

# Development of Uranium Milling and Conversion

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## Development of Uranium Milling and Conversion

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## ABSTRACT

The development and improvement of uranium milling and refining producing uranium tetrafluoride from ores by the wet process, without producing yellowcake as an intermediate product, have been carried out for over ten years with a small pilot plant (50 t-ore/day). In the past several years, a process for converting uranium tetrafluoride into hexafluoride has been developed successfully.

To develop the process further, the construction of an integrated milling and conversion pilot plant (200 t-U/year) started in 1979 and was completed in 1981.

This new plant has two systems of solvent extraction using tri-n-octylamine: one of the systems treats the pregnant solution (uranyl sulphate) by heap-leaching followed by ion exchange, and the other treats the uranyl sulphate solution by dissolving imported yellowcake.

The uranium loading solvents from the two systems are stripped with hydrochloric acid solution to obtain the concentrated uranium solution containing 100 g-U/l.

Uranyl sulphate solution from the stripping circuit is reduced to a uranous sulphate solution by the electrolytic method. In a reduction cell, uranyl sulphate solution and dilute sulphuric acid are used respectively as catholyte and anolyte, and a cation exchange membrane is used to prevent re-oxidation of the uranous sulphate.

In the following hydrofluorination step, uranium tetrafluoride,  $UF_4 \cdot 1-1.2H_2O$  (particle size: 50-100 $\mu$ ), is produced continuously as the precipitate in an improved reaction vessel, and this makes it possible to simplify the procedures of liquid-solid separation, drying and granulation.

The uranium tetrafluoride is dehydrated by heating to 350°C in an inert gas flow.

The complete conversion from  $UF_4$  into  $UF_6$  is achieved by a fluidized-bed reactor and a high value of utilization efficiency of fluorine, over 99.9 percent, is attained at about 400°C.

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## INTRODUCTION

In 1964, a small pilot mill (50 t-ore/day) for treating domestic uranium ores was constructed at the Ningyo-Toge mine in Okayama Prefecture, Japan.<sup>1)</sup>

This pilot mill had operated for over ten years, with the addition of several improvements and modifications in order to produce  $UF_4$  directly from ore without producing yellowcake. This process (PNC process) consists of leaching, solvent extraction, electrolytic reduction and hydrofluorination in a wet process as shown in Fig. 1, and has been proved to have three advantageous features as follows:

(1) Except for the final dehydration step, the process is carried out completely by the wet process (liquid-liquid system) and as every process step is simple, the operation and process control are easy.

(2) Because the major part of the process is operated at a temperature lower than  $90^\circ C$ , the tanks and vessels in the plant can be made of FRP (fiber reinforced plastic), which is non-corrosive for many chemicals and is cheap, while in the conventional dry process (gas-solid system) expensive equipment made of high nickel alloy is used in systems operating at high temperatures.

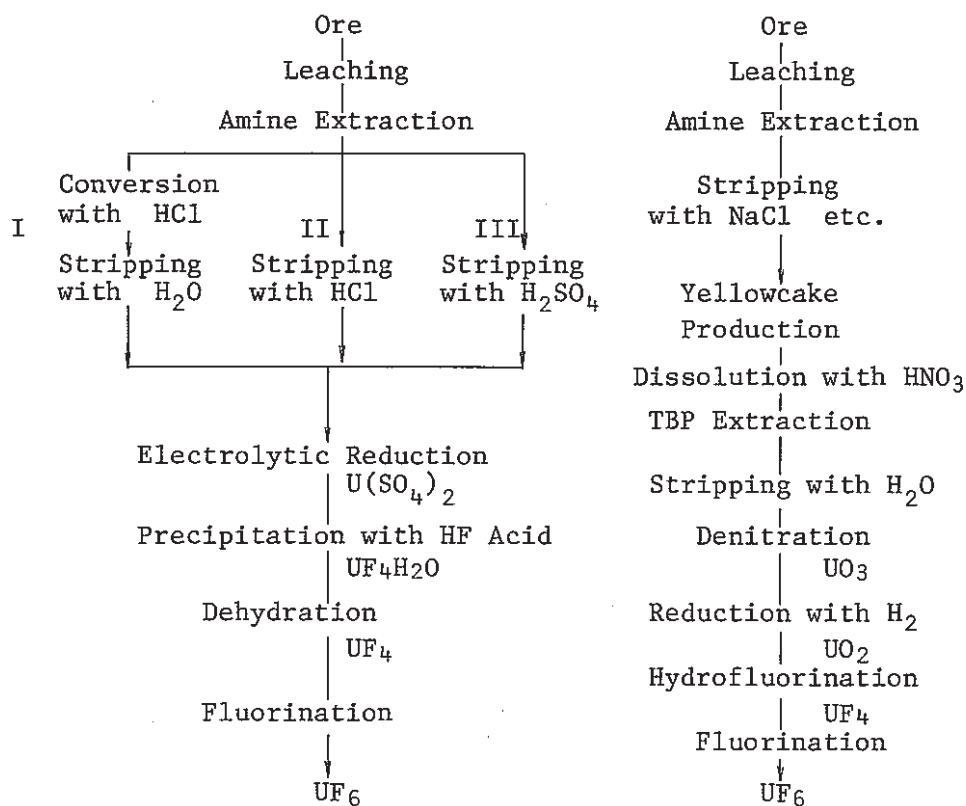


Fig. 1. Comparison of uranium processings from ore to  $UF_6$ .

(3) The uranium tetrafluoride powder is produced in a more reactive form for fluorine than the uranium tetrafluoride from the conventional dry process.

In the early 1970s, an experimental facility for converting  $UF_4$  into  $UF_6$  was constructed and it was developed successfully over several years. Thus, the development of an integrated process to obtain  $UF_6$  from uranium ore was achieved in a small pilot plant, in 1977.

Based on these results, construction of a new milling and conversion pilot plant (200 t-U/year) was completed in November, 1981, and it has operated favorably since its opening ceremony on March 26, 1982.

In this paper a summary of the integrated process and the vat leaching system supplying the pregnant solutions to the process is given.

#### VAT LEACHING AND ION EXCHANGE SYSTEM

The uranium mineralization of the Ningyo-Toge deposits is present mainly as autunite and ningyoite in tertiary conglomerate and sandstone, which are consolidated weakly.

The uranium minerals occur in the matrix of conglomerate and between grains of sandstone. The main gangue minerals are quartz, feldspar, clay minerals and hematite. Typically, the ore grade is 0.08 percent uranium. The ore is supplied for the vat leaching without crushing.

The uranium is extracted from the crude ore by percolation of the sulphuric acid solution. The leaching operation is carried out by three leaching vats, loading 500 t ore in each vat.

The vat is constructed with concrete, lined with acid-proof paint and timbers, and provided with a gravel filter at the bottom.

The uranium recovery was about 90 percent under the leaching conditions described in Table 1, and the acid consumption was expected to be 20 kg/t-ore.

Table 1. Comparison of leaching condition

	Conventional method	Heap leaching
Ore grain size	- 8 mesh (- 2.4 mm)	not crushed (crude ore)
Solution ratio (solution: ore m <sup>3</sup> /t)	0.62 - 0.67	0.26 - 0.35
Initial concentration of H <sub>2</sub> SO <sub>4</sub> (g/l)	45 - 60 per 20 - 40 kg/t-ore	58 - 76 per 20 kg/t-ore
Free SO <sub>4</sub> after leaching (g/l)	10 - 30	9 - 31
Retention time (hr)	3 - 4	24 - 72
Temperature (°C)	50	room temperature
Leaching ratio (%)	90 - 98	81 - 93
Total production of leaching solution (m <sup>3</sup> /t-ore)	2 - 3	1 - 1.9

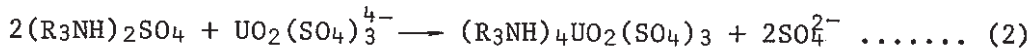
An ion-exchange process is used to concentrate uranium up to 3-5 g/l from a low concentrated uranium solution, such as a uranium-poor pregnant solution and wash water, and consequently to reduce solvent losses in the following amine solvent extraction section.

The uranium is loaded on the strong base anionic resins as anionic complex  $UO_2(SO_4)_3^{4-}$ , and is eluted with one mol/l sulphuric acid solution. Uranium in the eluate is then extracted with tri-n-octylamine, and the barren eluate "raffinate" is reused as an eluant of the ion exchange step.

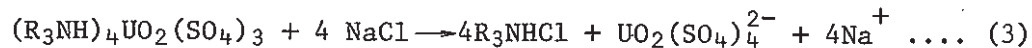
## SOLVENT EXTRACTION

In the conventional Amex process, the loaded uranium in the organic phase is stripped with chloride, carbonate or ammonium sulphate solution, as shown in Eqs. (1), (2), and (3).

Amine Extraction: (R: octyl radical)

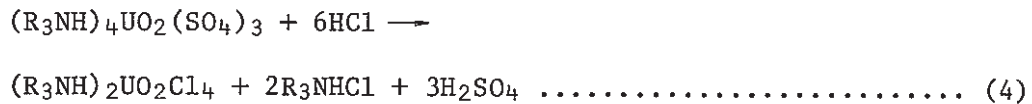


Stripping:



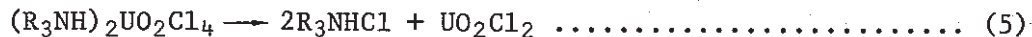
However, in the PNC (Power Reactor and Nuclear Fuel Development Corp.) process I, the loaded uranium in the organic phase is converted to a chloride complex by using 8 mol/l hydrochloric acid, as given in Eq (4).

Chloride Conversion:

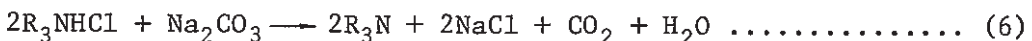


Uranium in the solvent after the conversion is readily stripped with water.

Stripping of Process I:



The organic phase after stripping is scrubbed with sodium carbonate solution, as the following chemical equation.



In the case of PNC Process I, two advantages are as follows:

(1) Because the organic phase extracts uranium twice, that is, in the forms of sulphate and chloride complexes, a high purity solution is obtained.

(2) Because of a high stripping effect, the uranium concentration in the stripping solution (100 g-U/l) is higher than that of the conventional Amex process.

It would be expected to have a high refining efficiency for treating the ore containing many impurities, such as thorium and boron etc.<sup>2)</sup>

Process II as shown in Fig. 1, has fewer stages than process I, and process II is used for most ores containing few impurities.

In Process II, the stripping is performed with hydrochloric acid without chloride conversion. The reaction is indicated by Eq. (7).

Stripping of process II:

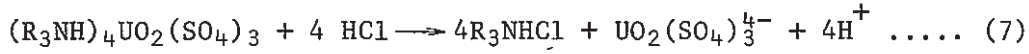


Figure 2 gives the explanations of chloride conversion and the stripping of process II.

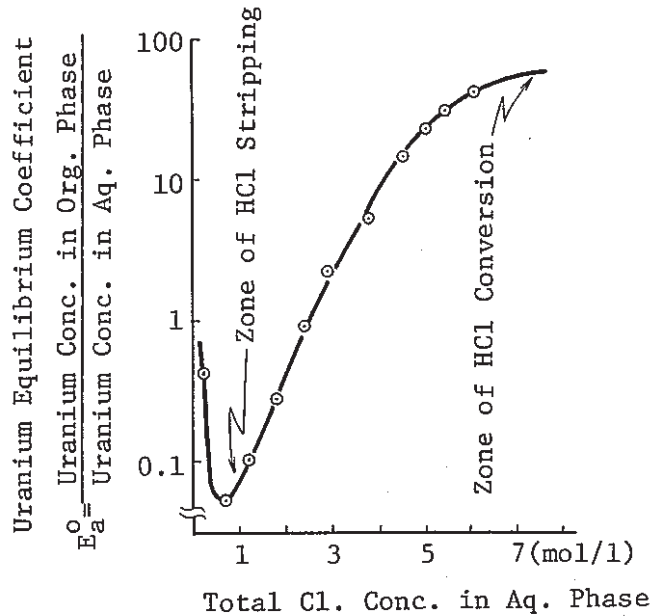


Fig. 2. Uranium behavior after loading step of  $UO_2(SO_4)_3^{4-}$

Process III does not require conversion and scrubbing.

However, a stripping solution with a higher concentration of sulphuric acid than the stripping solution in process I and II is required for the stripping stage in process III. The acidic solution, containing sulphuric and hydrofluoric acids discharged from the uranium tetrafluoride precipitation stage, can be separated into sulphuric and hydrofluoric acid by means of distillation. These acids are used.

#### ELECTROLYTIC REDUCTION

The uranium in the uranyl sulphate solution from the stripping section is reduced to tetravalent form by means of electrolytic reduction.

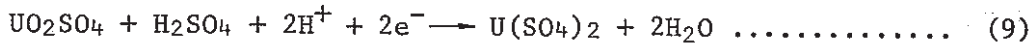
The electrolytic cell is divided into two compartments with a cation exchange membrane. The electrode reactions are as follows:



Anode:



Cathode:



Here, the membrane fulfills the function of preventing the re-oxidation of the uranous sulphate, to add to the cation exchange function.

An improved procedure for plating the electrode with noble metals was developed. Thinner and lighter bipolar electrodes were introduced into the cells, and lower manufacturing costs are expected.

As an experiment, a vertical layer-built electrolytic cell including the above-mentioned improvement was made. The improved cell resulted in decreases in leakages of electric current and solutions, and facilitated the inside check.

The chemical and physical stability of the ion exchange membrane was improved to achieve high current efficiency at the high reduction rate and stable performance of the electrolytic cell.

The electrolytic cell with several improvements, as mentioned above, was continuously operated for more than 1,000 hours without any malfunctions. About 70 percent of the current efficiency on average was attained with a reduction rate of 99.5 percent or more.

### HYDRO-FLUORINATION

A reaction vessel in which hydrated uranium tetrafluoride grains are continuously precipitated is shown schematically in Fig. 3.

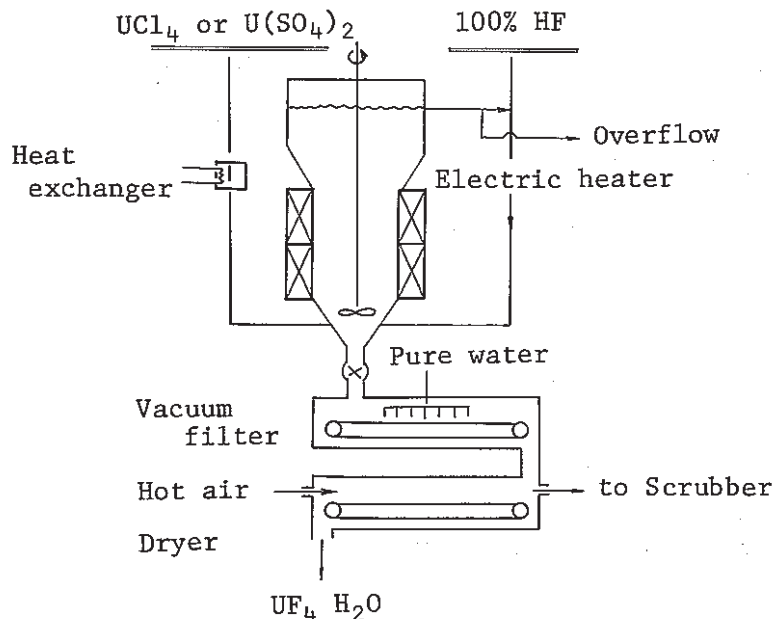
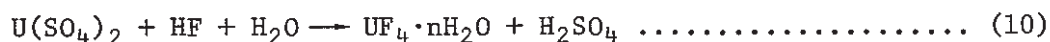


Fig. 3. The hydrofluorinator

The uranous solution and the hydrofluoric acid solution which is diluted with the discharged solution which overflowed from the reaction vessel are continuously fed into the reaction zone in the bottom part of the vessel.

The reaction (Eq. 10) takes place in the lower part of the vessel, and hydrated uranium tetrafluoride grains grow to 50-100 $\mu$  in diameter while suspended in the reaction zone.



The conditions for the formation of hydrated uranium tetrafluoride are as follows:

- (1) The grains have to be kept suspended within the reaction zone.
- (2) The supersaturated uranium tetrafluoride concentration in the solution has to be as low as possible; therefore, the concentration of hydrofluoric acid has to be diluted as much as possible.
- (3) The reaction temperature has to be kept at about 90°C.
- (4) The stirring has to be kept constantly at a speed which holds the grains suspended in the solution; however, the stirring must be slow enough that the grains are hardly present in the overflow solution.

The  $UF_4 \cdot nH_2O$  grains are separated from the mother liquor after a few hours in the reaction vessel. They are washed with pure water, filtered and dried. As the hydrated uranium tetrafluoride product has an excellent permeability, the product taken from the reaction vessel is fully scrubbed in a comparatively small quantity of water.

The dried product contains virtually no impurities, as shown in Table 2.

The hydrated  $UF_4$  was identified as  $UF_4 \cdot 1-1.2H_2O$  which is a mixture of the monoclinic type ( $UF_4 \cdot 3/4H_2O$ ), the cubic type ( $UF_4 \cdot 1 \ 1/2H_2O$ ), and the orthorhombic ( $UF_4 \cdot 2 \ 1/2H_2O$ ) type, by differential thermal analysis and thermogravimetric analysis and X-ray diffraction.

About 70-80 percent of the content of the crystallization water in the mixture is dehydrated at 150-200°C, and the rest is dehydrated at 350°C by means of heating in nitrogen gas flow.

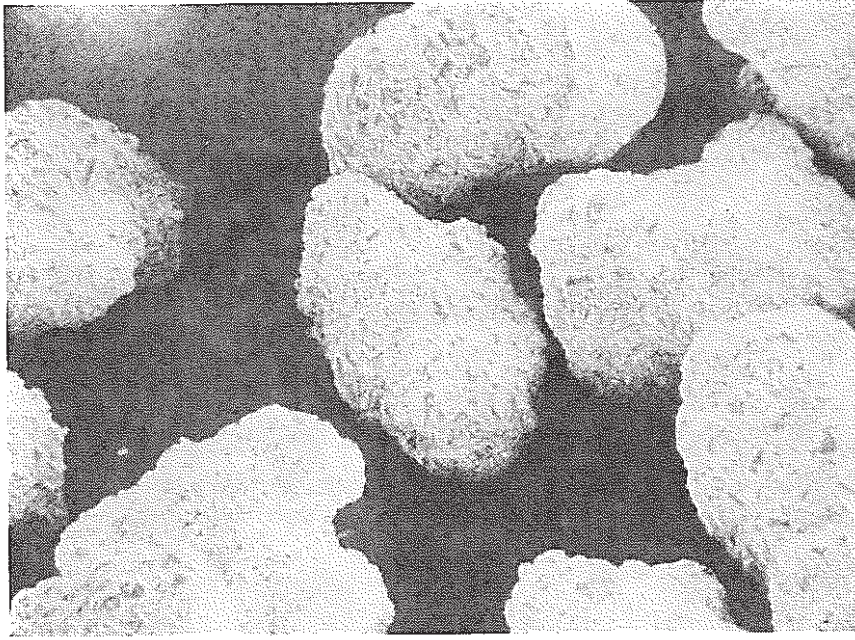
The scanning electron micrographs of the grains are shown in Figs. 4, 5, and 6.

Table 2. Typical analyses and specification of ore, intermediate and product

Item Element	Typical analysis				Specification	
	Grade of uranium ore (%)	Leaching solution (g/l)	UF <sub>4</sub> (ppm on a U basis)	UF <sub>6</sub> (ppm on a U basis)	UF <sub>4</sub> (ppm on a U basis)	UF <sub>6</sub> (ppm on a U basis)
					UKAEA	USAEC
Al	6.36	2.94	3.0	8	10	.
Ag	0.003	0.0007	<0.1	<0.01	0.2	.
B			<0.2		0.1	⊙
Ca	0.5	0.023	<0.1	20.3		.
Cd	0.0018	0.00059	<0.1	0.01	0.2	.
Cr	0.0062	0.0027	0.19	0.26	8	10.7
Cu	0.002	0.011	0.10	0.12	15	.
Fe	2.52	5.00	17.4	15.0	50	.
K	1.66	0.034	2.6	10	50	.
Mg	0.21	0.713	0.33	0.65	2	.
Mn	0.054	0.419	0.06	0.04	3	.
Mo	0.004	0.00076	0.39	0.10	3	1.4
Na	4.08	0.061	16	28.9	80	.
Ni	0.001	0.0059	0.1	0.16	30	.
Si	31.08	0.56	<8		15	100
Ti	0.15	Tr.	0.4		10	1
Th	0.0012	0.0016	<1			.
V	0.005	0.0024	<1	<0.4	3	1.4
Zn	0.022	0.0057	0.09	0.59	50	.
U	0.12	1.39				

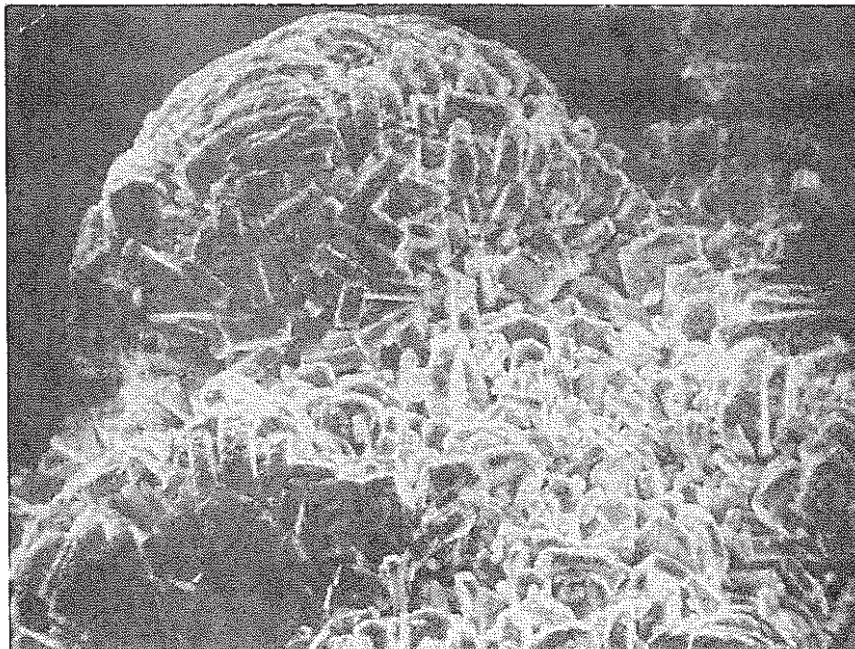
\*: Total of elements forming non-volatile fluorides <300ppm/U.

⊙: The specification requires that the total of impurities, expressed as boron equivalents, should not exceed 8 ppm on a U basis.



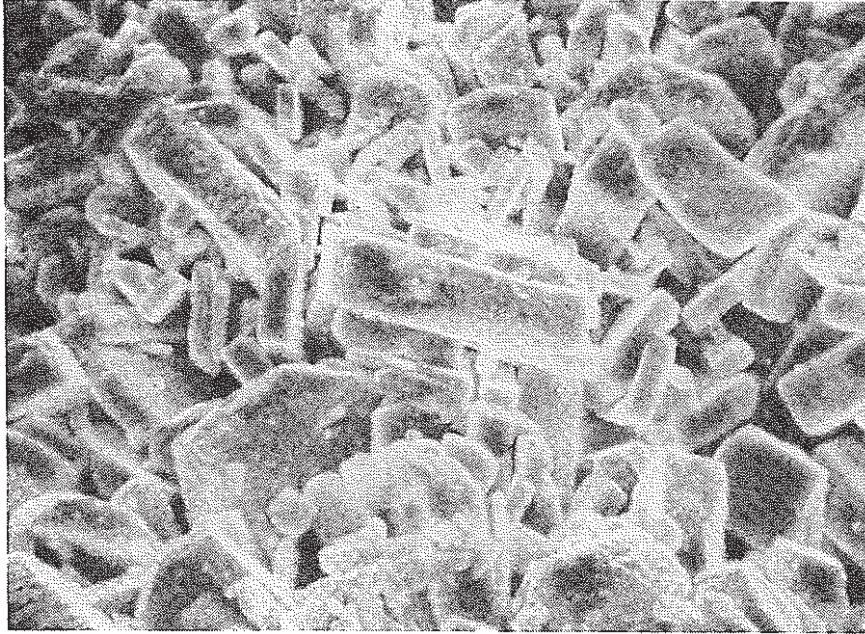
100 $\mu$

Fig. 4. Scanning electron micrograph of  
UF<sub>4</sub>·1-1.2 H<sub>2</sub>O particles



5 $\mu$

Fig. 5. Scanning electron micrograph  
of a part of one particle  
(UF<sub>4</sub>·1-1.2 H<sub>2</sub>O)



1  $\mu$

Fig. 6. Scanning electron micrograph  
of a part of one particle  
(dehydrated  $UF_4$ )



## DEHYDRATION

During dehydration of  $UF_4 \cdot nH_2O$ , some uranium oxide,  $UO_2$ , is formed with the following reactions between  $UF_4$  and  $H_2O$ , as shown in the equations (11) and (12).



The  $UO_2$  containing a small quantity of  $UF_4$  consumes fluorine gas at the  $UF_6$  conversion step, followed by the dehydration step, as shown in equations 11 and 12.



The fluidized-bed reactor was selected because the reactor dehydrates rapidly from the hydrated uranium tetrafluoride grains when fluidizing the grains in an upward nitrogen flow.

The rapid dehydration decreases the formation of uranium oxide.

The formation of uranium oxide by dehydration was approximately 0.8-1 wt% and 1-3 wt% with the batch and continuous treatments respectively, with the temperature within the range of 300-400°C, and the retention time calculated from an experimental formula to remove 99.9 percent of the crystallization water in uranium tetrafluoride. By experimental and theoretical analyses of the dehydration of  $UF_4 \cdot 1-1.2H_2O$  and of the formation of  $UO_2$ , the optimum condition (350°C, about 50 min) was found.

## FLUORINATION

Dehydrated  $UF_4$  is converted to  $UF_6$  by reacting with fluorine gas, as shown in Eq. 13. A fluidized-bed reactor was used for the conversion, because of the ease in controlling the heat transfer, compared with the flame type, and the residence time of  $UF_4$  particles.

The batchwise experiments have been performed with the fluidized-bed reactor (Fig. 7), with constant charged weights of  $UF_4$  and sintered  $Al_2O_3$  into the bed, on the conditions of holding the bed at a constant temperature and sending  $F_2$  and  $N_2$  gas mixture from the bottom of the reactor. The quantities of  $UF_6$  gas product and  $F_2$  were measured with a thermal conductivity cell.

The  $UF_6$  production rate is constant during the reaction period, and the reaction time  $t_f$  is directly proportional to initial feed inventory  $m_0$ . From the experimental results, the rate constant  $K$  which is proportional to  $1/t_f$  can be summarized as follows:

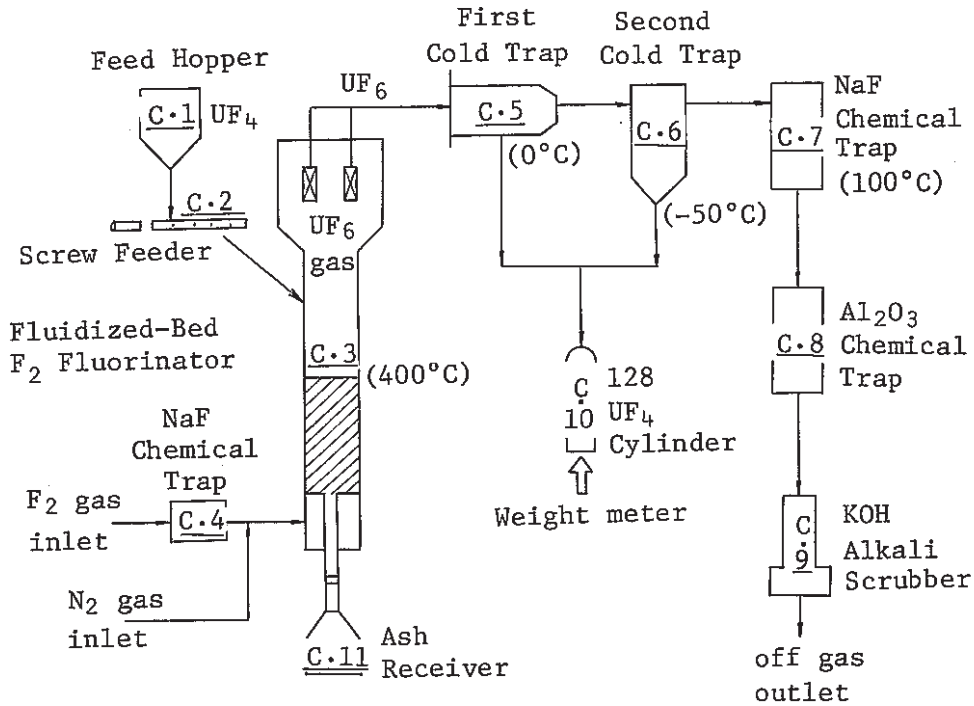


Fig. 7.  $UF_6$  conversion process

- i. Temperature dependence shows that K agrees closely with Arrhenius' equation and that the activation energy is 17.83 kcal/mole.
- ii. K is directly proportional to fluorine partial pressure and bed height of reaction zone.
- iii. The higher the dehydration temperature, the lower the reactivity.

From the above experimental results, the  $UF_6$  production rate by reaction between  $UF_4$  and  $F_2$  can be represented by the following empirical formula 15.

$$\text{"}UF_6 \text{ production rate"} \propto -dm/dt = K$$

$$K = 1.14 \times 10^6 \cdot F \cdot L \cdot \exp(-9.030/T) \dots \dots \dots (15)$$

where

- t: time (min)
- m: amount of feed  $UF_4$  into the reactor (g)
- K: rate constant (g/min)
- F: inlet  $F_2$  gas flow rate (NL/min)
- L: bed height at the state without flowing gas (cm)
- T: temperature (Kelvin degree)

The equation of fluorine utility efficiency in dependence of reaction temperature is theoretically introduced from Eq. 15, as follows:

$$E = F_o/F = 3.60 \times 10^6 \exp(-9.030/T) \dots \dots \dots (16)$$

where

- E: fluorine utility efficiency
- F<sub>0</sub>: stoichiometrical F<sub>2</sub> consumption rate (Nl/min)
- F: actual inlet F<sub>2</sub> gas flow rate (Nl/min)

After the batchwise experiments, continuous test operation of fluorination was performed under the condition of constant bed inventory. And it has been recognized that the test results agree approximately with the equation of fluorine utility efficiency (Eq. 16), as shown in Fig. 8.

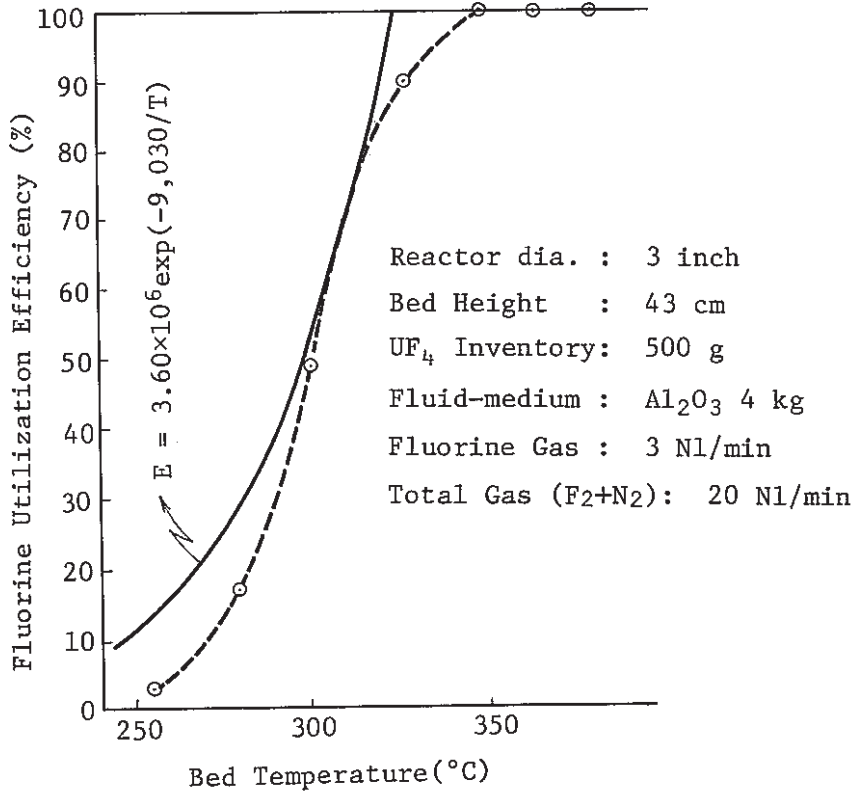


Fig. 8. Effect of temperature on utilization of fluorine

After many experiments and experiences, a high fluorine utilization efficiency of over 99.9 percent (less than 0.1 percent of unreacted fluorine) was finally attained in conditions of the relatively low temperature of 380°C and the usual UF<sub>4</sub> feed velocity of 0.1 kg/h cm<sup>2</sup>. The UF<sub>4</sub> powder produced by the PNC wet process, as mentioned above, has a high reactivity compared with the experimental data published by several researchers.<sup>4),5)</sup>

The behavior of impurities in the process was also investigated. The contents of the impurities after the refining and conversion are given in Table 2. The UF<sub>4</sub> and the UF<sub>6</sub> are products of high purities, and the low values of the impurities adequately satisfy UKAEA and USAEC specifications, as shown in Table 2.



## NEW PLANT OPERATION

To develop the PNC process, a new milling and conversion pilot plant (200 t-U/year) was built, and is now expanding and supplying  $UF_6$  to the adjacent uranium enrichment pilot plant in the Ningyo-Toge Works.

The flow-sheet of the plant is shown in Fig. 9. The new plant has been designed to treat uranium ores and imported yellow cake as its feed materials.

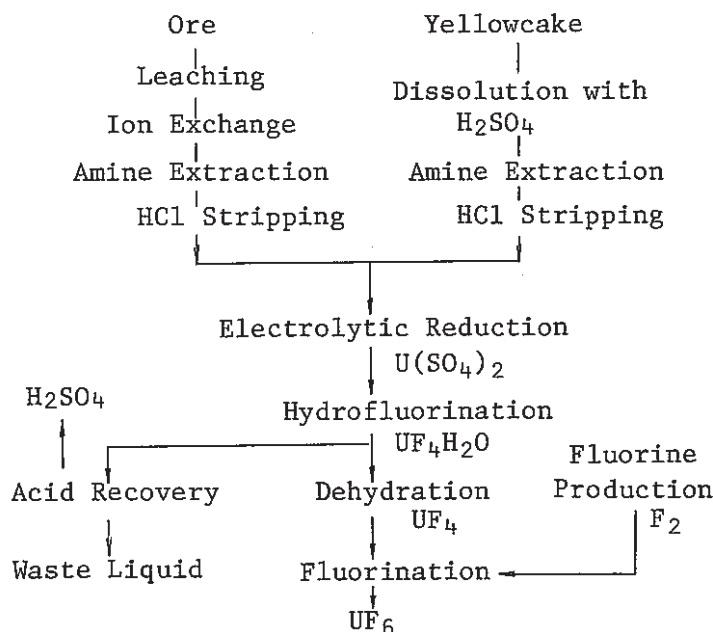


Fig. 9. Flowsheet of new milling and conversion pilot plant

The plant has two systems of solvent extraction using tri-n-octylamine; one treats the pregnant liquor (3-5 g-U/l) from the vat-leaching followed by ion exchange, and the other treats the uranyl sulphate solution (200 g-U/l) by the dissolution of yellow cake. In both solvent extraction systems, PNC process II was introduced, and mixer-settlers were used because of the ease of operation and analysis of the data from the operation. In the amine extraction section which treats the pregnant liquor from the ores, a sieve tray extraction tower was specially adapted in order to reduce the floor area and power consumption.

The stripping solution (100 g-U/l) from both solvent extraction systems is jointly fed to the electrolytic cell, in which the hexavalent uranium in the solution is reduced to tetravalent form. The reduction power consumption is about 1.5 kWh/kg-U, and the reduction rate is over 99.5 percent.

The tetravalent uranium solution is continuously reacted with hydrofluoric acid, and the uranium tetrafluoride, the reaction product, is dehydrated.

The conversion of UF<sub>4</sub> to UF<sub>6</sub> is accomplished in a fluidized-bed reactor, and the gaseous UF<sub>6</sub>, the final product, is trapped in the cold traps which are cooled to -10°C and -50°C. The data of impurities in the UF<sub>6</sub> produced with the PNC process are given in Table 3.

Table 3. Typical analyses of feed and product

Sample Element	Ore	Yellow cake		Product UF <sub>6</sub> ppm/U
	Ningyo-toge (%)	Niger ppm/U	China* ppm/U	
Al	6.9 - 9.0			<0.3 - 45.8
Ca	0.5 - 1.2	1200-3200	2 -20	0.9 - 17.0
Cd	0.001 - 0.002			<0.04 - 0.5
Cr	0.004 - 0.007			<0.04 - 1.5
Cu	0.001 - 0.003			<0.05 - 2.6
Fe	2.0 - 3.5	3100-3900	42 -62	<1.7 - 54.1
K	1.7 - 3.4	800-1000	11 -12	<0.4 - 36.5
Mg	0.21 - 0.47		0.6- 1.1	<0.1 - 15.2
Mn	0.05 - 0.06			<0.02 - 2.7
Mo	0.001 - 0.005	1500-2000	6 -12	<0.2 - 1.3
Na	1.0 - 4.2	28400-56100	0.7- 7	0.9 - 45.5
Ni	<0.001 - 0.002			<0.04 - 12.1
Ti	0.1 - 0.2		11 -28	<1
V	0.002 - 0.007	1500-2000	<0.2- 1.2	<0.2 - 1.2
Zn	0.01 - 0.02			<0.04 - 5.7
U(%)	0.07 - 0.13	72.5-74.2%	34.5-85.0%	67.3 - 67.6%

ppm/U: ppm on a U basis.

\*: the People's Republic of China.

The plant is operating satisfactorily and we are gradually obtaining important information for designing a commercial plant, to be constructed in the near future.

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