1126	0.0411
13	Ca	Ca $K\alpha$	0.1602	0.0342
14	Pt	Pt $L\alpha_1$	0.5771	0.0215
15	Th	Th $L\beta_1$	0.3496	0.0208
16	Zr	Zr $K\alpha$	1.0831	0.0179
17	P	P $K\alpha$	0.2141	0.0104
18	Nb	Nb $K\alpha$	0.4274	0.0063
19	Cu	Cu $K\alpha$	0.2730	0.0058

2.2 Properties of Aqueous Solutions of Cinnabar and HgS Reagent

2.2.1 pH and Eh

Measurements of pH and Eh were carried out for the aqueous and I^- solutions containing cinnabar and HgS reagent. The results are as follows :

For cinnabar ;

Aqueous solution : pH = about 8, Eh = 450mV

NaI solution : pH = about 9, Eh = 250mV

For HgS reagent ;

Aqueous solution : pH = about 6, Eh = 450mV

NaI solution : pH = about 7, Eh = 250mV

2.2.2 Point of Zero Charge (PZC)

PZC of aqueous solutions containing cinnabar and HgS reagent was measured by electrophoresis method and is pH 7.8 for cinnabar and pH 4.5 for HgS reagent, respectively.

2.3 Solubility of Cinnabar

2.3.1 Analytical Method of Hg

Analyses of Hg in solutions were carried out by atomic absorption spectroscopy method.

2.3.2 Hg Concentrations in Cinnabar Dispersed Solutions

Cinnabar dispersed solutions were shaken for an appropriate time in thermostat, followed by filtering. Concentrations of Hg in the filtrates were measured and found to be 400 ~ 2,000ppm, which is higher than that expected from the stability product of HgS, i.e., 10ppb. This result suggests that cinnabar contains Hg compound with higher solubility than HgS or materials which can change HgS to compound with high solubility.

2.3.3 ICP Analyses of Cinnabar Dispersed Solutions

The filtrates prepared in 2.3.2 were analyzed with ICP. The results showed that the filtrates contain elements of Ag, B, Br, Ca, Mg, S and Si.

2.3.4 Analyses of Anions in Cinnabar Dispersed Solutions

Anions containing in the filtrates prepared in 2.3.2 were analyzed by ion-chromatography. The presence of Cl^- , NO_3^- and SO_4^{2-} ions were revealed.

2.3.5 Column Experiments of Hg Elution from Cinnabar

Distilled water was made to flow through column packed with cinnabar. Concentrations of Hg in the eluents were analyzed. The results are shown in Fig. 2-1. The concentrations of Hg in eluents are about 80ppb in initial stage and decrease with the progress of elution, followed by holding constant at 18ppb. Constancy in Hg concentration is considered to be due to the dissolution of HgS in cinnabar. Shaded parts in Fig. 2-1 correspond to the Hg concentration of 7.0×10^{-7} mol/g, which may be attributed to the dissolution of Hg compound other than HgS.

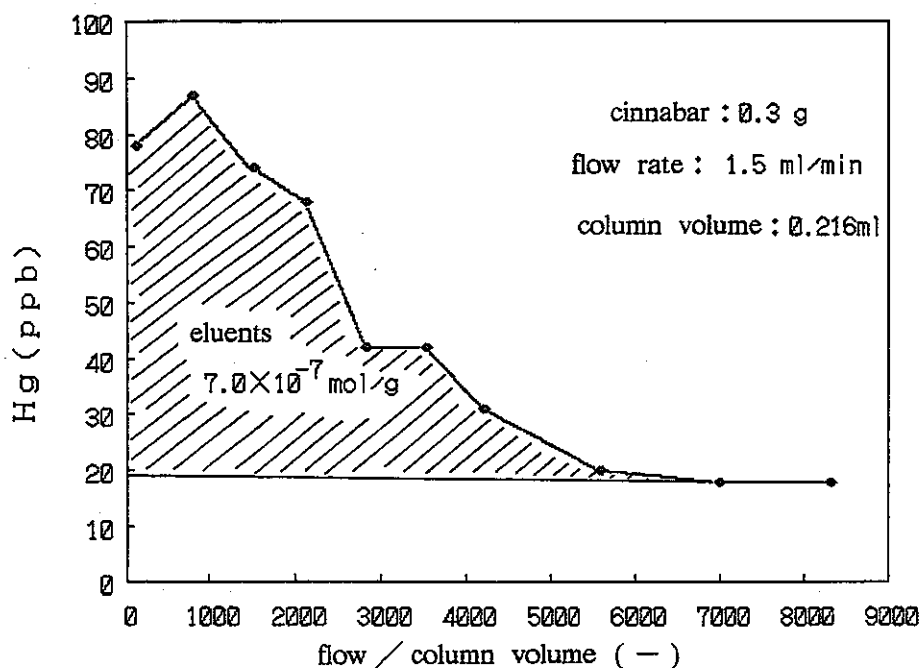


Fig. 2-1 Hg Elution from Cinnabar in Column Experiments

2.4 Experimental Study on Adsorption of I^- Ions in High Concentration

2.4.1 Time Dependence of I^- Ion Adsorption on Cinnabar

Figure 2-2 shows plots of adsorption ratio (%) against time (min) for the adsorption of I^- ions ($10^{-4} \sim 10^{-3}$ M) on cinnabar. It was found that the adsorption of I^- ions occurs very rapidly and that equilibrium is approached within 2 hours.

For example adsorption
for the case of $1.58 \times 10^{-3} M$ in about
10% after 2 hours.
Rd and adsorption
rate are calibrated
and the result is
shown in Fig 2-3.

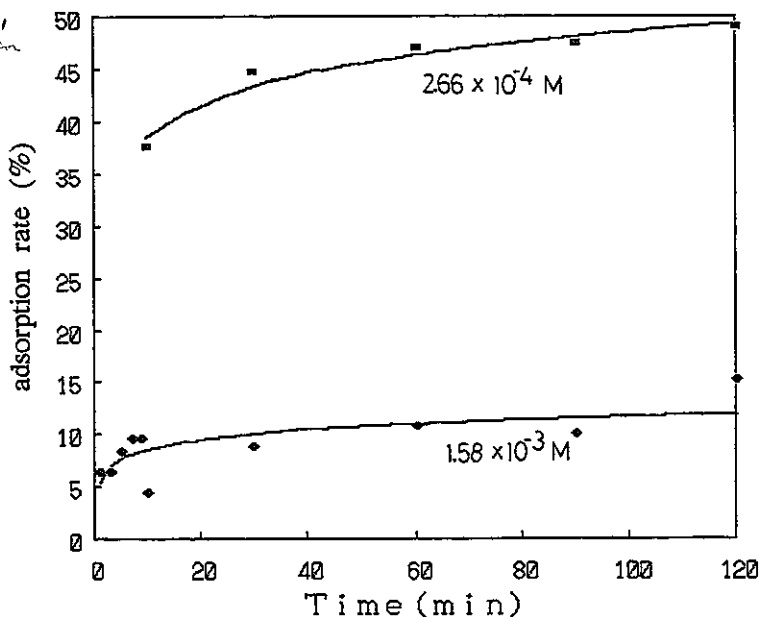
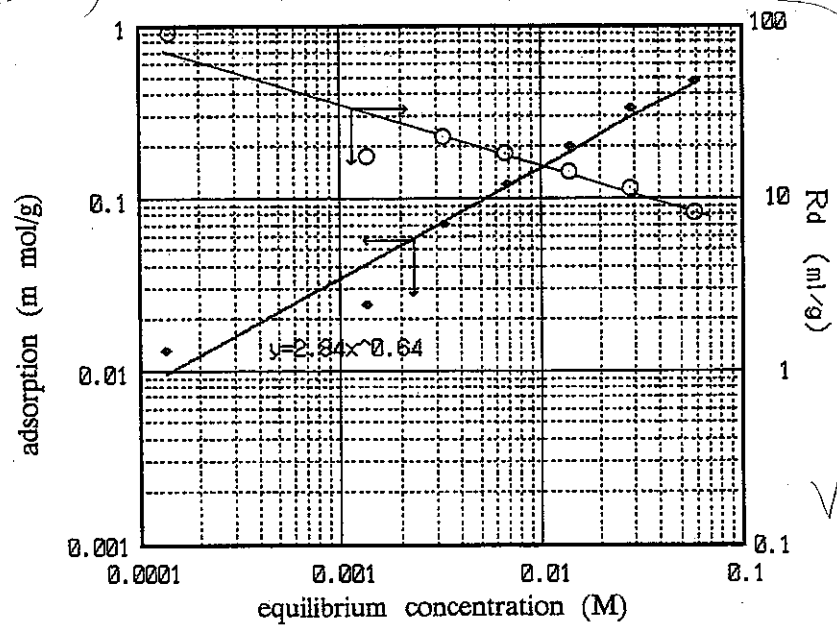


Fig. 2-2 Time Dependence of I⁻ Ion Adsorption on Cinnabar

2.4.2 Dependence of I⁻ Adsorption on Cinnabar on I⁻ Concentration

Experiments of I⁻ ion adsorption on cinnabar were carried out at various concentrations of I⁻ ions under L/S = 100, Temp. = 20 °C and immersing time = 2 h. The results are shown in Fig. 2-3. It was found that the amounts of I⁻ ions adsorbed increase with an increase in concentration, while the values of Rd decrease with increasing temperature. Furthermore, the plot in Fig. 2-3 shows that the relationship between W and C (equilibrium concentration) is expressed as follows :

$W = 2.84 \cdot C^{0.64}$



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濃度でなし、濃度では

W ←

Fig. 2-3 Dependence of I⁻ Adsorption on Cinnabar on I⁻ Concentration

2.4.3 Dependence of I⁻ Adsorption on Cinnabar on Temperature

Adsorption experiments of I⁻ ions on cinnabar were carried out at 20, 40, and 75 °C under the conditions, [I⁻] = 1.58 × 10⁻³ M and L/S = 16.7. The amounts of I⁻ ions adsorped were found to slightly increase with an increase in temperature.

2.4.4 Dependence of I⁻ Adsorption on Cinnabar on pH

The results of adsorption experiments at various pH show that cinnabar adsorbes I⁻ ions efficiently in acid solution and that the adsorption of I⁻ ions on HgS reagents do not take place in all pH region. This suggests that the adsorption on I⁻ ions on cinnabar is not due to HgS, which is a main component of cinnabar.

2.4.5 Effect of Coexistent Ions on I⁻ Adsorption on Cinnabar

12.7
12-22°C
10.22
In order to examine the effect of coexistent ions on I⁻ adsorption on cinnabar, the adsorption experiments of I⁻ ions were carried out in the solutions containing Cl⁻ ions at various concentrations. Experimental conditions are as follows :

[Cl⁻] = 2.82 × 10⁻³, 2.82 × 10⁻², and 2.82 × 10⁻¹ M ; [I⁻] = 1.58 × 10⁻³ M ; L/S = 16.7 ; Temp. = 20 °C ; immersing time = 2 h.

The existence of Cl⁻ ions was found to not affect the adsorption of I⁻ ions on cinnabar.

2.4.6 Adsorptivity of Pre-washed Cinnabar for I⁻ Adsorption

The amounts of I⁻ adsorped on pre-washed cinnabar are not different from those of cinnabar without washing treatment. This result suggests that the I⁻ adsorption on cinnabar is attributed to not the insoluble precipitation formed by reaction between I⁻ ions and eluted Hg species but some interactions between I⁻ ions and cinnabar.

2.5 Experimental Study on Adsorption of I⁻ Ions in Low Concentration

The adsorption experiments of I⁻ ions on cinnabar were carried out by using ¹²⁵I tracer. The solutions used in the experiments are as follows ; 1) distilled water containing ¹²⁵I tracer, 2) KI solution of 10⁻⁶ M, and 3) the artificial ground water shown in Table 2-15 (original report). The values of Rd were evaluated by following equation.

$$Rd = \frac{\text{blank (cpm)} - \text{supernatant solution (cpm)}}{\text{supernatant solutio (cpm)}} \times \frac{L \text{ (ml)}}{S \text{ (g)}}$$

The results are shown in Table 2-2.

Table 2-2 Adsorption Experiments by Using ^{125}I Tracer

samples	solutions	immersion time	p H	adsorption (%)	log R d
cinnabar	①	5 days	10.1	99.4	4.20
washed cinnabar	①	5 days	10.1	99.1	4.06
cinnabar	③	2 days	9.0	96.7	3.46
HgS reagent	②	2 days	8.7	25.9	1.54
HgS reagent	③	2 days	9.0	0	-

2.6 Adsorption Mechanism

The results mentioned above suggest that the adsorption of I^- ions on cinnabar is due to the formation of insoluble Hg_2I_2 .

3. Stability of Montmorillonite Containing Silver Thiourea Complexes and Its Adsorption Mechanism of I⁻ Ions

3.1 Chemical Form of Silver Thiourea Complex

3.1.1 Elemental Analyses

Elemental analyses of synthesized complex were carried out. The results are listed in Table 3-1 and indicate that the complex is [Ag(tu)₃]NO₃.

Table 3-1 Elemental Analyses of Silver Thiourea Complex

elements	C (%)	N (%)
experimental	9.1 ± 0.6	24.9 ± 0.9
theoretical		
[Ag(tu)]NO ₃	4.9	17.1
[Ag(tu) ₂]NO ₃	7.5	21.7
[Ag(tu) ₃]NO ₃	9.0	24.6
[Ag(tu) ₄]NO ₃	10.1	26.6

tu = thiourea

3.1.2 Coordination Structure of Silver Thiourea Complex

Structural studies were carried out using IR. Main absorption peaks are shown in Table 3-2. It is found that the peak due to C = S stretching shifts from 1,415.7 to 1,384.9 cm⁻¹ and that the peak assigned to CN stretching shifts from 1,471.7 to 1,489.0 cm⁻¹. These results suggest that the thiourea molecules coordinate to Ag through S in [Ag(tu)₃]NO₃.

Table 3-2 Main Adsorption Peaks of Thiourea and Silver Thiourea Complex

vibration type	wave number / cm ⁻¹	
	tu	[Ag(tu) ₃] (NO ₃)
NH ₂ bending	1614.4	1610.6
N-C-N stretching	1471.7	1489.0(w)
NH ₂ rocking		
N-C-N stretching	1415.7	1384.9(s)
C=S stretching		
N-C-N stretching		
NH ₂ rocking	1085.9	1101.4(w)
C=S stretching		
C=S stretching	731.0	715.6(s)
N-C-N stretching		

tu : thiourea

3.2 Preparation of Samples

The $\text{Ag}(\text{tu})_3^+$ solutions were prepared by adding solution (50 ml) of AgNO_3 (0.2 M) to solution (50 ml) of thiourea (2.0 M). Montmorillonite (5 g) was added to the complex solution, stirred and placed in dark place, followed by filtering. The adsorbents obtained were washed with distilled water or solution containing thiourea, followed by drying at 100°C .

The color of adsorbents changed from pale yellow to black with washing by distilled water. This phenomenon was considered to be due to the hydrolysis of $\text{Ag}(\text{tu})_3^+$ ions, because the hydrolysis products of silver ions change to Ag_2O with dryness.

3.3 Stability of Adsorbent

3.3.1 Batch Test

In the present experiment, montmorillonite and silver thiourea solution were mixed and the mixture was placed in the dark place for an appropriate time. After separation of solid phase by using glass filter, the solid was washed with distilled water or thiourea solution for 2 ~ 3 times. The concentrations of Ag^+ ions in the supernatant solution and filtrate were analyzed with ICP. The results are shown in Table 3-3 and indicate that 30% of complex prepared is contained in montmorillonite.

Table 3-3 Results of the Measurement of Ag^+ ions by ICP Method

	[Ag^+] / M			
	Sample 1	Sample 2	Sample 3	Sample 4
supernatant solution	0.0174	0.0174	0.0359	0.0422
first washed solution	0.0061	0.0069	0.0096	0.0107
second washed solution	0.0014	0.0020	0.0018	0.0019
third washed solution			0.0007	

3.3.2 Column Test

a) Experimental method

Adsorbents (0.1 g) prepared in 3.2 were packed in column and distilled water was made to flow through the column at 1.5 ml/min. The eluates from column were collected

by using fraction collector at 10 min intervals. Concentrations of Ag^+ ions in each eluate were analyzed by ICP method.

b) Experimental results

The results are shown in Table 3-4. As seen from Table 3-4, the amounts of Ag^+ ions eluted are relatively large and become constant with the progress of elution. This suggests that the silver thiourea complexes are present stably in montmorillonite unless the adsorbents are in contact with a large quantity of water.

Table 3-4 Eluents of Ag^+ ions from Montmorillonite Containing Silver Thiourea Complexes by Column Test

sampling time (min)	total flow (ml)	Ag^+ concentration (ppm)
0~10	15	6.88
10~20	30	0.0560
20~30	45	0.0525
30~40	90	0.0357
60~70	105	0.0301
140~150	225	0.0268
180~190	285	0.0250
240~250	375	0.0235
390~400	600	0.0240
990~1000	1500	0.0223

3.4 Experimental Study on Adsorption of I^- ions

3.4.1 Low Concentration System

a) Experimental method

The adsorbents (0.1 g) were added to the ground water or distilled water (10 ml) containing ^{125}I as the tracer. The mixtures were shaken for an appropriate time, followed by separating liquid phase by using ultrafiltration method. The radioactivities of filtrates were measured and used for evaluating the amounts of I^- ions adsorped.

b) Adsorbents

The adsorbents used in the present study are as follows :

- No. 1 : Complex impregnated montmorillonite (without washing)
- No. 2 : Complex impregnated montmorillonite (washing) — Sample 1
- No. 3 : Complex impregnated montmorillonite (washing) — Sample 2
- No. 4 : Complex impregnated montmorillonite (washing) — Sample 3

c) Artificial ground water

The artificial ground water was prepared by following the method used in PNC SJ 4262 90-001.

d) Experimental results

The results are summarized in Table 3-5.

Table 3-5 Adsorption Experiment of I⁻ ions by Using ¹²⁵I Tracer

samples	solutions	adsorption ratio (%)	logRd
No. 1	artificial ground water (pH=8.5)	94.5	3.24
No. 1	distilled water (pH=7.6)	99.6	4.43
No. 2	distilled water (pH=7.4)	99.3	4.15
No. 3	distilled water (pH=7.0)	99.2	4.12
No. 4	distilled water (pH=8.2)	39.6	1.82

3.4.2 High Concentration System

a) Experimental method

The adsorbents were added to the solution containing I⁻ ions of 10⁻³ M and the mixtures were shaken in a thermostat kept at 20 °C, followed by filtration. The concentrations of I⁻ ions in filtrates were measured using ion-chromatographic method. The adsorption ratio were calculated by using the following equation.

$$\text{Adsorption ratio (\%)} = \frac{([I^-] \text{ in sample}) - ([I^-] \text{ in filtrate})}{([I^-] \text{ in sample})} \times 100$$

b) Adsorbent

The adsorbents used in this experiment are Sample 4 prepared in 3.2.

c) Experimental results

The results are summarized in Table 3-6.

Table 3-6 Adsorption Experiment of I⁻ ions at High Concentration (10⁻³ M)

immersion time	adsorption ratio (%)	adsorption weight (mol/g)
1 min	41.6	4.16 x 10 ⁻⁵
10 min	53.6	5.36
60 min	53.0	5.30
24 hr	55.0	5.50
90 hr	52.2	5.22

Handwritten notes: 10³ M, 125, 42°C

3.5 Adsorption Mechanism

In order to examine the adsorption mechanism, studies on the structure of silver thiourea complex, the structure of complex in montmorillonite, the adsorption ratios of various adsorbents, and the assignment of products formed in montmorillonite were carried out. As a result, it was found that the complex synthesized is $[\text{Ag}(\text{tu})_3]\text{NO}_3$ and such a chemical form is maintained even in montmorillonite. In addition, the color of adsorbents was found to change from pale yellow to black with washing by water. This may be due to the hydrolysis of complex. The adsorption experiments showed that the adsorbents washed with water have adsorptivity superior to those washed with thiourea solution ~~and that the adsorption equilibrium is complete within 1 min.~~ From these results, it was supposed that the adsorption of I^- ions on the adsorbents is due to the compound formation between I^- ions and silver thiourea complex. The compound formed was considered to be chemical compounds other than AgI and AgIO_3 .

On the basis of the results mentioned above, the adsorption of I^- ions on the present adsorbents takes place through the diffusion of I^- ions into the montmorillonite layers and the formation of chemical compounds.

4. Adsorptivity of I^- ions on Inorganic Ion Exchangers

4.1 Ion Exchange Properties of Inorganic Ion Exchangers

Inorganic ion exchangers are classified into following six groups.

a) Multi-valence hydrate metal oxides

$MnO_2 \cdot nH_2O$, $TiO_2 \cdot nH_2O$, $Sb_2O_5 \cdot 4H_2O$, $ZrO_2 \cdot nH_2O$ and so on.

b) Acidic salts of metal (IV)

$M(H_2PO_4)_2 \cdot H_2O$ ($M = Ti, Zr, Sn, Ce$ and so on)

c) Heteropoly acid salts $HmXY_{12}O_{40} \cdot nH_2O$

12molybdophosphate and so on.

d) In soluble ferrocyanide

e) Synthetic aluminosilicate

- three dimensional cross-linked framework structure

- synthetic zeolites

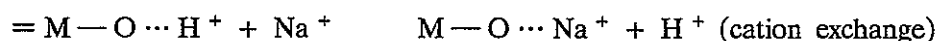
- two dimensional layer structure

- synthetic clay minerals, tobermorites

f) Others

synthetic apatites, hydrotalcites

The a) and f) groups of these ion exchangers are known to have the anion exchangeability. The materials of a) group are mainly synthesized by hydrolytic polymerization. The synthetic properties are dependent on first hydrolysis constants (K_1) of metal ions and solubility products (K_{sp}) of hydrous oxides (Fig. 4-1). The materials of a) group have the properties of anion, cation, or amphoteric ion exchange depending on the metal ions. The ion exchange reactions in the materials of group a) are expressed as follows :



These equations mean that the amounts of adsorption of cations and anions are

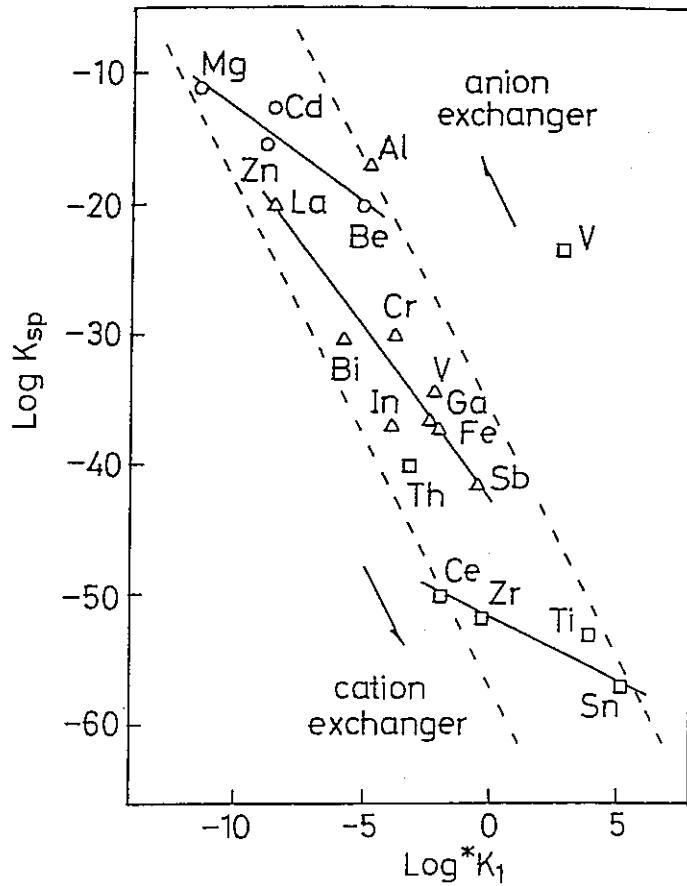


Fig. 4-1 Correlation between $\text{Log } K_{sp}$ of Hydrus Oxides and $\text{Log } *K_1$ of Central Metal Ions

o:divalent, Δ :trivalent, \square :tetravalent

K_{sp} :solubility product for hydrous oxide, L.G. Sillén and A.E.Martell, Stability Constants of Metal-Ion Complexes, special publ.No.17, 25 (1964).

$*K_1$: first hydrolysis constant of metal ions, C.F. Baes, Jr. and R.E.Mesmer, The Hydrolysis of Cations, Wiley, N.Y.(1976)

dependent on pH and that the adsorbents with high proton donicity serve as the cation exchangers. The proton donicity depends on the ^{donation} ~~valence~~ ^{charge} (Z) of metal (M) and the bond length (r) of M—O, the hydrous oxides composed of metal with large Z and small r function as the cation exchangers and those with small Z and large r act as the anion exchangers. Hence, it is expected that the hydrous metal oxides in upper side of Fig. 4-1 act as the anion exchangers and those in lower side serve as the cation exchangers.

4.2 Syntheses of Inorganic Ion Exchangers

In the present study, the following hydrotalcite compounds, i.e. $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$ $[A^{n-}_{x/n}mH_2O]^{x-}$ were synthesized, where Mg, Ni, Cu, Co, and Zn were used as divalent metal and Al, Fe, La, Bi, and Cr used as trivalent metal. The inorganic ion exchangers were synthesized by adding Na_2CO_3 solution to the solution containing metal salts.

4.3 Experimental Study on Adsorption of I^- Ions

4.3.1 Experimental method

Inorganic ion exchangers (0.1 g) were added to the KI solutions ($KI = 1 \times 10^{-6}$ M, 10 ml) or artificial ground water containing $^{125}I^-$ and soaked for 3 days at an appropriate temperature. After filtering, pH and radioactivity were measured. The Rd values were obtained from the following equation.

$$Rd = \frac{I_0 - I}{I} \times \frac{\text{Solution (ml)}}{\text{Exchanger (g)}}$$

where I is radioactivity (Bq/ml).

4.3.2 Results and discussion

The results are summarized in Table 4-1. As seen from this table, compounds of Mg-Bi system have the highest adsorption ratio. In the artificial ground water, Mg/Al and Mg/Bi compounds exhibit almost same adsorption ratio. The adsorption ratio of Mg/Bi in the artificial ground water is lower than that in the HI solution. This is due to the effect of coexistent ions. However, the adsorption ratio of Mg/Al increases in the artificial ground water. Further detail examination is necessary for the adsorption properties of Mg/Al compounds.

Adsorption Experiments of I^- ions on Inorganic Ion Exchangers

adsorbents	molar ratio	$1 \times 10^{-6} M$ KI solution		artical ground water	
		adsorption ratio (%)	equilibrium pH	adsorption ratio (%)	equilibrium pH
Mg/Bi ⁻	2:1	73.5	10.1	29.7	9.1
Mg/Fe	2:1	12.4	9.7	0	9.3
Mg/La	2:1	4.5	10.8	-	-
Mg/Cr	2:1	9.0	9.39	-	-
Mg/Al	6:2	9.8	8.2	27.1	9.0
Mg/Al	5:2	10.7	7.7	-	-
Mg/Al	4:2	11.7	7.3	-	-
Mg/Al	3:2	4.7	7.4	-	-
Ni/Al	2:1	7.5	7.5	-	-
Co/Al	2:1	6.1	7.4	-	-
Zn/Al	2:1	3.6	7.4	-	-
HTDD(H ⁺ type)**		9.3	7.1	-	-
HTDD(Na ⁺ type)**		11.4	6.7	-	-

- : unmesured

5. Hydrophobic Treatment on Surface of Fixation Materials for Radioactive Iodine and Its Leach Resistance

5.1 Preparation of Fixation Material

The materials for fixing radioactive iodine were prepared by impregnating porous styrene divinylbenzene polymer (SBP) particles with AgNO_3 solution, followed by drying and reducing Ag^+ to Ag metal. Iodine (200ppm) was fixed in this material at 130°C .

5.2 Measurements of Contact Angle

Measurement of contact angle is known as one of methods for assessing the hydrophobic property of materials. The powder technique was used for measuring the contact angles in the present study, because the present fixation materials are spherical particles. The contact angles (θ) were evaluated by the following equation.

$$\cos \theta = \frac{\gamma^\circ \rho h_m}{\gamma \rho^\circ h_m^\circ}$$

where γ , ρ , and h_m are surface tension, density, and height of liquid level, respectively.

Samples for measurements are SBP particles, Ag impregnated SBP, and Ag impregnated SBP adsorbed iodine. Each sample was powdered with agate mortar and the powdered samples were packed in the glass tube of 4.5 mm inner diameter and 30 cm long. The glass tube was placed vertically in distilled water for 10 days and the liquid level was measured. CCl_4 solvent was used as standard solution. Liquid level in CCl_4 solvent was 152 mm, while the rise of liquid level was not observed in the water. These results show that the present fixation materials are hydrophobic.

5.3 Leaching Properties

In order to examine the leach resistance of iodine fixation material (Ag impregnated SBP particles), iodine adsorbed particles were immersed in distilled water of 40 ml for an appropriate time at 20°C . The Ag concentration of liquid phase was measured with ICP. The results are shown in Table 5-1. The concentrations of Ag were found to be bigger

Table 5-1 Eluent of Ag^+ ion from Iodine Fixation Material

immersion time	Ag^+ ion	eluent ratio (%)
① 1 days	0.0265ppm(9.82×10^{-9} mol) (= 2.46×10^{-7} mol/l)	4.77×10^{-3} %
② 2 days	0.0450ppm(1.67×10^{-8} mol) (= 4.18×10^{-7} mol/l)	8.19×10^{-3} %
③ 3 day	0.0324ppm(1.20×10^{-8} mol) (= 3.00×10^{-7} mol/l)	5.88×10^{-3} %

calculated value from solubility product of AgI $[\text{Ag}^+] = 1.3 \times 10^{-8}$ mol/l

than that expected from the stability constant of AgI . This seems to be due to the following reasons :

- ① AgIO_3 , whose solubility is larger than that of AgI , was formed in the SBP particles.
- ② Unreacted Ag metal or AgNO_3 are still remained in SBP particles.

6. Summary

The results obtained from the present study are summarized as follows :

6.1 Cinnabar

- ① The adsorption of I^- ions on cinnabar takes place at the surface of cinnabar particles, where the precipitations with the reaction between I^- ions and Hg or other elements are not formed.
- ② The adsorption of I^- ions is not affected by increasing in temperature. This suggests that the adsorption is not due to the physical adsorption.
- ③ The adsorption of I^- ions is not affected by the coexistent ions. This indicates that the adsorption of I^- ions is not due to ion exchange.
- ④ The amount of I^- ions adsorped at equilibrium is about 10^{-5} mol/g, which is much lower than that of HgS contained in cinnabar. Iodide ions do not almost react with HgS reagent. These results suggest that the adsorption of I^- ions on cinnabar is not due to the reaction with the main component, i.e. HgS.
- ⑤ Element which can form insoluble compounds with I^- ions in cinnabar is only Hg.
- ⑥ The results in ①~⑤ suggest that the adsorption of I^- ions on cinnabar is attributed to the formation of insoluble Hg_2I_2 .
- ⑦ The value of Rd in the artificial ground water is 10^4 in low I^- concentration.

6.2 Montmorillonite Containing Silver Thiourea Complex

- ① Synthesized complex is $[Ag(tu)_3]NO_3$ (tu = thiourea).
- ② Basal spacing of montmorillonite is becomes wide with the impregnation of the complexes.
- ③ Ag ions in montmorillonite are leached out with the long contact with water.
- ④ The adsorption of I^- ions on this adsorbent is considered to be due to the formation of iodide compound with complex or hydrolysis products of complex.

6.3 Inorganic Ion Exchangers

- ① Various hydrotalcite compounds, which can adsorb selectively I^- ions, were synthesized.
- ② Compounds of Mg/Bi system have the highest adsorptivity in the synthesized hydrotalcite compounds.
- ③ In the ground water, the adsorptivity is decreased by the effect of coexistent ions.

6.4 Hydrophobic Iodine Fixation Materials

Hydrohobic materials are proposed as the leaching resistant materials for the iodine fixation. The low wetability of materials was confirmed by the measurements of contact angle. However, Ag ions were found to leach out from the surface in contact with water.