

Analysis of a Two-Phases System of Mass Transfer and Electro-Reduction of Uranium(VI) in Nitric Acid-Hydrazine Media

K.W. Kim, J.H. Yoo, and H.S. Park

Korea Atomic Energy Research Institute

J.D. Kim

Korea Advanced Institute of Science and Technology

H. Aoyagi and Z. Yoshida

Japan Atomic Energy Research Institute

(Received October 5, 1994)

질산-하이드라진 매질에서 우라늄(VI)의 물질전달과 전기적 환원을 갖는 이 상계의 해석

김광욱 · 유재형 · 박현수

한국원자력연구소

김종득

한국과학기술원

青柳壽夫 · 吉田善行

일본원자력연구소

(1994. 10. 5 접수)

Abstract

Simulation for a dynamic analysis of the electrolytic preparation of U(IV) in two-phases system, which consisted of mass transfer of U(VI) from TBP phase into HNO₃ solution and electrolytic reduction of U(VI) to U(IV) at a cathode in aqueous phase, was carried out in order to establish the most suitable operating condition and best electrode area as basic design data for the system. It was found that maintaining an appropriate mass transfer rate was more significant rather than enlarging the surface area of the cathode for more effective production yield of U(IV). The electrode area and the operation time affected deeply the production composition of U(IV) in the resulting aqueous phase. And optimal electrode areas were evaluated to meet production criteria of U(IV) of resulting solution in several system conditions. Though about 0.37M HNO₃ was preferable to prepare the solution of U(IV), nitric acid concentration should be higher than 0.5M to prevent a hydrolysis of U(IV) in the aqueous phase.

요 약

TBP 유기상으로 부터 질산용액으로 U(VI)의 물질 이동과 그 질산용액에서 U(VI)의 U(IV)으로

전해 환원과정을 갖는 두 상으로 구성된 계에서 U(IV)을 전해적인 방법으로 생산하기 위해 필요한 기본 설계 자료로서의 운전조건 및 전극면적 계산을 위한 계의 수치해석이 수행되었다. 효과적인 U(IV)의 생산수율을 위해서는 적절한 물질전달 면적을 유지시키는 것이 전극면적을 증가시키는 것보다 중요하였으며, 전극면적과 운전시간은 최종 수용액의 U(IV) 조성에 큰 영향을 주는 것을 알 수 있었다. 또한 여러 계의 조건에서 최종 용액의 U(IV) 생산 조건을 만족시키기 위한 최적 전극면적이 계산되었다. 수용상의 최적 질산 농도는 U(IV) 생산만을 위해서는 약 0.37M이나, 용액중의 U(IV)의 가수분해를 방지하기 위해 최소한 0.5M을 유지해야 함을 알 수 있었다.

1. Introduction

The electrolytic technique for preparation of U(IV) in nitric acid solution can be an important step in the *in-situ* electro-partitioning for separation of several elements, which could be used in the back-end fuel cycle.[1–3] This procedure involves the back-extraction of a target element accompanied with the reduction of the target element by U(IV) generated at the electrode. This electrolytic technique is also promising for some other applications such as hydrometallurgy of uranium ores[4] and electrochemical analysis. The *in-situ* electrolytic partitioning process for separation of some several elements may consist of two phases; U(VI) is loaded initially in the organic phase of 30 vol.% TBP[5], transferred to aqueous phase, and is reduced to U(IV) at an electrode only in the aqueous phase as the electrolytic reaction can not occur in organic phase.[6, 7] A titanium cathode is usually used in an electrolytic pulsed column or a mixer-settler of process-scale[1, 2, 8] because the material is highly resistant to corrosion in nitric acid media. The nitric acid solution generally contains hydrazine as a stabilizer for U(IV) and electron-donor to the anode.[1, 2, 6]

In order to analyze theoretically such system as *in-situ* electrolytic separation process, from which optimal electrode area and the most suitable operating conditions as basic design data of the system can be estimated, the simulation of the system phases should be performed carefully on the basis of kinetic data of electrolysis of U(VI) together with mass transfer model of U(VI) between two phases. Little information, however, is available with respect to the kin-

etic data for the reduction of U(VI) at Ti electrode because the measurement of clear and reproducible voltammogram for the quantitative wave-analysis is difficult due to oxide film on Ti electrode.[9] Even if any reported data about it, they might be considered to be incorrect because they didn't involve a correction of the oxide film effect on the reduction rate of U(VI). But more correct kinetic data for electrolytic reduction of U(VI) at the Ti electrode were estimated in our previous works.[9, 10, 23]

In present study, the dynamics of components U(VI) and U(IV) in the two-phases system were simulated with changes of several parameters such as electrode area, mass transfer area, the ratio of the two areas and nitric acid concentration in order to get the system information, the electrolytic reduction rate and the mass transfer rate of U(VI) being compared together. The rate of the electrolytic reduction and the mass transfer of U(VI) were compared with each other, and the electrode area which is required to meet the system criteria was estimated on the basis of the correct kinetic data for the reduction of U(VI) at Ti electrode.

2. Mathematical Expressions

The system shown in Fig. 1 defines a mechanism of two-phase system with mass transfer and the electro-reduction of U(VI). The mass transfer at the liquid/liquid is according to the two film theory. Several sound assumptions were used for simplicity as follows; (1) All components in bulk solution are homogeneous. (2) U(IV) generated at the electrode remains in aqueous phase because of low distribution coef-

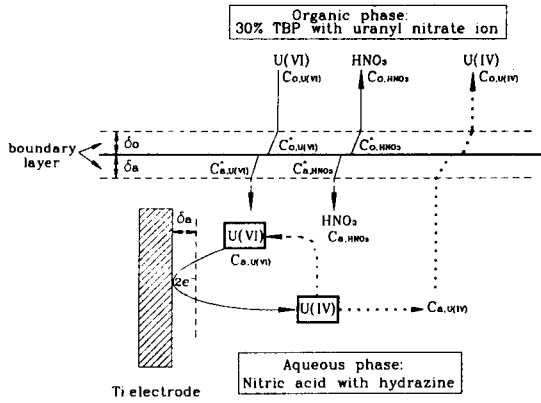


Fig. 1. Mechanism of the Two-Phases System with Mass Transfer and Electro-reduction of U(VI).

ficient of U(IV).[5] (3) There is no reoxidation of U(IV) by nitrous acid in the presence of sufficient amount of hydrazine.[1, 2, 11, 12] (4) Reactions of both U(VI) and HNO_3 with TBP at the interface are rapid and reversible so that the reactions are at equilibrium states.(5) There are no thermal and Marangoni effects[24] due to the interfacial reaction between U(VI) and TBP.(6) Mass transfer in boundary layers is in steady state because the layers are so thin with a suitable mixing, and is characterized by Fick's 1st law.(7) There is no electrolysis in the organic phase.[6, 7] (8) There is no electro-reduction of HNO_3 in the presence of hydrazine.[13, 14]

The governing equations can be expressed as follows.

$$V_o \frac{dC_{oj}}{dt} = V_o C_{oj} - J_{oj} A ; j = \text{HNO}_3, \text{U(VI)} \quad (1)$$

$$V_a \frac{dC_{aj}}{dt} = J_{aj} A - v_{\text{U(VI)}} ; j = \text{HNO}_3, \text{U(VI)} \quad (2)$$

$$V_a \frac{dC_{a,U^{IV}}}{dt} = v_{\text{U(VI)}} \quad (3)$$

$$|v_{\text{U(VI)}}| = |v_{\text{U(IV)}}| = \left| \frac{iS}{nF} \right| \quad (4)$$

$$\frac{i}{nF} = k_f C_a(O,t) = k_a C_{a,U(VI)} \quad (5)$$

where,

$$k_a = \frac{k_f k_m}{k_f + k_m} \quad (6)$$

$$k_f = a \exp \{ -[0.111 + 0.021 \ln(C_{\text{HNO}_3})] F/RT [E_{\text{app}} - E^o] \}^{(9,10)} \quad (7)$$

$$k_m = \frac{D_a U(VI)}{\delta_a} \quad (8)$$

$$C_{T,U} = C_{a,U(VI)} + C_{o,U(VI)} + C_{a,U(IV)} \quad (9)$$

$$C_{T,\text{HNO}_3} = C_{a,\text{HNO}_3} + C_{o,\text{HNO}_3} \quad (10)$$

$$\text{Initial condition 1 : } t=0 : C_{o,U(VI)} = C_{T,U},$$

$$C_{a,U(VI)} = 0, C_{a,U(IV)} = 0 \quad (11)$$

$$\text{Initial condition 2 : } t=0 : C_{o,\text{HNO}_3} = C_{(\text{HNO}_3)_0},$$

$$C_{a,\text{HNO}_3} = C_{(\text{HNO}_3)_0} \quad (12)$$

The flux of U(VI) and HNO_3 in steady state is

$$J_{oj} = \frac{D_{oj}}{\delta_o} [C_{oj} - C_{oj}^*] ; j = \text{HNO}_3, \text{U(VI)} \quad (13)$$

$$J_{aj} = \frac{D_{aj}}{\delta_a} [C_{aj} - C_{aj}^*] ; j = \text{HNO}_3, \text{U(VI)} \quad (14)$$

$$d_j = \frac{C_{oj}^*}{C_{aj}^*} ; j = \text{HNO}_3, \text{U(VI)} \quad (15)$$

The distribution coefficients of uranium and nitric acid can be estimated by Richardson' model in the SEPHIS code.[15]

The interfacial concentration corresponding to a given bulk concentration can be estimated by Eq.(16) derived from Eqs (13) to (15) together with (9) and (10) in a non-linear equation because the distribution coefficient is expressed as a complicated non-linear equation.

$$F(C_{aj}, C_{aj}^*, C_{Tj}) = [C_{Tj} - C_{aj} - d_k C_{aj}^*] - \frac{\delta_o}{\delta_a} \frac{D_{aj}}{D_{oj}} [C_{aj} - C_{aj}^*] = 0 ; j = \text{HNO}_3, \text{U(VI)} \quad (16)$$

The thicknesses of boundary layers of both phases should be obtained first for solving Eq.s (1) to (16), but it is difficult to measure both values simultaneously. Most of mass transfer coefficient data are for the aqueous side but few data for the organic side. In present study for the simulation of the general characteristics of the system, the information on the order of magnitude of mass transfer coefficient or thickness of both sides is enough instead of the absolute values. Thus, the relative values of the thicknesses as follows were taken into account. Under the identical forced-convection condition of both phases, the ratio of mass transfer coefficients or the boundary layer thicknesses of both phases can be expressed by Eq.(19) on the basis of a following relation.[16, 17]

$$N_{sh} = \text{Constant } N_{Re}^{1/2} N_{Sc}^{1/3}$$

The mass transfer coefficient can be expressed by Eq.(18)

$$k = \frac{D}{\delta} \propto D^{2/3} \rho^{1/6} \mu^{-1/6}$$

$$\frac{\delta_{oj}}{\delta_{aj}} = \left(\frac{D_{aj}}{D_{oj}} \right)^{1/3} \left(\frac{\rho_{aj}}{\rho_{oj}} \right)^{1/6} \left(\frac{\mu_{aj}}{\mu_{oj}} \right)^{-1/6}$$

$$\text{where, } j = \text{HNO}_3, \text{ U(VI)} \quad (19)$$

The reported values of $D_{a, \text{U(VI)}}$, $D_{o, \text{U(VI)-TBP}}$, D_{a, H^+} and $D_{o, \text{H}^+ \cdot \text{TBP}}$ are 4.5×10^{-6} , 1.5×10^{-6} , 3.6×10^{-5} , and $4.3 \times 10^{-6} \text{ cm}^2/\text{sec}$, and viscosity(μ) and density (ρ) of 1M HNO_3 solution and 30 vol.% TBP/n-dodecane solution with 30g/l U(VI) are 10.16 mP, 1.066g/cm³, and 20.63 mP, 0.856g/cm³, respectively.[18, 19]

These physicochemical data being employed, the ratio of boundary layer thickness in the organic phase to that in the aqueous phase, $\delta_{o,j} / \delta_{a,j}$, can be calculated to be 0.8079, or 0.5739 for U(VI) or nitric acid, respectively. Therefore, if the boundary layer thicknesses of one side of interface of the two phases is known, the thickness of another side could be estimated. The order of magnitude of the mass transfer coefficient in aqueous phase is known to be

about 10^{-3} cm/sec .[20] The relative boundary layer thickness of the organic phase can be approximated from a given mass transfer coefficient in the aqueous phase.

3. Simulation of the System

Two processes, i.e., mass transfer of U(VI) from the organic phase to aqueous phase and electro-reduction of U(VI) at the cathode, occur independently in the system. Accordingly, it is required to elucidate how the relative magnitude of the mass transfer rate and the electro-reduction rate affect the system behavior. Here, a ratio, Ra, of the mass transfer rate to the electro-reduction rate is defined as Eq.(20).

$$Ra = \frac{\text{mass transfer rate}}{\text{electro-reduction rate}} = \frac{J}{i/nF} \frac{A}{S} = \frac{V_a \frac{dC_{a, \text{U(VI)}}}{dt}}{V_a \frac{dC_{a, \text{U(IV)}}}{dt}} \quad (20)$$

If Ra is more than 1, the mass transfer rate is faster than the electro-reduction rate so that U(VI) is accumulated in the aqueous phase. Increasing the electro-reduction rate is necessary. If Ra is less than 1, the mass transfer rate is slower than the electro-reduction rate so that U(VI) is reduced to U(IV) completely but the energy efficiency becomes worse. Therefore, Increasing mass transfer rate is required. With Ra of less than 1, the mass transfer rate may be accelerated because the U(VI) in aqueous phase is consumed. If Ra is equal to 1, the operating condition is most suitable.

The controlled-potential electrolysis at -0.5 V vs. SSE was selected for this simulation on the basis of the results in the previous work.[9, 10]

3.1. Transient Concentration of the Components

Fig. 2 shows the simulation results on the changes of the concentrations of U(VI) and U(IV) in the

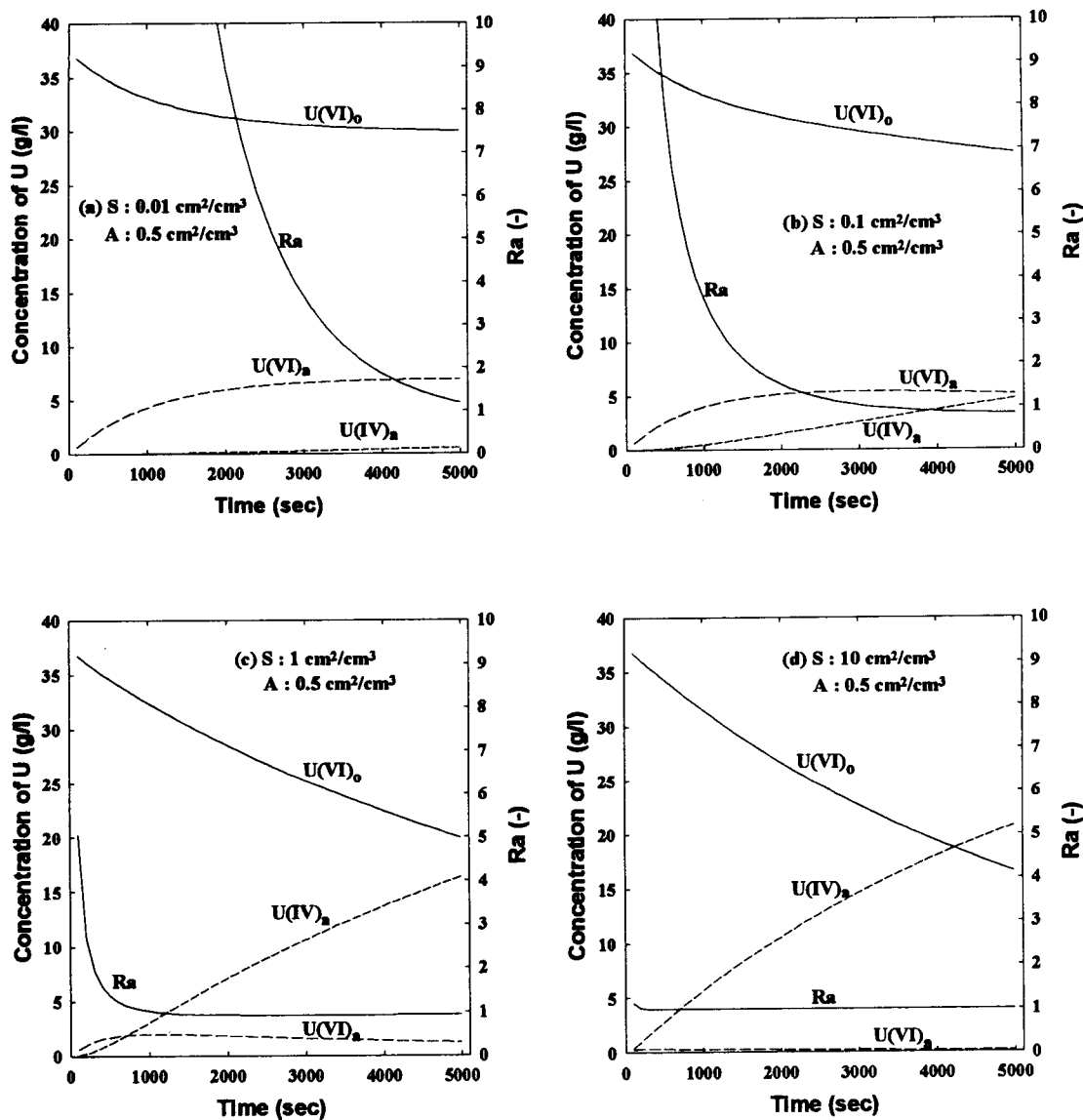


Fig. 2. Simulation for Transient Changes of $C_{a,U(VI)}$, $C_{a,U(IV)}$, $C_{o,U(VI)}$ and Ra with Increase of Operation Time. A: $0.5 \text{ cm}^2/\text{cm}^3$, S: Variable, $k_m: 1.8 \times 10^{-3} \text{ cm/sec}$, $C_{o,U(VI),t=0}: 37.5 \text{ g/l}$, $C_{a,HNO_3}: 1.0 \text{ M}$, $E_{app}: -0.5 \text{ V vs. SSE}$

aqueous phase, U(VI) in the organic phase, and the Ra as functions of operation time and electrode area per aqueous volume, S, under the condition of constant mass transfer area per unit aqueous volume, A of $0.5 \text{ cm}^2/\text{cm}^3$.

In this simulation, the electrode potential of $-0.5 \text{ V vs. Ag-AgCl/sat. KCl(SSE)}$ was adopted for the controlled-potential electrolysis of U(VI) to U(IV), taking into account the results of the previous works.[9, 10] When the electrode area is relatively small, com-

pared to mass transfer area per aqueous volume, A , most of the transferred $U(VI)$ is accumulated in aqueous phase from the beginning because the production rate of $U(IV)$ is not high enough. This is due to small electrode area as well as low concentration of $U(VI)$ and can be also explained by the Eq.(4) and (5) showing that the reduction is a function of electrode area, concentration of $U(VI)$, and nitric acid concentration in aqueous phase. In this case, the R_a value is large. However, as the time elapses, $U(VI)$ in aqueous phase increases so that the production rate of $U(IV)$ increases gradually, and the R_a approaches to 1. As the electrode area being increased i.e., the ratio of A/S being decreased, $U(IV)$ in the aqueous phase increases, and $U(VI)$ in organic phase decreases more rapidly because the difference of $U(VI)$ concentrations between at the interface and in the bulk phase increases due to the consumption of $U(VI)$ in aqueous phase through the electrolysis. The R_a rapidly approaches to 1 and then keeps the value throughout the operation, because the electro-reduction of $U(VI)$ itself depends on the concentration of $U(VI)$ in aqueous phase which is determined by the mass transfer of $U(VI)$ from the organic phase. This indicates that the mass transfer rate of $U(VI)$ is a determining step of the production rate of $U(IV)$ in the two phases system examined in the present study, though the electro-reduction rate is influenced also by the electrode area and the applied potential. It also means that keeping a suitable mass transfer rate of $U(VI)$ is required to meet a sufficient production yield of $U(IV)$ which is defined as $C_{a, U(IV)} / C_{a, U(VI), t=0}$. The production composition of $U(IV)$ in the resulting solution, which is defined as $C_{a, U(IV)} / (C_{a, U(VI)} + C_{a, U(IV)})$, is good at a large electrode area.

Fig. 3 shows the results similar to Fig. 2 as functions of operation time and mass transfer area per aqueous volume with a constant electrode area per unit aqueous volume, S of $0.5 \text{ cm}^2/\text{cm}^3$. As the mass transfer area being increased, i.e., the ratio of A/S being increased, $U(IV)$ in the aqueous phase in-

crease and $U(VI)$ in the organic phase decreases drastically, because the mass transfer rate of $U(VI)$ becomes faster so that the enough $U(VI)$ is supplied to change into $U(IV)$. Therefore, $U(VI)$ is effectively consumed in the aqueous phase so that the concentration of $U(VI)$ is low. In the case of large electrode area, the mass transfer area does not affect the R_a , because the electrolytic reduction rate of $U(VI)$ depends on the concentration of $U(VI)$ transferred from organic phase. The production yield in the resulting solution is good at a large mass transfer area but the production composition is not so good.

Fig. 4 shows the effect of nitric acid on the amount of $U(IV)$ produced in aqueous phase. As mentioned above, the reduction rate of $U(VI)$ at the electrode increases with increase of the nitric acid. However, the mass transfer rate of $U(VI)$ decreases with increase of nitric acid due to the increase of the distribution coefficient. Accordingly, an optimal nitric acid concentration should exist to attain maximum production rate of $U(IV)$. The produced $U(IV)$ culminates at about 0.37 M HNO_3 and then decreases rapidly. This suggests that the production rate of $U(IV)$ depends more strongly on the mass transfer rather than on the electro-reduction.

The nitric acid concentration, however, should be higher than 0.5 M to prevent a hydrolysis of $U(IV)$ in the aqueous phase.[21, 22] It was found from the simulation that other parameters such as electrode area, mass transfer area, and operation time, had no effects on the nitric acid concentration giving the peak production rate of $U(IV)$.

3.2. Production Yield and Production Composition of $U(IV)$

The operational parameters such as mass transfer area, electrode area, mass transfer coefficient, operation time, and the initial $U(VI)$ concentration in organic phase affect the production yield and the production composition of $U(IV)$ in the resulting aque-

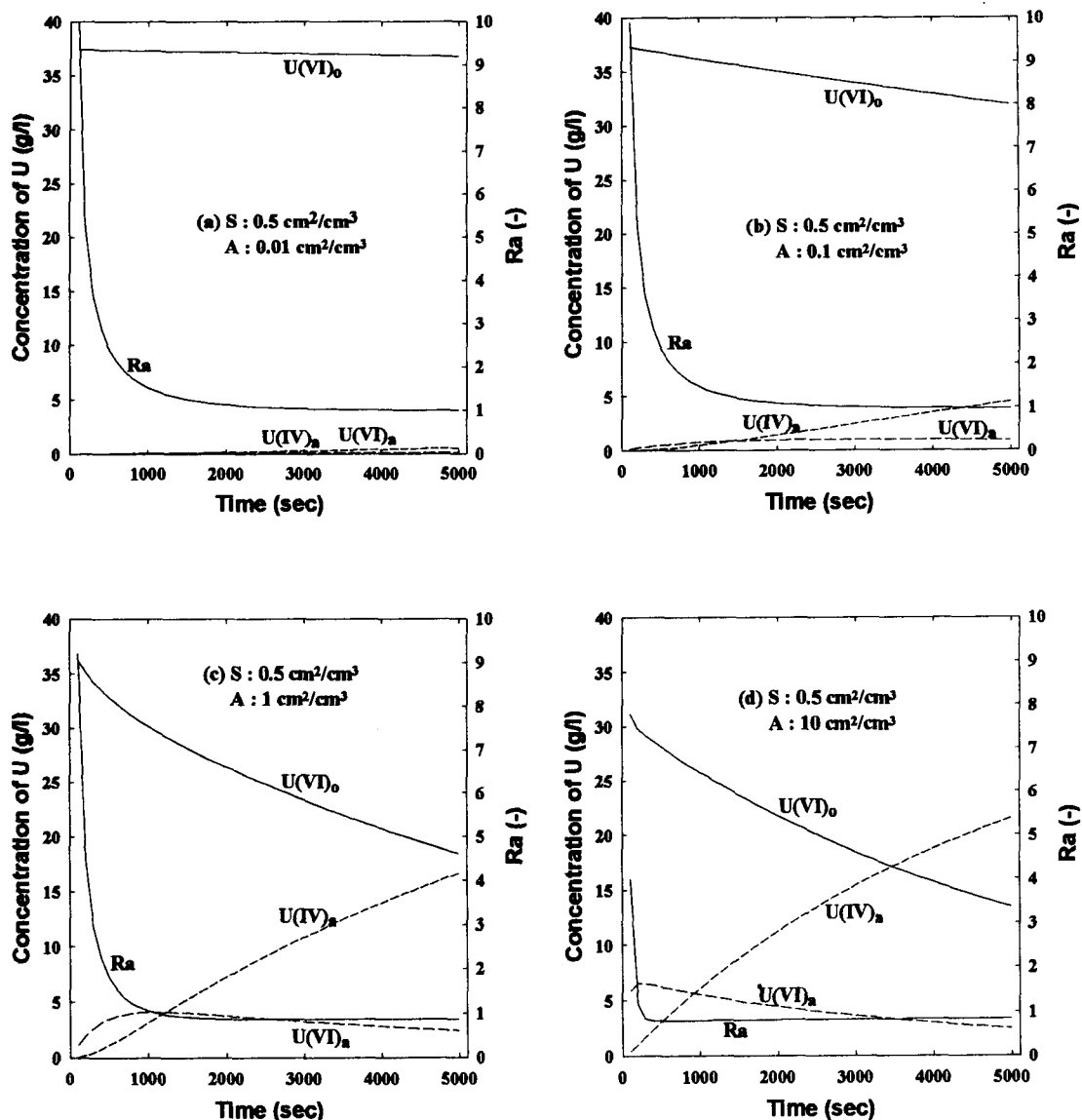


Fig. 3. Simulation for Transient Changes of $C_{a,U(VI)}$, $C_{a,U(IV)}$, $C_{o,U(VI)}$ and Ra with Increase of Operation Time. A: Variable, S: 0.5 cm²/cm³, k_m : 1.8×10^{-3} cm/sec, $C_{o,U(VI),t=0}$: 37.5 g/l, C_{a,HNO_3} : 1.0M, E_{app} : -0.5 V vs. SSE

ous phase. The final production yield and composition of U(IV) in aqueous solution should be premised according to the operational demands for the evaluation of a suitable electrode area. For example, in the partitioning part of the chemical reprocessing

process using electrolytic pulsed column or mixer-settler, the several operational parameters are usually fixed on the basis of preliminary experiments to establish a condition for the most suitable mass transfer. The complete electrolysis of U(VI) into U(IV) is not

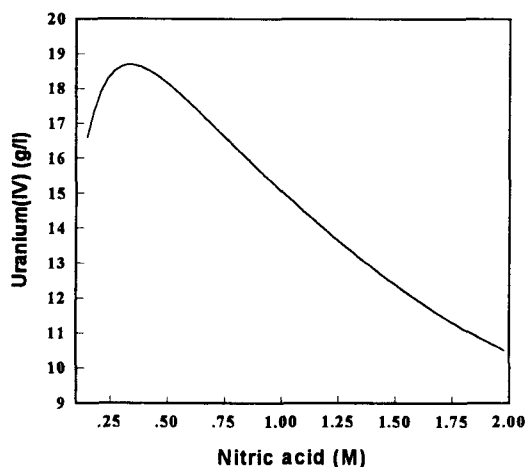


Fig. 4. Effect of Nitric Acid Concentration on the Production Rate of U(IV)
 $A: 1.0 \text{ cm}^2/\text{cm}^3$, $S: 0.5 \text{ cm}^2/\text{cm}^3$, $k_m: 2.0 \times 10^{-3} \text{ cm/sec}$, $C_{0,U(VI),t=0}: 40 \text{ g/l}$, $t: 4,000 \text{ sec}$, $E_{app}: -0.5 \text{ V vs. SSE}$

necessary for the separation of plutonium from uranium, because the concentration of uranium is much higher than that of the plutonium in the organic phase and the reduction rate of Pu(IV) to Pu(III) by U(IV) generated at the electrode is enough rapid. The most suitable electrode area in such case should be determined in order to optimize the construction cost and operation cost of the equipment satisfying the decided operating criteria. Such a optimal electrode area can be evaluated by this kind of simulation.

The simulation in this work was done with two parameters affecting the system significantly, i.e., mass transfer area per volume and operation time related to the residence time of organic phase in the system. Figure 5 shows the dependence of production yield and production composition of U(IV) on the electrode area with given mass transfer areas. The mass transfer area is usually decided in advance together with the mass transfer coefficient in the *in-situ* equipment to meet the best mass transfer. Under a given mass transfer condition, the electrode area needed to

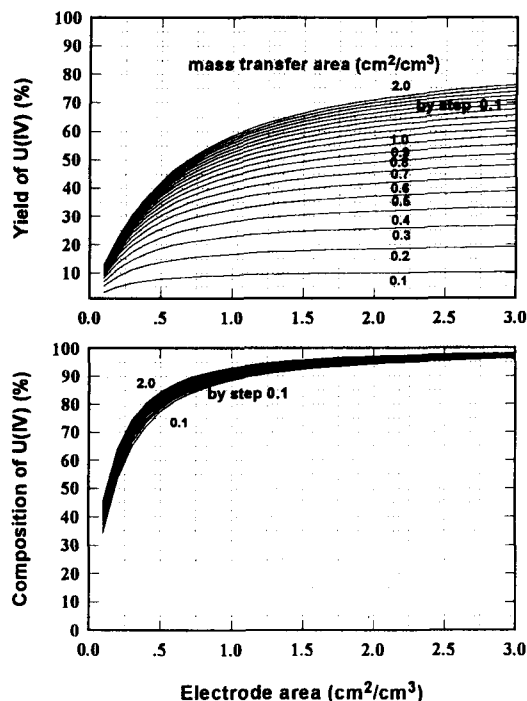


Fig. 5. Effect of Electrode Area on the Production Yield of U(IV) and the Production Composition of U(IV) with Various Mass Transfer Areas.

$k_m: 2.0 \times 10^{-3} \text{ cm/sec}$, $C_{0,U(VI),t=0}: 40 \text{ g/l}$, $t: 4,000 \text{ sec}$, $E_{app}: -0.5 \text{ V vs. SSE}$

attain the desired production yield and the production composition of U(IV) can be determined from these figures. The production yield does not change greatly at the small mass transfer area, but increases much with the increase of electrode area at the large mass transfer area. It means also that the production of U(IV) depends more strongly on the mass transfer rather than the electro-reduction. The production composition of U(IV) depends strongly on the electrode area, but little on the mass transfer area.

Figure 6 shows the effect of electrode area on the production yield and the production composition of U(IV) with various operation times. The operation time is directly related to the residence time of organic phase in the equipment so that it strongly affect

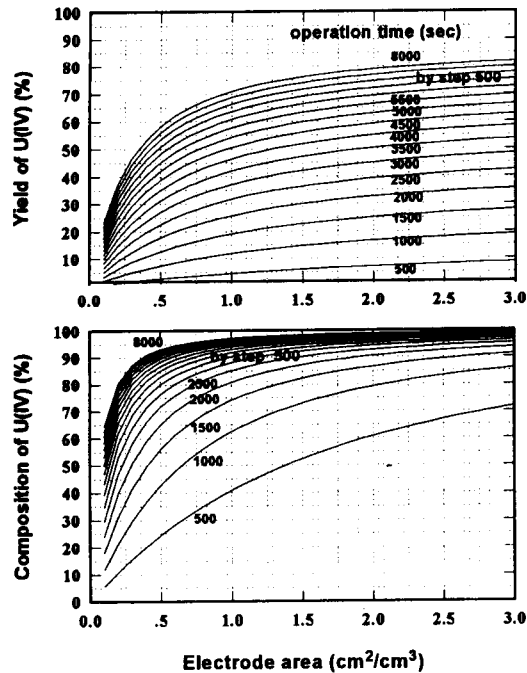


Fig. 6. Effect of Electrode Area on the Production Yield of U(IV) and the Production Composition of U(IV) with Various Operation Times.

A: $1.0 \text{ cm}^2/\text{cm}^3$, $k_m: 2.0 \times 10^{-3} \text{ cm/sec}$, $C_{0,U(VI),t=0}: 40 \text{ g/l}$, $E_{app}: -0.5 \text{ V vs. SSE}$

ts the production composition of U(IV). The residence time usually depends on drop size of organic phase, flow rates of aqueous phase and organic phase fed into the equipment.

In summation, the optimal electrode area can be estimated on the basis of the simulation, if the production composition and the production yield of U(IV) are decided to meet specific conditions for the separation of U/Pu or other two-phases systems.

4. Conclusion

In the two-phases system with mass transfer and electro-reduction of U(VI), a maintenance of suitable mass transfer rate was found to be more important rather than enlargement of electrode area to produce U(IV) optimally. However, large electrode area and

operation time affects the production composition of U(IV) in the aqueous phase after the electrolysis. Concentration of nitric acid should be kept as low as possible for more effective production of U(IV), but should be more than 0.5 M. Optimal electrode areas for the system were estimated as the electrode design criteria under various conditions.

Abbreviation and Definition

- A : mass transfer area per unit aqueous volume (cm^2/cm^3)
- C_k : concentration of species k in solution at time t (M)
- D_k : diffusion coefficient of species k (cm^2/sec)
- d_k : distribution coefficient of species k at interface (—)
- E_{app} : applied potential (V)
- $E^{\circ'}$: formal potential (V)
- F : Faraday constant (96,500 coulombs)
- i : current density (A/cm^2)
- j_k : mass flux of specie k at interface ($\text{mol}/\text{sec}/\text{cm}^2$)
- k_a : apparent heterogeneous rate constant (cm/sec)
- k_t : heterogeneous rate constant (cm/sec)
- k_m : mass transfer coefficient (cm/sec)
- N_{Re} : Reynolds number ($\rho dN/\mu$) (—)
- N_{Sc} : Schmit number ($\mu/\rho D$) (—)
- N_{Sh} : Sherwood number (kL/D) (—)
- S : electrode area per unit aqueous volume (cm^2/cm^3)
- R : gas constant ($\text{J}/\text{mol}/\text{K}$)
- R_a : ratio of mass transfer rate of U(VI) to electro-reduction rate of U(VI) (—)
- t : operation time (sec)
- T : absolute temperature (K)
- V : volume (cm^3)
- v : heterogeneous electro-reaction rate (mol/sec)
- α : transfer coefficient
- δ : thickness of boundary layer (cm)

ρ : density (g / cm³)
 μ : viscosity (g / cm / sec)

Subscript

a : aqueous phase
 o : organic phase
 T : total of system
 * : interface

References

1. He J.Y., Zang Q.X., Lo L.J., ACS Symp. Ser. 117, Actinide Separation, (1986)
2. Faumgartner F., Schmieder H., Radiochim. Acta, 25, 191, (1978)
3. Burkhart L., UCRL-15101, (1979)
4. Majima H., Awakura., Hirono S., Met. Trans. B, 17B, 41, (1986)
5. M. Bénédict, T. H. Pigford, H. W. Levi, "Nuclear Chemical Engineering", 2nd Ed. N.Y., Mc-Graw Hill Co., (1981)
6. H. Feess, H. Wendt, Chemie Ingenieur Technik, 53, 808, (1981)
7. G. Petrich, U. Galla, H. Goldacker, H. Schmieder, Chem. Eng. Sci., 41, 981 (1986)
8. N. Srinivasn, T.S. Laxminaranan, et. al., B.A.R.C. -373, (1968)
9. K.W. Kim, J.D. Kim, H. Aoyagi, Y. Toida, Z. Yoshida, J. Nucl. Sci. & Tech., 30, 6, 554, (1993)
10. K.W. Kim, J.D. Kim, H. Aoyagi, Z. Yoshida, J. Nucl. Sci. & Tech., 31, 4, 329 (1994)
11. L. Salmon, E.L. Mechero, Ind. Eng. Chem. Prog. Des. Develop, 9, 3, 345, (1970)
12. R.S. Ondrejcin, DP-602, (1960)
13. K.J.Z. Vetter, Phys. Chem. 194, 199 (1960)
14. J.A. Epstein, I.L. Sravin, Proceeding of 3rd United Nations International Conference on Peaceful Uses of Atomic Energy, 18, 436, (1964)
15. G.L. Richardson, J.L. Swanson, HEDL-TME 75-31, (1975)
16. I.F. McConvey, A.N. Haines, K. Scott, Chem. Eng. Res. Des., 67, 14, (1989)
17. A.H.P. Skelland, "Diffusional Mass Transfer", John Wiley & Sons Inc. (1974)
18. R.S. Ondrejcin, DP-653 (1961)
19. L.L. Burger, HW-62087 (1959)
20. T.C. Lo, M.H.I. Baird, C. Hanson, "Handbook of Solvent Extraction", N.Y., John Wiley & Sons, (1983)
21. J. Bruno, I. Casas, B. Lagerman, M. Munoz, Mat. Res. Symp. Proc., 84, 153, (1987)
22. E.H.P. Cordfunke, "The chemistry of uranium", N.Y. Elsevier Pub. Co., (1969)
23. K.W. Kim, E.H. Lee, Y.J. Shin, J.H. Yoo, H.S. Park, J. Korea Nuclear Society, 26, 3, 425 (1994)
24. Y. Nakaike, S. Takahashi, T. Tadaki, International Chemical Engineering, 17, 2, 260 (1977)