Studies on Treatment of Uranium Ores. I : Leaching of Uranium Ore from the Matsuiwa Mine

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Leaching of Uranium Ore from the Matsuiwa Mine*

Kingo SUDO and Akiichi KIGOSHI

The Research Institute of Mineral Dressing and Metallurgy

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Synopsis

Studies were made of several processes of extracting uranium with the uraniferrous ore from the Ryusei pit, Matsuiwa Mine, Miyagi Prefecture, assaying 0.081 per cent U.

Three series of experiments were carried out as follows:

(1) Pressure oxidation leaching of the uranium ore in carbonate solutions containing gaseous oxygen.

(2) Leaching the roasted ore in sulfuric acid.

(3) Pressure and atmospheric oxidation leachings of the ore in acids.

The results obtained show that the atmospheric oxidation leaching with dilute sulfuric acid was an attractive method for extraction of uranium from such low grade ore as this. By this method over 96 per cent of uranium, together with some copper and from 0.3 to 2 per cent of iron were extracted at 60°C in 6 hours.

The same results were obtained with nitric acid and the atmospheric leaching in water with oxygen recovered over 80 per cent of uranium.

I. Introduction

The present report is the first part of a series of studies on metallurgy of nuclear fuels. In this part several processes for extracting uranium from the uraniferrous ore from the Ryusei pit, Matsuiwa Mine, Miyagi Prefecture are studied. The results obtained show that an attractive method can be applied for this ore. It also suggests a method for the treatment of this kind of domestic ores.

II. Sample

The sample was the ore at positions whose radiation intensity is relatively strong in the Ryusei pit. It was ground by a jaw crusher and a ball mill. Its sieve analysis and chemical composition are given in Table 1. The following minerals were observed under a microscope: pyrite, pyrrhotite, arsenopyrite, quartz, muscovite, tourmaline and a little of hematite, scheelite, chalcopyrite, magnetite, marcasite, garnet and epidote. Uranium seemed to be contained as uraninite.

III. Experimental method

No reports dealing with uranium ores containing such a large amount of iron and sulfur have been published. Iron and sulfur which are contained chiefly as pyrite and pyrrhotite consume inevitably the oxidizing agent which is required in extraction of uranium. Iron is dissolved mostly as ferric ion by acid leaching.

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Ferric ion has been found to be extremely harmful[1],[2] to purification of uranium leach liquor by organic solvents or ion exchangers. Therefore, the three following methods were employed. These methods suppressed dissolution of iron as

Table 1. Analysis of the ore.

Mesh	Distribution (%)	U_3O_8 (%)	Fe (%)	Cu (%)	S (%)	Al_2O_3 (%)	WO_3 (%)	CaO (%)	MgO (%)	As (%)	SiO_2 (%)
+ 65	13.48	0.065	13.17	0.13	4.10	10.75	0.00	0.36	0.27	0.10	66.58
− 65+100	22.87	0.080	13.21	0.38	4.11	12.00	0.00	0.32	0.25	0.11	64.94
−100+150	21.00	0.105	15.99	0.94	3.96	18.37	0.10	0.35	0.25	0.09	54.03
−150+200	33.26	0.122	20.15	1.36	3.94	23.80	0.45	0.30	0.22	0.08	42.39
−200+275	7.06	0.067	22.29	2.24	4.02	24.15	0.45	0.28	0.21	0.12	38.19
−275	2.33	0.050	22.77	1.62	4.07	25.56	0.18	0.28	0.21	0.13	36.99
mean		0.096	16.96	0.95	4.01	18.27	0.21	0.32	0.24	0.10	52.83

ferric form.

First, the presence of oxygen under moderate pressure or a chemical oxidizing agent has been found particularly effective. Uraninite, for instance, reacts under these conditions as follows:

$$U_3O_8 + 1/2O_2 + 9CO_3^{--} + 3H_2O = 3UO_2(CO_3)_3^{----} + 6OH^-. \quad (1)$$

And the reaction of iron sulfide is given by the following equation:

$$2FeS_2 + 71/2O_2 + 8CO_3^{--} + 7H_2O = 2Fe(OH)_3 + 4SO_4^{--} + 8HCO_3^-. \quad (2)$$

In moderate amount, such reaction may be beneficial to the leaching, since it prevents dissolution of iron. And it assures the presence of some bicarbonate in the solution. Then the dissolution of uranium is promoted as follows:

$$U_3O_8 + 1/2O_2 + 3CO_3 + 6HCO_3^- = 3UO_3(CO_3)_3^{----} + 3H_2O, \quad (3)$$

and the reprecipitation of uranium by accumulation of OH^- is prevented. Such basic constituents as CaO and MgO may react with the carbonate, but in this case they are found to be negligible because of their little amount. The dissolution of silica from the ore may give rise to further carbonate consumption as follows:

$$SiO_2 + H_2O + 2CO_3^{--} = SiO_3^{--} + 2HCO_3^-. \quad (4)$$

This reaction, which is promoted by raising temperature, is undesirable, since the resulting solution is difficult to filter, and some uranium may be lost through occlusion into the silicates, which reprecipitate on cooling. Forward and Halpern[3] have found a particular advantage in this method on treating a pitchblend ore containing 6.45 per cent S, 28.0 per cent Fe and 4.72 per cent U. This uranium content is about fifty times higher than that in this experiment.

(1) J. D. Moore, J. Metals, **9** (1957), 757.
(2) A. M. Ross, Mining Eng., **9** (1957), 997.
(3) F. A. Forward and J. Halpern, Can. Mining Met. Bull., **10** (1953), 634.

Second, in treating ore by acid leaching, if the ore is preroasted, uranium may be extracted preferentially in the presence of moderate oxidizing agent as follows:

$$2U_3O_8+O_2+H_2SO_4=6UO_2SO_4+6H_2O, \quad (5)$$

since iron sulfide is converted to an insoluble oxide as follows:

$$2FeS_2+71/2O_2=Fe_2O_3+4SO_2. \quad (6)$$

Third, atmospheric acid leaching may extract uranium preferentially. Sulfuric acid leaching is recognized to be particularly suited to siliceous ore, while the acid may dissolve any iron and copper contained in ore. According to Forward and Halpern,[4],[5] however, it seems possible to find the optimum conditions which would permit the uranium to be extracted, leaving most of copper, iron and other impurities behind in the leach tailings.

These three methods were studied in this experiment. Samples were analyzed for uranium by the cellulose-column[6],[7] or ion-exchange methods[8],[9], by using spectrophotometer for final colorimetric determination. All other determinations were made by using standard analytical procedures. The extraction rate were determined in all cases by analyzing the both leach liquors and tailings.

IV. Results of experiments

1. Carbonate leaching

Leaching tests were carried out with a stainless steel autoclave of 5 liter capacity. The contents were agitated by an impeller, and heated by an electric heater. Ores were made up with 10 per cent sodium carbonate solution to a 25 per cent pulp density. The pulp was placed in the autoclave at oxygen pressure of 5 atm and stirred continuously at a given temperature. The results of the leaching for 6 hours are shown in Table 2. When the leaching temperature was elevated from 60 to 140°C, the extraction rate increased. Excessively high temper-

Table 2. Leaching rates at various temperatures, solution, 10%-Na_2CO_3; O_2 pressure, 5 atm.

Leaching temp. (°C)	Extraction (%)						
	U	Fe	Cu	S	Al_2O_3	WO_3	SiO_2
60	12.50	0.060	1.43	3.93	0.82	1.87	0.010
100	14.15	0.071	2.59	9.49	1.18	11.01	0.046
140	17.82	0.061	2.14	9.56	1.24	15.39	0.073
160	17.23	0.061	2.15	5.51	0.82	11.81	0.454

(4) F. A. Forward and J. Halpern, J. Metals, **7** (1955), 463.
(5) P. M. Gray, Trans. Inst. Mining Met., **65** (1955), 55.
(6) T. Hara, J. Chem. Soc. Japan, **3** (1957), 337.
(7) H. Kurama, Y. Isihara, B. Kominami, T. Isikawa and J. Ito, Bunsekikagaku, **1** (1957), 3
(8) S. Fisher and R. Kunin, Anal. Chem., **29** (1957), 400.
(9) H. T. Sein, R. J. Morris and W. Frew, Anal. Chem., **29** (1957), 443.

ature, however, should be avoided, since this results in an increase in the dissolution of silica. Fig. 1 shows the results obtained by a long time extraction at 140°C under the same conditions as above. It is seen that an increase in leaching

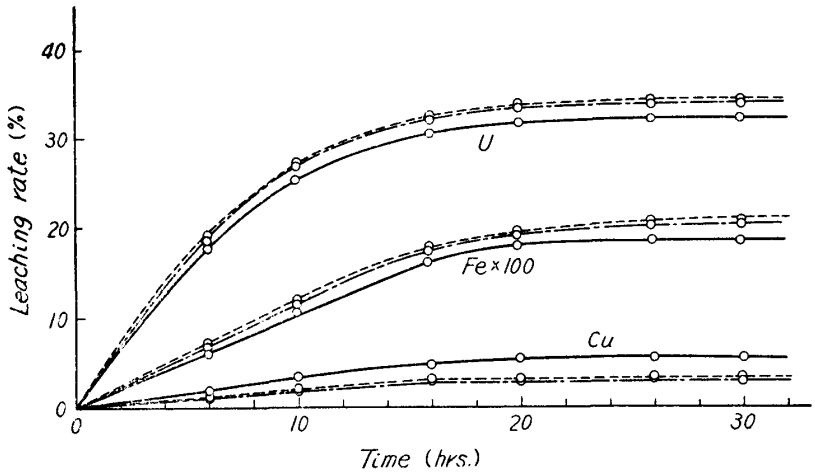

Fig. 1. Typical leaching rate curve at 140°C.
..... Na_2CO_3 100g/l.
——— Na_2CO_3 100g/l, $NaHCO_3$ 20g/l.
– – – – Na_2CO_3 200g/l, $NaHCO_3$ 20g/l.

rate becomes very slow after 20 hours and the extraction of uranium is about 30 per cent in such a case. A slight effect of addition of bicarbonate can be seen. The ore used is considered to be a slightly oxidized form of the ores from the Maeda pit, Matsuiwa Mine, in which uraninite crystals are usually surounded with pyrite[10]. When grinding the ore, outer oxidized layer of each ore particle can easily be cracked and eliminated, while the second layer, pyrite, seems to be rather difficult to destroy. It is clear that the dissolving reaction of pyrite is required to obtain higher uranium recovery. Accordingly, with carbonate leaching, even under oxygen pressure, poor recovery is naturally expected.

2. Sulfuric acid leaching after roasting

Some experiments on preliminary oxidizing roasting with a boat were done. A silica boat, on which the ore sample was placed, was inserted in the reaction tube of silica and heated by an electic resistance furnace which was kept at a desired temperature. Under an abundant supply of air at a constant flow rate, the outgoing gas containing sulfur di- and trioxide gas was analysed. Then quantity of sulfur oxidized for a given interval during the roasting was calculated. The results

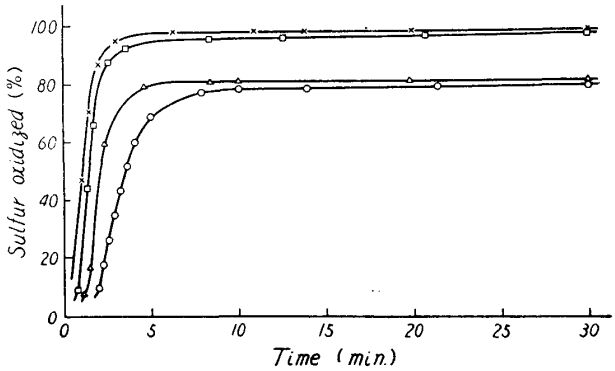

Fig. 2. Typical roasting curves.
× 850°C, □ 750°C, △ 650°C,
○ 550°C.

(10) M. Wada, H. Majima, T. Hashimoto, S. Koseki and N. Miyamoto, Bull. Res. Inst. Min. Dressing and Met., **13** (1957), 131.

are shown in Fig. 2. It is seen that sulfur in the ore particle can be oxidized almost completely in a few minutes above 750°C, while about 80 per cent of total sulfur below 650°. After roasting at 550, 650, 750 and 850°C for 30 minutes, each calcine was treated with 10 per cent sulfuric acid for 6 hours. From the results shown in Fig. 3, it is seen that the extraction of iron can be suppressed about 6 per cent by preroasting at 850°C, while that of uranium remains almost constant at 95 per cent. In this case, little effect of roasting time at 850°C can be observed as shown in Fig. 4. A slight decrease in extraction of both iron and uranium can be considered to be due to the presence of a small amount of silicate or ferrite which may be produced during the roasting. Fig. 5 shows the effect of concentration of acid on the leaching of calcine which was roasted at 850°C for 30 minutes.

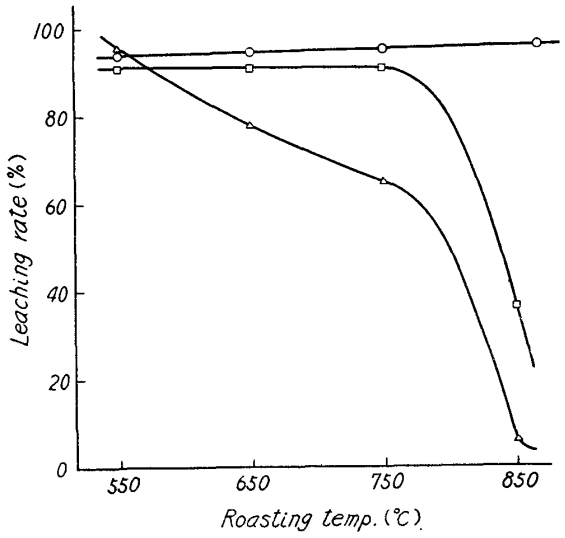

Fig. 3. Effect of roasting temperature on leaching rate.
○ U, △ Fe, □ Cu.

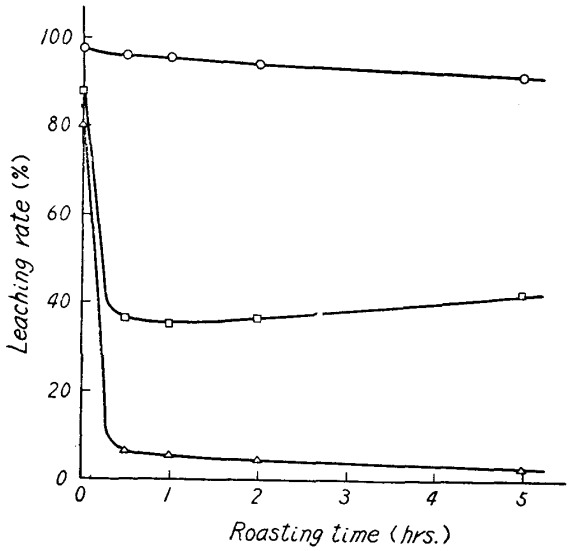

Fig. 4. Effect of roasting time on leaching rate.
○ U, △ Fe, □ Cu.

3. Pressure and atmospheric oxidation leachings with acid

Fig. 6 shows the results of leaching which were conducted in an autoclave under conditions of 25 per cent pulp density, 3.75N (about 10 per cent) sulfuric acid and 3 atm oxygen pressure for 6 hours. The highest extraction of uranium was obtained at 140°C. Concentration has a smaller effect on uranium extraction but produces great change in extraction of iron and copper.

Atmospheric pressure acid leaching was found to be of interest in the treatment of the ore. The pulp was placed in a beaker and stirred vigorously at 60°C. The pulp consisted of the ore and various concentrations of sulfuric acid or nitric acid. And oxygen was continuously blown into it as in the former case. These results, illustrated in Figs. 8 and 9 respectively, indicate that no troublesome method with an autoclave is needed, but rather

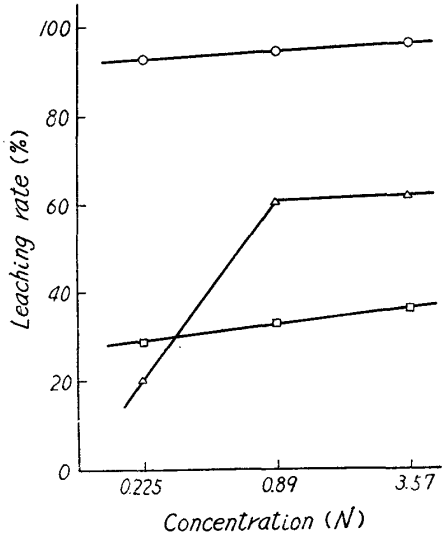

Fig. 5. Effect of acid concentration on leaching rate.
○ U, △ Fe×10, □ Cu.

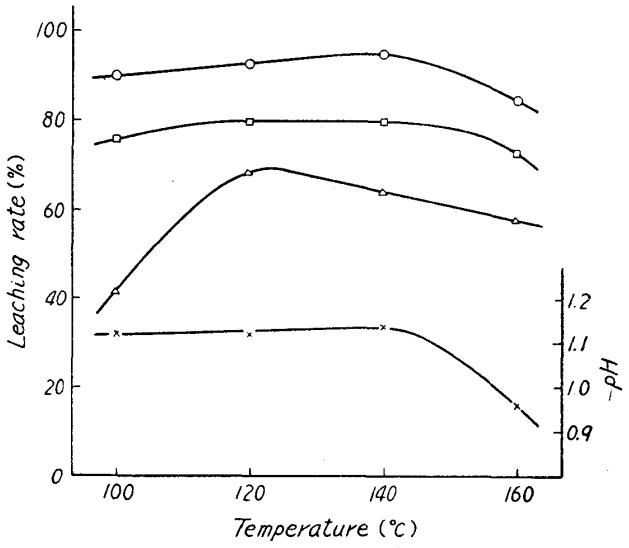

Fig. 6. Effect of leaching temperature.
○ U, △ Fe, □ Cu, × pH.

simple atmospheric oxidation leaching is an attractive method. The effect of pulp density from 25 per cent to 75 per cent solid in 0.112N sulfuric acid is shown in Fig. 10, and the concentration of each element in leach liquor is given in Table 3. From these results it is seen that over 96 per cent of uranium, together with some copper, is extracted and the extraction of iron can be kept below 2 per cent. Grinding the ore under 200 mesh was found to have no appreciable effect on the leaching.

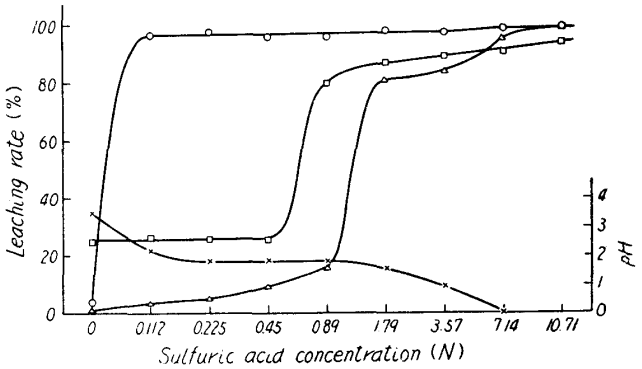

Fig. 7. Effect of sulfuric acid concentration on leaching rate.
○ U, △ Fe, □ Cu, × pH.

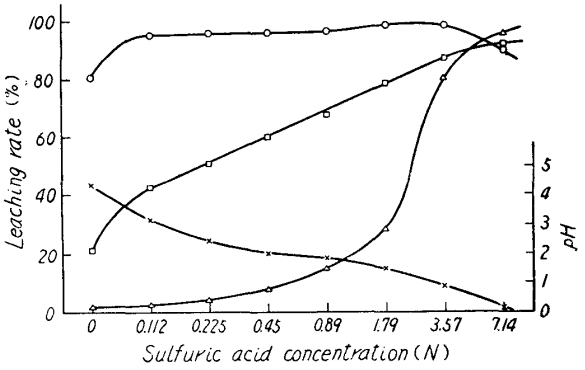

Fig. 8. Atmospheric oxidation leaching with sulfuric acid.
○ U, △ Fe, □ Cu, × pH.

Summary

Studies were made of several processes of extracting uranium with the uraniferrous ore from the Ryusei pit, Matsuiwa Mine, Miyagi Prefecture, assaying 0.081 per cent U. Three series of experiments were carried out; 1) Pressure oxidation leaching of

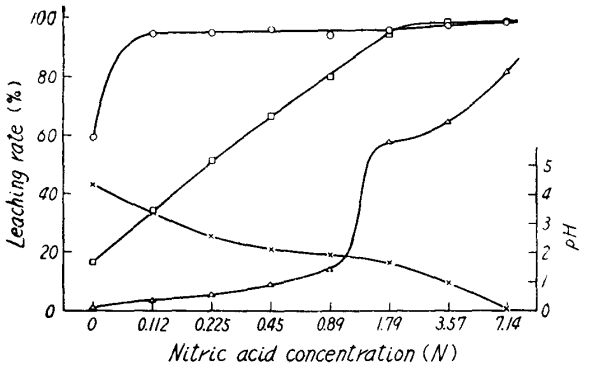

Fig. 9. Atmospheric leaching with nitric acid.
○ U, △ Fe, □ Cu, × pH.

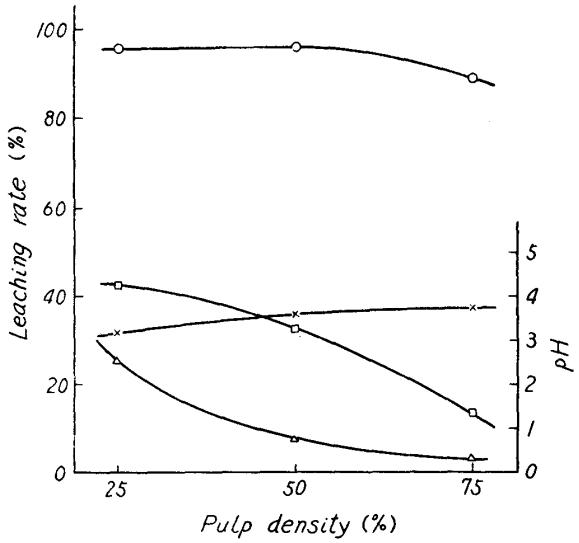

Fig. 10. Effect of pulp density on leaching rate.
○ U, △ Fe×10, □ Cu, × pH.

Table 3. Effect of pulp density on concentration of each element in leach liquor.

Pulp density (%)	Concentration (g/l)		
	U	Fe	Cu
25	0.26	1.44	1.36
50	0.78	1.26	3.11
75	2.17	1.72	3.89

the uranium ore in carbonate solutions containing goseous oxygen; 2) leaching the roasted ore in sulfuric acid; 3) pressure and atmospheric oxidation leachings of the ore in acid. From the results it was found that carbonate leaching and preroasting of the ore are not suitable and atmospheric oxidation leaching with dilute acid is an attractive method for extracting uranium from such low grade ore as this. By this method over 96 per cent of uranium, together with some copper and from 0.3 to 2 per cent of iron were extracted at 60°C in 6 hours. The same results were obtained with nitric acid and the atmospheric leaching in water with oxygen recovered over 80 per cent of uranium.

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