GENIORS
GEN IV integrated oxide fuels recycling strategies

First INSPYRE Summer School

Radiolytic Effects Affecting Reprocessing Performance

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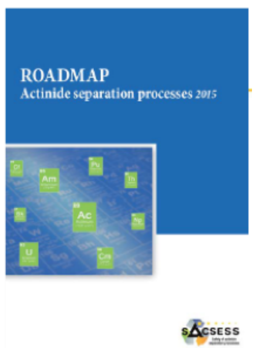
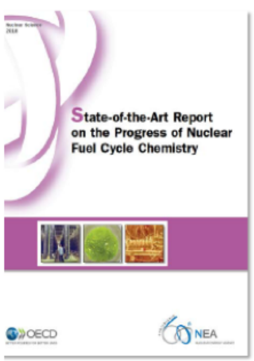
Outlines

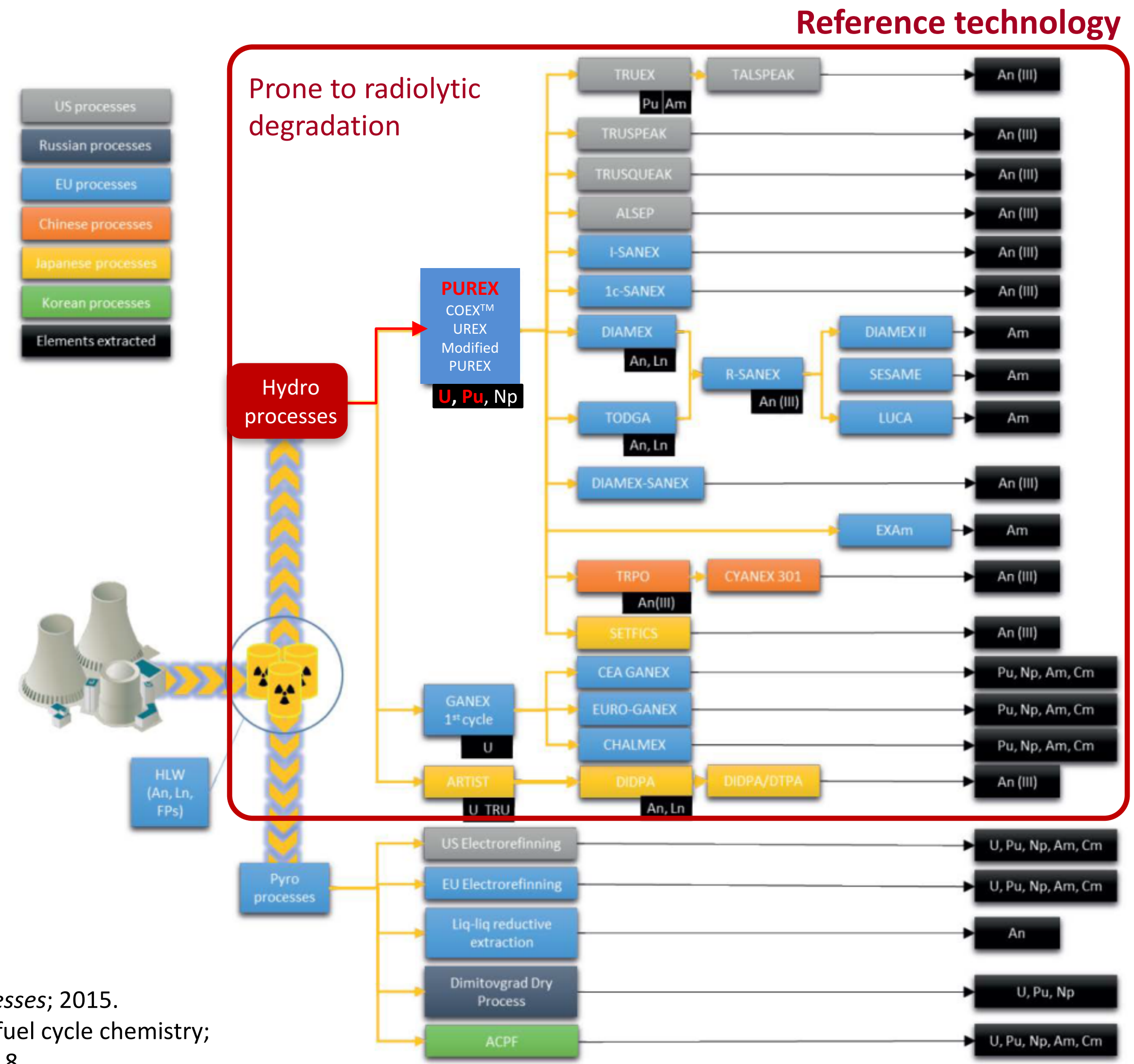
1. *Introduction*
2. *Degradation of solvents and long-term behavior*
3. *Stability studies*
4. *Stability studies along process development*
5. *Main conclusions*

1. Introduction

SEPARATION PROCESSES for nuclear fuel recycling







Joly, P.; Boo, E. *SACSESS roadmap — actinide separation processes*; 2015.
OECD-NEA State-of-the-art report on the progress of nuclear fuel cycle chemistry; NEA No. 7267, OECD, Nuclear Energy Agency (NEA), Paris: 2018.

1. Introduction

Extraction process development for nuclear fuel recycling

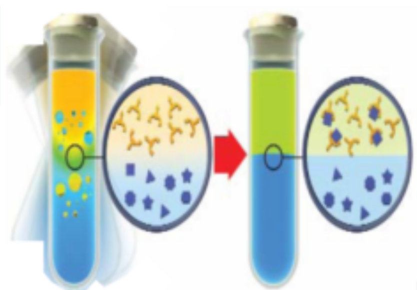
Steps and limiting points

System screening

Process development and optimization

Hot test

Scale-up



Batch experiments

Extracting and complexing properties

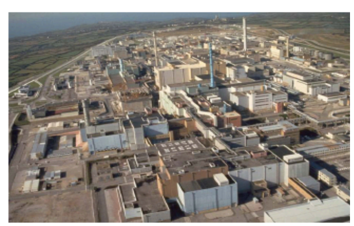
Industrial diluents

Good kinetics, viscosity, reversibility, etc.

Low synthesis cost

Stability: to keep its properties

Reprocessing plant



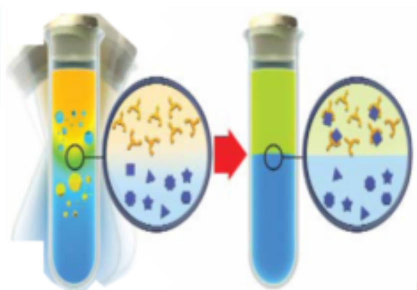
Industrial application

1. Introduction

Extraction process development for nuclear fuel recycling

Steps and limiting points

System screening



Batch experiments

Extracting and complexing properties

Process development and optimization

Process chemistry

Flowsheet design and modelling

Validation at lab scale

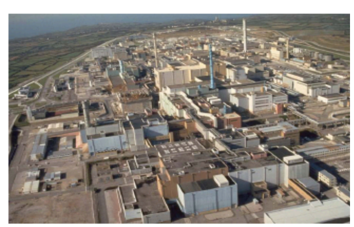
Contactors development

Hot test

Integrated experiments using real solutions

Scale-up

Reprocessing plant



Industrial application

2. Degradation of solvents and long term behaviour

What happens to a solvent during the process operation

Original performance

Evaporating or carry over effects to other phases

Thermal degradation

Chemical attacks

Hydrolytic degradation

Radiolytic degradation

Stability studies

Avoid loss efficiency

Identify unexpected behavior

Control security problems

Reduce costs

Important changes

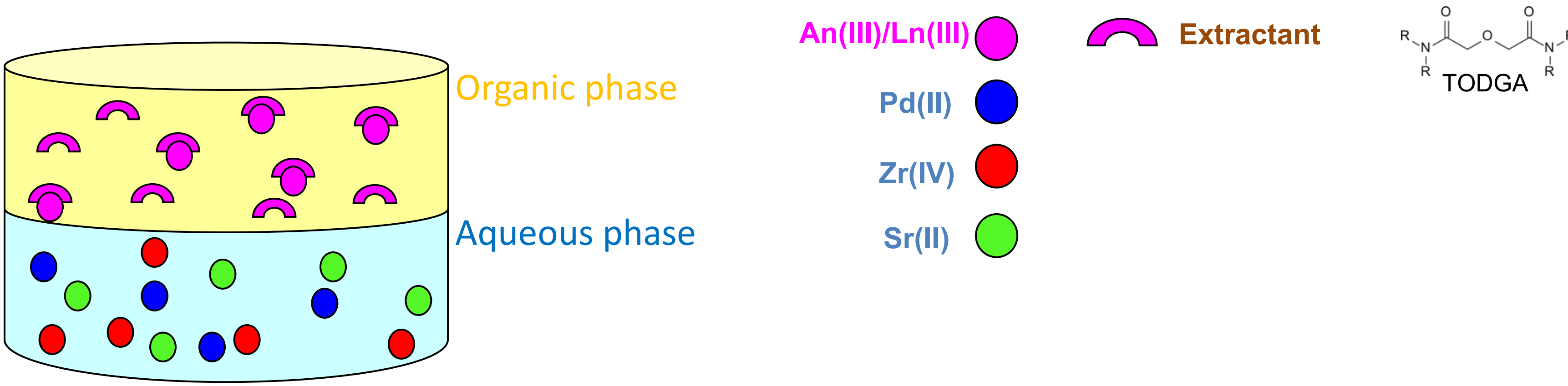
- **Changes in the composition:**

  Main ligand, new species formation and changes in metal oxidation states

- **Changes in physico-chemical and chemical properties**
- Increase of secondary waste and security issues to consider
- Increase of costs

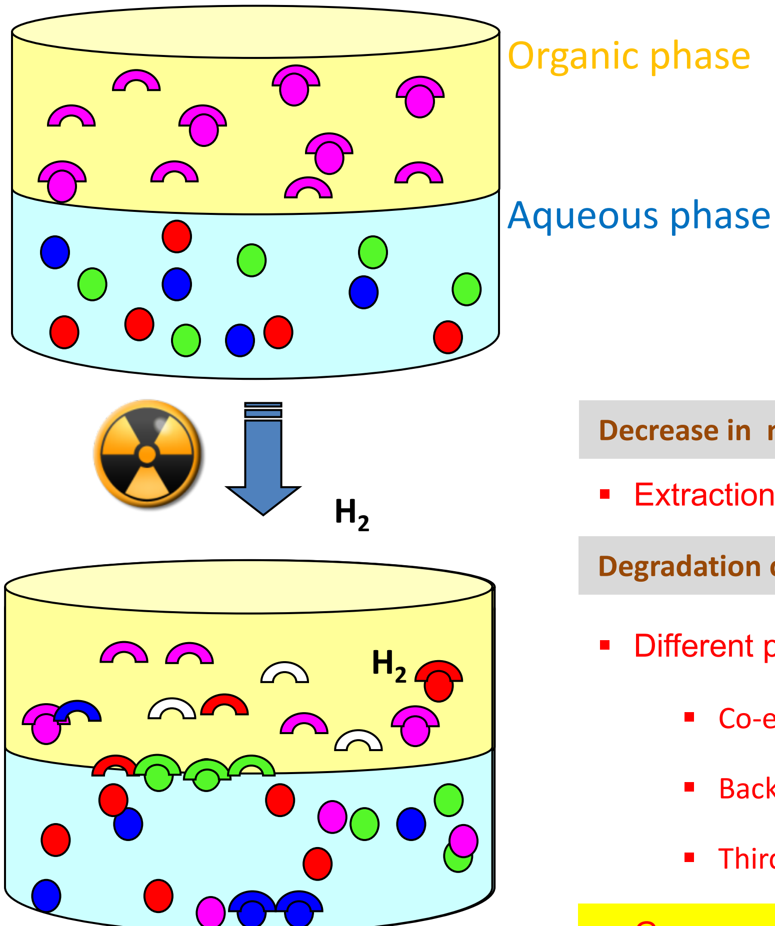
2. Degradation of solvents and long term behaviour

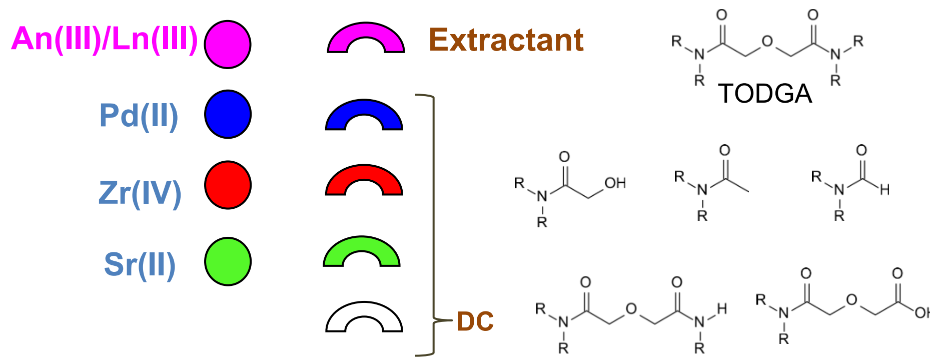
Changes in the composition: main ligand and degradation compounds



2. Degradation of solvents and long term behaviour

Changes in the composition: main ligand and degradation compounds





Decrease in main ligand concentration

- Extraction decrease ($D_{Ln/An}$)

Degradation compounds

- Different properties
  - Co-extraction of other metals (FPs)
  - Back-extraction problems
  - Third phase formation!!!!
- Gas generation

Safe long-term performance

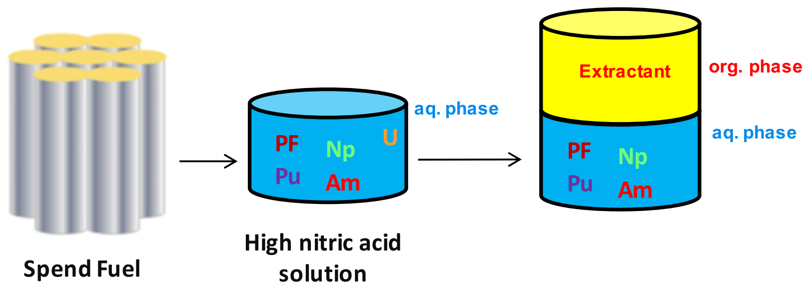
Study of DCs properties

- **Identify the most problematic**
- **Regeneration studies**

2. Degradation of solvents

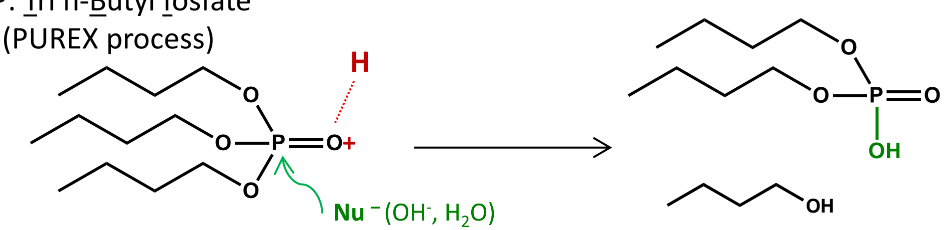
What are the mechanisms?

- **Hydrolytic degradation**
- **Radiolytic degradation**



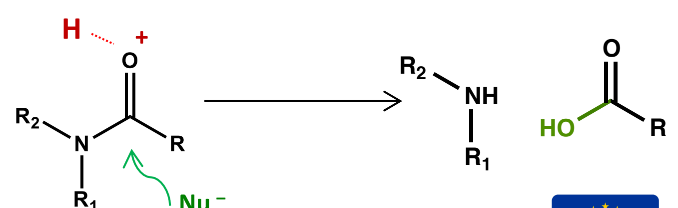
- **Oxidative reaction**
- **Hydrolytic reaction of functional groups of extractants**

TBP: Tri n-Butyl fosfate
(PUREX process)



Extractants for *Advance nuclear fuel reprocessing*

Amide
Malonamides (MA)
Diglycolamides (DGA)
Etc



2. Degradation of solvents

What are the mechanisms?

- **Hydrolytic degradation**
- **Radiolytic degradation**

▪ **Direct radiolysis**

S \/\/\→ S$^{+\bullet}$ + e$^{-\bullet}$, S = Extractant

RH \/\/\→ RH$^{+\bullet}$ + e$^{-\bullet}$, RH = diluent (dodecane, TPH, kerosene ,etc)

It occurs to an extent dictated by the abundance of the constituent in solution

▪ **Indirect radiolysis**

RH \/\/\→ RH$^{+\bullet}$ + e$^{-\bullet}$

RH$^{+\bullet}$ + S → S$^{+\bullet}$

Aerated conditions

Radical cations (RH$^{\bullet+}$)
Carbon-centered radicals (RH$^{\bullet}$)
Solvated electrons (e^-_{sol})
Reactive molecular species (H_2)

Organic media (Alkane radiolysis or organic diluents):

$CH_3(CH_2)_nCH_3$ - \/\/\→ e^-_{sol} + $\mathbf{CH_3(CH_2)_nCH_3^{\bullet+}}$ + $\mathbf{CH_3(CH_2)_nCH_2^{\bullet}}$ + $\mathbf{CH_3^{\bullet}}$ + $\mathbf{H^{\bullet}}$ + $\mathbf{H_2}$

Aqueous media (water or acid radiolysis) :

H_2O - \/\/\→ $\mathbf{^{\bullet}OH}$ + e^-_{aq} + $\mathbf{H^{\bullet}}$ + $\mathbf{H_2O_2}$ + H_3O^+ + $\mathbf{H_2}$

HNO_3 -\/\/\→ e^-_{aq} + $\mathbf{^{\bullet}NO_3}$ + $\mathbf{^{\bullet}NO_2}$ + $\mathbf{HNO_2}$ + $^{\bullet}O$

Oxidizing radicals
Reducing radicals
Reactive molecular species

2. Degradation of solvents

What are the mechanisms?

- **Hydrolytic degradation**
- **Radiolytic degradation**

  - **Direct radiolysis**

    $S \ \backslash/\backslash/\backslash\!\rightarrow S^{+\bullet} + e^{-\bullet}$, S = Extractant

    $RH \ \backslash/\backslash/\backslash\!\rightarrow RH^{+\bullet} + e^{-\bullet}$, RH = diluent (dodecane, TPH, kerosene ,etc)

    It occurs to an extent dictated by the abundance of the constituent in solution

  - **Indirect radiolysis**

    $RH \ \backslash/\backslash/\backslash\!\rightarrow RH^{+\bullet} + e^{-\bullet}$

    $RH^{+\bullet} + S \rightarrow S^{+\bullet}$

    Aerated conditions

    Radical cations ($RH^{\bullet +}$)
    Carbon-centered radicals ($RH^{\bullet}$)
    Solvated electrons (e^{-}_{sol})
    Reactive molecular species (H_2)

    $S^{+\bullet} \rightarrow$ Degradation products (CD)

    Higher molecular weight DC (additions, combination of radicals)

    Lower molecular weight DC (de-alkylation reaction, C-C/C-X bond excision reactions, etc)

2. Degradation of solvents

Factors governing the degradation

External parameters

Nature of the irradiation source

Irradiation dose and dose Rate

Temperature

Chemical parameters: Influence of the composition of solvents

Nature of the diluents (ionization potential, polarity, aromatic groups, etc)

Structure of the extractant

Concentration of extractant

Presence of additional ligands or phase modifiers

Metals complexation

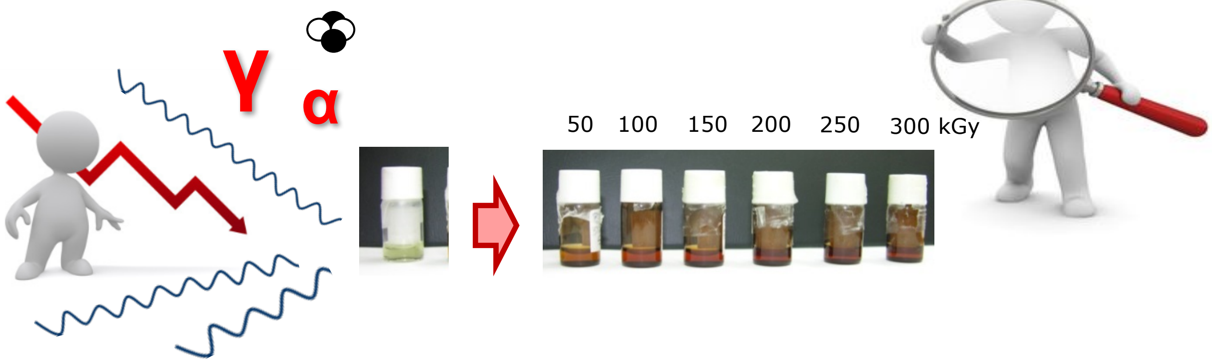
Effect of the atmosphere (oxygen)

Aqueous phase in contact

3. Stability studies

To simulate and study the effects to understand and predict

Simulate irradiation



How long?

What problems we have?

Why?

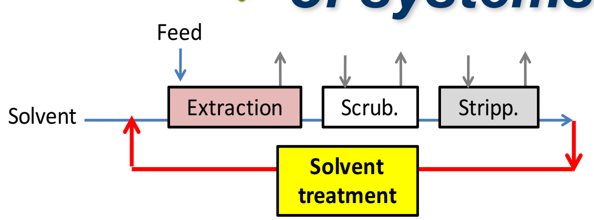
Modifying experimental conditions

To understand stability rules!!!

To find solutions!!!!

Improve systems

Regeneration of systems



Identify operative limits

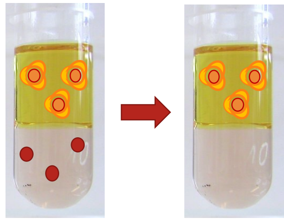
3. Stability studies

Different approaches to simulate effect of nuclear fuel radiation

<u>Type of radiation:</u>

- ❑ ALPHA radiation (in-situ radiation)
- ❑ He ion bean
- ❑ GAMMA radiation (^{60}Co or ^{137}Cs)

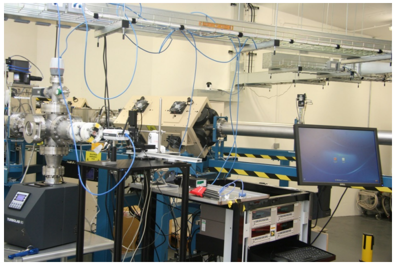
<u>In-situ radiation</u>

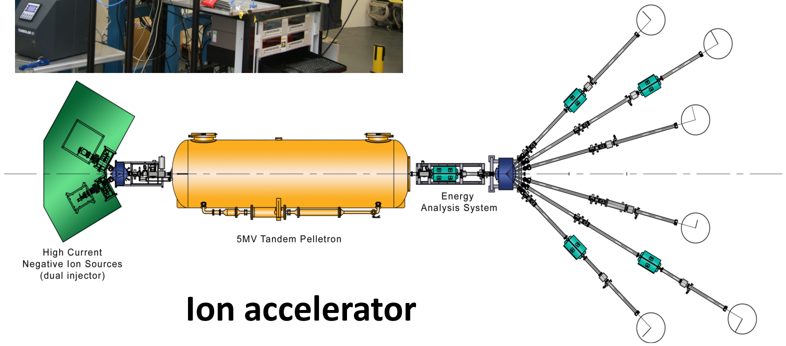


● = M^+ = At, Pu, Cm, etc

<u>Ex-situ radiation</u>

GAMMA radiation (^{60}Co)





Ion accelerator

3. Stability studies

Different approaches to simulate effect of nuclear fuel radiation

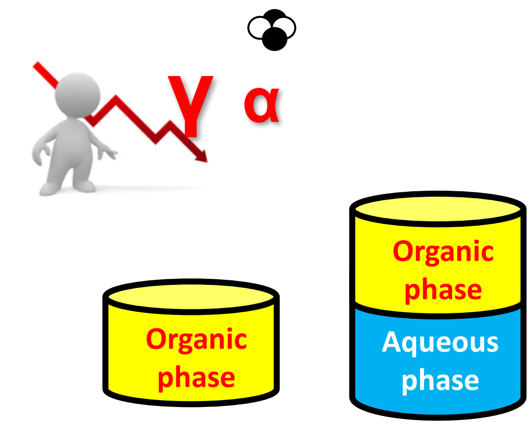
Type of radiation:

- ❑ ALPHA radiation (in-situ radiation)
- ❑ He ion bean
- ❑ GAMMA radiation (^{60}Co or ^{137}Cs)

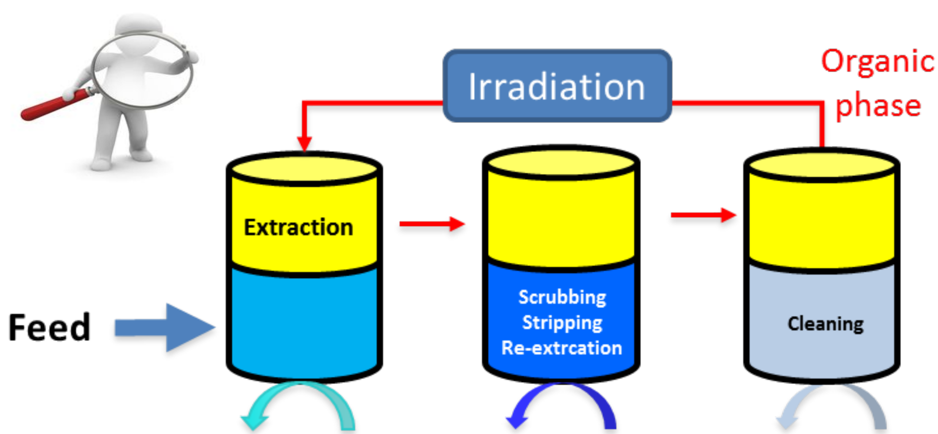
Design of experiments:

- ➢ Dose rate and integrated dose
- ➢ Static (batch) irradiation experiments
  - ➢ One or two phases in contact
- ➢ Dynamic irradiation experiments (loop tests)

Static experiments



Dynamic experiments



3. Stability studies

Different approaches to simulate effect of nuclear fuel radiation

<u>Type of radiation:</u>

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- He ion bean
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<u>Design of experiments:</u>

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<u>Facilities available in GENIORS consortium</u>

- SCK•CEN, Belgium
- Chalmers, Sweden
- Manchester (Dalton Cumbria), UK
- NNL, UK
- Náyade, CIEMAT, Spain
- INL, US, (GENIORS-DOE collaboration)
- Marcel, CEA, France

4. Stability studies along process development

System screening

Process development and optimization

Loops

Hot Test

Scale-up

Stability studies are necessary at each steps of process development

Industrial implementation

Key for a successful industrial implementation is an integrated approach of stability studies

4.1 Stability studies along process development: Batch experiments I

System screening

- Extraction behavior (**D_M, SF,** etc) as function of dose
- Decrease of main extractant concentration as function of dose

Alpha and gamma spectrometry and ICP-MS

Quantitative/semi-quantitative HPLC-MS/DAD and GC-MS

Influence of structure of extractants

- Presence of heteroatoms (O, P, N, S) introduces an additional weak point and leads to a lower overall radiolytic or hydrolytic stability.

  Ethers (CH_2-O-CH_2-)
- Presence of aromatic moieties could enhance the stability
- Lengthening the alkyl chains
  - It slightly increases resistance to degradation
  - It increases the yield of hydrogen production, (higher C–H cleavages)
  - It forms more lipophilic degradation compounds

4.1 Stability studies along process development: Batch experiments I

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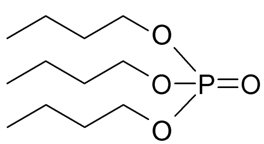
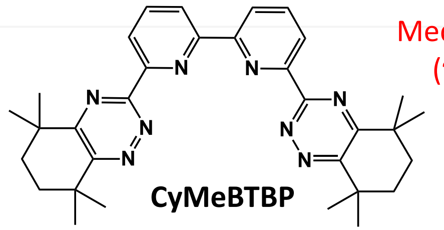
- Extraction behavior (**D_M, SF,** etc) as function of dose
- Decrease of main extractant concentration as function of dose



TBP: Tri n-Butyl fosfate

(PUREX process)

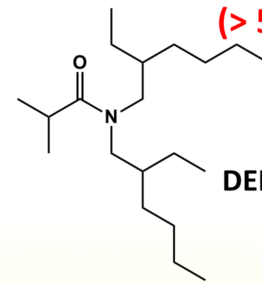
Very high stability



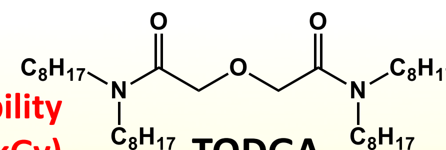
CyMeBTBP

Medium/low stability
(~ 100-300 kGy)

Very high stability
(> 500 kGy)



DEHiBA



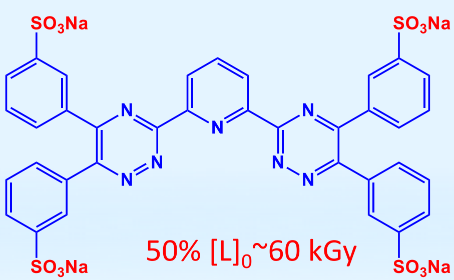
TODGA

High stability
(~ 500 kGy)

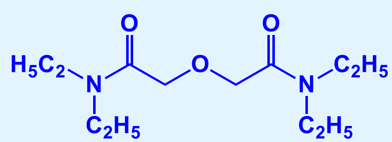
Hydrophobic

Water soluble

SO_3PhBTP



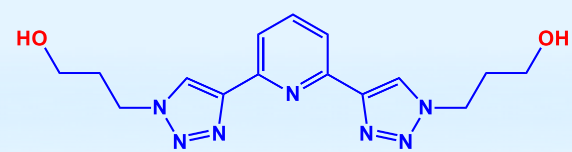
50% $[L]_0$~60 kGy



TEDGA

50% $[L]_0$~100 kGy

$D_{(M)}$ unaffected up to 200 kGy
50% $[L]_0$~100 kGy



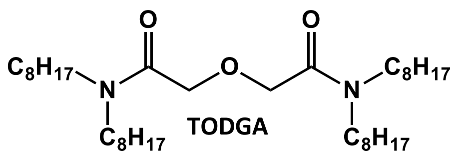
PTD

❖ In general, molecules in the aqueous phase are more affected by radiation

4.1 Stability studies along process development: Batch experiments I

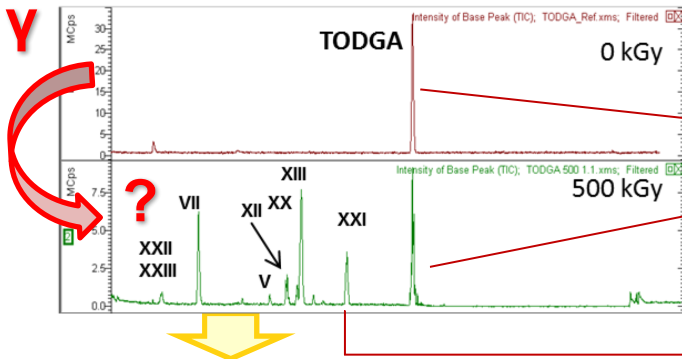
System screening

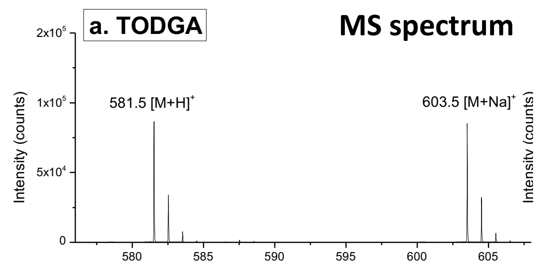
- Extraction behavior (**D_M, SF,** etc) as function of dose
- Decrease of main extractant concentration as function of dose
- **Identification of degradation compounds**

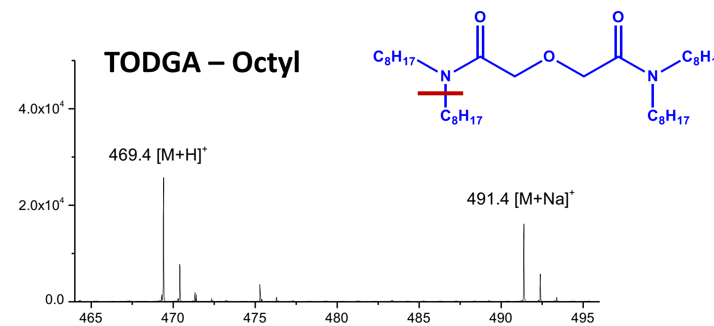


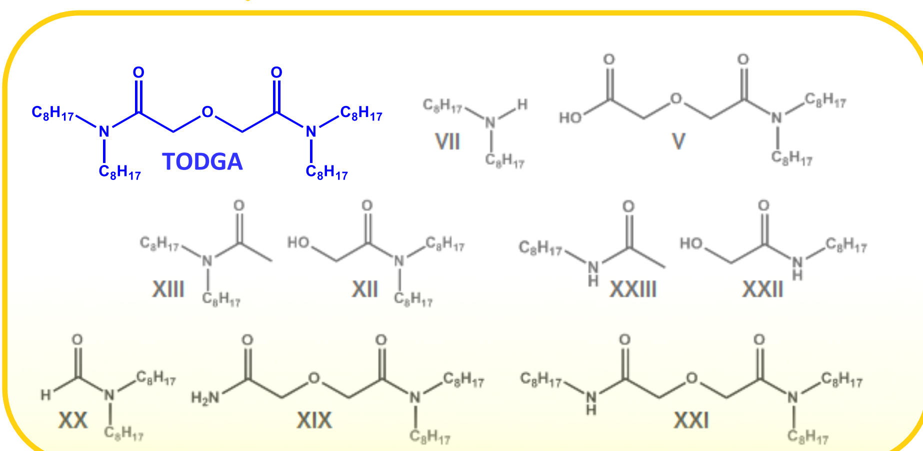
Mass Spectroscopy
- **Gas Chromatography (GC-MS)**
- **Liquid chromatography (HPLC-MS)**

HPLC-MS cromatogram





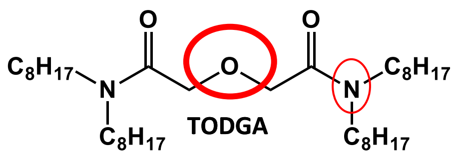




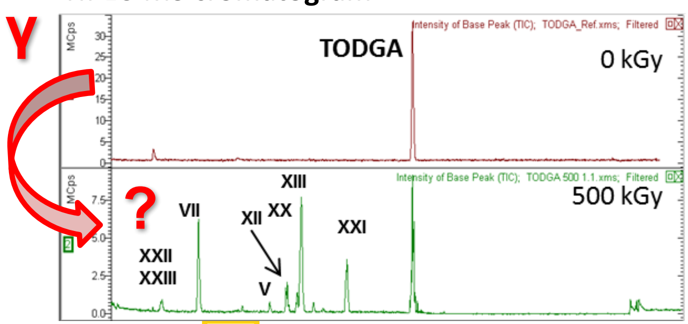
4.1 Stability studies along process development: Batch experiments I

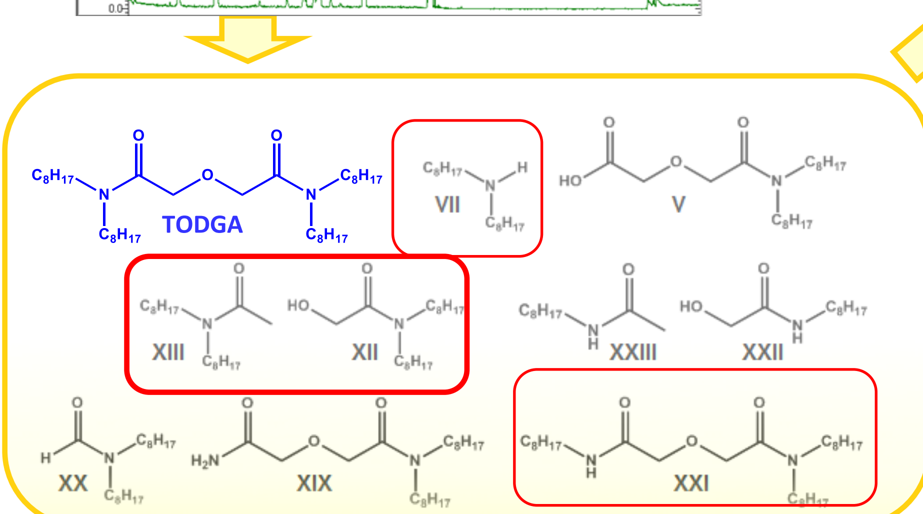
System screening

- Extraction behavior (**D_M, SF,** etc) as function of dose
- Decrease of main extractant concentration as function of dose
- **Identification of degradation compounds**
- **Weakest point of the molecule**
- **Effects of diluents, pre-treatment and phase modifier**

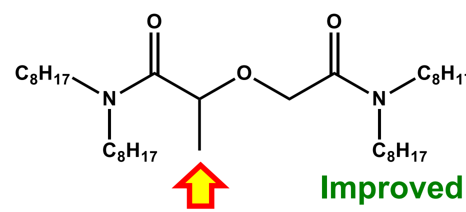


HPLC-MS cromatogram



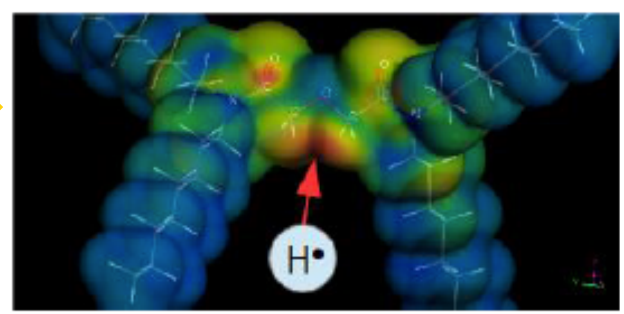


MeTODGA



Improved structures???

Modelling studies agree!!

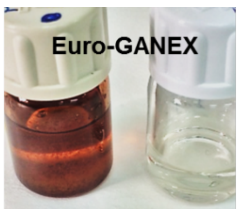


4.1 Stability studies along process development: Batch experiments II

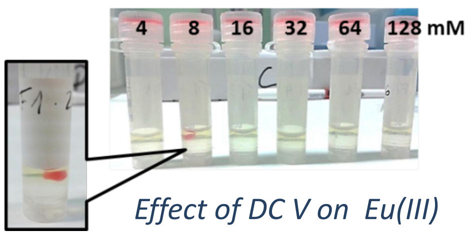
System screening

Process development and optimization

- Effects on the performance
  - Co-extraction or back extraction problems
  - 3º phase, kinetics, loading capacity
  - Phase Disengagement Time Ratio (DTR)
  - Density, viscosity and hydrodynamic
- Phase transferences or losses
- Possible accumulation of DCs

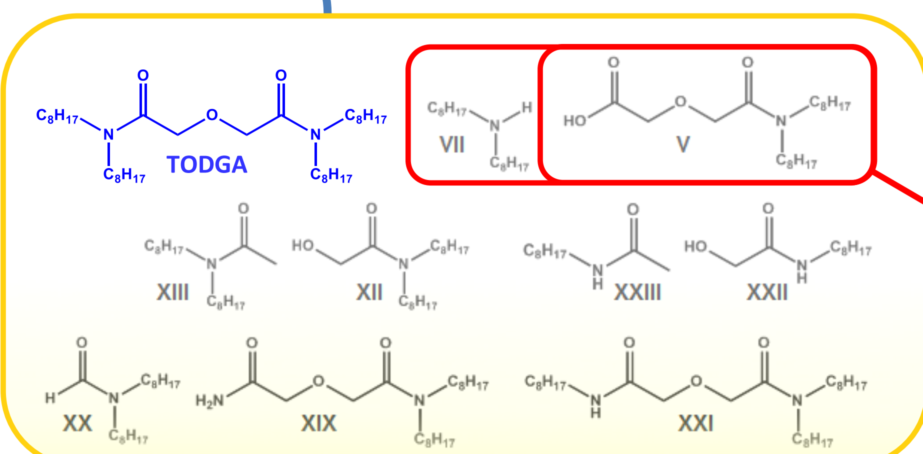


3 DCs responsible of insolubilities observed.



Effect of DC V on Eu(III) loading capacity

DCs properties



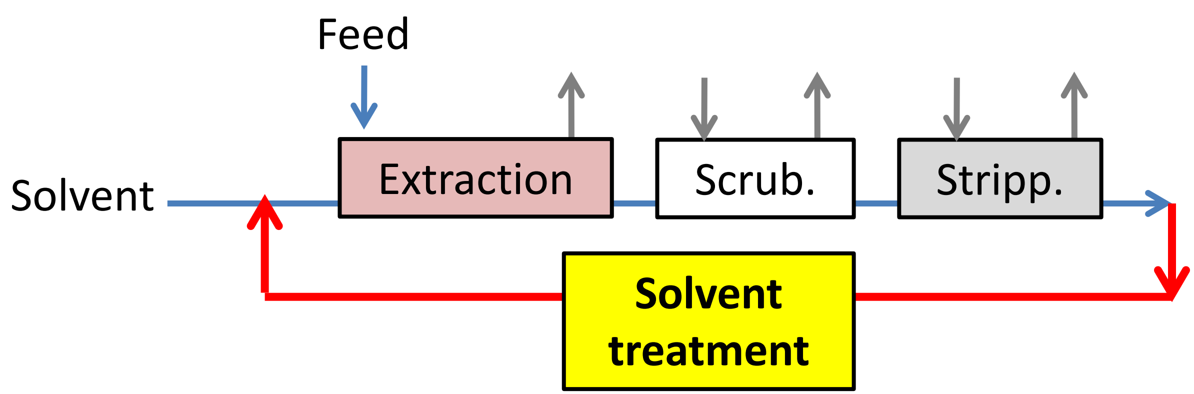
Accumulation:
More back-extraction stages would be necessary for Ln recovering

4.1 Stability studies along process development: Batch experiments II

System screening

Process development and optimization

- Effects on the performance
  - Co-extraction or back extraction problems
  - 3º phase, Kinetics, loading capacity
  - Phase Disengagement Time Ratio (DTR)
  - Density, viscosity and hydrodynamic
- Phase transferences or losses
- Possible accumulation of DCs
- **Optimization of the flowsheets**
  - Additional extraction, scrubbing or stripping steps
  - **Additional steps for clean-up**



Solvent treatment

- Basic washing
- Acidic washing

4.2 Stability studies along process development: Safety first!

System screening

Process development and optimization

Gas generation: H_2 production measurements

$$CH_3(CH_2)CH_3 \rightarrow CH_3(CH_2)CH_3, e_{solv^-}, CH_3(CH_2)CH_3, CH_3, H_2 \text{ etc}$$

$$H^{\bullet} + TODGA \rightarrow H_2 + TODGA^{\bullet}$$

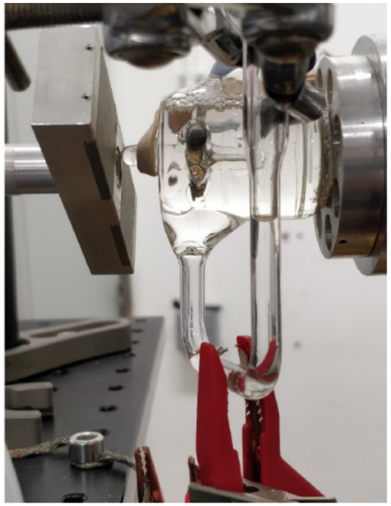
$$2e_{aq}^{-} + 2H_2O \rightarrow OH^{-} + H^{\bullet} + H_2 + \text{etc}$$

TODGA-based solvents

To understand its production:

- **Diluents effect**
- **Nitric acid effect**
- **Phase modifier effects**

He^{2+} Irradiations



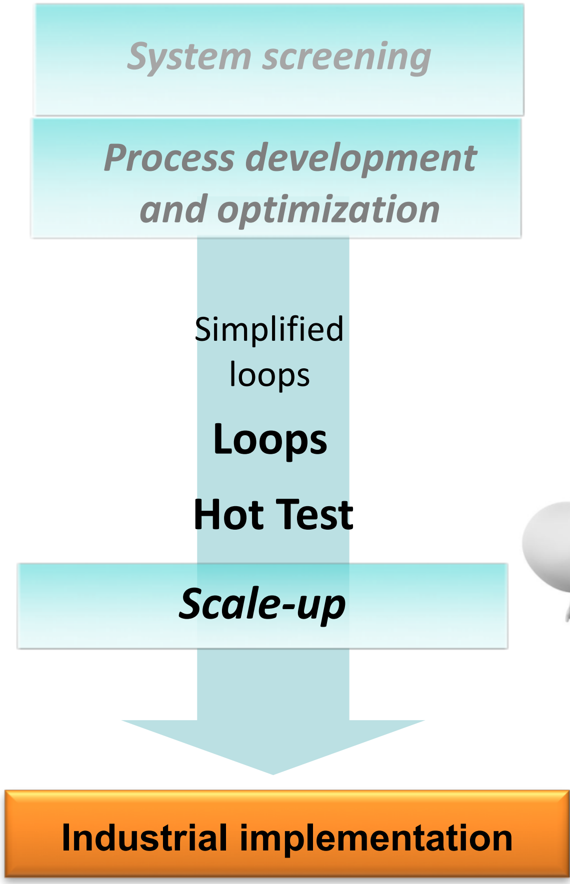
Gamma irradiation in static vessels

$+H_2$

U. Manchester, NNL and U. Lancaster collaboration

Daniel Whittaker *et. al.* 2nd Radical Behavior Workshop, Würzburg, Germany, April 19-20 th 2018

4.3 Stability studies along process development: Dynamic experiments



Continuous flowsheet implementations

Dynamic irradiation experiments

- Long term behavior of the solvent (D_M, SF, hydrodynamics, etc)
- Control of extractant concentration and adjust solvent supplies
- Effects of recycling treatment
- Monitor accumulation of products and their impact

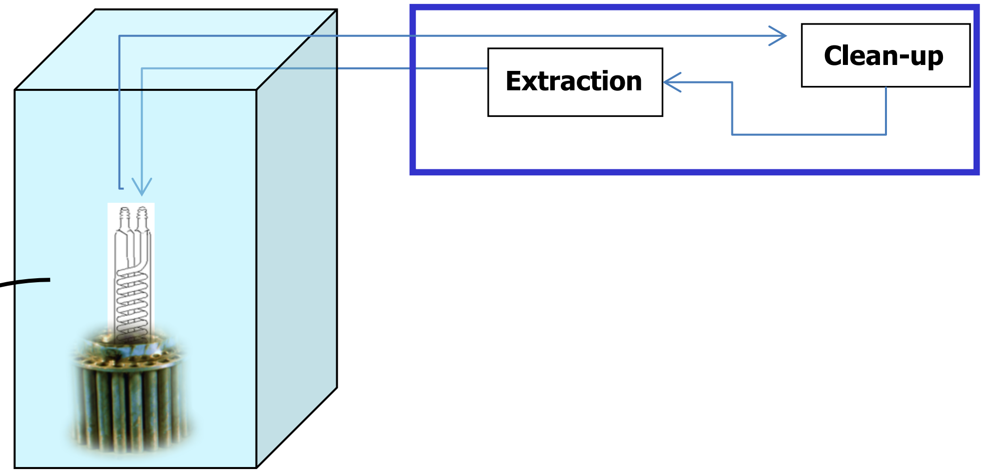
These experiments need an important setting-up and implementation!

4.3.1 Dynamic experiments: Simplified IRRADIATION LOOPS

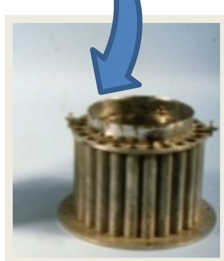
Dynamic experiments, γ Náyade irradiation facility, CIEMAT (Spain)

- Continuous irradiation (^{60}Co sources)
- Analysis
  - Solvent extraction properties and composition
    - Distribution ratios
    - Ligand concentration
    - Degradation products
    - Acid concentration

Náyade pool

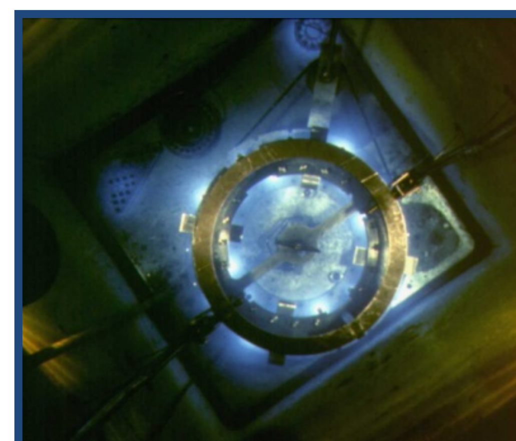


Irradiation device



Glass contactors

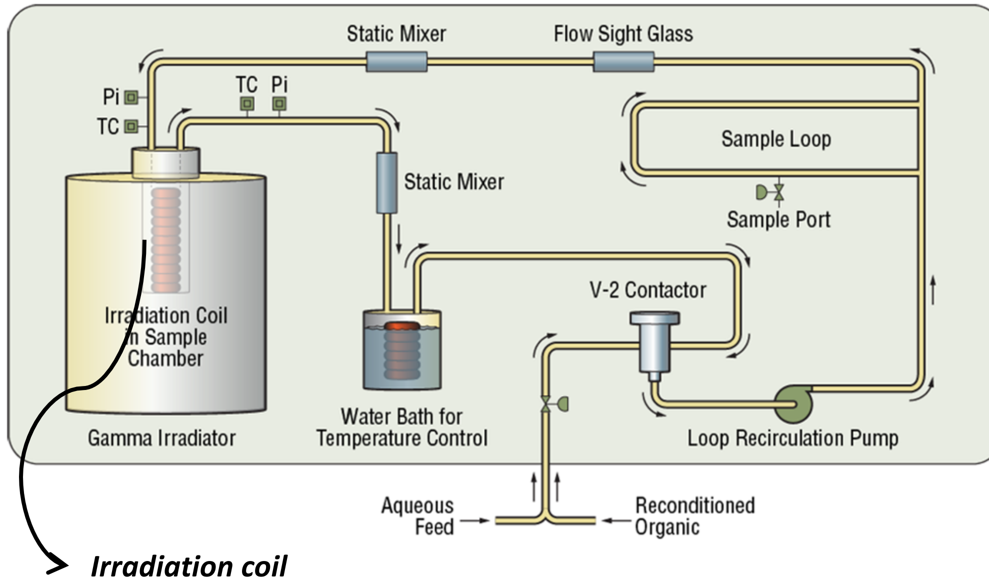
Glass coil



4.3.2 Dynamic experiments: IRRADIATION LOOPS I

Irradiation loop, INL (US)

- Continuous irradiation (^{60}Co sources)
- Continuous flowsheet simulation
- Analysis
  - Solvent extraction properties and composition
    - Distribution ratios
    - Ligand concentration
    - Degradation products
    - Acid concentration
  - Phase disengagement times



Irradiation coil

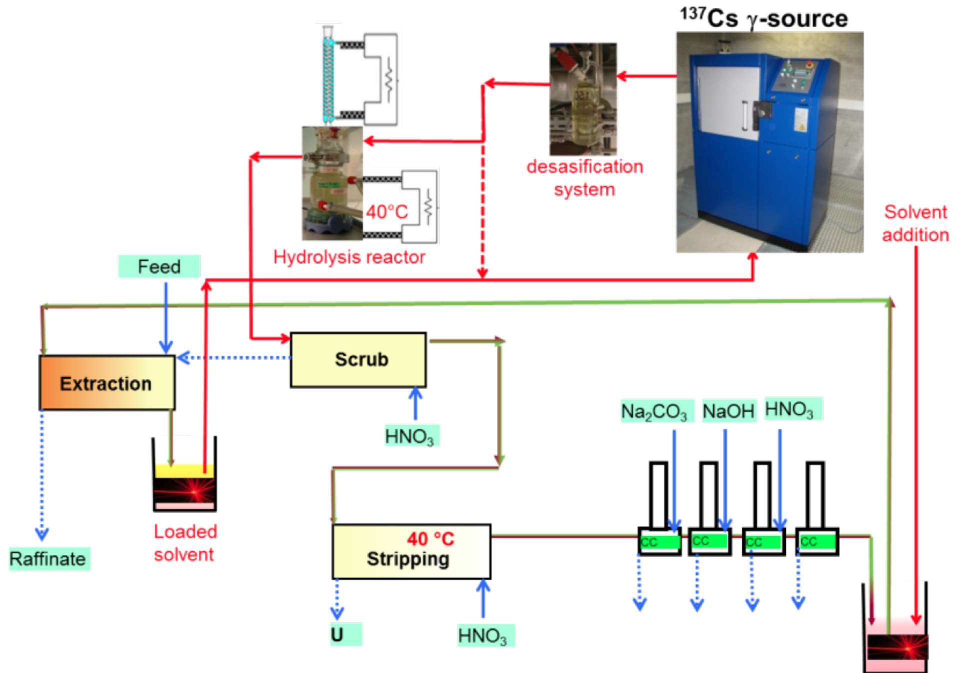
Reconditioning loop

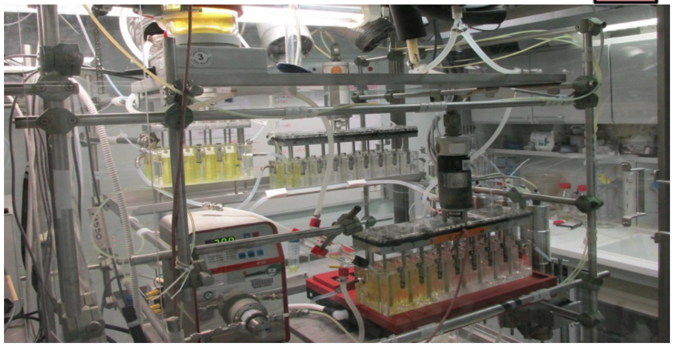
D. Peterman et.al. *Ind. Eng. Chem. Res.* **2016,** *55*, 10427−10435

4.3.2 Dynamic experiments: IRRADIATION LOOPS II

MARCEL γ Irradiation facility, CEA (France): A process platform

- Continuous irradiation (^{137}Cs sources)
- Continuous flowsheet simulation and implementations
  - Recycling and treatment of solvent
  - Control of extractant concentration and adjust solvent supplies
  - Monitor of breakdown accumulation products and impact on solvent properties
- Analysis
  - Distribution ratios
  - Ligand concentration
  - Degradation products
  - Physico-chemical properties
  - Gas generation
  - Hydrolysis reactor





M.C. Charbonel *et. al.* 2nd Radical Behavior Workshop, Würburg, Germany, April 19-20 th 2018

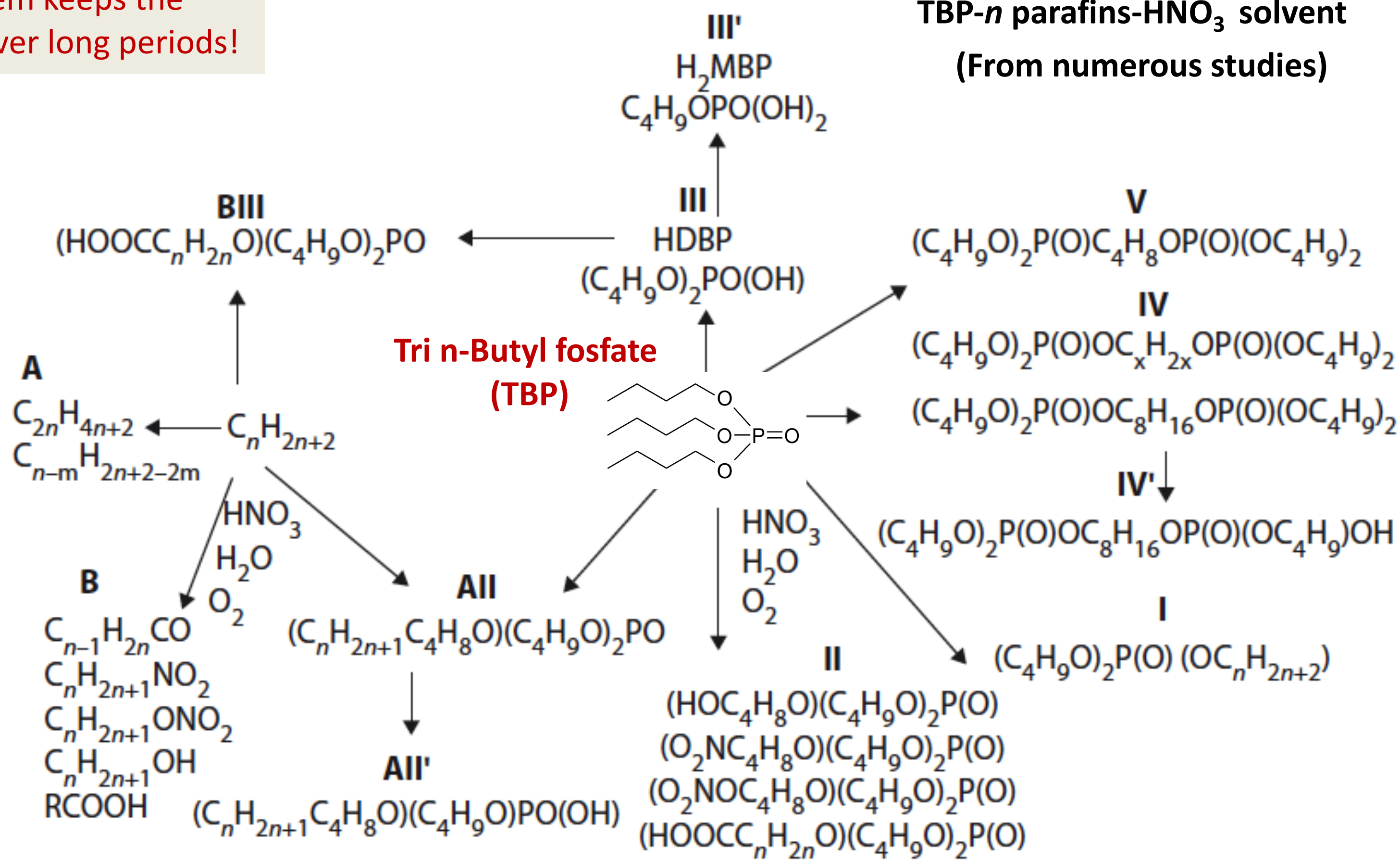
4.4 Example of integrated stability studies (PUREX process)

Industrial plants experience:

- Very high resistance!
- Extraction system keeps the performance over long periods!

Degradation compounds of TBP-*n* parafins-HNO_3 solvent

(From numerous studies)



L. BERTHON, M-C. CHARBONNEL. *Radiolysis of solvents used in nuclear fuel reprocessing*, Chapter 8 in Vol 19 Ion exchange and Solvent extraction, Ed. CRC Press, B. Moyer, 2010, pp 429-514.

4.4 Example of integrated stability studies (PUREX process)

Irradiation loop platform at CEA (France)

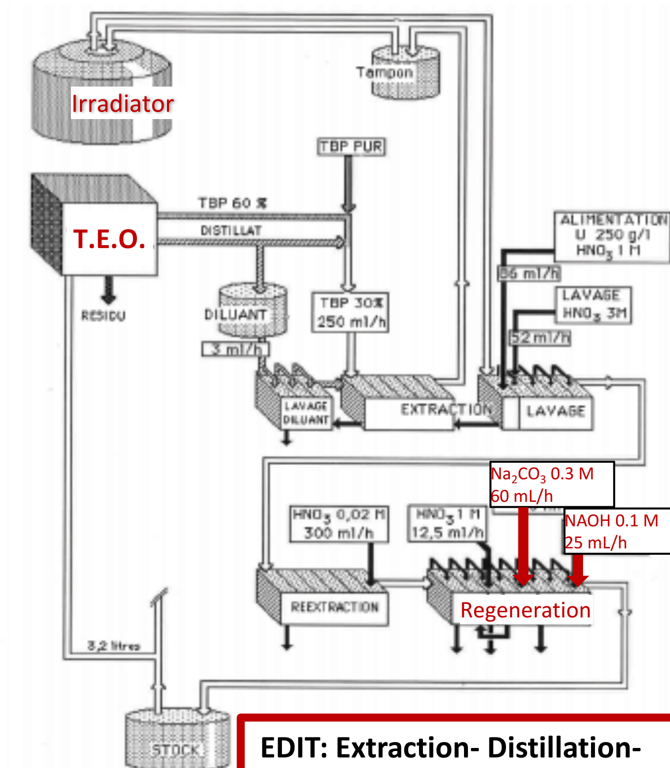
Advance solvent clean-up for PUREX process

Objectives

To check the efficiency basic washing + distillation solvent treatment

Evaluate degradation products accumulations after years

- Simulation of the 1st cycle of PUREX, U-Pu extraction
- Irradiation of solvent (840 mL) by ^{60}Co 8,6 kGy/h
- Treatment with distillation unit (1/3 of the solvent volume)- 3L of solvent – Scale 1/1000
- Simulation of 0.5 year in the plant, but higher irradiation to accelerate the degradation (**more than 2.5 years**)



EDIT: Extraction- Distillation-Irradiation-Treatment

Main results

- ✓ Stabilisation of physico-chemical properties
  - Efficiency of basic treatment: (RCOOH, HDBP,…)
  - Efficiency of TEO: compounds with low ebullition point, high-molecular-weight and Pu complexants
- ✓ Some degradation products non eliminated, **but no consequences on the process**

La Hague Plant results after more than 25 years:

Evolution of the solvent consistent with observations from EDIT test

Basic data obtained helps to find solutions, in case of malo-operations

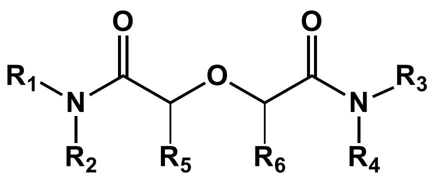
4.4 Example of integrated stability studies (Advanced processes)

Objectives

Integrated stability evaluation of NEW AVANCED PROCESSES for its implementation

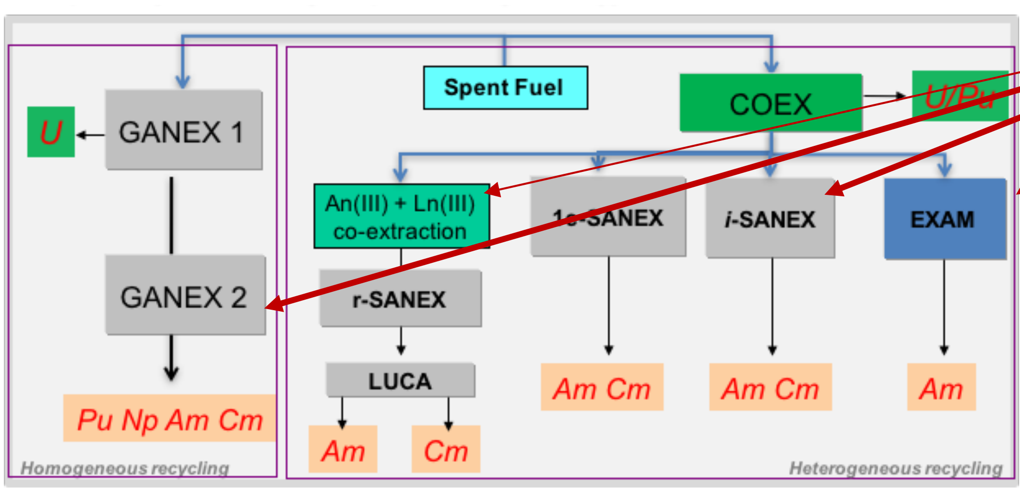
DGA-based solvents

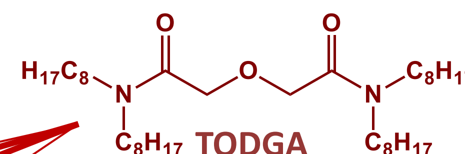
Japan, India, USA, Europe



- High affinity for An(III)/Ln(III)
- Easy and cheap synthesis
- CHON principle
- **Good hydrolytic/radiolytic resistence**
- Numerous process demonstrations and applications, worldwide, mainly using lipophilic DGAs

European hydrometallurgical recycling strategy

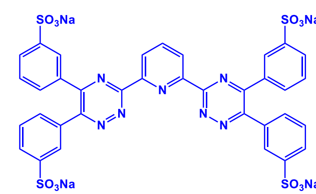




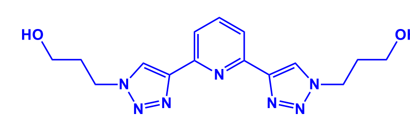
TODGA

+ phase modifiers

An stripping agents



SO_3PhBTP



PTD

4.4 Example of integrated stability studies (Advanced processes)

Stability studies objectives

Integrated evaluation of the robustness of the NEW AVANCED PROCESSES for their implementation

System screening

Process development and optimization

Loops

Hot Test

Scale-up

Industrial implementation

(ACSEPT, SACCSES, GENIORS projects)

DGA stability studies (*i*-SANEX and GANEX)

1- Behavior of the system
- *Extraction properties*
- *Physico-chemical performance*

2- Understand and improve the system
- *Composition of the system*
- *Remaining concentration of ligands*
- *Degradation compounds*
  - *Degradation pathways* → *Structural improvement*
  - *Effects on degraded solvent* → *Optimization of solvents*

A lot of experience and fundamental data!!!

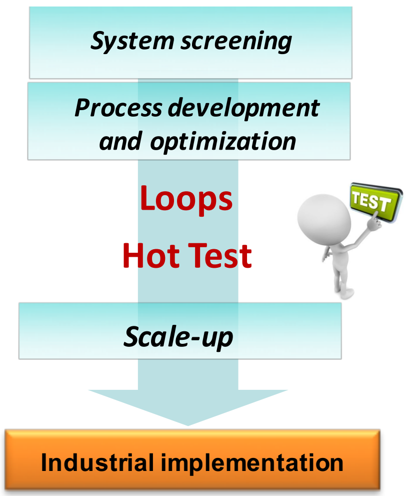
3- Long term behavior under relevant process conditions
- Better understanding of critical factors
- To find relevant process conditions to simulate
- To design a as simple possible loop tests, but realistic

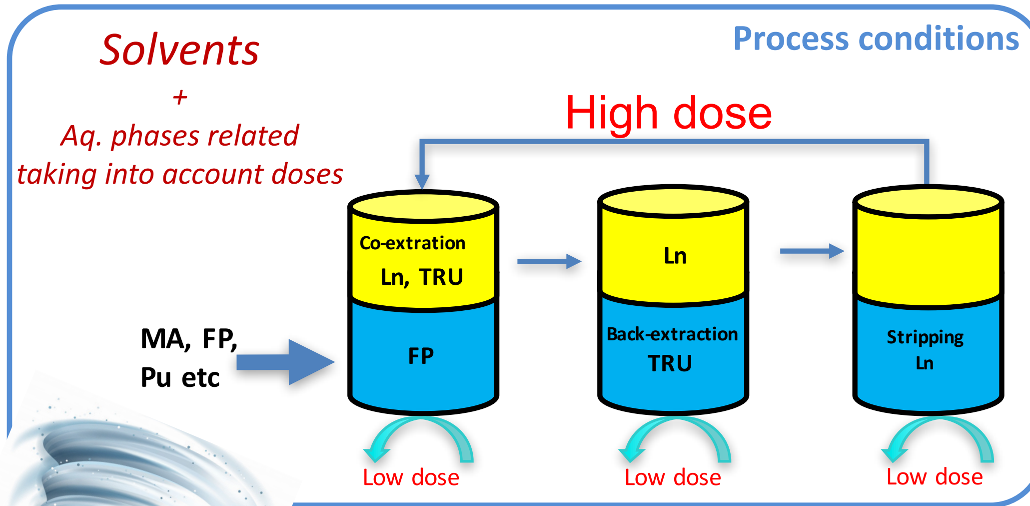
DOE and GENIORS irradiation collaboration

4.4 Example of integrated stability studies (Advanced processes)

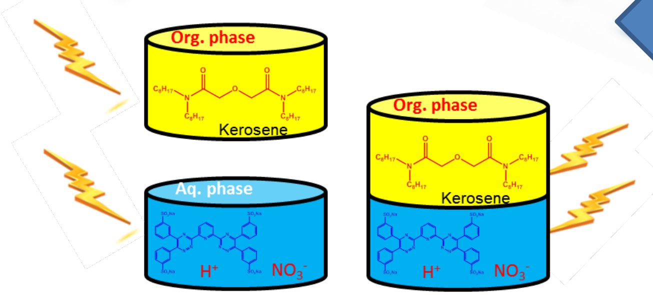
Stability studies objectives

Integrated evaluation of the robustness of the NEW AVANCED PROCESSES for their implementation



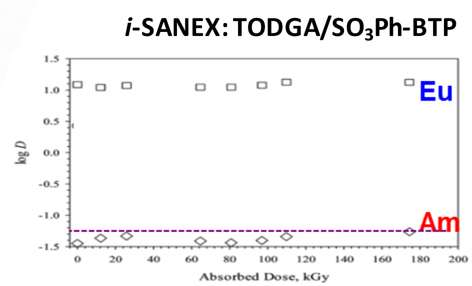


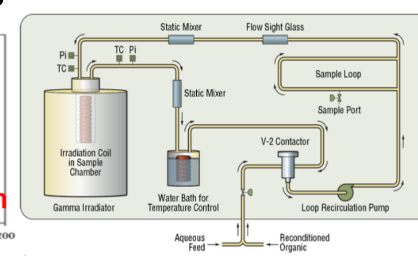
Batch experiments



Loops experiments

INL facility





D. Peterman, et al. *Ind. Eng. Chem. Res* 55.39 (2016): 10427-10435.

DOE and GENIORS irradiation collaboration

5. Conclusions

Development of an extraction process for nuclear fuel recycling ⟺ *Solvent degradation must be understood to control normal and mal-operation*

Studies of long-term behavior must be an integrated approach

- ❖ Stability of the molecules
- ❖ Identification of loses of efficiency
- ❖ Degradation products and their impact
- ❖ Identification of risks, limits and mal-operation situations
- ❖ Identification of recycling strategy

5. Conclusions

Development of an extraction process for nuclear fuel recycling ⟷ *Solvent degradation must be understood to control normal and mal-operation*

Studies of long-term behavior must be an integrated approach

- The stability must be considered not only from the quantitative but also from the qualitative aspect
- The objective is not a perfect resistance, but sufficient for an industrial implementation
- **Dedicated representative loop tests are of key importance before industrial implementation**

Reliable models from batch experiments → *Irradiation loop platforms*

Acknowledgment

All GENIORS partners

CEA	JRC-ITU	UEDIN
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CIEMAT	KIT	UNIPR
CNRS	LGI	ULEEDS
CTU	NNL	UREAD
ICHTJ	POLIMI	ULANC
IIC	SCK-CEN	EDF
IRSN	TWENTE	AREVA

Cooperation agreement with

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