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SEPARATION OF URANIUM ISOTOPES BY THE CHEMICAL EXCHANGE METHOD

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ABSTRACT

The basic chemical process and technology for producing 3-5% enriched uranium has been established, through advances which allowed increases in the electron-exchange and adsorption-desorption reaction rates, effective uranium adsorption band formation and maintenance, reduction of the mobile-phase dispersion, and reduction in the height of the separation unit, which is largely determined by the diffusion coefficient, the electron exchange reaction rate of uranium ions, and the non-uniform flow pattern in the adsorption band. Physical theory and experimental results show the attainment of a specific separation power of approximately 500 SWU/m^3·yr for the process, and the possibility of an enrichment cost of $41/SWU in its commercial-scale application as calculated with depreciation terms of 15 years for equipment and 45 years for buildings and interest payments at 8% on investment capital. Inherent advantages of the process, in addition to low enrichment cost, are simple, stable operation and facilitation of the nuclear fuel cycle, with efficient separation of uranium-235 from the other uranium isotopes of spent nuclear fuel and elimination of the need for UF_6 conversion.

INTRODUCTION

Research on the uranium isotope chemical exchange reaction was initiated in 1948 by Woodard (1), who studied the equilibrium constants of the isotope electron exchange reaction between uranyl and uranous ions. Subsequent studies on utilization of this equilibrium showed its enrichment factor in aqueous solutions to be in the range of 0.0010 to 0.0014 (2-4), and isotope separation experiments were performed on this basis by several researchers (4-6).

Research at Asahi Chemical on the chemical method of uranium enrichment began in 1972, based on its established ion-exchange technologies. About that time, an evaluation by the U. S. Atomic Energy Commission (7) reported that based on the previous experiments the chemical enrichment process would require several centuries to obtain 3% enrichment from natural uranium. Since the enrichment factor of the chemical enrichment method is so small, more than 5 million separation steps are necessary to obtain 3% enriched uranium. The development of the chemical uranium enrichment process (8, 9) thus required the establishment of multi-stage separation using an efficient equilibrium system and a high-speed adsorbent. Studies for this purpose on catalysts for acceleration of the electron-exchange reaction rate (10) and technologies for production of a highly efficient adsorbent with a controlled pore structure (9) led to improvement of the overall reaction rate by a factor of several thousand.

These results were applied to the design and construction of a semi-commercial plant with columns of 1 m diameter and 3 m height at Hyuga City, which began operational separation studies in 1986. The plant has since yielded some 17 kilograms of more than 3% enriched uranium and provided data which indicate the chemical process to be commercially feasible (11). Here we describe the key elements of the chemical enrichment process and its practical utilization.

BASIC PRINCIPLES

The chemical enrichment process is based on the isotopic equilibria between U^{4+} and UO_2^{2+} shown in Figure 1, with separation carried out in a column packed with an adsorbent and an aqueous

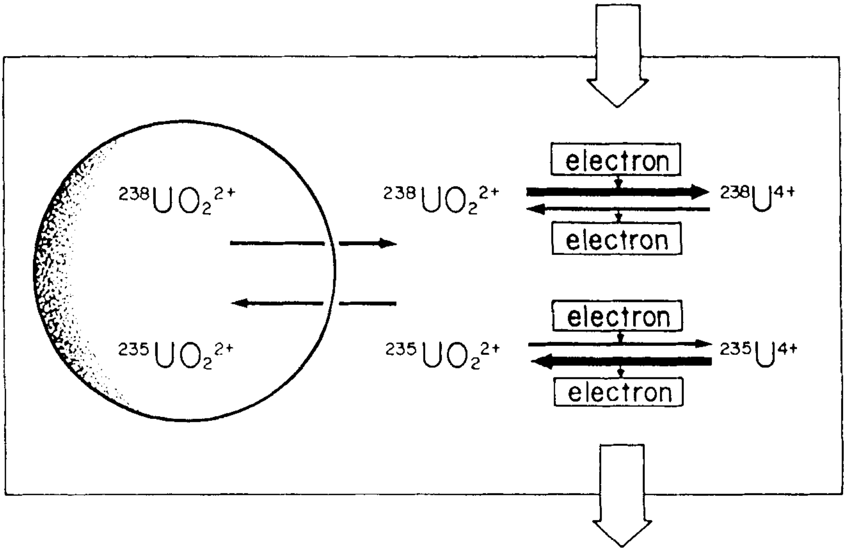

FIGURE 1. Basic isotopic equilibria of the chemical enrichment process.

solution. In a solution of U^{4+} and UO_2^{2+} ions, the hexavalent uranium-238 accepts electrons from a donor more readily than does hexavalent uranium-235, and thus tends to more readily undergo conversion to the tetravalent uranium ion. In the presence of an electron acceptor, on the other hand, the tetravalent uranium-235 ion tends to release electrons more easily than the tetravalent uranium-238 ion, and thus more readily undergo conversion to hexavalent uranium ion. The adsorbent has no direct preference for either isotope. It does, however, preferentially adsorb ions containing hexavalent uranium from a solution containing U^{4+} and UO_2^{2+}. The overall effect, therefore, is the occurrence of a slight increase in uranium-235 concentration by the adsorbent.

The chromatographic development is illustrated in Figure 2. Since the enrichment factor of the electron exchange reaction is only about 0.001, a very large number of separation units must be included

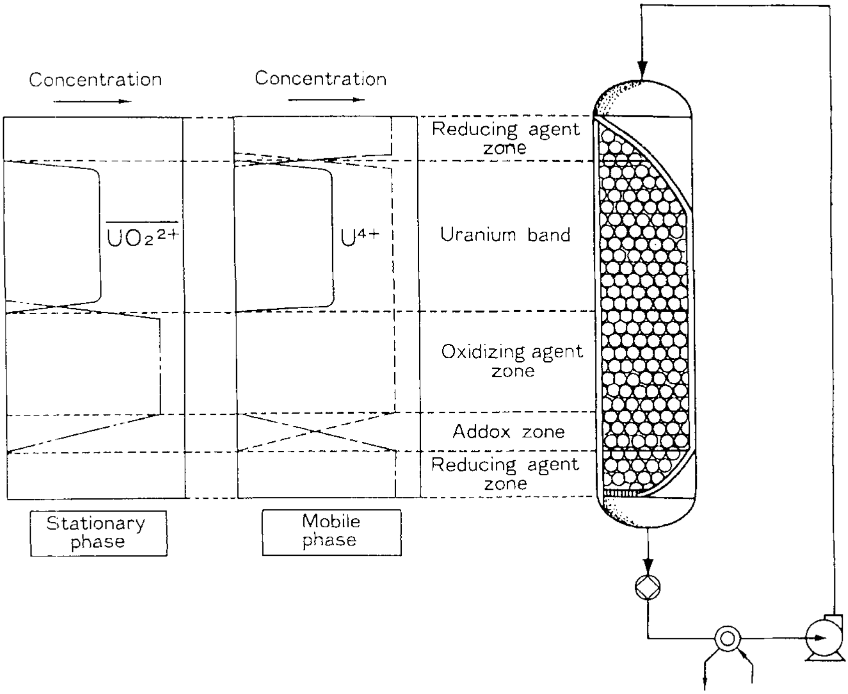

FIGURE 2. Component zones of the enrichment column.

in the uranium band containing $UO_2{}^{2+}$ in the adsorbed, or stationary, phase (12). Even with a band comprising some 6,500 of these separation units, several million development steps must be repeated in order to obtain 4% enriched uranium at the rear end of the band. At the rear end of the band, the electron donor gives up electrons to the hexavalent uranium ion. At the front end, the electron acceptor conversely oxidizes tetravalent uranium ion to obtain hexavalent uranium ion. As the band travels through the column, the uranium isotope profile is gradually developed until it reaches the stationary state, in which the enriched and depleted products are collected from the opposite end of the uranium band.

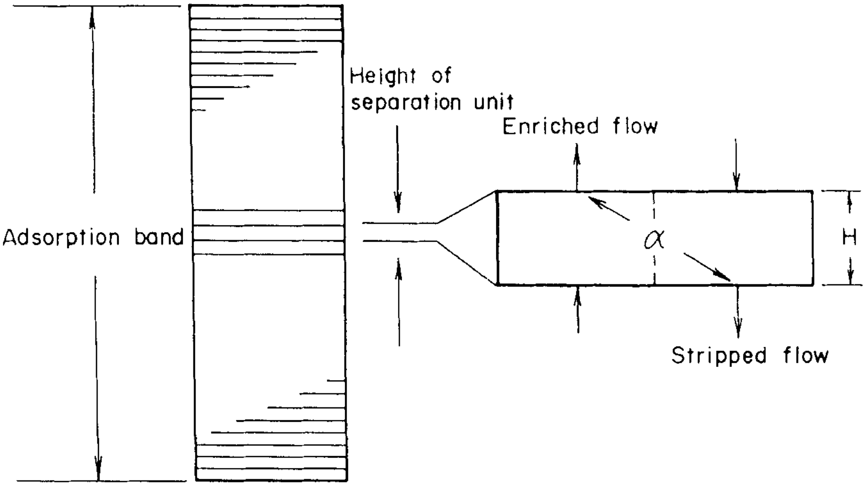

FIGURE 3. Conception of separation unit.

ENRICHMENT FACTOR OF THE SEPARATION UNIT

In separation of two target species, the separation factor is generally defined in terms of the ratio of the target species concentrations in the stationary phase at the top of the separation unit (f_2/f_1) and that in the mobile phase as it is about to leave the bottom (C_2/C_1), as

$$\alpha \equiv \frac{f_2/f_1}{C_2/C_1} \; . \tag{1}$$

It is the physical determiner of the height of the separation unit H, as shown in Figure 3, which is taken as the distance from the unit bottom at which the ratio between the target species concentration ratios in the two phases leaving the separation unit in the dynamic state, with the solution travelling down the column, equals the value of

TABLE 1. SYMBOLS DEPICTING URANIUM ION CONCENTRATIONS

	$(UO_2^{2+})_a$	$(UO_2^{2+})_s$	$(U^{4+})_s$	$(U^{4+})_a$
^{235}U	x_1	x_2	x_3	x_4
^{238}U	y_1	y_2	y_3	y_4
$^{235}U + {}^{238}U$	X_1	X_2	X_3	X_4

Subscripts: a, stationary phase; s, mobile phase

α obtained in the static state. The enrichment factor of the separation unit is defined as

$$\varepsilon_S = \alpha - 1 \tag{2}$$

The separation factor α may be expressed in terms of the isotope concentrations represented in Table 1, as

$$\alpha \equiv \frac{(x_1 + x_4)/(x_2 + x_3)}{(y_1 + y_4)/(y_2 + y_3)} \; . \tag{3}$$

Since no significant isotopic basis exists in the adsorption-desorption equilibria, and since the electron acceptance potential in the adsorbent is the same as that in the mobile phase, the relation of Eq. (3) may be approximated, in terms of the molar fractions in each phase, as

$$\begin{aligned} \alpha &= 1 + \varepsilon_S \\ &= \frac{(1 + \varepsilon_S)\, aX_1 + X_4\,(aX_2 + X_3)}{(aX_1 + X_4)\,\{(1 + \varepsilon_0)\, aX_2 + X_3\}} \end{aligned} \tag{4}$$

where $a = \{1 - N_0(1+\varepsilon_0)\}/(1-N_0)$, N_0 representing the molar fraction of ^{235}U in the feed uranium. If $\varepsilon_0 \ll 1$ and $N_0 \ll 1$, then Eq. (4)

may be written as

$$\varepsilon = \zeta \cdot \varepsilon_0 , \tag{5}$$

$$\zeta \equiv (X_1 X_3 - X_2 X_4) / \{ (X_1 + X_4) - (X_2 + X_3) \} . \tag{6}$$

The coefficient ζ represents the reduction in the enrichment factor resulting from incomplete adsorption of UO_2^{2+} and partial adsorption of U^{4+} from the mobile phase.

The value of the enrichment factor based on observed uranium enrichment efficiency was found to coincide with that calculated theoretically by Eq. (5) from measured uranium concentrations under the equilibrium between solution and adsorbent (9), which showed it to be in the range 0.0008 – 0.0012.

BASIC EQUATION OF CHEMICAL ENRICHMENT

The theoretical description of the chemical enrichment method is derived from the generally applied description of square-cascade separation as a fine, multi-stage process. If the average concentration of a target separation species in a separation unit at a certain position is taken as q_v, its concentration in the mobile phase of the unit is taken as C, and the distance of chromatographical development is taken as z, then the material balance for the distance z-Hd to z may be described by

$$Hd \, (q_{v+\Delta v} - q_v) = \Delta \, (C_{z-Hd} - C_z) , \tag{7}$$

where v represents the volume of solution added. Both C_{z-Hd} and $q_{v+\Delta v}$ can be expressed by Taylor's series developed to only two terms, since Hd and $\Delta \, v$ are relatively small in comparison with z and v, making it possible to express the relation.

$$\left(\frac{\partial q}{\partial v} \right)_z + \left(\frac{\partial C}{\partial z} \right)_r - \frac{Hd}{2} \left(\frac{\partial^2 C}{\partial z^2} \right)_v = 0 . \tag{8}$$

Translation of Eq. (8) to that of a moving coordinate system of the type generally applied in theoretical description of multi-stage separation yields an equation which includes a cross product in one term. It is therefore not amenable to formal solution, and is solved rather by variable-transformation linearization. In the limiting case of displacement chromatography in which the length of the adsorption band and the total concentration of the target species are both constant over time, solution of Eq. (8) yields

$$\frac{C_2}{C_{2,0}} = \frac{2\varepsilon_q N}{1 - exp(-2\varepsilon_q N)} exp(-2\varepsilon_q i) - \frac{4\varepsilon_q}{N}$$

$$\times\, exp(-2\varepsilon_q i) \sum_{m=1}^{\infty} - \frac{n\{1 - (-1)^m exp(\varepsilon_q N)\}}{(\varepsilon_q^2 + n^2)^2}$$

$$\times\, \{n cos(ni) - \varepsilon_q sin(ni)\}\, exp\{- \frac{\varepsilon_q^2 + n^2}{2(1+\varepsilon_q) j}\} \tag{9}$$

where N is the total number of separation units and i the relative position of the separation unit in the adsorption band, j represents the development stage, $\varepsilon_q = X\varepsilon_s$ with X being the mole fraction of the uranium ions in the stationary phase, and $n = m\pi/N$.

HEIGHT OF THE SEPARATION UNIT

The height of the separation unit, H, is defined as the height at which equilibrium is attained between the uranium isotope ratio in the stationary phase and that in the mobile phase. Factors such as low reaction rate and mobile-phase dispersion may be considered as tending to delay its attainment.

The components of the separation unit height illustrated in Figure 4, are defined as follows.

$$H = Ha + Hr + Hm{,}micro\, , \tag{10}$$

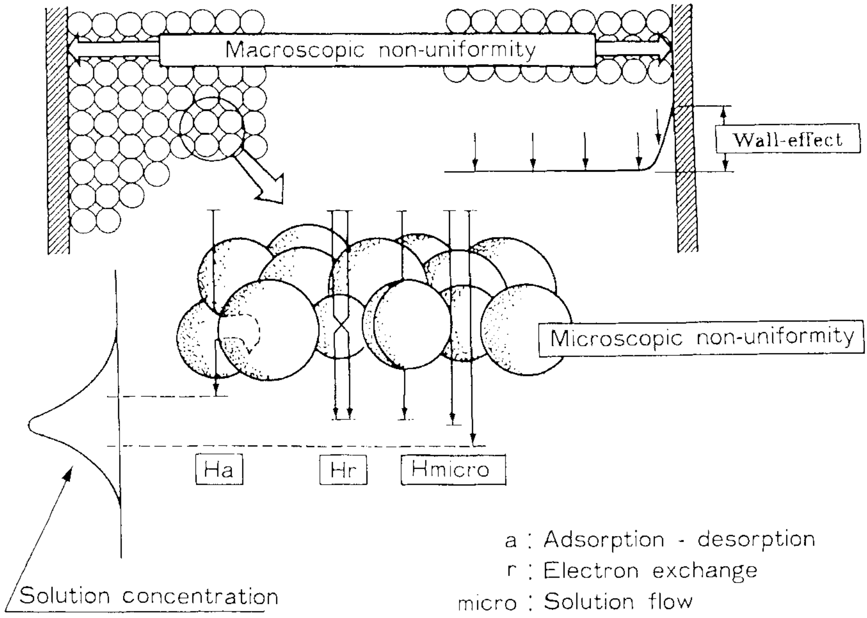

FIGURE 4. Components of separation unit height.

where Ha, Hr, and $Hm_{,micro}$ represent minute non-uniformities related to adsorption-desorption reactions, electron exchange reactions, and flow pattern, respectively. Ha and Hr can be represented as

$$Ha = \xi_a \frac{dp^2}{28D} u \tag{11}$$

$$Hr = \xi_r \frac{1}{k} u, \tag{12}$$

where ξ, D, dp, k and u are the localization factor, intra-adsorbent diffusion coefficient, particle diameter, reaction kinetic constant, and velocity of the uranium mobile phase, respectively.

Improvement of the adsorbent has lowered Ha to a current value of about 340 μm. The intra-adsorbent diffusion coefficient has been increased to more than 10^{-10} m^2s^{-1} from the level of 10^{-13} m^2s^{-1} found in commercial exchangers, essentially by optimizing the internal structure of the adsorbent. The pore diameter was optimized to maximize intra-pore ion mobility. In addition, the pore volume ratio was increased with no loss in physical strength, and the pore diameter distribution was sharpened.

A substantial reduction in Hr, to about 40 μm in the present semi-commercial plant, has been achieved through the development of electron exchange catalysts (10) and the utilization of temperature effects. $H_{m,micro}$ has been greatly decreased, to about 140 μm, by improvements related to (a) longitudinal diffusion, (b) intra-particle diffusion, (c) particle size distribution, (d) liquid viscosities, (e) interparticle channeling, and (f) velocity. These results allowed us to design and obtain a commercial plant separation column having about 10,000 separation units in the uranium band.

BACKMIXING

With the progress in the reduction on the separation unit height related to reactions and minute flow non-uniformities, elucidation and minimization of backmixing assume increasing importance. Dispersion due to backmixing is generally statistically represented using the second moment $m2$, which is defined as

$$m2 = \int_0^\infty (l - m1)^2 \, h(l) \, dl / m0, \tag{13}$$

where l is characteristic length, $m1$ the mean value of the distribution profile, $h(l)$ the length distribution function, and $m0$ the peak area of the distribution profile.

The height of the separation unit H may be represented in terms of the second moment $m2$, as

$$H = m2 / Lc, \tag{14}$$

where Lc represents the column length, but the related mixing

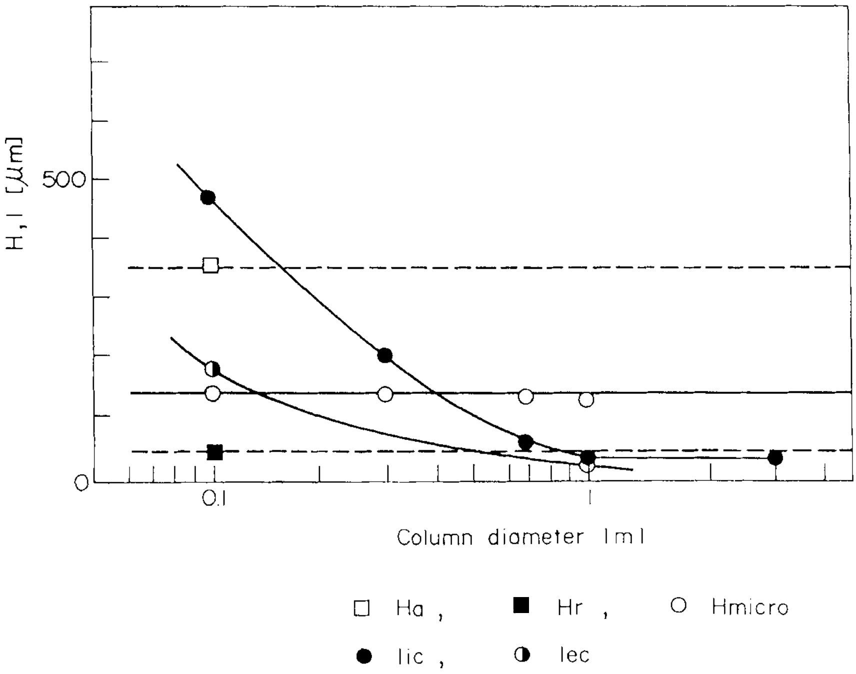

FIGURE 5. Column diameter and separation unit height.

phenomena are most appropriately considered and elucidated on a minute scale, as described above.

Macroscopic backmixing, on the other hand, is related primarily to the intracolumn wall effect and the extra-column equipment such as pipes and values. It is most appropriately represented by the backmixing term I, expressed as,

$$I = m2 / Lc \,, \tag{15}$$

$$Itotal = I\text{ic} + Iex \,, \tag{16}$$

where the subscripts *ic* and *ec* denote intra-column and extra-column, respectively. Macroscopically induced isotope backmixing (I_{ic}, I_{ec}), which is generally of particular concern in the development of industrial-scale isotope separation systems, has been shown in the course of our studies to decrease when the column diameter is increased as indicated in Figure 5. Both experimental results and theoretical description have led to accurate predictions of I_{ic} and I_{ec} based on statistical variance methods, and clearly indicate that the chemical enrichment process can be readily expanded to the industrial scale.

The intra-column backmixing has been shown experimentally to be highly dependent on the column diameter. Our studies have shown that solution flow near the column wall is quite distinctive in characteristics and slower than that farther inside of the column. We have also found that the thickness of the wall effect is constant, regardless of the column diameter. When the column diameter is increased to the semi-commercial scale, the wall effect no longer has any significant influence on the performance of the enrichment process.

The value of I_{eq} has been substantially reduced through extensive experiments and computational analyses of fluid dynamics related to equipment configurations and the hold-up of the liquids in the system. The experimental method consists essentially of injecting a tracer representing the delta-function input signal upstream from the equipment under observation, and measuring the output signal as a time-concentration function downstream from the equipment.

The relationship between the Reynolds number and the backmixing term I is shown in Figure 6. Experimental points are indicated by circles. The theoretical and experimental lines are derived from the relationship between the Reynolds number and the Peclet number. Under operating conditions, the Reynolds number ranges from 10^4 go 10^5. The I value per meter of pipeline was found to be about 0.1 μm/m. From these experiments, the value of I_{ec} has now been shown to be virtually negligible in equipment scale-up.

Flow patterns in equipment are numerically calculated by solving the Navier-Stokes equations. The government equations, which are the continuity equation and the Navier-Stokes equations, are expressed in an appropriately non-dimensionalized form as

$$\frac{\partial V}{\partial t} + (V \cdot grad)\, V = -grad\ p + \frac{1}{Re}\nabla^2 V \tag{17}$$

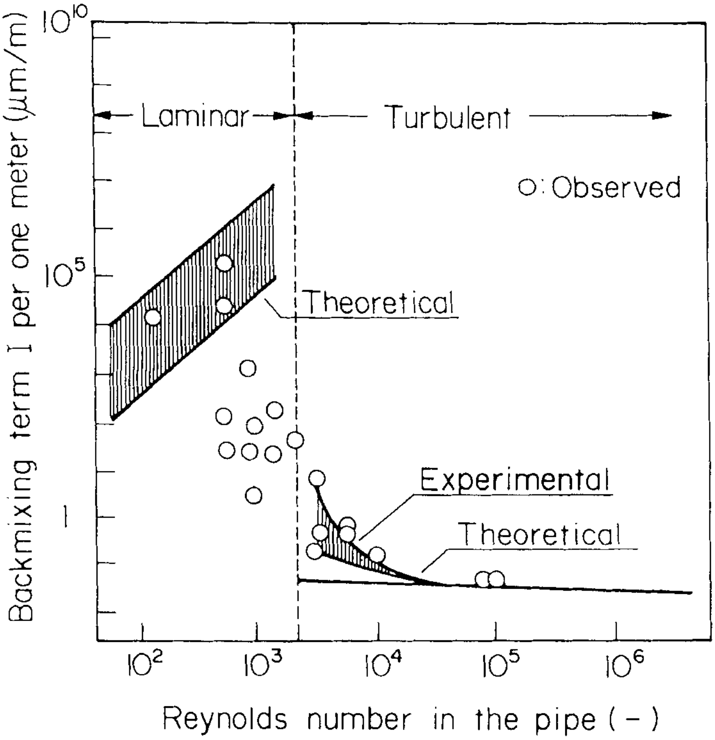

FIGURE 6. Intra-pipeline Reynolds number and backmixing.

and

$$div \cdot V = 0\,. \tag{18}$$

A semi-implicit scheme (13, 14) is utilized for the temporal integration of the Navier-Stokes equation. This scheme is equivalent to the Euler backward scheme except for the nonlinear convection terms. The convection term is linearized as

$$V \cdot gradV = V^{n+1} \cdot gradV^{n+1} \simeq V^{n} gradV^{n+1}\,. \tag{19}$$

These linearized equations are solved using a SOR scheme at each time-step. The computational study was applied to estimate the flow pattern of the equipment, and has contributed to the decrease of macroscopic backmixing to insignificant levels.

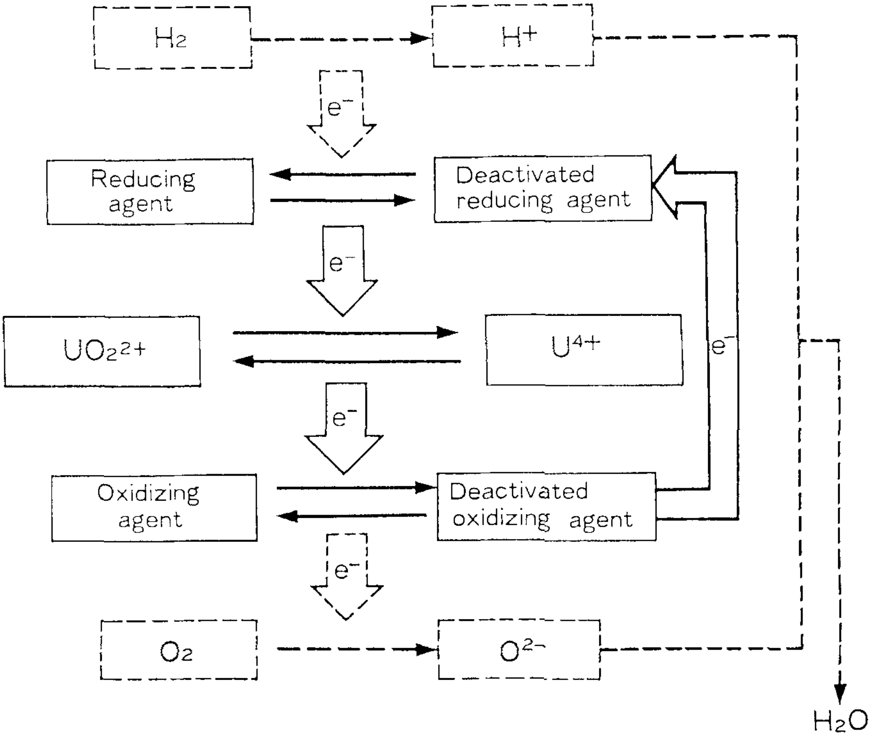

FIGURE 7. Electron cycle of isotope separation.

RECOVERY OF ENRICHMENT ENERGY AND THE SUPER PROCESS

In the chemical enrichment process, one mole of uranium ions can be stoichiometrically reduced by two mole of electrons. As shown in Figure 7, the electron flows essentially from hydrogen gas to the deactivated donor (the reducing agent), to the hexavalent uranium, to the activated acceptor (oxidizing agent), and finally to oxygen gas. The resulting hydrogen and oxygen ions combine, to form water. The redox energy is, inherently, the separation energy of the process. A new reaction was discovered, in which the potential of the electron of the

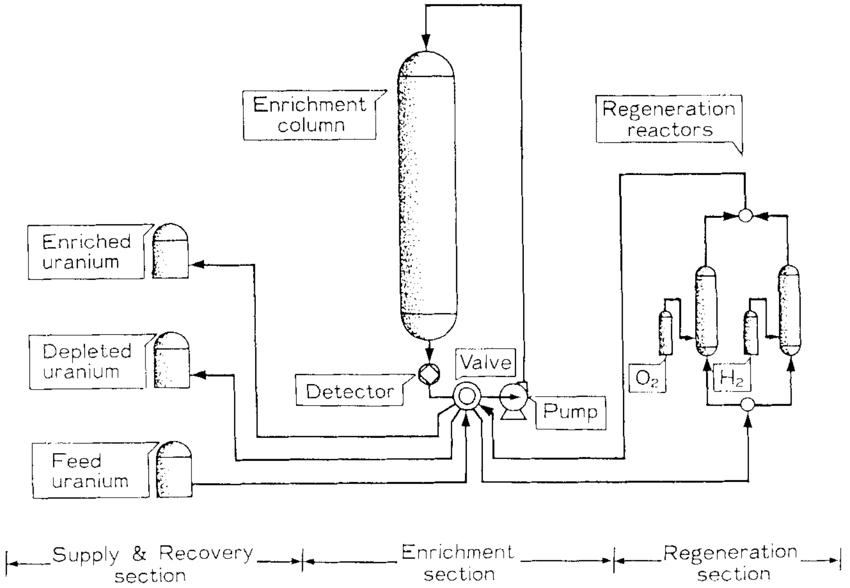

FIGURE 8. Super Process.

deactivated acceptor can be "pumped up" by the adsorbent to that of the electron donor. This is an inverse reaction, in the sense that the electron flow is from the low potential of the acceptor to the high potential of the donor. We now call this the "addox" reaction, as an abbreviation of adsorption and redox.

The Super Process version of the chemical enrichment process utilizes the addox reaction for energy recovery. In this system, the enrichment column has an addox zone in addition to the reducing agent zone, uranium band, and oxidizing agent zone. Particularly by inducing a strong addox reaction, it is possible to carry out continuous enrichment with only one enrichment column, as shown in Figure 8. The deactivated reducing agent, which has donated an electron to the hexavalent uranium, flows down the column relatively rapidly through the adsorbent particle interstices, and meets the deactivated oxidizing agent, which has gained an electron from tetravalent uranium. The

TABLE 2. COST OF COMMERCIAL PLANT

Product : 4.0% ^{235}U
Waste : 0.3% ^{235}U

Capacity	(million SWU/y)		9
Construction cost	(million $)		1880
Total enrichment cost	($/SWU)		41.2
Operation cost	($/SWU)		9.3
Electric power consumption		(46 kWh/SWU)	(3.7)
Oxygen and hydrogen consumption		(13 Nm^{3}O$_2$/SWU)	(3.6)
Other chemicals and utilities		(catalyst, adsorbent, pure water, fuel, etc.)	(2.0)
Depreciation cost	($/SWU)		29.9
Equipment		(46 kWh/SWU)	(18.3)
Buildings and others		(interest, tax, etc.)	(11.6)
Others	($/SWU)	(workers, etc.)	2.0

deactivated reducing agent and the deactivated oxidizing agent undergo the inverse reaction in the addox zone, as they continue to flow down the column. The reactivation reaction is not perfect, and a small supplementary reactivation by hydrogen and oxygen is required in the regeneration section. The Super Process offers major economic advantages, and allows the simplification of the process, a great reduction in the size of equipment, and a great saving in the enrichment energy.

PROCESS ECONOMY AND FACILITATION OF FUEL CYCLE

The chemical enrichment process, and particularly the great energy saving and simplification of the Super Process, permits highly economical plant installation and operation.

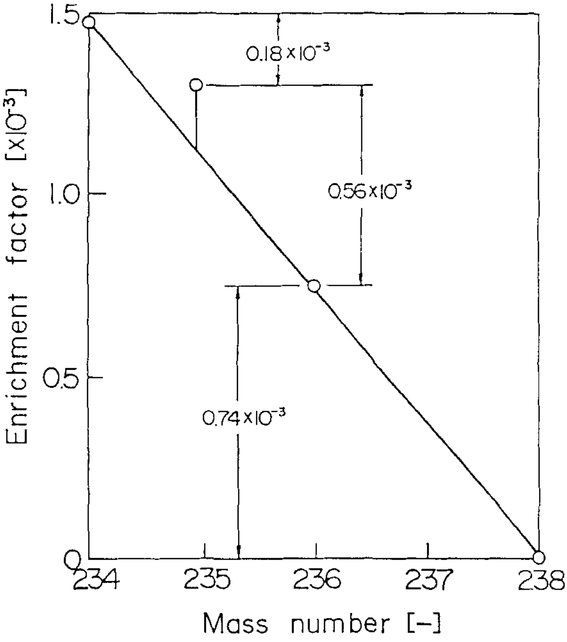

FIGURE 9. Enrichment factors for four uranium isotopes.

In the commercial plant design, based on experimental data obtained mainly by the semi-commercial plant, the specific separation power is estimated to be 500 SWU/y·m^3. As is shown in Table 2, the estimated construction cost and total enrichment cost of a 9 million SWU/y plant are $1,880 million and $41/SWU, respectively. Variable costs per SWU are calculated from unit consumptions of 13 Nm^3/SWU for oxygen, 26 Nm^3/SWU for hydrogen and 46 kWh/SWU for electric power. Depreciation terms are taken as 15 years for equipment and 45 years for buildings, and an interest rate of 8% for capital investment is assumed. The low construction and enrichment costs are attributable in large part to the utilization of the reversible equilibrium reaction as the basic mechanism of separation, rather than physical dynamics under the high accelerative forces employed in other uranium enrichment processes. The energy requirement for separation itself is therefore small, and the need for propulsion of process fluids is minimal and can be provided by several pumps.

The chemical enrichment process will also facilitate establishment of contribution to the nuclear fuel cycle. It eliminates UF_6 conversion and reconversion from the cycle, and can be readily applied to the reenrichment of uranium after its reprocessing. It can furthermore provide an effective means of separating uranium-236 from reprocessed uranium, and thus avoiding the adverse effect of this isotope on reactor efficiency with reenriched uranium. The relation between mass number and enrichment factor for uranium isotopes relevant to reenrichment is shown in Figure 9. As indicated the enrichment factor for separation of uranium-235 from uranium-236 has been found in operation of the chemical enrichment process to be considerably larger than that predicted from the difference in mass number alone. In its efficient removal of uranium-236, as well as its elimination of the need for UF_6, the chemical enrichment process is expected to be a significant contributor to the completion of the nuclear fuel cycle.

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