Long-term behaviour of extraction systems for nuclear fuel recycling

Hitos Galán, Andreas Geist

Nuclear Fission Division of CIEMAT, Spain
KIT-INE, Germany

Topical day

When partitioning meets transmutation

25 October 2018, Antwerp

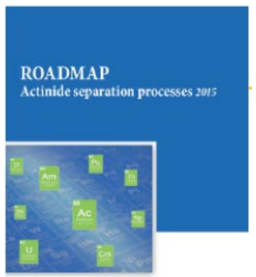
Funded by the Horizon 2020
Framework programme of the European Union
(Grant Agreement Number 730227)

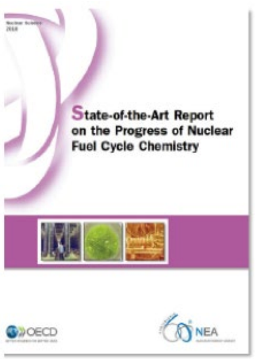
Outlines

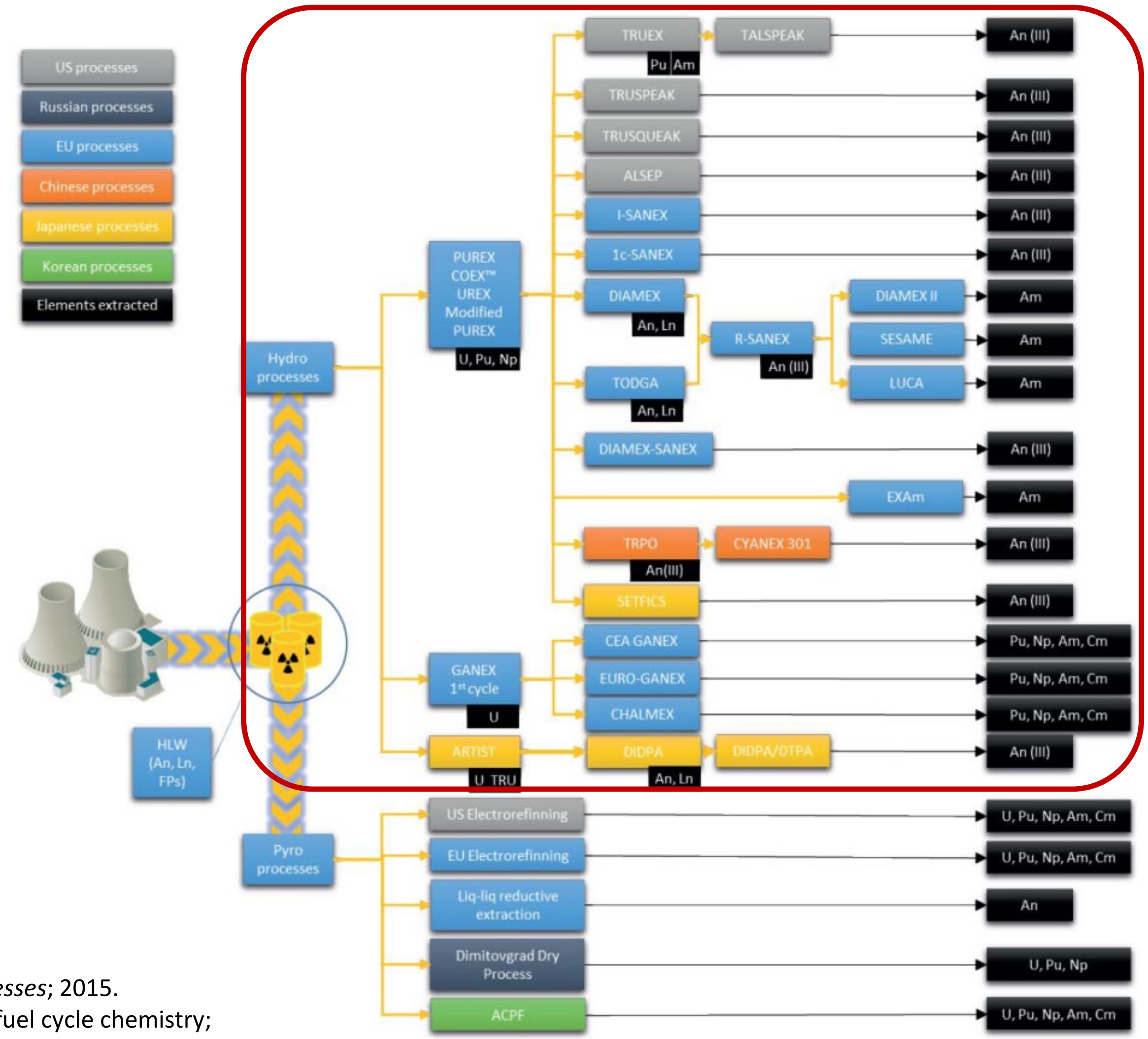
1. *Introduction*
   - *Extraction process development*
2. *Degradation of solvents and long-term behavior*
3. *Stability studies*
4. *Stability studies along process development*
5. *Main conclusions*

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

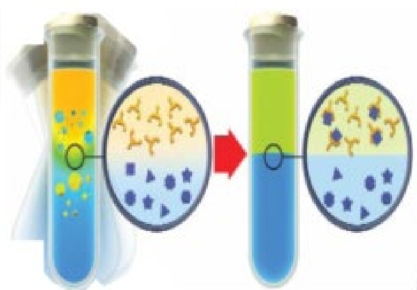
Steps and limiting points

System screening

Process development and optimization

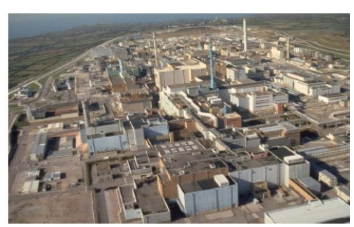
Hot test

Scale-up



Batch experiments

Reprocessing plant



Industrial application

Extracting and complexing properties

Industrial diluents

Good kinetics, viscosity, reversibility, etc.

Low synthesis cost

Stability: to keep its properties

GENIORS

1. Introduction

Extraction process development for nuclear fuel recycling

Steps and limiting points

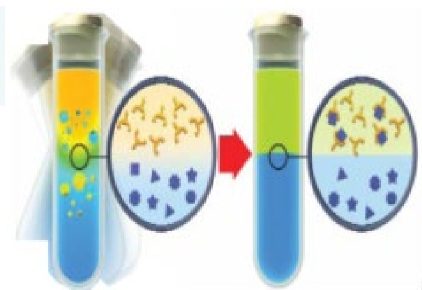
System screening

Process development and optimization

Hot test

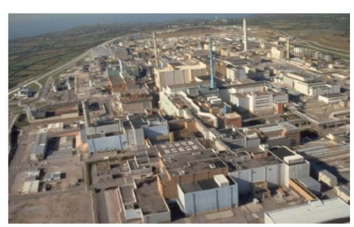
Scale-up

Industrial application



Batch experiments

Reprocessing plant



Extracting and complexing properties

Process chemistry

Flowsheet design and modelling

Validation at lab scale

Contactors development

Integrated experiments

using real solutions

GENIORS

2. Degradation of solvents and long term behaviour

What happens to a solvent during the process operation

Evaporation or carry-over effects to other phases

Thermal degradation

Chemical attacks

Hydrolytic degradation

Radiolytic degradation

Stability studies

Avoid loss efficiency

Identification of any unexpected behavior

Reduce costs

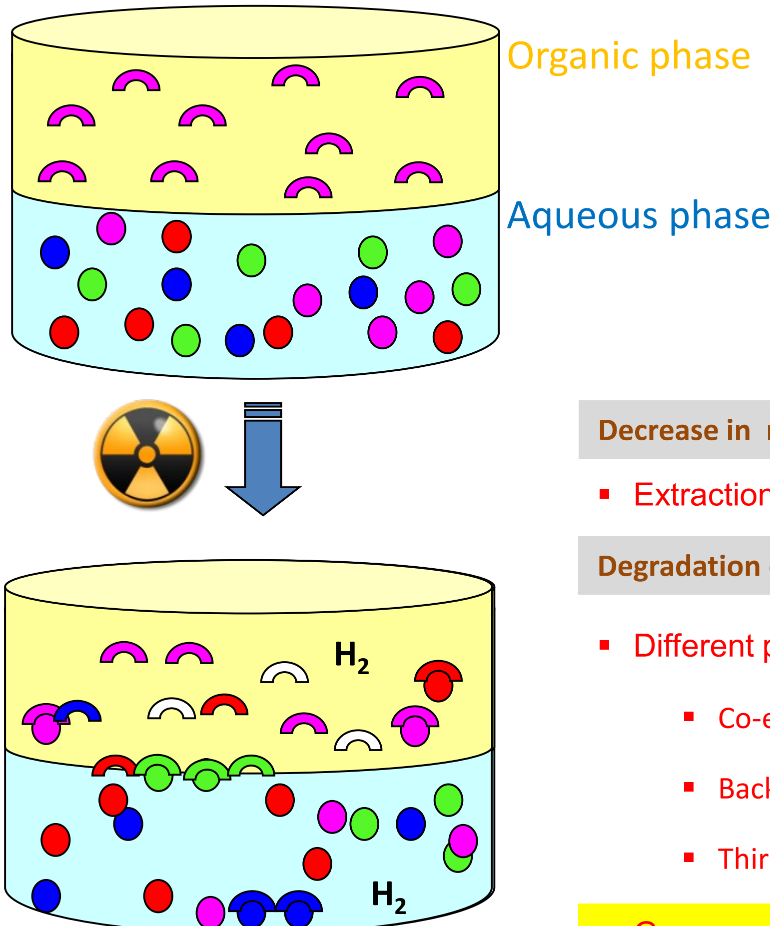
Important changes

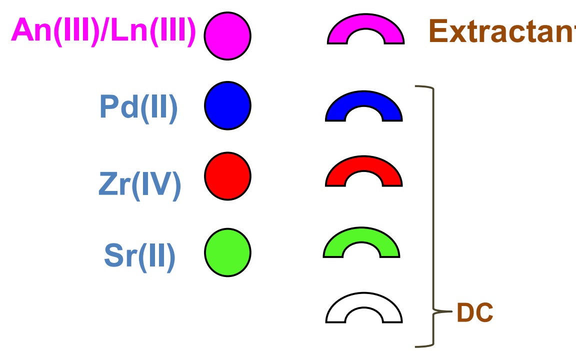
- Changes in the composition
- Changes in physico-chemical and chemical properties
- Increase of secondary waste
- Increase of costs

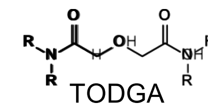
GENIORS

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

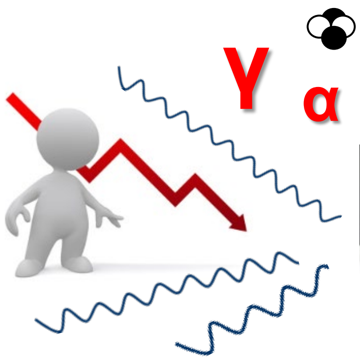
- Identify the most problematic
- Regeneration studies

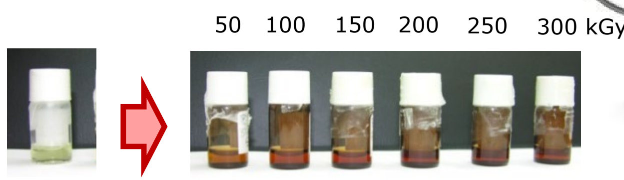
GENIORS

3. Stability studies

To simulate and study the effects to understand and predict

Simulate irradiation





How long?

Why?

What problems I have?

Modifying experimental conditions

To understand stability rules!!!

To find solutions!!!!

Improve systems

Regeneration of systems

Identify operative limits

GENIORS

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)

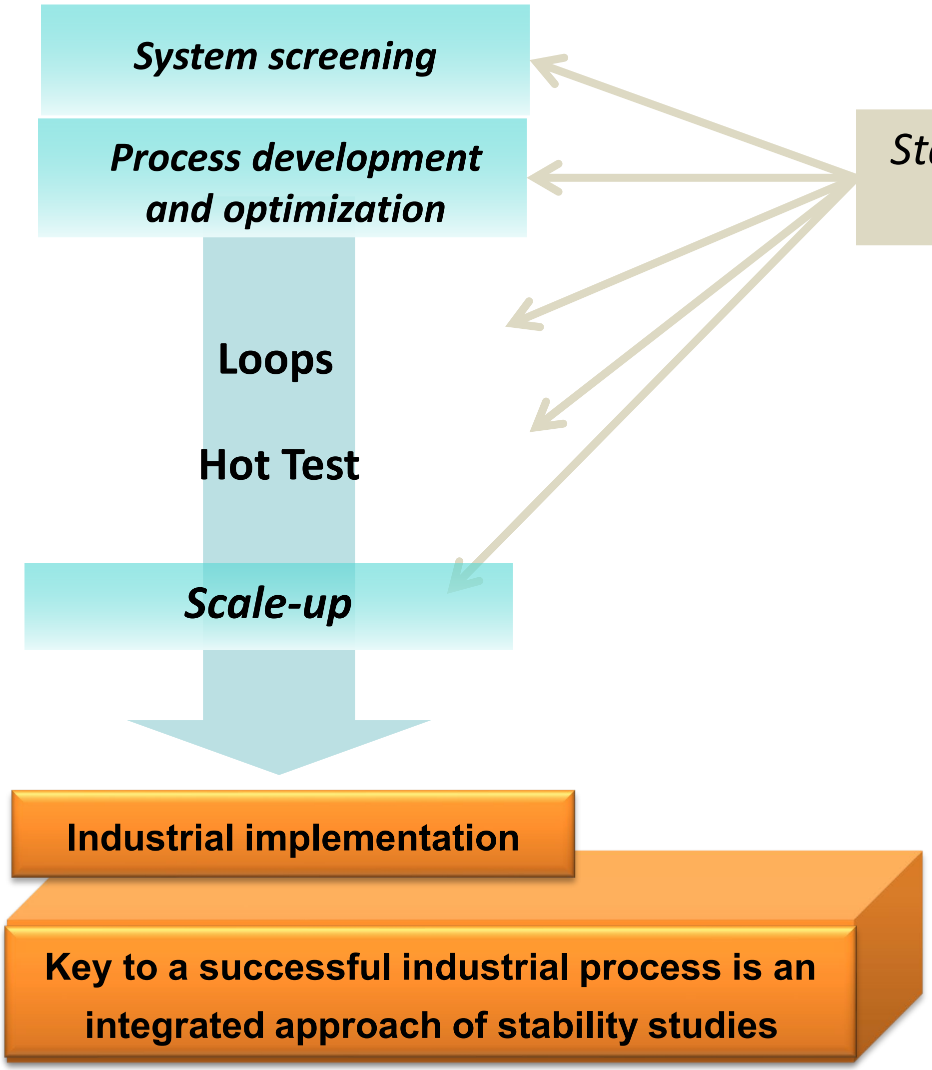
Design of experiments:

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

Facilities available in GENIORS consortium

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

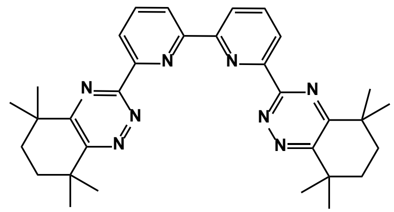
4. Stability studies a long process development



4.1 Stability studies a long process development: Batch experiments I

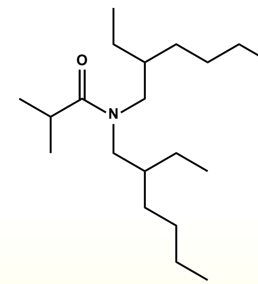
System screening

- Extraction decrease (D_M) as function of dose
- Decrease of main extractant concentration as function of dose



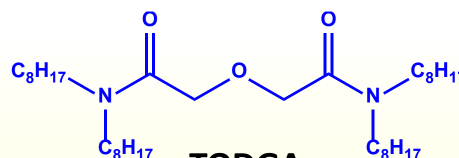
CyMeBTBP

Medium/low stability
(~ 100-300 kGy)



DEHiBA

Very high stability
(> 500 kGy)

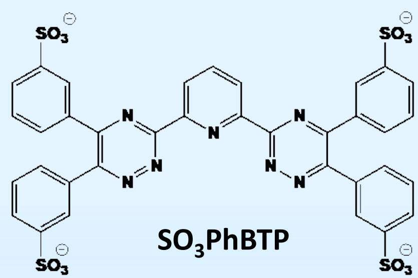


TODGA

High stability
(~ 500 kGy)

Hydrophobic

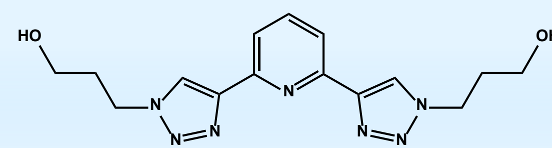
Water soluble



SO_3PhBTP

50% $[L]_0$~60 kGy

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



PTD

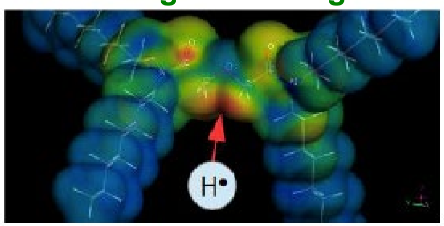
GENIORS

4.1 Stability studies a long process development: Batch experiments I

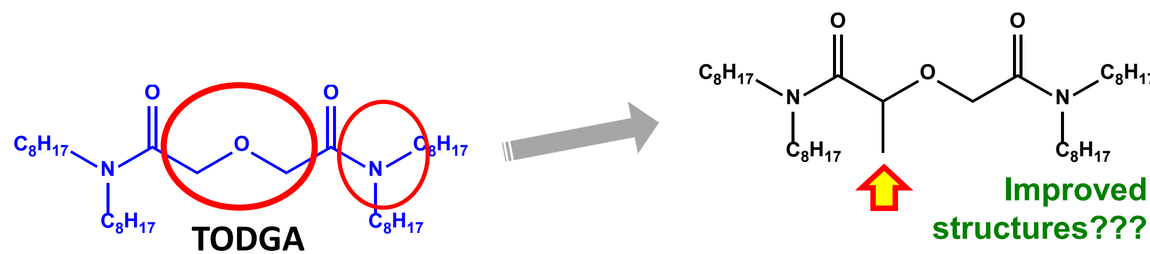
System screening

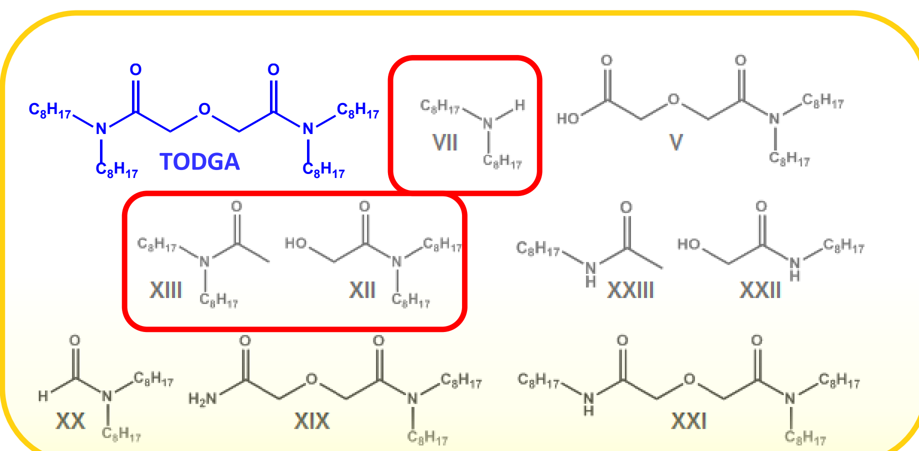
- Extraction decrease (D_M) as function of dose
- Decrease of main extractant concentration as function of dose
- **Identification of degradation compounds**
- **Weakest point of the molecule**
- **Effects of diluents, pre-treatment and phase modifier**

Modelling studies agree!!

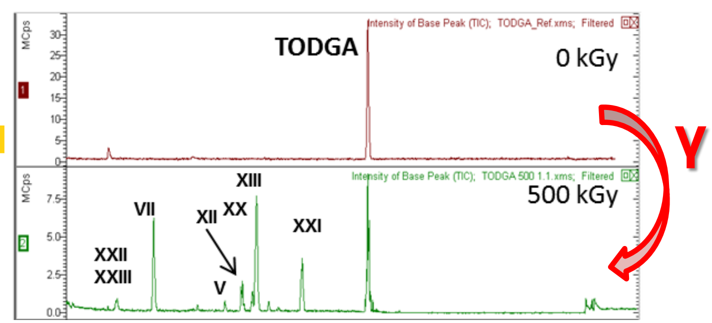


MeTODGA





HPLC-MS spectra



GENIORS

4.1 Stability studies a long process development: Batch experiments II

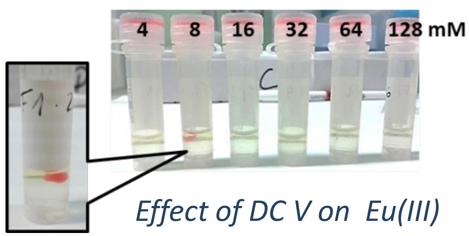
System screening

Process development and optimization

- Effects on the performance
- Phase transferences or losses
- Possible accumulation of DCs

- Co-extraction or back extraction problems
- 3º phase, kinetics, loading capacity
- Phase Disengagement Time Ratio (DTR)
- Density, viscosity and hydrodynamic

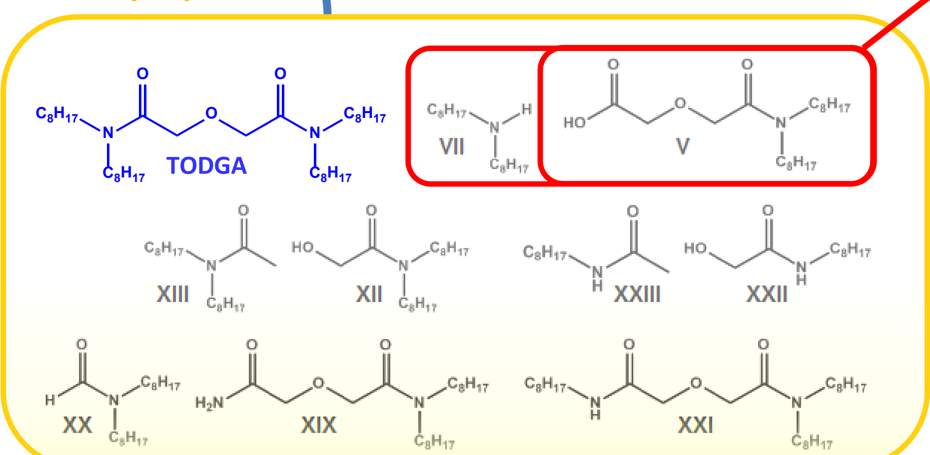
3 DCs responsible of insolubilities observed.



Effect of DC V on Eu(III) loading capacity

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

DCs properties



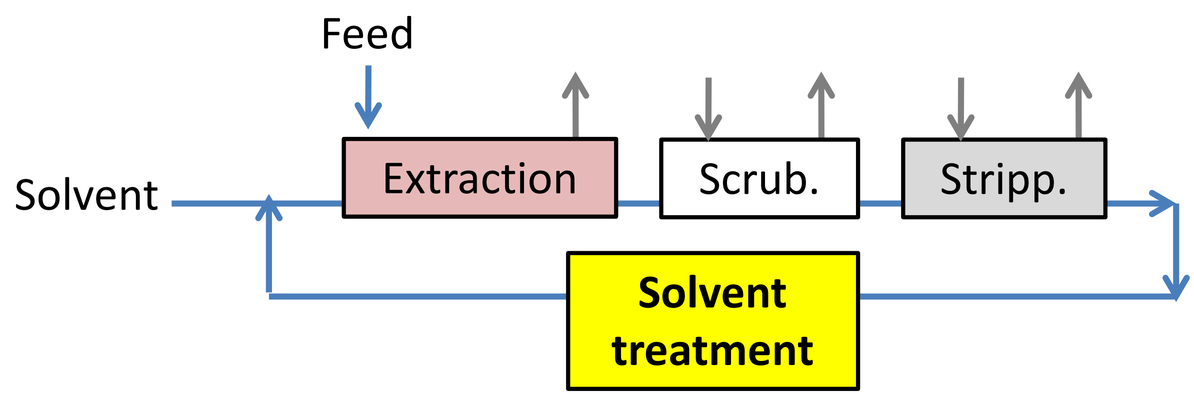
GENIORS

4.1 Stability studies a long 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 a long process development: Safety first!

System screening

Process development and optimization

Gas generation: H_2 production measurements

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

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

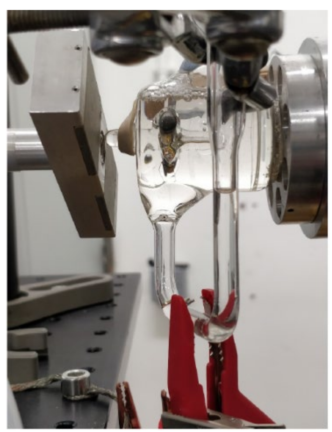
$$2e_{aq}^{-} + 2H_2O \rightarrow OH^{-} + H^{\bullet} + H_2 + \text{etc}$$

To understand its production:

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

U. Manchester, NNL and U. Lancaster collaboration:
TODGA-based solvents

He^{2+} Irradiations



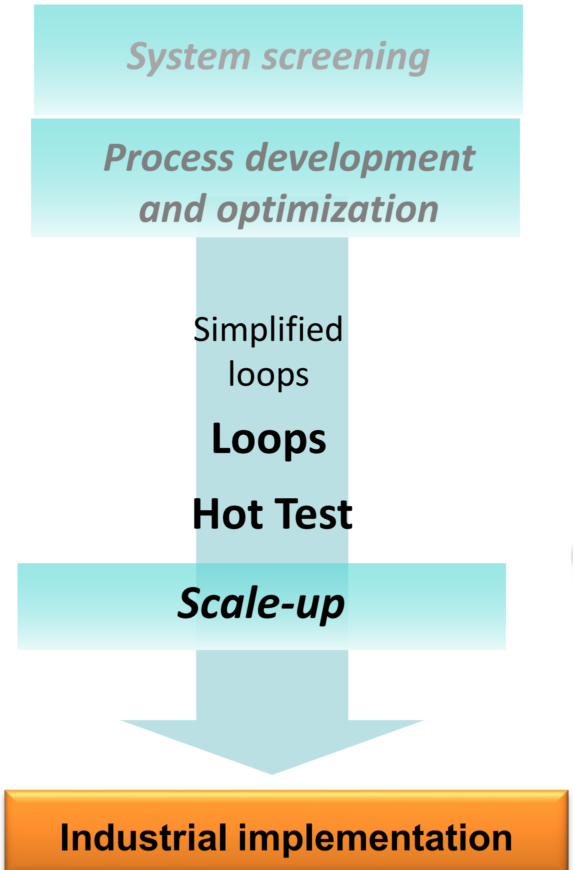
Gamma irradiation in static vessels

$+H_2$

GENIORS

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

4.3 Stability studies a long process development: Dynamic experiments



Continuous flowsheet implementations

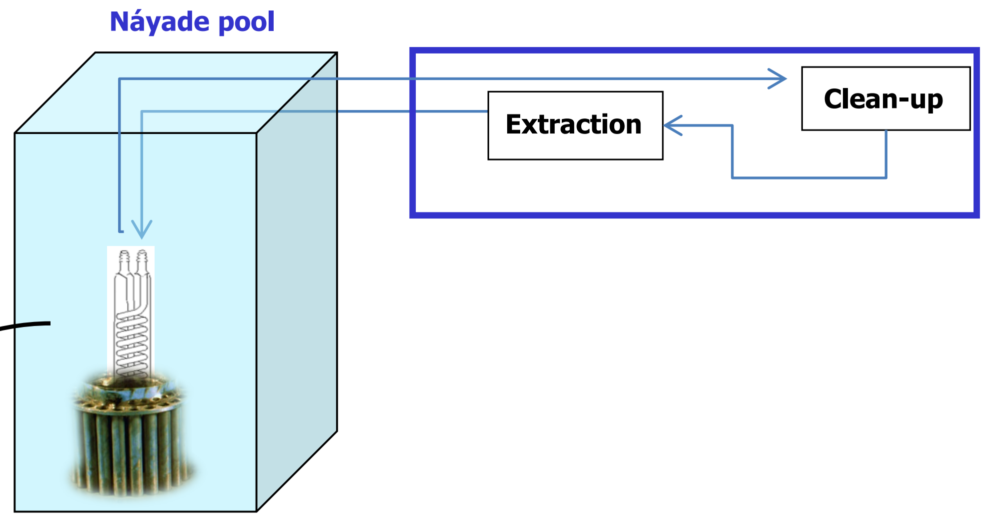
Dynamic experiments

- Control of extractant concentration and adjust solvent supplies
- Monitor accumulation of products and their impact
- Long term behavior of the solvent (recycling and treatment)

4.3.1 Dynamic experiments: Simplified IRRADIATION LOOPS

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

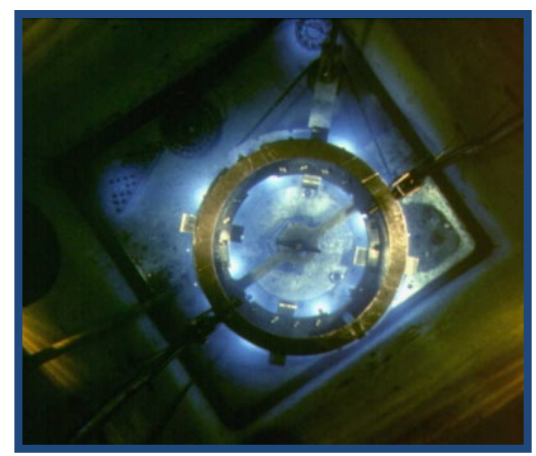
- Continuous irradiation (^{60}Co sources)
- Analysis
  - Solvent extraction properties
    - Distribution ratios
    - Ligand concentration
    - Degradation products
    - Acid concentration



Irradiation device

Glass contactors

Glass coil

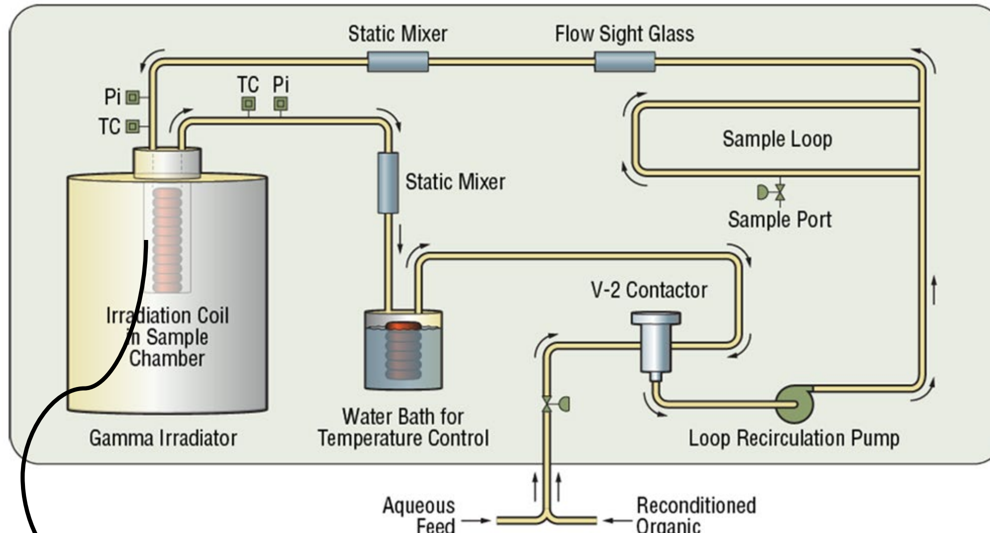


GENIORS

4.3.2 Dynamic experiments: IRRADIATION LOOPS I

Irradiation loop, INL (US)

- Continuous irradiation (^{60}Co sources)
- Recirculation under process-like conditions of irradiated mixed phases
- Analysis
  - Solvent extraction properties
    - Distribution ratios
    - Ligand concentration
    - Degradation products
    - Acid concentration
  - Phase disengagement times



Irradiation coil

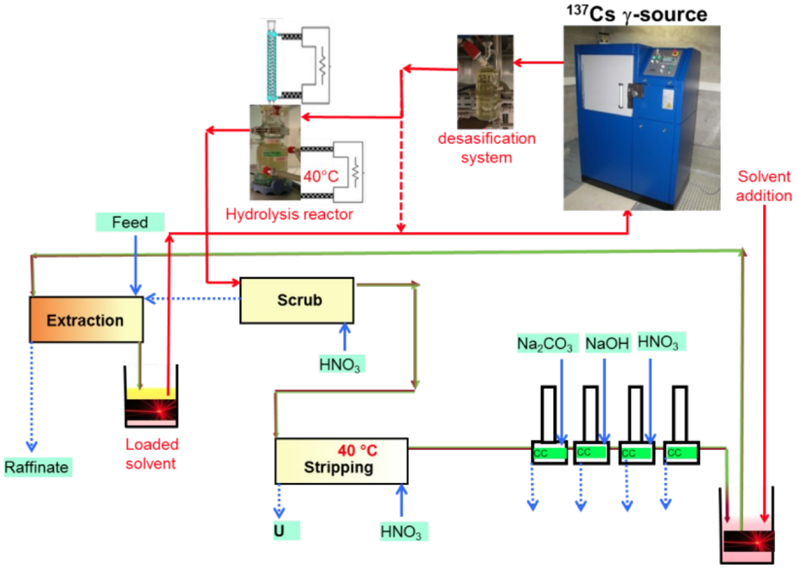
Reconditioning loop

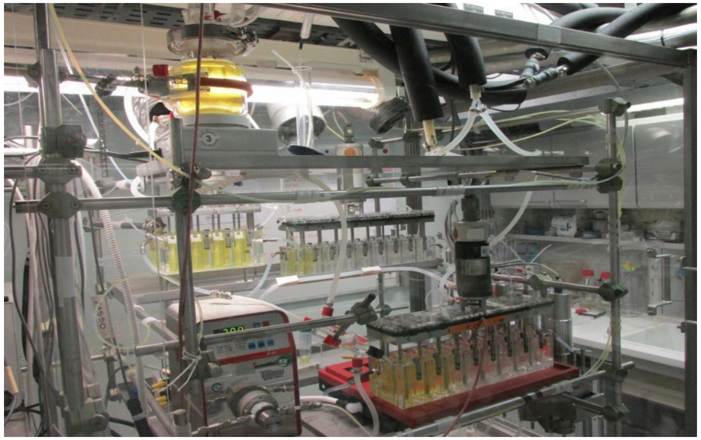
D. Peterman et.al. *Ind. Eng. Chem. Res.* **2016,** *55*, 10427−10435

4.3.2 Dynamic experiments: IRRADIATION LOOPS II

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

- Continuous irradiation (^{137}Cs sources)
- Continuous flowsheet 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





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

GENIORS

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 steps and evaluation of costs

Batch experiments → *Irradiation loop platforms*

GENIORS

Acknowledgment

All GENIORS partners

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

Cooperation agreement with

SYTRAD I
SYTRAD II

GENIORS

2nd half year meeting

Thank you for your attention

DOMAIN 1 coordinator

andreas.geist@kit.edu

WP2 leader

hitos.galan@ciemat.es

DOMAIN 2 coordinator

jean-marc.adnet@cea.fr

WP5 leader

che@chalmers.se

Project coordinator

stephane.bourg@cea.fr

Funded by the Horizon 2020
Framework programme of the European Union
(Grant Agreement Number 665906)