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A powerful tool to model and simulate solvent extraction operations

ABSTRACT

The PAREX code has been developed since the nineties by CEA and AREVA to describe the PUREX process implemented in the French fuel reprocessing plants. It enables the calculation, either in steady or transitory states, of the behaviour of the different elements of interest at each process step. The highly customised structure of the software allowed the implementation of various phenomenological models describing solvent extraction systems dedicated to uranium purification from crude ore to spent fuel. After qualification of the implemented models, the code was used to design flow sheets for safety demonstration analysis or for operational assistance. CEA is currently developing a new simulation platform to make the code PAREX perennial and associate it with tools included in a standardised computing background for their perpetuation and sharing of generic functionality. In particular, it is planned to develop validated databases to reference the scientific knowledge useful in modelling development. The platform will adapt the standard phenomenological complexity needed to simulate a reprocessing plant, real or virtual, share tools and improve the transposition from laboratory scale to industrial scale, thus decreasing the number of experimental studies required for the implementation of a process.

INTRODUCTION

The modelling of the solvent extraction process was initiated in the CEA more than 30 years ago to describe the mechanisms involved in the PUREX process (Plutonium Uranium Refining by Extraction). It was developed progressively in close partnership with experimental teams and lead to the development of simulating tools which were implemented together in the PAREX code. This simulating code is used to design flow sheets for safety demonstration analysis and for operational assistance. As mentioned previously, the development of the PAREX code was linked to the implementation of the PUREX process in the French reprocessing plants. More recently, its customisable structure was also exploited to describe other solvent extraction systems dedicated to actinide purification from crude ore to spent fuel.

With the help of two examples, the successive steps of the PAREX use from flow sheet design to industrial operator training through aid in facility design will be presented. The recent development of the 1st GANEX cycle devoted to the selective uranium extraction from a dissolution solution will be detailed. The aid in design of the plutonium purification cycle in La Hague UP2 plant, based on the PAREX code, will also be detailed.

SOLVENT EXTRACTION MODELLING

Phenomena implemented in the PAREX code can be sorted into four main fields:

- Solvent extraction mechanisms
- Chemical reactions in the homogeneous phase
- Mass transfer between the two phases
- Simplified hydrodynamics in the liquid-liquid contactors.

The first two fields describe the chemistry of extraction, which is the core of this modelling. The standard of description chosen to model these phenomena is a compromise between the means and the objectives. Thus, the models devoted to the chemical description can be more or less advanced according to the maturity of the solvent extraction systems. Those implemented in the PAREX code to describe both mass transfer and hydrodynamics are mostly the same whatever the process. On the one hand, modelling the transfer between two phases is based on the diffuse double layer theory. On the other hand, the discrete contactors (mixer-settlers or centrifugals) are described as continuous stirred-tank reactors and the axial dispersion model is applied to describe continuous contactors.

A phenomenological approach is used to model the chemistry of solvent extraction: the main mechanisms governing the behaviour of elements of interest are identified. The more recent example of such an approach was the modelling of the 1st GANEX cycle. The GANEX process (Group Actinide Extraction) was developed by the CEA for the

hydrometallurgical reprocessing of Generation IV spent nuclear fuels and the homogenous recycling of actinides **[1]**.The first cycle consists of a selective extraction of uranium (VI) from the dissolution solution before the actinide group separation (Np, Pu, Am, Cm), carried out in the second cycle prior to the co-conversion step **[2]**. The preliminary separation of uranium in the first cycle is required in order to recover this element at a high purity to adjust the uranium/other actinides ratio in the nuclear fuel. Additionally, the separation of the major constituents of spent fuels is helpful for the hydrodynamics of the second extraction cycle. The selective separation of uranium is carried out by solvent extraction using a N,N-dialkylamide DEHiBA (N,N-di-(ethyl-2-hexyl)isobutyramide), depicted in **Figure 1**. DEHiBA was selected for the 1st GANEX cycle because it shows a good compromise between a quantitative extraction of uranium, a high U(VI)/Pu(IV) selectivity ($SF_{U(VI)/Pu(IV)}$ ~ 80 at 3M HNO_3) and a high loading capacity for uranium **[3,4]**.

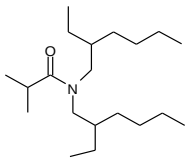

Figure 1 Structure of DEHiBA

Experimental distribution ratios obtained for nitric acid, uranium(VI), plutonium(III, IV), neptunium(V, VI) and technetium(VII) were described with a physicochemical model based on the application of the mass action law on each extraction equilibrium (**Equations 1 and 2**).

$$i\overline{E} + jH^+ + kM^{n+} + (j+k.n)NO_3^- + jH_2O \Leftrightarrow \overline{(E)_i(HNO_3)_j(M(NO_3)_n)_k(H_2O)_h} \quad \textbf{(1)}$$

$$K_{ijkh} = \frac{\left[\overline{(E)_i(HNO_3)_j(M(NO_3)_n)_k(H_2O)_h}\right]}{\left[\overline{E}\right]^i.a^j_{HNO_3}.a^k_{M(NO_3)_n}.a^h_{H_2O}} \cdot \frac{\overline{y_{ijkh}}}{\overline{y_E}^{\,i}} \quad \textbf{(2)}$$

$a_{M_pX_q}$: Activity of M_pX_q electrolyte

γM_pX_q : Stoichiometric activity coefficient of MpXq electrolyte

Due to the lack of data on water extraction, organic activity coefficients were neglected. Deviations from ideal behaviour in the aqueous phase were estimated by calculating the activity coefficient of each component according to the "simple solutions" concept. The latter is based on the outstanding experimental behaviour of isopiestic solutions, (solutions having the same water activity) first pointed out by Zdanovskii **[5]** and confirmed later by Stockes and Robinson **[6]**. The linear relation reported below is the mathematical expression of Zdanovskii's empirical rule. Solving it using an iterative procedure allows the estimation of the water activity of any mixtures since binary data of each electrolyte are known.

$$\sum_i \frac{C_i}{C_i^{bi}} = 1 \qquad \textbf{(3)}$$

C_i : Molarity of component i in the mixture (mol/L^{-1})

C_i^{bi} : Molarity of component i in the binary solution at the same a.w. as the mixture (mol/L^{-1})

Mikulin **[7]** demonstrated that the calculation of activity coefficients in mixtures with the help of the McKay-Perring relation **[8]** is solved most simply when Zdanovskii's rule holds. Thus, the estimated activity coefficient of an electrolyte in a mixture involves only binary data and electrolyte concentration.

The aqueous activity coefficients in binary solutions or in mixtures could be achieved respectively according to the Mikulin's relation by interpolating binary data. Nitric acid extraction was represented by taking into account the formation of three organic complexes. Modelling of actinide extraction involved complexes containing two extractants per metal in the case of actinides at the oxidation states of (VI) (U and Np) and (IV) (Pu and Th) and one extractant per metal with Pu(III) and Np(V). The extraction of pertechnetate was modelled by considering two organic complexes $(HTcO_4)(DEHiBA)_2$ and $UO_2(TcO_4)(NO_3)(DEHiBA)_2$ to accurately represent its distribution ratios.

FLOW SHEET DESIGN

The equilibrium constants optimised to represent extraction of nitric acid and metals were implemented into the PAREX code. Owing to the structure of the code, the chemical reactions involving the Np(VI)/Np(V) redox couple **[9]** and Tc(VII) **[10]** with hydrazine, previously modelled in the framework of the PUREX development, could be easily integrated.

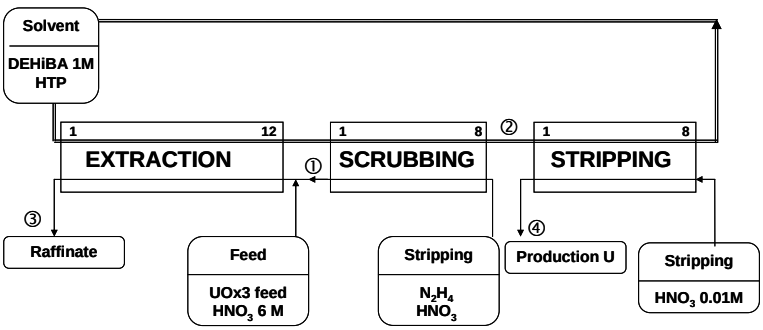

Figure 2 Flow sheet of the 1st GANEX cycle

With the help of this validated model, flow sheets were designed to demonstrate the ability of the DEHiBA to recover more than 99.9% of uranium from a dissolution solution with high decontamination factors towards the remaining fission products. The flow

sheet, illustrated in Figure 2, was carried out in laboratory scale mixer-settlers during a counter-current test to validate the extraction performance of DEHiBA in liquid-liquid discontinuous contactors from a UOx3 feed solution. The losses of uranium in raffinate and solvent outflows were lower than 0.002% and 0.003%, respectively, corresponding to a recovery yield of uranium higher than 99.99%. The decontamination factors vs Np, Tc and Pu are high enough with the help of hydrazinium nitrate in the scrubbing section. Uranium and technetium concentration profiles in the aqueous phase (and organic phase for uranium), obtained during the continuous hot test, are shown in **Figures 3 and 4** and compared with computed data for extraction, scrubbing and stripping parts of the flowsheet.

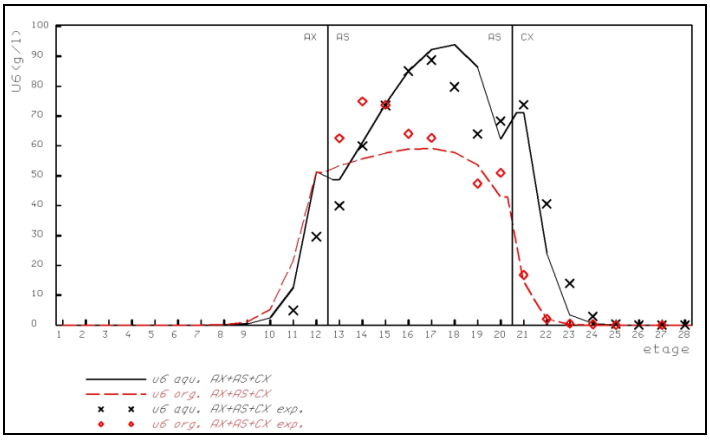

Figure 3 Experimental and calculated profiles of uranium concentrations in the aqueous and organic phases for the whole hot flow sheet

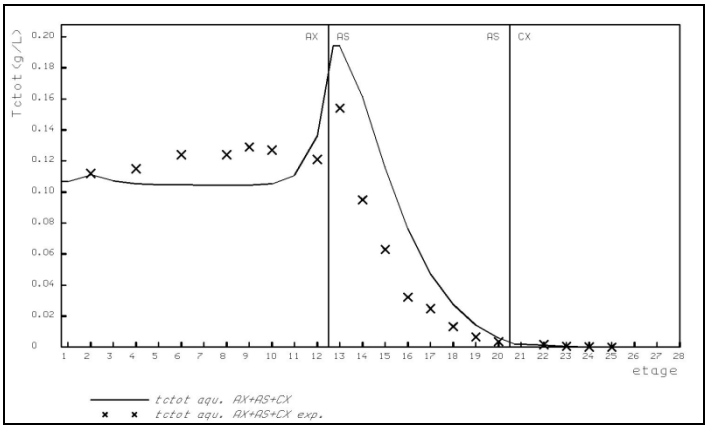

Figure 4 Experimental and calculated profiles of technetium concentrations in the aqueous phases for the whole hot flow sheet

These predicted values of uranium and technetium reproduced the experimental concentrations quite well, which confirm the validity of the model for uranium and technetium extraction by DEHiBA (extraction constants, kinetics and speciation). The good agreement between the experimental and calculated concentration profiles enables the extrapolation of the decontamination factors of Np, Pu and Tc for a flow sheet with two more scrubbing stages (ten instead of eight).

A similar approach was adopted to design the flow sheets of the extraction cycles involved in the PUREX process **[10]**: the first cycle was devoted to the uranium-plutonium splitting **[11,12]** and the plutonium purification cycle was recently implemented in La Hague plant **[13,14]**.

AID IN FACILITY DESIGN

A more recent example of the aid in facility design was the implementation of the plutonium purification in centrifugal contactors in the La Hague UP2-800 facility. The extension of the UP2 plant at La Hague plant includes a new plutonium purification cycle using multi-stage centrifugal extractors instead of the previous cycle implemented in mixer/settler banks. The benefits of this type of extractor are typically its compactness and the short residence time, limiting solvent degradation, particularly in the case of reprocessing high contents of plutonium-238.

Two types of reducing agents have been considered for the plutonium stripping operation: uranous nitrate and hydroxylamine nitrate. Uranous nitrate displays very fast reduction kinetics, ideal for the very short residence time of the phases in the centrifugal extractors. However, its extractability in the organic phase exacerbates the undesirable re-oxidation of plutonium, which is present in a high concentration in this stage of the process. Thanks to short residence times, the plutonium reduction reaction could occur with less undesirable re-oxidation mechanisms. Hydroxylamine nitrate (HAN) helps to minimise re-oxidation. However, the plutonium(IV) reduction kinetics obtained are slower than with uranous nitrate, making it necessary to check whether its use is compatible with the very short residence times of centrifugal extractors.

Preliminary flow sheets were elaborated using the PAREX code **[15]**. Series of tests were then carried out in single-stage laboratory centrifugal extractors to measure the plutonium stripping performance. The study of these test results led to modifying the first flow sheets. Test campaigns in an active pilot plant using the same type of contactors were then performed to improve the flow sheet design. All test results were analysed using the PAREX code and new operating parameters were then computed for a new active test in order to minimise the number of active tests **[13]**.

Inactive tests, followed by full-scale ones, were carried out to estimate the mass transfer efficiency of extractors and to quantify the heating phases resulting from the dissipation of mechanical energy in in the mixing chambers. The PAREX code was then used to scale

up the flow sheet for the industrial plant, taking into account the chemical model for plutonium behaviour resulting from the active tests and the characteristics determined in full-scale inactive tests. Feedback from industrial plant results shows very good separation performances **[14]**.

SAFETY ANALYSIS

Process development based on a modelling approach leads to a qualified simulation code that can be used to perform safety analysis of industrial plants **[16]**. This analysis can be performed in two steps. The first step is a parametric analysis to identify the sensitive parameters for the risk of plutonium accumulation, indicating the permissible level of maladjustment. These calculations are also devoted to identify process indicators which should be monitored during plant operation.

The second step is the study of transient regimes in case of severe malfunction to verify that process monitoring allows the early and reliable detection of any drift towards a plutonium build-up.

TRAINING SIMULATION

SIMULEX is a simulation tool built on the PAREX code, dedicated to training plant operators. Its user-friendly interface offers the possibility of altering the operating parameters and displaying the computing dynamic evolution of the process in those conditions (concentration profiles of one element in a contactor, or concentration evolution at a point of the process) **[16]**.

CONCLUSION AND PROSPECTS

The modelling approach for process development followed for decades offers an essential advantage owing to the general and transposable character of the knowledge thus capitalised in the models. The resulting simulation code proved to be an outstanding tool to industrial plant design as well as plant operation. The iterative approach between experience and modelling chosen for solvent extraction modelling should be maintained in future actinide separation process development. Further progress achieved in the comprehension of the mechanisms involved should indeed be taken into account.

CEA is currently developing a new simulation platform to make the PAREX code perennial and associate it with tools included in a standardized computing background for their perpetuation and sharing of generic functionality. In particular, it is planned to develop validated databases to reference the scientific knowledge useful in developing modelling. The platform will adapt the standard phenomenological complexity needed to simulate a reprocessing plant, real or virtual, share tools and improve the transposition from laboratory scale to industrial scale, thus decreasing the number of experimental studies required for the implementation of a process.

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