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Energy Consumption of Chemical Uranium Enrichment

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ABSTRACT

A quantitative study of chemical separation energy for enriching uranium-235 by the redox chromatography was conducted. Isotope exchange reactions between U^{4+}-UO_2^{2+} ions in the enrichment column are maintained by the redox reactions. The chemical separation energy is ultimately supplied by hydrogen and oxygen gas for regenerating redox agents. The redox energy for the isotope separation is theoretically predicted as a function of the dynamic enrichment factor observed in the chromatographic development of uranium adsorption band. Thermodynamic treatments of the equilibrium reactions implies an "inverse redox reaction" which can be enhanced by the chemical potential of the ion-exchange reaction of oxidant. Experimental results showed 30 to 90% recovery of the redox energy by the inverse reaction. These results will devise a simplified redox chromatography process where a number of columns in one module is reduced.

INTRODUCTION

The chemical separation of uranium isotopes by redox chromatography was judged by the Adhoc Committee of USAEC in 1972(1) to be definitely not competitive with gaseous diffusion as a means of enriching ^{235}U, due to an equilibrium time measured in centuries and extremely large power requirements. However, the efforts of the present authors, which have been mainly focused on minimizing the rate of the isotope exchange, have led to the development of a novel redox chromatography system that enables us to obtain 3% enriched uranium in a continuous operation lasting several months. The development was presented at the Symposium on Uranium Enrichment held by the American Institute of Chemical Enegineers in 1982(2) and also reported in published papers(3,4).

To further improve the separation efficiency, it has been necessary to elucidate the mechanism of chemical and isotopic equilibria between uranium and other metal ions in the redox chromatography, as well as the effect of the physical parameters which may govern the rate of enrichment.

Two forms of energy are required in the redox chromatography. One is the mechanical energy to pump fluids through the enrichment system composed of enrichment columns and redox reactors, and the other is the chemical energy of hydrogen and oxygen needed to regenerate the redox agents after they have refluxed the hexavalent and tetravalent uranium ions in the uranium adsorption band. Here we report the results of investigations on the basic equilibria in the redox system, the chemical energy required to maintain the isotope exchange reactions, and our recent conclusion that a large portion of the separation energy can be recovered by an inverse redox reaction induced by the adsorbent in the column.

ENRICHMENT FACTOR AND SEPARATION ENERGY

The basic reaction for uranium enrichment by chemical means can be represented by Eq.(1), as an expression of the isotopic equilibrium between hexavalent and tetravalent uranium ions. In the redox chromatography process, the isotopic equilibrium between the uranium ions on the adsorbent and those in the solution can also be represented by the isotopic reaction expressed as Eq.(2).

$$^{238}UO_2{}^{2+} + {}^{235}U^{4+} \rightleftarrows {}^{235}UO_2{}^{2+} + {}^{238}U^{4+} \quad : K_0 \tag{1}$$

$$^{238}U_a + {}^{235}U_s \rightleftarrows {}^{235}U_a + {}^{238}U_s \quad : K_s \tag{2}$$

where U_a is uranium on the adsorbent, U_s is uranium in the solution, and K_0 and K_s are isotopic equilibrium constants.

Using the abbreviated symbols given in Table 1 for the molar concentration of uranium ions, K_0 and K_s can be expressed as

$$K_0 \equiv 1 + \varepsilon_0 = \frac{x_2/x_3}{y_2/y_3} \tag{3}$$

$$K_s \equiv 1 + \varepsilon_s = \frac{(x_1+x_4)/(x_2+x_3)}{(y_1+y_4)/(y_2+y_3)} \tag{4}$$

where ε_0 and ε_s are defined as enrichment factors.

Eq.(4) can be considered as comprising several types of reactions, related to (a) the isotopic equilibrium of electron exchange between

TABLE 1
Abbreviated Symbols of Uranium Ions

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

tetra- and hexavalent uranium ions, (b) the isotopic equilibrium of adsorption-desorption reactions between the adsorbent and the solution phases, and (c) the phase equilibrium of hexavalent and tetravalent uranium ions. The isotopic equilibrium constant of the reactions between uranium ions on the adsorbent and those of the same chemical state in the solution is known to be ∿1.0(5), and the isotopic equilibrium constant in the adsorbent is assumed to be the same as that within the solution. The enrichment factor ε_S can therefore be expressed as(6)

$$\varepsilon_S = \frac{((1+\varepsilon_0)ax_1+x_4)(ax_2+x_3)}{(ax_1+x_4)((1+\varepsilon_0)ax_2+x_3)}\varepsilon_0 \tag{5}$$

$$\text{where} \qquad a = \frac{1-N_0(1+\varepsilon_0)}{1-N_0} \tag{6}$$

If $\varepsilon_0 \ll 1$ and $N_0 \ll 1$, Eq.(5) can be reduced to Eq.(7), in which the "localization coefficient" ξ_e corresponds to the bias between the hexavalent and tetravalent uranium ion concentrations in the two phases.

$$\varepsilon_S = \xi_e \cdot \varepsilon_0 \tag{7}$$

$$\text{where} \qquad \xi_e = \frac{x_1x_3-x_2x_4}{(x_1+x_4)(x_2+x_3)} \tag{8}$$

In the experiment, however, the observed value of the enrichment factor is smaller than that predicted by Eq.(7). The enrichment factor ε_d, termed the "dynamic enrichment factor", is therefore introduced to fill the discrepancy between the static phase equilibria and the dynamic balance of chemical species when the uranium adsorption band is developed in the enrichment column. The discrepancy is attributable to incomplete phase equilibria, which is particularly evident in a column too short to attain the steady state between chemical species, but also occurs in longer columns due to isotopic mixing generated by the turbulent fluid flow in valves and lines. The factor ε_d is dependent on the coefficient ξ_e and the "unsteady state coefficient" ξ_u which is introduced to express miscellaneous mixing effects. The factor can then be expressed as Eq.(9)(6).

$$\varepsilon_d = \xi_e \cdot \xi_u \cdot \varepsilon_0 \tag{9}$$

In a steady-state operation of the redox chromatography, three zones form in the enrichment column, the oxidizing agent zone, the uranium adsorption band and the reducing agent zone. The adsorbent selectively retains hexavalent uranium in the uranium adsorption band. The exchange of uranium isotopes between the liquid and solid phases occurs upon contact of the descending tetravalent uranium in the liquid phase with the hexavalent uranium in the solid phase. At each end of the uranium adsorption band, the hexavalent or tetravalent uranium is refluxed by contact with the oxidizing or reducing agent. The uranium isotopes are thus separated within the uranium adsorption band, with ^{235}U tending to collect at the reduction boundary and ^{238}U at the oxidation boundary.

The regeneration energy, the chemical energy to maintain U^{4+} and $UO_2{}^{2+}$ isotope exchange reactions, is determined by the process parameters of the dynamic enrichment factor ε_d, and the ^{235}U mole fractions of the feed and product streams. Eq.(10) shows the minimal reflux ratio, which is the ratio of total mass flow to product flow(6),

$$R_m = \frac{X_P - X_F}{\varepsilon_d \cdot X_F} \qquad (10)$$

where X_P and X_F are mole fractions of the product and the feed stream, respectively. The amount of deactivated redox agents has been found experimentally to be larger than that of the minimum reflux ratio. In the redox chromatography the redox agents have to be entirely regenerated by the reaction with hydrogen and oxygen, or by electrolysis. In the new process which is currently under development, most of the deactivated redox agents can be activated by an "inverse redox reaction" induced by the adsorbent in the enrichment column. The principle of this reaction is described below.

EQUILIBRIA AND INVERSE REDOX REACTION

In the course of chromatographic development of the uranium adsorption band in the enrichment column, the following three types of reactions occur.

Redox reactions

$$UO_2{}^{2+} + 2Ti^{3+} \rightleftarrows U^{4+} + 2TiO^{2+} \qquad (11)$$

$$U^{4+} + 2Fe^{3+} + 2H_2O \rightleftarrows UO_2{}^{2+} + 2Fe^{2+} + 4H^+ \qquad (12)$$

Complex-forming reactions

$$(M{\cdot}Cl_n)^{\nu-} + C\ell^- \rightleftarrows (M{\cdot}Cl_{n+1})^{(\nu+1)-} \qquad (13)$$

Ion-exchange reactions

$$(M{\cdot}Cl_n)^{\nu-} + \nu R^+ \rightleftarrows (M{\cdot}Cl_n)^{\nu} - R_\nu \qquad (14)$$

where R^+ represents an ion-exchange group fixed to the adsorbent, and ν is the charge number of a metal complex. All three of these reactions can be written as a unified addition equation as Eq.(15),

$$A + \nu \cdot X \rightleftarrows D \tag{15}$$

where A and D are metal or metal complex ions, and X is respectively an electron, ligand or anion-exchange group in the redox, complex-forming or ion-exchange reaction.

The equilibrium of each reaction can be expressed, by applying thermodynamic relations, as

$$\Delta\mu_X = \Delta\mu^\circ_{X,A/D} + \frac{RT}{\nu}\ln\frac{a_A}{a_D} \tag{16}$$

$$\text{where} \qquad \Delta\mu_X \equiv \mu^\circ_X - \mu_X \tag{17}$$

$$\text{and} \qquad \Delta\mu^\circ_{X,A/D} \equiv \mu^\circ_X + \frac{1}{\nu}(\mu^\circ_A - \mu^\circ_D) \tag{18}$$

and where μ°_X, μ°_A, and μ°_D are the standard chemical potentials of X, A and D, and a_A and a_D are the activities of A and D(7). The terms $\Delta\mu_X$ and $\Delta\mu^\circ_{X,A/D}$ are referred to as the reduction potential strength and the standard reduction potential strength, respectively. The $\Delta\mu^\circ$ values for the individual reactions, as observed and calculated by the authors, are shown in Table 2.

In order to calculate the equilibrium states of numerous chemical species in the redox chromatography, about 80 reactions represented by Eq.(15) must be solved for each imaginary separation step in the chromatographic development. The distribution function T_{i,n_j} of an arbitrary adduct species, by which the molar ratio of the i-th element having n_j units of the j-th addend to the "bare" ion of that element can be calculated, is derived from Eq.(16).

$$T_{i,n_j} = \exp\left(\frac{S_P - L_P}{RT}\right) \tag{19}$$

$$\text{where} \qquad S_P \equiv \sum_j \sum_{n_j} (\nu_{i,j}\Delta\mu^\circ_{i,n_j}) \tag{20}$$

$$L_P \equiv \sum_j \sum_{n_j} (\nu_{i,j}\Delta\mu_{i,n_j}) \tag{21}$$

The introduction of the distribution function T_{i,n_j} has been reported in our previous papers(7,8). The L-potential L_P in Eq.(19) is a function of the total sum of reduction potential strengths $\Delta\mu_X$ in the solution; the S-potential S_P is the sum of the standard reduction potential strengths. The S-potentials used in this study are shown in Table 3.

This distribution function suggests that the distribution of each species is determined only by the sum of the potential strengths of the individual reactions, regardless of their physico-chemical differences as redox reactions or ion-exchange reactions. It also provides the theoretical prediction of an "inverse redox reaction", in that the equilibrium state of the redox reaction depends not only on the standard reduction potential, E°, in solution but also on the selectivity to the adsorbent. The inverse redox reaction here is

TABLE 2
Calculated Results of Standard Reduction Potential Strength
(kJ/mol)

reaction	ion	number of addends (ν)						
		0	1	2	3	4	5	6
complex formation	TiO^{2+}	-	4.6	-0.5	-4.9	-9.3	-13.7	-
	Ti^{3+}	-	10.5	-1.5	-5.9	-10.4	-14.8	-19.3
	$UO_2{}^{2+}$	-	-3.7	-2.3	-6.8	-11.2	-15.6	-20.0
	U^{4+}	-	10.3	1.3	-3.1	-7.5	-11.9	-16.4
	Fe^{3+}	-	18.0	4.6	0.1	-4.3	-8.7	-13.1
	Fe^{2+}	-	8.8	-2.3	-6.7	-11.1	-15.5	-20.0
redox	TiO^{2+}/Ti^{3+}	11.8	17.7	16.6	15.5	14.5	13.4	-
	$UO_2{}^{2+}/U^{4+}$	24.2	31.2	33.1	34.9	36.8	38.6	40.5
	Fe^{3+}/Fe^{2+}	81.8	72.6	65.8	59.0	52.2	45.4	38.6
ion exchange	TiO^{2+}	-	-	-	3.6	1.9	1.3	-
	Ti^{3+}	-	-	-	-	12.4	9.0	7.9
	$UO_2{}^{2+}$	-	-	-	14.4	17.9	18.2	18.7
	U^{4+}	-	-	-	-	-	21.2	15.4
	Fe^{3+}	-	-	-	-	21.6	17.2	15.8
	Fe^{2+}	-	-	-	2.0	2.0	2.0	2.0

TABLE 3
Calculated S-potentials of Ions
(kJ/mol)

phase	ion	number of addends (ν)						
		0	1	2	3	4	5	6
solution	TiO^{2+}	0	4.6	4.3	-0.7	-10.0	-23.7	-
	Ti^{3+}	11.8	22.3	20.8	14.9	4.5	-10.3	-29.6
	$UO_2{}^{2+}$	0	-3.7	-6.0	-12.8	-24.1	-39.7	-59.7
	U^{4+}	48.4	58.8	60.1	57.0	49.5	37.6	21.1
	Fe^{3+}	0	18.0	22.6	22.7	18.4	9.7	-3.5
	Fe^{2+}	81.8	90.7	88.4	81.7	70.6	55.1	35.1
adsorbent	TiO^{2+}	-	-	-	3.0	-8.1	-22.4	-
	Ti^{3+}	-	-	-	-	16.8	-1.3	-21.7
	$UO_2{}^{2+}$	-	-	-	1.6	-6.2	-21.5	-41.0
	U^{4+}	-	-	-	-	-	58.7	36.6
	Fe^{3+}	-	-	-	-	40.0	26.9	12.3
	Fe^{2+}	-	-	-	83.7	72.5	57.0	37.0

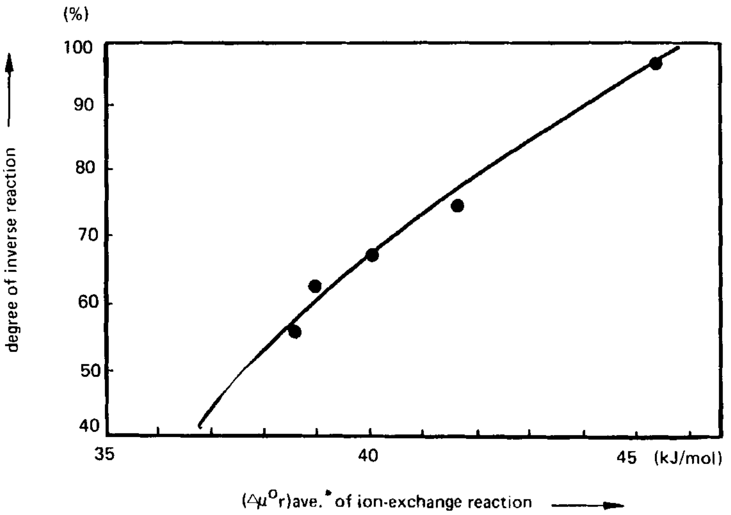

Fig.1 Degree of regeneration by inverse redox reaction
* average standard chemical potential of complexes

referred to the redox reaction where a mixture of deactivated redox agents can be activated to a large extent. The reaction is normally unfavored from the viewpoint of the standard reduction potential but favored in the presence of adsorbent if a large difference in adsorption selectivity is observed between the redox agents. The results of many experiments have shown this theoretical prediction to be valid. It was found in a preliminary batchweise experiment that ferrous (Fe^{2+}) and titanyl (T_iO^{2+}) ions in an acidic solution were converted to ferric (Fe^{3+}) and trivalent titanuim (T^{3+}) ions by contact with a fresh adsorbent. In addition, in a chromatography experiment for uranium enrichment, analysis of the effluent of mixed redox agents collected from the enrichment column showed regeneration of $T_i{}^{3+}$ ions to have occurred, and an equivalent amount of Fe^{3+} ions was found adsorbed on the adsorbent.

Some further study may be necessary to fully utilize the effect of the inverse redox reaction in the actual redox chromatography. The curve in Fig.1 shows the degree of the regeneration a_r, to be obtained by the inverse redox reaction, as a function of the standard reduction potential strength of ion-exchange reaction $\Delta\mu°_R$.
A regeneration at about 60% to the full redox energy has been observed in a continuous chromatographic development of a uranium band, and some advanced laboratory-scale experiments have also yielded the results of nearly 90% regeneration.

The regeneration of the redox agents by the inverse redox reaction results in a corresponding reduction in the isotope separation energy to be supplied by hydrogen and oxygen gas. As the optimum reflux ratio of a square cascade is about 1.5 times the minimum reflux ratio described by Eq.(10), the separation energy R_e required in an actual redox chromatography system can be expressed as follows.

$$R_e = \frac{1.5(1-\alpha_r)(X_P-X_F)}{\varepsilon_d \cdot X_F} \qquad (22)$$

A large excess of chemical energy is generally required to operate the chromatographic system, however. This type of redox chromatography can be conceived as a quasi-reversible process because of its recovery of separation energy.

The same effect may apply to other chemical isotope separation processes regardless of the element, due to the similarity of the chemical characteristics of ion-exchange reactions.

CONCLUSIONS

The conclusions of the present study are summarized and stated as follows:

1. The minimum reflux ratio of redox chromatography for uranium enrichment can be expressed in terms of the dynamic enrichment factor.
2. Equilibrium states of quite many complex ions in the redox chromatography can be expressed in terms of the reduction potential strengths, and the distribution function can then be derived to express concentrations of each complex.
3. Theoretical application of the distribution function strongly implies the possibility of inverse redox reactions in an ion-exchange column.
4. The inverse redox reaction was observed in the redox chromatography system, and regeneration of the redox agents at nearly 90% was achieved in some advanced laboratory-scale experiments.
5. About 60% reduction of the separation energy was achieved in the U^{4+} and $UO_2{}^{2+}$ isotope exchange reaction in a continuous run of the redox chromatography.

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