Development and Validation of a Flowsheet Simulation Model for Neptunium Extraction in an Advanced PUREX Process

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ABSTRACT
An Advanced PUREX process has been developed for separation and recycling of neptunium from spent nuclear fuel. This work presents a new flowsheet simulation model for the extraction of neptunium using centrifugal contactors, where mass transfer is modeled using two-film theory and a linear driving force. Distribution coefficients and neptunium redox reactions are modeled using published models. Mass transfer between the organic and aqueous phases in the phase separation zone is shown to have a negligible effect. The model is applied to a previously tested flowsheet and its predictions are shown to be in good agreement with the experimental results.

KEYWORDS
Advanced PUREX; centrifugal contactor; neptunium; solvent extraction; gPROMS

1. Introduction
The management of nuclear wastes, including spent nuclear fuel arising from nuclear power production, is a matter of global concern. Spent nuclear fuel can be either directly disposed of in a geological repository (the “open” fuel cycle) or reprocessed and the actinide elements recycled into new fuel (the “closed” fuel cycle). Recycling uranium and plutonium increases the sustainability of nuclear energy by vastly extending the available fuel reserves, and recycling the minor actinides (neptunium, americium, and curium) can substantially reduce the long-term radiotoxicity and heat loading of high-level wastes in the repository. Neptunium separation and recovery from spent nuclear fuel is specifically of interest because of the mobility of neptunium in the environment, its long half-life, and its relatively high concentration in spent fuel. Next-generation spent nuclear reprocessing technologies, therefore, need to address the separation and recycling of neptunium. The recovered neptunium can then be incorporated into mixed oxide fuels and fed into a fast neutron reactor for burning.

Currently, the well-known PUREX process is the standard method for industrial-scale reprocessing of spent nuclear fuels. In this process, uranium, plutonium, and other actinides are separated by extraction into tributyl phosphate (TBP) in a diluent organic phase from nitric acid aqueous solution. However, due to the differing solution stabilities and extraction properties of neptunium oxidation states and the complexity of their oxidation–reduction reactions in nitric acid, it is not easy to recover neptunium with a high recovery in this process. Current reprocessing plants, for example, only extract 60–80% of neptunium in the primary extraction section, with the remainder being lost to the fission product raffinate stream. Therefore, a simulation model is needed to predict neptunium extraction behavior in the PUREX process and to guide design of flowsheet modifications that better control neptunium in the process.

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Many models of the PUREX process, such as SEPHIS, SOLVEX, AMUSE, PAREX, and MIXSET, have been developed since the 1950s.\cite{16} However, few of these models are accessible in the open literature for reasons of commercial confidentiality, and these models are also typically limited to extraction of uranium and plutonium using mixer-settlers or pulsed columns as the contacting equipment. Increasingly, however, centrifugal contactors are seen as a next-generation extraction technology as they offer significant benefits in terms of low residual volumes and good mixing and separation of phases, although in active conditions they require greater maintenance and are less robust, being prone to blockage by solids, for instance.\cite{17-19}

While mixer-settler models can be used to describe centrifugal contactors, these models have some limitations. For example, most existing models predefine the phase holdup volumes, while holdup volumes in the separation unit of a centrifugal contactor depend on the weir diameters of the contactor and change with fluid flow rates. To address these shortcomings, this paper proposes a new centrifugal contactor model for neptunium extraction and presents the application of the model to investigate neptunium extraction in an advanced PUREX process (for which experimental data have been published\cite{13}). Further to previous work\cite{20}, our main contributions are to include in the model mass transfer kinetics and hydraulic calculations under a centrifugal force field on extraction. The simulation model is validated against experimental data\cite{13} and can be used to analyze the sensitivity of the neptunium separation to key operating parameters.

2. Model Development

2.1 Structure of Simulation Model

The simulation model is implemented in gPROMS due to its inherent modularity and ability to account for process dynamics. It is relatively straightforward to integrate models of several sub-processes into more complex process flow schemes in gPROMS.\cite{21} Figure 1 illustrates the overall flowsheet model in terms of three levels: process phenomena, process steps, and process units.

Chemical and physical phenomena are modeled to describe mass transfer, phase equilibrium (in terms of distribution coefficients), redox reactions, and physical properties. The mixture includes distributing components, namely, U(VI), Np(VI), Np(V), HNO$_3$ and HNO$_2$, while TBP and odorless

![Figure 1. Flowsheet model structure.](image-url)
kerosene are treated as nondistributing species in this work. The concentration of water in the organic phase is also assumed to be constant.

The second level concerns models of processing steps related to mixing and phase separation. Models for units in this level incorporate chemical engineering principles, such as mass balances and hydraulic behavior calculations within process units. The main models in this level, for the mixing zone and for the phase separation zones of the contactors, account for streams entering and leaving these zones.

The flowsheet level of the model addresses basic unit operations, including contactors, feed tanks, product tanks, stream mixing units, splitters, and the streams connecting these units. The flowsheet models in this level are created using click-and-drag interfaces in gPROMS, as in many process simulation software packages.

### 2.2 Physical Property Modeling

The physical property model is used to calculate liquid densities according to Eqs. (1) and (2).

- **Equation (1)**
  \[
  \rho = \rho_{H_2O} \left( 1 + \sum_{i=1}^{2} b_i C_{i,aq} + \sum_{i=1}^{2} p_i C_{i,aq}^{1.5} \right) \quad (1a)
  \]
  \[
  b_i = b_0^i \left( 1 + b_i^0 (T - 25) + b_i^0 (T - 25)^2 \right) \quad (1b)
  \]
  \[
  p_i = p_0^i \left( 1 + p_i^0 (T - 25) + p_i^0 (T - 25)^2 \right) \quad (1c)
  \]

- \( \rho_{H_2O} \) is the density of pure water at T °C.

Secondly, for the organic phase (where \( C_{i,or} \) denotes the organic phase concentration of species \( i \)), Eq. (2) predicts the liquid phase density in g/L:

\[
\rho = (\rho_{OK} \times (1 + (0.4307 C_{U,or} + 0.0318 C_{H,or} + 0.0706 C_{TBP,or}))
+ (0.0071 C_{U,or}^{1.5} - 0.0013 C_{H,or}^{1.5} + 0.0062 C_{TBP,or}^{1.5})) \times (1 - 9.8566 \times 10^{-4} \times (T - 25)
- 2.4242 \times 10^{-7} \times (T - 25)^2)
\]

\( \rho_{OK} \) is the density of odorless kerosene at 25°C.

### 2.3 Modeling of Neptunium Redox Reaction Kinetics

The Np redox reaction system is a rather complex system that has been studied many times over the past 60 years. In this simulation study, the aqueous phase model for the Np(V) oxidation reaction kinetics is modeled using Eq. (3), which indicates the reversible redox reaction between Np(V) and Np(VI), based on reaction rate equations derived by Koltunov for concentrations of 0.27–0.66 mM Np (63–156 mg/L) and 0.56–1.9 mM HNO \(_3\). Equation (4) describes the forward reaction rate, where the index of the H\(^+\) concentration, \( z \), is in the range 0.5–2, depending on extraction conditions. For nitrous acid concentrations of about 10\(^{-3}\) mol/L,
a value of \( z = 2 \) provides the most reasonable fit to experimental data.\cite{31} The backward reaction, Np(VI) reduction, is modeled as Eq. (5).\cite{32}

\[
\text{Np(V)} + \frac{3}{2} \text{HNO}_3 \rightleftharpoons \text{Np(VI)} + \frac{1}{2} \text{HNO}_2
\]

\[
\frac{dC_{\text{Np(V),aq}}}{dt} = 2.884 \times 10^{11} e^{-\frac{9972}{R T}} C_{\text{Np(V),aq}}^{0.5} C_{\text{HNO}_3,aq}^{0.5} C_{\text{H}^+,aq}
\]

\[
+ 5.405 \times 10^{11} e^{-\frac{10031}{R T}} C_{\text{Np(V),aq}}^{0.5} C_{\text{HNO}_3,aq}^{0.5} C_{\text{H}^+,aq}
\]

\[
\frac{dC_{\text{Np(VI),aq}}}{dt} = 2 \times 6.928 \times 10^{10} e^{-\frac{2065}{R T}} C_{\text{Np(VI),aq}}^{1.5} C_{\text{HNO}_3,aq}^{0.5} C_{\text{H}^+,aq}
\]

\[
+ 2 \times 2.497 \times 10^{12} e^{-\frac{3004}{R T}} C_{\text{Np(VI),aq}}^{1.5} C_{\text{HNO}_3,aq}^{0.5} C_{\text{H}^+,aq}
\]

The neptunium (V) oxidation reaction in the organic phase was modeled by Eqs. (6) and (7).\cite{32}

\[
\text{Np(V)} + \frac{3}{2} \text{HNO}_3 \rightarrow \text{Np(VI)} + \frac{1}{2} \text{HNO}_2
\]

\[
R_2 = -\frac{dC_{\text{Np(V),or}}}{dt} = 1.952 \times 10^{11} e^{-\frac{9972}{R T}} C_{\text{Np(V),or}}^{0.5} C_{\text{HNO}_3,or}^{0.5} C_{\text{H}_2\text{O},or}^{0.2}
\]

Based on the low solubility of water in the organic phase, which is a mixture of TBP and the diluent, and the index (−0.2) of the water concentration in Eq. (7), the concentration of water in the organic phase can be treated as a constant. In this model, specifically, \( C_{\text{H}_2\text{O},or} = 0.42 \text{ mol/L}. \)\cite{34} This assumption simplifies the calculations.

### 2.4 Distribution Coefficient Modeling

#### 2.4.1 HNO₃ and Uranium (VI)

Distribution coefficients of HNO₃ and uranium (VI) are calculated using the SEPHIS model.\cite{35,36} This model is known to be reliable and robust in calculations.\cite{36} These distribution coefficient models can be applied to organic mixtures containing 30% TBP at temperatures from 20 to 72°C, HNO₃ concentrations under 10.3 mol/L and uranium loadings less than 349 g/L.\cite{36}

#### 2.4.2 Neptunium (VI)

Distribution coefficients of neptunium (VI) are calculated using the model of Kolarik and Petrich.\cite{37} The extractant is limited to 30% TBP solution in an aliphatic diluent. The empirical equation is given by Eq. (8), where \( C_{\text{Np}^{5+},aq} \) is the analytical concentration of nitrate ions in the equilibrium aqueous phase according to Eq. (9) and where \( P_i \) are parameters of the model equation that can be fitted to experimental data using data regression methods.

\[
D_{\text{Np(VI)}} = \frac{P_1 C_{\text{Np}^{5+},aq}^{P_2}}{1 + P_5 C_{\text{Np}^{5+},aq}^{P_4} + P_5 C_{\text{Np}^{5+},aq}^{P_6} C_{U(VI),aq}^{P_7}} \exp\left(\frac{P_7}{1 + P_8 C_{\text{Np}^{5+},aq}^{P_9} C_{U(VI),aq}^{P_7}} \left(\frac{1}{T + 273} - \frac{1}{298}\right)\right)
\]

\[
C_{\text{Np}^{5+},aq} = 2C_{U(VI),aq} + C_{\text{HNO}_3,aq}
\]

The parameters of this neptunium (VI) distribution coefficient model, as used in this article, are based on a nonlinear fitting method applied to the data of Kolarik and Dressler,\cite{38} for which results are summarized in Table 2. Temperatures range from 25 to 60°C; uranium (VI) concentrations are 0–210 g/L; HNO₃ concentrations are 0.1–11 mol/L; the concentrations of Np(IV,VI) in the aqueous phase are less than 0.03 g/L. The presence of Pu(IV) is not considered in this regression. The average
relative deviation between the predicted values and the reported distribution coefficients in the dataset was \(-0.0332\).

### 2.4.3 Neptunium (V)

Although neptunium (V) is not easily dissolved in the TBP–diluent solvent phase,\(^{[10]}\) the organic phase oxidation of Np(V) converts extracted Np(V) in the organic phase to Np(VI), thereby changing the equilibrium concentrations of Np(V) and Np(VI). Hence, the extraction of Np(V), although very small, cannot be neglected in the process simulation. In this simulation, we used a nominal value of 0.01 for the distribution coefficient of Np(V), as given by Tachimori.\(^{[39]}\)

### 2.4.4 Nitrous Acid

Uchiyama\(^{[40]}\) suggested that the distribution coefficient for HNO\(_2\) can be calculated by Eq. (10), where, in this model, the free TBP concentration \(C_{\text{free TBP, or}}\) was calculated with the SEPHIS model.\(^{[36]}\)

\[
D_{\text{HNO}_2} \approx 25C_{\text{free TBP, or}}
\]  

(10)

### 2.5 Mass Transfer Kinetic Model

From the two-film theory for mass transfer, the mass transfer of species between two phases can be modeled as illustrated in Fig. 2. Note that transfer of species from the aqueous phase to the organic phase is known as extraction, while that in the opposite direction is known as backwashing (or back extraction or stripping). To simplify calculations, we assume that no reactions take place in the films; the mass transfer rate can be calculated by Eq. (11):\(^{[41]}\)

\[
E = K_{\text{OO}}Va(C_{\text{or}^*} - C_{\text{or}})
\]  

(11)

where \(K_{\text{OO}}\) is the overall mass transfer coefficient, \(V\) is the total volume in the vessel, \(C_{\text{or}}\) is the organic-phase bulk concentration, and \(C_{\text{or}^*}\) is the solute concentration in equilibrium with the bulk solute concentration in the aqueous phase.

The equilibrium concentration \(C_{\text{or}^*}\) was calculated using the distribution coefficient model; \(a\) is the interfacial area for mass transfer per unit volume of the liquid phase, given by Eq. (12):

\[
a = \frac{6\phi D}{d_{\text{vis}}}
\]  

(12)

---

**Table 2.** Model parameters for Np(VI) distribution coefficient model (Eq. 8).

| \(P_1\) | \(P_2\) | \(P_3\) | \(P_4\) | \(P_5\) | \(P_6\) | \(P_7\) | \(P_8\) |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 4.7801 | 1.0719 | 8.2218 × 10\(^{-4}\) | 4.0160 | 22.686 | 1.067 | 1461.3 | -1732.2 |
| 4.0160 | 22.686 | 1.067 | 1461.3 | -1732.2 | 188.1 |

---

**Figure 2.** Mass transfer between two phases.
where \( d_{vs} \) is the surface-mean diameter of dispersed phase drops and \( \varphi_{D} \) is the dispersed phase volume fraction in the vessel. We assumed the organic phase is the dispersed phase, so \( \varphi_{D} \) is equal to \( \varphi_{or} \). (This assumption is applied if the organic-phase volume fraction \( \varphi_{or} < 0.74 \);\(^{41} \) otherwise, if \( \varphi_{or} \geq 0.74 \), the dispersed phase would be the aqueous phase and \( \varphi_{D} = 1 - \varphi_{or} \).) For centrifugal contactors in the PUREX process, the average drop size, \( d_{vs} \), is in the range of \( 4 \times 10^{-5} \) to \( 6 \times 10^{-5} \) m.\(^{42} \) We assumed \( d_{vs} \) equals \( 4 \times 10^{-5} \) m regardless of which phase is dispersed.

Usually, the concentrations of the aqueous and organic phase at the interface are assumed to be in equilibrium.\(^{43-46} \) Dinh proposed that this hypothesis is not true and imposed pseudo-first-order interfacial extraction kinetics to improve the overall mass transfer rate calculation.\(^{47} \) However, the real interfacial compositions are seldom determined and therefore it is very difficult to distinguish between diffusive transfer and transfer with those interfacial extraction kinetics.\(^{47} \) In this work, the effects of the interfacial extraction kinetics are included in the mass transfer for the two phases. The overall mass transfer coefficient \( K_{OO} \) is a combination of the coefficients for the two phases, \( k_{or} \) and \( k_{aq} \) (Eq. 13), where \( D \) is the equilibrium distribution coefficient. The calculation of \( k_{or} \) and \( k_{aq} \) is not easy due to complex and uncertain mass transfer across the interface. This work assumes that the mass transfer coefficients of the two phases are equal, \( k_{or} \approx k_{aq} = k \), giving Eq. (14):

\[
\frac{1}{K_{OO}} = \frac{1}{k_{or}} + \frac{D}{k_{aq}} \tag{13}
\]

\[
K_{OO} = \frac{k}{1 + D} \tag{14}
\]

Theoretically, the aqueous phase and organic phase mass transfer coefficients can be predicted using mass diffusion theory. However, due to lack of parameters and reliable data specifically related to neptunium extraction in the centrifugal contactor (e.g., diffusion coefficients, interfacial tension, and viscosities), we did not calculate mass transfer coefficients for aqueous and organic phases in this work. Instead, a constant value was specified for the mass transfer coefficient of each species in each contactor.

### 2.6 Mixing Zone Model

Centrifugal contactors\(^{48} \) are designed for solvent extraction and have a spinning rotor and a stationary housing wall. Two immiscible liquids flow into the gap between the rotor and the wall and are quickly dispersed in the turbulent two-phase flow created by the rotation of the rotor. Mass transfer between two phases occurs in this zone.

The flows in the mixing zone of a centrifugal contactor are highly turbulent. Therefore, it is assumed that the concentrations of each component in each phase within the mixing zone are equal to those in the effluent, as in the continuously stirred tank reactor (CSTR) model.\(^{49} \) We also assumed that mixing and mass transfer processes in the mixing zone were isothermal. The organic and aqueous phases were modeled separately, so the mixing zone was modeled as having two feeds and two product streams as well as two phases within the zone, as shown in Fig. 3. The feed or draw of a centrifugal contactor stage can be dealt with outside the CSTR model by an independent stream mixer unit or splitter in the process unit level model, as illustrated in Fig. 1.

![Figure 3. Schematic of the mixing zone model in a centrifugal contactor.](image-url)
The model comprises separate material balances for each species in each phase, taking into account material flows, reactions, and mass transfer rates (Eqs. 15 and 16) where: $N_{i,aq}$ and $N_{i,or}$ are the molar flow rates of component $i$ in the aqueous phase and organic phase, respectively; $F_{i,aq}^{in}$ and $F_{i,aq}^{out}$ are the inlet and outlet aqueous phase molar flow rates of component $i$; $F_{i,or}^{in}$ and $F_{i,or}^{out}$ are the inlet and outlet organic phase molar flow rates of component $i$, and $R_{i,aq}$ and $R_{i,or}$ are the reaction rates of $i$ in aqueous phase redox reactions and organic phase redox reactions. $E_{i}$ is the rate of mass transfer of component $i$ between two phases, calculated using the mass transfer kinetic model presented before. The thick arrow in Figure 3 indicates the direction of mass transfer: in the model, mass transfer from the aqueous phase to the organic phase (extraction) is expressed with a positive value of $E$ and conversely the mass transfer from the organic phase to the aqueous phase (backwash) is expressed with a negative value of $E$. $V_{aq}$ and $V_{or}$ are the aqueous and organic phase holdup volumes, respectively; $V$ is the total holdup volume of two phases; $t$ is time.

\[
\frac{dN_{i,aq}}{dt} = F_{i,aq}^{in} - F_{i,aq}^{out} + V_{aq}R_{i,aq} - E_{i} \tag{15}
\]

\[
\frac{dN_{i,or}}{dt} = F_{i,or}^{in} - F_{i,or}^{out} + V_{or}R_{i,or} + E_{i} \tag{16}
\]

We also assumed that the outlet organic-to-aqueous ratio is the same as the holdup organic-to-aqueous ratio and the total holdup is close to constant, which is measured by the experiment. The aqueous phase molar flow rate is related to the volumetric flow rate by Eqs. (17) and (19) and the organic phase molar flow rate is related to the volumetric flow rate by Eqs. (20–22) where $MW_{i}$ is the $i$ species molecular weight and Eqs. (19) and (22) are calculated using the physical property models.

\[
N_{i,aq} = V_{aq} \cdot C_{i,aq} \tag{17}
\]

\[
V_{aq} = \frac{\sum (N_{i,aq} \cdot MW_{i})}{\rho_{aq}} \tag{18}
\]

\[
\rho_{aq} = f_{aq}(T, N_{i,aq}) \tag{19}
\]

\[
N_{i,or} = V_{or} \cdot C_{i,or} \tag{20}
\]

\[
V_{or} = \frac{\sum (N_{i,or} \cdot MW_{i})}{\rho_{or}} \tag{21}
\]

\[
\rho_{or} = f_{or}(T, N_{i,or}) \tag{22}
\]

Aqueous and organic phase outlet molar flow rates are given by Eqs. (23) and (24), where $S$ is the volumetric flow rate.

\[
F_{i,aq}^{out} = S_{aq}^{out} \cdot C_{i,aq} \tag{23}
\]

\[
F_{i,or}^{out} = S_{or}^{out} \cdot C_{i,or} \tag{24}
\]

The total holdup volume is given by Eq. (25).

\[
V = V_{aq} + V_{or} \tag{25}
\]

The total outlet volume flow rate is given by Eq. (26), the phase ratio by Eq. (27), and the outlet flow rate by Eq. (28).

\[
S^{out} = S_{aq}^{out} + S_{or}^{out} \tag{26}
\]

\[
\frac{S_{or}^{out}}{S_{aq}^{out}} = \frac{V_{or}}{V_{aq}} \tag{27}
\]
Reactions and mass transfer rates are given by Eqs. (29–31).

\[
R_{i,aq} = f_{aq}^R(T, C_{aq}) \quad (29)
\]

\[
R_{i,or} = f_{or}^R(T, C_{or}) \quad (30)
\]

\[
E_i = f^E(T, C_{aq}, C_{or}, k_i) \quad (31)
\]

Extraction in the mixing zone was, therefore, modeled using the equations given in Eqs. (15–31).

### 2.7 Phase Separation Zone Model

Phase separation occurs in the rotor of a centrifugal contactor under centrifugal force. Recent research on flow conditions inside the centrifugal contactor have focused on two-phase flow but seldom addressed extraction.\(^{[50–53]}\) Also, in the modeling of neptunium extraction, as redox reactions occur in both phases, the residence times of each phase in the phase separation zone are significant. This means the holdups of organic and aqueous in this zone must be considered in a good model of a contactor. Liquid holdups inside a centrifugal contactor are controlled by the heavy phase and the light phase weirs, flow rates of the two phases, and rotation speed.\(^{[16]}\) This work assumed that the rotation speed is sufficient to ensure full phase separation, so the rotation speed is not explicit in the model. Other parameters are addressed in the phase separation zone model of the centrifugal contactor.

As Fig. 4 shows, we treated the two phases in the phase separation zone of the centrifugal contactor as two independent CSTRs in which holdup volumes are controlled by flow rates and weir diameters. As the phase entrainment usually is very low in a well-operated centrifugal contactor,\(^{[54]}\) we assumed there was no phase entrainment in any of the outlet flows. We also assumed that there was no mass transfer of species between two phases in the separation zone of the centrifugal contactor but there could still be redox reactions proceeding in both phases.

Each phase was modeled as a CSTR with the mass balance for each phase as given in Eqs. (32–33):

\[
\frac{dN_{i,aq}}{dt} = F_{i,aq}^{in} - F_{i,aq}^{out} + V_{aq} \cdot R_{i,aq} \quad (32)
\]

\[
\frac{dN_{i,or}}{dt} = F_{i,or}^{in} - F_{i,or}^{out} + V_{or} \cdot R_{i,or} \quad (33)
\]

Similar to the mixing zone model, the relationship of molar flow rate to volumetric flowrate for the aqueous and organic phases can be described by Eqs. (17–22) and the neptunium redox reactions.
occurring in each phase can be calculated with Eqs. (29) and (30). Again, the aqueous and organic phase outlet flow rates can be calculated according to Eqs. (23) and (24).

The aqueous and organic phase holdup volumes in the separation zone of a centrifugal contactor are controlled by its geometric structure and flow rates, as Fig. 4 shows. They can be calculated by Eq. (34), assuming the centrifugal contactor is operated at a suitable rotation speed and flow rate, considering the hydrostatic equilibrium at the level of the heavy phase exit, $h_{aq}^*$, and given the centrifugal acceleration ($G = 4\pi^2 \omega^2 r$):

$$
\int_{H-h_{aq}^*}^{H} 4\pi^2 \omega^2 \rho_{aq} r dr = \int_{H-h_{aq}^*}^{H-h_{or}} 4\pi^2 \omega^2 \rho_{aq} r dr + \int_{H-h_{or}}^{H-h_{aq}} 4\pi^2 \omega^2 \rho_{or} r dr
$$

where $H$ is the radius of the rotor.

Integrating, rearranging, and normalizing $h_{aq}^*$, $h_{aq}$, and $h_{or}$ with respect to $H$: $h_{aq}^* = h_{aq} / H$, $h_{aq} = h_{aq} / H$ and $h_{or} = h_{or} / H$, we obtained

$$
h_{aq}^* = 1 - \sqrt{1 - \left(2h_{aq} - h_{aq}^2 + \frac{\rho_{or}}{\rho_{aq}} (2h_{or} - 2h_{aq} h_{or} - h_{or}^2)\right)}.
$$

Equations (36) and (37) relate $h_{aq}$ and $h_{or}$ to the holdup volume of the aqueous and organic phases, respectively, where $L$ is the length of the rotor:

$$
V_{aq} = \pi \cdot L \cdot H^2 \cdot \left(1 - (1 - h_{aq})^2\right)
$$

$$
V_{or} = \pi \cdot L \cdot H^2 \cdot \left((1 - h_{aq})^2 - (1 - h_{aq} - h_{or})^2\right)
$$

The total volume $V_{n,r}$ inside the rotor used for phase separation is

$$
V_{n,r} = \pi \cdot L \cdot H^2 \cdot \left(1 - (1 - H_{or})^2\right)
$$

Therefore, we can replace $L$ and $H$ with $H_{or}$ ($H_{or}$ normalized with respect to $H$) and $V_{n,r}$ as follows:

$$
\frac{V_{aq}}{V_{n,r}} = \frac{2h_{aq} - h_{aq}^2}{(2 - H_{or})H_{or}}
$$

Assuming $SC = \frac{(2 - H_{or})H_{or}}{V_{n,r}}$, which is a constant for a contactor, as $H_{or}$ and $V_{n,r}$ are dimensions of a contactor, we can calculate the aqueous and organic phase holdup volumes as

$$
V_{aq} = \frac{2h_{aq} - h_{aq}^2}{SC}
$$

$$
V_{or} = \frac{2h_{or}(1 - h_{aq}) - h_{or}^2}{SC}
$$

The total molar flow rates for aqueous and organic phases are calculated by Eqs. (42) and (43), where $cd_{aq}$ and $cd_{or}$ are valve constants of the aqueous outlet and organic outlet, respectively.

$$
S_{aq}^{out} = \begin{cases} 
    cd_{aq} (h_{aq}^* - H_{aq}), & \text{if } h_{aq}^* > H_{aq} \\
    0, & \text{if } h_{aq}^* \leq H_{aq}
\end{cases}
$$

$$
S_{or}^{out} = \begin{cases} 
    cd_{or} (h_{or} + h_{aq}^* - H_{or}), & \text{if } h_{or} + h_{aq}^* > H_{or} \\
    0, & \text{if } h_{or} + h_{aq}^* \leq H_{or}
\end{cases}
$$

These equations (Eqs. 32, 33, 35, and 40–43 together with Eqs. 17–24, 29, and 30) describe the phase separation zone in a centrifugal contactor with no mass transfer of species between the two phases.
The parameters of this model are the heavy phase and light phase weir diameters (normalized with respect to the radius of the rotor) and the total internal volume of the rotor. These variables all depend on the structure and size of the contactor.

In the advanced PUREX process experiments, two types of 1-cm-diameter annular centrifugal contactors were used: standard length rotor contactor and long length rotor contactor. In our simulation, the normalized heavy phase weir diameter was set to 0.68, based on the literature value. The normalized diameter of the light phase weir was set to 0.99 (to set the light phase level very close to the axis of the rotor). The total internal volume of the rotor is 4 mL for a standard length rotor and 5.3 mL for a long rotor, and the valve constants of the aqueous and organic outlets were set to high values to minimize the difference between liquid level and the weir height in order to avoid calculation failure. We then modeled the centrifugal contactor as a mixing zone model connected with a phase separation zone model and used this combined model to build a flowsheet simulation process model.

3. Model Validation

3.1 Mass Transfer Coefficient

The mass transfer between two phases is very fast in the PUREX process if no chemical reaction occurs. For example, the SEPHIS model is based on an ideal stage and has been successfully applied to describe the PUREX process. Research on centrifugal contactors also showed that this type of contactor could reach high extraction efficiencies (defined as the ratio of the amount of uranium actually extracted to the amount of uranium extracted if the two phases reach equilibrium). It is thus reasonable to assume that phase equilibrium can be reached in a centrifugal contactor in the absence of chemical reactions. Therefore, the mass transfer coefficients of nonreacting species, such as uranium, were set to ensure that the time to reach equilibrium was less than the residence time in the contactor.

The centrifugal contactor used in our neptunium extraction experiments has a 2 mL (standard rotor) or a 2.3 mL (long rotor) mixing zone volume and was operated at a total flow rate of 4 mL/min (single-stage experiment) to 4.5 mL/min (multistage experiment) and a residence time of about 26 s.

Figure 5 shows simulation results for a range of test cases with various thin film mass transfer coefficients in a stand-alone mixing zone model using the chemical system of U–HNO₃–TBP–

![Figure 5](image_url)

Figure 5. Results of dynamic simulations using different mass transfer coefficients for U(VI). Mixing volume: 2mL; initial O/A holdup ratio: 1:1; Temperature: 20°C; C\(_{\text{HNO}_3,\text{aq,initial}}\) = 5 mol/L; C\(_{\text{U (VI),aq,initial}}\) = 1.24 mol/L; 30 % TBP; C\(_{\text{U (VI),or, initial}}\) = 0 mol/L; C\(_{\text{HNO}_3,\text{or, initial}}\) = 0 mol/L.
odorless kerosene. Figure 5 shows that if the mass transfer coefficient for uranium is set to greater than $2 \times 10^{-5}$ m/s, the uranium concentration in the organic phase is constant after 4 s. That is, if the mass transfer coefficient is set as $2 \times 10^{-5}$ m/s or higher, uranium extraction easily reaches equilibrium in the contactor mixing zone. Therefore, we selected $2 \times 10^{-5}$ m/s as the mass transfer coefficient value for uranium. The most appropriate values for the mass transfer coefficients for species that participate in chemical reactions, such as neptunium, HNO$_3$ and HNO$_2$, will be discussed in the next section.

### 3.2 Mass Transfer Coefficients of Species With Reaction

To parameterize mass transfer coefficients for neptunium, nitric acid, and nitrous acid, results of two-phase single centrifugal contactor stage experiments$^{[13]}$ (specifically experiment 6 in Table 3 of Taylor et al.$^{[13]}$) have been used. In the single-stage experiment, the aqueous phase was recycled, while the organic phase passed through the contactor, as illustrated in Fig. 6. The solvent was 30% TBP–odorless kerosene with 0.917 mol/L nitric acid and 10 mmol/L nitrous acid. The initial Np(V) and nitric acid concentrations in the aqueous phase were 0.2 g/L and 5 mol/L, respectively. There was no nitrous acid in the aqueous phase before starting the extraction experiment. The centrifugal contactor was a 1 cm diameter rotor centrifugal contactor with a 2 mL mixing zone and a 4 mL phase separation zone$^{[13,31]}$ and a total hold up of the aqueous phase external to the reservoir of 14.5 mL. The operating temperature was set to 20°C.

The flow rates of aqueous and organic phases into the contactor were both 2 mL/min. Before the start of the simulation, it was assumed that the contactor was spinning at a suitable rotation speed and the mixing zone of the contactor was full, with a 1:1 ratio of the aqueous and organic phases. The liquid levels of the two phases in the separation zone were assumed to be equal to the heights of the light and heavy phase weirs, respectively. No mass transfer or chemical reactions began before $t = 0$.

We simulated this experiment with different mass transfer coefficients and compared the relative Np(V) concentration in the sample point to experimental results to evaluate the model and investigate the effects of mass transfer coefficients. As shown in Fig. 7, it was found that the mean square error (MSE, defined in Eq. 44) between the experimental and simulation results was not sensitive to the value of the mass transfer coefficients of nitric acid, neptunium (V), and neptunium (VI) within the range of $2 \times 10^{-9}$ to $2 \times 10^{-1}$ m/s. The value of the mass transfer coefficient used for uranium, $2 \times 10^{-5}$ m/s, was therefore deemed suitable for use in the simulations.

$$MSE = \frac{1}{n} \sum_{j=1}^{n} \left( \frac{C_{\text{Np(V)}; \text{aq}; \text{cal}} - C_{\text{Np(V)}; \text{aq}; \text{expt}}}{C_0} \right)^2$$

As Np(VI) is extracted more easily into the organic phase than Np(V), Np(V) in the aqueous phase was mainly oxidized to Np(VI) and then extracted by TBP; only small quantities of Np(V) were

**Figure 6.** Single-stage test flowsheet.$^{[13]}$
extracted directly. Predicted reaction rates of the aqueous phase oxidation of Np(V) and reduction of Np(VI), as well as the rate of extraction of Np(VI) into the organic phase, are plotted in Fig. 8. It is shown that both the Np(V) oxidation reaction rate and Np(VI) reduction reaction rate are significantly lower than the rate of Np(VI) extraction during the single-stage experiment. Also, the net oxidation rate of neptunium in the aqueous phase was almost equal to the calculated oxidation reaction rate in the aqueous phase due to the very low reduction reaction rate of Np(VI) in the aqueous phase under these conditions.

Although the distribution ratio of Np(V) in the 30% TBP–diluent solution is very low, Np(V) in the organic phase can also be oxidized to Np(VI). This reaction will reduce the Np(V) concentration in the organic phase and cause more Np(V) to transfer from the aqueous phase to the organic phase. This process is modeled as a sequential process of Np(V) extraction following oxidation in the organic phase. The simulation results presented in Fig. 9 show that the Np(V) extraction rate is faster than the Np(V) oxidation rate in the organic phase. This means that the controlling step in this sequence of processes is Np(V) oxidation in the organic phase rather than Np(V) extraction. Hence, the simulation results will be insensitive to the Np(V) mass transfer coefficient selected.

Figure 7. Mean square error between experimental and simulation results with various mass transfer coefficient settings for Np(V), Np(VI), HNO₃, and HNO₂. If not specified, k is set to 2 × 10⁻⁵ m/s; kₜ₃₂ is set to 1 × 10⁻⁶ m/s.

Figure 8. Neptunium aqueous phase redox reaction rates and Np(VI) extraction rate in the contactor mixing zone. kₜ₃₂ = 1 × 10⁻⁸ m/s; other mass transfer coefficients are set to 2 × 10⁻⁵ m/s.
Figure 7 shows that the simulation results are sensitive to the value of the mass transfer coefficient $k_{\text{HNO}_2}$ of HNO$_2$, with the MSE showing a minimum value about $1 \times 10^{-8}$ m/s and higher or lower values giving large MSEs. The impact of the selected value for $k_{\text{HNO}_2}$ on the single-stage simulation is illustrated in Fig. 10 for values of $k_{\text{HNO}_2}$ between $1.5 \times 10^{-10}$ and $2 \times 10^{-5}$ m/s. The selected value of the nitrous acid mass transfer coefficient of $1 \times 10^{-8}$ m/s is seen to lead to a good agreement with the experimental data.

In the experiment$^{[13]}$, the initial nitrous acid concentration in the aqueous phase was zero. Since the aqueous phase was recycled from the reservoir to the contactor and the incoming organic solution contained 10 mmol/L HNO$_2$, the aqueous phase nitrous acid concentration is not zero, due to a combination of backwashing (nitrous acid extracted from the organic phase by the aqueous phase) and the oxidation reaction of Np(V). Figure 11 compares the rates of HNO$_2$ backwashing from the organic phase with the generation of HNO$_2$ by the Np(V) aqueous phase oxidation reaction. The simulation result suggests that the backwashing rate of HNO$_2$ is much
greater than the generation rate of HNO₂ from the Np(V) aqueous phase oxidation reaction under these conditions.

3.3 CSTR Sections in Separation Zone

The separation zone of a centrifugal contactor may be modeled as a CSTR or as a plug-flow region, which may be modeled approximately as a series of CSTRs. Figure 12 shows that the concentration predicted by models of one CSTR and of three CSTRs in series are almost identical. Therefore, a single CSTR was adopted in this work.

3.4 Mass Transfer in the Phase Separation Zone

Mass transfer of species between two phases in the phase separation zone is treated by combining the mixing and phase separation zone models presented before. As there is only a little turbulence in the phase separation zone, it is reasonable to assume that there are no new drops generated and the dispersed phase drops are directly fed from the mixing zone of the contactor. In the phase separation zone, the dispersed phase drops combine to generate a new bulk phase. This means that the organic bulk phase composition does not affect the composition of organic drops dispersed in the aqueous phase, and vice versa.

The simplest way of modeling the phase separation zone is to assume that all material leaving the mixing zone only undergoes phase separation (i.e., mass transfer does not take place). This work instead assumes that part of the material leaving the mixing zone only undergoes phase separation (in the phase separation zone), while the remaining part of the material does not immediately separate but passes to a mixing unit where mass transfer between the two phases takes place before phase separation occurs. Figure 13 illustrates the concept, showing the phase separation zone modeled using a phase separation zone in parallel with a mixing zone.

The mixing fraction is defined as the fraction $f$ of material leaving the mixing zone and entering the mixing unit. Since the residence times of the mixing unit and the phase separation unit must be equal, $f$ also describes the volume fraction of the mixing unit within the whole phase separation zone. When this mixing fraction is zero, this means that there is no mass transfer between two phases in the phase separation zone.

Figure 11. Comparison of rates of HNO₂ accumulation in the aqueous phase due to HNO₂ backwashing from the organic phase and generation through Np(V) oxidation in the contactor mixing zone; $k_{\text{HNO}_2} = 1 \times 10^{-8}$ m/s; other mass transfer coefficients are set to $2 \times 10^{-5}$ m/s.
A single-stage centrifugal contactor was modeled using various mixing fractions for the phase separation zone. However, Fig. 14 shows that the model predictions were in closest agreement with the experimental results for a mixing fraction of zero. This suggests the mass transfer between two phases in the phase separation zone is negligible, that is, that phase separation is carried out very effectively within the centrifugal contactors, given the strong centrifugal forces and short residence times. Therefore, subsequent simulations neglected mass transfer of species between two phases in the phase separation zone.

3.5 Multistage Flowsheet Simulation

The single-stage model described before was then implemented in the gPROMS process modeling platform to represent a multistage neptunium extraction flowsheet proposed for the primary extraction and scrubbing section of an advanced PUREX process. The experimental data for this flowsheet\cite{13} are used to validate the model.
The flowsheet is summarized in Fig. 15 and Tables 3 and 4. Aqueous Neptunium (V) is fed with nitric acid and uranium in stream F1, and stream F2 adds NaNO₂ to the feed stage to simulate the generation of nitrous acid by radiolysis in a real system. (The laboratory tests used surrogate feeds with HNO₂ added to the feeds rather than spent nuclear fuel solutions where HNO₂ automatically arises from HNO₃ radiolysis). Stream A1 is an aqueous nitric acid solution fed to stage 1 in the HS bank as the scrubbing stream. Stream A2 is fed to stage 7 in the HA1B bank to simulate nitrous acid generated by radiolysis. S1 is the organic phase feed. SP is the solvent product containing extracted uranium and neptunium; AP is the aqueous product. HS bank (stages 1–4), is the scrubbing section, in which water-soluble fission products are backwashed from the organic phase, while HA1A, HA1B, HA2, and HA3 banks are extraction banks, in which uranium and neptunium are extracted by TBP. HS bank and HA1A and HA1B bank are heated to 50°C to improve the oxidation of Np(V).

The flowsheet was first simulated using the same mass transfer coefficients as those determined during the validation of the single-stage contactor model, as described in Sections 3.1 and 3.2. Although the predictions were in good agreement with the experimental results for the flowsheet,[13] there were some discrepancies on the feed stage. These may be attributed to poor mixing and mass...
transfer on the feed stage.\[59\] The reason for poor mass transfer in the feed stage is that the organic phase fed to the feed stage is almost saturated by nitric acid and therefore there is a large backwash flux of nitric acid from organic phase to aqueous phase, which is opposite to the uranium extraction flux. In concentrated solutions, this flux will reduce the mass transfer rate\[43\].

Therefore, a second simulation was carried out, where the mass transfer coefficients are the same as in the first simulation, apart from those for uranium and neptunium on the feed stage (stage 5). In the second simulation, the value for uranium is reduced from $2 \times 10^{-5}$ m/s to $1.3 \times 10^{-6}$ m/s. The Np\(\text{(VI)}\) distribution coefficient is calculated from the aqueous uranium and nitric acid concentrations at equilibrium. However, the aqueous-phase uranium concentration is abnormally high; therefore, in Simulation 2, the Np\(\text{(VI)}\) distribution coefficient to be set to a higher value $1 \times 10^{-8}$ m/s than would correspond to an equilibrium uranium aqueous concentration.

The simulated stage-by-stage aqueous- and organic-phase neptunium and uranium concentration profiles are plotted in Figs. 16–19 and compared with experimental data for a run time of 4 h.\[13\] These modeling results can be seen to be in good agreement with the experimental results,\[13\] including on the feed stage, when using updated mass transfer coefficients for uranium and neptunium\(\text{(VI)}\) on the feed stage.

Figure 20 shows the predicted Np\(\text{(V)}\) and Np\(\text{(VI)}\) profiles in the aqueous and organic phases using the updated feed stage mass transfer coefficients. These simulation results indicate that neptunium in the aqueous phase is mainly Np\(\text{(VI)}\) in the HS and HA1 banks (stages 1–8) but Np\(\text{(V)}\) in the HA2 and HA3 banks (stages 9–14). This is because neptunium, present almost completely as Np\(\text{(V)}\) in the feed (streams F1 and F2), is quickly oxidized to Np\(\text{(VI)}\) in HA1 and the generated Np\(\text{(VI)}\) is extracted into the organic phase, thus moving the redox reaction away from equilibrium and promoting Np\(\text{(V)}\) oxidation in the aqueous phase. The extracted Np\(\text{(VI)}\) is not reduced in the organic phase; therefore, it is retained through the scrubbing section HS. HA1 and HS were also heated to ~50°C to accelerate the oxidation reaction.\[60\] HA2 and HA3 were not heated and, as there was no additional nitrous acid feed to these banks, the rate of oxidation of the residual Np\(\text{(V)}\) was low. These simulation results indicated that the reaction and distribution coefficient models capture these temperature and concentration effects well.

### Table 4. Operating parameters and initial conditions of multistage process.

|                | HS  | HA1A | HA1B | HA2  | HA3  |
|----------------|-----|------|------|------|------|
| Stages         | 4   | 2    | 2    | 4    | 2    |
| Mixing zone volume, mL | 2   | 2.67 | 2.67 | 2.67 | 2    |
| Rotor inside volume, mL  | 4   | 5.3  | 5.3  | 5.3  | 4    |
| Temperature, °C             | 50  | 50   | 50   | 25   | 25   |
| Initial mixing zone liquid Holdup (mL) | 1   | 1.33 | 1.33 | 1.33 | 1    |
| Organic phase               | 1   | 1.33 | 1.33 | 1.33 | 1    |
| Initial phase separation Zone relative liquid level | 0.68 | 0.68 | 0.68 | 0.68 | 0.68 |
| Organic phase               | 0.99| 0.99 | 0.99 | 0.99 | 0.99 |
| Initial aqueous phase       |     |      |      |      |      |
| U(\text{VI}), mol/L         | 0   | 0    | 0    | 0    | 0    |
| Np(\text{V})*, mol/L       | $1 \times 10^{-9}$ | $1 \times 10^{-9}$ | $1 \times 10^{-9}$ | $1 \times 10^{-9}$ | $1 \times 10^{-9}$ |
| Np(\text{VI}), mol/L       | 0   | 0    | 0    | 0    | 0    |
| HNO$_2^*$, mol/L           | $1 \times 10^{-9}$ | $1 \times 10^{-9}$ | $1 \times 10^{-9}$ | $1 \times 10^{-9}$ | $1 \times 10^{-9}$ |
| HNO$_3$, mol/L             | 3.53| 3.53 | 3.53 | 3.53 | 3.53 |
| Initial organic phase       |     |      |      |      |      |
| U(\text{VI}), mol/L         | 0   | 0    | 0    | 0    | 0    |
| Np(\text{V}), mol/L        | 0   | 0    | 0    | 0    | 0    |
| Np(\text{VI}), mol/L       | 0   | 0    | 0    | 0    | 0    |
| Np(\text{V})*, mol/L       | 0   | 0    | 0    | 0    | 0    |
| Np(\text{VI}), mol/L       | 0   | 0    | 0    | 0    | 0    |
| TBP, mol/L                  | 1.09| 1.09 | 1.09 | 1.09 | 1.09 |

*Values set to $1 \times 10^{-9}$ to avoid dividing by zero during calculations.
It may be observed that the model overpredicts uranium and neptunium aqueous phase concentrations in the HS bank (stages 1–4). Reasons for this overprediction may relate to the high O/A ratio in the HS bank (stages 1–4): at a higher O/A ratio, the continuous phase is more likely to be the organic phase\cite{41} and the size of aqueous-phase droplets is likely to be larger than the assumed (constant) values, with and smaller interfacial area and lower mass transfer. Figures 21 and 22 test this hypothesis: as the assumed droplet size in the HS bank is increased, the model predicts aqueous-phase U and Np concentrations more accurately in the HS bank. However, the source of discrepancies for predicted organic-phase concentration profiles is unclear.

4. Conclusions

A new simulation model has been developed to describe neptunium extraction in an Advanced PUREX process that uses centrifugal contactors. The simulation has been implemented in gPROMS software, a standard modern platform for chemical engineering process modeling and simulation.\cite{21}

The simulation model has been developed in a modular form to facilitate adaptation and development of the models. The models have been validated using the data from single contactor stage and multistage experiments published in the open literature.\cite{13} This model now can be applied to the

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Figure 16. Aqueous phase neptunium concentration profile.
Figure 17. Organic phase neptunium concentration profile.

Figure 18. Aqueous phase uranium concentration profile.
development and modification of PUREX-type flowsheets to optimize neptunium control within the extraction-scrubbing section of the flowsheet.

The simulation results confirm that a centrifugal contactor can be modeled as a mixing zone connected to a phase separation zone model, where mass transfer between the organic and aqueous phases in the phase separation zone is negligible. The simulation results for a single-stage contactor are shown to be in good agreement with published experimental results\(^{[13]}\) when the mass transfer coefficient values of U(VI), Np(VI), Np(V), HNO\(_3\) are set as \(2 \times 10^{-5}\) m/s and a lower value for the mass transfer coefficient of HNO\(_2\), \(1 \times 10^{-8}\) m/s, is used. The single-stage simulation results also indicate that HNO\(_2\) produced as a consequence of Np(V) oxidation is not significant compared to HNO\(_2\) backwashed from the organic phase.

The single-stage model, when applied within a multistage cascade, also shows good agreement with the experimental results from flowsheet trials\(^{[13]}\). The modeling results suggest that the feed-stage peak in the aqueous phase uranium and neptunium concentration profiles can be explained in terms of poor mass transfer of uranium and neptunium (VI) in this stage and can be modeled adequately by using reduced values of the uranium and neptunium mass transfer coefficients in this stage.

![Figure 19. Organic phase uranium concentration profile.](image1)

![Figure 20. Multistage simulation results (simulation 2); calculated Np(V) and Np(VI) profiles.](image2)
A number of assumptions have been made in the development of this model to simplify the calculations. First, an existing model\textsuperscript{[40]} for nitrous acid extraction was used. A constant neptunium (V) distribution ratio and constant water concentration in the organic phase were also assumed, based on previous reports.\textsuperscript{[34,39]} These assumptions are likely to lead to some errors in the calculated organic and aqueous phase concentrations of key species. Secondly, the mass transfer coefficients have been fitted to minimize the mean square error compared to experimental data. This has led to assumptions that uranium mass transfer is sufficiently fast that it reaches equilibrium in a single stage, that the mass transfer coefficients for HNO\textsubscript{3}, Np(V) and Np(VI) are the same as those for uranium and that mass transfer of nitrous acid is much slower. Thirdly, Np(V) oxidation in the aqueous phase is described using a kinetic model modified from that of Koltunov, where the value of $z$ is taken as 2.\textsuperscript{[29]} The low mass transfer coefficient for HNO\textsubscript{2} is of particular concern. The nitrous acid yield from nitric acid radiolysis is also not considered. Future refinements of the model will address these assumptions to improve the fit of the flowsheet model to experimental data, and should aim to extend the applicability of the model to a wider range of process conditions.
List of symbols

\( a \)  \hspace{2em} \text{Interfacial area for mass transfer per unit volume of liquid phase, } 1/\text{m} \\
\( b \)  \hspace{2em} \text{Coefficients in Kumar's aqueous phase density equation}^{22} \\
\( C \)  \hspace{2em} \text{Concentration, mol/L, if not specified} \\
\( cd \)  \hspace{2em} \text{Valve constant} \\
\( D \)  \hspace{2em} \text{Distribution coefficient for molar concentration units} \\
\( d_{vs} \)  \hspace{2em} \text{Surface-mean diameter of dispersed phase, m} \\
\( E \)  \hspace{2em} \text{Extraction rate, mol/s} \\
\( f \)  \hspace{2em} \text{Mixing unit volume fraction of phase separation zone} \\
\( F \)  \hspace{2em} \text{Molar flow rate in and out, mol/s} \\
\( h, \bar{h} \)  \hspace{2em} \text{Liquid level (m) and normalized liquid level inside contactor rotor} \\
\( h', \bar{h}' \)  \hspace{2em} \text{Liquid level (m) and normalized liquid level in exit of rotor} \\
\( H \)  \hspace{2em} \text{Rotor radius, m} \\
\( H_{aq}, \bar{H}_{aq} \)  \hspace{2em} \text{Heavy phase weir height (m) and normalized height} \\
\( H_{or}, \bar{H}_{or} \)  \hspace{2em} \text{Light phase weir height (m) and normalized height} \\
\( k \)  \hspace{2em} \text{Mass transfer coefficient for single phase, m/s} \\
\( K_{00} \)  \hspace{2em} \text{Overall mass transfer coefficient, m/s} \\
\( L \)  \hspace{2em} \text{Length of rotor of the centrifugal contactor, m} \\
\( N \)  \hspace{2em} \text{Moles in extractor or containers, mole} \\
\( p \)  \hspace{2em} \text{Coefficients of aqueous phase density equation of Kumar and Koganti}^{22} \\
\( P \)  \hspace{2em} \text{Parameters of distribution coefficients of the model of Kolarik}^{38} \\
\( r \)  \hspace{2em} \text{Radial distance, m} \\
\( R \)  \hspace{2em} \text{Reaction rate, mol/L/s} \\
\( S \)  \hspace{2em} \text{Volume flow rate, L/s} \\
\( S_0 \)  \hspace{2em} \text{Minimum flow rate, L/s} \\
\( SC \)  \hspace{2em} \text{Dimension constant of a centrifugal contactor} \\
\( t \)  \hspace{2em} \text{Time, second} \\
\( T \)  \hspace{2em} \text{Temperature(°C)} \\
\( V \)  \hspace{2em} \text{Volume, L} \\
\( V_n \)  \hspace{2em} \text{Normal volume, L} \\
\( \rho \)  \hspace{2em} \text{Density, g/L} \\
\( \omega \)  \hspace{2em} \text{Rotation speed, 1/s} \\
\( \phi \)  \hspace{2em} \text{Fraction} \\

Superscripts:

\( \text{in} \)  \hspace{2em} \text{Feed} \\
\( \text{out} \)  \hspace{2em} \text{Outlet} \\
\( * \)  \hspace{2em} \text{At equilibrium} \\

Subscripts:

\( \text{aq} \)  \hspace{2em} \text{Aqueous phase} \\
\( C \)  \hspace{2em} \text{Continuous phase} \\
\( \text{cal.} \)  \hspace{2em} \text{Calculation result} \\
\( D \)  \hspace{2em} \text{Dispersed phase} \\
\( \text{expt.} \)  \hspace{2em} \text{Experimental result} \\
\( i \)  \hspace{2em} \text{ith component} \\
\( j \)  \hspace{2em} \text{jth data point} \\
\( \text{or} \)  \hspace{2em} \text{Organic phase}
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