GENIORS, assessing the MOX fuel reprocessing in GEN IV systems

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and all the GENIORS Partners

GEN IV Fast Neutron Reactors + ADS in Europe

SFR
Sodium-cooled fast reactor

GFR
Gas-cooled fast reactor

LFR
Lead-cooled fast reactor

Reference fuel: MOX
Potential Future Fuel Cycles

DISSOLUTION

U, Pu

SEPARATION

MA

CONVERSION, FABRICATION

IRRADIATION

Specific Reprocessing

DISSOLUTION

ADS
Different separation process options developed worldwide

Reference aqueous separation process routes in Europe

- An(Ill) + Ln(III) coextraction (DAMEX)
- An(Ill)/Ln(III) separation (r-SANEX)
- An(Ill) selective Stripping (l-SANEX)
- Am selective Stripping (EXAm)

Homogeneous recycling = grouped separation GANEX

Heterogeneous recycling = enhanced partitioning DAMEX/SANEX
The FP7-SACSESS reference process flowsheets
GENIORS

FROM FUEL TO FUEL
MOX FOR GEN IV
GEN IV Integrated Oxide fuels recycling strategies

6/2017 – 5/2021
24 Partners, 11 countries
Budget 7,5M€, EU grant 5M€

Cooperation agreement with DOE (I-NERI project),
Our strategy: Chemistry and Philosophy…

“Everything should be made as simple as possible, but not simpler”
- Albert Einstein
The ambition of GENIORS: a down-selection approach

GENIORS SELECTED SCIENCE BASED STRATEGIES for Pu multi recycling and minor actinide recycling of oxide fuels in GEN IV fast reactors in order to save the uranium resource and minimize the volume and radicotoxicity of the final nuclear waste
The structure of GENIORS
WP1 - Fission product behaviour

- Investigating the solution and extraction chemistry of key fission products. Improving the actinide/fission product separation
- Further optimizing the separation processes.

**extraction chemistry** of Ru, Tc, Pd, Sr, Ag for the TODGA, GANEX and SANEX system.

Study of the speciation of FP in organic solvents and in nitric acid solutions by different analytical tools. Data are necessary to define an equilibrium model for the implementation of process related flow-sheets.

**optimisation of scrubbing steps** using well known masking agents. During the partitioning of trivalent actinides from High Active Raffinate (HAR) solutions, most processes have to cope with an undesirable co-extraction of some of the fission products. New polyaminocarboxylic ligands will be synthesised and tested under process relevant conditions.
- Ensuring a safe long-term performance of a chemical system submitted to radiation.
- Improving the resistance of the ligands as well as the systems where they are involved will be the main goal. Solvent degradation may lead to many undesirable effects, for that, the identification of loses of efficiency, the behaviour troublesome degradation products or mal operation situation due to degradation will be the key issues.

Studies will be limited to only ligands and/or chemical systems approved.

- Radiolysis & degradation products
- Destruction of organics
- Gas generation
WP3 - Solvent extraction chemistry

Improving the understanding of the reference chemical systems for advanced solvent extraction separation processes for their optimisation: grouped separation of the actinides (EURO-GANEX), separation of the minor actinides (i-SANEX), or separation of americium only (EURO-EXAM).

It includes:

- the understanding of extraction chemistry to support concept process flowsheets
- the acquisition of extraction data to support the conception of process flowsheets, and
- the identification of process options for clean-up of solvents to allow them to be recycled on plant.
Better understanding of the phenomena occurring at the solid/liquid interfaces during spent nuclear fuel reprocessing in order to support potential processes.

It will be divided in two main topics.

• **dissolution step.** It will be examined not only considering direct interactions between the chemical species coming from the solid and the solution, but also through the development of catalytic reactions at the interface.

• **conversion of actinides** by precipitation of original precursors coming from new chemical processes based on wet chemistry routes.
- Integrating the data coming from DM1
- Determining the specific conditions to develop a relevant and safe process flowsheet from these data,
- Integrating the solvent extraction process with the surrounding processes (1st solvent extraction cycle, solvent wash cycle, conversion), accounting for the interfaces between processes, and equipment, including on-line analysis.

- Hydrodynamics and stability in processes
- Technology and analysis
- Flowsheet and models
WP6 - Process Optimisation and testing including interface between SX process(es)

- Optimising the efficiencies and safety of separation processes developed under the SACSESS project (*i.e.* i-SANEX, EURO-GANEX, EXAm, CHALMEX) The main emphasis is on process development through flowsheet testing.

- Optimising the reference separation processes, particularly where significant simplification is possible or replacement of non-CHON ligands by CHON molecules can be proposed. It also includes extension of process envelopes to more challenging GenIV feeds and integration of the minor actinide SX cycles with upstream and downstream stages, particularly where interfaces may cause issues.

- **Homogeneous recycling**
- **Heterogeneous recycling**

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<th>CHALMERS</th>
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<th>JRC-ITU</th>
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Providing relevant dissolution and conversion processes linkable with the separation processes.
When necessary, interfaces between dissolution/separation and separation/conversion will be considered.

- **Conversion issues of solutions from SX-process:** development of safe synthesis routes, destruction of prejudicial organics from SX-process and characterization of synthesized MABB precursors
- **Dissolution of model compounds**
- **Interface between SX and conversion**
- **Actinides materials for fuel fabrication**
- Developing processes towards industrialisation studies that consider the holistic impacts of the flowsheet are necessary.
- Assessing and illustrating the holistic effects on the nuclear fuel cycle that occur from fundamental changes to the chemistry at the heart of its key processes. Appropriate technology deployment and consideration of potential issues and impediments to industrialisation will also be assessed.

- Concept Design of a Euro-GANEX Plant
- Comparing SX processes for heterogeneous recycling
- Process Mapping Studies
- “Sim-plant” – engineering simulation of integrated plants
- Impact Studies
- Developing an emerging process towards industrialisation. It is essential to understand from the outset what the safety implications of the process are and where efforts need to be focused to understand further the risks which need to be mitigated through flowsheet design and engineering.

- Studying these requirements for both normal and mal-operations across the fuel cycle from head end dissolution through to powder formation for fuel manufacture.

- **Safety Review of a Euro-GANEX plant**
- **Hazard Analysis and Criticality Studies**
- **Quantification of Corrosions Risks in EURO-GANEX and EXAm Processes**
Integrating the work done in GENIORS in a more global approach by creating synergies with other European and international initiatives and by Involving the stakeholders.

• **Clustering with other European projects and international initiatives** - Through seminars and workshops organised on selected key topics, GENIORS will create synergies with H2020 project such as INSPYRE. A specific collaboration will be established with the US-DOE (and particularly Sigma Team on actinide partitioning and recycling) in continuation of the collaboration already established with SACSESS.

• **Stakeholders/end-users Events** - Two dedicated events will be organised gathering the stakeholders potentially interested by the output of GENIORS will be organised at mid-term and at the end of the project.
WP12 - T&E and Knowledge management

- Ensuring researchers on the project get access to the best facilities and knowledge.
- Capturing the knowledge generated by the project and provide as wide an access as possible to this.

- **Travel bursaries and secondment grants**
- **Think-Tank** : The aim of this task is to move beyond the traditional chalk and talk workshop or single topic training event and focus on the critical thinking skills of the early career researchers. This will be achieved by conducting a think tank event on the best way to address the key research challenges for implementing the technologies and processes under development in the programme. The output will be a statement on how to address these challenges.
GENIORS

A FEW EXAMPLES
TODGA: Very strong complexation with actinides (III), (IV), (VI) ➔ used at low concentration ➔ limited An loading

DMDOHEMA: Phase modifier to avoid 3rd phase formation by TODGA at high acidity and high loading

SO3-BTP: strip selectively the An from the organic phase – potential issues with sulphur at conversion step

CDTA: Keep FP in the feed solution
Simplifying EURO-GANEX!
Why not one single molecule at the extraction?

Increasing the loading capacity of TODGA

- Increased chain length strongly affects the limiting organic concentration.
- A point is reached where the organic phase seems to be stable – with Nd....
- Chain length (number of C) is limited by the increasing viscosity. Especially at high loadings

Decreasing the complexation strength

- Groups inserted at central carbons exert steric hindrance and thereby affects complexation strength.
- D-values drop orders of magnitude inserting two methyl groups.

Side chains have an impact!!

Central groups have an impact

10a = TWE21, R1 = Me, R2 = H
10b = TWE14, R1 = R2 = Me

mTDDGA!
### TODGA vs mTDDGA

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TODGA-GANEX</th>
<th>mTDDGA-GANEX</th>
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<tbody>
<tr>
<td>Organic formulation</td>
<td>TODGA (0.2M) + DMDOHEMA (0.5M) mixture</td>
<td>Only mTDDGA (0.5M)</td>
</tr>
<tr>
<td>Diluents</td>
<td>kerosene</td>
<td>n-dodecane</td>
</tr>
<tr>
<td>Pu loading limit</td>
<td>~ 20 g/L</td>
<td>32 g/L</td>
</tr>
<tr>
<td>3rd phase formation</td>
<td>Yes, at high Pu and acid conc.</td>
<td>No, even at high Pu and acid conc.</td>
</tr>
<tr>
<td>Acidity</td>
<td>0.01-3.0 M</td>
<td>0.01-6.0 M</td>
</tr>
<tr>
<td>D value for Sr, Mo, Fe</td>
<td>~ 1</td>
<td>~0.1 (10 times lower)</td>
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**mTDDGA could be a promising candidate for a simplified organic formulation for future EURO-GANEX process.**
Replacing the SO3-BTP

Process performances

- Experiments with macro-concentrations of $^{241}$Am (1 mM), $^{152}$Eu spike, in presence of 0.02M lanthanides for i-SANEX process;

- Experiments with macro-concentrations of $^{241}$Am (1 mM) and $^{239}$Pu (10 mM), $^{152}$Eu spike, in presence of 0.02M lanthanides for EURO-GANEX process;

Radiolytic stability studies

to go further in the radiochemical stability of PTD-based extracting system
to confirm the identity of the observed PTD degradation products
to study the generation of gaseous products from irradiated TODGA-PTD system
1. An inventory of the description of each loop as well as the current status of operation of each loop
2. An inventory of methods/methodologies of assessing the dose-rate for each loop
3. A definition of a common system to study
4. A common source of extractants, diluents and acids must be identified and used by all the partners involved.
5. A rough flowsheet will be provided by Andreas Geist (simplified flowsheet based on the Juelich process), where he will point-out where there is not sufficient data. This flowsheet is supposed to be adapted to each LOOP and reported on the outcome
6. Each Loop will report if the system can be run in the respective facilities
7. Each loop should report an estimate date for starting the test
System studies

- Developing processes towards industrialisation studies
- Assessing and illustrating the holistic effects on the nuclear fuel cycle that occur from fundamental changes to the chemistry at the heart of its key processes.

• Concept Design of a Euro-GANEX Plant
• Comparing SX processes for heterogeneous recycling
• Process Mapping Studies
• “Sim-plant” – engineering simulation of integrated plants
• Impact Studies
Process safety

- Developing an emerging process towards industrialisation.
- Studying these requirements for both normal and mal-operations across the fuel cycle

• Safety Review of a Euro-GANEX plant
• Hazard Analysis and Criticality Studies
• Quantification of Corrosions Risks in EURO-GANEX and EXAm Processes
Fuel cycle integration

Integrating the work done in GENIORS in a more global approach by creating synergies with other European and international initiatives and by Involving the stakeholders.

- Clustering with other European projects and international initiatives – including collaboration with the

- Stakeholders/end-users Events - Two dedicated events will be organised gathering the stakeholders potentially interested by the output of GENIORS will be organised at mid-term and at the end of the project.

Joint workshops with DOE
DGA extraction chemistry
Diluent issues
Exchanges + summer school with H2020 INSPYRE project on oxide fuel materials
Our Events

The Radical Behaviour Workshop, May 2018, Wûrtzburg
Stakeholders event and topical day on P&T, October 2018, Antwerp
Think-tank on process safety issues, October 2018, Antwerp
INSPYRE – GENIORS school, May 2019, TU-DELFT
Process flow-sheets, modelling and simulation

Based on the reference process flow-sheet analysis (GANEX/EUROGANEX, EXAM/EUROEXAM, I-SANEX), we will discuss the methodologies we can use for improving a processes

It will cover among others
process modelling
chemical system optimisation
...

Milano, Italy, 4-6 November 2019
contact@geniors.eu
Conclusion

- GENIORS is built on the legacy of SACSESS and previous projects
- GENIORS focuses on GEN IV fuel reprocessing issues
- GENIORS acquires the maximum of data to build processes on sound scientific basis
- GENIORS exploits the data to provide system studies and ensure the safety of the selected processes
- GENIORS continues to invest in the young generation
Save the date & submit your abstract!

7–12 June, Montpellier (France)

www.atalante2020.org