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Modelling of americium stripping in the EXAm process

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Abstract

The EXAm process aims at recovering americium alone contained in the PUREX raffinate. The americium stripping model has been revised to take into account a change of stripping aqueous phase and up-to-date experimental results conducted within DRCP to improve knowledge about complexes.

This work represents a first approximation at modelling americium stripping. The modelling work has led to synthesize the knowledge on chemical phenomenology and adopt assumptions that best reflect experimental results. The modelling has been implemented in PAREX code in order to simulate this step to prepare and understand tests to be carried out in mixer settlers.

Keywords: EXAm; americium stripping; DMDOHEMA; HDEHP; DTPA

1. Why the modelling of americium stripping has to evolve

The EXAm process [1][2], developed within the framework of the 2006 Waste Management Act, aims at recovering americium alone contained in the PUREX raffinate. Thanks to an organic phase composed of two extractants, DMDOHEMA (0.6M) and HDEHP (0.3M), americium is extracted in high-acid conditions and then

stripped selectively into a low acidic aqueous phase containing complexing agents. Figure 1 shows the different steps of the EXAm process.
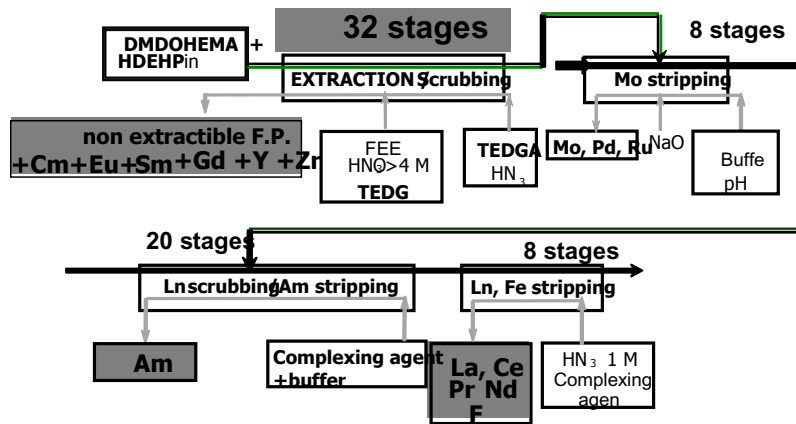

Fig. 1. EXAm flowsheet

The americium stripping model, in presence of "light"lanthanides (La, Ce, Pr, Nd) which are also extractable, has been revised to take into account the following elements :

- Change of stripping aqueous phase to minimize the impact of residual complexing reagents on conversion : "HEDTA / citric acid" has been replaced by "DTPA 0.01M / malonic acid 0.3M", which are easier to eliminate.
- Consideration of up-to-date experimental results conducted within DRCP to improve knowledge about complexes formed between americium / "light" lanthanides and DMDOHEMA / HDEHP on one hand and DTPA on the other hand.

Nomenclature

EXAm   an heterogeneous recycling, where americium alone is recovered (extraction of Am)

GANEX   a homogeneous recycling, where all the actinides are separated from the fission, corrosion, and

activation products via a "group separation" (GANEX concept) in order to fabricate mixed actinide fuel for fast

reactors (Group actinides extraction). Concept in two cycles: GANEX1 (uranium recovery) and GANEX2

(plutonium and minor actinides recovery)

2. Approaches adopted to build the model

2.1. Early model

A former model was developed for GANEX2 process (DMDOHEMA and HDEHP are the extractants like in EXAm) to simulate separation between actinides and lanthanides in low-acid conditions [3]. According to this model, at a given temperature, extraction phenomena were supposed to be identical for all actinides (+III) and

lanthanides (+III): extraction equilibrium was evaluated for europium (element for which data is most numerous) and then equilibriums for other elements were deduced from europium by proportionality.

Based on batch experiments, each cation was assumed to be complexed in organic phase by 3 dimers $(M(DEHP)_3(HDEHP)_3)$. Following pilot tests, this stoichiometry was revised to 2.5 dimers $(M(DEHP)_3(HDEHP)_2)$ to obtain a better agreement between experiment and modelling. In both cases, three protons were exchanged. To improve retention of certain metals in the aqueous phase, a 1:1:1 complex with citric acid and HEDTA is produced. An adduct, involving DMDOHEMA and HDEHP, with lower extraction properties is assumed to be formed: as this phenomenon was previously unknown, its effect was taken into account by a mathematical expression.

At the end, a mathematical law, including all phenomena, was implemented:

$$\left[\overline{(M,DEHP_3,HDEHP_2)}\right] = K_M \frac{\left[\overline{HDEHP}\right]_{free}^{2.5}\left[H^+\right]\left[M\right]_{total}}{\left[HEDTA\right]_{total}\left[citric\_acid\right]_{total}110^{\left[\overline{DMDOHEMA}\right]}}$$

This "all-in-one" model was difficult to modify to include new phenomena and new molecules (i.e. DTPA). To benefit from up-to-date knowledge about complexes formed, it was decided to use a more phenomenological approach, as was already done for the "americium extraction / curium scrubbing" step.

2.2. Integration in overall EXAm model

When varying the acidity of the aqueous phase, the extraction by the mixture of the two extractants shows a behaviour different from those of the two single extractants: a synergistic effect occurs for nitric acid concentrations of 0.5 mol/L (Am) and 1.0 mol/L (Eu) while an antagonistic effect becoming marked at lower acidity [4].

For this reason, the "americium extraction / curium scrubbing" model [5] cannot be used and it was necessary to develop a specific model for low acidic condition steps, such as americium stripping. What is more, effects of each extractant cannot be studied separately.

2.3. Scope of this model

Modelling work has been focused on extraction mechanisms independently of kinetics. Only americium and "light" lanthanides are taken into consideration. Iron and zirconium are foremost supposed to remain in the organic phase. Steps upstream are supposed to operate correctly, ensuring absence of elements like molybdenum and ruthenium.

The model has been developed in two steps:

- Extraction by a mixture of DMDOHEMA/HDEHP.
- Complexation reactions in the aqueous phase by DTPA are added to the previous modelling.

As values of the extraction constants were unknown, the following guideline was applied:

- To facilitate evaluation of the extraction constants, the model was simplified as much as possible.
- The complexation constants by DTPA were evaluated, by using the extraction constants previously determined, and then compared to values found in literature. This was one means to check the relevance of the model (hypotheses, values of contents, etc.).

Whenever necessary, SCILAB© software was used to decide between different possibilities, which one best reflects experimental results.

3. Extraction by DMDOHEMA/HDEHP

3.1. Hypotheses of the extraction model

3.1.1. Complexes formed between cations, DMDOHEMA and HDEHP

Mixed species with DMDOHEMA and HDEHP, thermodynamically more stable than HDEHP complexes, are preferentially formed [4]. Based on experiments with neodymium, europium and americium, M(DMDOHEMA)$_x$(DEHP)$_3$(HDEHP)$_y$, x $\in$ [1;3], y $\in$ [0;3] complexes were proposed in the organic phase [4].

It was pointed out that one nitrate may substitute to one DEHP$^-$: for this initial model, at low acidic conditions (pH around 2.5), this possibility was disregarded.

Two models were implemented in SCILAB$^©$: one for M(DEHP)$_3$HDEHP$_3$, as considered in the early model, and one for M(DMDOHEMA)(DEHP)$_3$. In most cases, for HDEHP complex, experimental data and model evaluations cannot be concealed. Otherwise, for a mixed complex with a single DMDOHEMA, comparison with experience was satisfying, when cation concentrations were below around 0.2M.

Furthermore, considering the concentrations of extractants in the EXAm process (0.6M for DMDOHEMA and 0.3M for HDEHP) and the stoichiometry of these extractants in complex, HDEHP is the limiting extractant towards loading capacity: in order to implement the easiest model, complexes involving several malonamide were left out.

There was an experimental uncertainty on the number of HDEHP involved in mixed complexes (from 0 to 3). Model results were compared and best results were obtained with y = 0 for HDEHP.

Finally, with this complex, 3 protons are released in the aqueous phase for each cation extracted.

3.1.2. How to model antagonistic effect in low acidic conditions?

Antagonism observed can only be interpreted by the presence of competitive equilibrium such as the formation of mixed DMDOHEMA-HDEHP species, which consumes free HDEHP [4]. This adduct does not extract cations. In the lack of further information, a 1:1 adduct was taken into consideration.
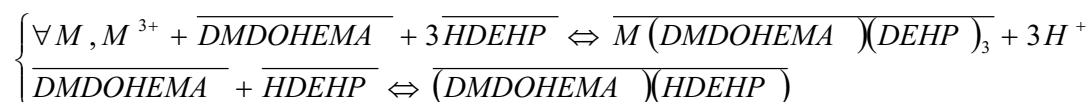
3.1.3. Some phenomena left out

The following phenomena were disregarded:

- Binuclear complexes. For higher concentrations of cations (one experiment at 1M), binuclear complexes were observed with HDEHP alone. For PUREX raffinate, where the total concentration of cations is lower than 0.2M, this assumption is acceptable. But, errors may occur in case of concentrated feed solution.
- Water extraction and the synergetic effect between the two extractants in this case. As the model is based on concentrations and not chemical activities, this hypothesis is supposed acceptable.
- Aggregate of DMDOHEMA or HDEHP. They appear to bring complexity with no direct link to the way cations behave.

3.1.4. Chemical system to solve

To sum up, the following chemical reactions are taken into account:

$$\begin{cases} \forall M, M^{3+} + \overline{DMDOHEMA} + 3\overline{HDEHP} \Leftrightarrow \overline{M(DMDOHEMA)(DEHP)_3} + 3H^+ \\ \overline{DMDOHEMA} + \overline{HDEHP} \Leftrightarrow \overline{(DMDOHEMA)(HDEHP)} \end{cases}$$

The next step is to determine equilibrium constants for adduct and each cation.

3.2. Determination of equilibrium constants

Equilibrium constants were determined by the method of least squares implemented in SCILAB[©] software. The following four-step methodology was used:

- Computation of organic concentrations by solving the above system (aqueous concentrations and total extractant concentrations are input elements).
- Relative difference is evaluated between computation and experimental organic concentrations and quadratically added.
- Solutions given by SCILAB[©] optimization algorithms depend on initial vector of equilibrium constants. To be sure to obtain the absolute minimum, a grid method was applied to determine the initial vector which minimizes root-mean square.
- Finally, "leastsq" SCILAB[©] function optimized parameter values.

Table 1 presents parameters obtained so far.

Table 1. parameters obtained for "DMDOHEMA/HDEHP" extraction model

Chemical element	Number of experiments	Equilibrium constant (L.mol^{-1})
Americium	2	0.39
Cerium	4	0.126
Neodymium	6	0.54
Europium	8	1.67
Adduct	18	0.07

4. Extraction by DMDOHEMA/HDEHP with DTPA as complexing reagent

4.1. Hypotheses of extraction model with DTPA

4.1.1. Modelling of DTPA complexing effect

The principle is to add a reaction in the aqueous phase to take into account complexing effects of DTPA on each element.

$DTPA^{5-}$ is the main specie of DTPA aging as complexing reagent. $DTPA^{4-}$ is also quoted in literature [6]: a simulation with SCILAB[©] shows few effects of the phenomenon on experiment / modelling agreement. Consequently, $DTPA^{4-}$ effect is foremost disregarded.

4.1.2. Modelling of buffering elements

Malonic acid is used as buffer. Experimentally, changes in concentration of malonic acid do not alter distribution factors: malonic acid would not be involved in complexation.
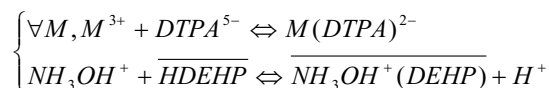
A base is added in the aqueous feed solution, containing DTPA and malonic acid, to reach pH 2.5. Two bases were experimented: NaOH and NH_2OH (hydroxylamine).

- NaOH has no effect on equilibrium. However, the presence of sodium is detrimental to the downstream process (conversion).
- Hydroxylamine is involved in the reaction. If this phenomenon is left out, significant differences between experiment and simulation are observed. Two possibilities were first assumed: action of NH_2OH as co-complexing reagent with DTPA; extraction of NH_3OH^+ by HDEHP, consuming free HDEHP. Simulation did not allow a choice between these two assumptions. However, NH_2OH complex did not seem to be strong

(contrary to DTPA): considering the very low concentration of NH_2OH at pH 2.5, this assumption was forsaken. Implementation of NH_3OH^+ extraction by HDEHP gave correct results. In this case, one proton is released for each NH_3OH^+ extracted.

4.1.3. Chemical system to solve

The two following equations are added to the system presented in part 3 (the first one for complexing reactions with DTPA, the second one for NH_3OH^+ extraction):

$$\begin{cases} \forall M, M^{3+} + DTPA^{5-} \Leftrightarrow M(DTPA)^{2-} \\ NH_3OH^+ + \overline{HDEHP} \Leftrightarrow \overline{NH_3OH^+(DEHP)} + H^+ \end{cases}$$

4.2. Determination of thermodynamic constants

The same method of determination as in part 3 is applied here. Table 2 presents parameters obtained so far. Complexing constants are given in logarithmic scale.

Table 2. Parameters obtained for "DMDOHEMA/HDEHP/DTPA/malonic acide" extraction model

Chemical element	Number of experiments	Equilibrium constant (L.mol^{-1})
NH_3OH^+	22	0.02

Chemical element	Number of experiments	Complexing constant (model)	Complexing constant (literature)
Americium	46	23.5	23.45 [7], 23.1 [8], 22.92 [9], 22.9 [10]
Cerium	50	20.82	21.65 [7], 20.33 [8], 20.4 [10]
Neodymium	4	23.73	21.6 [8], 21.96 [9], 21.69 [10]
Europium	50	22.86	22.93 [7], 22.39 [8], 22.40 [9], 22.49 [10]

5. Conclusion – prospects

Figure 1 shows a good agreement between experimental results and modelled data. It is clear from comparison of complexing constants that the model seems to be representative of americium, cerium and europium behaviours in process. Consequently, equilibrium constants without complexing reagents obtained for these elements appear to be reliable.
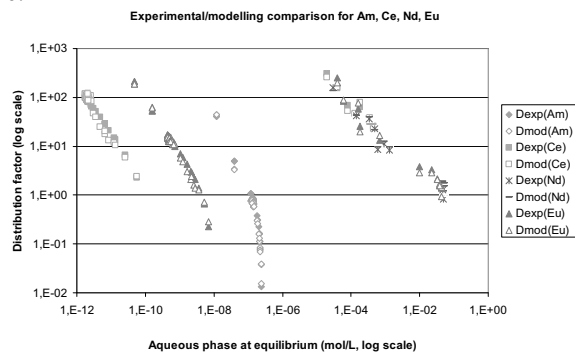

Fig. 1. Experimental/modelling comparison for americium, cerium, neodymium and europium

The complexing constant evaluated for neodymium is not satisfying. Theoretically, it must increase with atomic number for lanthanides. The determination of this constant must be first consolidated by further experiments. By construction, some limitations can be pointed out:

- All experiments were made with 0.6M DMDOHEMA and 0.3M HDEHP.
- Without DTPA, equilibrium acidities of experiments are higher (from 0.05M to 0.25M) than process working point (pH 2.5): precipitate appear at low acidity for "batch" experiments. On the contrary, with DTPA, the model relies on experiments with equilibrium pH between 1.6 and 3.1.
- The model is designed for no concentrated feed solution (total concentration of cations up to 0.2M).

This work represents a first approximation at modelling Am stripping in the EXAm process. Obviously, later comparison with experiment/pilot/hot tests will identify the weaknesses of the model and necessary improvements. The modelling has been implemented in PAREX code in order to simulate this Am selective stripping step to prepare and understand tests to be carried out in mixer settlers.

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