Simulation of electro-mixer-setter for the partitioning of uranium and plutonium in PUREX process

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Received 12 July 2003; revised received 13 February 2004; accepted 2 April 2004

The mathematical basis for a computer code PUSEP (Plutonium Uranium Solvent Extraction Program) for the analysis of partitioning cycle of PUREX process involving in-situ electrochemical reduction of uranium and plutonium is described in the present investigation. The basis of development of model equations 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. The components considered in the model equations are U(VI), U(IV), Pu(IV), Pu(III), nitric acid and hydrazine. Computer code provides transient behaviour of mixer-settler contactor from the start-up conditions to the steady-state conditions. The code has been validated with the experimental data available in literature. The calculated results are consistent with the experimental results considering the major components mentioned above.

IPC Code: B01D 59/38, G06F 17/00

Keywords: PUREX process, uranium, plutonium, partitioning, simulation

The PUREX (Plutonium Uranium EXtraction) process has been widely used world over to reprocess (separation of uranium and plutonium from fission products) the irradiated fuel arising from nuclear reactor. The head-end of the PUREX process involves dissolution of the fuel in nitric acid to yield a solution containing heavy metal (uranium and plutonium) nitrates and the acidity is adjusted to 3 to 4 M HNO₃ which is favourable for extraction of uranium and plutonium. This solution is then contacted with 30% tri-n-butyl phosphate (TBP) in n-dodecane using counter-current extraction. The uranium and plutonium are co-extracted from aqueous nitrate solution into organic (TBP) phase as U(VI) and Pu(IV) nitrates to achieve separation from fission products. Further, it is necessary to separate uranium and plutonium from each other and also purify them separately for the end use. Stripping of plutonium (transfer of Pu to aqueous phase) from metal rich organic phase is accomplished by selectively reducing the plutonium to poorly extractable trivalent species [Pu(III)] by means of a reducing agent (i.e., by ferrous sulphamate, hydroxylamine nitrate or uranous nitrate) or by in-situ reduction (electrochemical reduction). The extent to which separation of plutonium from uranium is achieved depends upon the distribution coefficients of the species involved under the prevailing conditions of partitioning cycle.

PUREX solvent extraction flowsheet has been 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. In majority of the cases it helps in cutting down costly and hazardous (from the nuclear safety point of view) experimental runs required. Some of the important computer codes developed in the past for simulating PUREX solvent extraction systems are SEPHIS and its modifications¹,², PUBG³, PUMA⁴, SOLVEX⁵, SIMPSEX⁶, etc, and all of them designed for mixer-settler contactors. Except for PUMA, all these codes provide transient response of a contactor from some initial conditions to the steady-state conditions. 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 PHWR fuel reprocessing. Applicability of this code is limited only to extraction and stripping

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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. SIMPSEX code was developed inhouse by Kumar and Koganti et al. to simulate and analyze the FBR flowsheets pertaining to high plutonium concentration. The unique feature of this code is that it is equipped with a diagnostic module for checking the limits of third phase formation and Pu(IV) polymerization and a thermodynamic model based on activity coefficients is used for the estimation of distribution coefficients for key components [uranium (VI), plutonium(IV) and nitric acid]. However, applicability of the SIMPSEX code is limited only to extraction and stripping contactors of the PUREX process.

None of the above-mentioned codes have the capability of handling electrolytic partitioning of uranium and plutonium. In the reprocessing of spent nuclear fuel from PHWR having about 0.3% Pu and balance being U, partitioning of U/Pu is conventionally carried out after the 1st cycle extraction step and the separated streams of uranium and plutonium will have further purification steps. Externally generated uranous [U(IV)] is generally used as reducing agent for U/Pu partitioning in the contemporary salt free reprocessing flowsheet. Normally, large quantity of uranous (more than 6-10 times of stoichiometry) is required to achieve effective separation between U and Pu. Due to high content of Pu in FBR fuels (about 25-30% Pu), addition of large excess of externally generated uranous is not feasible option as it poses problems like criticality and related size limitations. In addition, large quantity of product uranium has to be recycled. The only option is to employ electrochemical in-situ reduction process in the partitioning step of the fast reactor reprocessing plant to achieve separation between uranium and plutonium. In-situ reduction process has several advantages over other methods. The process is simple to operate, easy to control remotely and waste management cost is low as there is no external chemical addition for reduction purpose.

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. Most of the published information is from Karlsruhe, Germany. While research efforts in reprocessing of spent nuclear fuels in many countries have waned due to various reasons, in India interest in nuclear power from FBRs is increasing considering limited resources of uranium and the vast resources of thorium. For FBR programs to be successful and economically viable, closing of the back end of the fuel cycle is an essential requirement and in this context reprocessing technology of FBR fuels assumes greater importance. Since, partitioning is one of the important steps of fuel reprocessing, development of a computational model is necessary to address this step.

In the present work, mathematical basis for a computer code PUSEP (Plutonium Uranium Solvent Extraction Program) for the separation of uranium and plutonium from each other is described. The basis of model equations development involves countercurrent multicomponent extraction with coupled 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 code generates transient concentration profiles from the initial conditions to steady-state conditions. Though calculation of steady-state profiles via transient behaviour 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.

Electrochemical in-situ reduction process

Electrochemical in-situ reduction et al Pu(IV) and U(VI) for the separation of U and Pu offers several advantages over other methods. Its main advantage lies in the reprocessing fuels with high plutonium content, such as FBR fuels. In this process neither product uranium recycle nor additional U(IV) feeds are necessary. Local depletion of stabilizer and reductant has never been observed (the reductant is homogeneously produced within the extractor from process inherent U(VI)). It is also reported that, in comparison with the hydroxylamine process Pu is completely stripped even from the HDBP complex in
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), HNO₃, and hydrazine] distribution in aqueous and organic phases is accompanied with redox reactions involving uranium, plutonium, nitric and nitrous acids and hydrazine. Additional complications occur due to the presence of technetium (Tc). This fission product, which is present in significant amounts in the dissolver solution, behaves differently from other fission products as it changes valency in nitric acid medium. Tc gets co-extracted with U(VI), Pu(IV) and catalyses the destruction of hydrazine by nitric acid.

Flow scheme in electrochemical mixer-settler

The flow scheme in the reductive separation of U & Pu in electrochemical mixer-settler is shown in Fig. 1. The organic (generally 30% TBP in n-dodecane) feed containing extracted U(VI) and Pu(IV) and small amount of nitric acid from the previous extraction cycle enters the mixer-settler bank at an intermediate stage. For the operation of partitioning mixer-settler bank, (Fig. 1) the extraction section lies left of the feed point or in the direction of the feed flow whereas scrub section lies on the right side of the feed point. The extraction section of the mixer-settler bank is equipped with the electrodes. The whole extractor casing is made of titanium and acts as cathode. In the settling chamber, the anode is placed in an anodic space lined with ceramic isolating material, where electrochemical reaction takes place. Due to selective placing of the anode in the settling chamber, electrolysis takes place preferentially in the aqueous phase of the settler compartment. Platinum or platinized Ti, Ta is used as the anode. 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) 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) re-oxidation by nitrous acid, which is produced during electrolysis as well 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.

The function of the scrub section is to re-extract the uranium that distributed to aqueous phase leaving the feed stage. This is accomplished by bringing in fresh solvent as the scrub. With the sufficient number of stages available and the favourable flow ratio and distribution ratios for U(VI), the uranium contamination of the plutonium product can be reduced to ppm level. In the extraction section of mixer-settler bank, concentrations of 0.2 to 0.6 M HNO₃ and in scrubbing section of 1.0 to
1.5\textit{M} HNO\textsubscript{3} should be considered as optimum acidities.

To simulate partitioning process, detailed models of the distribution equilibria for the species involved under the prevailing conditions of partitioning cycle, the mass transfer kinetics and the redox reactions are needed. The species U(IV), U(VI), Pu(III), Pu(IV), HNO\textsubscript{3}, HNO\textsubscript{4}, hydrazine are to be incorporated into the model equations.

**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. The distribution coefficient is defined as the ratio of the solute concentrations in organic phase to the aqueous-phase, which are in equilibrium. 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\textsubscript{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), Pu(IV), Pu(III) and HNO\textsubscript{3} in presence of hydrazine nitrate employing TBP as extractant. The distribution data of U(VI), Pu(IV) and nitric acid in the system uranyl nitrate-plutonium nitrate-nitric acid-30\% TBP in an alkane diluent is available in literature as the “1981 Purex Distribution Data Index”\textsuperscript{4}, which is the collection of more than 4000 data points. This data bank may serve to make reliable mathematical models for calculating distribution coefficients.

The basis of uranium and plutonium separation is found in the order of distribution coefficients (\(D\)) as,

\[ D_{\text{Pu}^{\text{IV}}(\text{aq})} > D_{\text{Pu}^{\text{III}}(\text{aq})} > D_{\text{HNO}_3(\text{aq})} > D_{\text{Pu}^{\text{IV}}(\text{org})} > D_{\text{Pu}^{\text{III}}(\text{org})} > D_{\text{HNO}_3(\text{org})} > D_{\text{Pu}^{\text{III}}(\text{org})} > D_{\text{Pu}^{\text{IV}}(\text{org})} > D_{\text{HNO}_3(\text{org})} \]

The distribution of species between the aqueous and the organic phases are modelled on the basis of following reaction equilibria,

\[
\text{UO}_2^{2+} (\text{aq}) + 2\text{NO}_3^- (\text{aq}) + 2\text{TBP} (\text{org}) \rightleftharpoons \text{UO}_2\text{(NO}_3^-)_2\text{TBP} (\text{org}) \] \text{(1)}

\[
\text{U}^{3+} (\text{aq}) + 4\text{NO}_3^- (\text{aq}) + 2\text{TBP} (\text{org}) \rightleftharpoons \text{U(NO}_3^-)_4\text{TBP} (\text{org}) \] \text{(2)}

\[
\text{Pu}^{4+} (\text{aq}) + 4\text{NO}_3^- (\text{aq}) + 2\text{TBP} (\text{org}) \rightleftharpoons \text{Pu(NO}_3^-)_4\text{TBP} (\text{org}) \] \text{(3)}

\[
\text{Pu}^{4+} (\text{aq}) + 3\text{NO}_3^- (\text{aq}) + 3\text{TBP} (\text{org}) \rightleftharpoons \text{Pu(NO}_3^-)_3\text{TBP} (\text{org}) \] \text{(4)}

\[
\text{H}^+ (\text{aq}) + \text{NO}_3^- (\text{aq}) + \text{TBP} (\text{org}) \rightleftharpoons \text{HNO}_3\text{TBP} (\text{org}) \] \text{(5)}

Higher solvate of nitric acid HNO\textsubscript{3}.2TBP and HNO\textsubscript{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\textsuperscript{5}.

The apparent equilibrium constants, which are defined as the multiplication product of the equilibrium constants and the activity coefficients in suitable power for Eqs (1) through (5) are represented as follows,

\[
K_{\text{UVI}} = \frac{[\text{UO}_2\text{(NO}_3^-)_2\text{TBP}]}{[\text{UO}_2^{2+}][\text{NO}_3^-]^2}[\text{TBP}^2] \] \text{(6)}

\[
K_{\text{U(VI)}} = \frac{[\text{U(NO}_3^-)_4\text{TBP}]}{[\text{U}^{4+}][\text{NO}_3^-]^4}[\text{TBP}^2] \] \text{(7)}

\[
K_{\text{Pu(IV)}} = \frac{[\text{Pu(NO}_3^-)_3\text{TBP}]}{[\text{Pu}^{4+}][\text{NO}_3^-]^3}[\text{TBP}^1] \] \text{(8)}

\[
K_{\text{Pu(III)}} = \frac{[\text{Pu(NO}_3^-)_2\text{TBP}]}{[\text{Pu}^{3+}][\text{NO}_3^-]^2}[\text{TBP}^1] \] \text{(9)}

\[
K = \frac{[\text{HNO}_3\text{TBP}]}{[\text{H}^+][\text{NO}_3^-][\text{TBP}^1]} \] \text{(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:

\[
D_{\text{UVI}} = \frac{[\text{UO}_2\text{(NO}_3^-)_2\text{TBP}]}{[\text{UO}_2^{2+}]} = K_{\text{UVI}}[\text{NO}_3^-]^2[\text{TBP}^1] = K_{\text{U(VI)}}[\text{TBP}^1] \] \text{(11)}

\[
D_{\text{Pu(IV)}} = \frac{[\text{Pu(NO}_3^-)_4\text{TBP}]}{[\text{Pu}^{4+}]} = K_{\text{Pu(IV)}}[\text{NO}_3^-]^4[\text{TBP}^1] = K_{\text{Pu(IV)}}[\text{TBP}^1] \] \text{(12)}
\[
D_{\text{pure}} = \frac{[\text{Pu(NO}_3)_4]_2 \text{TBP}}{[\text{Pu}^{IV}]_2} = K_{\text{pure}} \text{[NO}_3^-][\text{TBP}]^2 \tag{13}
\]

\[
D_H = \frac{\text{[HNO}_3 \text{TBP]}}{[\text{H}^+]} = K_H \text{[NO}_3^-][\text{TBP}] = K_H \text{[TBP]} \tag{14}
\]

\[
D_{\text{pure}} = \frac{[\text{Pu(NO}_3)_4]_2 \text{TBP}}{[\text{Pu}^{IV}]_2} = K_{\text{pure}} \text{[NO}_3^-][\text{TBP}]^2 \tag{15}
\]

In order to correlate apparent equilibrium constant in a better way, Richardson grouped \(K\) and \([\text{NO}_3^-]^x\) (where \(x\) is power of \([\text{NO}_3^-]\) for the respective solute) together as one parameter as \(K^x\).

The quantity \([\text{TBP}]\) is the concentration of uncombined or free TBP, which is obtained by TBP balance as,

\[
[\text{TBP}] = ([\text{TBP}] - 2([\text{UO}_2(NO_3)_2] \text{TBP}) - 2([\text{Pu}(NO_3)_4] \text{TBP}) - ([\text{HNO}_3] \text{TBP}) - 3([\text{Pu}(NO_3)_3] \text{TBP}]) \tag{16}
\]

Substitutions from Eqs (11-15) into Eq. (16) results in

\[
[\text{TBP}] = 2K_{\text{PuIV}}([\text{UO}_2(NO_3)_2]) \text{TBP} - 2K_{\text{PuIV}}([\text{U}^{IV}]) \text{TBP} - K_H([\text{H}^+]) \text{TBP} - 3K_{\text{PuIV}}([\text{Pu}^{IV}]) \text{TBP}\tag{17}
\]

where \([\text{TBP}]_0\) is the initial concentration of TBP. Rearranging gives:

\[
Q[\text{TBP}]^2 + P[\text{TBP}] + (1+R)[\text{TBP}] - [\text{TBP}]_0 = 0 \tag{18}
\]

where,

\[
P = 2(6K_{\text{UO}_2} + K_{\text{UO}_2}([\text{U}^{IV}]) + 3K_{\text{PuIV}}([\text{Pu}^{IV}])) \tag{19}
\]

\[
Q = 2K_{\text{PuIV}}([\text{Pu}^{IV}]) \tag{20}
\]

\[
R = K_H([\text{H}^+]) \tag{21}
\]

Eq. (18) represents a cubic equation in \([\text{TBP}]\) 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.\(^{17}\) (for \(U^{VI}\), \(U^{IV}\), \(Pu^{IV}\), \(Pu^{III}\) and \(\text{HNO}_3\)) 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.

### Chemical and electrochemical reactions

Possible chemical and electrochemical reactions, which occur during electrochemical process, are as follows:

#### Electrochemical reactions

- At cathode:
  \[
  \text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- = \text{U}^{IV} + 2\text{H}_2\text{O} \tag{22}
  \]
  \[
  \text{Pu}^{IV} + \text{e}^- = \text{Pu}^{III} \tag{23}
  \]
  \[
  2\text{H}^+ + 2\text{e}^- = \text{H}_2 \uparrow \tag{24}
  \]
  \[
  3\text{H}^+ + \text{NO}_2^- + 2\text{e}^- = \text{HNO}_2 + \text{H}_2\text{O} \tag{25}
  \]

- At anode:
  \[
  \text{Pu}^{IV} = \text{Pu}^{IV} + \text{e}^- \tag{26}
  \]
  \[
  \text{N}_2 + 3\text{H}_2^0 = \text{N}_2 \uparrow + 3\text{H}^+ + 3\text{e}^- \tag{27}
  \]
  \[
  2\text{H}_2\text{O} = 4\text{H}^+ + \text{O}_2 \uparrow + 4\text{e}^- \tag{28}
  \]

#### Chemical reactions

- \(U^{IV} + 2\text{Pu}^{IV} + 2\text{H}_2\text{O} = \text{UO}_2^{2+} + 2\text{Pu}^{3+} + 4\text{H}^+ \tag{29}\)
- \(2\text{Pu}^{IV} + 2\text{N}_2\text{H}_4 = 2\text{Pu}^{IV} + 2\text{NH}_3 + \text{N}_2 \uparrow + 2\text{H}^+ \tag{30}\)
- \(4\text{Pu}^{IV} + \text{N}_2\text{H}_3 = 4\text{Pu}^{IV} + \text{N}_2 \uparrow + 5\text{H}^+ \tag{31}\)
- \(\text{Pu}^{3+} + \text{HNO}_3^- + \text{H}^+ = \text{Pu}^{4+} + \text{NO} \uparrow + \text{H}_2\text{O} \tag{32}\)
- \(4\text{Pu}^{3+} + 2\text{HNO}_3^- + 4\text{H}^+ = 4\text{Pu}^{4+} + \text{N}_2 \uparrow + 3\text{H}_2\text{O} \tag{33}\)
- \(2\text{Pu}^{3+} + 3\text{HNO}_3^- = 2\text{Pu}^{IV} + 2\text{NO}_3^- + \text{H}_2\text{O} \tag{34}\)
- \(\text{U}^{IV} + 2\text{HNO}_3^- = \text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{H}^+ \tag{35}\)
Table 1- Rate expressions of electrochemical and chemical reactions

<table>
<thead>
<tr>
<th>No.</th>
<th>Rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cathodic reduction of Pu(IV) [ \frac{d[\text{Pu(IV)}]}{dt} = -k_a [\text{Pu(IV)}] ]</td>
</tr>
<tr>
<td></td>
<td>( k = 13.8 \text{ cm}^2 \text{ h}^{-1} ), ( a_1 ) is specific area of cathode ( \text{cm}^{-1} )</td>
</tr>
<tr>
<td>2</td>
<td>Cathodic reduction of U(VI) [ \frac{d[U(VI)]}{dt} = -k_a [U(VI)] ]</td>
</tr>
<tr>
<td></td>
<td>( k = 0.48 \text{ cm}^2 \text{ h}^{-1} )</td>
</tr>
<tr>
<td>3</td>
<td>Anodic re-oxidation of Pu(III) [ \frac{d[\text{Pu(III)}]}{dt} = -k_a [\text{Pu(III)}] ]</td>
</tr>
<tr>
<td></td>
<td>( k = 15 \text{ cm}^2 \text{ h}^{-1} ), ( a_1 ) is specific area of anode ( \text{cm}^{-1} )</td>
</tr>
<tr>
<td>4</td>
<td>Reduction of Pu(IV) by U(IV) ( \text{Aq. Phase} ): [ \frac{d[\text{Pu(IV)}]}{dt} = \frac{k[\text{Pu(IV)}][\text{U(IV)}]}{[\text{UO}_2^2+][\text{Pu}^3+]} ]</td>
</tr>
<tr>
<td></td>
<td>( k = 9.12 \times 10^{10} \text{ mol} \text{ L}^{-1} \text{ h}^{-1} ), ( E_a = 104 \text{ kJ/mol} )</td>
</tr>
<tr>
<td>5</td>
<td>Reduction of Pu(IV) by hydrazine [ \frac{d[\text{Pu(IV)}]}{dt} = \frac{-k_1[\text{Pu(IV)}][\text{N}_2\text{H}_5^+]}{[\text{HNO}_2^+][\text{Pu}^3+]} ]</td>
</tr>
<tr>
<td></td>
<td>( k_1 = 2.28 \text{ h}^{-1} ), ( E_a = 93 \text{ kJ/mol} )</td>
</tr>
<tr>
<td>6</td>
<td>Oxidation of Pu(III) by HNO(_2) [ \frac{d[\text{Pu(III)}]}{dt} = -k[\text{Pu(III)}][\text{HNO}_2^+] ]</td>
</tr>
<tr>
<td></td>
<td>( k = 8640 \text{ mol} \text{ L}^{-1} \text{ h}^{-1} ), ( E_a = 59 \text{ kJ/mol} )</td>
</tr>
<tr>
<td>7</td>
<td>Reaction of HNO(_2) with hydrazine [ \frac{d[\text{HNO}_2^+]}{dt} = \frac{-d[N_2H_5^+]}{dt} = -60 \text{ kJ/mol} ]</td>
</tr>
</tbody>
</table>

Where \( a_1 \) and \( a_2 \) are the specific cathode and anode area. The values of rate constants for electrochemical reactions listed above are functions of the degree of agitation of the fluid and of the applied current. \( K_p \) and \( K_u \) are hydrolysis and dissociation constants for Pu and U respectively.

\[ N_2H_5^+ + HNO_2 = HN_3 + H^+ + 2H_2O \quad \text{(36)} \]

\[ HN_3 + HNO_2 = N_2 + N_2O + H_2O \quad \text{(37)} \]

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\(^{12}\). 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\(^{24}\), but like Pu(III), U(IV) is relatively easily re-oxidized to U(VI) by \( \text{N}_2\text{O}_5 \) or \( \text{HNO}_3 \) in nitric acid solution. A scavenger for \( \text{HNO}_2 \), such as hydrazine, sulfamic acid or urea is therefore added to partitioning system to stabilize U(IV) and Pu(III).
Hydrazoic acid (HN₃) is an undesirable byproduct of the hydrazine-nitrous acid reaction. It is extractable in TBP, and most of that formed in TBP extraction contactors will leave in the solvent phase. Hydrazoic acid will react further with an excess of nitrous acid according to the reaction (Eq. 37).

**Basis for mathematical model used in PUSEP**

Equations based on an idealized model for mixer-settlers incorporating distribution coefficients of the species involved and redox reactions are to be solved in order to obtain concentration profiles of the species. Fig. 2 shows qualitatively the scheme of the mixer-settler model. Following simplifying assumptions have been made:

- complete mixing is assumed in mixer compartment of mixer-settler unit.
- stage residence times are sufficiently long so that diffusional resistances can be ignored.
- mass transfer due to extraction occurs only in mixer compartment and the components are always at equilibrium between the phases.
- the flow rates are assumed to be constant across the mixer-settler bank.
- only in the aqueous phase of the settler compartment electro-reduction of U(VI) and Pu(IV) take place.
- autocatalytic oxidation of Pu(III) by nitrous acid is not taken into consideration. It is assumed that in presence of hydrazine auto-oxidation of Pu(III) is suppressed.
- no provisions are made for entrainment of phases and solvent degradation products.

**Program structure of PUSEP**

The PUSEP code is written in MATLAB (running in Windows 2000 on a 650 MHz P-III Processor). The program structure (modules of program) of the PUSEP code is shown in Fig. 3. Model equations (38-40) are solved simultaneously using fourth order Runge-Kutta scheme with appropriate distribution coefficients and rate expressions in order to obtain concentration profile of each component across the stages of mixer-settler bank. The Runge-Kutta integration scheme is very useful in calculating the concentration profiles and is very stable. It consumes considerable amount of time, particularly in the case of partitioning contactors where both chemical reaction and mass transfer between phases are occurring.

**Discussion**

All the computer codes use the common convention that the aqueous stream flows from the lower to the higher numbered stages, the organic stream...
Main Program (PUSEP.m)
This program solves the model equations using fourth order Runge-Kutta scheme. It is interactive with the user. The initial concentration profile in the extractor and the parameters (such as flow rates, TBP%, Temperature, volume of mixer-settler unit, number of stages etc.) that will be used by the model equations are to be provided here. This program calls the ModelEq.m function, passes the parameters to it, and receives back the results. It writes the results in a formatted form and generates plots.

ModelEq.m
This is a function file, which contains model equations to be solved. This function calls DistC.m, Rate.m and RateS.m (with input parameters).

RateM.m
This function files contains rate expressions, which calculates rates of chemical reactions occurring in mixer.

DistC.m
This is a function file, which contains distribution coefficient correlations. This function calls NRpoly.m for finding out the roots of cubic equation.

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

NRpoly.m
This is general function file, which determines the roots of a polynomial by Newton-Raphson method. This function is portable so that it can be called by other input-output programs and/or from the MATLAB workspace (with parameters).

Fig. 3 — Computational algorithm of PUSEP

flowing in opposite direction. Similar convention is followed in the present investigation.

Comparison of calculated results with available experimental data
Simulation of almost all the published experimental results 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 good agreement was observed with all the experimental results. Only two examples of experimental results based on 20 and 30% TBP flowsheet are considered here for the discussion. Figs 4 & 5 show 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. The deviations in the plutonium profile in the low concentration 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 PUSEP is limited to mass transfer equilibrium. 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. In addition the predictions of Pu species concentrations from the distribution correlations are generally inaccurate in this region.

Further deviations from equilibrium are accounted by a transfer function that has a form \( K_\text{overall} a_j(Y_{aq} - Y_j) \), where \( K_\text{overall} \) 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
**Fig. 4.** — Comparison of calculated and experimental profiles in a 16-stage IB contactor. Experimental data from KFK-2082 (Fig. 23, Ref. 11) based on 20% TBP in n-dodecane. The feed stream is at 10th stage and the feed concentrations are U: 49.6 g/L and Pu: 2.33 g/L. The organic scrub is 20% TBP in n-dodecane. The strip solution concentrations are HNO₃: 0.4 M and N₂H₄: 0.26 M. The respective flow rates are 0.75, 0.156 and 0.12 L/hr respectively for feed, organic scrub and strip.

**Fig. 5.** — Comparison of calculated and experimental profiles in a 16-stage IB contactor. Experimental data from KFK-2082 (Fig. 24, Ref. 11) report, based on 30% TBP in n-dodecane. The feed stream is at 9th stage and the feed concentrations are U: 81.4 g/L and Pu: 0.52 g/L. The organic scrub is 30% TBP in n-dodecane. The strip solution concentrations are HNO₃: 0.26 M and N₂H₄: 0.2 M. The respective flow rates are 0.75, 0.15 and 0.081 L/hr respectively for feed, organic scrub and strip.
attempts\textsuperscript{17} to account for deviations from mass transfer equilibrium in chemical modelling did not explicitly account for mass transfer rates, a primary characteristic of a solvent extraction contactor operating away from equilibrium.

Theoretical studies on methods of correlating mass transfer area and mass transfer coefficients with hydrodynamic parameters such as dispersed phase hold up, viscosity and flow rates are required in order to account for deviations from mass transfer equilibrium in model equations.

In all the simulation calculations, values of specific cathode and anode area used were 0.01 and 0.6 cm\textsuperscript{2} respectively. 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. For the typical cases illustrated by Figs 4 & 5 the strip solution concentrations are HNO\textsubscript{3}: 0.4 M, N\textsubscript{2}H\textsubscript{5}+: 0.26 M and HNO\textsubscript{3}: 0.26 M, N\textsubscript{2}H\textsubscript{5}+: 0.2 M respectively.

**Transient profiles**

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. Fig. 6 shows the calculated concentration profile of Pu(III) in aqueous phase at different interval of time along with the experimental results in a 16 stage IB contactor. Experimental data is from KFK-2082 report (Fig. 24, Ref. 11).

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. Following comments are offered with regard to partitioning contactors,

1. The factors affecting the performance of partitioning contactor are: U-Pu ratio,
concentration of HNO₃ in aqueous strip solution, flow ratios and total volume flow rate (residence time). The most significant influence on the separation (DF of Pu) was found to be the residence time. All other parameters are less important when varied within reasonable limits. A decrease in total volume flow rate causes complex interactions in counter-current extractor due to increase of residence time for both phases.

i. Increasing nitric acid concentration lowers U and Pu re-extraction from the organic phase, thereby less U(VI) is available for electrolytic reduction which takes place in the aqueous phase only. Lower U(IV) concentrations reduce Pu(IV) reduction and thus separation. By an increase of the U feed concentration this effect may be compensated in certain cases.

ii. Increased Pu feed concentration for a given flow rate obviously requires a larger supply of reductant for compensation. But it also increases the salting-out effects by the higher Pu(III) concentration, therefore reducing re-extraction and separation.

iii. A rise in temperature increases reaction rates but may have complicated effects on fluid dynamics, extractability and re-oxidation rate.

iv. Hydrazine may be necessary to prevent re-oxidation, but hydrazine also acts as a salting-out agent and therefore reduces separation.

v. The ratio of area of cathode to anode is to be chosen as large as possible to reduce anodic oxidation of Pu(III).

Simulation results for the proposed partitioning cycle of fast breeder test reactor (FBTR) reprocessing plant:

Lead Mini Cell (LMC) at Reprocessing Group, IGCAR, Kalpakkam is meant for the reprocessing of mixed carbide fuel (70% PuC+30% UC) FBTR fuel. The proposed LMC flowsheet employs three co-decontamination cycles followed by electrolytic partitioning of U/Pu and a uranium purification cycle. All the co-decontamination cycles employ 16-stage centrifugal extractor bank in each cycle, whereas 16-stage electro-mixer settler developed in house will be used for partitioning cycle. Simulation calculations using PUSEP were performed in order to determine optimum flowsheet conditions for the partitioning cycle. Calculated results are presented in the Fig.8. Verification of calculated results could not be done, as no
experimental results exist in literature for such a high concentration of plutonium in partitioning cycle.

Conclusions

A new computer simulation code PUSEP (Plutonium Uranium Solvent Extraction Program) has been developed and has been used to calculate concentration profiles in partitioning contactors of PUREX process involving in-situ electrochemical reduction of uranium and plutonium. The model equation development involves countercurrent multicomponent extraction coupled with chemical and electrochemical reactions. The model is specific to mixer-settler contactors and is restricted to mass transfer equilibrium. At present, the solutes/components considered in the model equations are U(VI), U(IV), Pu(IV), Pu(III), nitric acid and hydrazine. Computer code provides transient behaviour of mixer-settler contactor from some initial conditions to the steady-state conditions. Calculated profiles of uranium [total uranium i.e., U(IV)+U(VI)], U(IV), and acid are in reasonably good agreement with the published experimental results. The deviations observed in the plutonium profile in the low concentration zone may probably are due to slow strip rate of Pu-HDBP complex and uncertainty in the estimation of distribution coefficient in low concentration region. 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. Further studies are in progress to incorporate auto-oxidation of Pu(III) by HNO₃ in partitioning contactors.

Acknowledgement

Authors wish to express sincere thanks to Dr. H.K. Sahu of Material Science Division (MSD), IGCAR, for his valuable suggestions during the program development stage.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>aqueous flow rate, L/h</td>
</tr>
<tr>
<td>a₁</td>
<td>specific area of anode, cm²</td>
</tr>
<tr>
<td>a₂</td>
<td>specific area of cathode, cm²</td>
</tr>
<tr>
<td>D</td>
<td>organic flow rate, L/h</td>
</tr>
<tr>
<td>D</td>
<td>distribution coefficient</td>
</tr>
<tr>
<td>E₀</td>
<td>activation energy, kJ/mol</td>
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<tr>
<td>hₒ</td>
<td>volume of aqueous phase in mixer, L</td>
</tr>
<tr>
<td>hₘ</td>
<td>volume of organic phase in mixer, L</td>
</tr>
<tr>
<td>Hₛ</td>
<td>volume of aqueous phase in settler, L</td>
</tr>
<tr>
<td>Hₘ</td>
<td>volume of organic phase in settler, L</td>
</tr>
<tr>
<td>K</td>
<td>apparent equilibrium constant</td>
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<tr>
<td>kₚ</td>
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<tr>
<td>kₚₛ</td>
<td>hydrolysis constant for plutonium</td>
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<tr>
<td>kₛ</td>
<td>dissociation constant for uranium</td>
</tr>
<tr>
<td>Σrₐₐ</td>
<td>net rate of reaction of solute in aqueous phase of mixer, mol L⁻¹ h⁻¹</td>
</tr>
<tr>
<td>Σrₘₘ</td>
<td>net rate of reaction of solute in organic phase of mixer, mol L⁻¹ h⁻¹</td>
</tr>
<tr>
<td>Σrₛₛ</td>
<td>net rate of reaction of solute in aqueous phase of settler, mol L⁻¹ h⁻¹</td>
</tr>
<tr>
<td>Σrₛₘ</td>
<td>net rate of reaction of solute in organic phase of settler, mol L⁻¹ h⁻¹</td>
</tr>
<tr>
<td>Σrₘₙ</td>
<td>net rate of electrochemical reaction of solute, mol L⁻¹ h⁻¹</td>
</tr>
<tr>
<td>t</td>
<td>time, h</td>
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<tr>
<td>ΣU</td>
<td>total uranium [U(IV)+U(VI)] concentration, g/L</td>
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<tr>
<td>Vₘ</td>
<td>volume mixer, L</td>
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<td>Vₛ</td>
<td>volume settler, L</td>
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<tr>
<td>X</td>
<td>solute concentration in aqueous phase, mol/L</td>
</tr>
<tr>
<td>Y</td>
<td>solute concentration in organic phase, mol/L</td>
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<tr>
<td>[TBP]ᵢ</td>
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<tr>
<td>[TBP]ₔ</td>
<td>free TBP concentration, mol/L</td>
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</table>

References


