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MODELLING OF URANIUM/PLUTONIUM SPLITTING IN PUREX PROCESS

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MODELLING OF URANIUM/PLUTONIUM SPLITTING IN PUREX PROCESS

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A mathematical model simulating the highly complex uranium/plutonium splitting operation in PUREX process has been achieved by the french "Commissariat à l'Énergie Atomique". The development of such a model, which includes transfer and redox reactions kinetics for all the species involved, required an important experimental work in the field of basic chemical data acquisition. The model has been successfully validated by comparison of its results with those of specific trials achieved (at laboratory scale), and with the available results of the french reprocessing units operation. It has then been used for the design of french new plants splitting operations.

INTRODUCTION

The simulation of the different operations of the Purex process by a computer program is a very useful tool today, not only for the definition of the process flowsheets and for safety analyses, but also in the related areas of the definition of the control systems and even aid in process operation on the industrial site. In fact, simulation calculations make it possible and easy to :

- determine the "parameters of state" of a process, sensitive and prompt indicators of any change in the process (optimisation of the number, type and location of the sensors),
- define the optimal procedures concerning exceptional events : shutdowns, startups, rate changes (sequence optimisation by choosing between different scenarios),
- contribute effectively to the training of future operators (model/-control console coupling for the most "sensitive" facilities),
- set up a solid, reliable "knowhow base" usable as a reference to aid operators in taking decisions (Expert Systems for diagnosis and guidance for optimising the activities of the operator in "degraded" operation).

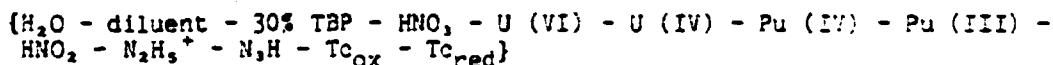
The uranium-plutonium partition operation is one of the key steps of the Purex process, and is also one of the most complex, owing to the variety of the chemical and physico-chemical mechanisms involved. Simulation by a computer program is here, more than anywhere, a real need for proper process mastery.

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The program presented here simulates the uranium-plutonium splitting with uranous nitrate in a battery of mixer-settlers.

OPERATION PRELIMINARY ANALYSIS

The partition operation involves a large number of chemical species, and we have restricted our analysis to the following system :



Two types of mechanism take place in the operation :

- Partition of solutes between phases ;
- Redox reactions in which the different chemical species can participate in each of the phases.

The construction of a model simulating this operation hence requires the knowledge of three types of chemical and physico-chemical data :

- data on the partition coefficients of all the extractible species,
- data on the interphase transfer kinetics of the species,
- data on the kinetics of the redox reactions occurring between the species.

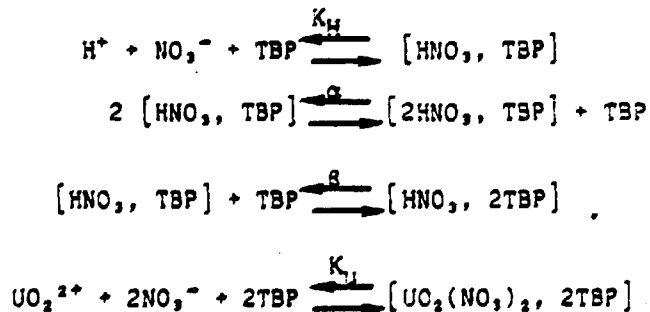
Moreover, it is also necessary to describe the phase flow in the unit, and hence to make assumptions concerning the hydraulic behaviour of the contactor.

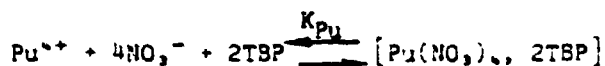
SPECIFICATIONS OF THE MODEL

1 - Partition coefficients

The system analysed contains eight extractible solutes (HNO₃ - U (VI) - U (IV) - Pu (IV) - Pu (III) - HNO₂ - N₃H - Tc) and one unextractible solute (hydrazine). The large number of solutes, the interactive character of their partition, and the absence of data on the complete system, led us to develop a model that serves to simulate the partition coefficients.

This semi-empirical model was developed from the one used in the SEPHIS code [1], of which we updated the parameters and expanded the field of application. The model is based on the identification of the apparent equilibrium constants as a function of the nitrate ion concentration (or rather the "nitrate salting out effect"). For example, the extraction of the species in the restricted system {H₂O- 30 % TBP - HNO₃ - U(VI) - Pu(IV)} is simulated as follows :





For which the following are defined :

$$K_{\text{H}} = \frac{[\text{HNO}_3, \text{TBP}]}{[\text{H}^+][\text{TBP}]}$$

$$\beta = \frac{[\text{HNO}_3, 2\text{TBP}]}{[\text{HNO}_3, \text{TBP}][\text{TBP}]}$$

$$\alpha = \frac{[2\text{HNO}_3, \text{TBP}][\text{TBP}]}{[\text{HNO}_3, \text{TBP}]^2}$$

$$K_{\text{U}} = \frac{[\text{UO}_2(\text{NO}_3)_2, 2\text{TBP}]}{[\text{UO}_2^{2+}][\text{TBP}]^2}$$

$$K_{\text{Pu}} = \frac{[\text{Pu}(\text{NO}_3)_6, 2\text{TBP}]}{[\text{Pu}^{4+}][\text{TBP}]^2}$$

$$K_{\text{PuOH}} = \frac{[\text{Pu}(\text{OH})^{3+}][\text{H}^+]}{[\text{Pu}^{4+}]}$$

K_{H} , α , K_{U} , K_{Pu} , K_{PuOH} are expressed as functions of a "nitrate salting out effect" variable, here defined by :

$$n_A = a(\text{H}^+) + b(\text{UO}_2^{2+}) + c(\text{Pu}^{4+})$$

Where a, b and c represents the respective "salting out effect factor" of nitric acid, uranium (VI) and plutonium (IV).

The values of each of these parameters or functions have been identified to fit the large available amount of partition coefficients determinations.

Remark : The concentrations are expressed in moles per litre of free solvent insted of molar concentrations.

2. Transfer kinetics

The transfer kinetics is taken into account by means of the following expression of the flow crossing the exchange area :

$$F = V_d \cdot K.A.(y^* - y)$$

V_d = volume of dispersed phase

A = specific exchange area/dispersed phase

K = overall transfer coefficient

y = substance concentration in the organic phase

y^* = substance concentration in equilibrium, with the aqueous phase

Remarks : The value of the product $K.A$ is one of the model's parameters ; it should be adjusted, for each extractible specie, according to mixer's performance. For example, we found $K.A = 1 \text{ s}^{-1}$ for uranium (VI) in our alpha active rig (cf. further) under correct hydraulic conditions ; this value is in very good agreement with both K and d_{12} published determinations [2] [3].

However, it must be noticed that for industrial mixers, the residence time of the dispersed phase is so high that we don't need an accurate determination ; the results are quite insensitive to this parameter in the field of its probable values.

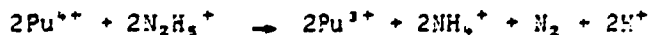
3. Redox reactions

The different reactions can be classified in four types :

- "functional" reactions : reactions which produce Pu (III),
- "interference" reactions : reactions which oxidise Pu (III) and U (IV),
- "useful" reactions : reactions which inhibit the interference reactions,
- "interference side" reactions : reactions which could be qualified as "interference" of "useful" reactions (destruction of hydrazine by technetium).

"Functional" reactions

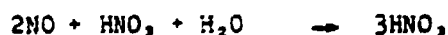
We have two reducers of plutonium (IV) in the medium under investigation, uranium (IV) and hydrazine. The reactions are written :



Since the reduction kinetics of plutonium by hydrazine is much slower than by uranium (IV), we ignored it in the present model.

"Interference" reactions

To correctly simulate (especially in the organic phase) the oxidation reaction of Pu(III) by nitric acid, catalysed by nitrous acid (autocatalytic reaction), we described it by a set of three reactions :



As for the oxidation of uranium (IV) in the presence of plutonium, this reaction is already described by the above set of three reactions, if we add the reduction reaction of plutonium (IV) by uranium (IV) ("functional" reaction). To describe the oxidation of uranium (IV) in the absence of plutonium, we introduced the reaction :



"Useful" reactions

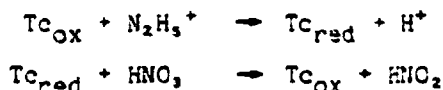
Two reactions lead to the destruction of nitrous acid and hence inhibit the oxidation reactions. These are :



Since the kinetics of the destruction of nitrous acid by hydrazoic acid is much slower than by hydrazine, we ignored it in the present model.

"Interference side" reactions

In the medium analysed, technetium participates in many redox reactions understood to varying degrees. Nevertheless, its main action is to catalyse the destruction of hydrazine by nitric acid [4]. In our model, we therefore simulate its action only by the reactions :



NB : For each of the reactions selected, the kinetics was formulated from available experimental determinations.

4. Specific assumptions

The balance equations of the model were based on the following assumptions :

1. The mixers and settlers (aqueous and organic phases) are considered as perfectly mixed cells.
2. Phase separation is perfect in the settlers (no phase entrainment).
3. No mass transfer occurs in the settlers.
4. The volume of the dispersed phase in the mixer is defined by the equation :

$$V_d = \frac{Q_d}{Q_t}$$

where :

V_d = volume of dispersed phase

Q_d = flow rate of dispersed phase

Q_t = total throughput (aqueous + organic)

QUALIFICATION OF THE MODEL

The different parameters were adjusted and the model validated by comparison with the tests conducted in our laboratories, and with the operating results of the UP2 plant. As an example, we give below to the comparison of the model with one of the tests which served to validate the model.

Presentation of the test

The test concerned was carried out according to the diagram in figure 1. The battery had 16 identical stages, the mixers had a volume of 3.5 cm³, and the settlers a volume of 50 cm³.

Results

The results of the comparison are shown in figures 2 to 6. We can see that on the whole, the model performed very well, although some slight discrepancies were nevertheless found on certain profiles.

CONCLUSIONS

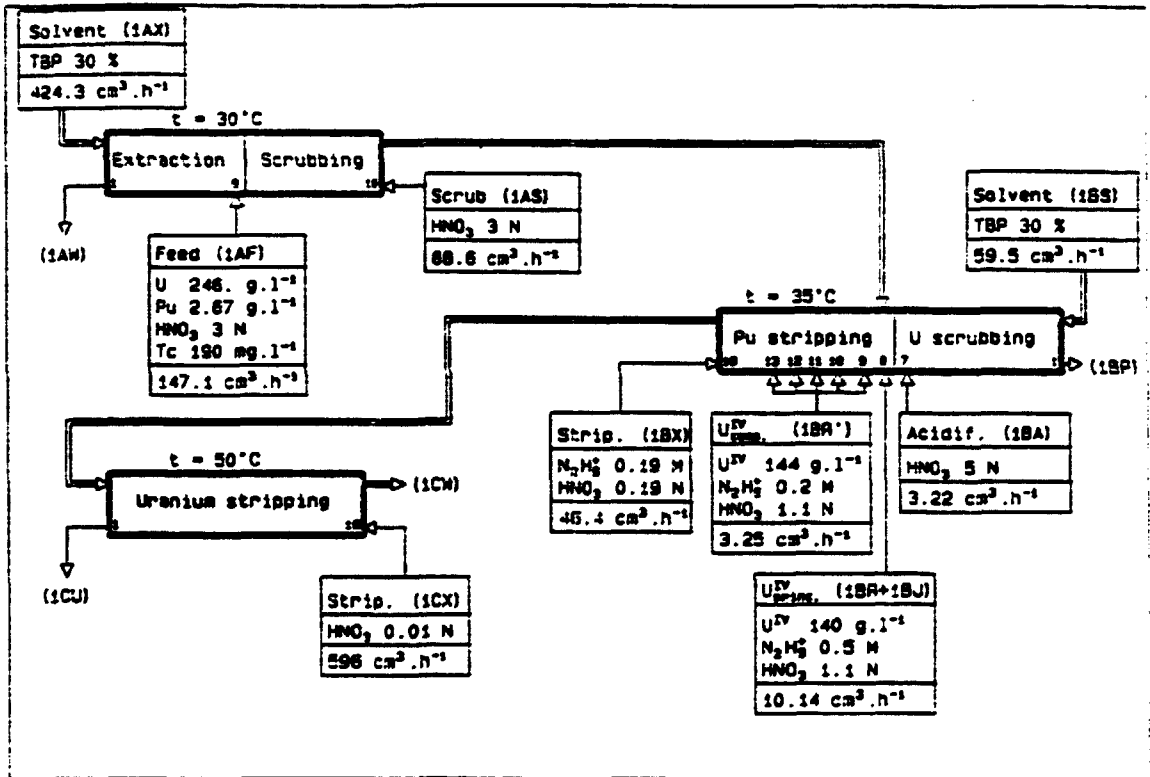
We have now a computer program simulating the reductive stripping of plutonium by uranous nitrate. Its validation is testified by the very good agreement between calculated and experimental concentration profiles, both for alpha active applied experiments and for plant operation results. Although its accuracy has to be improved for some particular species, which requires further experimental investigations - kinetics laws for hydrazine/uranium (IV) reactions for example -, it already appears as an outstanding and qualified tool for industrial uranium/partition studies, and has brought an essential contribution into the design of such an operation for the UP3 french reprocessing plant.

NOMENCLATURE

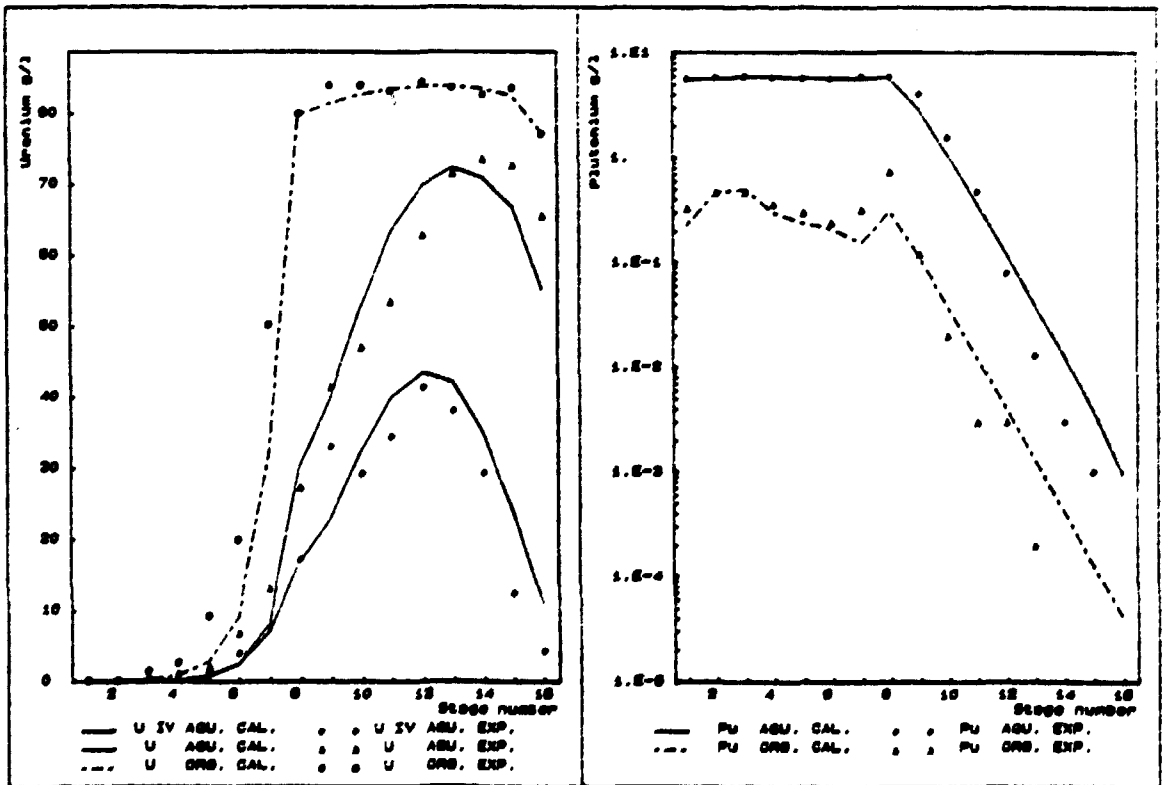
- n_A : "nitrate salting out effect" parameter
 a,b,c... : nitrate salting out effect" factors
 F : Mass transfer flowrate
 V_d : Volume of dispersed phase
 A : specific interfacial area
 K : Mass transfer coefficient
 y : solute concentration in the organic phase
 x : solute concentration in the aqueous phase
 Kd : partition coefficient of the solute
 y* : defined by $y^* = Kd \cdot x$
 d_{32} : Sauter diameter
 Q_t : total throughput
 Q_D : dispersed phase throughput

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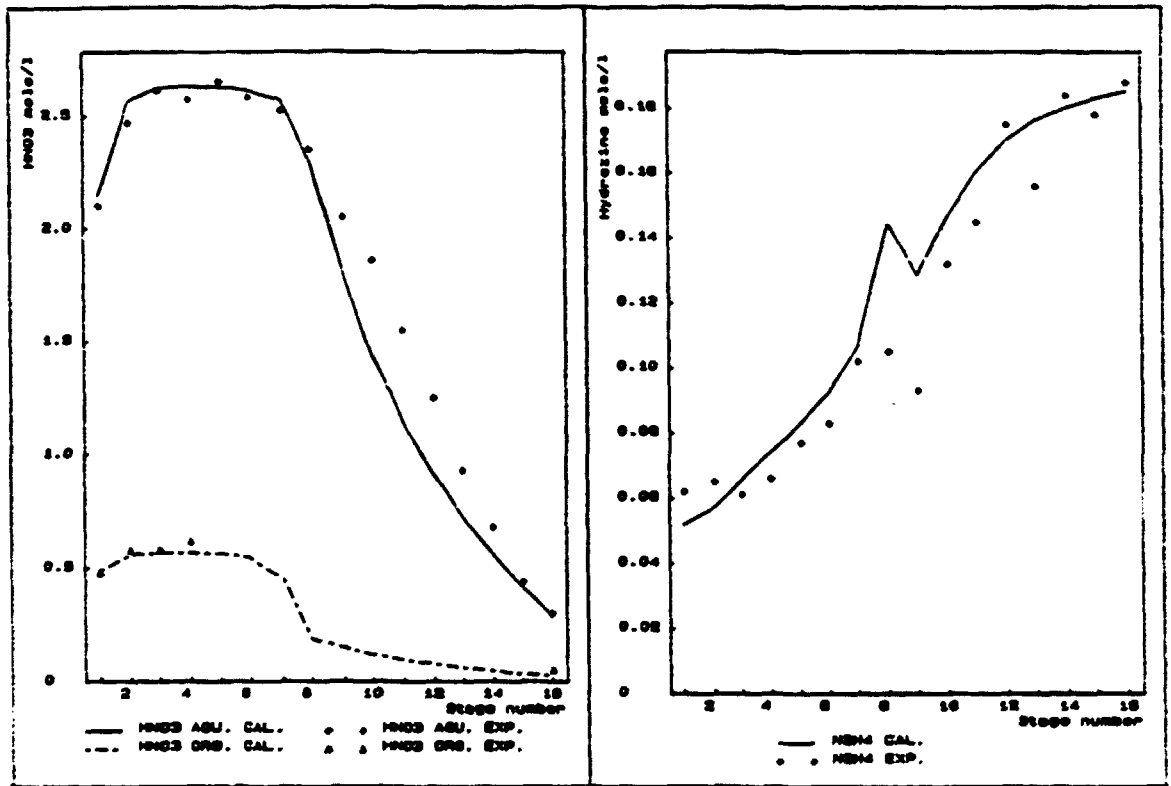


1. ALPHA-ACTIVE EXPERIMENTAL FLOWSHEET FOR MODEL QUALIFICATION



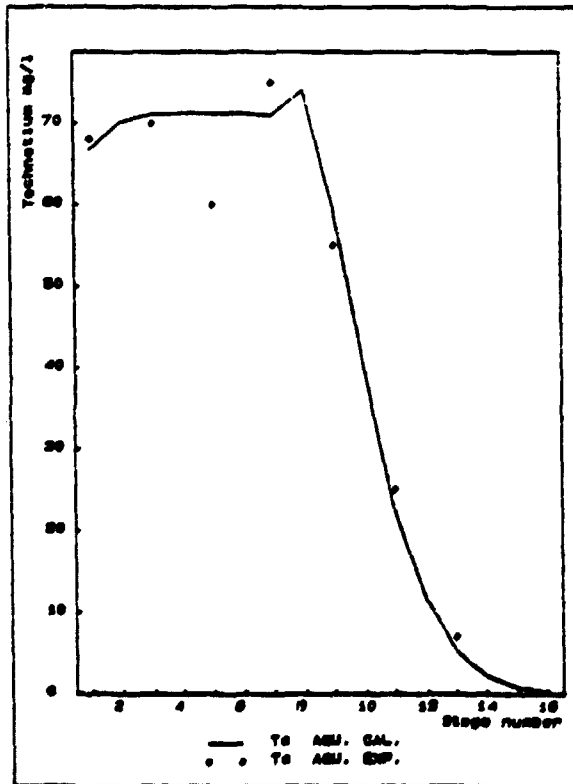
2. URANIUM PROFILES

3. PLUTONIUM PROFILES



4. NITRIC ACID PROFILES

5. HYDRAZINE PROFILES



6. TECHNETIUM PROFILES