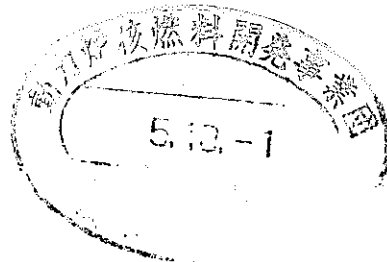Executive Summary

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

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A Study on the Migration of Iodine Species of
Various Chemistry Forms in Geological Media (V)

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Abstract

The present study has been carried out to establish the final disposal methods for the wastes containing radioactive iodines. In the previous studies, cinnabar (spain) and montmorillonite containing Ag-thiourea complex were selected as the artificial barrier materials. In the present report, the adsorption mechanisms of two adsorbents were studied in more detail. Furthermore, various synthetic inorganic ion exchangers were also examined as the model materials of I^- ion adsorbents. The results are summarized as follows :

1. Detail examination for I^- ion adsorption behavior of cinnabar
   ① In available cinnabars, only spain one has an adsorptivity to I^- ion.
   ② The cinnabar adsorbent has the selective adsorptivity to I^- ion.
   ③ It takes 40 days to reach the adsorption equilibrium.
   ④ The amount of adsorbed I^- ions decreases with the rise of pH, and the desorption of I^- ions from cinnabar is not observed. These results suggest that the adsorption of I^- ions on cinnabar is not due to the ion exchange but the compound formation.
   ⑤ Heat treatment of cinnabar results in a lowering of the adsorptivity. This suggests that the adsorption of I^- ion on cinnabar is due to the chemical reactions with Hg (I) compound.

2. Examination for the adsorption of I^- ion on the montmorillonite containing Ag-thiourea complex
   ① This adsorbent has the selective adsorptivity to I^- ion.
   ② The amount of adsorbed I^- ions is in excess of that of Ag in the adsorbent.
   ③ The pH of solution containing adsorbent changes from 4.3 to 8.6 with increasing the amount of adsorbed I^- ions.
   ④ In the IR spectra and XRD patterns of adsorbent, new peaks appear with increasing the amount of adsorbed I^- ions. This suggests that certain compounds are formed with the adsorption of I^- ion.
   ⑤ It seems that the adsorption of I^- ions on this adsorbent is attributed to the compound formation with the reaction between I^- ions and Ag-thiourea complexes and the formation of interaction sites with the intercalation of complex.

3. Adsorption mechanism of I^- ion in inorganic ion exchangers
   ① The compounds of Mg／Bi system, which have high adsoptivity to I^- ion, are bismustite-like compound.
   ② The adsorption of I^- ion on Mg／Bi compounds shows the anti-langmuir isotherm.
   ③ The adsorption reaction occurs exothermically.

CONTENT

1. Introduction

For the purpose of establishing the final disposal methods for the wastes containing radioactive iodines, various literature survay and experiments for obtaining basic data have been carried out. In the previous experiments, it was found that the adsorption content in equilibium of I^- ions on cinnabar is relatively low, around 10^{-5} mole/g, that the adsorption is not affected by the coexistent anions, and that the Kd value for I^- ions in the low concentration is 10^4 even under the groundwater environment. Furthermore, it was suggested that the I^- ion adsorption of cinnabar is not due to the reaction with HgS but Hg(I) compounds such as Hg_2S. In the montmorillonite containing Ag-thiourea complex, the Kd value for I^- ions in the low concentration was found to be 10^3 and the adsorptivity was suggested to be attributed to the reaction between I^- ions and the Ag-thiourea complex or the hydrolysis products. In the synthetic inorganic ion exchangers, the compounds of Mg/Bi system were found to be have high adsorptivity, while the adsorptivity decreases owing to the effect of coexistent anions. In spite of these informations, however, the adsorption mechanisms of cinnabar and montmorillonite with the Ag-thiourea complex have not been completely clarified. In the present study, the adsorption mechanisms of the above adsorbents were examined in more detail and furthermore the adsorption behavior of synthetic inorganic ion exchangers was investigated as the model compounds of I^- ion selective adsorbents.

2. Detail Examination of the Adsorption Behavior of I^- Ions on Cinnabar

2.1 Preparation of adsorbents and characterization

2.1.1 Grounding and Sieving

Three kinds of cinnabars (Spain, U.S.A, Mexico) were used in the present study. These cinnabars were grounded and sieved into four fractions, that is, 250 μm (60 mesh), 125 μm (120 mesh), 74 μm (200 mesh), and 37 μm (400 mesh).

2.1.2 Measurement of Hg content in cinnabars

Cinnabars were dissolved by aqua regia and the Hg concentrations were measured by ICP. The results are listed in Table 2-1. In the Mexican cinnabar, the undissolved residues are almost zero. This is due to the fact that the main phase of Mexican cinnabar is $CaCO_3$.

Table 2 — 1   Hg content in various cinnabars

Origin	Particle size (μm)	Hg Content (Wt%)	undissolved residue (Wt%)
Mexico	37~74	5.71	~0
U.S.A	37~74	52.1	26.6
Spain	37~74	27.7	58.1

2.1.3 Composition analyses of cinnabar with XRD and FT-IR

Composition analyses of cinnabars were carried out by using FT-IR and XRD. The spain cinnabar was found to be mixture of SiO_2 and HgS. The main component of U.S.A cinnabar was confirmed to be HgS. The main phase of Mexican cinnabar was found to be $CaCO_3$ (Calcite).

2.1.4 Measurements of specific surface areas

The surface area of cinnabar samples dried for 1 hr at 105 ℃ were measured by BET method. The results are shown in Table 2-2 and indicate that the surface area of cinnabar is relatively small.

Table 2 — 2 Specific surface areas

Sample	Surface area (m^2/g)
125~250 μ m	0.16
74~125 μ m	0.28
37~74 μ m	0.67
37 μ m under	1.36

### 2.1.5 Mineralogical analyses with microscope

The mineralogical analyses of cinnabars were carried out using microscope. The results suggest that the mineralization of Spain cinnabar is achieved for short time at relatively low temperature, and that the minerallization of U.S.A cinnabar was undergone for long time at relatively high temperature.

2.2 Buffer action of cinnabar

The pH values of solutions dispersed cinnabars are as follows :

Spain : 8.5, U.S.A : 9.5, Mexico : 9.7

The pH chanages with addition of acid and alkaline solutions to the dispersed solutions are shown in Fig. 2-1 and indicate that the buffer actions of U.S.A and Spain cinnabars are relatively strong. This is explained by the following reaction

$$- OH + H_2 O + X^- \rightarrow OH_2^+ \cdot X^- + OH^-$$
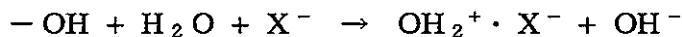
Hence, anions such as I^- ions are expected to be adsorbed on cinnabar in the low pH region.

2.3 Experiments for the adsorption of I^- and Cl^- ions

2.3.1 Experimental method

Adsorption experiments were carried out by batch method as follows. Cinnabars were charged into the solution containing ions and standed for an appropriate time, followed
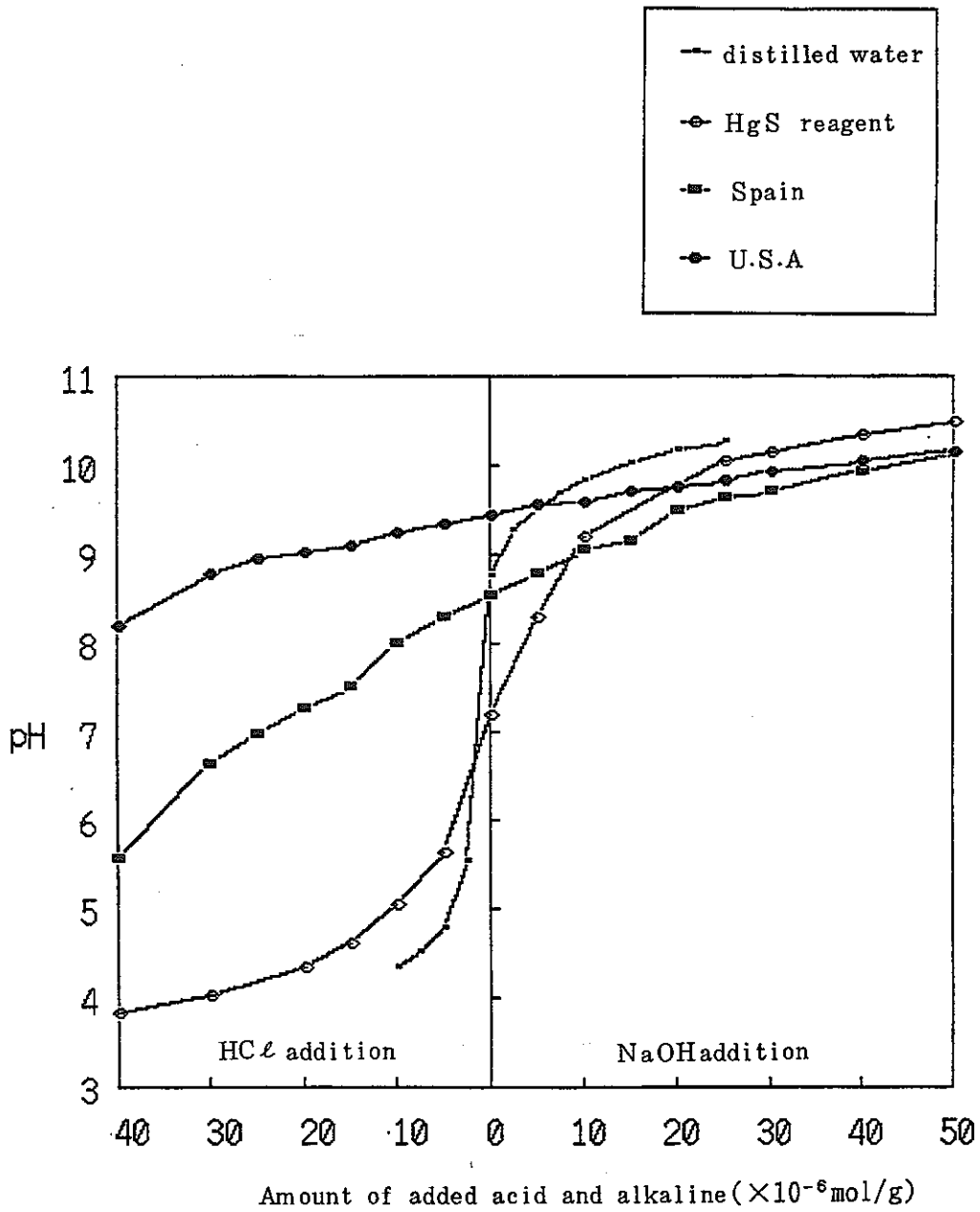
Fig, 2−1　Buffer action and ion exchange ability of cinnabar.

by filtration. The I^- ion concentrations in the filtrates were measured by ion chromatographic method. For the experiment in the low concentration region, [125] I tracer was used.

The distribution ratio, Rd (Kd), was estimated by the following equation.

$$Rd \ (m\ell /g) = \frac{\text{Initial conc.} - \text{Equilibrium conc.}}{\text{Equilibrium conc.}} \times \frac{\text{Volume of solution}}{\text{Weight of adsorbent}}$$

2.3.2 Adsorptivity of cinnabar

In the solution containing Cl^- and I^- ions (Cl^-, I^- : 1.0×10^{-5} M), I^- ions were adsorbed by only Spain cinnabar and Cl^- ions were not adsorbed by cinnabars used in the present experiment. The HgS reagent did not adsorb I^- ions.

2.3.3 I^- ion adsorption capacity in the equilibrium

The equilibrium adsorption capacity for I^- ions of Spain cinnabar (37-74 μm) was found to be 2.0×10^{-5} mole/g for initial concentration of $I^- = 5.0 \times 10^{-4}$ M. It was estimated to take 2 weeks to reach to equilibrium.

2.3.4 Adsorption isotherm

Figure 2-2 shows the plots of amount of adsorbed I^- ions vs. $[I^-]$ in equilibrium and indicates that it takes about 40 days to reach to equilibrium and that the saturated adsorption capacity is 6×10^{-5} mole/g, and suggests that the adsorption takes place in the Langmuir type.

2.3.5 pH dependence and desorption properties

Figure 2-3 shows the pH dependence in I^- adsorption and indicates that the adsorption capacity decreases with an increase in pH value. This phenomenon is compatible with that in the surface complex model.

Hence, the I^- desorption behavior of adsorbent was examined by adding alkaline solution. Even in the high pH region, the I^- ions were not desorbed from the adsorbent. This result suggest that the I^- adsorption is irreversible.

2.3.6 Effect of coexistent ions

The adsorption experiments were carried out in the coexistent system of Cl^- and I^- ions. It was clarified that the I^- adsorption is not affected by the existence of Cl^-.

2.3.7 Effect of particle size of cinnabar

The I^- adsorption on cinnabar is dependent of the particle size of cinnabar.

2.3.8 Adsorption properties of heated cinnabar

The I^- adsorptivity of cinnabar decreases with heating cinnabar at more than 100 ℃ and the cinnabar heated at 450 ℃ loses the adsorptivity to I^- ion. These results suggest that the adsorptivity is due to the interaction between I^- ions and the unstable Hg compounds in cinnabar.

Experimencal Conditions

initial$[I^-]$ = 2.0×10^{-4} M
initial$[I^-]$ = 5.0×10^{-4} M
initial$[I^-]$ = 1.0×10^{-3} M
initial$[I^-]$ = 2.0×10^{-3} M
L/S = 100
Temp : 25℃
Sample : Spain cinnabar

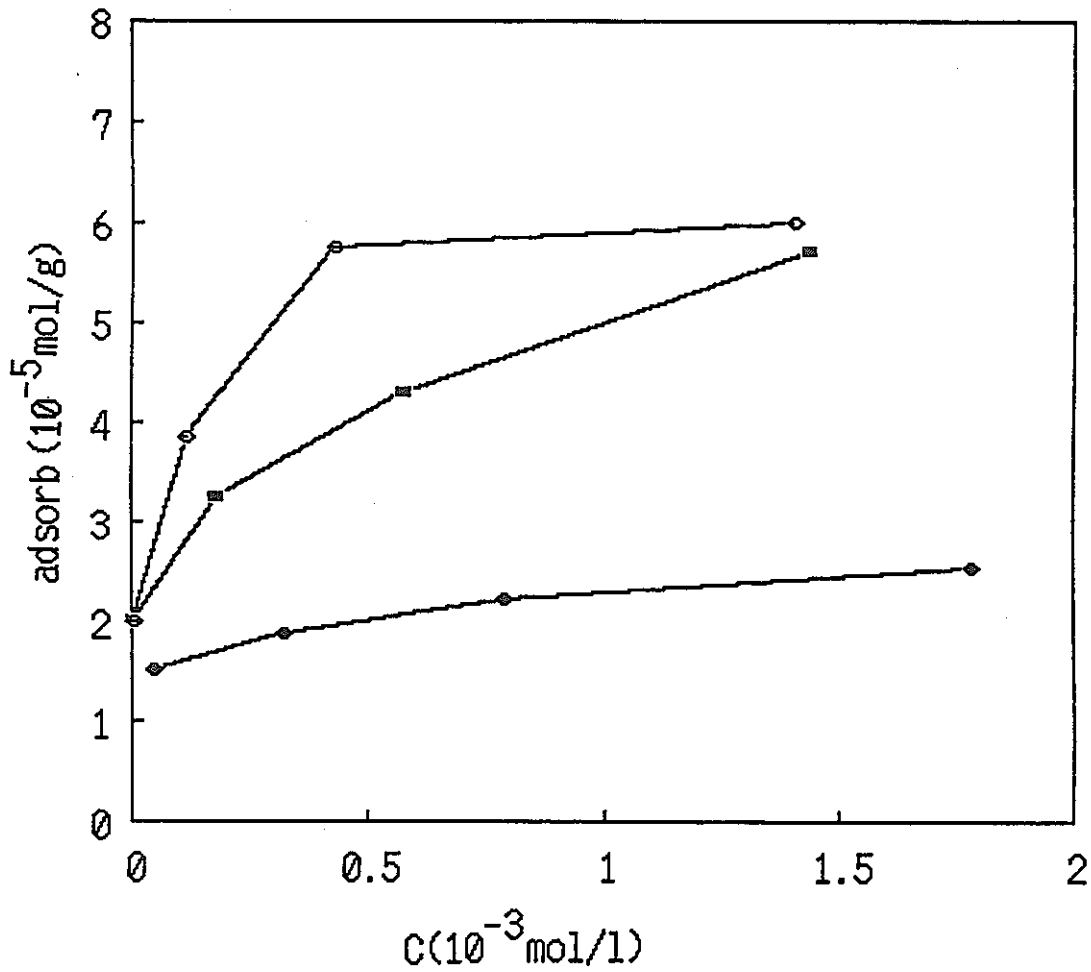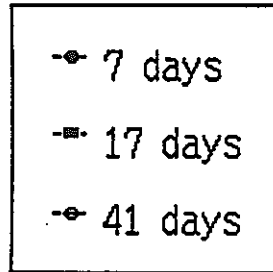-•- 7 days
-■- 17 days
-○- 41 days

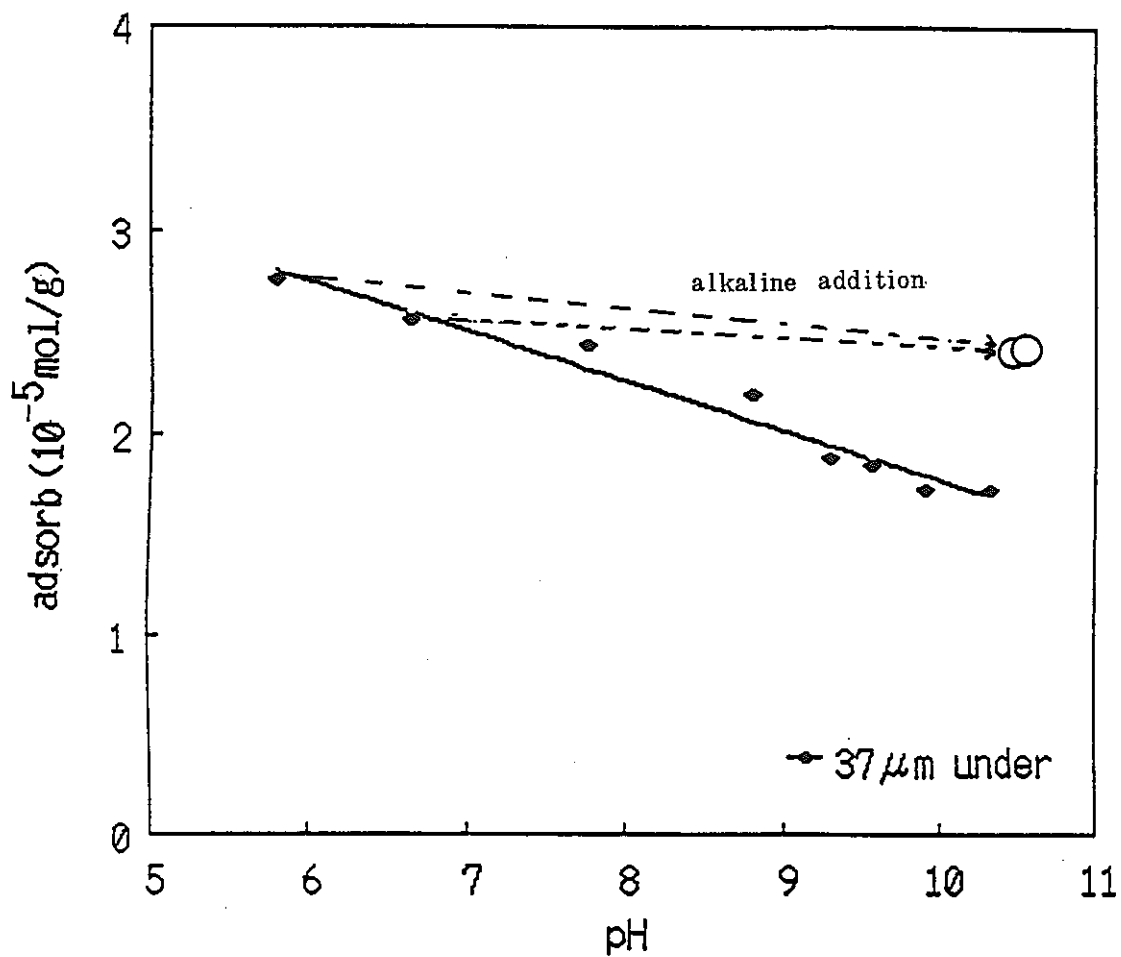Fig. 2−2 Adsorption isotherm of I^- ion on Spain cinnabar(37〜74μm)

Fig. 2−3 Irreversibility in I^- adsorption of cinnabar

Experimental conditions

・initial$[I^-] = 5.0 \times 10^{-4} M$

・L/S = 100

・Standing condition ： 25℃−3 weeks

2.3.9 I⁻ adsorptivity of synthetic cinnabar

The I⁻ adsorptivity of spain cinnabar was considerd to be due to the interaction between I⁻ ions and Hg(I) compounds of low thermal stability. Hence, thesynthetic cinnabar was preparaed by mixing SiO'$_2$ (50wt%), HgS (45wt%), and Hg$_2$Cl$_2$ (5wt%) and its adsorptivity to I⁻ ions was examined. As a result, the temperature dependence in adsorptivity of cinnabar was reproduced. However, it was not confirmed that the I⁻ adsorptivity of cinnabar is attributed to the reaction of I⁻ ions with Hg$_2$Cl$_2$.

2.4 Experiments for the adsorption of I⁻ ion in low concentrations

The adsorption experiments in low I⁻ concentrations (10^{-4}, 10^{-5}, and 10^{-6} M) were carried out using ^{125}I tracer. The results are shown in Table 2-3. The pH dependence in I⁻ adsorptivity of spain cinnabar was examined and the results are listed in Table 2-4. It was clarified that the pH dependence is bigger than that in high I⁻ concentrations.

Table 2-3　Adsorption experiments of I⁻ ions in cinnabar

Origin	Particle size	Adsorption ratio (%)	Kd (ml/g)
Spain	37 μm under	77.5	346.3
U.S.A	37 μm under	30.3	43.7

Initial[I⁻]=1.0×10^{-4} M, Soaking time : 20 days

Table 2-4　pH dependence of I⁻ adsorption in Spain cinnabar

pH	Adsorption ratio (%)	Kd (ml/g)
6.95	90.7	990.3
7.64	87.4	720.0
8.55	73.9	289.9
9.21	62.5	169.1
9.86	40.2	68.3
9.98	43.1	77.7
10.13	16.8	52.1
10.25	38.4	65.2

Soaking time : 20 days, Partide size : 37 ~ 74 μm ,

Initial[I⁻]=1.0×10^{-4} M

2.5 Consideration of adsorption mechanism

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

① the adsorptivity to I^- ions of spain cinnabar was highest of three kinds of cinnabars

② the time taken to reach the adsorption equilibrium was 20-40 days.

③ the saturated adsorption capacity was relatively low, i.e., 6.0×10^{-5} mole/g.

④ the adsorption isotherm showed the Langmuir curve.

⑤ the adsorptivity of cinnabar was found to depend on the grounding method. This was considered to be due to the difference in surface area.

⑥ the adsorptivity of cinnabar was found to decrease with an increase in pH.

⑦ the adsorption of I^- ions on cinnabar was irreversible.

⑧ the I^- ions was found to be adsorbed slightly on the U.S.A cinnabar.

⑨ the adsorption of I^- ions on cinnabar was not affected by the coexistent anions such as Cl^- ion.

⑩ the heat treatment of cinnabar at more than 100 ℃ resulted in decrease of I^- adsorptivity of cinnabar.

⑪ the elution of Na^+ ions with the adsorption of I^- ions was not observed.

⑫ In the synthetic cinnabar (SiO_2 +HgS+Hg_2Cl_2), the decrease in adsorptivity with heating was reproduced.

⑬ the elution of Cl^- ions with I^- adsorption was observed in the synthetic cinnabar, while such a phenomenon was not observed in Spain cinnabar.

From these results, the I^- adsorptivity of cinnabar is supposed to be due to the interaction between I^- ions and Hg(I) compounds in cinnabar.

3. Examination for the Adsorption of I^- Ion on the Montmorillonite Containing Ag-thiourea Complex

3.1 Preparation of adsorbent

The adsorbent was prepared as follows. The $AgNO_3$ solution (0.2M, 50 ml) was poured into the thiourea solution (0.2M, 50 ml), followed by addition of an appropriate amount of montmorillonite. The slurry solution was stirred for an appropriate time in the dark, followed by filtration with glass filter. The obtained solid was washed with distilled water and dried in vacuo at 50 ℃ .

The analyses of adsorbent prepared were carried out using XRD and FT-IR. It was confirmed that the Ag-thiourea complexes are impregnated into montmorillonite and that the thiourea molecules coordinate to Ag^+ through S in Ag-thiourea complex.

3.2 Ag content in adsorbent

Two kinds of adsorbents (sample 1 and 2) were dissolved by HF solution. The Ag concentrations in solutions were measured with ICP. The Ag contents in Sample 1 and 2 were found to be 2.0 and 9.7wt%, respectively.

3.3 Experiments for adsorption of I⁻ ion

The I⁻ adsorption experiments for the adsorbents were carried out by batch method. The following solutions were used in the present experiments.

① $[NaI]=1.0 \times 10^{-2}$ M

② $[NaI]=7.5 \times 10^{-3}$ M $[NaCl]=2.5 \times 10^{-3}$ M

③ $[NaI]=5.0 \times 10^{-3}$ M $[NaCl]=5.0 \times 10^{-3}$ M

④ $[NaI]=2.5 \times 10^{-3}$ M $[NaCl]=7.5 \times 10^{-3}$ M

⑤ $[NaI]=1.0 \times 10^{-3}$ M $[NaCl]=9.0 \times 10^{-3}$ M

⑥ $[NaI]=5.0 \times 10^{-4}$ M $[NaCl]=9.5 \times 10^{-3}$ M

3.4 Results and Discussion

In order to examine the adsorptivity to I⁻ and Cl⁻ ions of the present adsorbents, the adsorption capacity (the amount of adsorbed anions (mole) / adsorbent (1g)), the adsorption ratio (the concentration of adsorbed I⁻ or Cl⁻) / the initial concentration of I⁻ or Cl⁻, %), the reaction ratio (the ratio of complexes reacted with I⁻ or Cl⁻, %) were evaluated and are listed in Table 3-1.

$$\text{Reaction ratio} = \frac{\text{the amount of adsorbed I}^- \text{ or Cl}^- \text{ (mole)}}{\text{the amount of complexes in the adsorbent (mole)*}} \times 100$$

* : (the amount of adsorbent used) × (Ag content (wt%)) / 107.87

Table 3－1 Anion Adsorptivity of Sample 1 (7 day soaking)

system	anion	amount of adsorption (mole/g)	adsorption ratio (%)	reaction ratio (%)
2	I⁻	4.03×10^{-4}	38.4	217
	Cl⁻	–	–	–
3	I⁻	3.52×10^{-4}	44.5	189
	Cl⁻	–	–	–
4	I⁻	2.83×10^{-4}	52.8	152
	Cl⁻	–	–	–
5	I⁻	1.86×10^{-4}	71.9	100
	Cl⁻	–	–	–
6	I⁻	9.05×10^{-5}	89.6	49
	Cl⁻	–	–	–
7	I⁻	4.31×10^{-5}	86.2	23
	Cl⁻	8.00×10^{-6}	0.9	4.3
8	I⁻	6.58×10^{-4}	32.9	355
	Cl⁻	–	–	–

The results of the adsorption experiments and the analytical data obtained from XRD and FT-IR measurements are summarized as follows :

- the adsobents have the selective adsorptivity to I^- ions.
- the pH of aqueous solution containing the adsorbent is 4.5-5.5, while the pH value increases with the adsorption of I^- ions.
- In the adsorption experiments of I^- ions in the high concentrations, the I^- ions more than stoichiometrical amount were adsorbed on the adsorbents. This result suggests that the interaction sites with I^- ions except for the Ag-thiourea complex are formed with the intercalation of complex into montmorillonite.
- It was found from XRD measurements that the new compound is formed in the adsorbent with the adsorption of I^- ions and that the basal spacing of adsorbents decrease from 18 Å to 13 Å with an increase in the amount of adsorption of I^- ions.
- the measurement of IR spectra showed that the new compound is formed by I^- adsorption and the new IR signals appear at 1,408 and 696 cm^{-1} with I^- adsorption.

## 4. Exchange adsorption for iodide on synthetic inorganic ion exchangers

4.1 Ion exchange properties of double hydroxide hydrates

The following compounds have been known as synthetic inorganic ion exchangers : a) hydrous oxides of multivalent metals, b) acid salts of tetravalent metals, c) heteropoly acid salt, d) insoluble ferrocyanides, e) synthetic aluminosilicates, f) others (synthetic apatite, hydrotalcites, and so on). Of these exchangers, compounds belonging to the groups of a and f show the anion exchange properties.

The compounds with the brucite layered structure have been the present subject for the ion exchange properties. The deficient charge responsible for the anion exchange properties was generated by substitution with Al^{3+} and other trivalent metal ions in the brucite layer and the high basicity was utilized for the materials design. These ions have been known as superconducting layered oxide. La^{3+} and Bi^{3+} were also studied for its substitution in the layered structute. These M^{3+}-substituted materials were studied as anion exchangers.

4.2 Synthesis of ion exchangers

A group of M^{3+}-substituted compounds in the $Mg(OH)_2$ brucite layer has been known as a hydrotalcite-like compound (HT). The HT phase has the chemical composition of

$$[M^{2+}_{1-R} M^{3+}_R (OH)_2]^{R+} [(R/n)A^{n-} \cdot mH_2O]^{R-},$$
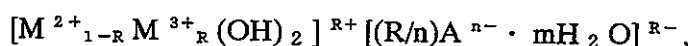
where the value of R depends on the combination of divalent and trivalent metal ions. Mg, Ni, Cu, Co and Zn as the divalent metals, and Al, Fe, La, Bi and Cr as the trivalent metals were used for synthesis. The precipitate was allowed to form by adding

Na_2CO_3 solution to the mixed solution of the nitrates. It was aged for a few days, filtered and air-dried for crystallization. Synthetic apatite (IXE 1000) was supplied by TOA GOSEI Ltd.

4.3 Experimental procedure of adsorption

Adsorption experiments were carried out for iodide in the presence of bicarbonate which is one of the predominant species in the ground water environment. A 0.100g portion of the exchanger was equilibrated with $(KI+KHCO_3)$ mixed solution for 3 days at 30, 45 or 60 °C. After attaining the steady state concentration, an aliquot of the supernatant solution was determined for I^- by the neutron activation analysis or the argenometry.

4.4 Results and discussion

The previous report described high selectivity towards I^- on Bi-based compound in $KHCO_3$ media. A comparison has been made for the % adsorption of I^- on five adsorbents in mixed solution of $(10^{-4}$ N $KI+0.01N$ $KHCO_3)$ in Table 4-1. The adsorption is largely different, depending on the compound, and the affinity is found to increase in the order of

$$MgAl < CoBi < IXE \ll ZnBi < MgBi.$$

A group of ZnBi and MgBi showed an increased selectivity in comparison with other compounds.

The XRD pattern of the MgBi adsorbent is similar to that of bismutite, and so carbonate ions are possibly involved in the uptake of I^-. The commercially available chemical, bismuth oxide carbonate (bismutite), was tested for uptake of Cl^-, Br^- and I^- (table 4-2). However, the adsorption selectivity of bismutite was low (uptake 0.01 meq/g) against the expectation, indicating a surface adsorption for these ions. Therefore, MgBi and related compounds found in the present work are different from the bismutite in respect to the ion-exchange properties and active sites. These considerations lead to the conclusion that they are new type of adsorbent showing selectivity towards halides in bicarbonate solution.

The adsorption isotherm of the MgBi compound was revealed for I^- at 25, 45 and 60 °C (Fig. 4-1). All the isotherms were in anti-Langmuir type and showed a weak interaction with adsorption sites in the crystal lattice. The temperature dependence of the selectivity was negative and the selectivity was lowered with increase in the temperature. The adsorption was the exothermic reaction in the temperature range studied.

Table 4-1   Affinity of several inorganic ion exchangers toward I⁻

Sample	% uptake
MgBi	40 ± 1
ZnBi	24 ± 0.5
IXE	4.2 ± 0.2
CoBi	2 ± 0.4
MgAl	1.8 ± 1.7

Table 4-2   Affinity of bismutite ($Bi_2O_2CO_3$) toward Cl^-, Br^- and I^-

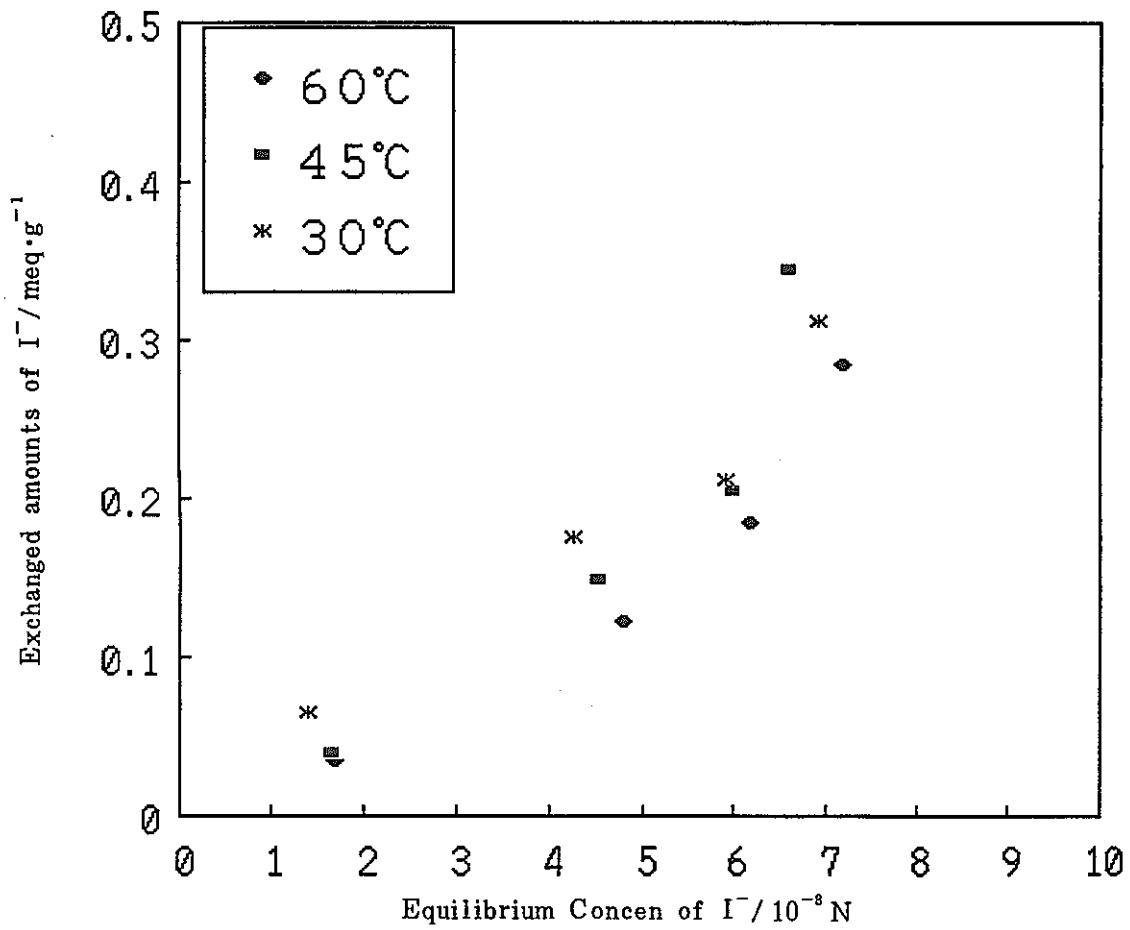| Ion	Equil.concn./N	Uptake/meq g⁻¹
I⁻	1.88×10^{-3}	0.011
Br⁻	1.86×10^{-3}	0.014
Cl⁻	1.93×10^{-3}	0.006

Fig. 4－1　Exchange adsorption of I⁻ by MgBi compound
in （KI＋KHCO₃）mixed solution