Translated from *Uspekhi Khimii* **58** 747–766 (1989) U.D.C. 546.791.02

The separation of uranium isotopes by chemical isotopic exchange

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ABSTRACT. Data on the separation of uranium isotopes by chemical isotopic exchange have been reviewed. Promising methods for enriching uranium have been compared.

The bibliography contains 120 references.

Contents

I. Introduction 441
II. Theoretical principles of the separation of uranium isotopes by chemical isotopic exchange 441
III. The separation of uranium isotopes by ion exchange 442
IV. The isotopic fractionation of uranium in electron exchange processes 443
V. The separation of uranium isotopes in the UF_6-NOUF_6 system 448
VI. Other methods 448
VII. Comparison of the methods 449

I. Introduction

The industrial production of enriched uranium is based on gas diffusion (GD).[1] In many countries, however, an intensive search is being carried out to find other methods of enrichment making it possible not only to lower the cost per separative work unit (kg S. W. U.) but also to decrease considerably the consumption of raw material and energy.[1–3] As alternatives to GD, methods based on the use of the centrifuge, lasers, effusion phenomena, a rotating plasma, and chemical isotopic exchange (CIE) are being examined.[2,3] Their theoretical principles and the possibility of their practical application have been examined in a number of reviews,[2–12] and there is an extensive patent literature. The greatest interest in CIE is being shown in Japan and France,[5,6] but published systematic reviews of this topic are inadequate. Some publications[3,5,12–18] deal only with individual aspects of the use of CIE to separate uranium isotopes, and ten years have passed since the publication of the review by Filippov and co-workers,[6] which deals most fully with this problem. In this period, many new and interesting publications have appeared, which not only develop the ideas presented in earlier work but also propose various fundamentally new approaches to the solution of the problem of separating uranium isotopes by chemical methods.

Of all the methods used to separate uranium isotopes, only CIE does not require the use of gaseous compounds or the atomic vapour of uranium. The regular features observed in the isotopic enrichment of uranium by CIE may be useful in the development of methods for separating the isotopes of heavy elements which for any reason do not form stable volatile compounds.

The aim of the present review is to analyse published data on the separation of uranium isotopes by chemical isotopic exchange and to compare promising methods for enriching uranium.

II. Theoretical principles of the separation of uranium isotopes by chemical isotopic exchange

In principle, chemical methods for separating isotopes may be based on kinetic or thermodynamic isotope effects arising in chemical transformations. In both cases the magnitude of the isotope effects is determined by the differences in the zero-point energies of the vibrations of the bonds in the isotopic molecules involved in the reactions.[1,19] Since the difference in the masses of the isotopic forms of molecules or ions is small, the interatomic distances and force constants of the bonds can with good accuracy be regarded as invariant.[19]

The CIE methods used at present are mainly based on thermodynamic isotope effects, since a single separation step is reversible. In this case the separation of isotopes can easily be made a multi-stage process by using counter-current separating systems. Moreover, the expenditure of energy in these processes is determined chiefly by the organisation of the phase reversal.[19]

In schemes for enriching uranium by CIE, the most widely encountered systems are those in which the isotopic exchange takes place between forms which do not react chemically and which are selectively distributed between two phases. The equilibrium constant of the isotopic exchange reaction (K) and hence the isotope separation coefficient (α) can be calculated by statistical thermodynamics.[1,19] In particular, for the heavy hydrogen isotopes, use is made of the approximate Bigeleisen–Mayer equation,[19] from which it follows that the values of $\ln\alpha$ are proportional to the square of the reciprocal of the mass of the isotope. Thus for CIE reactions in uranium compounds, very low values of α can be expected. The observed isotopic effects can be increased, however, by making use of complex processes in which the values of α for the elementary reactions act in the same direction and increase the overall effect. To determine the regular features of the change in the values of α in CIE processes, it has been proposed that isotopic exchange reactions be classified using three factors: the oxidation state of the element, the nature of the coordinated ligand, and the configuration of the coordination sphere.[20–22] The highest values of α should be achieved in systems in which the compounds being compared differ from one another to the greatest extent in terms of all three factors. The element in the

higher oxidation state should be combined with σ,π-donor ligands (N, O, F), and should form an unsaturated coordination sphere. For the element in the lower oxidation state, the coordinated ligands should have σ,π-donor and weak π-acceptor properties (Cl, Br, I, S, Se), and the coordination sphere should be close to saturation. Under real conditions, only a certain approximation to the optimum systems is possible, since the selection principles are contrary to the requirements for thermodynamic stability. Systems containing elements in different oxidation states are most promising, systems containing complexes with different configurations occupy second place, and systems differing only in the ligands are least promising.

A theoretical analysis of the values of α in isotopic fractionation in $U^{IV}-U^{VI}$ systems has been carried out.[23-26] The values of K have been calculated for the reactions:[23]

$$[^{235}U(H_2O)_8]^{4+} + [^{238}UO_2]^{2+} \rightleftarrows [^{238}U(H_2O)_8]^{4+} + [^{235}UO_2]^{2+},$$
$$^{235}U(H_2O)_4Cl_4 + [^{238}UO_2]^{2+} \rightleftarrows {}^{238}U(H_2O)_4Cl_4 + [^{235}UO_2]^{2+}.$$

At 20 °C, ^{235}U should be concentrated as UO_2^{2+} if the distances $U-H_2O$ in $[U(H_2O)_8]^{4+}$ and $U(H_2O)_4Cl_4$ are shorter than 2.26 Å and 2.30 Å respectively. X-Ray diffraction data indicate that these conditions are satisfied. The wavenumbers of the doubly degenerate (ν_2) and antisymmetric (ν_3) vibrations of the U−O bonds have been used to calculate the ratios of the reduced partition functions (RPF) of the UO_2^{2+} ion in its compounds with ClO_4^-, Cl^-, NO_3^-, and SO_4^{2-}.[24] The contribution of ν_3 to the RPF is 85% at 25 °C, and increases with increase in temperature. The equilibrium constants of the CIE reactions involving UO_2^{2+} are sensitive to changes in ν_2 resulting from complex formation. The separation coefficient for the isotopes ^{235}U and ^{238}U in U^{IV}–U^{VI} systems in the presence of cation exchangers is given by the expression[25,26]

$$\ln\alpha = \ln\alpha' + \ln[1 + (K-1)/(1+\bar{\rho})] + \ln[1 + (K^{-1}-1)/(1+\rho)], \quad (1)$$

where α' is the separation coefficient for the system containing only uranyl ions, K the equilibrium constant of the CIE reaction between U^{IV} and U^{VI} in solution, and ρ and $\bar{\rho}$ the molar ratios of U^{VI} and U^{IV} in solution and in the ion exchanger respectively.

It follows from Eqn. (1) that the influence of K on α is greater, the greater the difference between ρ and $\bar{\rho}$, that is the higher the selectivity of the sorption of the ionic forms of uranium. The concentration profiles of the elution curves, and equations relating the concentrations of the ith isotope to the position of the band in the column have been obtained, and the way in which the overall separation coefficient is related to the local values of α and the time taken to establish the steady state has been determined.[26,27]

To select the best method for separating uranium isotopes, it is also necessary to take account of economic factors. It has been suggested[5] that to be competitive, CIE methods must satisfy the following requirements:

1) the values of α should be not less than 10^{-3};

2) the chemical forms taking part in the exchange should be stable and should be distributed selectively between the phases;

3) the time for which uranium is involved in an elementary step should not exceed 1 min;

4) an effective means of phase reversal must be available.

The average consumption of energy should be about 5 eV per atom for reflux streams of high intensity.

III. The separation of uranium isotopes by ion exchange

1. Reactions involving U^{VI}

The results of experiments on the separation of uranium isotopes in a system formed by a uranyl salt solution and a sulphonic acid cation exchanger were published in 1954.[28] UO_2^{2+} was eluted through a column of Dowex 50 × 8 resin (50–100 mesh) in the Cu-form using a 5×10^{-3} M solution of $(NH_4)_2MgA$, where H_4A = EDTA. For a UO_2^{2+} band length of 28 cm and a migration distance of 90 cm, the specimen was enriched in the ^{235}U isotope from 4% to 5% at the front of the band. The isotopic fractionation took place as a result of the isotopic exchange reaction

$$[^{238}UO_2A]_s^{2-} + [^{235}UO_2]_r^{2+} \rightleftarrows [^{235}UO_2A]_s^{2-} + [^{238}UO_2]_r^{2+},$$

where the subscripts 's' and 'r' refer to the solution and resin phases respectively. In this system, phase reversal is described by the following equations:

$$[UO_2A]_s^{2-} + Cu_r^{2+} \rightarrow [UO_2]_r^{2+} + CuA^{2-} \text{ (sorption)}, \quad (2)$$
$$[UO_2]_r^{2+} + (NH_4)_2MgA \rightarrow [UO_2A]_s^{2-} \text{ (desorption)}. \quad (3)$$

Equilibria (2) and (3) are displaced to the right, so that both band fronts remain sharp during the elution, and no change in the band length takes place. This method of elution was called the Spedding method, after one of the authors.[28] In the process studied, the value of α for $^{235}U/^{238}U$ reached 1.002. It was later established[29] that in fact, $\alpha = 1.00006 \pm 0.00005$. The Spedding method has also been used to study isotopic replacement reactions in a cation exchanger–solution system using a column of length 1–2 m filled with Amberlite IR-120 or Dowex 50 × 8 resin in the H^+-form.[30] The sorption was carried out from $UO_2(NO_3)_2$, UO_2Cl_2, $UO_2(ClO_4)_2$, and $UO_2(SO_4)$ solutions. Solutions of ammonium acetate, citrate, and tartrate were used as eluants. The values of α obtained varied in the range 1.0001–1.0004. The values of α obtained using Dowex 50 × 8 resin were higher than those obtained using Amberlite IR-120.

Table 1. Isotopic enrichment in UO_2^{2+}–cation exchanger systems.[31-34]

Eluant	pH	Rate of elution, ml h^{-1}	Length of migration, cm	Rate of movement of the band, cm h^{-1}	$10^4\,\varepsilon$
Perchlorate	—	—	—	—	0.0±0.1
Chloride	7	9.5	197	1.85	0.25±0.1
Tricarballylate	—	—	—	—	0.66±0.1
Acetate	5	6.9	197	0.51	0.88±0.1
Glycollate	7	7.8	198	0.83	1.03±0.1
Lactate	7	7.0	203	0.80	1.42±0.15
Citrate	—	—	—	—	1.80±0.15
Malonate	7.5	6.3	200	1.4	2.18±0.2

Note. LS-6 cation exchanger (H^+-form, 100–200 mesh), 25 °C, column diameter 1 cm, eluant concentration 0.1 M; $\varepsilon = \alpha - 1$.

The Spedding method has been used to study the isotopic fractionation of uranium in a uranyl–cation exchanger system with elution by solutions of ammonium carboxylates or $NiCl_2$.[31-34] The results are given in Table 1. Enrichment in ^{235}U takes place at the

elution front, that is the carboxylate form of the uranyl complexes is enriched. The correlation between $\varepsilon = \alpha - 1$ and the wavenumbers ν_3 (cm^{-1}) of the antisymmetric vibrations of the UO_2^{2+} group in the complexes is given by the equation

$$\varepsilon = 4.62 \cdot 10^{-6}(960 - \nu_3),$$

where 960 cm^{-1} is the value of ν_3 in the resin phase. The data in Table 1 show good agreement with the results of a study[35] in which the eluant used for UO_2^{2+} sorbed on Dowex 50 resin was 0.07–0.22 M ammonium α-hydroxyisobutyrate solution (pH 2–6). The enrichment in ^{235}U took place in the solution phase, and the value of ε, (1.9–0.6) × 10^{-4}, depended on the pH of the eluant.

The isotopic fractionation of uranium in UO_2^{2+}–cation exchanger systems with desorption by complex-forming reagents is also being studied in China.[36] It has been found[37] that the isotopic effects in UO_2^{2+}–anion exchanger systems are lower than those in cation-exchange chromatography.

Table 2. Isotopic fractionation of uranium in U^{IV}–cation exchanger systems.[38–41]

Eluant solution	Temperature, °C	Percentage cross-linking of resin	Length of column, m	Enrichment in $^{235}U^*$ relative to natural uranium, %
0.3 M NH_4Cl, HCl	30	10	12	4.9
0.45 M NH_4Cl, HCl	60	12	12	5.5
0.4 M NH_4Cl, HCl	—	15	12	6.2
0.15 M Na_2SO_4	40	20	10	3.3
0.2 M Na_2SO_4	30	16	10	2.9
0.2 M NaCl, 0.28 M HCl	—	20	8	2.8
0.2 M NaCl, 0.27 M HCl	—	10	5	1.4
0.28 M HCl	—	16	12	2.4
0.18 M H_2SO_4	35	16	10	2.0
1 M H_2SO_4	—	5	10	1.5
0.01 M NaF, 0.5 M H_2SO_4	—	—	4	1.1
Lactic acid 0.6 M	30	10	10	4.2
Sulphosalicylic acid 0.4 M	75	15	10	5.1
Citric acid				
0.1 M	60	12	10	4.6
0.5 M	—	—	4	0.8

*The enrichment takes place in the 'trailing' part of the elution curve.

2. Reactions involving U^{IV}

Japanese workers[38–41] have developed methods for separating uranium isotopes in U^{IV}–cation exchanger systems with elution by various complex-forming reagents (Table 2). Strongly acidic styrene–divinylbenzene cation exchange resins with different degrees of cross-linking have been used. In contrast to the systems containing UO_2^{2+}, with U^{IV} the enrichment in ^{235}U takes place in the resin phase, and the values of ε are lower for U^{IV} than for the uranyl ion. If U^{IV} is desorbed using pure H_2SO_4 solutions, marked spreading of the uranium zone is observed, so that solutions of $MgSO_4$ or an $H_2SO_4 + MgSO_4$ mixture have been proposed as eluants.[39,40] The value of ε when an $MgSO_4 + H_2SO_4$ mixture was used was 5×10^{-5}.[39]

In the elution of U^{IV} with solutions of citric,[41] malonic, and lactic[42] acids, the elementary separation coefficient decreases with increase in temperature. The values of ε are approximately the same for all three acids. The value for citric acid is 6×10^{-5} at 50°C.[41]

A method for separating uranium isotopes in a U^{IV}–anion exchanger system has been patented.[43] Uranium(IV) was sorbed on a chloromethylated or aminated styrene–divinylbenzene anion exchange resin from a solution containing NH_4HSO_4. The uranium was desorbed using an $NH_4HSO_4 + H_2SO_4$ mixture. In a column of length 10 m, enrichment in the ^{235}U isotope by 10% relative to the original concentration took place at the front of the elution curve.

Thus the single-stage separation coefficients of uranium isotopes in ion-exchange systems containing different ionic forms of the metal in the same oxidation state are too low for these systems to be used on the industrial scale. Recently, however, systems in which the enrichment coefficient ε reaches 10^{-3} have been found. Thus in the isotopic exchange reaction between U^{VI} extracted by a 0.1 M solution of the macrocyclic polyether dicyclohexyl-18-crown-6 in 1,2-dichloroethane and U^{VI} in an aqueous solution containing 3.1–3.9 M HCl, enrichment of the organic phase in the ^{235}U isotope was observed, and the calculated value of α was 1.002 ± 0.004.[44] In the corresponding system containing U^{IV}, enrichment of the organic phase in the light isotope was again observed, and the coefficient α was 1.001 ± 0.0003.[45] An interesting feature is that the separation coefficients for $^{235}U/^{238}U$ and $^{40}Ca/^{42}Ca$ in the systems containing the crown ether were found to be close to one another (α = 1.0010 ± 0.0002 for $^{40}Ca/^{42}Ca$).[46] The reasons for these high isotopic effects in the uranium systems are not yet clear.

IV. The isotopic fractionation of uranium in electron exchange processes

1. The U^{IV}–U^{III} system

The values of α can be increased considerably by using systems in which uranium is present in different oxidation states in the compounds undergoing exchange. The U^{IV}–U^{III} system has been proposed as one such system.[47–51] The different oxidation states are separated using ion exchange resins[47] or various extracting agents.[47–51]

In the ion exchange method, U^{IV} is sorbed from 8 M HCl solution, and U^{III} remains in the aqueous phase. When a cation exchanger is used, U^{III} is sorbed, and U^{IV} remains in the aqueous solution containing 0.25 M H_2SO_4. In both cases, U^{IV} is enriched in the ^{235}U isotope. The values obtained for α were 1.0024 and 1.0020 for the anion exchanger and the cation exchanger respectively. In practice, it is difficult to use ion exchangers, because of the instability of U^{III}.

It is recommended that in extraction systems, U^{IV} be transferred to the organic phase as its complexes with alkyl phosphates, phosphine oxides, phosphonates, or phosphinates. The organic diluents used are benzene, toluene, dodecane, or kerosene. The results of the experiments are given in Table 3. The isotopic fractionation involves the reaction

$$^{235}U^{III}_{aq} + {}^{238}U^{IV}_{org} \rightleftarrows {}^{235}U^{IV}_{org} + {}^{238}U^{III}_{aq}.$$

Since appreciable rearrangement of the structure of the species involved in the exchange is not required, this reaction is rapid, and its kinetic charactersitics are determined by the inter-phase transfer time. Irrespective of the extracting agent, the U^{IV} compound is enriched in the light isotope ^{235}U.

It is desirable that the separation of uranium isotopes in extraction systems be carried out by the counter-current method; the aqueous phase should contain 0.1–2.5 M UCl_3 and 4–9 M HCl, and the organic phase 0.1–1 M U^{IV}. To prevent the oxidation of U^{III}, the process must be carried out in a nitrogen atmosphere, and the reagents should be free from ions which catalyse the oxidation of U^{III}. It has also been suggested that reagents combining with oxygen should be introduced into the system.

It is recommended that phase reversal be carried out electrochemically.[51] Zinc amalgam (1.1–1.8% Zn) can be used as the cathode to reduce U^{IV} in the aqueous phase. The solution used for the electrolysis should contain 4–5 M $ZnCl_2$. Under these conditions, liberation of gas does not take place in the reduction of U^{IV}. The anode for oxidising U^{III} may consist of lead, lead amalgam, graphite, mercury, or tantalum; the best characteristics are shown by lead.

2. The CHEMEX process

In 1977 it was reported that an industrial method had been developed in France for obtaining uranium with a low degree of enrichment (up to 3.5% ^{235}U) from natural raw material by isotopic exchange in an extraction system (the CHEMEX process).[52] Later, various characteristics of this process were described in more detail.[18,53–56] The isotopic exchange between U^{IV} in the organic phase and U^{III} in the aqueous phase is carried out in plastic pulsation counter-current columns with a diameter of 1.2 m and a height of 30 m. Organophosphorus compounds are used as the extracting agents. The rate of the overall process is determined by the kinetics of inter-phase transfer. The kinetic charactersitics give an efficiency of up to 200 kg S. W. U. per year for a column volume of 1 m^3. The value of the single-stage separation coefficient reaches 1.0025. Phase reversal is achieved electrochemically in a cell with a graphite anode and a dropping mercury cathode. U^{IV} is reduced in the aqueous phase. The self-oxidation of U^{III} is prevented using a patented method.[50] The overall scheme of the CHEMEX process is shown in Fig. 1.

The cascade for the production from natural uranium of 250 000 kg S. W. U. per year of product with an enrichment of 3.5% in ^{235}U includes 20 identical extraction columns. The production of 50 tons of uranium with an enrichment of 3.5% requires 250 tons of natural uranium. 200 tons of depleted uranium (0.2% ^{235}U) are produced. The output is doubled by combining two identical cascades in a module (Fig. 2). The expected energy consumption is 300 kW per kg S. W. U.

The French Atomic Energy Commission proposes in 1990 to begin the construction of a plant with a capacity of 10^6 kg S. W. U. per year, consisting of two parallel modules and containing 80 exchange columns. The contruction will cost 25–30 million dollars. To develop the method, a model assembly was constructed in 1970, and in March 1985 a pilot plant consisting of a module with dimensions one tenth of those of the industrial assembly was brought into operation in Pierrelatte.[51] The main disadvantages of the method are in the loss of uranium in the technological cycle, and the low rate of the process, which requires the use of large-scale equipment and large quantities of uranium. The time required for the equilibrium state to be established is several months.

3. The $U^{IV}-U^{VI}$ system

a) The kinetics of electron transfer between U^{IV} and U^{VI}

In the development of the Manhattan project, it was established[58] that the equilibrium constant (K) of the exchange reaction

$$[^{238}UO_2]^{2+} + {}^{235}U\,(IV) \rightleftarrows [^{235}UO_2]^{2+} + {}^{238}U\,(IV) \qquad (4)$$

differs from 1 and is equal to 1.0012–1.0013. At that time, however, this reaction could not be used to obtain enriched uranium, because of the low values of the enrichment coefficient and the very long equilibration time.

Table 3. Separation of uranium isotopes by extraction in the $U^{IV}-U^{III}$ system.[50]

Extracting agent*	Diluent	Concentration of U^{IV} in the organic phase, M	Composition of the aqueous phase	Temperature, °C	Phase contact time, s	α
TBP	benzene	0.4	0.4 M U(III), 7 M HCl	21	15	1.0030
TBP (50%)	dodecane	0.2	0.2 M U(III), 7 M HCl	—	49—132	1.0026
TBP (40%)	kerosene	0.4	0.4 M U(III), 7 M HCl	21	15	1.0025
TBP (42%)	xylene	0.42	2.35 M U(III), 0.13 M U(IV), 1.55 M HCl	35	30	1.0028
TBP (50%)	toluene	0.42	0.4 M U(III), 8 M HCl	—	30	1.0026
n-Butyl di-isobutylphosphonate (40%)	dodecane	0.55	1 M U(III), ** 0.125 M U(IV), 4.6 M HCl	20	60	1.0025
TOPO (10%)	toluene	0.12	0.11 M U(III), 0.01 M U(IV), 5 M HCl	25	60	1.0024
Di-n-pentyl sulphoxide (2 M)	tetrachloroethane	0.44	0.43 M U(III), 0.16 M U(IV)	25	60	1.0020
Di-2-EHHP (30%)	toluene	0.08	0.08 M U(III), 4.5 M HCl, 6 M HBr	20	300	1.0020
Tri-2-methylbutyl phosphate	dodecane	0.67	0.7 M U(III), 8.2 M HCl	30	60	1.0027

*TBP = tributyl phosphate, TOPO = trioctylphosphine oxide, di-2-EHHP = di-2-ethylhexyl hydrogen phosphate.
**The given ratio between the organic and aqueous phases is 0.5.

The kinetics of the isotopic exchange reaction (4) in homogeneous solutions have been studied in considerable detail.[6] Only the main conclusions about the kinetics and mechanism of reaction (4) will be examined in the present review.

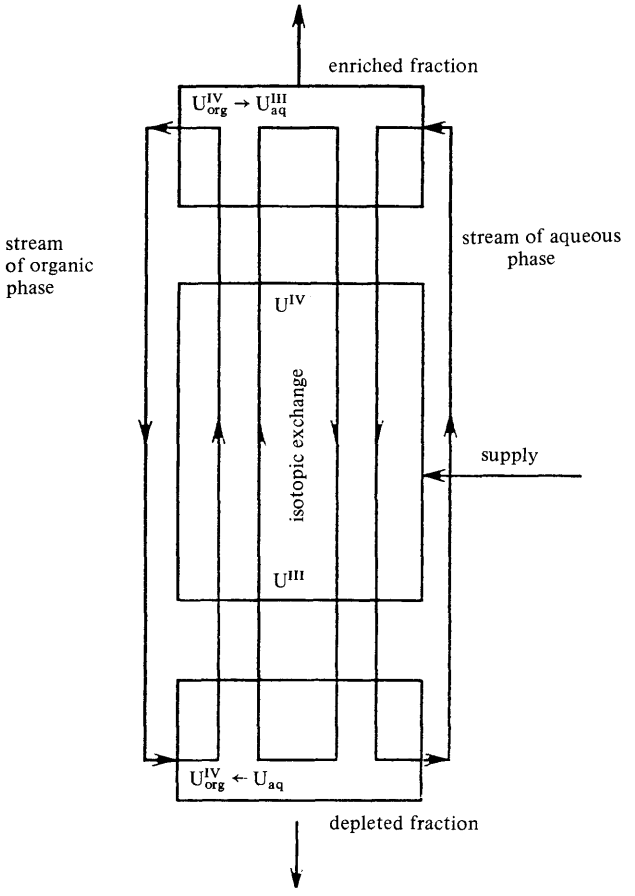


Figure 1. Diagram of the streams in the extraction column of the CHEMEX process.[18]

The order of the reaction between U^{IV} and U^{VI} with respect to the concentration of the reagents is usually fractional. In solutions with a relatively low acidity (2 M acid), its rate (R) is inversely proportional to the cube of the H^+ concentration. It has been suggested that in this acidity range the isotopic exchange mechanism includes the hydrolysis of U^{IV}. In hydrochloric acid solutions with an HCl concentration greater than 3 M, R increases with increase in the acid concentration. It has been suggested that under these conditions the exchange involves chloro-complexes of U^{IV} and U^{VI}. In H_2SO_4 and $(NH_4)_2C_2O_4$ solutions, isotopic exchange takes place between U^{IV} and U^{VI} sulphate and oxalate complexes respectively. In water–acetone and water–ethylene glycol mixtures, the orders of the reaction with respect to U^{IV}, U^{VI}, and H^+ show a complex dependence on the concentration of the organic solvent; the highest values of R are observed for a concentration of the organic component of 30–40%. The rate of reaction (4) increases considerably on ultraviolet irradiation of the solution.

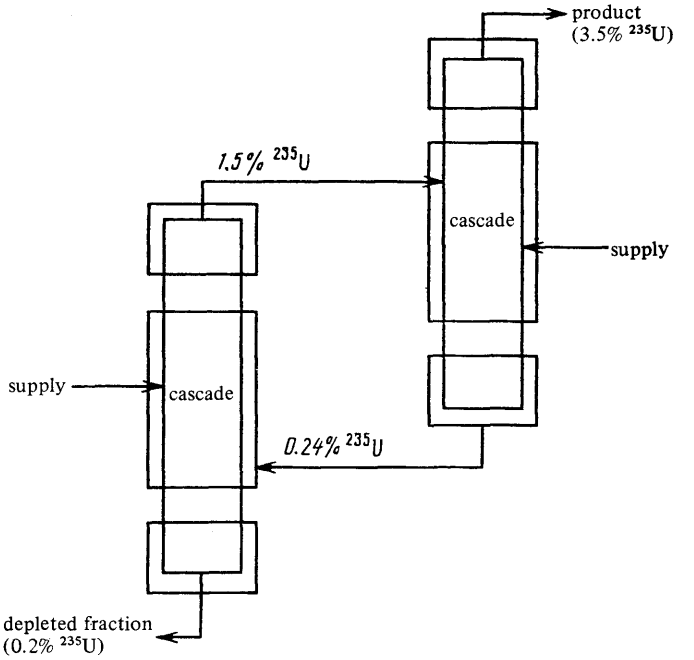


Figure 2. Industrial module of the CHEMEX process.[5]

Most authors consider that electron transfer between U^{IV} and U^{VI} involves the formation and subsequent disproportionation of U^{V}.[6]

Japanese workers studied the kinetics of isotopic exchange between U^{IV} and U^{VI} in the presence of Dowex 5 × 4 cation exchange resin[59] and Dowex 2 × 8 anion exchange resin.[60] The isotopic exchange process in the cation exchange resin involves two stages: exchange in the resin phase between U^{IV} and U^{VI}, and exchange between U^{IV} in the resin and U^{VI} in the solution. The rate of exchange in the resin phase is 10^3–10^4 times that of the corresponding reaction in the solution. The rate of exchange in the resin depends markedly on the acidity of the solution, but a corresponding relationship is not observed for the exchange in the solution. The apparent activation energies of these stages are 24.5 kJ mol^{-1} and 58.4 kJ mol^{-1} respectively.

The reaction in the anion exchange resin is described by the scheme:

$$\begin{aligned} &^{238}U(IV)_r + {}^{235}U(VI)_r \rightleftarrows {}^{235}U(IV)_r + {}^{238}U(VI)_r, \\ &^{238}U(IV)_s + {}^{235}U(IV)_r \rightleftarrows {}^{235}U(IV)_s + {}^{238}U(IV)_r, \\ &^{235}U(VI)_r + {}^{238}U(IV)_s \rightleftarrows {}^{235}U(IV)_s + {}^{238}U(VI)_r. \end{aligned} \quad (5)$$

The rate constant of reaction (5) at 30 °C is 7.3×10^{-4} litre mol^{-1} min^{-1}, which is much lower than the rate constant of the exchange in a homogeneous solution under analogous conditions. The explanation given for this phenomenon is that the concentration of acid in the resin phase is lower than that in the solution.[60] The activation

energy of reaction (5) is 96.2 kJ mol^{-1}, which is close to that in solution (101–105 kJ mol^{-1}). It has been suggested that the mechanisms of isotopic exchange in the solution and in the anion exchange resin are similar.

Isotopic exchange between U^{IV} and U^{VI} in systems containing AV-17-10P anion exchange resin in 6 M HCl solution, KU-8-2P cation exchange resin in 0.5 M HCl solution, and titanium phosphate in 0.7 M H_2SO_4 solution has been studied under static conditions.[61–63] In hydrochloric acid solutions at 25 °C in the absence of catalysts, practically no exchange takes place, but in the presence of titanium phosphate and sulphuric acid the rate of exchange is fairly high ($k = 1.5 \times 10^{-3}$ litre mol^{-1} s^{-1}). It is suggested that the limiting stage of the exchange is the reaction between U^{IV} sorbed on titanium phosphate and U^{VI} in the aqueous phase. In 6 M HCl solutions the rate of isotopic exchange increases considerably in the presence of Fe^{II} salts, but this effect is not observed in 0.5 M HCl solutions.

Table 4. Influence of catalysts on the rate of isotopic exchange in the $U^{IV}-U^{III}$ system.

Catalyst	Concentration of catalyst, M	Concentration of HCl, M	Temperature, °C	k, litre mol^{-1} min^{-1}	k/k_0^*	Refs.
$FeCl_2$	2.5	1	55	9.5	179	[65, 66]
	0.1	2	50	0.082	58	
$CuCl_2$	0.1	4	70	1.4	175	[68]
VCl_3	0.05	4	70	0.17	21	[68]
$CrCl_3$	0.1	4	70	0.01	1.25	[66—68]
p-Benzoquinone	0.05	1.7	90	2.0	1.2	[67]
Hydroquinone	0.1	4	90	0.53	4.8	[69]
Alloxan	0.1	2	50	0.37	65	[67, 69]
$VCl_3 + CrCl_3$	0.05+0.1	4	70	0.38	48	[66]
$FeCl_2$ + alloxan	0.1+0.02	2	50	0.24	170	[66, 69]
$FeCl_2 + CrCl_3$	0.07+0.2	2	50	0.18	129	[66, 67]
$FeCl_2$ + LiCl + γ-picoline	0.7+2.5+0.3	1.5	55	14.0	264	[67]
$FeCl_2$ + LiCl + piperidine	0.7+2.5+0.3	1.5	55	14.8	279	[67, 68]
$FeCl_2$ + ethanol (40%)	1.0	4	55	42.4	820	[67, 69]

* k_0 is the exchange rate constant under corresponding conditions in the absence of a catalyst.

The rate of electron exchange between U^{IV} and U^{VI} can be increased considerably using various catalysts. Thus the reaction between U^{IV} sorbed by a cation exchange resin and U^{VI} in solution is catalysed by the nitrate ion.[64] Detailed studies have shown that the reaction is catalysed by various metal cations, for example Cu^{II}, In^{III}, Tl^{I}, Sn^{IV}, V^{III}, Nb^{V}, As^{III}, Cr^{III}, Mo^{V}, Mn^{II}, Pd^{II}, Hg^{II}, Sb^{III}, Bi^{III}, Zr^{IV}, Re^{V}, Ru^{III}, and Fe^{II},[65–67] and by various organic compounds, such as dicarboxylic or sulphonic acids, hydroxyacids, acids containing N,S-donor atoms and salts of these acids, furans,[68,69] derivatives of quinone and hydroquinone, catechols, and alloxans.[67,69] The concentration of catalyst varies in the range 0.05–3 M.[70] The use of a mixture of catalysts often gives a synergic effect, the magnitude of which depends markedly on the catalysts.[66,67] The catalystic systems are chosen so that the difference in the potentials for the U^{IV}/U^{VI} couple and the redox couple of the catalyst is 0–0.05 V.[67,71] The data in Table 4 show that in a number of cases the rate of the isotopic exchange between U^{IV} and U^{VI} can be increased by a factor of almost 1000. Since the mechanism of isotopic exchange in the $U^{IV}-U^{VI}$ system has not been reliably established, the nature of the action of the catalysts is not yet fully understood. Thus the search for the best catalytic systems is carried out mainly by trial and error.

b) Isotopic effects in the $U^{IV}-U^{VI}$ system

A method for separating uranium isotopes by CIE, in which equimolar quantities of the original U^{IV} and U^{VI} salts are mixed in the light at 25–75 °C and pH 1.5–1.9 has been described.[72] After 1 h, exchange is stopped by adding 3 M HCl solution. The oxidation states of uranium are separated by precipitating U^{IV} with a 5% excess of oxalic acid. In nine separation steps the ^{235}U concentration increases from 0.7052% to 0.7090%.

The exchange reaction was also carried out in 0.207 M H_2SO_4 for 20 h at 35 °C in the dark in a nitrogen atmosphere.[72] Uranium(IV) was precipitated using hydrofluoric acid. For the separation of ^{235}U and ^{238}U, $\alpha = 1.0013 \pm 0.0004$. Similar experiments were carried out in perchloric acid solutions,[74] where the value of α was 1.0012.

Isotope fractionation in the $U^{IV}-U^{VI}$ system in the presence of 0.05 M $CuBr_2$ as catalyst has been studied.[70] The experimental scheme is shown in Fig. 3. Dowex 50W × 4 was used as sorbent. After eight-fold repetition, the ^{235}U enrichment factor was 1.0042. It is suggested[73] that the value of α in the $U^{IV}-U^{VI}$ system is independent of the ligands coordinated to uranium.

Gonda and Kakihana[75] passed 0.05 M solutions of trioctylamine (TOA) or TBP in benzene, saturated with U^{IV} and U^{VI}, through ion-exchange columns with a length of 100 cm and a diameter of 1.2 cm, filled with Dowex 21K anion exchange resin, at a rate of 25 ml h^{-1}. In the system containing TBP, the solution at the outlet from the column was enriched in ^{235}U by a factor of 1.017 compared with the original solution. When TOA was used, the filtrate was depleted in the light isotope ($\alpha = 0.987$). Since in the system containing TBP the anion exchange resin sorbs mainly U^{VI}, in the TOA$-U^{IV}$ system ^{235}U is apparently concentated as $[UO_2]^{2+}$.

When a solution containing 0.5 M H_2SO_4, 0.03 M NaF, and equimolar quantities of U^{IV} and U^{VI} was passed at a rate of 0.5 ml min^{-1} through a column of length 100 cm filled with a cation exchange resin, the resin sorbed mainly U^{IV}.[76] At the outlet from the column, the ^{235}U enrichment factor was 1.009. With increase in the rate of elution to 2 ml min^{-1}, the enrichment factor decreased to 1.000333.

In the counter-current method for separating the isotopes,[77] uranium(IV) sorbed by a strongly acidic cation exchanger moves downwards, and an aqueous solution of U^{VI} moves upwards. In the upper part of the column, U^{VI} slightly enriched in ^{235}U is removed, reduced to U^{IV}, and sorbed on the cation exchanger used in the second column. Uranium(IV) depleted in ^{235}U is removed from the lower part of the first column, oxidised to U^{VI}, and passed to the second column.

A slightly different counter-current method for separating uranium isotopes has been proposed.[78] In this method, the cation exchanger with U^{IV} sorbed on it again moves downwards, but an oxidising agent containing 1% H_2O_2 moves upwards. U^{IV} is oxidised to U^{VI}, desorbed from the resin, and moves upwards with the eluant. Uranium(VI) in the upper part of the column is enriched in the light isotope.

The isotopic fractionation of uranium in counter-current columns makes it possible to carry out a multi-stage process. In the $U^{IV}-U^{VI}$ system, however, this cannot be achieved by using a stationary layer of ion exchanger. For example, Fujii and

co-workers[79] sorbed U^{VI} on a strongly basic macroporous ion exchanger placed in a column with a length of 100 cm and a diameter of 1 cm. Uranium was eluted with a solution containing 0.1–0.12 M $TiCl_3$ and 4–5 M HCl at a rate of elution in the range 3.75–12.3 ml h^{-1}. When the eluant comes in contact with the resin, U^{VI} is reduced to U^{IV}. Since U^{IV} is weakly sorbed by the anion exchanger under the conditions of the experiments, most of it is transferred to the aqueous phase and moves with the eluant. The movement of U^{IV} is accompanied by isotopic exchange between U^{IV} in the aqueous phase and U^{VI} in the exchanger phase. If the rate of attainment of isotopic equilibrium is sufficiently high, isotopic fractionation takes place repeatedly during the passage of the front,[70] as a result of which U^{IV} is enriched in the ^{235}U isotope in the tail of the elution curve. The values of ε obtained at 70 °C and 87 °C were 7.3×10^{-4} and 7.0×10^{-4} respectively. The number of theoretical plates in the experiments varied from 570 to 990, depending on the rate of elution and temperature.

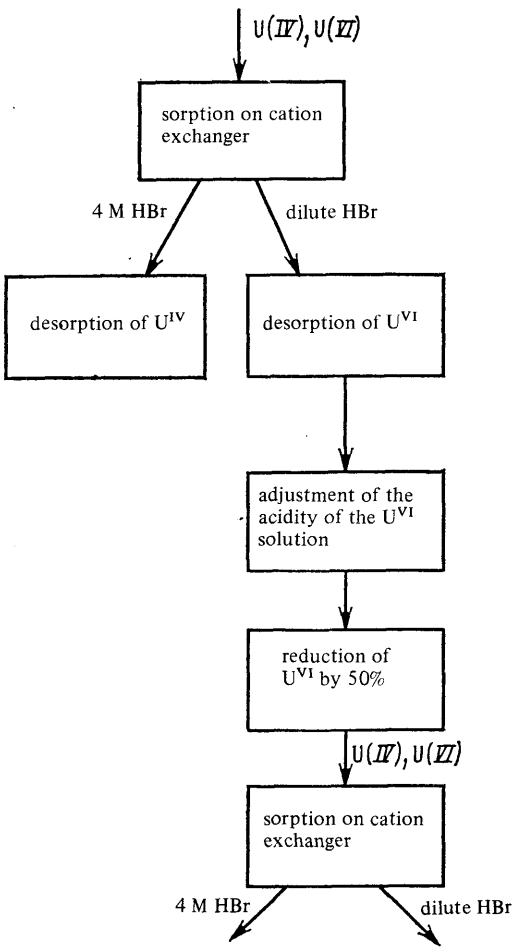


Figure 3. Diagram of the experiment to study isotopic effects in the $U^{IV}-U^{VI}$ system.[70]

Similar experiments were carried out with a cation exchanger in the U^{IV}-form.[64] 0.1 M $Fe(NO_3)_3$ solution was used as eluant. During the elution, U^{IV} was oxidised to U^{VI}, and was washed from the column. Enrichment in ^{235}U took place at the front of the elution curve.

Ponta and Calusaru[80] passed a solution of a U^{VI} salt through a column filled with a cation exchanger in the Ti^{III}-form. U^{VI} was reduced to U^{IV} and sorbed on the resin, and Ti^{III} was converted into TiO^{2+} and washed from the column. The observed isotopic effect is determined by the superposition of the relatively large isotopic effect of the electron exchange between U^{IV} in the resin and U^{VI} in the solution on the weaker isotopic effect of opposite sign due to the reduction of U^{VI} by Ti^{III}.

The methods of separation described above have proved unsuitable for industrial application, however. A method for separating uranium isotopes based on the continuous movement of a uranium zone along a column[81] filled with Dowex 50W-X8 cation exchange resin in the Ti^{III}-form was patented in 1972. When a solution of U^{VI} is passed through the column, the U^{VI} is reduced to U^{IV}, which is sorbed by the resin. As a result, a U^{IV} zone is produced in the upper part of the column. A solution of $FeCl_3$, which oxidises the sorbed uranium, is then passed through the column. The U^{VI} formed is transferred to the solution, and moves with the eluant to the boundary between the zones of uranium and the reducing agent Ti^{III}, where U^{VI} is again reduced to U^{IV} and sorbed by the cation exchanger. The uranium zone moves continuously along the column, and selective distribution of the uranium isotopes takes place at its boundaries as a result of isotopic exchange between U^{IV} from the resin and U^{VI} from the solution. Enrichment in ^{235}U takes place at the boundary between the zones of uranium and the reducing agent. The results of similar experiments carried out by other workers,[82–84] show good agreement with these data.[81]

The chromatographic separation of uranium isotopes according to the above scheme[81] has also been carried out using anion exchange resins.[85–88] In the experiments of Fukuda and co-workers,[88] the zone of uranium, present as anionic complexes of U^{VI}, moved along a column filled with a strongly basic anion exchanger in the Fe^{III}-form. A Ti^{III} solution was used as eluant. The HCl concentration lay in the range 9–4 M, and the temperature in the range 15–83 °C. $FeCl_2$ solution was used to catalyse the isotopic exchange. Enrichment in the light isotope took place in the 'trailing' part of the zone. The values of ε obtained at 30, 50, and 87 °C were 7.8×10^{-4}, 6.8×10^{-4}, and 7.0×10^{-4} respectively. Fe^{III}, Tl^{III}, Mo^{VI}, Sb^{V}, Cr^{VI}, Ce^{IV}, and Hg^{II} were proposed as oxidising agents, and Ti^{III}, V^{II}, V^{III}, Nb^{III}, Cr^{II}, and Cu^{I} as reducing agents.[89] The eluted mixture is treated with oxygen to regenerate the oxidising agent. The reducing agent is regenerated by hydrogen in the presence of catalysts (Pt, Ru, Rh, Pd, Os, or Ir).[89]

4. The ACE process

In 1972, the Japanese firm Asahi Chemical Industry began to develop an industrial method for obtaining uranium with a low degree of enrichment.[14] This method has been called the ACE process.[14] The method is based on isotopic exchange between U^{IV} and U^{VI}. Both cation exchangers and anion exchangers are used to separate the ionic forms of uranium. The firm has developed new highly effective resins giving the process improved kinetic characteristics, which make it economic.

A pilot plant for enriching uranium by CIE (one tenth of the size of the industrial assembly) was brought into operation in Japan in 1985.[90] The capacity of the assembly is 1–2 thousand kg S. W. U. per year. The cost of construction was about 15.8 million dollars.[91] The cascade consists of four columns with a height of 3 m and a diameter of 8 m (Fig. 4), filled with anion exchange resin. The sphericity and dimensions of the particles are varied along the length of the column.[92] Fe^{III} is used as oxidising agent, and Ti^{III} as eluant. The time required to establish the steady state to obtain uranium with an enrichment of 3% is 20–90 d, and the expenditure of energy is 105–180 kW. h per kg S. W. U.[93] To obtain uranium with an enrichment of 93%, the time taken to establish the steady state is 9–10 years.[13]

V. The separation of uranium isotopes in the UF_6—$NOUF_6$ system

Nugent[94] and Ogle[95] found that in the isotopic exchange between UF_6 and $NOUF_6$, relatively high isotopic fractionation of uranium takes place, and the light isotope is concentrated in the UF_6. Nugent[94] carried out the experiments in a column with a small diameter, filled with $NOUF_6$ in anhydrous HF. A solution of UF_6 in Freon-114, which is denser than the solution in the column, was dispersed in the upper part of the column. Isotopic exchange takes place as the drops fall. The value found for α was 1.0016. Similar results were obtained using the complexes $NOUF_7$ and NO_2UF_7 instead of $NOUF_6$. Ogle[95] used solutions of UF_6 in trichlorotrifluoroethane, dichlorotetrafluoroethane, or perfluorotributylamine. The data obtained by Ogle show good agreement with those obtained by Nugent.[94] A scheme for an assembly for separating uranium isotopes, based on the above method, has been proposed.[96] The values of α in the UF_6(gas)—$NOUF_6$(solid) system at 25 °C and 70 °C are 1.0016 and 1.0011 respectively.[73] The rate of exchange increases in the presence of HF. The main obstacle to the practical utilisation of the exchange between UF_6 and $NOUF_6$ is the high stability of $NOUF_6$ in anhydrous HF solutions towards oxidising agents.[94,98] The oxidation of $NOUF_6$ is necessary to organise phase reversal. F_2, ClF_3, ClF_5, BrF_3, and BrF_5 have been proposed as oxidising agents.[98] The problem of the repeated utilisation of NO has not yet been solved.[98] Moreover, the time taken to establish isotopic equilibrium is fairly long (~2 h), even in the presence of HF. These difficulties make it unlikely that an economic industrial method for separating uranium isotopes based on the reaction between UF_6 and $NOUF_6$ will be developed in the near future.

VI. Other methods

Many workers have used a combination of ion exchange and various electrochemical processes to increase isotopic effects. Thus a method in which isotopic exchange between U^{IV} and U^{VI} is combined with counter-current electromigration has been described.[99] After the electrochemical cell had operated for 1400 h, the ^{235}U concentration in the anode compartment increased by a factor of 1.0007. The method is uneconomic, compared with gas diffusion. Uranium isotopes have also been separated by electromigration using cation exchange membranes.[100] The authors cited suggested that the use of ion exchange membranes should increase the efficiency of isotopic fractionation, since the solvation of uranium ions in the membrane is less extensive than in solution, so that the differences in the masses of the isotope-containing forms should be greater for separation in the membrane. For the fractionation of ^{235}U and ^{238}U by this method α = 1.00006.

The theory of the separation of isotopes by electromigration in an ion exchanger–solution system has been developed, with allowance for the association of the ions and the formation of ion pairs, and also for isotopic exchange between ionic forms in solution and in the exchanger phase.[101]

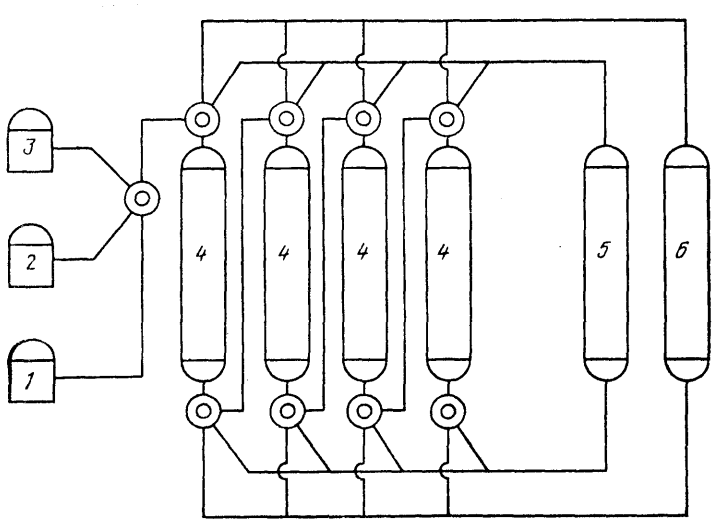


Figure 4. Diagram of the cascade of the ACE process:[2] *1*, vessel for depleted uranium; *2*, vessel for enriched uranium;, *3*, vessel for natural uranium; *4*, separating columns; *5,6*, columns for regenerating the oxidising agent and the reducing agent.

A combination of ion exchange and electrophoresis has been used.[102] Natural U^{IV} chloride was sorbed on the cation exchanger, and then eluted with a mixture of glycine and $CaCl_2$. A voltage was applied to the ends of the chromatographic column (current density 2–3 mA cm^{-2}); the cathode was situated in the upper part. The concentration of ^{235}U at the cathode after 3, 10, and 20 h was 0.736, 0.744, and 0.750 mol% respectively.

A cyclic process involving electro-adsorption and electro-desorption on porous electrodes having a highly developed surface and ion-exchange properties has been proposed for separating uranium isotopes.[103] The sorption–desorption cycles are synchronised with the periodic change in the direction of the flow of liquid, so that a concentration gradient is created along the column.

A kinetic isotopic effect has been detected in the sorption of $[UO_2]^{2+}$ on ion exchange resins under static conditions.[104,105] The sorbents used were the strongly acidic cation exchange resin Amberlite IR-120 in the H^+-form and the strongly basic anion exchange resin Amberlite IRA-400 and the weakly basic anion exchange resin Amberlite IRA-93 in the OH^-, Cl^-, or SO_4^{2-} forms. The ratio of the concentrations of ^{235}U and ^{238}U changed during the sorption. The time dependence of the separation coefficient α shows an extremal point, whose position depends on many factors. When the cation exchange resin was used, the maximum values of α were observed 2 min after contact with the solution, and with the anion exchange resins the smallest value of α was observed after 5–10 min. After passing the extremal point, the ratio $^{235}U/^{238}U$ returned to the original value. The values of α at the extremal points when Amberlite IR-120, IRA-93, and IRA-400 were used were 1.02, 1.03, and 0.99 respectively. The same authors patented similar methods for separating uranium isotopes, based on the kinetic isotopic effect in the sorption of $[UO_2]^{2+}$ on a carboxylic acid cation exchanger on an acrylic base[106] and on an anion exchanger consisting of a structured copolymer of glycyl methacrylate and amines.[107]

The values of α obtained in the works cited[104–107] are more than 10–100 times the uranium isotope enrichment coefficients in equilibrium processes with electron transfer. The nature of the observed phenomenon is not yet clear.

It has been found[108] that the rate of formation of uranyl hydroxide acetate as a result of the irradiation of $UO_2(CH_3COO)_2$ solution with visible light is different for ^{235}U and ^{238}U. The observed phenomenon was attributed to the magnetic isotope effect.

The lack of data on the magnitude and sign of this effect, however, does not make it possible to relate it directly to magnetic phenomena. Moreover, U^{VI} is reduced to U^{IV} when uranyl acetate solutions are irradiated with light. The authors cited[108] did not take account of this process. It follows from the theory of magnetic isotope effects[109] that their highest values are achieved when various conditions are observed. Firstly, the constants of the hyperfine interaction (HFI) with the magnetic nuclei of different isotopes in intermediate radical pairs should differ considerably from one another. Secondly, the HFI constants for one of the isotopes should have high values. Thirdly, the generation of triplet radical pairs is necessary, since their recombination is always preceded by a singlet–triplet interconversion, which leads to the most effective selection of the isotopes.

Until recently, there was lack of agreement on the electronic state of the excited uranyl group.[110] In particular, it was stated that as a consequence of strong spin–orbit coupling, the existence of a characteristic spin in the many-electron uranium atom was impossible. It has been shown,[111] however, that the application of an external magnetic field under certain conditions leads to a decrease in the yield of U^{IV} in the photoreduction of the uranyl group under the influence of N,N-diallyl-N,N-dimethylammonium chloride. The sign of the magnetic effect proves unambiguously the existence of a triplet state of the excited uranyl ion, which on photoreduction gives a triplet radical pair. Thus the appearance of magnetic isotope effects is probably possible in principle in the photoreduction of UO_2^{2+}. The search for specific systems in which these effects are greatest is obviously necessary.

VII. Comparison of the methods

According to the estimates of various specialists, even at the low rates of development of nuclear energy, the annual requirements of the capitalist countries for enriched uranium will be 30 million kg S. W. U. by 1990, and 60 million kg S. W. U. by the year 2000.[12] The production of enriched uranium will be increased both by modernising existing gas-diffusion (GD) plants and by introducing assemblies based on new principles. At the present time, three gas-diffusion plants are operating in the USA (Oak Ridge, Paducah, Portsmouth), and three in Western Europe, of which two are in France (Pierrelatte, Tricastin), and one in Britain (Capenhurst). The production of enriched uranium by GD in the EEC countries is controlled by the international organisation Eurodiff.

In 1970, Britain, West Germany, and the Netherlands established the firm Urenco to develop the ultracentrifuge (UC) method for separating uranium isotopes. In 1979, this firm began to operate two demonstration assemblies in Capenhurst (Britain) and Almelo (The Netherlands), which by 1987 had produced approximately 2 million kg S. W. U. of enriched uranium.[42] A pilot plant with an output of 75 000 kg S. W. U. per year using the UC method is operating in Nintyo-Toge, Japan. In 1985, the Japanese firm PNC began the construction of a similar plant with a planned output of 200 000 kg S. W. U. per year.[113] It is planned to provide 30% of Japan's requirements for enriched uranium from plants using the UC method.

In the USA, approximately 2.6 million dollars have been spent in the construction of a UC plant in Portsmouth.[114] It was planned to bring the first cascade of the plant with an output of 13.2 million kg S. W. U. per year into operation in 1988. The Department of Energy of the USA, however, decided to halt the development of the UC method.[114,115] A method based on the selective photo-ionisation of the atomic vapour of uranium under the influence of laser radiation (AVLIS) was chosen for industrial application in the nineteen-nineties.[115] The main advantages of the AVLIS method over UC is the lower capital expenditure and the lower cost of production per kg S. W. U., and also the greater flexibility for improvement of the method and a gradual increase in output.[115] The very high values of α (see Table 5) make it possible to use depleted uranium from GD plants as the starting material for the AVLIS process.[116] In the USA it is planned to begin in 1988 the construction of a plant using the AVLIS method with a planned output of 10 million kg S. W. U. per year.[115] A similar programme for separating plutonium isotopes is also being developed.[12] It is proposed to begin work on this in 1990. In 1984, 71.9 million dollars were spent on the development of this program. The AVLIS process is also being studied in France,[115] Japan,[117] and Britain.[118]

Representatives of Urenco state, however, that by the late nineteen-eighties the new generation of centrifuges will make it possible to achieve the same economic characteristics as the AVLIS process.[119]

Table 5. Comparison of methods for separating uranium isotopes.[2,5,7,116]

Method*	Level of development	α	Energy consumption, kW per kg S.W.U.	Capital expenditure, dollars per kg S.W.U.	Cost of product, dollars per kg S.W.U.
GD	principal method	1.003	2400—2500	250	95
UC	large-scale plants being brought into production	1.005	100—135	400	90
SJ	construction of large-scale plants being planned	1.015	3000—3600	350	125
SSJ	ditto	1.025	4000	—	—
AVLIS	demonstration assembly being constructed	~100**	50—150	60—70	25—30
MLIS	laboratory studies	2—4	235	—	—
CHEMEX	demonstration assembly in operation	1.002	300	325	60—65
ACE	ditto	1.001	105—180	—	—
PM	laboratory studies	1.1	330	—	—

*GD = gas diffusion, UC = ultracentrifuge, SJ = separating jet method, SSJ = supersonic jet method, AVLIS = selective laser photo-ionisation, MLIS = selective laser photo-dissociation, PM = plasma method; ** separation coefficient without allowance for losses 10^3-10^4.

In addition to AVLIS, the selective laser photo-dissociation of UF_6 vapour (the MLIS process) is also being developed. This method has certain advantages over AVLIS, since UF_6 is extremely volatile.[5] The MLIS process does not give such high values of α as the AVLIS process, however (see Table 5), so that it is necessary to increase the number of stages. The MLIS process is being studied in the Institute of Physical and Chemical Studies in Japan.[120] It is proposed to develop the MLIS method to the AVLIS level.

The separating jet (SJ) method has been developed in West Germany since the mid nineteen-fifties. In 1975, Brazil and West Germany agreed to construct a demonstration plant for enriching uranium by this method.[3] Table 5 shows that the SJ method is the most expensive of the alternative methods.

The supersonic jet (SSJ) method is being developed in the United Arab Republic, where a pilot plant with a planned output of about 300 thousand kg S.W.U. per year has been constructed. Insufficient technical information has been published on this process.

Attempts have been made to separate uranium isotopes in a strongly ionised rotating column of uranium plasma or in the plasma of a low-pressure arc with a hollow cathode (PM).[3] The details of the mechanism of the separation of the isotopes in the plasma are not yet clear, because of the complexity of its structure. The technical problems associated with the use of uranium compounds in a plasma have not been solved.

Comparison of different methods for separating uranium isotopes shows that the chief advantages of CIE methods are the simplicity of the equipment, the use of traditional technology and non-aggressive reagents, and the economic features.[3] Their disadvantages are the low values of α, the long times taken to establish equilibrium, and the complexity of the methods for phase reversal. The developers of the CHEMEX and ACE processes, however, have managed to overcome the difficulties and to develop competitive methods for enriching uranium (see Table 5). The CHEMEX process gives the cost of 1 kg S.W.U. at the level of 60% of the cost of 1 kg S.W.U. in the Eurodiff plants.[115] An advantage of the ACE process over the CHEMEX process is the simplicity of phase reversal, since the latter process requires the use of additional equipment to carry out the redox reactions (electrolyser, etc.).[90] Table 5 shows that the energy used in the ACE process is much lower than that in the CHEMEX process. At the same time, the value of ε for the CHEMEX process is twice that for the ACE process.

Because of these disadvantages, it cannot be said that CIE methods occupy a leading place in the technology of uranium enrichment. These simple and economic methods may prove useful, however, in countries where the requirements for uranium with a low degree of enrichment are low and where there is no need to develop a large-tonnage capital-intensive technology such as GD or UC. Moreover, CIE methods may possibly find application when combined with other promising methods such as laser methods in the early stages of the production of uranium with a low degree of enrichment, when it is necessary to process very large volumes of the starting material.

The possibilities provided by chemical methods for separating uranium isotopes have not been exhausted. In particular, much can still be achieved using processes based on kinetic isotopic effects.

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