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# Development of a New Process for the Selective Extraction of Uranium from Phosphate Rocks

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## Introduction and context

Chemistry of Uranium in phosphoric acid

Limits and optimization of the Oak Ridge process (reference)

## Development of a new process

Laboratory Parametric Studies

Modelling of the extraction with DEHCNPB

Flowsheet design

Counter-current test in PROUST platform

## Conclusions

# Introduction and Context

## ■ Uranium concentration in phosphoric acid ores: production and resources

Country	Estimated production in 2010 (Mt P <sub>2</sub> O <sub>5</sub> )	Total reserves (Mt P <sub>2</sub> O <sub>5</sub> )
Algeria	2.0	2200
Australia	2.8	82
Brazil	5.5	340
China	65	3700
Egypt	5	100
Israël	3	180
Jordania	6	1500
Morocco	26	50000
Russia	10	1300
South Africa	2.3	1500
Syria	2.8	1800
Tunisia	7.6	100
USA	26.1	1400
Other countries	11.7	865
<b>Total</b>	<b>176</b>	<b>65000</b>



**4 millions tons of potentially « recoverable » uranium**

### ■ But low U concentration

(mainly 60 to 200 ppm)

- **Production of U** as a by-product of phosphoric acid production commercially competitive but limited at **10 ktU/ year** (20% current world demand)

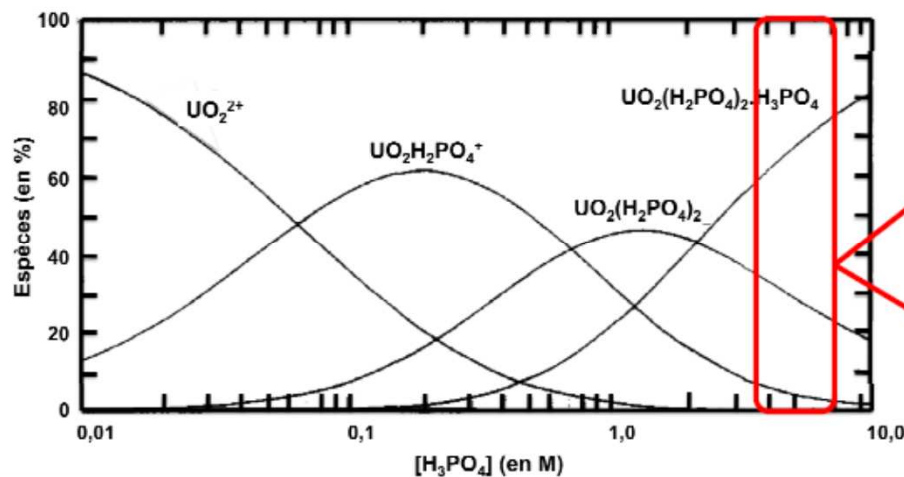
(S. Gabriel, A. Bashwitz, G. Mathonnière, F. Fizaine, T. Elouet Resources Policy 38 (2013) 458-469)

Source AIEA Safety Reports Series N°78

- U considered as impurity vs other cations as Ca, Mg, Fe, Al

Elément	Concentration (g/L)	Elément	Concentration (g/L)
Ca	3.3	Al	1.8
Mg	2.8	Na	0,4
Fe	2.2	U	0.14

- Strongly complexed in  $\text{H}_3\text{PO}_4$  (26-32%  $\text{P}_2\text{O}_5$  (4-5.5 M  $\text{H}_3\text{PO}_4$ ))



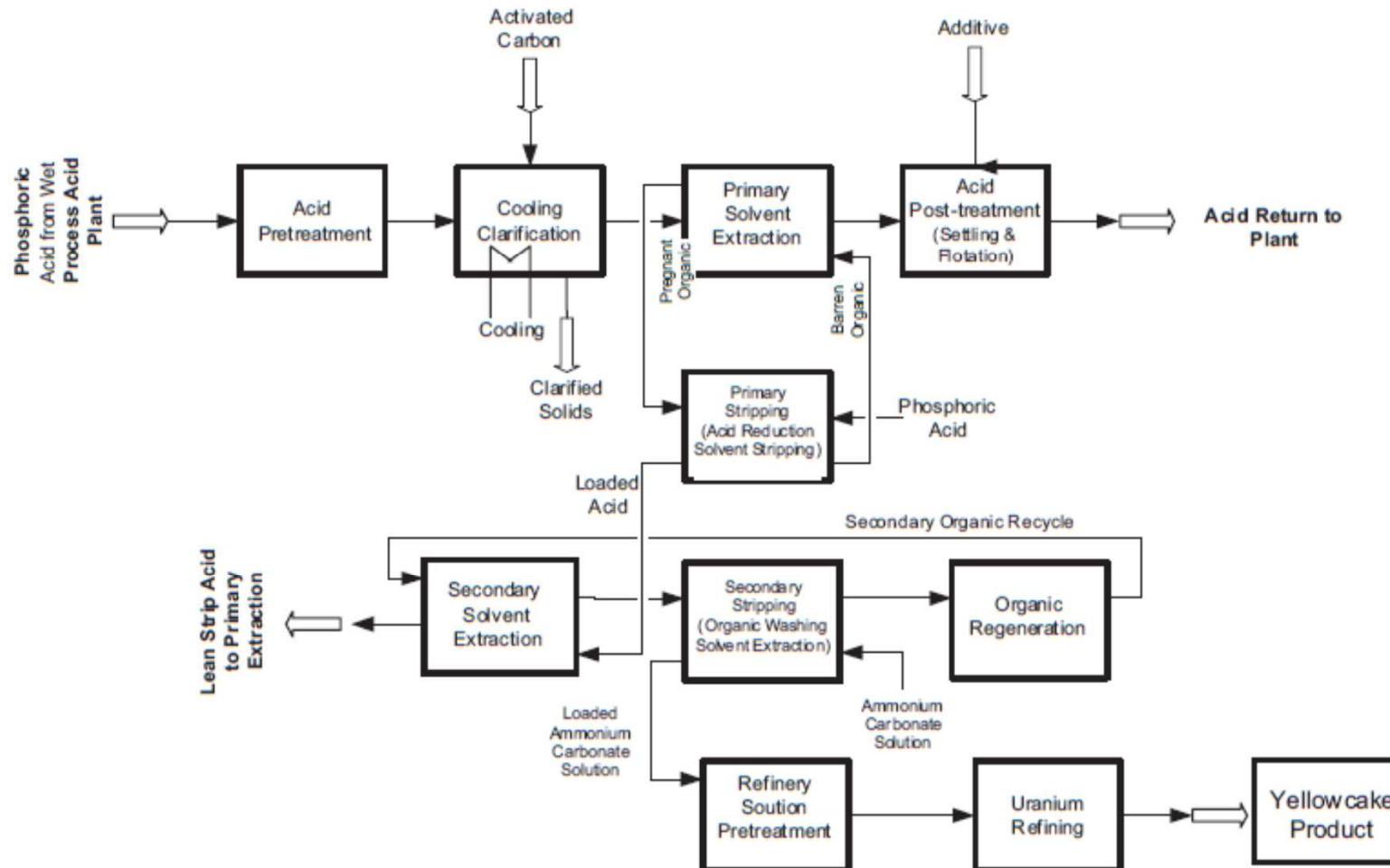
Thamer (JACS, 1957, 79, 4298) :

- ◆  $\text{UO}_2(\text{H}_2\text{PO}_4)_2$  Minor specie
- ◆  $\text{UO}_2(\text{H}_2\text{PO}_4)_2(\text{H}_3\text{PO}_4)$  Major

Elyahyaoui et al. J. Less-Com. Met., 1987, 135, 147) :

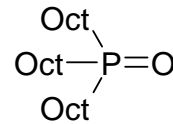
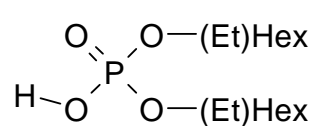
- ◆  $\text{UO}_2(\text{H}_2\text{PO}_4)_2\text{H}_3\text{PO}_4$  minor
- ◆  $\text{UO}_2(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)_2^+$  major

# Uranium recovery from phosphoric acid by solvent extraction



# Limits of reference process

- Separation of U from industrial phosphoric acid by synergistic mixture of organic solvent



Oak Ridge or  
URPHOS process

HDEHP – TOPO 4/1

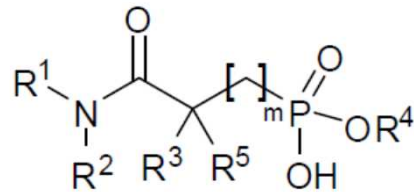
- AREVA Mines asks CEA to improve the reference process
  - $D_U$  not high enough to allow only one Separation/Purification cycle
  - $D_{Fe}$  too high which involves insoluble cruds during U step

- Screening of alternative extractants

- Mono and diamides tested but were not efficient enough because of strong complexation of  $\text{UO}_2^{2+}$  by phosphates
- Optimisation of the molecules of the reference system (but if  $D_U$  😊 then  $SF_{U/Fe}$  😞 )

# New concept of molecules

- Concept of bifunctional molecules developed by CEA and ICSM : amido-phosphonates for AREVA



Amido-phosphonates

Patented molecule  
PCT WO 2013/167516 A1  
6/5/2013 (national) and  
14/11/2013 (international)

- Combination of cationic exchanger and neutral donor functions on a single ligand
  - Modification of extraction mechanisms (increase of  $D_U$  and U/Fe selectivity)
- Optimization of the design of amidophosphonates
  - Study of molecular design and influence of chemical properties
    - Length and ramifications of alkyl chains on amid group ( $R^1$  and  $R^2$ )
    - spacer length and degree of steric hindrance on the spacer ( $m$ ,  $R^3$  and  $R^5$ )
    - length of alkyl chain of free phosphonic acid functions ( $R^4$ )

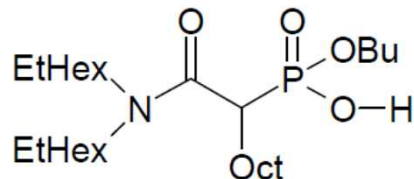
# Laboratory Parametric Studies

## ■ Preparation of synthetic solutions

- Organic solutions by dilution of extractant in aliphatic diluent (without addition of modifier)
- Aqueous solutions of phosphoric acid by mixing concentrated solutions of  $\text{H}_3\text{PO}_4$ , U and Fe as phosphates (Fe spiked with  $^{59}\text{Fe}$  for improving detection limits with gamma spectrometry)

## ■ Distribution ratios measurements by batch experiments

- Solutions vigorously shaken (O/A=1) to obtain good emulsion (30 min)
- Concentrations of U and Fe measured by ICP-AES before and after contact
  - Organic concentrations estimated after 2 successive stripping first to strip Fe and second to strip U
- Fe distributions measured also by gamma spectrometry  $^{59}\text{Fe}$
- **Screening tests** with various designs of molecules and evaluation of performances :  $D_{\text{U}}$ ,  $D_{\text{Fe}}$ ,  $FS_{\text{U/Fe}}$ , solubility in aliphatic ligand, decantation
- Choose of **DEHCNPB** as optimised amido-phosphonate





# First screening tests

## ■ Comparison of extraction performances between the synergistic reference system (HDEHP/TOPO) and DEHCNPB

### ■ Experimental conditions

- Synthetic aqueous solution 250 mg/L U(VI) + 2,5 g/L Fe(III) + 5 M H<sub>3</sub>PO<sub>4</sub>
- 1 hour of shaking contact at 22-23°C and O/A=1

### ■ D<sub>U</sub> and SF<sub>U/Fe</sub> much higher with DEHCNPB and for lower concentrations

	[U] initial (mg/L)	[Fe] initial (mg/L)	D <sub>U</sub>	D <sub>Fe</sub>	SF <sub>U/Fe</sub>
HDEHP/TOPO (4/1) 0.25 M	250	2500	3.8	0.02	200
DEHCNPB 0.1 M	290	3100	72	0.01	6500
DEHCNPB 0.25 M	3920	5240	150	0.02	7500

D<sub>U</sub> x 19  
SF<sub>U/Fe</sub> x 32,5

D<sub>U</sub> x 39  
SF<sub>U/Fe</sub> x 37,5

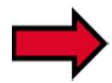
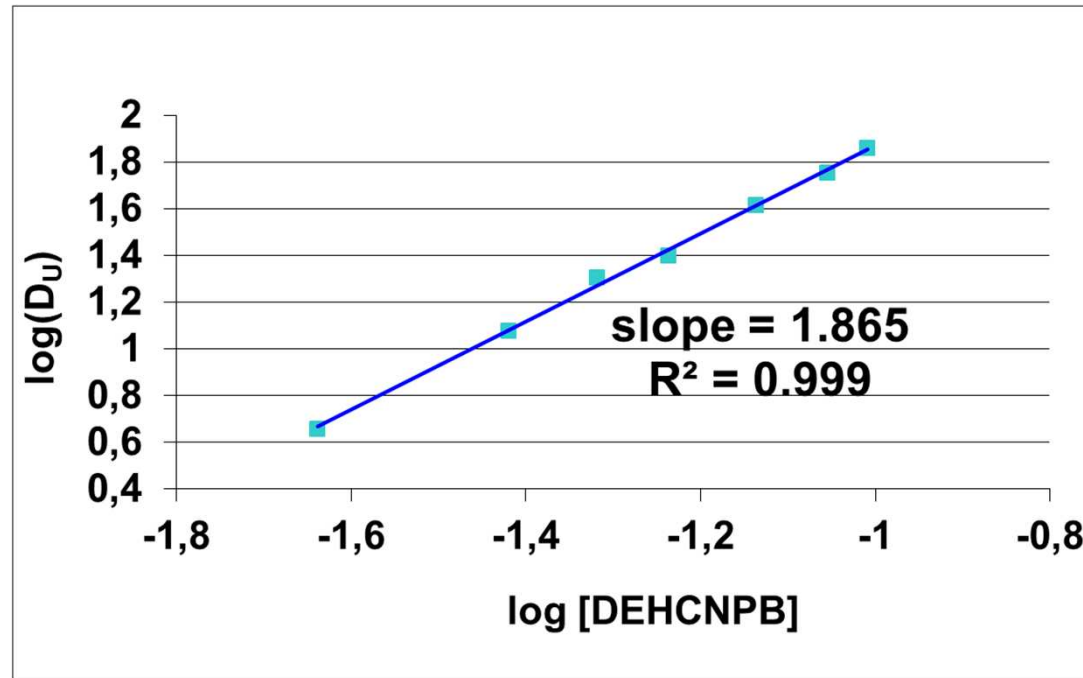
➔ DEHCNPB very promising molecule

# Batch Equilibrium Studies

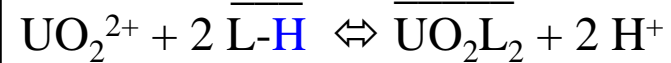
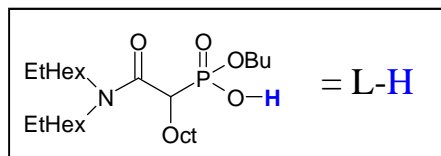
## Influence of DEHCNPB concentration on uranium extraction

$D_U$  at 5 M  $H_3PO_4$  and [DEHCNPB] varying from 0.01 to 0.1 M

Experimental conditions  
Org : 0.1 M DEHCNPB /  
dodécane  
Aqu. : 280 mg of U(VI)/L  
+ 2.5 g/L of Fe(III)  
+ 5 M  $H_3PO_4$   
A/O=1, T=22.5-23°C



Slope close to 2 confirms that  $UO_2^{2+}$  is extracted by 2 molecules of DEHCNPB with the release of 2 protons in aqueous phase

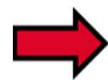
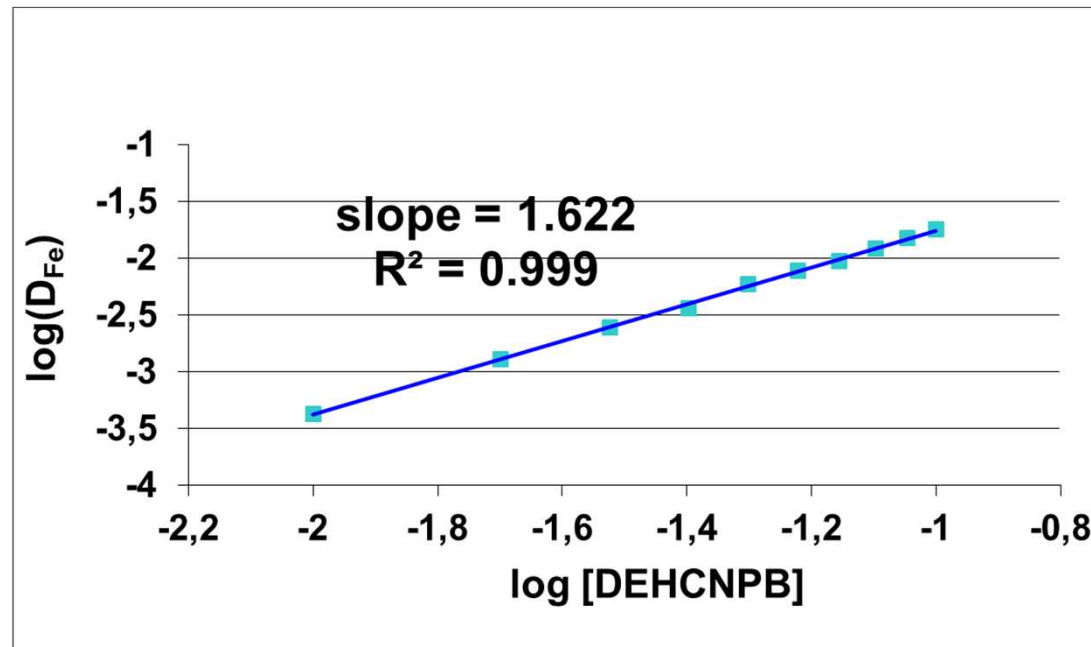


suggested equilibrium

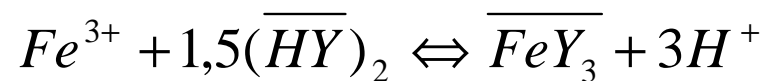
# Batch Equilibrium Studies

- Influence of DEHCNPB concentration on iron (III) extraction
  - $D_{Fe}$  at 5 M  $H_3PO_4$  and [DEHCNPB] varying from 0.01 to 0.1 M

Experimental conditions  
 Org : 0.1 M DEHCNPB /  
 dodécane  
 Aqu. : 100 MBq/L  $^{59}Fe$  +  
 5 M  $H_3PO_4$   
 A/O=1, T=22.5-23°C



**Slope close to 1.6 shows that  $Fe^{3+}$  ion would be extracted by 1 or 2 molecules of DEHCNPB**



suggested equilibrium

# Batch Equilibrium Studies

## ■ Influence of uranium loading

- Solvent with 0.1 M DEHCNPB/dodecane contacted with increasing concentrations of U at 5 M H<sub>3</sub>PO<sub>4</sub>
  - Loading capacity close to **5 g/L of U in organic phase** without third phase formation
  - 4 or 5 molecules of DEHCNPB coordinate U (DEHCNPB probably organized as dimers)

## ■ Test with a genuine industrial phosphoric acid solution

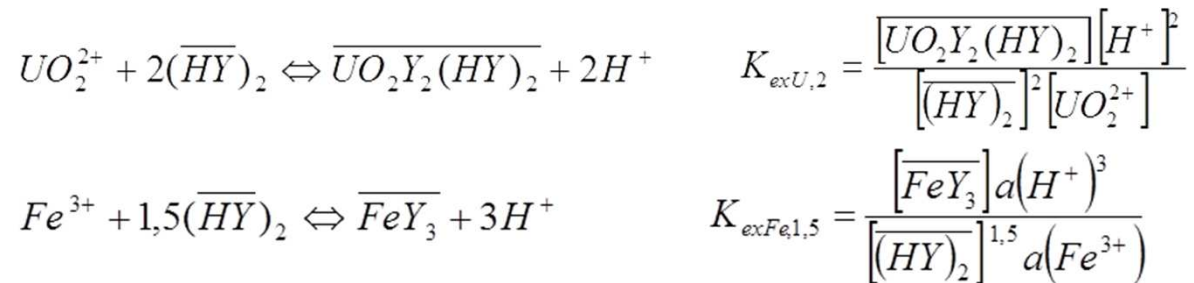
- Composition of an industrial phosphoric acid solution

Elements	U	Fe	Mo	Cr	Zn	Cd	Al	V	Ti	Zr
Conc. (mg/L)	155	2470	6	276	393	19	1880	264	55	44
D <sub>M</sub>	>100	0.02	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

- Results very close to those obtained with synthetic solutions
  - great selectivity of DEHCNPB for U
  - only Mo is slightly extracted (D<sub>Mo</sub> = 0.15) but SF<sub>U/Mo</sub> remains high (> 600) and Mo present as traces in phosphoric solutions

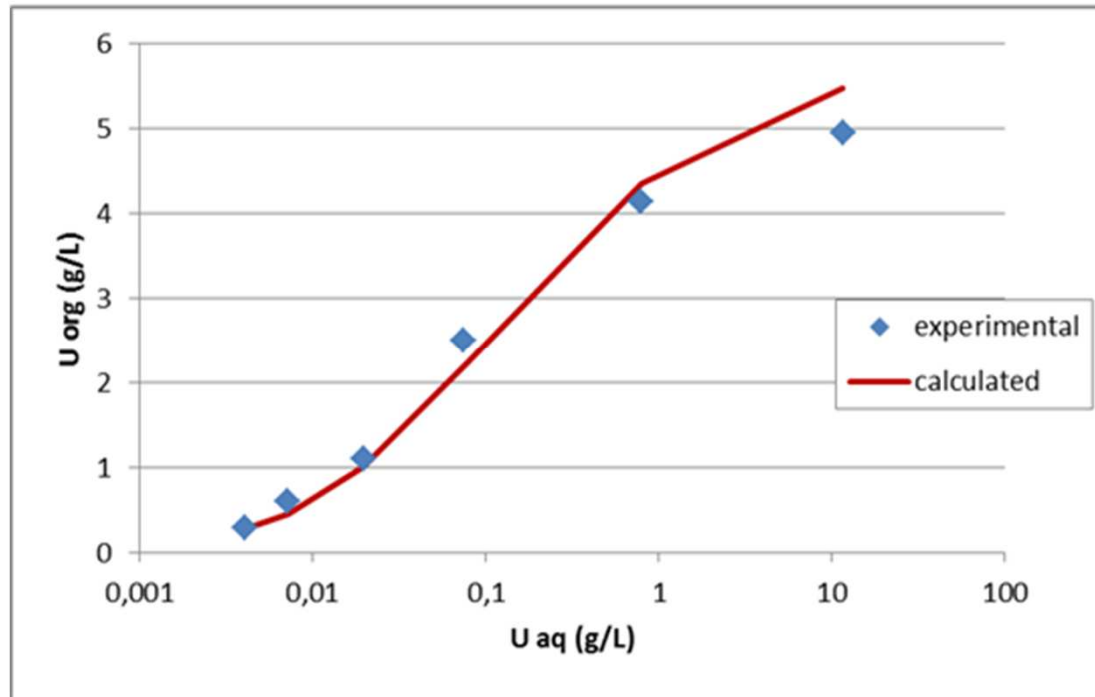
# Modelling of the extraction with DEHCNPB

- Extraction mechanisms suggested by laboratory parametric studies
- **Goal of modelling**
  - optimize thermodynamics constants of the different extraction equilibrium for each step of the flowsheet
- **Cationic exchange between U and DEHCNPB (HY)** considered in proton dimer form
- Global forms of equilibriums of U and Fe, with associated thermodynamic constants are given below



- **Optimization of constants**
  - Application of the mass action law for each element
  - Minimizing the differences between experimental and calculated organic data
  - Resolution of mass balances according to Scilab calculation software to determine the free concentrations

- Comparison of experimental and calculated data for the isotherm of uranium extraction

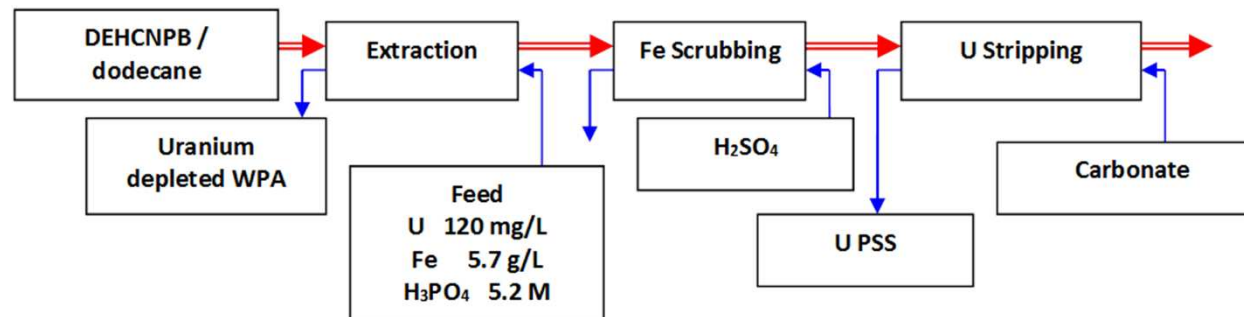


Far from saturation (process conditions), modeling of  $D_U$  is in very good agreement with experimental isotherm

Experimental and calculated U extraction isotherm with 0.1 M DEHCNPB/TPH and 5 M  $H_3PO_4$  at 25°C

- Similar modelling were performed for iron scrubbing and U stripping
- Study of the influence of temperature on U and Fe extraction
- Extraction of phosphoric acid by DEHCNPB neglected after titration experiments

- Model implemented into PAREX simulation code to elaborate a flowsheet at laboratory scale
- Design of a flowsheet with 3 main steps
  - Uranium extraction by DEHCNPB
  - Iron scrubbing by  $H_2SO_4$
  - Uranium stripping by carbonate ( $Na_2CO_3$ )



- Process devices and analytical measurements
  - 3 PMMA Laboratory scale mixer settlers with perforated stainless steel blades
  - Extraction step heated at 35°C
  - Iron scrubbing and Uranium stripping steps heated at 45°C
  - Flow rates controlled by weight measurements

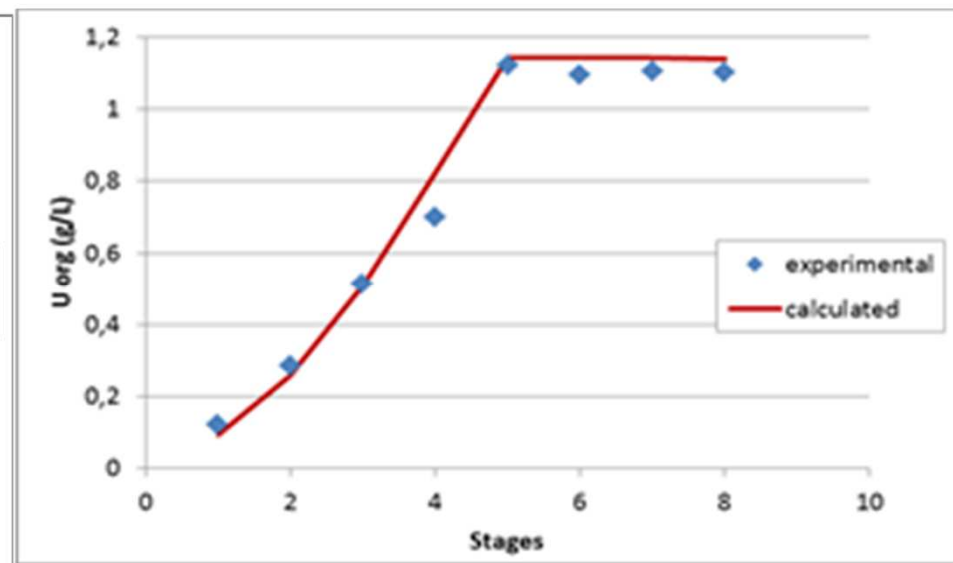
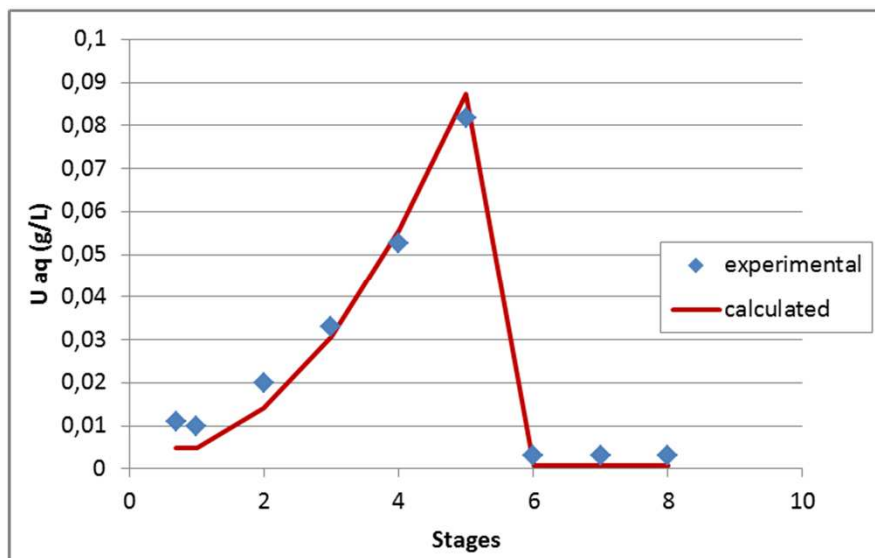
# Counter-current test in Proust platform





# Experimental results of flowsheet tested

- On line analysis shows that steady state was reached for U
- Very successful test : more than 91% of U recovered and concentrated from 0.12 to 5.6 g/L
- Good decontamination of U from Fe and other impurities
  - Fe/U = 0.04% < ASTM specifications (0.15%)
- No cruds observed in stripping section and good hydrodynamic behaviour
- Comparison of experimental and calculated profiles with the PAREX code shows good agreement which validate the extraction model developed



Experimental and calculated uranium aqueous (left) and organic (right) profiles after the counter-current test with an industrial phosphoric acid

- **Amido-phosphonate DEHCNPB is very promising for U extraction from phosphoric acid**
  - Selective extraction of U even among high concentrations of iron in genuine 5 M  $\text{H}_3\text{PO}_4$  solution :  $[\text{Fe}]/[\text{U}]$  reduced from 30 (feed) to  $4.3 \cdot 10^{-4}$  (product)
- **Parametric laboratory studies**
  - Characterize the stoichiometry of extracted complex in organic phase
  - Propose extraction mechanisms
- **Model developed and implemented in CEA PAREX code**
  - Modelling and flowsheet design
- **Counter-current test on PROUST platform in G1 facility with genuine industrial phosphoric solution**
  - Treatment of an industrial phosphoric acid in laboratory-scale mixer-settlers
  - Very promising performances of the run with good U recovery (91%) and good decontamination ( $[\text{Fe}] / [\text{U}] < \text{ASTM specifications}$ )
  - **Experimental and calculated profiles of U and Fe in good agreement**
- **Experiments in progress to optimize this flowsheet**

Thank you for your attention

## Acknowledgements

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