FR8502206

CHEMICAL PROPERTIES OF NEPTUNIUM APPLIED TO NEPTUNIUM MANAGEMENT IN EXTRACTION CYCLES OF PUREX PROCESS.

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Alternative ways of managing neptunium in the Purex process are discussed. Main coordination and redox properties of neptunium in nitric medium are reviewed. Kinetics results with reagents consistent with "salt free process" are presented with emphasis on the influence of uranium and plutonium ions, including results about some peculiar behaviour of neptunium in TBP (the so-called cation-cation complexes). Attempts to fit chemical engineering models to neptunium metabolism in extraction equipment (mixer-settlers and pulsed columns) are described.

INTRODUCTION

Until 1980, the potential radiotoxic hazard of the neptunium 237 produced in the irradiated fuel was considered negligible as compared to the plutonium and americium ones [1,2,3] - Recent revision [4] of the neptunium transfer factor from the gastro-intestinal tract to blood made it one of the most dangerous nuclide - Due to its ionic form (NpO_2^+) it shows an ability to migrate easier than the other actinides in the underground that increases the long term risk for this isotope. Americium [241], which gives neptunium [237] by α decay shows the same potential hazard.
Research programms have been developped in many countries about the actinides partitioning from the high level wastes generated by the reprocessing. Alternatives purposes are either to ensure a better conditioning for these isotopes or their transmutation in fast breeder reactor. But the aim of this contributi n will stay in the frame of the reprocessing carried out in actual plants or to be build next years. Our purpose is to examine the alternative ways of the neptunium in the course of the reprocessing related to the knowledge of its main chemical properties and attempts to fit chemical engineering models to neptunium metabolism in extraction equipment.

The figure 1 schematizes the alternative ways of the neptunium in the reprocessing. Due to increasing plutonium contents in actual irradiated fuels (LWR and FBR) the U/Pu partitioning is included in the first extraction cycle in order to minimize criticality problems. Another important point to underline is the development of "salt free" process in order to minimize the volume of radioactive wastes. In figure 1, the way number one for the neptunium is the direct discharge with fission products. But in presently operated plants only about 10 - 20 % neptunium goes this way. This is related

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to extraction parameters and principally a redox reaction with the nitric medium.

Ways number 2 and 3 are especially determined by the reagent used for the U/Pu partitioning Ferrous ion has been used in the past but it presented disadvantages : sulfate ions were introduced that corrodes stainless steel and that salt increased the volume of the wastes. Today two reagents are considered : uranous nitrate and hydroxylammonium nitrate. With uranous nitrate, neptunium takes the way number 2 and follows uranium stream – With hydroxylammonium nitrate that is the third way. For a better understanding of these different behaviours we shall make a short review of the main chemical properties of the neptunium related to the extraction cycles of the reprocessing.

STATE OF ART IN THE NEPTUNIUM CHEMISTRY RELATED TO THE REPROCESSING

Valency states

Redox potentials in $HClO_4$ 1M are summarized on the figure 2. The trivalent state cannot be observed in nitric medium except as transient species.

The pentavalent state exists as NpO_2^+ ion which is the most stable form of the neptunium. Oxydation to hexavalent state as NpO_2^{2+} takes place with a simple electronic exchange. But reduction to neptunium Np^{4+} involves the break of Np-O bonds. So, this step is generally slow. Conversely the oxydation of the Np^{4+} is slow too.

In reprocessing solution there is often mixtures of two valency states Np (V + VI) or Np(V + IV) and the behaviour of the neptunium appears very complicated due to their different affinity for the organic solvent.

Neptunium extraction by tributylphosphate (TBP)

On figure 3, actinides : uranium, neptunium and plutonium have been arranged from left to right with increasing ability to extraction by TBP. Neptunium V, the most stable species, is the less extractable – so that neptunium can be extracted either in oxidizing medium as Np VI or in reducing medium as Np IV. In intermediate media it will be difficult to predict its behaviour.

Distribution coefficients of neptunium (IV), (V) and (VI) in the absence of uranium are collected on table 1. Neptunium IV and VI distribution data in the presence of large amount of uranium [5] are shown in figure 4.

But generally redox reactions occur during extraction cycles. Also, in order to build chemical engineering model, it is necessary to know kinetics of such a reaction.

Redox chemistry of the neptunium in the reprocessing

On the table 2 the redox reactions involved in the reprocessing are summarized.

- Disproportionation of NpO_2^+

This slow reaction is equilibrated. It strongly depends on the acidity:

$$2\ NpO_2^+ + 4\ H^+ \rightleftharpoons Np^{4+} + NpO_2^{2+} + 2H_2O \tag{1}$$
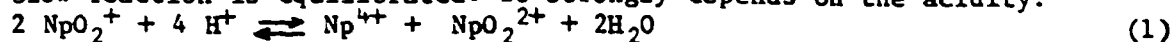
Values of the equilibrium constant are weak (from 1.4×10^{-4} to 4.6×10^{-4} in the range 5.5 to 8.0 M HNO_3 [6] and for acidities under 4M HNO_3 this reaction will be negligible.

- Oxydation by nitric acid.

Redox system of the nitrogen oxides is complicated.
With neptunium V the overall reaction is

$$NpO_2^+ + 3/2\ H^+ + 1/2\ NO_3^- \rightleftharpoons NpO_2^{2+} + 1/2\ HNO_2 + 1/2\ H_2O \tag{2}$$
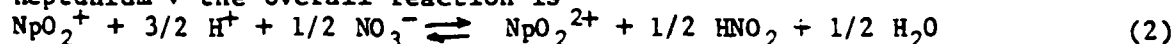
The apparent constant at 25°C

$$Kapp = \frac{[Np(VI)] \cdot [HNO_2]^{1/2}}{[Np(V)] \cdot [HNO_3]^2}$$

increases from 3.2×10^{-4} to 9.3×10^{-4} mole$^{-1}.5.1^{1.5}$ when acidity varies from 1 to 4 M [7]. This reaction is rather fast when nitrous acid concentration is about 10^{-3} M which is the order of magnitude observed in the solution of the irradiated fuel. The rate depends on the ratio $[HNO_2]/[Np(V)]$ and has been expressed by the equation:

$$-d[Np(V)]/dt = 1.8 \times 10^{-3}[H^+]^{1.3}[NO_3]^2[HNO_2] \cdot [Np(V)]/\{[HNO_2]+[Np(V)]\}$$

mole.1^{-1}.mn^{-1} at 25°C, with an activation energy equal to 15 kcal.mole^{-1}[8]. That reaction is responsible for the neptunium extraction in the first cycle. In the mixture Np(VI+V), the neptunium VI is extracted and the equilibrium (2) is continuously shifted to the right hand.

Neptunium can be refluxed almost completely with waste stream by addition of nitrous acid to shift the equilibrium to the left hand. This process have been experimented in Savannah River [9]. It presents many disavantages
  - extraction cycle involves high uranium saturation of solvent at the feed stage that makes a dangerous build-up of plutonium.
  - nitrous acid is introduced as sodium nitrite that increases the wastes and sodium content in the fission product.
  - nitrous acid is not convenient for the subsequent U/Pu partitionning and can speed up solvent degradation.

Nitric oxydation of the tetravalent neptunium is slow at room temperature :

$$Np^{4+} + 1/2\ NO_3^- + 3/2\ H_2O \longrightarrow NpO_2^+ + 1/2\ HNO_2 + 5/2\ H^+ \tag{3}$$
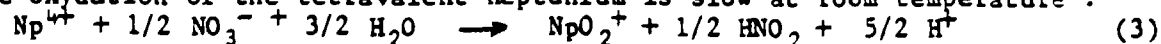
Iron is a catalyst above 10^{-5} M. The kinetic equation has been expressed as:
$$-d[Np(IV)]/dt=1.9\times10^{-3}[HNO_2]^{-1/2}[Np(IV)] \cdot [Np(V)]\ mole.1^{-1}.mn^{-1}$$

at 22°C with an apparent activation energy equal to 25.1 ± 2.6 kcal/mole [8]. Mechanism involve NpV disproportionation which is the limiting step for high HNO_2 concentrations. This reaction essentially takes place in evaporator after the partitioning. cycle.

Reduction reactions

In the U/Pu separation, and in plutonium purification cycles, powerful reducing agents are used. Uranous nitrate and hydroxylammonium nitrate have been chosen, as convenient for salt free process. With these reagents, plutonium is reduced to trivalent state, which can react with neptunium ions.

- Reaction with Pu III

The reaction is equilibrated:

$$NpO_2^+ + Pu^{3+} + 4 H^+ \rightleftharpoons Np^{4+} + Pu^{4+} + 2H_2O \tag{4}$$
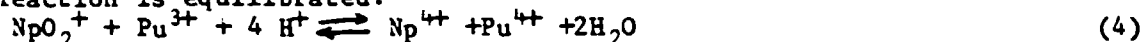
At 69.5°C ($\mu = 2$) in nitric acid, its velocity has been expressed by the equation :

$$-d[Np(V)]/dt = 5,15[Np(V)] \cdot [Pu(III)] \cdot [H^+]^{-1.3} \text{ mole.l}^{-1}.\text{mn}^{-1}$$

with 20.3 kcal/mole as energy of activation.[10]

Data have been published for the reverse reaction [11]. In the range of acidity 0.7 to 2.0 M HNO_3, at 39°C, the rate of this reverse reaction may be expressed by the equation :

$$-d[Np(IV)]/dt = 70[Np(IV)] \cdot [Pu(IV)]/[HNO_3]^4 \text{ mole.l}^{-1} \text{ mn}^{-1}$$

The value of the activation energy was found equal to 34.6±0.5 kcal/mole. With plutonium III concentrations above 5g/l, like in plutonium backwashing, the reduction of neptunium V by plutonium III predominates as compare to the reduction of neptunium V by uranous or hydroxylammonium nitrate.
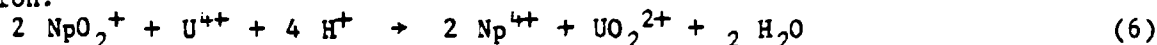
- Reaction with uranous nitrate

In aqueous solution, the neptunium VI reduction to neptunium V is fast :

$$2NpO_2^{2+} + U^{4+} + 2H_2O \rightarrow 2NpO_2^+ + UO_2^{2+} + 4H^+ \tag{5}$$
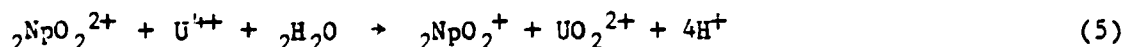
In perchloric medium [12] its equation of rate can be expressed by :

$$d[Np(V)]/dt = 1.3 \times 10^3 [Np(VI)] \cdot [U(IV)] \cdot [H^+]^{-0.97} \text{ mole.l}^{-1}\text{mn}^{-1}$$

The reduction of the neptunium V to neptunium IV is much slower. The overall reaction:

$$2 NpO_2^+ + U^{4+} + 4 H^+ \rightarrow 2 Np^{4+} + UO_2^{2+} + 2 H_2O \tag{6}$$

Its mechanism is very complicated. The rate of the reaction has a minimum value at intermediate acidity (0.5 to 1 M HNO_3). This behaviour has been explained [13] by neptunium III formation as transient species _ So that, the main product, Np IV acts as an accelerating reagent in weakly acid media (less than 1 M HNO_3). The kinetic equation proposed at $[H^+]$ greater than 1 M, (acidities used in plutonium cycles) is:

$$d[Np(IV)]/dt = \{1.6[H^+]^{-2} + 1.42 [H^+]\} \cdot [Np(V)] \cdot [U(IV)] \text{ mole.l}^{-1}\text{mn}^{-1}$$

at 56°C, with an activation energy equal to 9.6±0.3 kcal/mole. But in the frame of the U/Pu partitioning other facts must be taken into account.

Both U(VI) and Pu III act as catalysts. In the case of U(IV)-U(VI) systems we have in addition photochemical reactions induced by room lights of the laboratory, that accelerate the reduction of the neptunium. Of course, this phenomenon is not observed in metallic industrial contactors.

Conversely the catalytic influence of the plutonium III makes simpler the system. In fact, with large amounts of plutonium in aqueous solution the previously cited reaction (4) predominates.

In organic medium we have also redox reactions. Both Np(VI) and U (IV) are easily solvated by TBP solutions. Our spectrophotometric data on 30 % TBP solutions in dodecane showed the direct reduction of the Np(VI) to Np(IV)as:

$$Np(VI)org + U(IV)org \rightarrow Np(IV)org + U(VI) \ org$$

Typical order of magnitude for the time of half reaction was found to be about 1 minute.

Neptunium behaviour has been studied in laboratory scale U/Pu partition with U(IV) as a reducing agent, both in mixer-settler and pulsed column. The main part of the neptunium follows the uranium stream. This is qualitatively explained by:
  . Residence times in the extractors are long enough to get almost completely Np(IV)
  . In the solvent washing of the Pu(III) stream, O/A ratio is adjusted to extract U(IV) despite the low values of its distribution coefficient and then Np(IV) is extracted toward uranium organic stream.
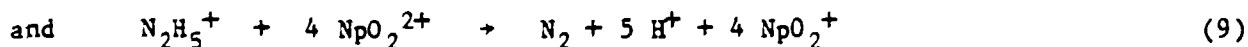That is the way number 2 on the figure 1.

Runs in small pulsed columns pilot have demonstrated decontamination factors of 100 for the plutonium with respect to the neptunium.

In this case it is necessary to manage a special section in the next cycle of uranium purification in order to eliminate the neptunium. This can be done by stabilizing the neptunium continuously at pentavalent.

Reduction by hydrazinium nitrate

At moderated acidity and room temperature the reduction from V to IV is very slow. So, it is interesting to use hydrazinium nitrate to get almost pure Np(V) from V-VI state mixture.

Two parallel reactions occur with Np(VI)

$$2 \ N_2H_5^+ + 2 \ NpO_2^{2+} \rightarrow N_2 + 2 \ NH_4^+ + 2 \ NpO_2^+ + 2H^+ \tag{8}$$

$$\text{and} \qquad N_2H_5^+ + 4 \ NpO_2^{2+} \rightarrow N_2 + 5 \ H^+ + 4 \ NpO_2^+ \tag{9}$$

The first one predominates under conditions of large excess of hydrazine used in the processes. In that case the rate of reduction is described by the equation:

$$d[Np(V)]/dt = 8.3 \ [Np(VI)].[N_2H_5^+].[H^+]^{-1.3} \ mole.l^{-1}mn^{-1}$$

in the range of $[H^+]=0.5 - 2$ M at ionic strength 2 and 20°C. The activation energy between 20 and 40°C was found to be 16.8 kcal/mole [14].The presence of uranium VI has no effect. This reaction have been checked in the course of a miniscale second uranium cycle. The feed contained uranium VI and neptunium V + VI. Diluted hydrazinium nitrate was introduced continuously with the feed and in the scrubbing section. Uranium was found decontaminated with respect to the neptunium with factors in the range 10 to 25. (See table 3).

Reduction by hydroxylammonium nitrate

Hydroxylammonium nitrate may be used in the same way as hydrazinium nitrate for the neptunium reduction from VI to V.In uranium cycles this reagent can give decontamination with respect to both neptunium and plutonium.

Neptunium VI reduction by hydroxylammonium occurs faster than reaction with hydrazinium. Koltunov [15] described the reaction rate by the equation:

$$-d[Np(VI)]/dt = 92.1 \ [Np(VI)].[NH_3OH^+].[H^+] \ mole.l^{-1}.mn^{-1}$$

at 15°C (μ=2) with 19.6 kcal/mole as energy of activation.So in a partionning cycle using hydroxylammonium nitrate the limiting reaction for neptunium will be the reduction from V to IV. In excess,hydroxylammonium ion is oxidized to nitrogen [16]

$$2 \ NpO_2^+ \ + \ 2 \ NH_3OH^+ \ + \ 4H^+ \rightarrow \ 2 \ Np^{4+} + N_2 + 6 \ H_2O \qquad (10)$$
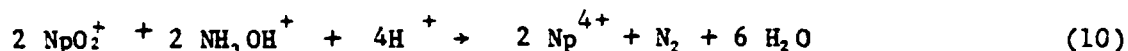
The overall equation for its velocity has been expressed as:

$$-d[Np(V)]/dt = 0.045[Np(V)].[NH_3OH^+].[H^+]^{1.65} \ mole.l^{-1}.mn^{-1}$$

at 92°C (μ=4).

The value 25.2±1.2 kcal/mole was found for the energy of activation.
In fact, with large amounts of plutonium III the reduction of the neptunium V goes using a different pathway and the velocity is well described using the rate equation related to the reaction (4).In biphasic systems, plutonium IV and neptunium IV are partly extracted by the solvent that shifts completely the equilibrium to the right-hand in the aqueous stream.

Cation-cation complexes.

So called cation-cation complexes have been pointed out more than twenty years ago [17]. Specially between uranium VI and neptunium V or between neptunium VI and neptunium V were investigated using spectrophotometry and it has been shown that formation of these complexes obeys the law of mass action [18] but with a weak apparent constant of equilibrium (K=3.0 and 3.7 for UVI-NpV and NpVI-NpV complexes). In aqueous solutions such complexes give very small change in the neptunium behaviour-except for analysis using direct spectrophotometry in concentrated solution of uranium.

Recent studies [19] have shown large enhancement of the apparent equilibrium constant of these complexes in organic medium (about 100 for U VI-NpV complex in 30 % TBP solution). Increasing concentrations of TBP and H_2O in the organic solvent decrease the complexing.This is illustrated by the figure 5. Studies about their influence on redox reaction of the neptunium in organic phases are in progress. But scouting works showed for instance that the neptunium VI is reduced by nitrous acid in TBP medium if uranium is present in significant amount.

Another interesting cation-cation complexes is the bi-nuclear complexe NpV-Ru(NO)III which has a slow kinetic of formation [19]. It is reinforced by DBP (degradation product of the TBP) and could be one possible way to explain ruthenium retention in the used solvent of plants.

MODELISATION OF NEPTUNIUM BEHAVIOUR IN THE CYCLES OF THE PUREX PROCESS

As seen before, neptunium ions are subjected to change of oxidation state in most of the extraction cycles. These reactions are fast enough to be significant and too slow to reach the equilibrium.

Distribution data and kinetic data are not sufficient to compute an extraction in which change of oxidation state occurs. Volumes of apparatus and pipes, nature of emulsion in these devices are needed: the assumption of "ideal stage" is too short and HTU or NTU are meaningless.

Neptunium behaviour in the first extraction

It depends upon the reaction between pentavalent neptunium and nitric acid described earlier. As Nitrous acid has an influence on the equilibrium and rate-laws, data have been determined on its distribution between aqueous phases of nitric acid and hexavalent uranium and organic ones of TBP [20].

The model design assumes:
- no extraction of the pentavalent neptunium
- consequently no redox reaction in the organic phase

Four steps are considered :
1. Oxidation of NpV to NpVI in aqueous phase,
2. Reduction of NpVI to NpV in aqueous phase,
3. Extraction of NpVI from aqueous phase to solvent,
4. Back-extraction of NpVI from solvent to aqueous phase.

This model has been developped for mixer-settlers only. The mixer part is assumed to be a Continuous Perfectly Stirred Tank (C.P.S.T.) with aqueous and organic inlets and one emulsion outlet. As the chemical rate is rather slow, step 1 and 2 are considered as limiting and steps 3 and 4 are assumed infinitely fast in the mixer part. In the settler part, the rates of steps 3 and 4 are conversely assumed nil. Most of the calculations has been made assimilating the aqueous part of the settler to a CPST. Some attempts to calculate with an alternate model for settler (plug-flow) failed to exhibit significant differences.

In the settler there is no neptunium exchange between solvent and aqueous phase so that the redox reaction is close to equilibrium and any model is convenient. Nevertheless with the CPST assumption the whole model is linear with respect to neptunium concentrations and computation is therefore more straightforward.

More than 20 runs were conducted with miniature pilot of mixer-settlers. The agreement between calculated and experimental results is good except in the washing section of runs with uranium. The figure 6 shows one run without uranium and one run with uranium - in which calculated results underestimate the reduction reaction of Np VI by HNO_2 in the washing section.

Two explanations can be proposed:
- photochemical reduction of uranium VI, inducing reduction of neptunium VI.
- contribution of the cation-cation complexation of Np V by UVI in the solvent. Without uranium, the reduction of Np V by HNO_2 in the solvent is very weak, because the equilibrium (2) is shifted on the right hand due to the strong Np VI and HNO_2 solvation by the TBP. The equilibrium constant in the solvent can be estimated by the following calculation:

$$K \text{ aqueous} = \frac{\left[Np(VI)aq\right] \cdot \left[HNO_2 aq\right]^{1/2}}{\left[Np(V)aq\right] \cdot \left[HNO_3 aq\right]^2}$$

$$K \text{ organic} = \frac{\left[Np(VI)org\right] \cdot \left[HNO_2 org\right]^{1/2}}{\left[Np(V)org\right] \cdot \left[HNO_3 org\right]^2}$$

$$K \text{ organic} = \frac{D\left[Np(VI)\right] \cdot \left[D(HNO_2)\right]^{1/2}}{D\left[Np(V)\right] \cdot \left[D(HNO_3)\right]^2} \times K \text{ aqueous}$$

Where $D[Np(V)]$, $D[Np(VI)]$, $D(HNO_2)$ and $D(HNO_3)$ are the distribution coefficients of the different species. With 3M HNO_3 in aqueous phase and 25°C we find
$$K \text{ organic} = 6.2 \times 10^4 \times K \text{ aqueous} = 41 \text{ mole}^{-1.5}.l^{1.5}.$$
So that the ratio $Np(V)/Np(VI)$ is very small.

With uranium the cation-cation complexation of the NpV acts as a sink. The reaction (2) is therefore shifted on left hand producing a noticeable amount of pentavalent neptunium. Explorating works on the kinetics of the reaction (2) showed that its rate in organic medium has the same order of magnitude than in aqueous medium.

Neptunium behaviour in uranium extraction cycle in the presence of hydrazine nitrate.

We consider the feed of such extraction as a mixture of neptunium V et VI in the uranium solution. Hydrazine nitrate in the aqueous stream of the washing section can provide selective decontamination owing to the irreversible reduction of the neptunium to pentavalent state. This reaction (8) has been described earlier. Modeling this decontamination in mixer-settlers is easy: the model already discussed before is convenient and the calculations are even simpler because the reaction is irreversible. Using this model we can compare calculated results with scale laboratory mixer-settlers and industrial scale devices, taking into account the internal recycling of the aqueous phase in each stage in the washing section. This important parameter which exists only in the industrial apparatus favours the chemical reaction so that laboratory equipments give noticeably pessimistic neptunium decontamination factors.

To check consequences on the performances by using pulsed columns instead mixer-settlers, six runs with pulsed columns ($\emptyset$ 25 mm) were conducted and compared with mixer-settlers runs in laboratory. Results collected in table 3 show that, in pulsed columns, the neptunium decontamination factor doesn't seem to be dependent upon the hydrazine nitrate concentration, contrary to the mixer-settlers runs. As the aqueous phase was the continuous one with low retention factors (8 to 14 %) residence times of the aqueous stream in the washing column were about 80 mn (less than 2 minutes for the solvent). The reaction (8) with half time varying from 0.6 to 12 mn is almost complete. Therefore mass transfer was the limiting step.

We elaborated a rough model assuming that distribution factor and mass transfer coefficient are constant in the washing section. We assumed that the interface area is proportionnal to the retention ratio.

It is worth noting that the general solution has the form:
$$[Np(VI)aq] = A.\exp(-\alpha.L) + B.\exp(\beta.L)$$

Where A, B, α, β are positive constants and L is the lenght of the washing column. With increasing hydrazine nitrate concentrations the rate of the reduction increases, and becomes much faster than transfer, therefore accuracy of the calculation on the term $B.\exp(\beta.L)$ becomes very poor.

So that, we devised a method which is convenient for high values of the reduction rate. This is a kind of steady state approximation which mixes up chemical reaction and mass-transfer kinetics. We consider the figure 7. In a "slice" of column of thickness dL, we assume the balance of the mass flow follows this rule:
$$\emptyset (NpVI \text{ org} \rightarrow NpVIaq) = (NpVI \text{ aq} \rightarrow NpV \text{ aq})$$

So that:

$$[NpVI \text{ aq}].(L+dL) = [NpVI \text{ aq}].L$$

then, the general solution is:

$$\left[NpV\ aq \right] = C.\ exp\ (-\gamma.L)$$

The model allowed us to compute a mass-transfer coefficient which conversely was used to recalculate the runs with very good agreement with experimental data.

In a industrial column it is clear that rate of mass-transfer will be better than in a laboratory and therefore the chemical reaction will be limiting but performances will be increased.

Neptunium behaviour in U/Pu partitioning

Modelisation of U/Pu partitioning is in progress. This is a three bodies model complicated with plutonium changes of valency.
So, until now, no model has been developped for the neptunium behaviour in cycles which involve plutonium and neptunium redox reactions. That's too much intricated. Only approximate valuation can be made using the assumption that reduction of the neptunium to tetravalent state is complete and using the values of the distribution coefficients shown on figure 4.

CONCLUSION

Qualitative chemical behaviour of the neptunium in the reprocessing is well known. Large part of the data needed to compute its quantitative behaviour exists today as distribution coefficients and kinetics data of the redox reactions. However, some data are lacking to get enough accuracy in the calculations. Ranges of the measurements do not fit exactly with these of the extraction cycles of the plants and, particularly kinetics data and equilibrium constants of redox reactions in organic medium have to be more investigated. As we noticed earlier, the performances may be different in industrial equipment from those computed with laboratory data.Also,it must be kept in mind that significant mass-transfer data are generally collected on large rigs and not in laboratory where conversely chemical data are measured.In fact the use of models more and more sophisticated can help this scale transposition. In the other hand, in reprocessing plant, where high decontamination factors are demanded, it is fictitious to calculate models assuming perfectly clean solvent. Degradation products, dibutylphosphoric acid (DBP) for instance modify the behaviour of elements traces: the better the decontamination the smaller are the concentrations and more the DBP enhances the extraction of the polluants. The cation-cation complexe neptunium V - ruthenium nitrosyle is especially formed slowly and stabilized by DBP. Such a compound can makes significant differences with computed results.Data on the rate of formation of the DBP,its coordination chemistry in both organic and aqueous solutions,its influence on kinetics of the redox reactions have to be collected and took into account. So, the main limitations don't come from chemical engineering but from chemistry.

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Table 1.

Distribution coefficients of Np(IV), Np(V), Np(VI) between nitric acid and 30 vol. % TBP in dodecane at 22°C [5] [7]

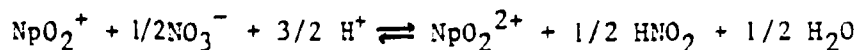| Aqueous HNO_3 concentration at equilibrium (mole/l)	Distribution coefficients		
	Np(IV)	Np(V)	Np(VI)
0,5	0,20		2,2
1	0,75	0,012	5,3
2	2,1	0,0145	12,5
3	3,5	0,0175	17
4	5,2	0,020	20
5	7,1		22

Table 2.

Main redox reactions of neptunium in extraction cycles of the reprocessing

Disproportionation : slow and equilibrated reaction

$$2 \; NpO_2^{+} + 4 \; H^{+} \rightleftharpoons NpO_2^{2+} + Np^{4+} + 2 \; H_2O$$
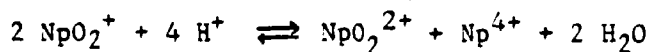
Oxidation by nitric acid : slow and equilibrated reactions

$$NpO_2^{+} + 1/2 NO_3^{-} + 3/2 \; H^{+} \rightleftharpoons NpO_2^{2+} + 1/2 \; HNO_2 + 1/2 \; H_2O$$

$$Np^{4+} + 1/2 \; NO_3^{-} + 3/2 \; H_2O \rightleftharpoons NpO_2^{+} + 1/2 \; HNO_2 + 5/2 \; H^{+}$$

Reduction by uranous nitrate
in aqueous phase : Np(VI) → Np(V)   very fast
                      Np(V) → Np(IV)   slow (faster with Pu)

in organic phase : Np(VI) → Np(IV)   fast

Reduction by hydrazinium nitrate
                      Np(VI) → Np(V)   fast
                      Np(V) → Np(IV)   very slow

Reduction by hydroxylammonium nitrate
                      Np(VI) → Np(V)   fast
                      Np(V) → Np(IV)   slow (faster with Pu)

TABLE 3. COMPARISON OF NEPTUNIUM DECONTAMINATION FACTORS OBTAINED IN DIFFERENT
URANIUM CYCLES RUNS IN LABORATORY WITH MIXER SETTLERS OR PULSED COLUMNS
(SCRUBBING ACIDITY 1.5 M HNO_3 IN EVERY RUN).

| Extractor type	θ C	HNO_3(M) in the feed	$N_2H_5^+$(M) in scrubbing	Ratio O/A Extn	Sc	D.F. Np	Feed contents
Mixer -settler	30-33°C	1,5	0,1	1,57	6,5	100	U 185 g/1, Np 1 g/1, Pu 1 g/1, $NaNO_2$ 5.10^{-3}M
Mixer -settler	30-33°C	1,5	0,035	1,57	6,5	10	U 185 g/1, Np 1 g/1, Pu 1 g/1, $NaNO_2$ 5.10^{-3}M
Mixer -settler	35°C	2,5	0,001	2	5,2	3	U 300 g/1, Np 77 mg/1, Pu 21 mg/1, $N_2H_5^+$ 2.10^{-3}M (introduced with the feed)
Pulsed column	25°C	2,5	0,040	2,2	6,4	26	U 298 g/1, Np 263 mg/1, Pu 63 mg/1, Fe 21 mg/1 $N_2H_5^+$ 2.10^{-3}M (introduced with the feed)
Pulsed column	25°C	2,52	0,098	2,2	6,4	15	U 309 g/1, Np 210 mg/1, Pu 57 mg/1, Fe 11 mg/1, $N_2H_5^+$ 2.10^{-3}M (introduced with the feed)
Pulsed column	25°C	2,52	0,0047	2,2	6,4	10	U 309 g/1, Np 210 mg/1, Pu 57 mg/1, Fe 10 mg/1, $N_2H_5^+$ 5.10^{-3}M (introduced with the feed)
Pulsed column	25°C	1,55	0,038	2,2	6,4	20	U 300 g/1, Np 262 mg/1, Pu 56 mg/1, Fe 46 mg/1, $N_2H_5^+$ 0
Pulsed column	25°C	1,5	0,097	2,2	6,4	19	U 300 g/1, Np 267 mg/1, Pu 57 mg/1, Fe 7,1 mg/1 $N_2H_5^+$ 0
Pulsed column	25°C	1,5	0,005 à 0,024	2,2	6,4	15	U 298 g/1, Np 222 mg/1, Pu 42 mg/1, Fe 4,3 mg/1, $N_2H_5^+$ 5.10^{-3}M (introduced with the feed)

FIGURE I .DIFFERENT WAYS FOR THE NEPTUNIUM.
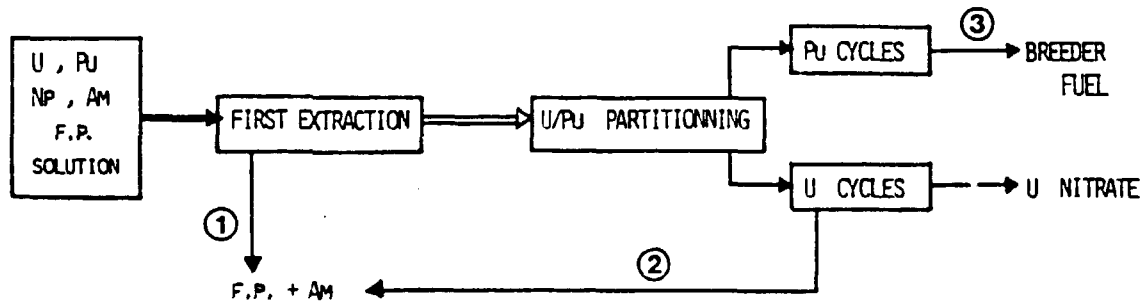
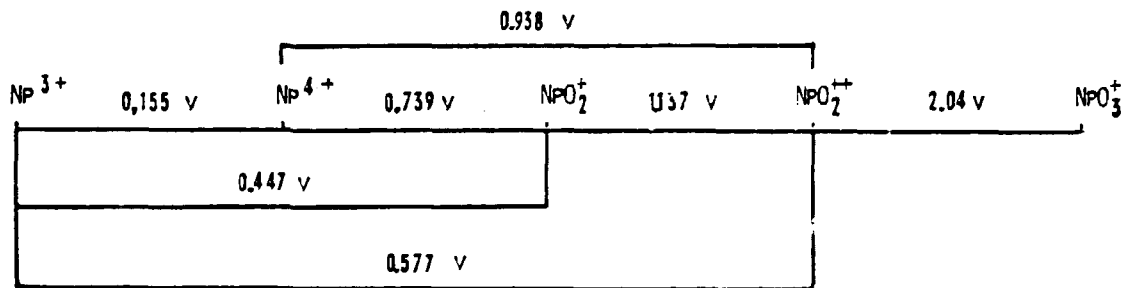FIGURE 2. POTENTIAL DIAGRAM OF NEPTUNIUM IN $HClO_4$ I M.

FIGURE 3 . EXTRACTABILITY IN TBP OF URANIUM,NEPTUNIUM AND PLUTONIUM.
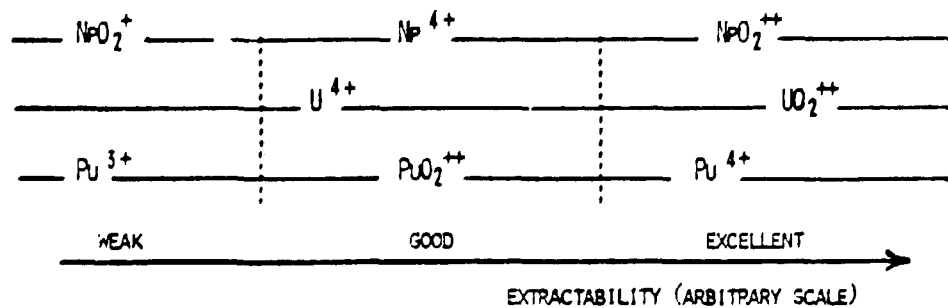
FIGURE 4. DISTRIBUTION COEFFICIENTS OF Np^{IV} AND Np^{VI} BETWEEN 30 VOL.% TRIBUTYLPHOSPHATE IN DODECANE AND NITRIC SOLUTIONS AS A FONCTION OF ORGANIC URANIUM CONCENTRATIONS.
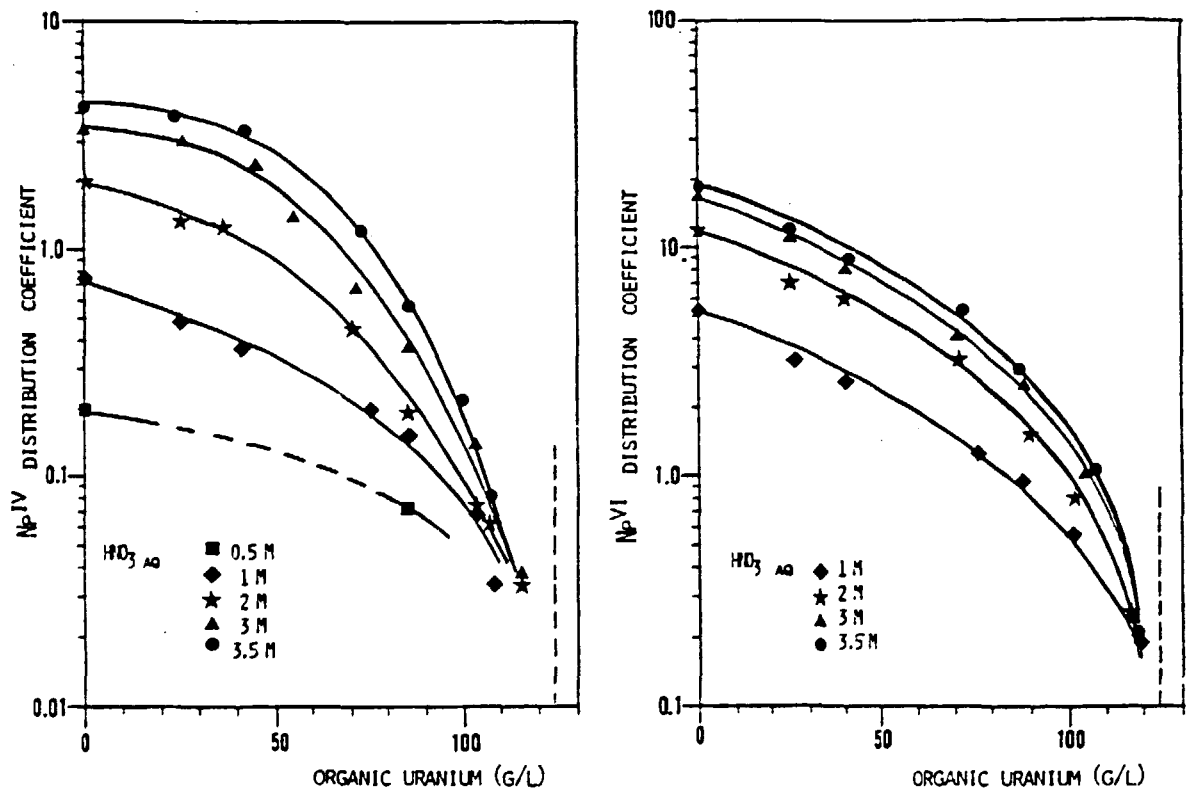

FIGURE 5. WATER INFLUENCE ON THE $Np^{V}-U^{VI}$ COMPLEX STABILITY (IN 30 VOL.% TBP IN DODECANE, RANGE OF URANIUM CONCENTRATIONS FROM 0.0045 TO 0.319 M).
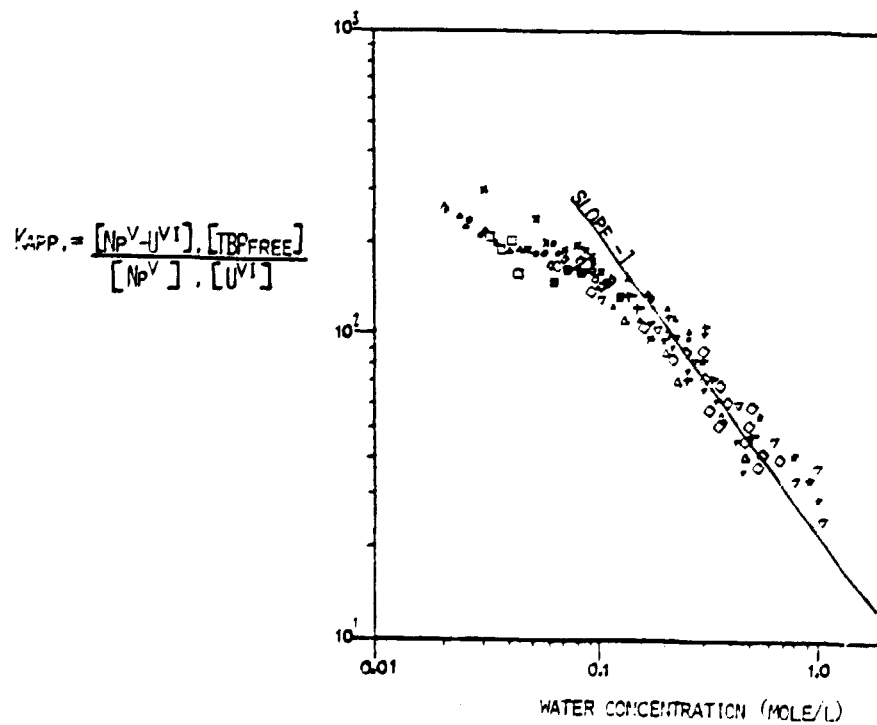
$$K_{APP.} = \frac{[Np^{V}-U^{VI}] \cdot [TBP_{FREE}]}{[Np^{V}] \cdot [U^{VI}]}$$

FIGURE 6. COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED PROFILE
OF NEPTUNIUM, IN THE FIRST EXTRACTION CYCLE.

ORGANIC PHASE: ■ EXPERIMENTAL --- CALCULATED
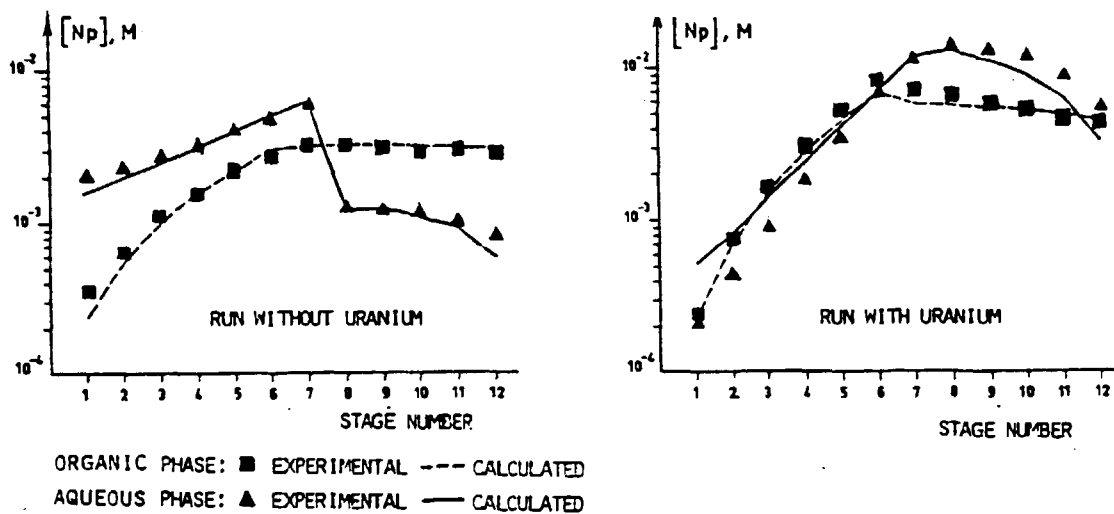AQUEOUS PHASE: ▲ EXPERIMENTAL ── CALCULATED

FIGURE 7 . SCHEMATIC FLOW DIAGRAM IN A SLICE OF COLUMN.