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B. Fries, C. Marie, V. Pacary, H. Mokhtari, Mc. Charbonnel. Understanding of iron extraction mechanisms from phosphate and sulfuric media using DEHCNPB. PhD day AREVA Mines, Jun 2016, Paris, France. PhD day AREVA Mines, 2016. hal-02417823

**HAL Id: hal-02417823**

**<https://hal.science/hal-02417823v1>**

Submitted on 18 Dec 2019

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# Understanding of iron extraction mechanisms from phosphate and sulfate media using DEHCNPB

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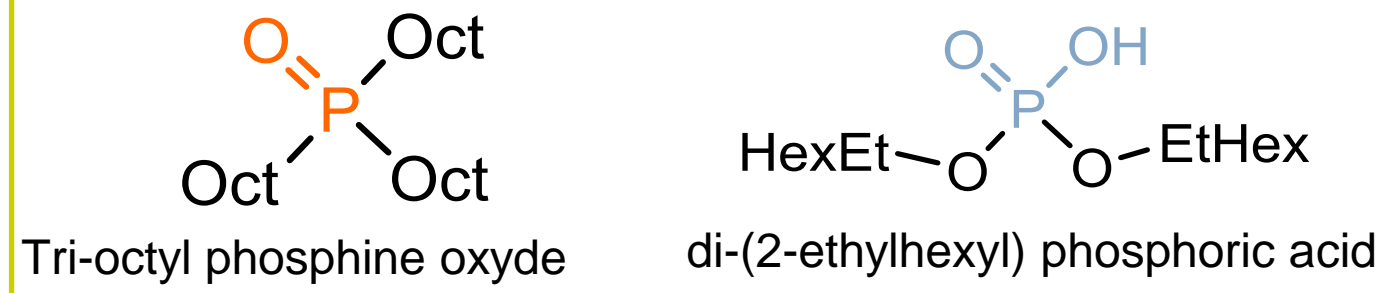
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## Context

### ► Uranium extraction from phosphate ores

- ◆ Low amount of U, but large quantity available (~4Mt)<sup>[1]</sup>
- ◆ Uranium with high amounts of other metals (U/Fe selectivity)

### ► Historic process: Synergistic mixture HDEHP/TOPO

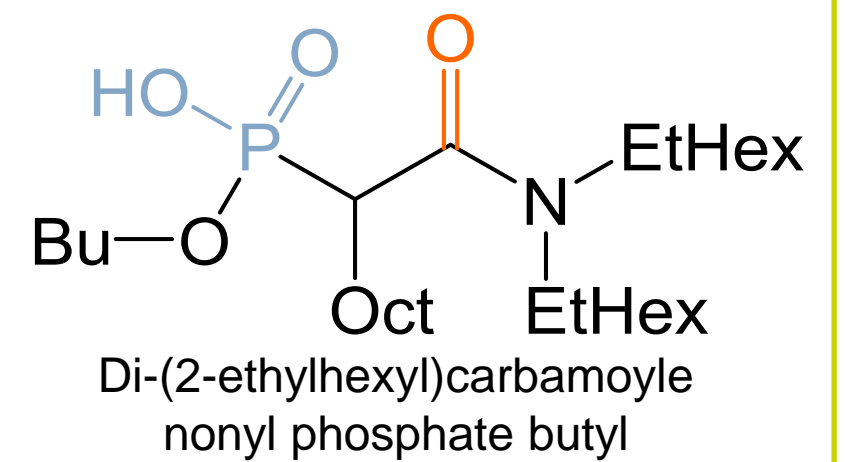


#### Drawbacks :

- ⇒  $D_U = \frac{C_U^{org}}{C_U^{aq}}$  not high enough (~4)\*
- ⇒ insufficient selectivity  $SF_{U/Fe} = \frac{D_U}{D_{Fe}} \sim 200^*$

### ► Novel bifunctional extractant: DEHCNPB [2]

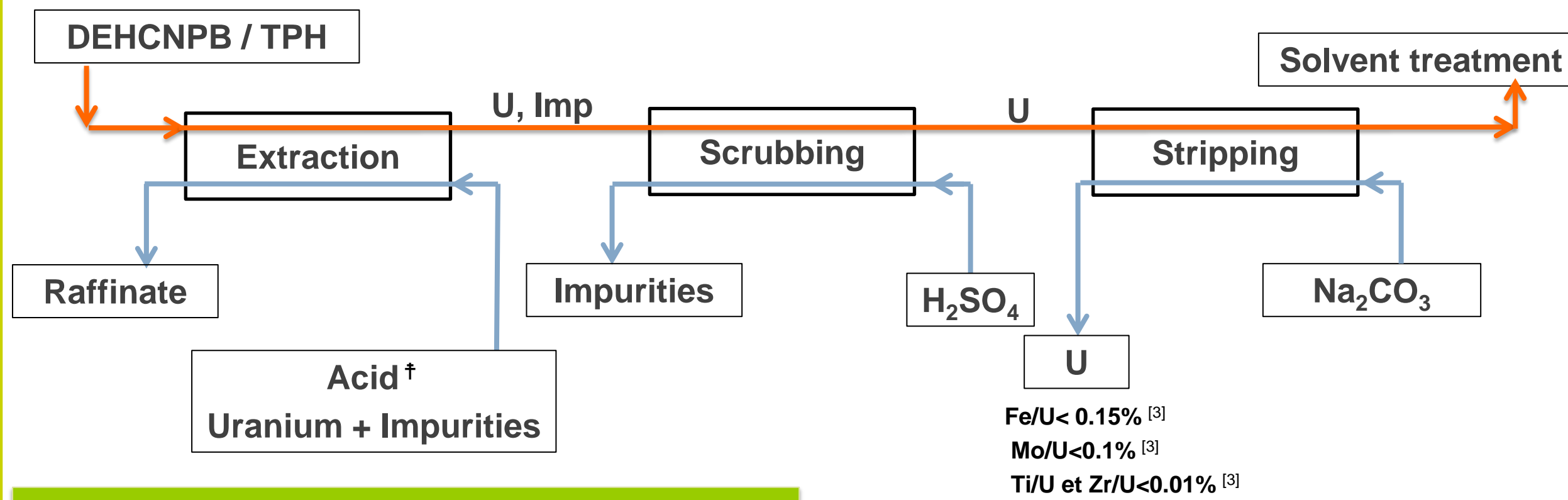
- ⇒  $D_U \sim 20x$  higher than with HDEHP/TOPO\*
- ⇒  $FS(U/Fe) \sim 35x$  higher\*
- ⇒ Pilot scale trial demonstration



⇒ Used for the extraction of uranium from sulfuric medium

**Lower performances of the « sulfate » process → U leaks in raffinates**

## U extraction process



## Objective Explain the differences between the two processes

Understanding of extraction mechanisms, speciation in organic phases  
Development of a thermodynamical model simulating both processes

### ► Uranium extraction by DEHCNPB in TPH

- ◆ ↑ Phosphoric medium: [H<sub>3</sub>PO<sub>4</sub>]=5M
- ◆ ↑ Sulfuric medium: [SO<sub>4</sub><sup>2-</sup>]=1.4M, pH = 1

### ► Iron scrubbing

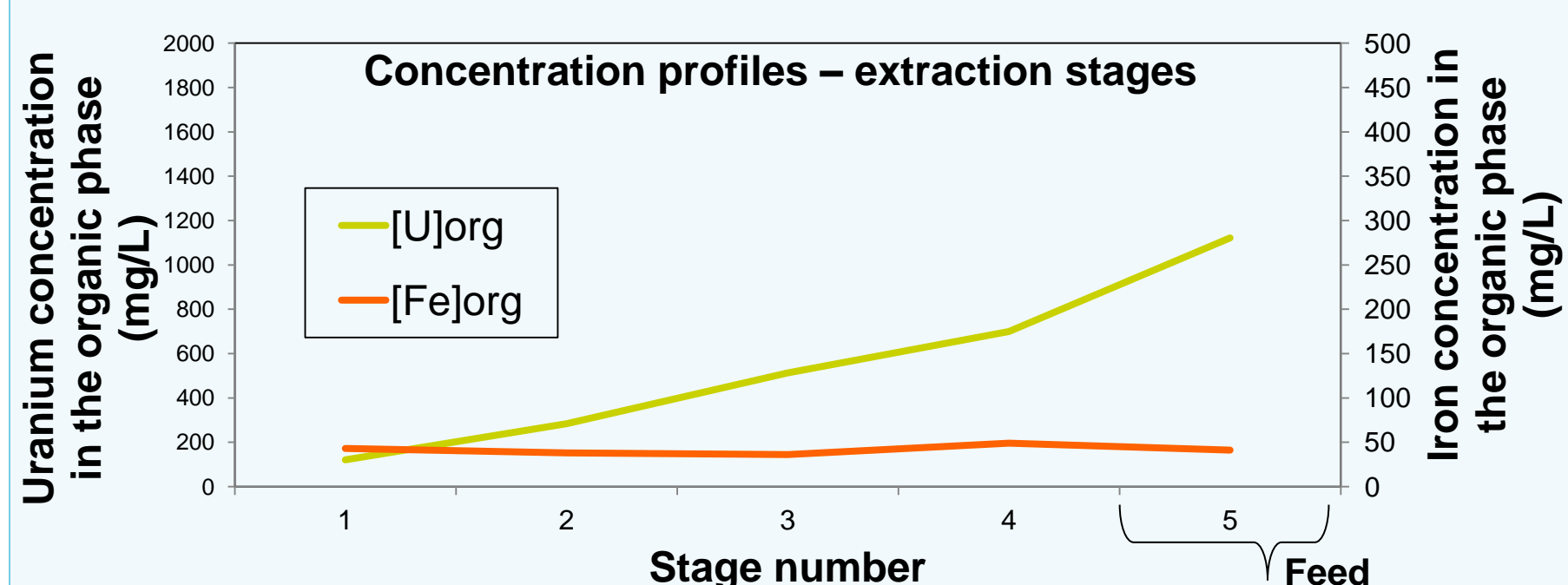
- ◆ Scrubbing of extracted iron by concentrated sulfuric acid

### ► Stripping of uranium in alkali medium (carbonates)

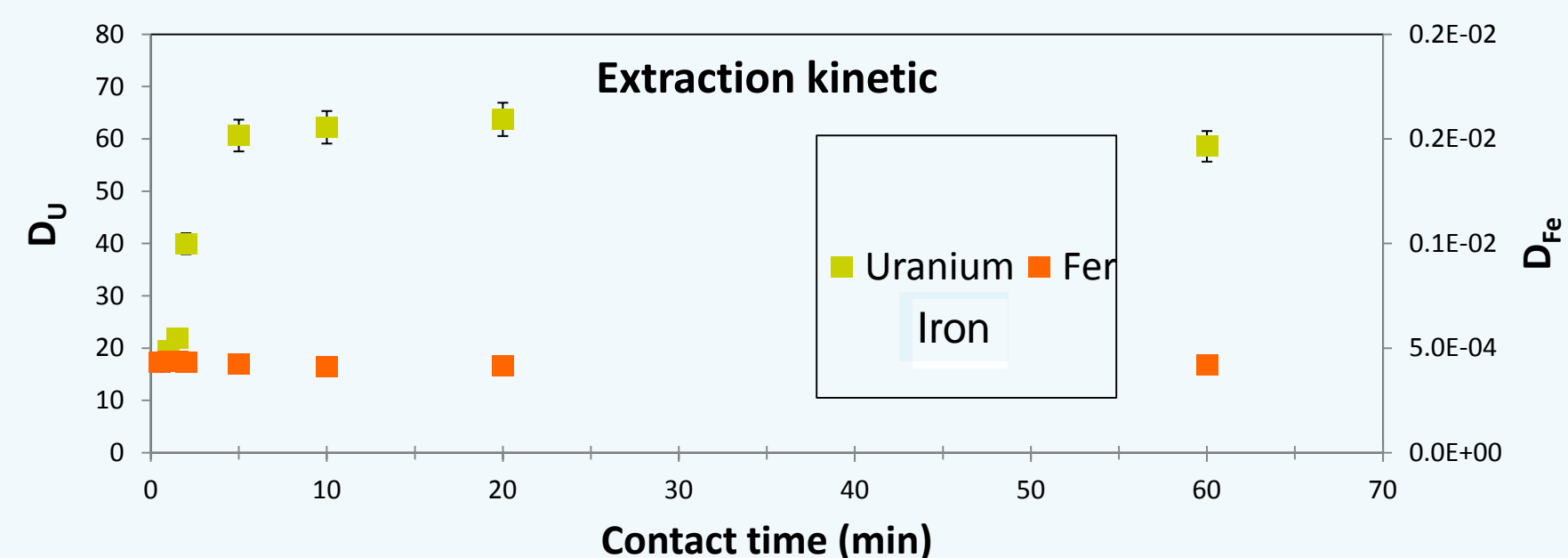
- ◆ Back-extraction of uranium in aqueous phase (concentrated U)

## Experimental studies

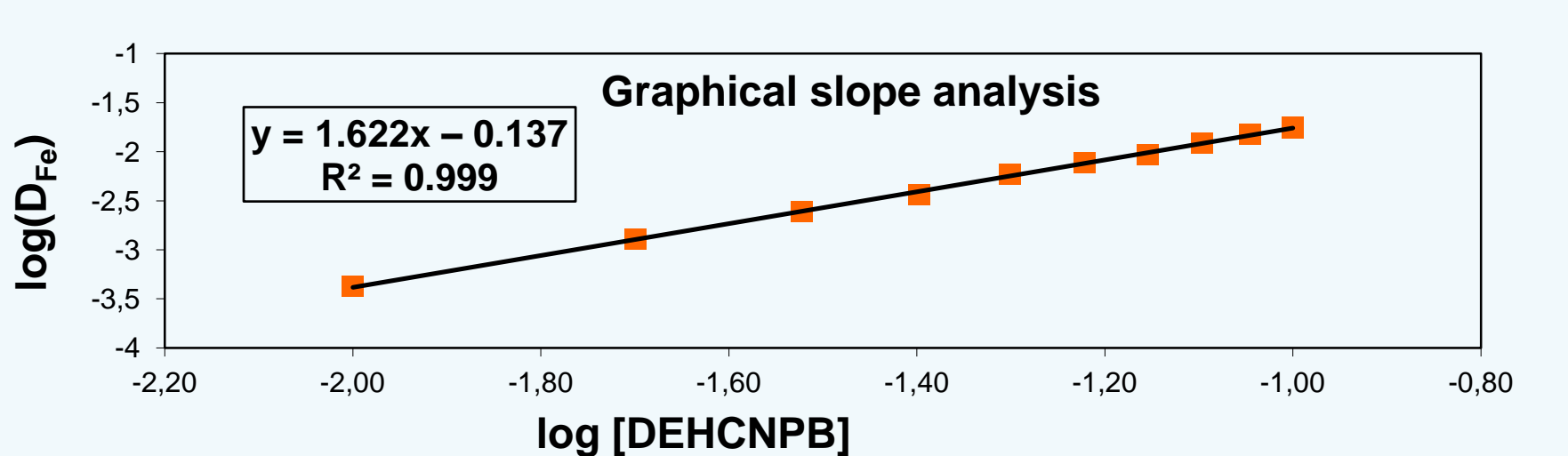
### Phosphoric medium



Uranium and iron extraction profiles during pilot scale trials; solvent: DEHCNPB 0.1M / Dodecane. Feed solution: industrial phosphoric acid, H<sub>3</sub>PO<sub>4</sub> 5M, C<sub>U</sub>=119ppm, C<sub>Fe</sub>=5.7g/L, O/A=0.1 ; T=40°C



Uranium and iron distribution coefficients as a function of extraction time; solvent: DEHCNPB 0.1M / TPH. Aqueous phase: [H<sub>3</sub>PO<sub>4</sub>]=5M, C<sub>U</sub>=1g/L, C<sub>Fe</sub>=10g/L ; O/A=1 ; T=25°C.



Logarithmic plot of iron distribution coefficient as a function of extractant concentration; solvent: DEHCNPB 0.01M - 0.1M / TPH. Aqueous phase: [H<sub>3</sub>PO<sub>4</sub>]=5M, C<sub>Fe</sub>=3g/L ; O/A=1 ; T=25°C.

### ► Comparative study

#### During the pilot scale trials

⇒ Uranium leaks

Step	Phosphate process	Sulfate process
Extraction	10 ppm	23 ppm
Stripping	< 3 ppm	70 ppm

⇒ Sulfate medium: Higher [Fe]<sub>org</sub>

⇒ How does the initial media influences the extraction of iron?

#### Extraction kinetic

⇒ Contact time required to reach equilibrium

Element	Phosphate medium	Sulfate medium
U	5 min	5 min
Fe	Unmeasurable	40 min

⇒ Sulfate medium: Higher D<sub>Fe</sub> and D<sub>U</sub> ↓ when iron reaches equilibrium

⇒ Selectivity issue?

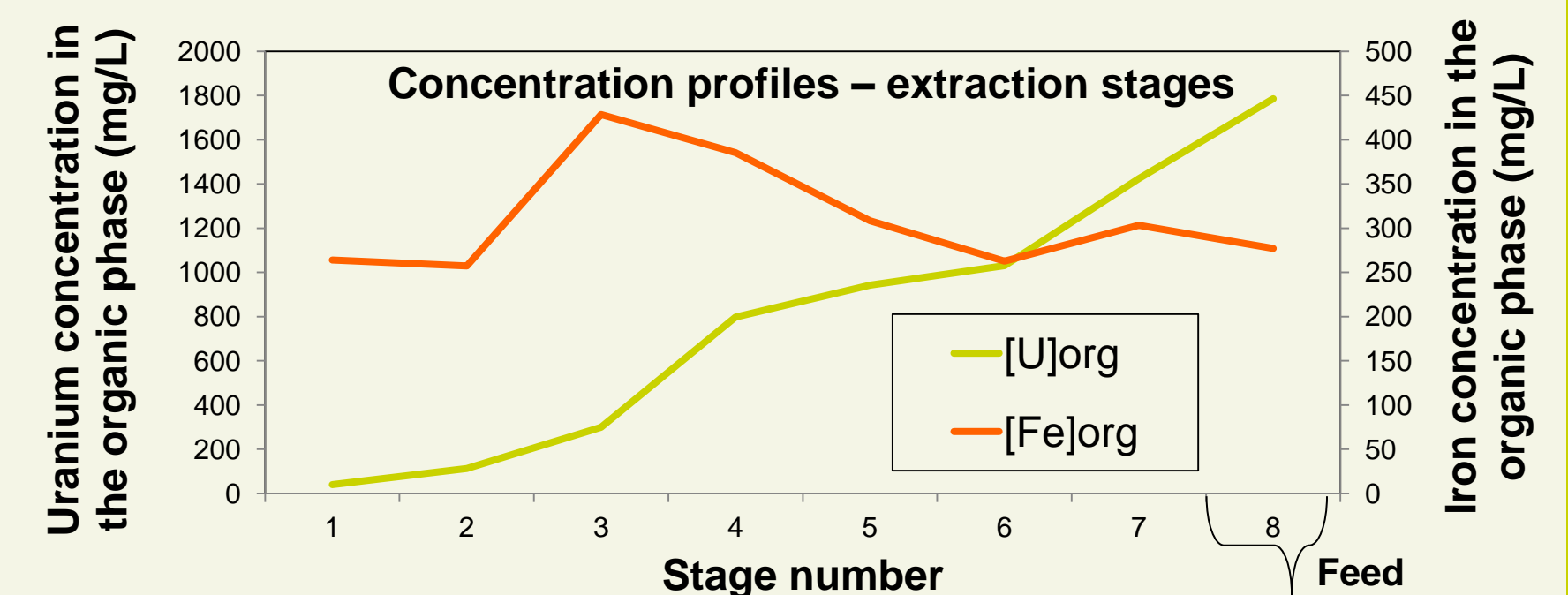
#### Average stoichiometries

##### Graphical slope analysis

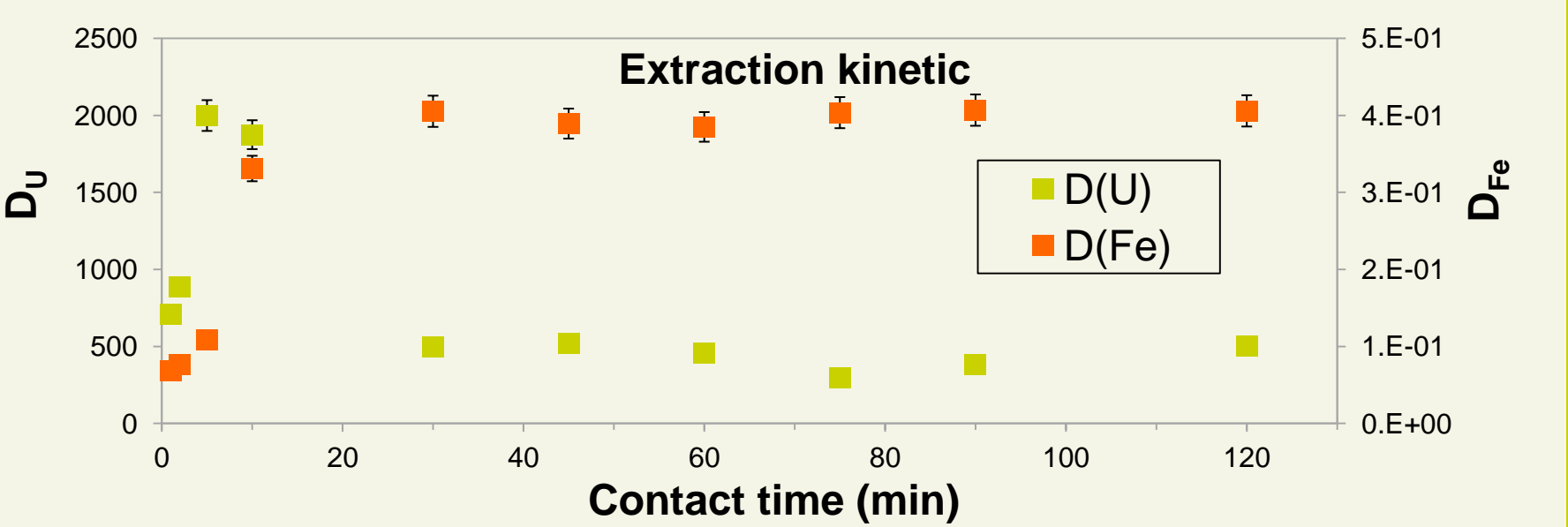
$$\log(D_{Fe}) \propto n \cdot \log([HL]_{libre})$$

⇒ Lower average stoichiometries of Fe-DEHCNPB complexes formed from the sulfate medium.

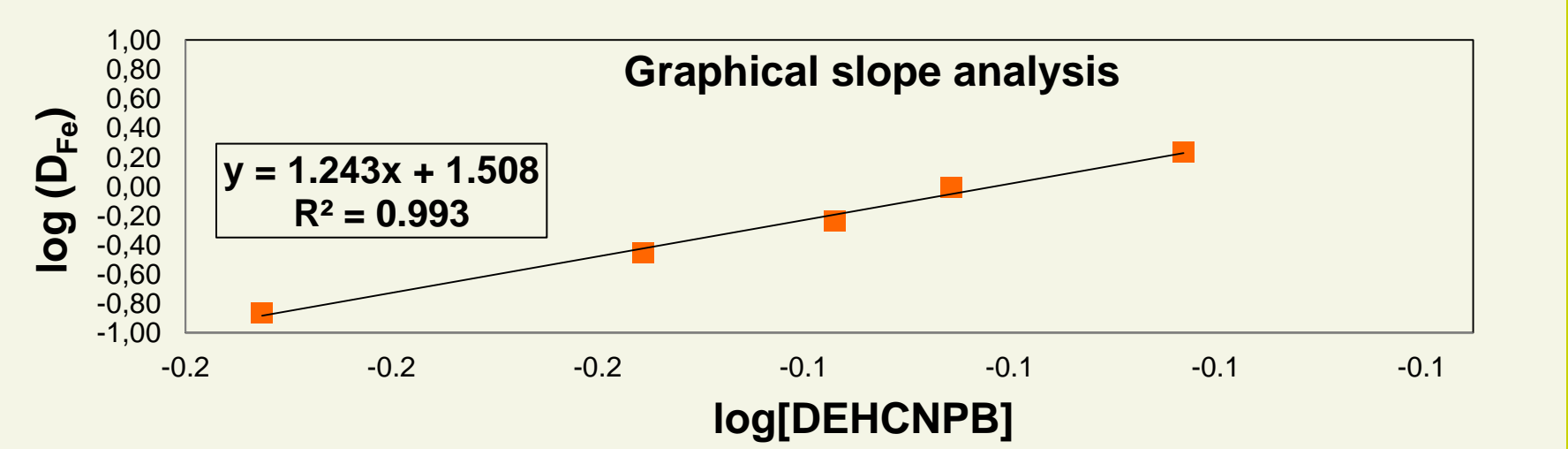
### Sulfuric medium



Uranium and iron extraction profiles during pilot scale trials; solvent: DEHCNPB 0.05M / TPH. Feed solution: Synthetic « Imourane » solution, [SO<sub>4</sub><sup>2-</sup>]=1.42M, pH=1, C<sub>U</sub>=360ppm, C<sub>Fe</sub>=4.1g/L, O/A=0.125 ; T=25°C



Uranium and iron distribution coefficients as a function of extraction time; solvent: DEHCNPB 0.1M / TPH. Aqueous phase: [SO<sub>4</sub><sup>2-</sup>]=1.6M, pH=1, C<sub>U</sub>=1g/L, C<sub>Fe</sub>=10 g/L ; O/A=1 ; T=25°C.

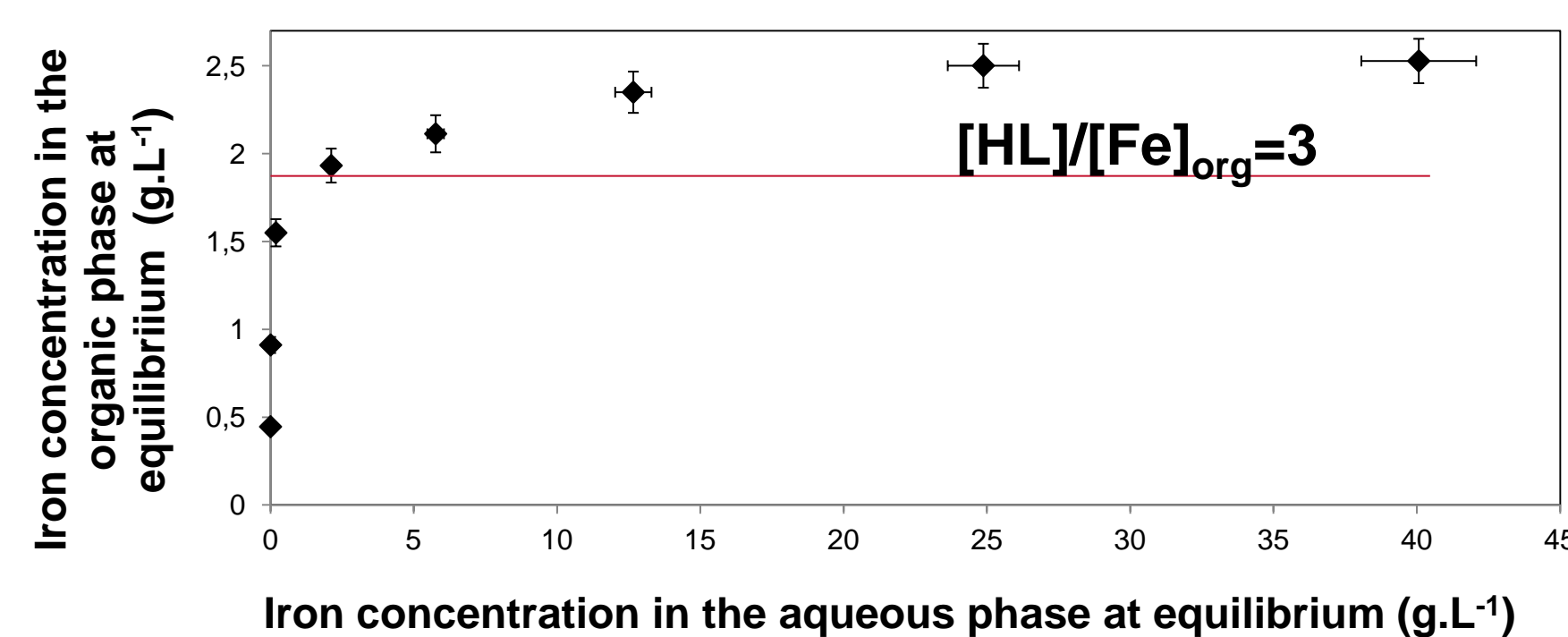


Logarithmic plot of iron distribution coefficient as a function of extractant concentration; solvent: DEHCNPB 0.022M-0.25M / TPH. Aqueous phase: [SO<sub>4</sub><sup>2-</sup>]=1.7M, pH=1, C<sub>Fe</sub>=3.8g/L ; O/A=1 ; T=25°C.

### ► Different iron extraction mechanisms according to the initial medium?

### ► Iron extraction from a sulfuric medium

- ◆ Hypothetical mechanism:  $Fe^{3+} + 3HL \leftrightarrow FeL_3 + 3H^+$
- ◆ Experiments ⇒ [HL]/[Fe]<sub>org</sub>=2.3 at saturation of the organic phase



Iron extraction isotherm. Solvent: DEHCNPB 0.1 M / TPH. Aqueous phase: [SO<sub>4</sub><sup>2-</sup>]=1.7M, pH=1, C<sub>Fe</sub> from 0.5g/L to 50g/L ; O/A=1 ; T=25°C.

### ◆ Hypotheses :

#### ✗ Extraction of Fe<sup>2+</sup>

Solution potential measurements allowed to estimate that 5% to 15% of iron is divalent in the sulfuric medium

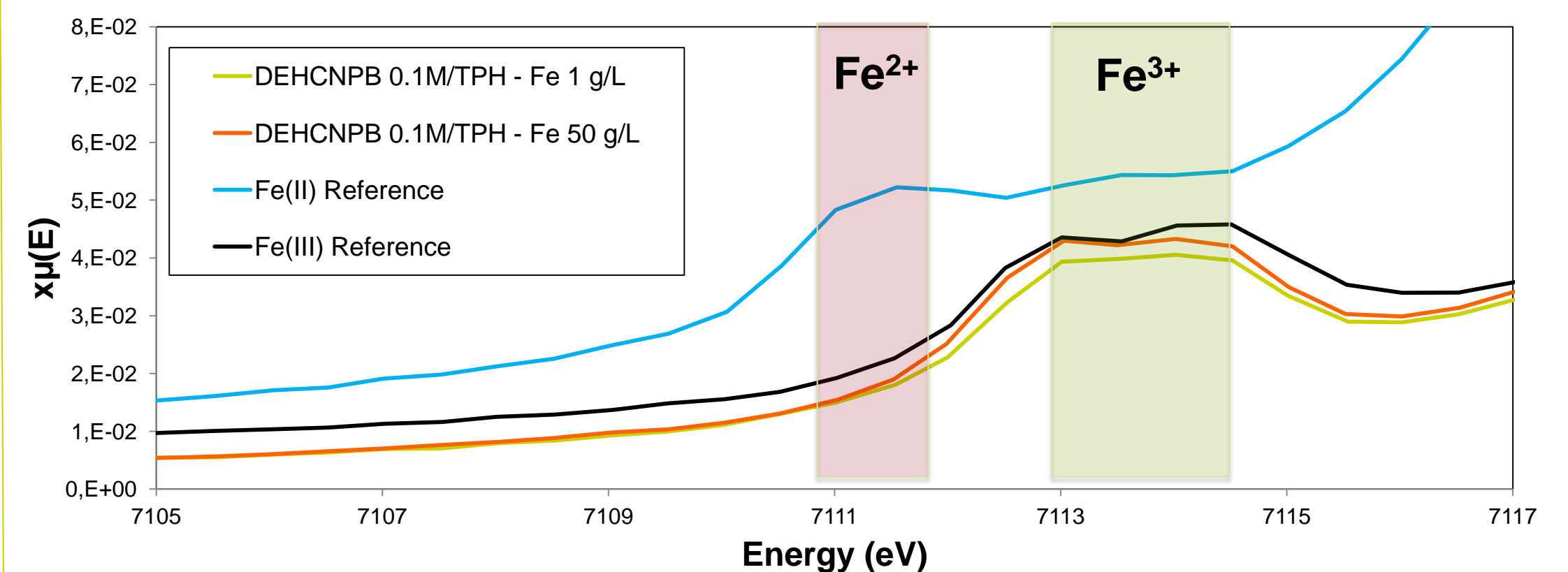
#### ✓ Co-extraction of SO<sub>4</sub><sup>2-</sup>

Direct measurement of sulfur Sulfur in organic phases at equilibrium thanks to ICP-AES

⇒ Extraction of FeSO<sub>4</sub><sup>+</sup> ?

### ► Determination of iron oxydation state in organic phases<sup>[4]</sup>

- ◆ XANES measurements: Only trivalent iron is present in the organic complexes



Samples : DEHCNPB 0.1M/TPH after extraction of iron from a sulfuric medium. Fe(II) reference: Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub> 0.05M with Hydroxylamine 1M. Fe(III) reference: Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> 0.05M with hydrogen peroxide 1M

## Conclusion

- ⇒ Two processes with ≠ performances → Uranium leaks in raffinates
- ⇒ Iron is suspected of interfering with uranium extraction from a sulfuric medium
- ⇒ Different iron extraction mechanisms depending on the initial medium
- ⇒ Predominant iron specie in sulfuric acid FeSO<sub>4</sub><sup>+</sup> is most likely extracted

## Perspectives

- Quantification of sulfur in the organic phase in a way to determine [SO<sub>4</sub><sup>2-</sup>]/[Fe<sup>3+</sup>] ratio (ICP-AES)
- Study of the extraction of water during the extraction of iron (Karl-Fischer)
- EXAFS measurements of organic phase to validate proposed structures of complexes
- Comparison with iron extraction from the phosphoric medium using an analog molecule

### References

- [1] : Gabriel.S et al., *Annals of Nuclear Energy*, 58., p213-220,2013. [3] : Norme ASTM C967-08.  
[2] : Brevet PCT WO 2013/167516 A1 ; 14/11/2013. [4] : Wilke. M et al., *American Mineralogist*, 86, pp714-730, 2001