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ARTICLE

U(VI) Leaching from Uranium-Containing Sludge by using Aqueous Carbonate Solution

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Many kinds of uranium-bearing waste are generated from uranium fuel-fabrication facilities. Sludge wastes, especially silica and iron sludges, contain high uranium concentrations. This research examined leaching of U(VI) from the sludge wastes by using aqueous carbonate solution, in which U(VI) was dissolved as stable uranyl carbonate complexes. The effects of the solution temperature and Na_2CO_3 concentration on the U(VI) leaching ratio were investigated. Based on the experimental results, the leaching mechanism and optimal leaching conditions are discussed.

KEYWORDS: uranyl carbonate, Na_2CO_3, uranium-bearing waste, silica sludge, iron sludge

I. Introduction

Uranium fuel-fabrication facilities, including those in which uranium fluoride is converted to uranium oxide, generate various types of uranium-bearing waste, such as sludges from waste solution treatment and incinerated ash.1) The sludge wastes are produced when uranium-bearing waste solutions are treated by coagulation and precipitation of U(VI). Iron sludge is treated by adding Fe(III) to acid waste solution, and then NaOH is used to coprecipitate U(VI) with Fe(III) hydrolysis products. For silica sludge, a sodium silicate solution is used to neutralize the acid waste solution, forming a gelatinous precipitate that contains U(VI).

In 2018, a survey of waste generation over the next 30 years was conducted across fuel-fabrication facilities in Japan. Iron sludge is expected to be the main waste, with the largest amount of over 400 tons in the various types of waste generated by the facilities until 2048.2) The amount of silica sludge generated is expected to be over 70 tons by 2048, and its uranium concentration is high; 64% of silica sludge has a specific activity of 10^3 to 10^4 Bq/g.2)

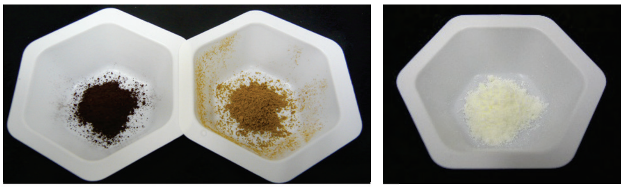
Following disposal, uranium-bearing waste is expected to remain radioactive because of the long life of uranium nuclides. Therefore, the U(VI) concentration in the sludge must be reduced, and it is necessary to develop methods for removing uranium from uranium-bearing waste.

We propose U(VI) leaching from the sludges by using alkaline carbonate solution as a method for the removal of uranium. U(VI) forms stable uranyl carbonate complexes in carbonate solution.3, 4) It is expected that immersing the sludge in carbonate solution will leach U(VI) selectively from the sludge matrix into the solution as $UO_2(CO_3)_3^{4-}$. In this research, U(VI) leaching from simulated iron sludge and silica sludge using Na_2CO_3 and $NaHCO_3$ solution is examined. Based on the experimental results, the leaching mechanism and optimal leaching conditions are discussed.

II. Experimental

1. Preparation of Simulated Sludge

Uranyl nitrate solution was made by dissolving U_3O_8 in HNO_3. Then, $FeCl_3{\cdot}6H_2O$ in 0.1 M (M = mol/L) HNO_3 was mixed with the uranyl nitrate solution. NaOH solution was added to the Fe(III) and U(VI) solution until neutralization was complete. Next, Fe(III) hydrolysis products were generated and U(VI) was coprecipitated. After overnight aging, the precipitate was separated from the solution by filtration and was dried at 383 K. The dried precipitate was ground to a powder with an agate mortar and pestle and used as simulated iron sludge. Two simulated iron sludges were prepared with uranium contents of 4.58wt% and 9.62wt%. The uranium content was evaluated as the weight percentage of loaded uranium in the sludge. A photograph of the simulated iron sludge is shown in **Fig. 1**.



4.58wt% uranium 9.62wt% uranium
iron sludges

3.38wt% uranium
silica sludge

Fig. 1 Photographs of the simulated iron sludges (left) and the simulated silica sludge (right).

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Simulated silica sludge was prepared as follows. Sodium silicate solution (about 38%) was added to the uranyl nitrate solution until a gelatinous precipitate appeared. The solution pH was adjusted to around 5 by using HNO_3 and sodium silicate solution. After overnight aging, the precipitate was recovered by filtration and dried at 383 K. The dried precipitate was ground to a powder and used as the simulated silica sludge. The uranium content of the simulated silica sludge was 3.38wt% and a photograph is shown in Fig. 1.

Table 1 Leaching experiment conditions for the simulated iron sludge and simulated silica sludge

Sludge	U content (wt%)	Leachate	Temperature (K)
Iron sludge	4.58	1 M Na_2CO_3 1 M $NaHCO_3$	323, 343, 363
	9.62	1 M Na_2CO_3 1 M $NaHCO_3$	323, 343, 363
Silica sludge	3.38	1 M Na_2CO_3 1 M $NaHCO_3$ 1:1 mixed solution^a	323
		0.1 M Na_2CO_3	323, 343, 363
		0.5, 0.6, 0.7, 0.9 M Na_2CO_3	323

^{a}1:1 mixed solution: 1:1 v/v mixture of 1 M Na_2CO_3 and 1 M $NaHCO_3$.

2. Leaching Experiment and Analysis

The experimental conditions are listed in **Table 1**. Na_2CO_3 or $NaHCO_3$ solution, or a 1:1 v/v mixture of 1 M Na_2CO_3 and 1 M $NaHCO_3$ was used as the leachate. The carbonate solution was put in a glass flask and the solution was agitated with a mixing impeller at 300 rpm under a constant temperature maintained by a heating mantle or hot plate. The sludge (1 g) was added to the carbonate solution (100 mL). At various intervals, a portion of the solution was sampled through a syringe filter. The same volume of fresh solution as was withdrawn was added to the flask to maintain the solution volume. The U(VI) concentration in the solution was analyzed by a spectrophotometric method with Arsenazo III color-producing reagent.[5)] The amount of leached uranium from the simulated sludge was calculated by Eq. (1).

$$M_n = [\mathrm{U}]_n \times V + \sum_{i=1}^{n-1} ([\mathrm{U}]_i \times V_i) \qquad (1)$$

Here, M_n is the total amount of leached uranium at the n^{th} sampling, V is the volume of the solution in the flask, V_i is the sampling volume of the i^{th} sample, and $[\mathrm{U}]_n$ and $[\mathrm{U}]_i$ are the U(VI) concentrations at n^{th} and i^{th} samples, respectively. The uranium leaching ratio, R_L, was calculated by Eq. (2).

$$R_L = \frac{M_n}{W_0 \times C_0} \qquad (2)$$

Here, W_0 and C_0 are the weight of the simulated sludge and the uranium content ratio in the simulated sludge, respectively.

After the leaching experiment, the residual sludge in the flask was recovered by filtration and was air-dried at room temperature. The ratio of residual sludge, R_r, was calculated by Eq. (3).

$$R_r = \frac{W_r}{W_0} \qquad (3)$$

Here, W_r is the weight of the residual sludge.

Infrared spectra of the simulated sludge and the residual sludge were analyzed by attenuated total reflection Fourier transform infrared (FTIR) spectroscopy (FT/IR-4100, JASCO). The pure chemicals Fe(III) α-oxyhydroxide (α-FeOOH, Kojundo Chemical Laboratory), Fe(III) oxide (Fe_2O_3, Sigma-Aldrich), and silicon dioxide (SiO_2, Fujifilm Wako Pure Chemical) were also analyzed by FTIR spectroscopy.

III. Results and Discussion

1. Iron Sludge

(1) Leaching Experiment

Leaching of U(VI) from the simulated iron sludge containing 4.58wt% uranium by using 1 M Na_2CO_3 or 1 M $NaHCO_3$ solution was examined at several different temperatures. The time evolution of the leaching ratio is shown in **Fig. 2**. The U(VI) leaching ratio was higher at higher temperatures. There was no significant difference between Na_2CO_3 and $NaHCO_3$ in the U(VI) leaching behavior. At 363 K for 4 h, the U(VI) leaching ratio was 88% in 1 M Na_2CO_3 and 94% in 1 M $NaHCO_3$.

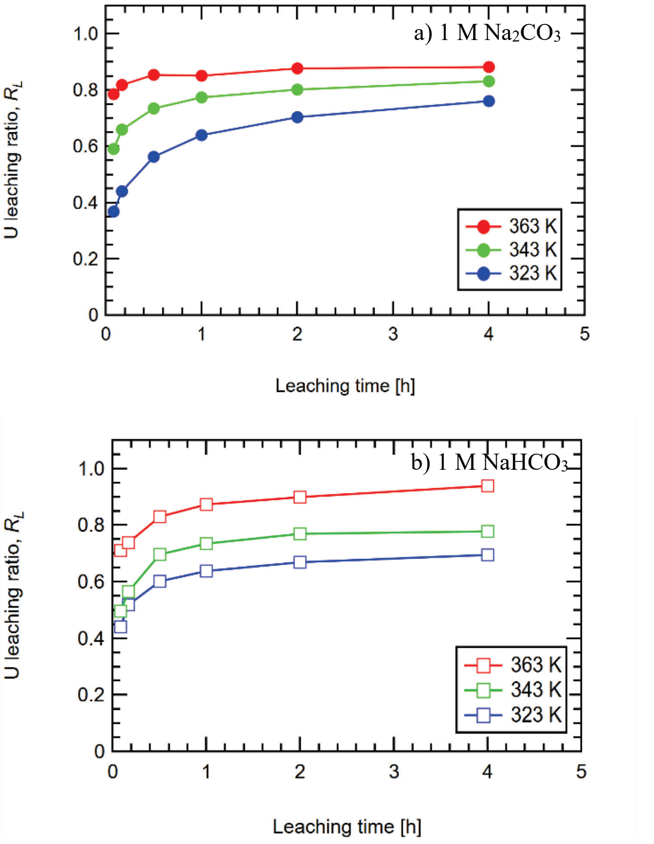

Fig. 2 Uranium leaching ratio of the 4.58wt% uranium simulated iron sludge, a) in 1 M Na_2CO_3 solution, b) in 1 M $NaHCO_3$ solution, at different temperatures.

Table 2 Uranium leaching ratio and ratio of residual sludge of the 4.58wt% uranium simulated iron sludge after 4 h

Leachate	Temperature (K)	Uranium leaching ratio, R_L (%)	Ratio of residual sludge, R_r (%)
1 M Na_2CO_3	323	76.1	99.3
	343	83.2	100.3
	363	88.3	102.5
1 M $NaHCO_3$	323	69.5	96.1
	343	77.9	98.5
	363	93.9	99.4

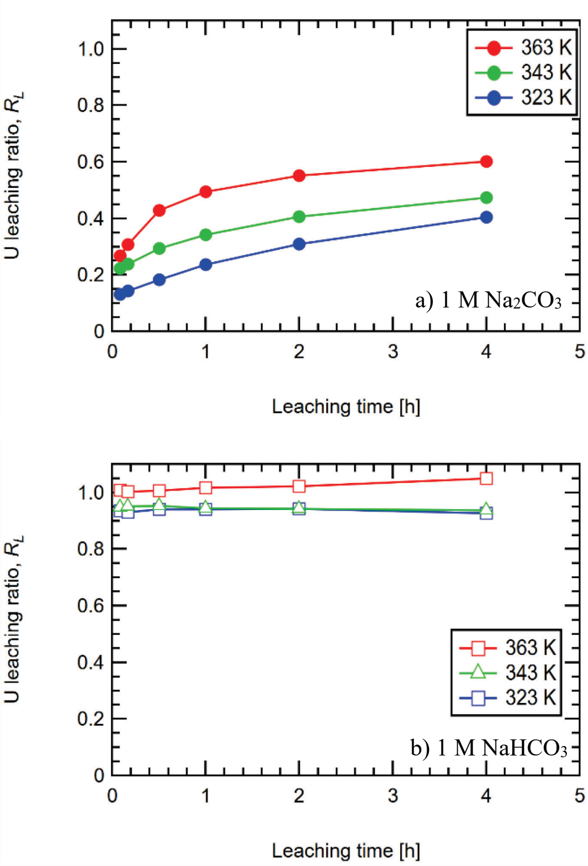

Fig. 3 Uranium leaching ratio of the 9.62wt% uranium simulated iron sludge, a) in 1 M Na_2CO_3 solution, b) in 1 M $NaHCO_3$ solution, at different temperatures.

Table 3 Uranium leaching ratio and ratio of residual sludge of the 9.62wt% uranium simulated iron sludge after 4 h

Leachate	Temperature (K)	Uranium leaching ratio, R_L (%)	Ratio of residual sludge, R_r (%)
1 M Na_2CO_3	323	40.5	90.1
	343	47.4	94.8
	363	60.1	101
1 M $NaHCO_3$	323	92.8	85.0
	343	93.7	85.8
	363	105	87.2

After the leaching experiment, the residual sludge was recovered and weighed. The ratios of residual sludge and U leaching ratios are listed in **Table 2**. Over 95% of the sludge was recovered at each temperature; therefore, only uranium was leached from the simulated iron sludge by using carbonate solution.

Figure 3 shows the results of the leaching experiment with the simulated iron sludge containing 9.62wt% uranium. The U(VI) leaching ratio with 1 M Na_2CO_3 gradually increased with time, and the ratio increased with the solution temperature. At 363 K for 4 h, 60% of U(VI) was leached. In contrast, the U(VI) leaching ratios for 1 M $NaHCO_3$ were high from the beginning of the experiment. At 323 and 343 K, over 90% of U(VI) was leached, and at 363 K the leaching ratio was 100%. The uranium in the simulated iron sludge was immediately leached by 1 M $NaHCO_3$. The residual ratio of the sludge was over 90% for 1 M Na_2CO_3 and 85% for 1 M $NaHCO_3$ (**Table 3**). Therefore, U(VI) was selectively leached from the simulated sludge.

(2) FTIR Spectroscopic Studies

The 4.58wt% uranium iron sludge was a different color from the 9.62wt% uranium iron sludge (Fig. 1). The chemical species of components in the sludge were expected to be different. To obtain qualitative information about the species, the FTIR spectra of the simulated iron sludge and the residue of the leaching experiment in 1 M $NaHCO_3$ at 363 K were measured.

Figure 4 shows the FTIR spectra for the 4.58wt% uranium iron sludge. For reference, Fe_2O_3 was also measured by FTIR spectroscopy. The spectrum of the 4.58wt% uranium sludge was similar to that of the residue, from which 94% of uranium was removed. The FTIR spectra showed characteristics of the Fe(III) chemical structure. The tail of the peak at around 500 cm^{-1} was consistent with that of Fe_2O_3 and was assigned to the Fe-O bond.[6)] Therefore, the main component of the 4.58wt% uranium iron sludge was expected to be Fe_2O_3.

Figure 5 shows the FTIR spectra for the 9.62wt% uranium iron sludge with α-FeOOH as a reference. The spectra of the 9.62wt% uranium iron sludge and residue were comparable and consistent with the spectrum of α-FeOOH. Two peaks at 790 and 890 cm^{-1} were assigned to the Fe-O-H bond.[6)]

Lam et al. mentioned that uranium atoms were incorporated into the Fe_2O_3 structure via substitution of an iron atom during coprecipitation of U(VI) and Fe(III) at a low uranium content,[7)] whereas they suggested that U(VI) was weakly adsorbed on the precipitate surface at a high uranium content. Therefore, it can be expected that uranium atoms are incorporated in the Fe_2O_3 structure for the 4.58wt% uranium iron sludge. In the 9.62wt% uranium iron sludge, the major species in the sludge was α-FeOOH, and U(VI) in α-FeOOH may be easily dissolved in a weakly alkaline solution, such as $NaHCO_3$ solution. Leaching behavior differed between Na_2CO_3 and $NaHCO_3$, and the state of U(VI) in the sludge and the leaching mechanisms were not clear.

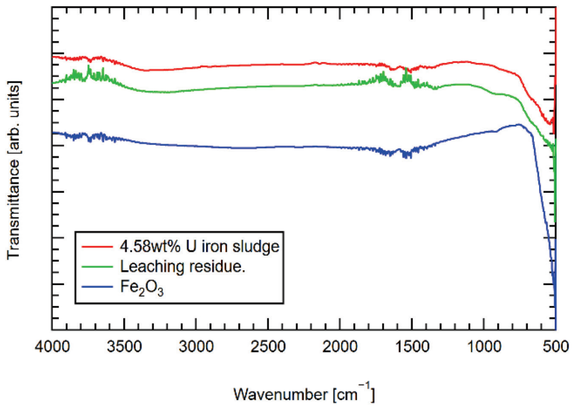

Fig. 4 IR spectra of the 4.58wt% uranium simulated iron sludge, the residue of the leaching experiment, and Fe_2O_3. The residue was obtained by leaching at 363 K in 1 M $NaHCO_3$.

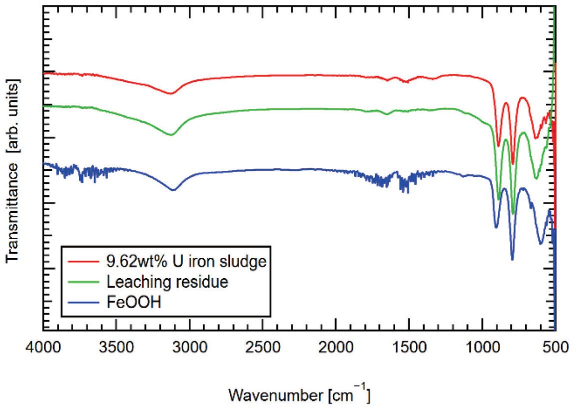

Fig. 5 IR spectra of the 9.62wt% uranium simulated iron sludge, the residue of the leaching experiment, and α-FeOOH. The residue was obtained by leaching at 363 K in 1 M $NaHCO_3$.

2. Silica Sludge

(1) Leaching Experiment

Figure 6 shows the time evolution of the uranium leaching ratio in the simulated silica sludge for 1 M Na_2CO_3, 1 M $NaHCO_3$, and a 1:1 v/v mixture of 1 M Na_2CO_3 and 1 M $NaHCO_3$. In 1 M Na_2CO_3, the leaching ratio was 91.3% after 4 h. Even under the same conditions, in 1 M $NaHCO_3$ or the 1:1 mixed solution, the leaching ratio was only around 40%. Na_2CO_3 solution was suitable for the leaching of uranium in the simulated silica sludge. The temperature dependence was examined in 0.1 M Na_2CO_3 as the leachate. In this solution, the carbonate concentration was sufficient for the leached U(VI) to exist as carbonate complexes. The results are shown in **Fig. 7**. The solution temperature caused an increase in the leaching rate. At 363 K, almost 50% of uranium was immediately leached from the silica sludge, and the ratio remained the same after 4 h.

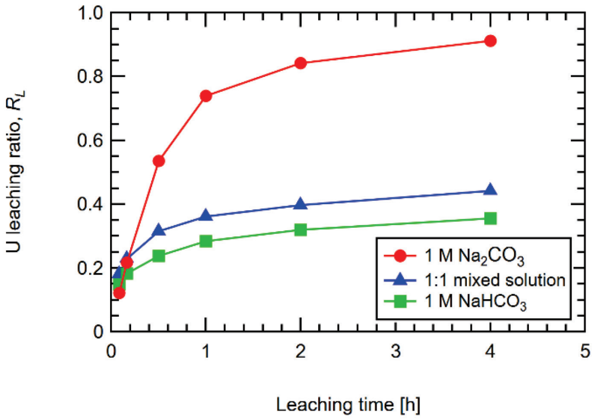

Fig. 6 Uranium leaching ratio in the simulated silica sludge against elapsed time for 1 M Na_2CO_3, 1 M $NaHCO_3$, and 1:1 mixed solution of 1 M Na_2CO_3 and 1 M $NaHCO_3$ at 323 K.

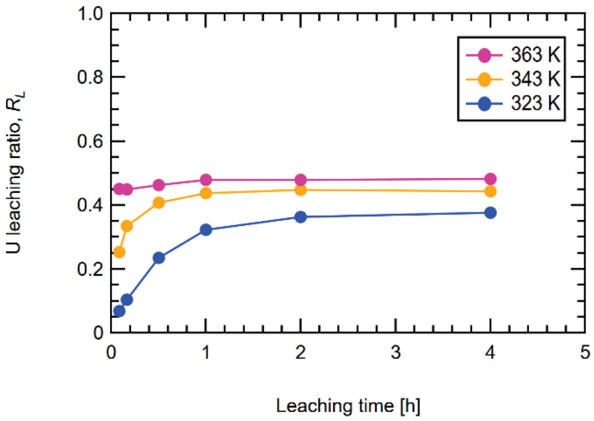

Fig. 7 Temperature dependence of the uranium leaching ratio in the simulated silica sludge for 0.1 M Na_2CO_3.

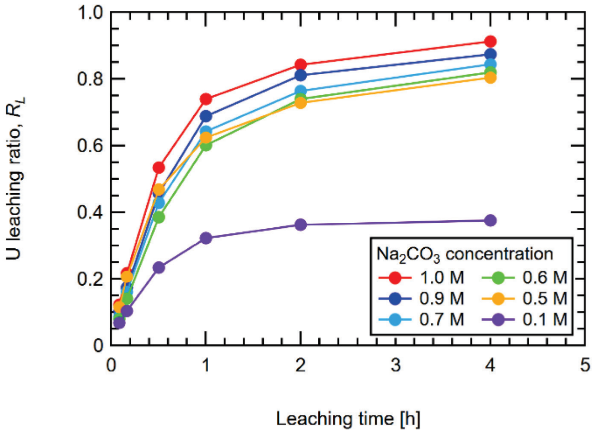

Fig. 8 Effect of Na_2CO_3 concentration on the uranium leaching ratio in the simulated silica sludge at 323K.

Figure 8 shows the uranium reaching ratio as a function of Na_2CO_3 concentration. For 0.5 M Na_2CO_3, 80% of the uranium leached after 4 h, and the ratio gradually increased to 90% as the Na_2CO_3 concentration increased to 1.0 M. Uranium leaching was affected by the Na_2CO_3 concentration rather than the solution temperature. After leaching at various Na_2CO_3 concentrations, the residual sludge was recovered and weighed. **Fig. 9** shows the uranium leaching ratio and the ratio of residual sludge. The sum of the uranium leaching ratio and the ratio of residual sludge was around 1 in each condition, indicating that uranium leaching in the simulated silica sludge was accompanied by dissolution of the sludge matrix. Based on the uranium leaching ratio and the ratio of residual sludge, the uranium content in the residue was 2.97wt%, which was lower than the initial value of 3.38wt%. In our recent experiment using actual silica sludge produced in a facility, a high U(VI) leaching ratio with a high ratio of residual sludge were achieved in high-concentration Na_2CO_3 solution.8) One of reasons for the difference between the simulated sludge and the actual one is expected to be the difference in chemical composition caused by the different sludge generation process between them. The details of the differences are being investigated.

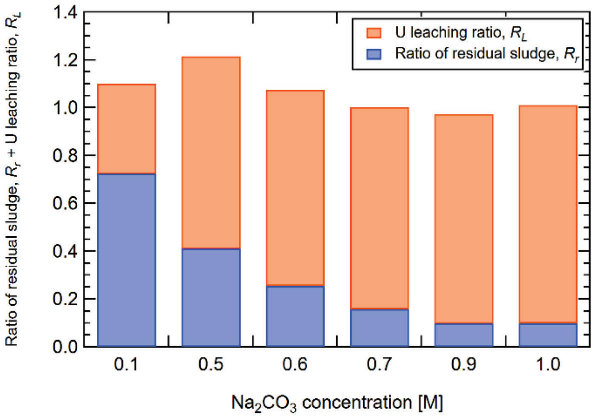

Fig. 9 Uranium leaching ratio and ratio of residual sludge for leaching experiments of silica sludge at various Na_2CO_3 concentrations at 323 K for 4 h.

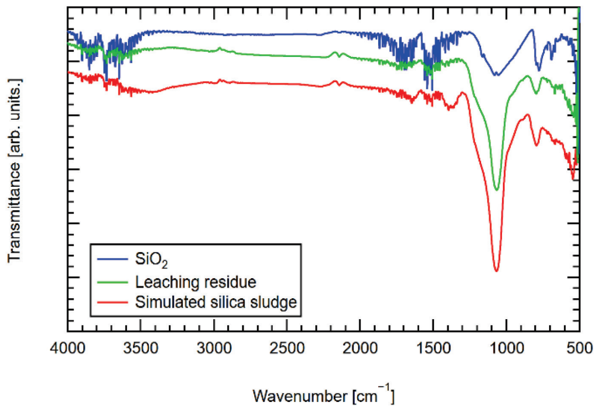

Fig. 10 IR spectra of the 3.38wt% uranium simulated silica sludge, the residue of the leaching experiment, and SiO_2. The residue was obtained at 323 K in 1 M Na_2CO_3.

(2) FTIR Spectroscopic Studies

The simulated silica sludge and the residue obtained from a leaching experiment were analyzed by FTIR spectroscopy. **Figure 10** shows the FTIR spectra with the SiO_2 spectrum as a reference. The simulated silica sludge spectrum was consistent with the residue spectrum, and both spectra were similar to the SiO_2 spectrum. The strong peak at 1050 to 1070 cm^{-1} was attributed to the Si-O-Si bond in amorphous SiO_2.9-10) U(VI) in the sludge was not identified in the FTIR spectra because the characteristic peak of U(VI) species may overlap with SiO_2 absorption band.

If the matrix of the simulated silica sludge consists of SiO_2, SiO_2 will dissolve in highly alkaline solutions, such as Na_2CO_3, rather than $NaHCO_3$ or the 1:1 mixed solution, resulting in a high U(VI) leaching ratio.

IV. Conclusion

Iron sludge and silica sludge containing U(VI) were prepared as simulated uranium-bearing waste. Leaching experiments were conducted, in which the uranium in the sludge was removed by using Na_2CO_3 and $NaHCO_3$ solution.

For the 4.58wt% uranium iron sludge, the leaching behavior in Na_2CO_3 and $NaHCO_3$ solutions was similar. High temperature caused an increase in the leaching ratio; after 4 h at 363 K, the leaching ratio in 1 M Na_2CO_3 solution was 88% and that in 1 M $NaHCO_3$ solution was 94%. For 9.62wt% uranium iron sludge, the leaching ratio was 60% in 1 M Na_2CO_3 solution at 363 K for 4 h, whereas the ratio was near 100% for 1 M $NaHCO_3$ solution, irrespective of the temperature. Under our experimental conditions, the ratio of residual iron sludge remained high. Therefore, U(VI) was selectively leached from the simulated iron sludge. The Fe(III) species in the sludge strongly affected the leaching. α-FeOOH was the main component of the 9.62wt% uranium iron sludge, and it was easy to dissolve in $NaHCO_3$. In contrast, the main component of the 4.58wt% uranium iron sludge was Fe_2O_3, the uranium atom strongly bound to the Fe_2O_3 structure, and U(VI) leaching was affected by the solution temperature.

Compared with the $NaHCO_3$ solution, the Na_2CO_3 solution had the advantage of leaching U(VI) from the silica sludge. The U(VI) leaching ratio in 1 M Na_2CO_3 reached 90% after 4 h at 323 K, and the ratio of residual sludge was 10%. Therefore, U(VI) leaching occurred together with the dissolution of the silica sludge matrix. The main component of the silica sludge was amorphous SiO_2, and thus highly alkaline solutions, such as Na_2CO_3, caused dissolution of SiO_2. Even though the silica sludge matrix inevitably dissolves in the carbonate solution for U(VI) leaching, leaching is still expected to decrease the uranium content in the residual sludge.

Acknowledgment

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