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Process modeling of in-situ electrochemical partitioning of uranium and plutonium in purex process: benchmark results with uranium reduction

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ABSTRACT

In-situ reduction of plutonium and uranium for the separation of U/Pu is suitable for plutonium-rich fuels such as FBR fuels. The mathematical basis for a computer program **PUSEP** (**P**lutonium **U**ranium **S**olvent **E**xtraction **P**rogram) for the analysis of partitioning cycle of PUREX process involving in-situ electrochemical reduction of uranium and plutonium is described in the present investigation. Model equations have been developed on the basis of the idealized model for mixer settlers incorporating distribution coefficients and redox reactions of the species involved and solved numerically to obtain concentration profiles of components. The validity of the model equations and associated computer program is tested by carrying out experiments in a proto type 20-stage electrolytic ejector mixer-settler operating without diaphragm for the electro reduction of uranium. The stage-wise experimental concentration profiles of U(VI), U(IV) and nitric acid were obtained and compared with the theoretical predictions. A reasonably good agreement is achieved between experimental and predicted concentration profiles.

Keywords: Purex process; Nuclear fuel processing; Modeling and simulation of SX process; Electrochemical partitioning

1. Introduction

The PUREX process which uses a mixture of tri-*n*-butyl phosphate (TBP) and a hydrocarbon diluent to extract uranyl nitrate is the most widely used process for reprocessing the nuclear spent fuels. In this process partitioning of U and Pu (i.e., separation of U and Pu from each other) is based on the fact that U(VI), U(IV) and Pu(IV) form strong organic complexes with TBP whereas Pu(III) forms a relatively weak TBP complex. The reduction of Pu(IV) to Pu(III) is achieved by means of a reducing agent (i.e., by ferrous sulfamate, hydroxylamine nitrate, uranous nitrate etc.) or by in-situ reduction (electrochemical reduction). The classical reducing agent for plutonium is ferrous sulfamate but it introduces a large amount of corrosive ions which leads to numerous troubles. The externally generated reductant U(IV) is ideally suited for high separation efficiency for fuels of low plutonium content such as pressurised water reactor (PWR) fuels, but normally large quantity of uranous (more than 6–10 times of stoichiometry) is required to achieve effective separation between uranium and plutonium. Hence, for fast reactor fuels, with 21–28% plutonium, large quantity of product uranium has to be recycled. The alternate option is to employ electrochemical in-situ reduction process in the partitioning

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step to achieve separation between uranium and plutonium. This process is simple to operate, easy to control remotely with low recycle load. It is also reported that, in comparison with the hydroxylamine process Pu is completely stripped even from the HDBP complex in the electrochemical process [1]. Moreover, the Pu product concentration can be increased above 40 g/l in the electrochemical process, which is not possible with the other candidate processes.

The design of PUREX solvent extraction flowsheet is greatly facilitated by the development of computer codes to do the tedious stage-by-stage equilibrium calculations involving multi solutes. It is a valuable tool for simulating various conditions and to arrive at optimum flowsheet conditions, minimizing the requirement of the number of experimental runs. Some of the important computer codes developed in the past for simulating PUREX solvent extraction system are SEPHIS and its modifications, PUBG, PUMA, SOLVEX, etc, and all of them developed for stage-wise contactors [2–6]. Each of these codes is addressed to a specific case. For example, SEPHIS (Version 3) was developed primarily for the analysis of diluted type extraction flowsheet meant for pressurised heavy water reactor (PHWR) fuel reprocessing. Applicability of this code is limited only to extraction and stripping contactors of PUREX process. Whereas the modified version of the SEPHIS code (SEPHIS MOD-4, which uses improved distribution coefficient relations), PUBG and PUMA are capable of simulating extraction, stripping and partitioning cycles of PUREX process. The use of either, hydrazine stabilized hydroxylamine nitrate (HAN) or externally generated uranous [U(IV)] as a reducing agent to partition plutonium from uranium is incorporated in these codes.

A number of studies on in-situ electrochemical reduction of uranium and plutonium have been carried out in USA, China, Germany, and many other countries [7–11]. Most of the published information is from Karlsruhe, Germany. As there is no code existing in the open literature on in-situ electrochemical partitioning, hence a computer program has been developed to address this step. In the present work mathematical basis for a computer code PUSEP (**P**lutonium **U**ranium **S**olvent **E**xtraction **P**rogram) for the separation of uranium and plutonium from each other and the experimental validation is described.

2. Mathematical modeling of electrochemical in-situ reduction process

In electrochemical in-situ reduction process the plutonium is chemically and electrochemically reduced to lower valence state and is back-extracted into the aqueous phase. Within an electro-reduction mixer-settler Pu(IV) reduction results from the following three reactions:

(i) Direct electrochemical Pu(IV) reduction,
(ii) Indirect Pu(IV) reduction by U(IV) [electrochemically formed],
(iii) Reduction of Pu(IV) by hydrazine.

The major fraction of Pu(IV) reduction is caused by U(IV) formed electrochemically within the extractor. Hydrazine reduces Pu(IV) much more slowly than does U(IV). It is common to add hydrazine as a holding reductant to prevent Pu(III) reoxidation by nitrous acid, which is produced during electrolysis as well as during dissolution step. In addition hydrazine also acts as a salting-out agent and therefore reduces separation. Hence, an optimum concentration of hydrazine must be chosen in order to improve separation efficiency. Partitioning of uranium and plutonium is a complicated process as the components [i.e., U(IV), U(VI), Pu(III), Pu(IV), Pu(V), Pu(VI), HNO_3, and hydrazine] distribution in aqueous and organic phases is accompanied with redox reactions involving uranium, plutonium, nitric and nitrous acids and hydrazine.

To simulate partitioning process, detailed models of the distribution equilibria for the extraction of multicomponent, chemical and electrochemical redox reactions rates and mass transfer kinetics are needed. In the present work mathematical basis of a computer program PUSEP (**P**lutonium **U**ranium **S**olvent **E**xtraction **P**rogram) for the analysis of partitioning cycle of PUREX process involving in-situ electrochemical reduction of uranium and plutonium is described. The development of model equations involves countercurrent multi component countercurrent extraction coupled with chemical and electrochemical redox reactions. The main components considered in the model equations are U(VI), U(IV), Pu(IV), Pu(III), nitric acid and hydrazine. The variable valance elements like Tc and Ru, though affect the performance of reductive stripping stages used to separate plutonium and uranium, their effect is insignificant. It is also to be noted that there is no sufficient data with respect to reaction kinetics and their distribution behaviour in the literature, and hence not incorporated in the model equations. The code generates transient concentration profiles from the initial conditions to steady-state conditions. The calculation of steady-state profiles through transient behavior provides important information about the variation of solute concentration with time in the contactor bank which otherwise cannot be obtained from the steady-state solutions. Transient calculations can only provide the information about unsafe accumulation of solute if any.

2.1. Distribution equilibria

A necessary prerequisite for any realistic simulation of counter-current extraction in the PUREX process is a reliable relation for the distribution coefficients of the species involved. Although a number of models of distribution coefficient for PUREX system have been presented in the literature, they are of limited use since they are generally restricted to only narrow concentration ranges. A thermodynamic model for distribution coefficients (representing equilibrium constants in terms of activity coefficients) is needed that could predict accurately the simultaneous extraction behaviour of U(VI), Pu(IV), HNO_3 and Pu(III) under reductive conditions of partitioning cycle of PUREX process. Limited data is available in literature on the simultaneous extraction of U(VI), U(IV), Pu(IV), Pu(III) and HNO_3 in presence of hydrazine nitrate employing TBP as extractant. The distribution coefficient data bank "1981 Purex Distribution Data Index", which is the collection of more than 4000 data points, serves to make reliable mathematical models for calculating distribution coefficients [12]. The distribution of species between the aqueous and the organic phases are modeled on the basis of following reaction equilibria,

$$\begin{aligned}&UO_2^{2+}(aq) + 2NO_3^-(aq) + 2TBP(o)\\&\leftrightarrow UO_2(NO_3)_2\,2TBP(o)\end{aligned} \tag{1}$$

$$\begin{aligned}&U^{4+}(aq) + 4NO_3^-(aq) + 2TBP(o)\\&\leftrightarrow U(NO_3)_4\,2TBP(o)\end{aligned} \tag{2}$$

$$\begin{aligned}&\cdots\ {}^{4+}(aq) + \qquad {}_3^-(aq) + \qquad\quad (o)\\&\leftrightarrow Pu(NO_3)_4\,2TBP(o)\end{aligned} \tag{3}$$

$$Pu^{3+}(aq) + 3NO_3^-(aq) + 3TBP(o) \leftrightarrow Pu(NO_3)_3\,3TBP(o) \tag{4}$$

$$H^+(aq) + NO_3^-(aq) + TBP(o) \leftrightarrow HNO_3TBP(o) \tag{5}$$

Higher solvate of nitric acid HNO_3 2TBP and HNO_3 3TBP are not considered because they are not expected to be significant under the conditions prevailing in the Purex streams. Evidence for such species is summarized in Ref. [13]. The apparent equilibrium constants, which are related with the thermodynamic ones and the activity coefficients in suitable power for Eqs. (1) through (5) are represented as follows:

$$K_{U(VI)} = \frac{[UO_2(NO_3)_2 2TBP]}{[UO_2^{2+}][NO_3^-]^2[TBP_f]^2} \tag{6}$$

$$K_{U(IV)} = \frac{[U(NO_3)_4 2TBP]}{[U^{4+}][NO_3^-]^4[TBP_f]^2} \tag{7}$$

$$K_{Pu(IV)} = \frac{[Pu(NO_3)_4 2TBP]}{[Pu^{4+}][NO_3^-]^4[TBP_f]^2} \tag{8}$$

$$K_{Pu(III)} = \frac{[Pu(NO_3)_3 3TBP]}{[Pu^{3+}][NO_3^-]^3[TBP_f]^3} \tag{9}$$

$$K_H = \frac{[HNO_3TBP]}{[H^+][NO_3^-][TBP_f]} \tag{10}$$

Here square brackets indicate the molar concentration of each species. Distribution coefficients (the ratio of the organic to aqueous phase concentrations) of the species are given as:

$$\begin{aligned}D_{U(VI)} &= \frac{[UO_2(NO_3)_2 2TBP]}{[UO_2^{2+}]} = K_{U(VI)}[NO_3^-]^2[TBP_f]^2\\&= K'_{U(VI)}[TBP_f]^2\end{aligned} \tag{11*}$$

$$\begin{aligned}D_{U(IV)} &= \frac{[U(NO_3)_4 2TBP]}{[U^{4+}]} = K_{U(IV)}[NO_3^-]^4[TBP_f]^2\\&= K'_{U(IV)}[TBP_f]^2\end{aligned} \tag{12*}$$

$$\begin{aligned}D_{Pu(IV)} &= \frac{[Pu(NO_3)_4 2TBP]}{[Pu^{4+}]} = K_{Pu(IV)}[NO_3^-]^4[TBP_f]^2\\&= K'_{Pu(IV)}[TBP_f]^2\end{aligned} \tag{13*}$$

$$D_H = \frac{[HNO_3TBP]}{[H^+]} = K_H[NO_3^-][TBP_f] = K'_H[TBP_f] \tag{14*}$$

$$\begin{aligned}D_{Pu(III)} &= \frac{[Pu(NO_3)_3 3TBP]}{[Pu^{3+}]} = K_{Pu(III)}[NO_3^-]^3[TBP_f]^3\\&= K'_{Pu(III)}[TBP_f]^3\end{aligned} \tag{15*}$$

The quantity $[TBP_f]$ is the concentration of uncombined or free TBP, which is obtained by TBP balance as,

$$\begin{aligned}[TBP_f] = [TBP_o] &- 2[UO_2(NO_3)_2 2TBP]\\&- 2[U(NO_3)_4 2TBP] - 2[Pu(NO_3)_4 2TBP]\\&- [HNO_3TBP] - 3[Pu(NO_3)_3 3TBP]\end{aligned} \tag{16}$$

where $[TBP_0]$ is the initial concentration of TBP. Substitutions from Eqs. (11)–(15) into Eq. (16) results in

$$\begin{aligned}[TBP_f] = [TBP_o] &- 2K'_{U(VI)}[UO_2^{2+}][TBP_f]^2\\&- 2K'_{U(IV)}[U^{4+}][TBP_f]^2 - 2K'_{Pu(IV)}[Pu^{4+}][TBP_f]^2\\&- K'_H[H^+][TBP_f] - 3K'_{Pu(III)}[Pu^{3+}][TBP_f]^3\end{aligned} \tag{17}$$

Rearranging gives:

$$Q[TBP_f]^3 + P[TBP_f]^2 + (1 + R)[TBP_f] - [TBP_o] = 0 \tag{18}$$

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*In order to correlate apparent equilibrium constant in a better way Richardson [14] grouped *K* and $[NO_3^-]^x$ (where x is power of $[NO_3^-]$ for the respective solute) together as one parameter as *K*′.

where,

$$P = 2\left(K'_{U(VI)}[UO_2^{2+}] + K'_{U(IV)}[U^{4+}] + K'_{Pu(IV)}[Pu^{4+}]\right) \quad (19)$$

$$Q = 3K'_{Pu(III)}[Pu^{3+}] \quad (20)$$

$$R = K'_H[H^+] \quad (21)$$

Eq. (18) represents a cubic equation in [TBP_f] which can be solved algebraically or, numerically to determine the amount of free TBP. Since the K' values in above equations are not true equilibrium constants as they are based on concentration rather than activities, they have been correlated in number of ways in the literature. Correlations of SEPHIS-MOD4 and Geldard et al. (for U(VI), U(IV), Pu(IV), Pu(III) and HNO_3) are found to be reasonably satisfactory and are applicable to wide range of solute concentration and volume percent of TBP and are used for the estimation of distribution coefficients of the species in the present work [15].

2.2. Chemical and electrochemical reactions

Some of the important chemical and electrochemical reactions, which occur during electrochemical process, are as follows:

Electrochemical reactions

At cathode:

$$UO_2^{2+} + 4H^+ + 2e^- = U^{4+} + 2H_2O \quad (22)$$

$$Pu^{4+} + e^- = Pu^{3+} \quad (23)$$

$$2H^+ + 2e^- = H_2\uparrow \quad (24)$$

$$3H^+ + NO_3^- + 2e^- = HNO_2 + H_2O \quad (25)$$

At anode:

$$Pu^{3+} = Pu^{4+} + e^- \quad (26)$$

$$N_2H_5^+ = N_2\uparrow + 5H^+ + 4e^- \quad (27)$$

$$2H_2O = 4H^+ + O_2\uparrow + 4e^- \quad (28)$$

Chemical reactions

$$U^{4+} + 2Pu^{4+} + 2H_2O = UO_2^{2+} + 2Pu^{3+} + 4H^+ \quad (29)$$

$$2Pu^{4+} + 2N_2H_5^+ = 2Pu^{3+} + 2NH_4^+ + N_2\uparrow + 2H^+ \quad (30)$$

$$4Pu^{4+} + N_2H_5^+ = 4Pu^{3+} + N_2\uparrow + 5H^+ \quad (31)$$

$$Pu^{3+} + HNO_2 + H^+ = Pu^4 + NO\uparrow + H_2O \quad (32)$$

$$4Pu^{3+} + 2HNO_2 + 4H^+ = 4Pu^{4+} + N_2O\uparrow + 3H_2O \quad (33)$$

$$2Pu^{3+} + 3HNO_3 = 2Pu^{4+} + 2NO_3^- + HNO_2 + H_2O \quad (34)$$

$$U^{4+} + 2HNO_2 = UO_2^{2+} + 2NO\uparrow + 2H^+ \quad (35)$$

$$N_2H_5^+ + HNO_2 = HN_3 + H^+ + 2H_2O \quad (36)$$

$$HN_3 + HNO_2 = N_2\uparrow + N_2O\uparrow + H_2O \quad (37)$$

Rate expressions for the above mentioned electrochemical and chemical reactions of significance, which are incorporated in the model equations, are given in Table 1.

The reduction of U(VI) to U(IV) proceeds in parallel with plutonium reduction. The kinetic studies have shown that electrochemical reduction of U(VI) and Pu(IV) follow a first order law [11]. The formation of U(IV) in addition to Pu(III) is advantageous and is desirable because, it itself reduces Pu(IV) to Pu(III) chemically and improves plutonium back-extraction into aqueous phase. The reduction of U(VI) to U(IV) is described thermodynamically irreversible, but like Pu(III), U(IV) is relatively easily re-oxidized to U(VI) by N_2O_4 or HNO_2 in nitric acid solution [16]. A scavenger for HNO_2, such

Table 1
Rate expressions of electrochemical and chemical reactions

No.	Rate expression
1	Cathodic reduction of Pu(IV) [11]: $\frac{d[Pu(IV)]}{dt} = -ka_c[Pu(IV)]$ $k = 13.8$ cm/hr, a_c is specific area of cathode cm^{-1}
2	Cathodic reduction of U(VI) [11]: $\frac{d[U(VI)]}{dt} = -ka_c[U(VI)]$ $k = 0.48$ cm/hr
3	Anodic re-oxidation of Pu(III) [11]: $\frac{d[Pu(III)]}{dt} = -ka_a[Pu(III)]$ $k = 15$ cm/hr, a_a is specific area of anode cm^{-1}
4	Reduction of Pu(IV) by U(IV) [17]: (Aq. Phase): $\frac{d[Pu(IV)]}{dt} = -\frac{k[Pu(IV)][U(IV)]}{([HNO_3]+K_P)([HNO_3]+K_U)}$ $k = 9.12*10^5$ mol/l/hr, $E_A = 104$ kJ/mol *Organic phase:* The organic phase reaction is not well known. It is assumed to be a factor of 100 times slower than the aqueous reaction [18]
5	Reduction of Pu(IV) by hydrazine [19] : $\frac{d[Pu(IV)]}{dt} = -\frac{k[Pu(IV)][N_2H_5^+]}{([HNO_3]+K_p)}$ $k = 2.28$ hr^{-1}, $E_A = 93$ kJ/mol where K_P and K_U are hydrolysis and dissociation constants for plutonium and uranium respectively

as hydrazine, sulfamic acid or urea is therefore added to partitioning system to stabilize U(IV) and Pu(III).

2.3. Model equations

The development of model equations involves countercurrent multi-component extraction coupled with chemical and electrochemical reactions. It is assumed that complete mixing is assumed in mixer compartment of mixer-settler unit and mass transfer due to extraction occurs only in mixer compartment and the components are always at equilibrium between the phases when they leave the stage. Stage residence times are sufficiently long so that diffusional resistances can be ignored. It is also assumed that only in the aqueous phase of the settler compartment electro-reduction of U(VI) and Pu(IV) take place and in presence of hydrazine autoxidation of Pu(III) by nitrous acid is suppressed. The flowrates are assumed to be constant across the mixer-settler bank. Entrainment of phases and the effect of solvent degradation products (particularly HDBP) are not considered in the present model. Fig. 1 shows qualitatively the scheme of the mixer-settler model. Material balance equations based on an idealized model for mixer-settlers can be written as:

Mass balance equation for mixer

$$\frac{dX_{mj}}{dt} = \frac{1}{(h_a + h_0 D_j)}\Big[A(X_{j-1} - X_{mj}) + O\left(Y_{j+1} - Y_{mj}\right) + h_a \sum r_{amj} + h_0 \sum r_{omj}\Big] \quad (38)$$

Mass balance equation for settler

$$\frac{dX_j}{dt} = \frac{A}{H_a}(X_{mj} - X_j) + \sum r_{aj} + \sum r_{ej} \quad (39)$$

$$\frac{dY_j}{dt} = \frac{O}{H_o}(Y_{mj} - Y_j) + \sum r_{oj} \quad (40)$$

where, $j = 1,2,3\ldots n$ (number of stages)

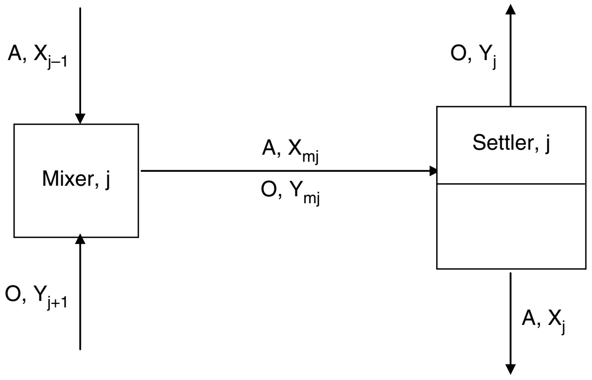

Fig. 1. Mass balance around a stage of mixer-settler.

The above equations are used in the computational algorithm for a single stage of mixer-settler bank. These unsteady mass balance equations are written for six solutes which are present (U(VI), U(IV), Pu(IV), Pu(III), HNO_3, and hydrazine) and are solved simultaneously in order to obtain concentration profile around the stages of mixer-settler. Except hydrazine all other components are getting distributed and their distributions are mutually dependent on each other. In the present model contribution from nitrous acid has not been considered, as no suitable distribution coefficient correlation is available in the literature.

All the computer codes use the common convention that the aqueous stream flows from the lower to the higher numbered stages, the organic stream flowing in opposite direction. Similar convention is followed in this code also. The developed computer program is written in MATLAB and model equations (38)–(40) are solved numerically using ordinary differential equation solver program ODE-45 with appropriate distribution coefficients and rate expressions (as listed in Table 1) for the six components in order to obtain concentration profile of each component around the stages of the mixer-settler. The initial conditions for calculations are taken as the conditions when all the stages are filled with strip solutions. The subroutines of the computer program (PUSEP) and their functions are described below.

ModelEq.m: This is a function file, which contains model equations (38–40) to be solved. It receives input parameters from the main program, like initial concentration profile in the extractor, flow rates, volume TBP%, temperature, volume of mixer-settler unit, number of stages etc. that will be used by the model equations. This function calls DistC.m, RateM.m and RateS.m (with input parameters).

DistC.m: This is a function file, which contains distribution coefficient correlations and calculates distribution coefficients of all components except hydrazine. It is interactive with subroutine ModelEq.m.

RateM.m: This function files contains rate expressions, which calculates net rate of chemical reactions occurring in mixer. It is interactive with subroutines ModelEq.m and DistC.m.

RateS.m: This function files contains rate expressions, which calculates net rate of chemical and electrochemical reactions in occurring in settler.

3. Validation of the model equations

Simulation of almost all the published experimental flowsheets [11] concerning to electrolytic partitioning of Pu/U were carried out in order to test the validity of the model equations and associated computer program. A reasonably fair to good agreement was observed with all the experimental results. A typical example of experimental data as shown in Fig. 2 based on 20 vol% TBP flowsheet is considered here for the discussion [11].

In this, a 16 stage mixer-settler bank with stages one to ten of mixer settler bank is equipped with electrodes is used for partitioning experiments, a loaded organic feed with conditions given in Fig. 2.

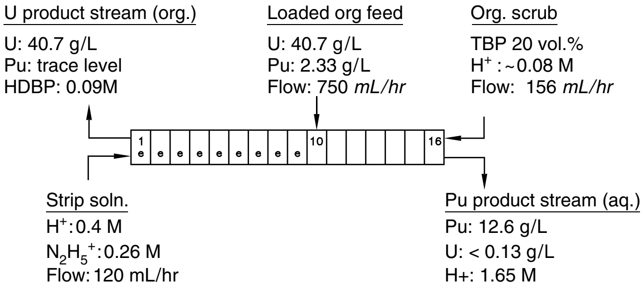

Fig. 2. Experimental data from **KFK-2082** (Fig. 23, Ref. 11) based on 20% TBP in *n*-dodecane.

Fig. 3 shows the comparison between experimental and calculated profiles. It can be seen that calculated values of uranium [total uranium i.e., U(IV)+U(VI)], U(IV), and nitric acid are in reasonably good agreement with the experimental results. Figs. 3(c) shows the calculated concentration profile of Pu(III) in aqueous phase at different interval of time along with the experimental profile. It is noticed that, Pu-product solution concentration (concentration of solution comes out from stage 16) and concentration profile of Pu(III) from stage no. 10 to 16 (called BS section) remains unchanged after about 3 h, whereas in BX section (for the stages from stage no. 1 to 9) variation in concentration profile with time is observed and it remains unchanged after 13 h. It is also observed from the Fig. 3(c) that calculated profile of Pu(III) compares better corresponding to time equal

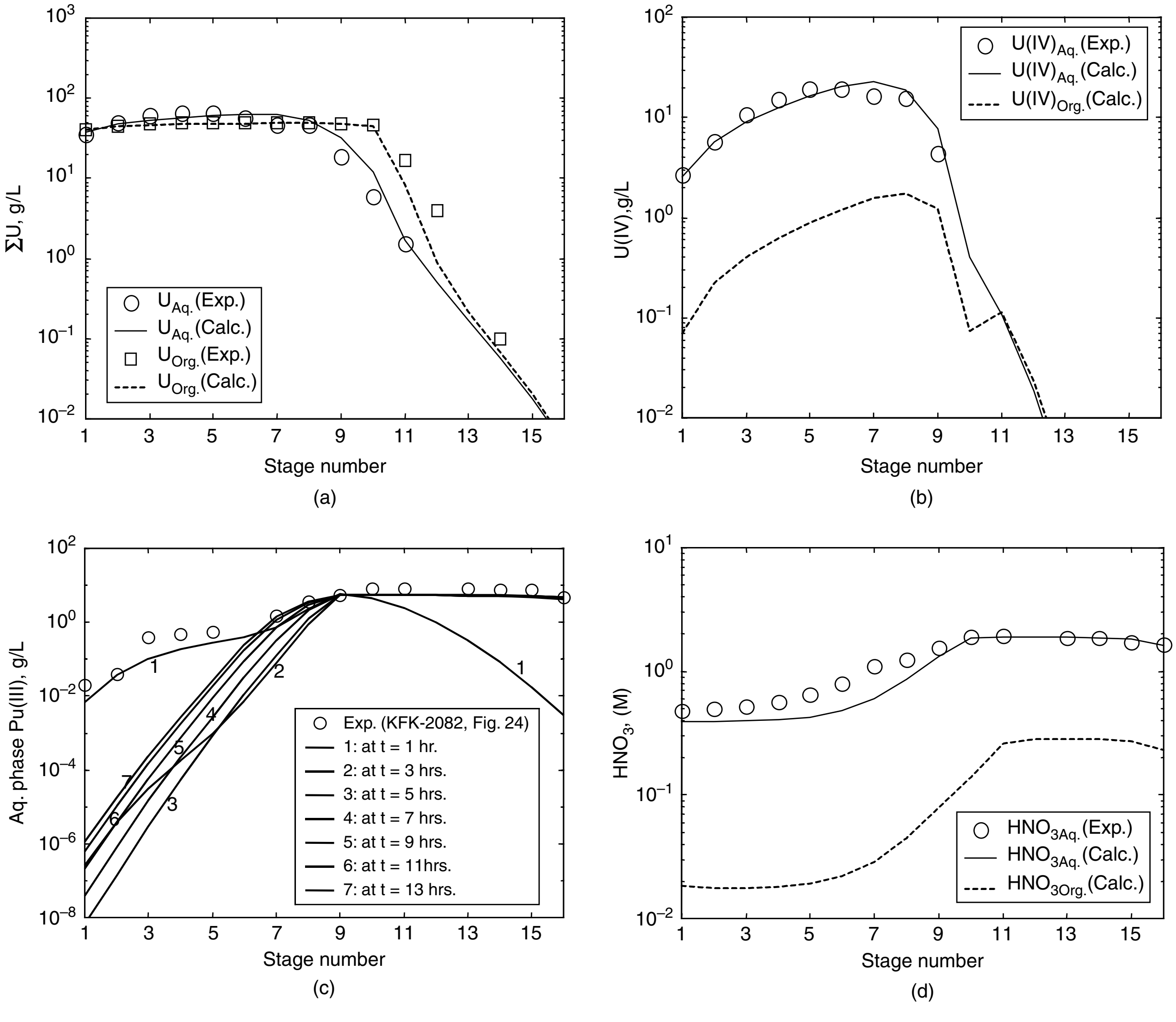

Fig. 3. Comparison of calculated and experimental profiles in a 16-stage 1B contactor.

to 13 h. In the reported experimental data, time of sampling of experimental profiles, nitric acid concentration in loaded organic feed and the initial conditions in the stages have not been specified. The initial conditions for the calculations are taken as the conditions when all the stages of mixer-settler unit are filled with the strip solution. In simulation calculations values of specific cathode and anode area used were 0.01 and 0.6–0.8 cm^{-1} respectively whereas as the actual specific cathode area is reported to be 1.8 cm^{-1} [11]. The difference between assumed and actual specific cathode area may be attributed to low current efficiency.

The deviations in the plutonium profile in the low concentration region, are probably due to slow strip rate of Pu-HDBP complex and uncertainty in the estimation of distribution coefficient in low concentration region. Since, strip rate of plutonium from Pu-HDBP complex is not known and therefore could not be incorporated in the model equations.

The calculation performed using developed program is limited to mass transfer equilibrium and is applicable to only stage-wise contractor. Most of the contemporary computerized chemical models used for simulating concentration profiles in mixer-settler contactors do not account for deviations from mass transfer equilibrium. The fact that in the extraction from the aqueous to organic phase, the measured concentrations are generally higher than the calculated values for stages between the feed stream and the aqueous waste stream (i.e., in low concentration region) suggests deviations from mass transfer equilibrium.

Further deviations from equilibrium are accounted by a transfer function that has a form $K_{xj}a_j(y_{eq}-y_j)$, where K_{xj} is the overall mass transfer coefficient based on Y-phase in the j'th mixer, a_j is the mass transfer area in the j'th mixer and the last part is the difference between the actual organic phase concentration and equilibrium concentration. Early attempts to account for deviations from mass transfer equilibrium in chemical modeling did not explicitly account for mass transfer rates, a primary characteristic of a solvent extraction contactor operating away from equilibrium [20]. Theoretical studies on methods of correlating mass transfer area and mass transfer coefficients with hydrodynamic parameters are required in order to account for deviations from mass transfer equilibrium in model equations.

The comparison between the experimental results and the calculated results demonstrated that the model and algorithm presented here is a useful tool for design, optimization and evaluation of flowsheet for partitioning step. However, caution should be applied in using the computer results particularly the predicted plutonium profiles at low acidities where disproportionation and hydrolysis can have significant effects. Moreover partitioning of plutonium from uranium is a complex process, there are several factors such as acidity, residence time, A/O ratio, temperature U/Pu ratio etc. which influence the performance of partitioning contactor, some compromises had to be made in fitting the experimental data because of limitations inherent in the computer program; as it does not include the effect of re-oxidation in the solvent, effect of solvent degradation products and it does not include a provision of backmixing.

4. Studies at IGCAR

A laboratory scale electrolytic mixer-settler made in polypropylene block operating without diaphragm was designed and developed at Reprocessing Group of Indira Gandhi Centre for Atomic Research, Kalpakkam to carry out studies on electrochemical portioning of uranium and plutonium of FBR fuels. The operation of the designed unit is tested for its performance by carrying out experiments with in-situ reduction of uranium before using it for electro-reduction uranium and plutonium ions. The performance obtained with uranium solution would probably suggest that no technical difficulty would arise in case of electrochemical separation of plutonium from uranium in Purex process for FBR fuels because, electrochemical reduction of uranium is more difficult than plutonium as it involves two electron transfer process also breaking of bond between uranium and oxygen.

A schematic diagram of one stage of mixer-settler bank is shown in Fig. 4. The mixer-settler unit has 20 stages with mixer having volume of about 15 ml and settler having volume of about 45 ml. An anodic space is provided by the side of each settler compartment as shown in Fig. 4. The anode compartment is interconnected to settler at bottom which ensures only aqueous phase is in contact with the anode and this also avoids the use of diaphragms to isolate cathode and anode which is related to voltage drop and the undesirable heating of the process stream. The cathode used is made of perforated titanium plates (with 3 mm holes) stacked together in the form of a cartridge having geometrical area of about 55 cm^2 is placed at the bottom of settling chamber such that it is always in contact with aqueous phase. The anode is made of platinum gauge of rectangular shape having geometrical area of about 13 cm^2.

At the bottom of each cylindrical mixer of mixer-settler unit is fitted with an ejector with short diffuser which performs as a mixing as well as inter-stage pumping device. The mixing device is isolated from the rest of mixer except through diffuser. This ensures that both continuous and dispersed phases pass through the diffuser so that good dispersion is achieved in the rest of the mixer section. The motive end of each ejector is connected through a pipe to a common header, which in turn is connected to a pressure and vacuum source

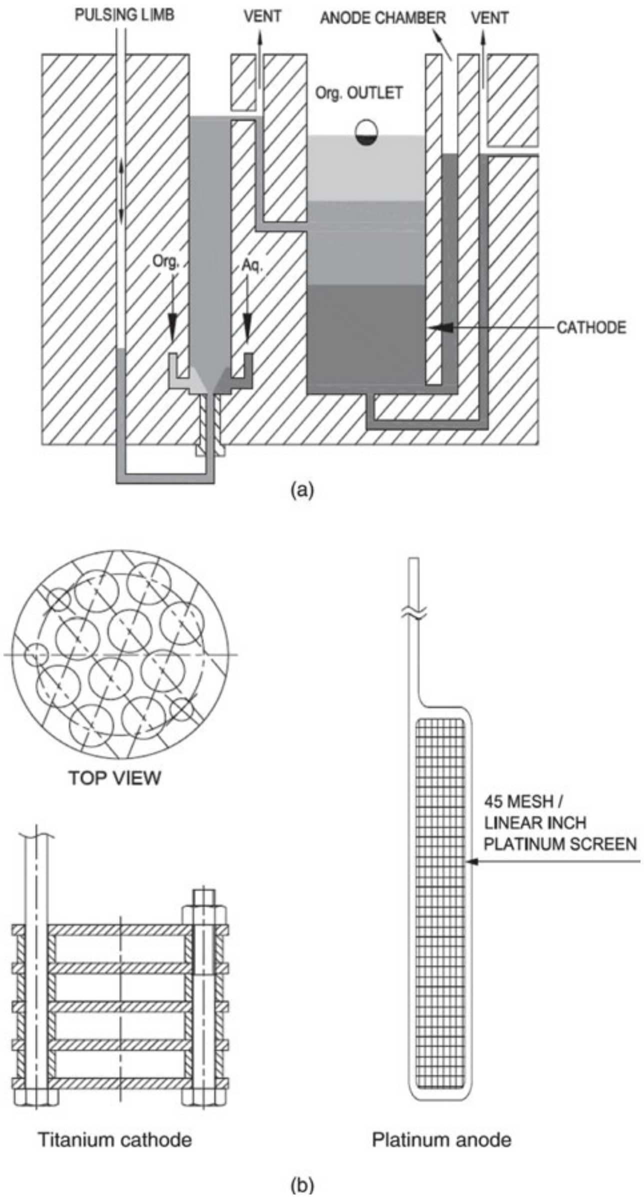

Fig. 4. Schematic diagram of (a) one stage of mixer-settler bank (b) cathode and anode geometry.

through a 2-way 3-port solenoid valve. A timer varies the frequency of the pulse, and by changing the pressure and vacuum to solenoid valve amplitude of the pulse can be changed.

Once the pulsing starts, the bottom portion of the mixer will develop a few inches of vacuum and the liquid level in the feed lines (to mixer) is lowered so that the aqueous and organic phases flow over the weirs and flow to the corresponding mixer, thereby, eliminating the need of inter-stage pumps. Depending upon the experimental conditions the interface in the settling chamber could be adjusted by lowering or raising a screw which is provided in the aqueous outlet limb.

During the experiments care was taken to maintain the level of interface level such that cathode is fully immersed in aqueous layer.

5. Experimental results

The 20-stage mixer-settler with parameters described above was used for validating the code with uranium solute before taking up flowsheet runs with U-Pu solutions. By following the concentration profiles of solutes, the code can be validated for the process except that for plutonium, which can be validated in the subsequent studies. Total four experimental runs were carried out, three runs with aqueous feed containing uranyl nitrate at different feed concentrations and one run with as loaded organic feed. After completely assembling the electro-mixer-settler, few test runs with 30% TBP in NPH and nitric acid (about 4 M) were made for checking, pulsing behaviour and mass transfer performance. Stages one to thirteen of mixer settler bank is equipped with electrodes and the position of the interface in settler is maintained such that electrode is fully dipped in the aqueous phase. A typical flow scheme of in-situ reduction of uranium solution in the electrolytic mixer-settler is shown in Fig. 5.

Valveless metering pumps were used for precisely pumping the feed, organic and strip solutions after prior calibration. A Power supply unit: 10 V, 15 A was used for constant voltage DC power supply during electrolysis.

Initially for about 2½ h, the unit was run with only nitric acid (~4 M HNO_3) in the feed with other respective input flow streams (organic and strip) in order to establish the acid profile in the stages of mixer-settler. After that feed solution containing uranyl nitrate was introduced at 14th stage mixer-settler bank and the electrolysis started by passing the current using a DC power supply. A constant voltage of about 10 V was applied which was required to maintain a constant current density of about 5 mA/cm^2 during the electrolysis [9]. After, about of 8 h of operation of electrolytic mixer-settler stage samples of aqueous and organic phases were taken and analyzed for free acidity, U(IV) and U(VI) concentration. The feed containing uranium in nitric acid in the case aqueous feed or loaded organic containing uranium was introduced at 14th stage of

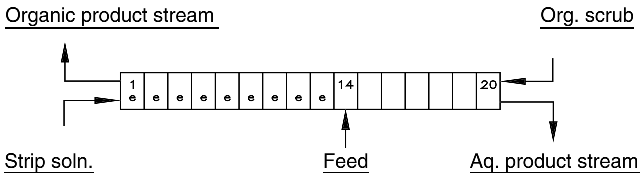

Fig. 5. A typical flow scheme for in-situ reduction.

mixer-settler unit for all the experimental runs. For the preparation of organic feed to electrolytic unit one extraction run was also performed in the same mixer-settler unit.

All the reagents and chemicals during experimental studies were of AR grade. Free HNO_3 in the aqueous and organic samples was estimated with standardized NaOH solution by using phenolphthalein as an indicator, after complexing the uranium with potassium oxalate solution. U(IV) was estimated in sulphuric acid medium by potentiometric titration with potassium dichromate using Ferroin indicator. U(VI) was estimated by Davis Grey method. HDBP concentration in the organic phase was estimated by using Ion chromatography.

A typical flow scheme of in-situ reduction of uranium solution in the electrolytic mixer-settler is shown in Figs. 6(a) & 7(a) respectively for electrolysis with aqueous and loaded organic as feed.

Comparison of experimental and calculated concentration profiles of U(VI), U(IV) and nitric acid is shown in Figs. 6(b) & 7(b).

It is observed from these figures that highest concentration of U(IV) is found be in 13th stage which just before the feed stage.

The calculated results also follow similar trends and the agreements between experimental and calculated profiles of components are reasonably good. From the flowshets [Figs. 6(a) & 7(a)] it also is observed that there is presence of di-butyl phosphate of about 300–400 ppm in organic outlet stream which might be produced from the degradation of TBP in electrolysis.

The important observations to make from the results presented in Figs. 6(b) & 7(b) is that when feed to the electrolytic mixer-settler is in the form aqueous or load organic there is almost similar performance is achieved as obvious from similar trends of concentration profiles. However, there is difference in concentration of U(IV) in aqueous outlet streams (from 20th stage) in these two cases, this is largely due to the fact that extractor is not operating at same A/O ratio and also the initial conditions (initial stage concentrations) were not same in the two cases described above.

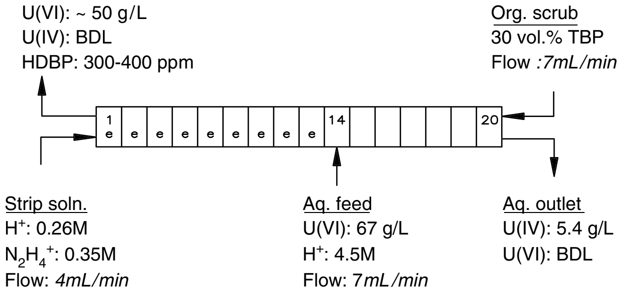

Fig. 6(a). A typical experimental flowsheet conditions (electrolysis with aq. feed).

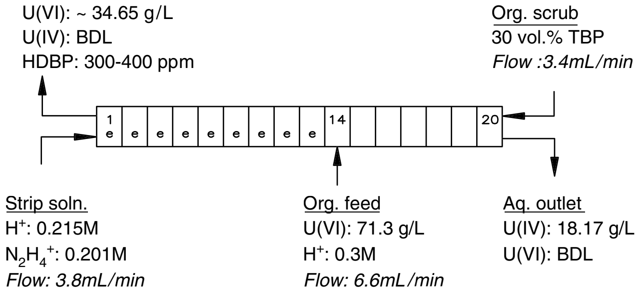

Fig. 7(a). Experimental Flowsheet Conditions (electrolysis with loaded organic as feed).

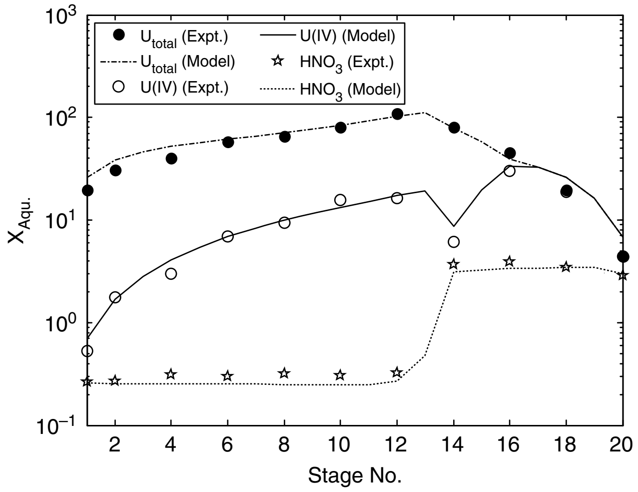

Fig. 6(b). Comparison of experimental and predicted concentration profiles of U(total), U(IV) and HNO_3 in stages of electrolytic mixer-settler.

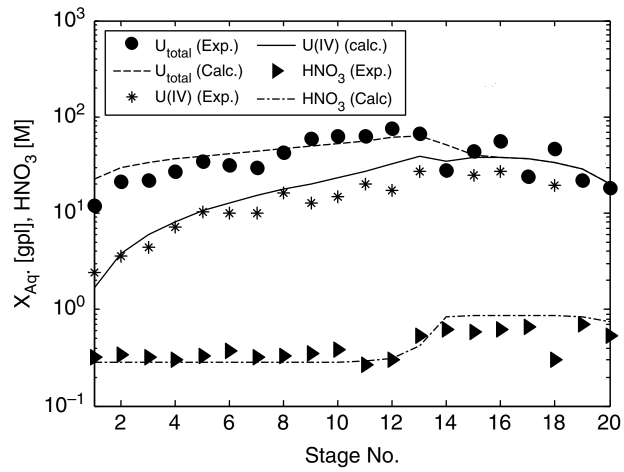

Fig. 7(b). Comparison of experimental and predicted concentration profiles of U(total), U(IV) and HNO_3 in stages of electrolytic mixer-settler.

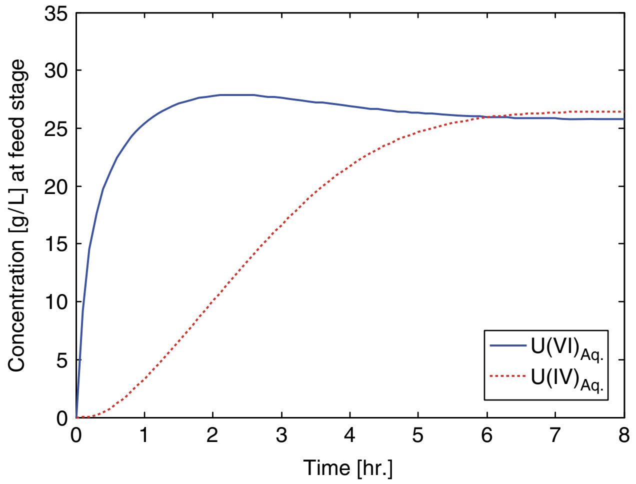

Fig. 8. Transient concentration profiles of aqueous phase concentration of U(VI) and U(IV) at feed stage (14th stage).

5.1. Transient profiles

Fig. 8 shows the calculated transient profiles of U(VI) and U(IV) at feed stage for the flowsheet conditions described in Fig. 7(a).

In real situation changes in feed concentrations and flow rate will lead to transient conditions in the contactor. It is important to know what the maximum concentration is likely, where it will occur and when it will occur. In addition transient calculations can also be utilized to optimize startup and shutdown conditions.

Though calculation of steady-state profiles via transient behavior consumes a considerable amount of computer time, particularly in the case of partitioning contactors where both chemical reaction and mass transfer between phases are occurring, but it provides important information about the variation of solute concentration with time in the contactor bank which otherwise cannot be obtained from the steady-state solutions. Transient calculations can only provide the information about unsafe accumulation of solute if any.

The important observation to make from this figure is that it is possible to predict the time and the corresponding stage where the peak concentration of a particular solute will appear.

6. Conclusions

Based on the mathematical model a computer program has been developed for the analysis of partitioning cycle of PUREX process. The model equation development involves countercurrent multi-component extraction coupled with chemical and electrochemical reactions. The model is specific to mixer-settler contactors and is restricted to mass transfer equilibrium. Model equations and associated program have been validated with published experimental data involving uranium and plutonium Also it was demonstrated that uranium could be successfully predicted in 20-stage electrolytic mixer-settler. The theoretical predictions agree well with the experimental ones. The comparison between the experimental results and the calculated results demonstrated that the model and algorithm presented here might be a useful tool for design, optimization and evaluation problem in a solvent extraction system. However, caution should be exercised in using calculated results because of the inherent limitations of the computer program as it does not include the effect of autocatalytic oxidation of Pu(III) by nitrous acid and effect of solvent degradation products. Further, model equations do not include provision of backmixing and effects of Tc, Zr, and Ru on the process. The discrepancies between the calculated and experimental values in the low concentration region are observed which could be attributed to uncertainty in estimating the distribution coefficient values and entrainment of the phases. Moreover, the distribution coefficient correlations for U(VI), U(IV), Pu(IV), Pu(III) and HNO_3 used in the model equations for predicting stage profiles have standard deviations greater than 10% .

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Symbols

A — Aqueous flow rate, l/hr
a_a — Specific area of anode, cm^{-1}
a_c — Specific area of cathode, cm^{-1}
D — Distribution coefficient
E_A — Activation energy, kJ/mol
h_a — Volume of aqueous phase in mixer, l
h_o — Volume of organic phase in mixer, l
H_a — Volume of aqueous phase in settler, l
H_o — Volume of organic phase in settler, l
K — Apparent equilibrium constant
K' — Pseudo equilibrium constant
K_P — Hydrolysis constant for plutonium
K_U — Dissociation constant for uranium
O — Organic flow rate, l/hr
Σr_{am} — Net rate of reaction of solute in aqueous phase of mixer, mol/l/hr

Σr_{om} — Net rate of reaction of solute in organic phase of mixer, mol/l/hr

Σr_{a} — Net rate of reaction of solute in aqueous phase of settler, mol/l/hr

Σr_{o} — Net rate of reaction of solute in organic phase of settler, mol/l/hr

Σr_{e} — Net rate of electrochemical reaction of solute, mol/l/hr

t — Time, hr

ΣU — Total uranium [U(IV)+U(VI)] concentration, g/l

V_m — Volume of mixer, l

V_s — Volume of settler, l

X — Solute concentration in aqueous phase, mol/l

Y — Solute concentration in organic phase, mol/l

$[\mathrm{TBP}]_0$ — Initial TBP concentration, mol/l

$[\mathrm{TBP}]_f$ — Free TBP concentration, mol/l

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