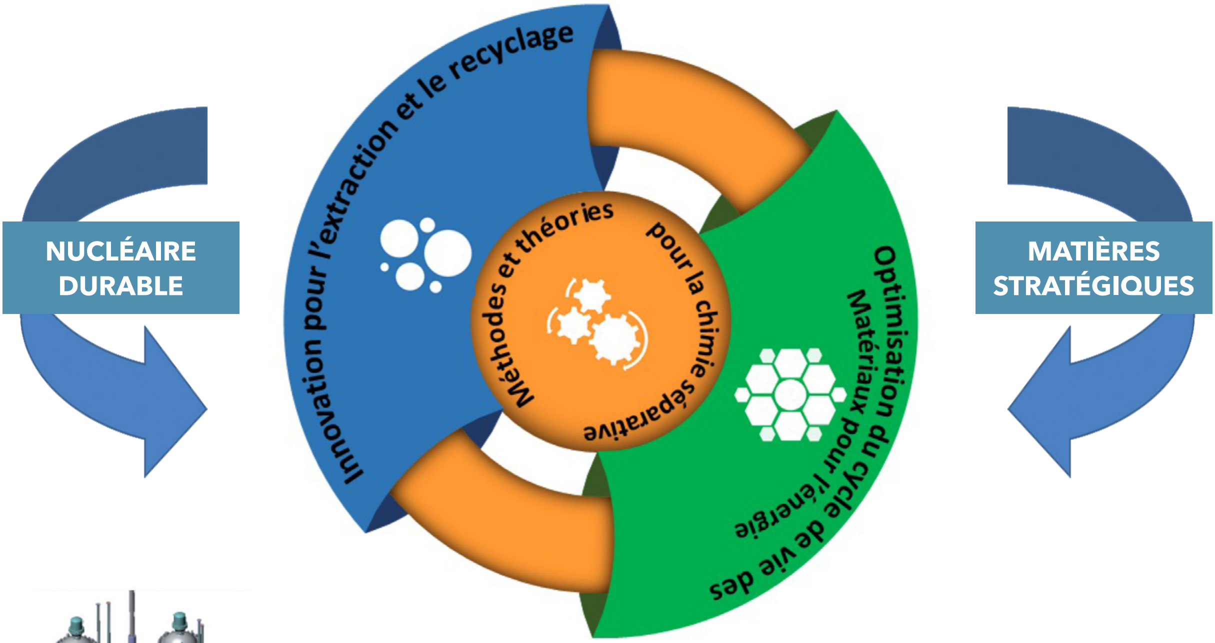
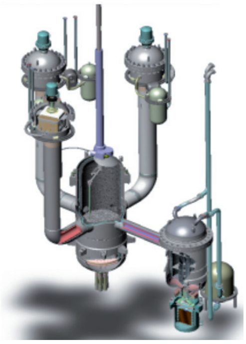
INSTITUT DE CHIMIE SÉPARATIVE DE MARCOULE

CHIMIE ET PHYSICO-CHIMIE DU RECYCLAGE

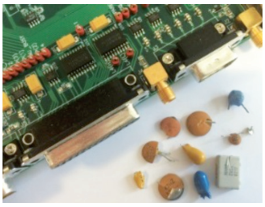
ÉNERGIES DÉCARBONÉES

ÉCONOMIE CIRCULAIRE





Progresser dans une chimie et une physico-chimie au service des **procédés** et des **matériaux pour l'énergie**… Appliquer nos compétences à la chimie du **recyclage** et de la **décontamination** en général.

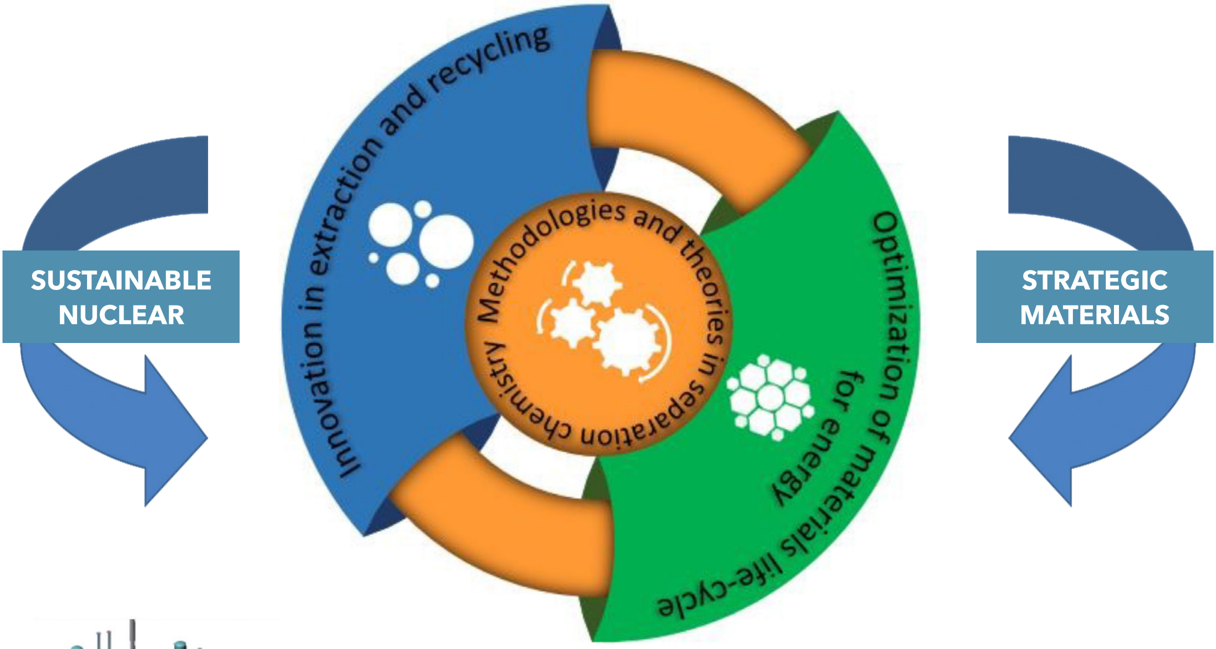


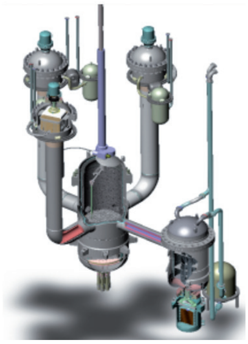
Pour une recherche intégrée aux ambitions du CEA, du Pôle Chimie université de Montpellier

CHEMISTRY AND PHYSICAL CHEMISTRY OF RECYCLING

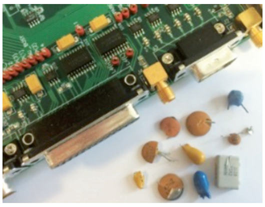
DECARBONATED ENERGY

CIRCULAR ECONOMY





To progress in a chemistry and physico-chemistry at the service of **processes and materials for energy...** To apply our skills to the chemistry of **recycling and decontamination** in overall.



For an integrated research to the CEA, the Montpellier University Chemistry cluster ambitions.

INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCOULE

RAPPORT SCIENTIFIQUE 2021 - 2024
SCIENTIFIC REPORT

Personnel de l'ICSM
ICSM staff

INSTITUT DE
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MARCOULE

PRÉFACE

L'unité mixte de recherche «Institut de chimie de séparation de Marcoule» a été créée conjointement par le CEA, le CNRS, l'Université de Montpellier et l'Ecole Nationale Supérieure de Chimie de Montpellier en mars 2007. Le bâtiment a été inauguré en juin 2009 avec en janvier 2010, l'autorisation de démarrer des expériences incluant quelques grammes d'uranium appauvri et de thorium naturel. Depuis, au rythme des appels à projets nationaux et internationaux, l'ICSM vise à développer une recherche fondamentale avec comme objectif principal de «proposer des choix» pour le développement de procédés de chimie de séparation dans les domaines des énergies décarbonées. L'intégration des enjeux d'une énergie nucléaire durable et les défis d'une économie circulaire dans son ensemble sont de réelles opportunités d'innovation et permettent d'afficher l'ICSM avec une reconnaissance unique en France et une visibilité internationale.

Les huit équipes de recherche travaillent donc toujours dans le sens des questions scientifiques ouvertes telles que définies et publiées par l'académie française (missions scientifiques contractuelles). La chimie de séparation, une branche de la chimie physique, est un domaine clé de la «chimie verte», et est fortement liée aux nanosciences, aux colloïdes et aux interfaces puisque toutes les séparations proviennent d'un transfert de phase: liquide-liquide, liquide-solide ou même liquide-air. La chimie de séparation est à la base des technologies du recyclage, tandis que le recyclage est à la base de l'économie circulaire et que l'économie circulaire est la seule stratégie durable dans un monde aux ressources limitées. Tous les scientifiques, ingénieurs, techniciens et étudiants ont pour objectif commun d'acquérir les connaissances nécessaires à l'amélioration des méthodes dans ce domaine.

En décembre 2024, l'ICSM rassemblait une centaine de personnes, dont 43 permanents (20 CEA, 14 CNRS, 9 UM / ENSCM) et 56 non permanents répartis en doctorants (33), post-doctorants-ATER-CDD (11), apprentis (11) et administratifs (1) (38 CEA, 11 CNRS et 7 UM/ENSCM). En outre, plus de 25 étudiants en licence et master rejoignent les huit équipes pendant quelques mois chaque année dont une dizaine du master de chimie à Montpellier sur « Chimie Séparative, matériaux et procédés ».

Depuis la première édition 2006 à Montpellier, des écoles pratiques en chimie de séparation et en instrumentation ainsi que des ateliers thématiques sont (co)organisées par l'ICSM, souvent en période d'été. Au cours de ces 4 dernières années on peut encore lister de nombreuses écoles thématiques qui deviennent régulières, d'ateliers et de conférences comme listées dans le chapitre « Teaching and workshops », le signe d'une dynamique pédagogique forte à l'institut.

Ce rapport, émis tous les 2 ans, donne ici un aperçu d'une sélection des projets en cours (projets nationaux ANR, PEPR et européens) et des travaux publiés sur 4 ans glissant et ce depuis janvier 2021. Nos études sont regroupées sous trois axes qui constituent actuellement les piliers de notre activité de recherche et de formation et définis par i) l'Innovation dans l'extraction et le recyclage, ii) Optimisation du cycle de vie des matériaux pour l'énergie et iii) les Méthodologies et théorie de la chimie de séparation.

Stéphane Pellet-Rostaing

Olivier Diat

FOREWORD

The joint research unit "Marcoule Institute for Separation Chemistry" was created jointly by CEA, CNRS, University of Montpellier and Ecole Nationale Supérieure de Chimie de Montpellier in March 2007.

The structure was officially opened in June 2009, and studies with a few grams of naturally occurring thorium and depleted uranium were allowed to begin in January 2010. Since ICSM seeks to develop fundamental research with the rhythm of national and international calls, with as main goal to «propose new options» for the development of separation chemical processes in the decarbonated energies domains. The integration of a sustainable nuclear energy issues and the challenges of a circular economy in its overall are real opportunities for innovation and with unique recognition in France and international visibility. The eight research teams still work in the direction of the scientific open questions as defined and published by the French academy. Separation chemistry, a branch of physical chemistry, is a key part of « green chemistry », and strongly linked to nanosciences, colloids and interfaces since all separations are sourced in phase transfer: liquid-liquid, liquid-solid or even liquid-air. Separation chemistry is the basis of recycling technologies, while recycling is the basis of circular economy and circular economy is the only sustainable strategy in a world of limited resources. All scientists, engineers, technician and students have the common goal to gain the knowledge needed to improve methods in this field.
In December 2024, the ICSM will have a staff of about one hundred, including 43 permanent staff (20 CEA, 14 CNRS, 9 UM / ENSCM) and 56 non-permanent staff, with 33 PhD students (33), 11 post-doctoral/ATER/CDD students (11), apprentices 11) and administrative staff (1) (38 CEA,11 CNRS and 7 UM/ENSCM). In addition, more than 25 undergraduate and graduate students join the eight teams for a few months each year, including about ten students in the master's degree programme in chemistry in Montpellier entitled "Separation Chemistry, materials and processes".

Since the first edition in 2006 in Montpellier, practical schools in separation chemistry and instrumentation as well as thematic workshops have been (co) organised by the ICSM. Over the last 4 years, there have been a number of thematic schools, which are now becoming a regular feature, as well as workshops and conferences, as listed in the 'Teaching and workshops' section and which is a sign of the strong pedagogical dynamic at the institute.

This report issued every 2 years gives here an overview of the selected ongoing projects (national and European projects) and the work published over 4 sliding years and this since January 2022. Our studies are grouped under three axes, which constitute the pillars of our research and training activity and are defined by 1) Innovation in extraction and recycling, 2) Optimization of materials life-cycle for energy and 3) Methodologies and theory of separation chemistry.

Stéphane Pellet-Rostaing

Olivier Diat

PRÉSENTATION DE L'ICSM

La production d'énergie à partir de combustibles fossiles dont l'impact négatif sur le climat et l'environnement est aujourd'hui inacceptable. Elle est accompagnée de nouvelles exigences en matière de sécurité des installations et de gestion de leurs déchets, mais également de la nécessité d'un recyclage, considéré jusqu'à présent comme exceptionnel, mais qui doit devenir la règle universelle et économiquement acceptable. Elle confronte les scientifiques à une demande sociétale forte pour des solutions maîtrisées en matière de technologies pour les énergies décarbonées, inscrite dans les lois françaises sur la transition énergétique du 13 juillet 2005 et 18 août 2015.
Le « nucléaire durable » du futur, fermant le cycle, reposera sur des avancées dites « en rupture » *via* une chimie séparative mettant en jeu des fluides complexes mis en œuvre dans des dispositifs optimisés.
Au-delà du domaine nucléaire et dans un monde fini en ressources naturelles, fermer les cycles relève d'une démarche de tri sélectif maitrisé, qu'il s'agisse de séparation ionique, moléculaire ou colloïdale. Recycler les matières dites « stratégiques » comme les terres rares, les platinoïdes et autres métaux précieux ou certains métalloïdes comme le germanium, le gallium ou l'antimoine est un premier défi d'importance pour cette chimie séparative qui relève des nanosciences.

Dans le but de développer une recherche fondamentale au service des « utopies nécessaires » de la chimie pour l'énergie, l'unité mixte CEA/CNRS/UM/ENSCM créée en 2007 est aujourd'hui constituée de huit équipes travaillant en synergie :

- *Systèmes hybrides pour la séparation (Damien BOURGEOIS)*
- *Chimie des ions aux interfaces actives (Pierre BAUDUIN)*
- *Tri ionique par des systèmes moléculaires auto-assemblés (Stéphane PELLET-ROSTAING)*
- *Sonochimie dans des fluides complexes (Tony CHAVE)*
- *Nanomatériaux pour l'énergie et le recyclage (Xavier DESCHANELS)*
- *Interfaces des matériaux en évolution (Nicolas CLAVIER)*

Ces groupes s'appuient sur deux équipes transverses de méthodologies autour de l'observation dans l'espace réel (microscopies), l'espace réciproque (diffusion rayons X, neutrons et lumière) et sur la modélisation statistique en conditions réelles représentatives de l'utilisation en température, activité de l'eau… :

- *Etude de la matière en mode environnementale (Xavier Le GOFF)*
- *Modélisation et chimie théorique (Jean-François DUFRÊCHE).*

En réponse à une demande sociétale sans cesse en évolution face aux défis énergétiques et environnementaux actuels et futurs, les recherches menées à l'ICSM participent à déconstruire l'image polluante et dangereuse de la chimie dans le domaine de l'extraction et de la purification de matières valorisables. L'ICSM se doit d'anticiper et de proposer des solutions aux verrous scientifiques permettant une diminution drastique des pollutions et de l'empreinte environnementale des procédés de la chimie séparative. La diminution du coût énergétique des procédés mis en œuvre, une meilleure gestion de l'eau, la limitation de la quantité et du volume de déchets, l'utilisation de matières premières renouvelables y sont des challenges majeurs. L'ICSM travaille à la découverte de méthodes de synthèses originales et plus efficaces, à la mise en œuvre de méthodes d'activations comme les techniques ultrasonores et micro-ondes, à l'optimisation et à l'intensification de procédés, au développement de théories et de méthodes d'analyse toujours plus performantes, à des techniques de traitement des matières et effluents de plus en plus efficientes. Cet effort doit s'intensifier et se rationaliser, en particulier vers le développement des interfaces, source d'innovation majeure résultant du croisement de compétences. Au cours de la dernière période de quatre ans, l'intégration des objectifs, l'utilisation des compétences développées dans les méthodes de caractérisation de l'environnement ainsi que dans la théorie de la méso-échelle ont été de plus en plus considérées. De plus, la distinction faite depuis la création de l'ICSM entre «comprendre», c'est-à-dire démontrer la puissance prédictive de modèles basés sur des principes premiers et «optimiser», c'est-à-dire démontrer la faisabilité de nouveaux systèmes chimiques dans l'extraction sélective, incluant ainsi les principes «de chimie et d'ingénierie verte» s'est avérée être pertinente.

En conséquence, trois axes de réflexion et de coopération en équipes ont naturellement émergé dont le premier centré sur «l'innovation dans l'extraction et le recyclage ».

Comme indiqué ci-dessus, optimiser nécessite de mieux comprendre et prévoir en associant développement expérimental et théorie. L'innovation à l'ICSM, illustrée par un nombre toujours élevé de brevets déposés (plus d'une trentaine entre 2021 et 2024) et un certains nombres d'articles proposant des idées en rupture (association/synergisme de ligands, formation de clusters ioniques spécifiques, démarche d'up-cycling) ne pourrait être proposée sans les corrélations fortes entre observation et théorie. En pratique, l'émergence a été possible grâce aux outils utilisés dans la physique statistique des interfaces, par exemple via les ondelettes aléatoires gaussiennes ainsi que la prise en compte systématique de l'énergie libre et modélisé dans un cadre général intitulé «ienaïque» avec une certaine similitude avec la neutronique, l'électrochimie et la nanoscience.

Ainsi, le second axe rassemblant des compétences autour de «Méthodologies et théorie de la chimie de séparation» ne cesse de s'étoffer grâce à un grand nombre de protocoles expérimentaux, tels que la mesure et le calcul des molécules d'extraction «perdues» non actives dans la séparation, ou de nouvelles méthodes de séparation sans agent d'extraction/tensioactif classique. Non moins importantes sont les avancées récentes dans les domaines de la microscopie électronique de surface couplée à des analyse d'image et des cellules spécifiques (humidité relative contrôlée ou température élevée) avec des permettant la caractérisation précise de propriétés physico-chimiques telles que l'auto-guérison, le frittage, la dissolution, la réactivité chimique par des expériences *in situ*.

Aucun processus de séparation ne peut être réalisé sans la connaissance de la «durabilité des matériaux», c'est-à-dire des matériaux qui doivent résister à des contraintes extrêmes et à une longue utilisation, non seulement dans le cycle de vie du combustible nucléaire, mais aussi dans celui de tous les matériaux nécessaires aux technologies des énergies alternatives. Le cycle de vie de toutes les technologies mises en œuvre doit être étudié et maîtrisé comme proposé dans l'axe «Optimisation du cycle de vie des matériaux pour l'énergie». Les interfaces solides/solides, solides/liquides et solides/gaz sont ici considérées puisque les propriétés physiques et chimiques de ces matériaux (durabilité, robustesse, capacité de confinement et de rétention...) dépendent de leur synthèse, c'est-à-dire de la nature des précurseurs (colloïde, solution, émulsion...) au matériau final (fritté, poreux, poudre, film mince).

Un certain nombre de projet de recherche étudiés au cours de ces quatre dernières années ont donc été regroupées par axe afin de faciliter l'ordre de leur lecture.

L'Institut de Chimie Séparative de Marcoule, créé en 2007, est actuellement dirigé par Stéphane Pellet-Rostaing et ce depuis 2013. Situé à 110 km au NE de Montpellier et à 25 km au Nord d'Avignon, l'ICSM fait partie du **Pôle de Chimie de l'université de Montpellier** et faisait partie du LABEX **« Chemisyst »** (2012 – 2022) sur la chimie des systèmes moléculaires et interfaciaux. Ayant démarré effectivement ses activités de recherche en janvier 2010, l'Institut est dimensionné pour accueillir en 2022 une cinquantaine de permanents dont environ 40 chercheurs, ingénieurs et techniciens, environ 10 administratifs, technicien et ingénieurs d'exploitation et autant de non-permanents thésards et post-doctorants.

Les propositions de stages au niveau master, post-doc et thèses sont accessibles sur le site **www.icsm.fr**.

ICSM PRESENTATION

It is currently undesirable to produce energy using fossil fuels because of their detrimental effects on the ecology and climate. It comes with additional criteria for the security of the facilities and the management of their wastes, as well as the necessity for recycling, which was previously thought to be an exception but now must be the standard and an economically viable practice. It presents scientists with a significant social demand for managed solutions in carbon-free energy technology, as reflected in French laws on energy transition from July 13, 2005, and August 18, 2015. Future «sustainable nuclear power,» which completes the fuel cycle, will rely on ostensibly «breakthrough» developments in separation chemistry, involving complex fluids in optimized devices.

Beyond the nuclear sector and in a world with limited natural resources, closure cycles are a part of a regulated extraction/separation/purification process with its two linked side-processes, dissolution and reformation of materials. As long as primary and secondary resources are involved, ionic, molecular, or colloidal dissolution and separation have to be understood and modeled predictively in order to allow growth of the recycling industry, as the core of the circular economy. One of the initial challenges in this separation chemistry, which belongs to the nanosciences, is recycling so-called «strategic» materials like germanium, gallium or antimony.

In order to develop a fundamental research for the «necessary utopia» of chemistry for energy, the joint unit CEA/CNRS/UM/ENSCM created in 2007 consists of eight teams working in synergy:

- *Hybrid Systems for separation (Damien BOURGEOIS)*
- *Ions at active interfaces (Pierre BAUDUIN)*
- *on separation by self-assembled molecular systems (Stéphane PELLET-ROSTAING)*
- *Sonochemistry in complex fluids (Tony CHAVE)*
- *Nanomaterials for energy and recycling processes (Xavier DESCHANELS)*
- *Evolution of surfaces of materials (Nicolas CLAVIER)*

These six teams that are highly specialized firmly associated to two transverse teams focusing on methodologies of microscopic observation in real space, and reciprocal space as well as statistical physics modelling to represent real conditions of use such as temperature, water activity and so on:

- *Material study by environmental methods (Xavier Le GOFF)*
- *Modeling and theoretical chemistry (Pr. Jean-François DUFRÊCHE).*

The research done at ICSM contributes to dismantling the polluting and dangerous picture of chemistry in the field of extraction and purification of recoverable materials in response to an ever-changing societal demand in a clean energy as well as environmental issues. ICSM must anticipate and propose solutions to the scientific challenges that will allow a drastic reduction in pollution and the environmental footprint of separation chemistry processes. Reducing the energy cost of the processes used, a better water management, limiting the quantity and volume of waste and using renewable raw materials are major challenges for the institute. ICSM is working on the discovery of original and more efficient synthesis methods, the implementation of activation methods such as ultrasonic and microwave techniques, the optimisation and intensification of processes, the development of ever more efficient analysis theories and methods, and increasingly efficient techniques for treating materials and effluents. This effort must be intensified and rationalised, in particular towards the development of interfaces with other expertises, a major source of innovation resulting from the crossing of skills. During the last four-year period, the integration of objectives, the use of skills developed in environmental characterisation methods and in mesoscale theory have been increasingly considered. Furthermore, the distinction made since the creation of the ICSM between «understanding», i.e. demonstrating the predictive power of models based on first principles, and «optimising», i.e. demonstrating the feasibility of new chemical systems in selective extraction, thus including the principles of «green chemistry and engineering», has proven to be relevant.

As a consequence, a first cluster of competence and cooperation centered on "Innovation in Extraction and Recycling" naturally emerged. As stated above, one first needs to understand and predict. Innovation at the ICSM, illustrated by the continuing high number of patents filed (more than a thirty between 2021 and 2024) and a number of articles proposing breakthrough ideas (association/synergism of ligands, formation of specific ionic clusters, up-cycling approach) would not be possible without the strong correlations between observation and theory. In practice, emergence has been possible thanks to the tools used in the statistical physics of interfaces, for example via Gaussian random wavelets, as well as the systematic consideration of free energy and modelled in a general framework entitled 'ienaic' with a certain similarity to neutronics, electrochemistry and nanoscience. Due to a large number of experimental protocols, such as the measurement and calculation of «lost» extraction molecules that are not active in the separation or new separation techniques without a conventional extraction agent/surfactant, the second axis gathering competences around «Methodologies and theory of separation chemistry» continues to expand. Recent developments in the fields of surface electron microscopy coupled to image analysis and the development of specific experimental cells (with a controlled relative humidity or achieving elevated temperature) have made it possible to precisely characterize physico-chemical properties such as self-healing, sintering, dissolution, and chemical reactivity through *in situ* experiments.

Without understanding of «durability of materials,» or materials that should endure tremendous constraints and long usage, no separation process can be constructed. This applies to all materials required in alternative energy technologies as well as those used in the life cycle of nuclear fuel. Every technology that has been put into use needs to have its life cycle studied and mastered, as suggested in the cluster «Optimization of materials life-cycle for energy». Since the physical and chemical characteristics of these materials (durability, robustness, ability to confine and filter, etc.) depend on their synthesis, i.e., from the nature of the precursors (colloid, solution, emulsion, etc.) to the final material, solid/solid, solid/liquid and solid/gas interfaces (sintered, porous, powder, thin film) are taken into consideration in this cluster activities.

A number of the research projects investigated over the past four years have therefore been gathered by axis in order to make easier their reading.

The Institute for Separation Chemistry of Marcoule has been created in 2007 and is nowadays managed by Stéphane Pellet-Rostaing since 2013. Located 110 km NE of Montpellier and 25 km north of Avignon, ICSM is a component of the **"Pôle de Chimie"** of Montpellier University was one of the partners of the Excellence laboratory **"Chemisyst"** 2012-2022, devoted to the Long Range chemical interactions (LRI) in "molecular and interfacial systems chemistry". Having effectively started its research activities in January 2010, the Institute was sized to hold in 2022 about fifty permanent staff including about 40 researchers, engineers and technicians, about 10 administrative, technical, operational and safety engineers and as many non-permanent PhDs and post-docs.

Open national and international PhD and post-doc positions are available on web-site:
www.icsm.fr.

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ICSM – PERMANENTS 2021 - 2024

Equipe DIR

Directeur	PELLET-ROSTAING Stéphane	Gestionnaire	MENASRIA Aurélie
Directeur Adjoint	DIAT Olivier 01/19	ISI	DIAS Mathilde
Adj. Directeur	ASOU-POTHET Marielle 11/22 ->	ISI	MARCHAL Nicolas
Assistante	HAON Véronique 12/20 ->	Exploitation	PESCE Claude 01/20 ->
Gestionnaire	VIDAL Alice	Exploitation	LAROZAS Daniel 03/21 ->

Equipe 1 - LHYS

Chef d'équipe	BOURGEOIS Damien 01/22
CR	MEYER Daniel 12/22 ->
Chercheur	SIMONNET Marie 07/23 ->
Chercheur	CARBONI Michaël
MDC	MAYNADIE Jérôme

Equipe 2 – L2IA

Chef d'équipe	BAUDUIN Pierre
Chercheur	DIAT Olivier
MDC	GIRARD Luc
IE	JONCHERE Alban
IE	PASQUIER Coralie 01/21 ->

Equipe 3 - LTSM

Chef d'équipe	PELLET-ROSTAING Stéphane
Directeur de recherche Professeur INSTN	ZEMB Thomas -> 10/24
MDC	ARRACHART Guilhem
Technicienne	BAUS-LAGARDE Béatrice
Chercheur	DOURDAIN Sandrine
IE	GIUSTI Fabrice 07/18 ->

Equipe 4 - LSFC

Chef d'équipe	CHAVE Tony
Chercheur	NIKITENKO Serguei
Chercheur	PFLIEGER Rachel
Chercheur	VIROT Matthieu

Equipe 5 - LNER

Chef d'équipe	DESCHANELS Xavier
Chercheur	CAUSSE Jérémy -> 05/24
IE	REY Cyrielle
MDC	TOQUER Guillaume

Equipe 6 - LIME

Chef d'équipe	CLAVIER Nicolas
MDC	CLAPAREDE Laurent
PR	DACHEUX Nicolas
CR	MESBAH Adel *-> 03/21*
Chercheur	SZENKNECT Stéphanie

Equipe 7 – L2ME

Chef d'équipe	LE GOFF Xavier
Ingénieur	BRAU Henri-Pierre -> 09/24
Chercheur	REBISCOUL Diane
IE	LAUTRU Joseph
IR	PODOR Renaud
IE	MAYNADIE Sandra
Ingénieur	ODORICO Michaël
IE	QUINTARD Guilhem 09/21 ->

Equipe 8 - LMCT

Chef d'équipe	DUFRECHE Jean-François
Chercheur	DUVAIL Magali
Chercheur	SIBOULET Bertrand

CEA
CNRS
UM ENSCM
Autres
Partis

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ICSM – NON PERMANENTS 2021 - 2024

EQUIPE DIR

CDD ITA
ROUSSIGNE Elisabeth 02/07/2018-01/06/2021
SCHAPPLER Mireille 02/11/2020-01/05/2021
PLESSE Nathalie 15/11/2021-31/12/2022
BONNET Quentin 15/12/2023-30/06/2024

APPRENTI
BADAROUX Rémy 01/09/2022 – 31/08/2023
FOURNEAU Baptiste 09/09/24-04/07/25
ROQUES Alexis 30/09/2024-05/09/2025

EQUIPE 2 L2IA

APPRENTI
CARTIER Amélie 06/09/2021-31/08/2023
DEMONET Loreleï 01/09/2022-31/08/2023
DEMONET Loreleï 18/09/2023-29/08/2024

CDD ITA
MASMOUDI Abderazak 04/11/2021-03/11/2022
LIADOUZE Camille 27/09/2021-26/03/2022

CDD CHERCHEUR
GOMES RODRIGUES Donatien 18/04/2016-31/08/2017
REGNIER Emilie 07/10/2019-06/10/2021

DOCTORANT
HOHENSCHUTZ Max 03/01/2018-02/01/2021
CHAZAPI Ioanna 21/10/2019-20/01/2023
SKORZEWSKA Klaudia 21/10/2019-20/01/2023
LAMONERIE Julien 01/10/2020-01/10/2023
FROGIER Raimoana 01/10/2021-30/09/2024
LEGRAND Valentin 01/10/2022 – 31/09/2025
MA Xiaochuan 12/12/2023-11/12/2026
MULLER Bastian 02/12/2024-01/12/2027

POST-DOCTORANT ou CHERCHEUR
FAKHOURI Hussein 02/05/23-01/05/2025
WINKLER Robert 01/03/2024-11/10/2024

EQUIPE 1 LHYS

APPRENTI
MEDJOUEL Sabrine 02/09/2021-01/09/2024
LAGAE-CAPELLE Eléonore 01/10/2018-30/09/2021
CISSE Khady 16/09/2024-29/08/2025
GIRARDET Bastien 02/09/2024-31/08/2027

CDD ITA
MORTADA Bouchra 19/07/2021-18/07/2023
BRUNET –MANQUAT Anthony 01/02/2022-31/07/2023
PIERRE Valentin 01/03/2022-28/02/2024
BASTIEN JALLY 08/09/2022-07/09/2023
AUDEVARD Jérémy 06/09/2023-05/09/2026
MONEUSE Marie 12/02/2024-17/12/24

DOCTORANT
CHEVALIER Aline 16/10/2017-15/01/2021
DURAIN Julie 16/10/2017-14/02/2021
RE Elisa 04/10/2017-05/01/2021
MOUSSAOUI Sayed-Ali 02/10/2018-30/12/2021
LORIGNON Fabrice 31/10/2018-30/12/2021
MAKOMBE Elizabeth 04/11/2019-03/02/2023
MARTIN ROMO Y MORALES Mickael 02/11/2020-01/11/2023
RIANT Tennessee 02/11/2020-01/11/2023
MONEUSE Raphaël 01/12/2020/-30/09/2023
HENRY Mathéo 02/10/2023-01/10/2026
KHODER Marwa 15/11/23-14/11/26
PROZSA Ervin 01/10/24-30/09/27
FASOLA Raphaëlle 04/11/24-03/11/27
GOLFIER Lucile 04/11/24-03/11/27

POST-DOCTORANT ou CHERCHEUR
NIKOLAIEVSKI Dmytro 02/01/2024-01/01/2026

CEA
CNRS
UM ENSCM
Autres
Partis

EQUIPE 3 LTSM

APPRENTI
PITON Raphaëlle 01/09/2020-31/08/2022
MONEUSE Marie 19/09/22-18/09/23
DROUOT Bastien 18/09/23 au 31/08/25

CDD ITA
LELONG Evan 18/10/2021-17/10/2022
SROUR Hassan 01/10/2021-30/09/2022
NDEBULIA WATCHOU Frantz 17/05/2021-16/11/2021
DELESTRAS Guillaume 01/07/2022-31/07/2022
FLEURY Clément 08/01/24-07/01/2026
GAUTIER Maud 26/08/2024-30/06/2025
LEBRUN Nils 01/10/2024-30/06/2025

POST-DOCTORANT ou CHERCHEUR
ARRAMBIDE CRUZ Carlos 01/07/2020-30/09/2021
LELONG Evan 17/10/2022-17/10/2024
LIN Jun 19/08/2023-18/02/2024
DUARTE RODRIGUEZ Alysson 04/11/24-03/05/2026

DOCTORANT
FELINES Nicolas 16/10/2017-15/01/2021
LU Zijun Quentin 07/11/2017-06/01/2021
BEN-GHOZI BOUVRANDE Justine 23/10/2018-22/10/2022
OYE AUKE Ruth 01/10/2018-30/12/2021
XING Chen Océane 08/10/2018-07/10/2022
BELFQUEH Sahar 10/12/2018-09/03/2022
EL MAANGAR Asmae 14/11/2018-31/01/2022
GINOT Loriane 02/11/2021-01/11/2024
STEMPLINGER Simon 04/11/2019-03/11/2022
COUTURIER Julien 01/01/2021-31/12/2023
EL KHOUEIRY Claudine 01/10/2020-01/10/2023
GUERINONI Elise 21/10/2020-20/10/2023
LE MIRE David 02/11/2020-01/11/2023
THIMOTEE Marine 03/10/2022-30/09/2025
BERNICOT Baptiste 01/10/2022-30/09/2025
FAUVEL Eléa 04/11/2024-03/11/2027
BAKAYOGO Aboubakar 08/10/2024-07/10/2027

EQUIPE 4 LSFC

CDD ITA
SLEIMAN Noura 15/07/2019-14/07/2020

CDD CHERCHEUR
BAYLE Simon 16/01/2023-15/07/2024
KALAWOUN Hamed 01/10/2024-31/03/2026

DOCTORANT
EL HAKIM Sara 22/11/2018-21/11/2021
COT-AURIOL Manon 21/10/2019-20/02/2023
HERR Sophie 04/11/2019-03/02/2023
MARGATE Julien 05/10/2021-04/10/2024
SALAME Rita 02/11/22-01/11/25
ZAHIR Noura 1/01/2023-03/06/2024
NZODOM-DJOZING David 01/11/22-30/10/25

EQUIPE 6 LIME

APPRENTI
BALME Kévin 01/09/2021-31/08/2022
ZANNOUH Wassima 01/09/2021-23/08/2022
TRONYO Marie 01/09/2022-31/08/2023
SCHUPPE Laura 01/09/2022-23/08/2023
GUILLARD Valentine 01/098/2023-31/08/2025
DIAZ Ilona 19/08/2023-31/08/2025

CDD ITA
DI MASCIO Lara 14/09/2020-13/09/2022
ANZALONE Eddie 14/09/2020-30/01/2022
IMBERT Paul-Henri 14/09/2020-13/12/2022
COLOMBEAU-BEDOS Thomas 10/01/2022-09/01/2023

DOCTORANT
MASSONNET Malvina 15/10/2018-14/10/2021
KACZMAREK Thibault 15/10/2018-14/10/2021
ASPLANATO Pierre 10/2019-10/2022
MONTAIGNE Théo 21/10/2019-20/10/2022
ROCHE Alison 01/10/2020-30/09/2023
BARRAL Thomas 19/10/2020-18/10/2023
BENARIB Sofian 21/10/2020-18/10/2023
HISAINY Mohammad 04/10/2021-03/10/2024
HOURS Charles 12/2019-12/2022
GILLET Célia 15/10/2018 – 14/10/2021
CAPRANI Raphaël 02/10/2020-01/10/2023
DESAGULIER Marie-Margaux 02/10/2020-01/10/2023
CALLEJON Lorenzo 16/10/23-15/10/26
FULCHIRON Mathias 16/10/23-15/10/26
LAFFONT Dorian 21/10/24-20/10/27
AVALLONE Arthur 21/10/24-20/10/27
NAVAS Camille 21/10/24-20/10/27

CEA
CNRS
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Autres
Partis

EQUIPE 5 LNER

APPRENTI
RAFFO Freddy 01/09/2022-31/08/2022

CDD ITA
MADINIER Sylvain 25/03/2024-24/03/2025

DOCTORANT
LU Zijie Martin 01/10/2017-30/09/2021
LIN Jun 15/10/2018-15/01/2022
TRATNJEK Toni 21/10/2019-20/10/2022
DIDIER Florian 01/10/2019-30/09/2022
HAUTECOUVERTURE Anna 19/10/2020-18/10/2023
ROCH Rayan 02/11/2021-01/11/2024
DE LAHARPE Pierre 02/11/2022-01/11/2025
ZRIOUIL Oumaïma 21/10/2024-20/10/2027
AZEDIOUI Aya 01/10/2023-30/09/2026
AL AMOURI Hiba 01/10/2022-30/09/2025

POST-DOCTORANT
RUSSO Baptiste – 14/12/2020-13/06/2022
KHODER Hassan 02/11/2020-01/11/2021
SINGARAVELU Chandra Mohan 17/12/2018-05/02/23
MANSAS Clémentine 04/01/21-03/01/23
LIN Jun 19/04/2022-18/10/2022

EQUIPE 7 L2ME

APPRENTI
HASSAK Siham 1/10/2020-30/09/22
EL BOUASSI Kaïs 18/09/2023-31/08/2024
AGNIEL Emile 02/09/2024-31/08/2025
TACCARD Léane 02/09/2024-29/08/2025

CDD ITA
NOTEZ Philippe 02/10/2023-30/11/2025

DOCTORANT
MENDONCA Jérôme 02/09/2019-30/10/2022
BARBIER Hélène L2ME/LIME 02/10/23 - 01/10/26
TSAPI METCHOP Vanele 02/10/23-01/10/26
KRAEMER Christin 27/11/23-26/11/26
B ODAPATI Laxmi 01/10/2024-30/09/27

POST-DOCTORANT ou CHERCHEUR
PINAUD Laetitia 04/01/2021-03/07/2022
TARON Mélanie 20/06/2022-19/06/2024
PEIRERA MACHADO Norma 02/05/2022-01/05/2023

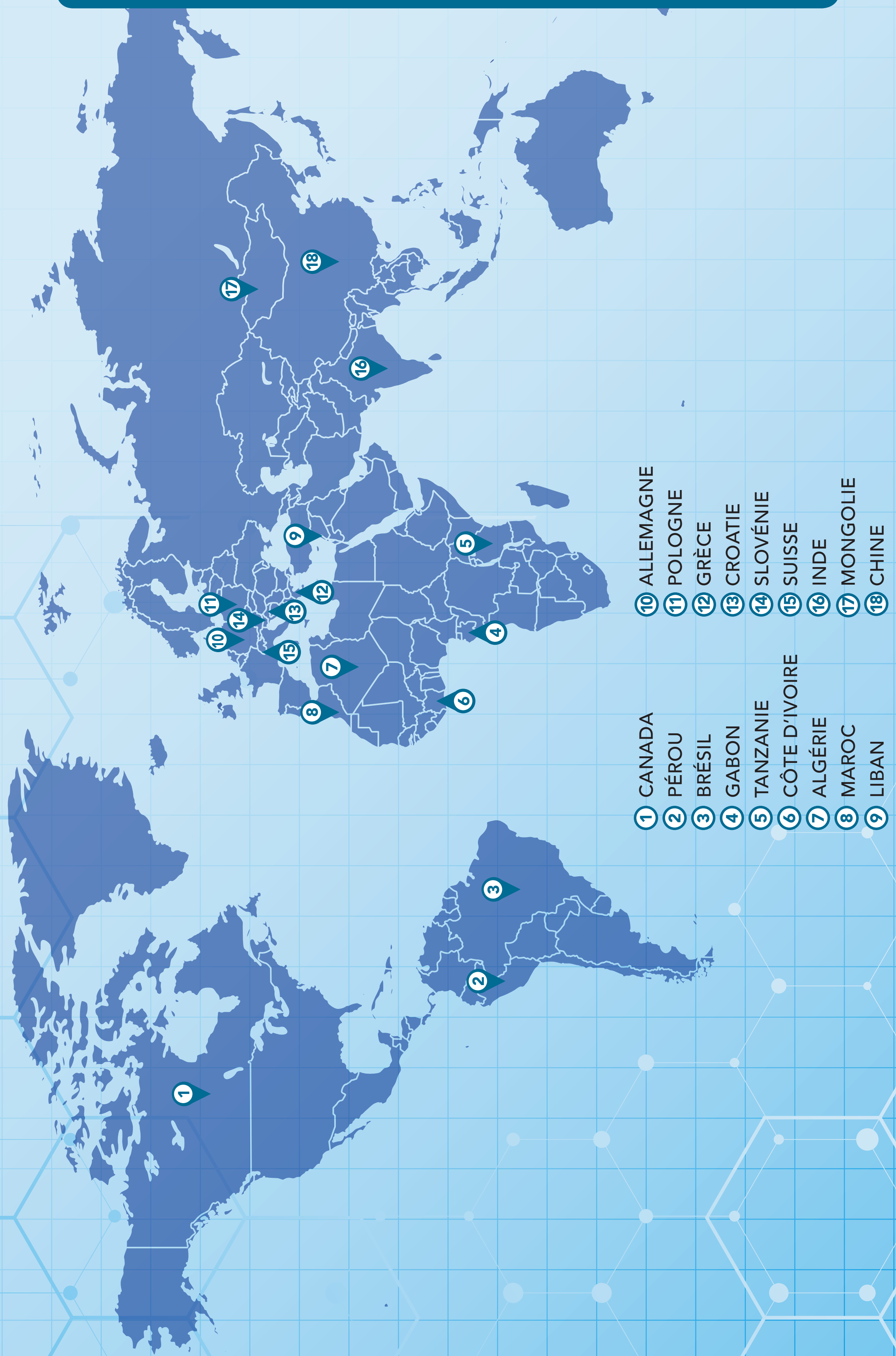
EQUIPE 8 LMCT

DOCTORANT
COQUIL Mathilde 10/2017-01/2021
VATIN Marin 15/10/2018-14/10/2021
HILAIRE Lolita 15/10/2018-14/10/2021
WANG Kunuy 01/10/2019-30/09/2022
JAMI Ludovic 01/10/2019-30/09/2022
COLLE Thomas 02/11/2020-01/11/2023
GUILLAM Erwann 17/10/22->16/10/25
ŽIBERNA Lara 03/10/2022-02/10/2025
SZCZEPAN Gustave 02/10/23-01/10/26
RODRIK Geoffroy 02/10/23-01/10/26
KLEIN Jordan 02/10/23-01/10/26

POST-DOCTORANT ou CHERCHEUR
FOUCAUD Yann 09/12/2019-08/12/2020
LE CROM Sébastien 01/02/2021-31/07/2022
DE ARAGAO Emilia 01/05/2023-30/04/2024

ORIGINE GÉOGRAPHIQUE DU PERSONNEL DE L’ICSM

GEOGRAPHICAL ORIGIN OF ICSM STAFF (SINCE 2007)



1. CANADA
2. PÉROU
3. BRÉSIL
4. GABON
5. TANZANIE
6. CÔTE D’IVOIRE
7. ALGÉRIE
8. MAROC
9. LIBAN
10. ALLEMAGNE
11. POLOGNE
12. GRÈCE
13. CROATIE
14. SLOVÉNIE
15. SUISSE
16. INDE
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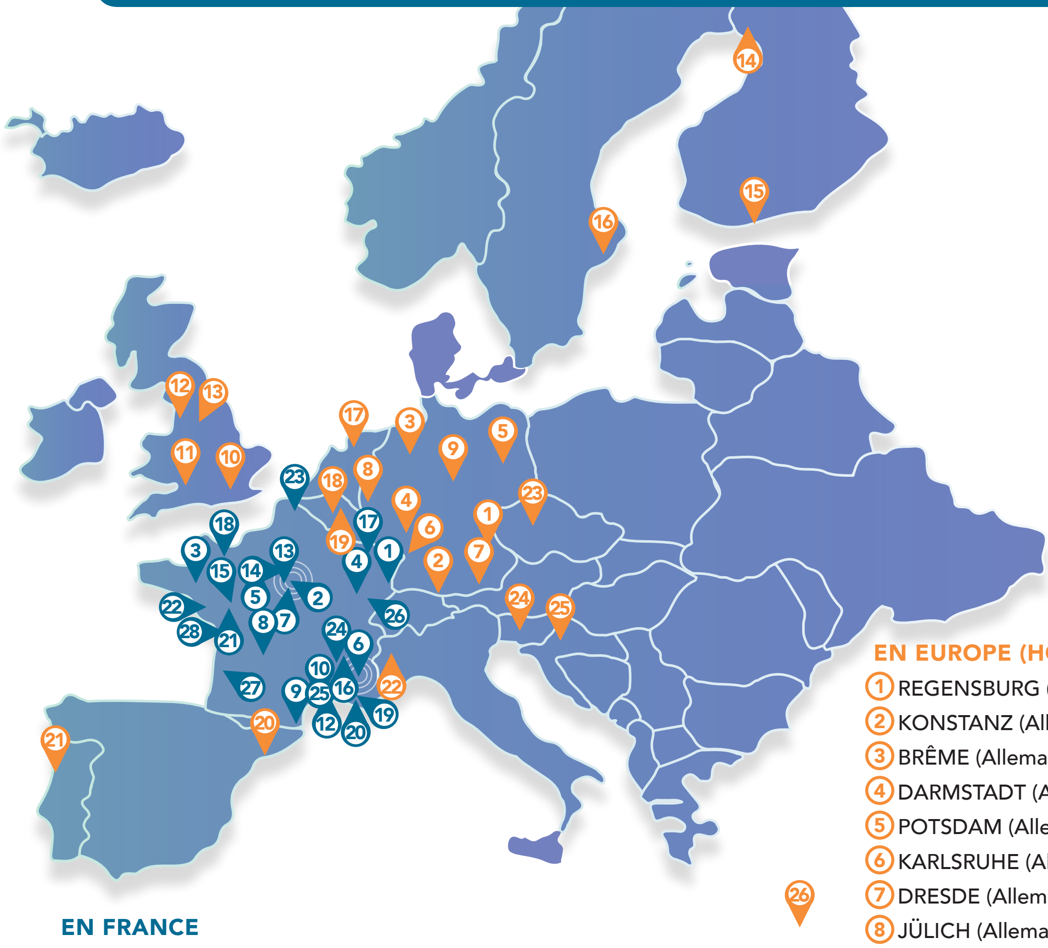
18. CHINE

COLLABORATIONS ACTIVES AVEC DES PARTENAIRES NATIONAUX, EUROPÉENS ET INTERNATIONAUX

ACTIVE COLLABORATIONS WITH NATIONAL, EUROPEAN AND INTERNATIONAL PARTNERS



EN FRANCE

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② PARIS
③ RENNES
④ NANCY
⑤ ORLÉANS
⑥ GRENOBLE
⑦ ORSAY
⑧ LIMOGES
⑨ PERPIGNAN
⑩ MONTPELLIER
⑪ NIMES
⑫ AVIGNON
⑬ SACLAY
⑭ VERSAILLES
⑮ TOURS
⑯ CHAMBERY
⑰ METZ
⑱ CAEN
⑲ AIX EN PROVENCE
⑳ MARSEILLE
㉑ POITIERS
㉒ NANTES
㉓ LILLE
㉔ ST ETIENNE
㉕ CAVAILLON
㉖ BESANÇON
㉗ BORDEAUX
㉘ LA ROCHELLE

INTERNATIONALES (HORS EUROPE) :

Berkeley (EU), San José (EU), Washington (EU), Oak Ridge (EU), Seattle (EU), Stanford (EU), Davis (EU), Trois-Rivières (Canada), Tucuman (Argentine), Melbourne (Australie), Canberra (Australie), Sydney (Australie), Beyrouth (Liban), Jamshedpur (Inde), Ibaraki (Japon), Singapour, Conakry (République de Guinée)

EN EUROPE (HORS FRANCE) :

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③ BRÊME (Allemagne)
④ DARMSTADT (Allemagne)
⑤ POTSDAM (Allemagne)
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⑦ DRESDE (Allemagne)
⑧ JÜLICH (Allemagne)
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⑮ HELSINKI (Finlande)
⑯ STOCKHOLM (Suède)
⑰ DELFT (Pays-Bas)
⑱ BRUXELLES (Belgique)
⑲ LOUVAIN (Belgique)
⑳ BARCELONE (Espagne)
㉑ AVEIRO (Portugal)
㉒ POLITO (Italie)
㉓ PRAGUE (République Tchèque)
㉔ LJUBLJANA (Slovénie)
㉕ ZAGREB (Croatie)
㉖ NICOSIE (Chypre)

LES MISSIONS SCIENTIFIQUES CONTRACTUELLES DE L'ICSM

Dans le but de développer la recherche fondamentale au service d'un nucléaire durable et économe de matières, le CEA, le CNRS et les deux établissements publics d'enseignement associés à ce projet, l'Université de Montpellier et l'Ecole Nationale Supérieure de Chimie de Montpellier, se groupent pour créer l'Institut de Chimie Séparative de Marcoule, autour de huit équipes ayant pour mission de rechercher des solutions sur des verrous identifiés dans les procédés actuels autour du cycle du combustible nucléaire et de progresser dans la connaissance fondamentale associée. A terme, le but est l'émergence de technologies en rupture dans le domaine de la chimie séparative applicables à l'ensemble du cycle du nucléaire de 4ème génération et extensibles pour le mix énergétique au-delà des procédés directement liés à l'électronucléaire seulement. Ainsi, les études de l'ICSM concernent également les énergies renouvelables économes de ressources et sans impact sur l'effet de serre et, d'une façon générale, la chimie pour le développement durable par une approche influencée par les progrès cognitifs très importants durant ces vingt dernières années dans le domaine des nanosciences. Les acquis scientifiques escomptés dans le domaine de l'énergie renouvelable déboucheront sur de nouvelles technologies utilisables pour l'extraction ou le recyclage des métaux stratégiques. Aux procédés de recyclage sont associés des matériaux d'usage, dont l'évolution des surfaces et donc le cycle de vie doit être prédictible sous stress chimique, thermique ou radioactif.

THÉMATIQUE 1

SYSTÈMES HYBRIDES POUR LA CHIMIE SÉPARATIVE (LHYS)

Cette thématique propose l'étude des propriétés de systèmes moléculaires et supramoléculaires auto-assemblés, à base de métaux (d et f) avec pour objectif principal d'appréhender au mieux les mécanismes sous-jacents à la séparation d'éléments d'intérêt. Il s'agit de déterminer le rôle des interactions entre un centre métallique et ses environnements proches et lointains dans un processus d'organisation de la matière afin de comprendre un comportement de séparation de métaux, et mettre à profit cette organisation pour contrôler les propriétés de structure et de réactivité des matériaux moléculaires obtenus.

Les systèmes d'étude expérimentale considérés sont notamment des solutions organiques composées de divers précurseurs moléculaires, permettant la solubilisation d'un métal sous forme d'un complexe moléculaire. Par leur structure moléculaire, ces systèmes doivent permettre la modulation des interactions entre un métal et son environnement à différentes distances et échelles d'énergies. Les interactions principales d'intérêt sont les interactions métal-molécule (chimie moléculaire) et molécule-molécule (chimie supramoléculaire). Dans le cadre de la chimie séparative, l'assemblage spécifique entre un métal et des systèmes moléculaires polyfonctionnels permet la formation d'un polymère hybride solide de type polymère de coordination, à partir d'éléments en solution. Ces systèmes permettent alors la séparation des métaux par auto-assemblage spécifique lié au champ cristallin du métal et non uniquement lié à des grandeurs de la physique classique (électrostatique, polarisation et dipôle). Cette approche ouvre la voie d'un tri des métaux par «précipitation» piloté par la géométrie de coordination et ouvre un nouveau champ d'investigation des propriétés physiques et chimiques de ces objets, plus particulièrement dans le domaine des nouvelles technologies de l'Energie décarbonées.

D'une manière générale, cette recherche a pour objectif de dépasser l'étude de la seule liaison de coordination dans un complexe métallique où l'ion est en interaction au niveau des nuages électroniques avec un «site complexant» identifié, modélisable au niveau quantique, et doit s'étendre aux interactions au-delà du premier voisin, modélisable au niveau mésoscopique, pour former soit des phases complexes spécifiques à un métal dans un solvant, soit des assemblages spécifiques type polymère de coordination.

THÉMATIQUE 2

CHIMIE DES IONS AUX INTERFACES ACTIVES (L2IA)

La chimie aux interfaces - ou chimie colloïdale des fluides complexes - est en pleine mutation. Une opportunité est donc ouverte par les progrès de cette chimie, en particulier dans le cas de l'extraction liquide/liquide. L'effort de recherche est à focaliser sur la caractérisation de la distribution à l'échelle nanométrique des ions et colloïdes près des interfaces macroscopiques, aussi bien sur les aspects statiques que dynamiques, avec un effort important sur l'aspect cinétique de transfert entre deux milieux fluides non miscibles. Déclinée dans le cas des actinides et des lanthanides, cette problématique est d'importance pour le tri ionique associé au cycle du combustible mais aussi pour de nombreux cas de dépollution et recyclage. On passerait, pour l'adsorption des ions en solution, de la démarche purement expérimentale à l'établissement de modèles prédictifs, aussi bien sur des fluides complexes ultra-divisés froids (non radioactifs) que des systèmes méso et microporeux chauds qui pourront être étudiés expérimentalement dans Atalante. Dans les domaines non-nucléaires liés aux énergies alternatives, les progrès dans cette direction cognitive sont porteurs de progrès en décontamination et en éco-extraction notamment.

THÉMATIQUE 3

TRI IONIQUE PAR LES SYSTÈMES MOLÉCULAIRES AUTO-ASSEMBLÉS (LTSM)

Dans les procédés associés au recyclage – nucléaire ou non -, lorsqu'un ion en solution est en équilibre à travers une interface avec une dispersion de complexants en conditions d'usage, la phase aqueuse ainsi que la phase non-aqueuse sont des solutions loin de l'idéalité. Ce sont des systèmes moléculaires organisés : micelles, microémulsion, colloïdes, cristaux liquides, que l'on peut considérer par la thermodynamique statistique comme des « nanophases » réactives. Ces nanophases dispersées présentent des effets coopératifs très puissants et sélectifs, qui sont la base des procédés de tri ionique efficaces et maîtrisés. Mais, via des « effets tunnel » dus aux espèces adsorbées aux interfaces, ces nanophases sont aussi à l'origine du peu d'efficacité en termes de flux massiques des méthodes de tri ionique. La compréhension des mécanismes physico-chimiques qui gouvernent le tri ionique doit ainsi permettre le design et la synthèse de systèmes chélatants optimisés, mis en œuvre dans les procédés d'extraction/séparation considérés biphasiques (liquide/liquide, solide/liquide) ou monophasiques (membranaire, flottation, précipitation). L'activité globale de l'équipe LTSM est ainsi dédiée à la problématique de la séparation d'ions par transfert entre phases liquides, dont l'une au moins est un fluide complexe auto-assemblé. A travers la conception, la synthèse et l'optimisation de structures moléculaires chélatantes, cette équipe s'intéresse à la compréhension et à la maîtrise des phénomènes qui influencent le tri ionique par des équilibres spécifiques d'ions entre deux fluides séparés par une interface, conditionnés par des systèmes moléculaires organisés. La sélectivité comme la cinétique d'extraction, qui résulte de la combinaison d'interactions locales avec les plus proches voisins et d'interactions « longue distance » telles que les forces de dispersion (effets de type Hofmeister alias chaotrope/cosmotrope, forces d'hydratation) sont alors abordées.

Au-delà du domaine purement nucléaire, ces effets sélectifs sont étudiés et mis en œuvre dans différents procédés liés au recyclage de matières associées à la production d'énergie et, plus généralement, dans les optiques de développement durable, par exemple en décontamination ou pour le recyclage sélectif des métaux stratégiques au-delà des applications liées à l'électronucléaire, c'est-à-dire comprenant aussi les énergies alternatives.

THÉMATIQUE 4

SONOCHIMIE DANS DES FLUIDES COMPLEXES (LSFC)

La cavitation acoustique observée dans les liquides soumis à des ultrasons de puissance conduit à des conditions extrêmes au sein des bulles, au moment de leur implosion, qui sont à l'origine de la réactivité chimique inhabituelle (sonochimie) ainsi que de l'émission de lumière, connue sous le nom de sonoluminescence. La mesure du spectre de sonoluminescence permet de sonder l'intérieur des bulles, d'obtenir des informations sur les températures atteintes et sur la présence d'espèces excitées.

En effet, chaque bulle de cavitation peut être considérée comme un microréacteur chimique à plasma qui ne nécessite pas l'addition de réactifs spécifiques et ne génère pas de déchets supplémentaires, respectant ainsi les principes de l'industrie nucléaire du futur et de la chimie «verte».

Une des potentialités de la sonochimie réside en la synthèse de matériaux monodispersés composés de sous-unités de taille nanométrique. En effet, en fonction des conditions opératoires, des nanoparticules avec des propriétés contrôlées (catalytiques, magnétiques, etc.) peuvent être synthétisées, ceci grâce aux espèces réactives formées *in situ* ainsi qu'aux effets thermiques locaux très importants autour des bulles de cavitation. La combinaison des ultrasons et des catalyseurs nanostructurés permet d'améliorer significativement l'efficacité des réactions catalytiques grâce à une dispersion efficace de la phase active et l'activation de surface de catalyseur.

A proximité de surfaces solides macroscopiques, les bulles de cavitation sont susceptibles d'imploser asymétriquement et de donner ainsi naissance à des micro-jets de liquide venant frapper violemment les surfaces solides. Combinés aux ondes de chocs résultant de l'implosion sphérique de bulles plus éloignées de surface, ceux-ci peuvent mener à des phénomènes tels que l'érosion de surface, la fracturation de grains, l'augmentation du transfert de masse, ou encore la diminution des couches de diffusion. De par sa simplicité d'utilisation et d'insertion potentielle dans une étape de procédé industriel, l'apport des ultrasons est aujourd'hui considéré aussi dans le domaine du nucléaire. Entre autres, le phénomène de cavitation acoustique pourrait contribuer à faciliter la dissolution du combustible nucléaire du futur ou améliorer la décontamination de déchets industriels.

THÉMATIQUE 5

NANOMATÉRIAUX POUR L'ENERGIE ET LE RECYCLAGE (LNER)

Cette thématique porte sur la recherche relative aux nanomatériaux utilisés dans le domaine de l'énergie (matériaux d'usage) et intervenant dans les procédés de recyclage. Les thématiques de recherche couvrent les méthodes innovantes de synthèse de matériaux structurés à différentes échelles, leur fonctionnalisation, leur caractérisation et l'étude des phénomènes mis en jeu lors des différentes étapes d'élaboration, complétées par l'étude de leurs propriétés d'intérêt et de leur comportement.

L'ensemble des études menées au sein de cette équipe est relatif à des composites de nature (porosités, phases hybrides, oxydes, carbures..), de taille (nano, méso et/ou micro) et de structure (ordonnée ou amorphe) contrôlées et présentant une ou plusieurs fonctionnalités (chimie séparative, propriétés optiques renforcées, incorporation d'éléments actinides…). Par ce type de structure hiérarchique, les propriétés physiques (fissuration, tenue à l'irradiation, propriétés optiques) mais aussi chimiques (extraction, lixiviation) de ces matériaux présentent des performances hautement non linéaires par rapport à celles des matériaux massifs, rendant ainsi possible le modelage de ces propriétés en fonction des applications souhaitées. Dans tous les cas, pour concevoir ces matériaux, les avancées de la chimie « douce » (sol-gel, colloïdale, émulsion, hydrothermale,…) sont mises en œuvre afin d'obtenir des réactivités lentes et contrôlées permettant alors une caractérisation précise et parfois « *in situ* » des différentes étapes réactionnelles et donc une meilleure maîtrise du matériau final. Cette démarche multi-échelle s'applique aussi vers les matériaux auto-cicatrisants ou auto-réparants utilisés dans le domaine de transformation ou de stockage de l'énergie.

THÉMATIQUE 6

INTERFACES DE MATÉRIAUX EN EVOLUTION (LIME)

La conception de nouveaux procédés et de nouveaux matériaux pouvant être mis en œuvre à des températures et des pressions significativement plus élevées devrait permettre de réaliser les avancées technologiques nécessaires au développement des réacteurs nucléaires du futur. Ces mêmes matériaux devront alors présenter des propriétés permettant de résister à plusieurs types d'agressions : thermique, chimique, radiative, ...

Les thématiques développées au sein du laboratoire ont donc pour principal objectif de décrire et de comprendre les phénomènes siégeant aux interfaces de matériaux d'intérêt pour le nucléaire : interfaces solide/solide au cours d'étapes de frittage (densification) et interfaces solide/liquide lors d'opérations de dissolution ou d'étapes de lixiviation ou d'altération sous contraintes. Il s'agit alors d'appréhender la synthèse puis la densification d'un matériau en regard des propriétés d'usage requises pour une application donnée.

Les expérimentations relatives aux interfaces solide/solide s'inscrivent principalement dans l'étude du frittage à travers les différents mécanismes intervenant lors de la densification d'un matériau (consolidation de l'objet, grossissement de grains, réduction de la porosité). Dans ce cadre, le couplage d'expérimentations *in situ* et ex situ permet non seulement d'analyser les différentes étapes de la densification et d'obtenir des données le plus souvent uniquement accessibles par modélisation mais également d'aboutir à l'obtention de cartes de frittage (« carte d'identité microstructurale » d'un matériau représentant la taille de grains vs. taux de densification) dans un délai très court. Il en découle alors une optimisation des conditions expérimentales en fonction de la microstructure désirée.

Concernant l'évolution des interfaces solide/liquide, il s'agit de permettre à terme l'optimisation des propriétés de certains matériaux utilisés (ou à utiliser), notamment pour l'aval ou l'amont du cycle électronucléaire. Pour cela, la démarche développée consiste à coupler une approche cinétique à travers l'établissement de l'expression multiparamétrique de la vitesse de dissolution avec une approche thermodynamique visant à déterminer des données associées aux phénomènes de saturation siégeant aux interfaces. Dans ce cadre, le volet cinétique inclut la mise en évidence des paramètres affectant l'interface en évolution aussi bien en solution (pH, Eh, complexants, T, …) que ceux associés au solide (structure et défauts structuraux, microstructure). Les expériences menées en conditions proches de la saturation visent, quant à elles, à identifier les phases néoformées potentielles issues de la dégradation des matériaux en cours de dissolution puis d'acquérir les données thermodynamiques associées à leur solubilité. Il s'agit principalement d'évaluer leur impact sur les relâchements élémentaires en solution.

Cette démarche transversale initialement mise au point sur des matériaux présentant un intérêt pour l'amont ou l'aval du cycle du combustible électronucléaire (phases minérales uranifères d'intérêt, combustibles, matrices de confinement spécifique, …) a pour vocation à être étendue à d'autres champs d'activité notamment à ceux relevant de la chimie séparative hors nucléaire.

THÉMATIQUE 7

ETUDES DE LA MATIÈRE EN MODE ENVIRONNEMENTAL (L2ME)

Dans ce nouveau Laboratoire d'Etudes de la Matière en Mode Environnemental (L2ME), la fusion des compétences et savoir-faire correspond à la volonté de coupler les informations microscopiques et macroscopiques obtenues par l'ensemble des techniques expérimentales disponibles au sein du L2ME, à partir d'un socle de compétences de microscopie électronique à balayage en mode environnemental. Il s'agira de décrire encore plus précisément le comportement de l'échantillon en maîtrisant, lors de l'enregistrement des mesures, les paramètres physiques auxquels est soumis l'échantillon (température, taux d'humidité, nature des gaz, pression…).

Le contrôle des paramètres de l'environnement d'un échantillon ouvre le champ de l'expérimentation *in situ* et l'accès à la détermination de grandeurs physiques originales. Les avancées récentes en microscopies à rayons X et électroniques permettent de voir directement des agrégats supra-moléculaires en solution avec une résolution inégalée à ce jour. L'apport de ces modes d'imageries à la compréhension fine de certaines propriétés des matériaux (auto-cicatrisation, frittage, dissolution) ou à l'observation de la morphologie d'objets résultant de l'auto-association de molécules est essentiel.

Une analyse chimique couplée à une imagerie pour l'étude des surfaces en évolution permet un suivi des mécanismes de réarrangement de surface, allant de la description des mécanismes de dissolution des matériaux jusqu'à de réelles expériences de recuit des matériaux *in situ*.

La caractérisation multi-échelle de la matière, du nanomètre au micron, repose sur une maîtrise des mesures dans l'espace réciproque dans une large dynamique d'intensité et de vecteur de diffusion. Ici, diffusion aux petits angles et diffraction utilisant des rayons X durs nécessaires pour l'étude d'éléments de Z élevés doivent être utilisées conjointement pour la caractérisation multi-échelle statistique des matériaux permettant de contourner les effets dus au choix d'images représentatives. A ce niveau, des grandeurs physico-chimiques allant jusqu'aux potentiels d'interaction, aux interfaces fractales et aux courbures peuvent être déterminées directement, en contrôlant conjointement température et activité du solvant.

Les matériaux divisés, leurs surfaces, les fluides, leurs mélanges et les associations faibles de molécules ayant des propriétés de transport ionique particulières ne peuvent être modélisés avec succès qu'après une caractérisation statistique de haute sensibilité même en cas de faible contraste, elle-même couplée avec une description microscopique précise des objets.

Au-delà de la collaboration étroite avec les équipes spécialisées, la pratique et l'interprétation physique et chimique des spectres de diffusion-diffraction et des images de microscopie sont une discipline scientifique à part entière, conduisant à des recherches propres dans les nanosciences et des collaborations scientifiques directes avec des équipes externes à l'ICSM. L'équipe permet aussi d'apporter un soutien à l'utilisation de grands instruments (sources de rayons X et de neutrons) pour les recherches menées dans les autres équipes.

THÉMATIQUE 8

MODÉLISATION MÉSOSCOPIQUE ET CHIMIE THÉORIQUE (LMCT)

La modélisation à l'échelle mésoscopique est nécessaire à toute modélisation prédictive : elle s'impose non seulement pour l'étude des états d'équilibre que pour la prédiction des propriétés de transport dans le cadre des systèmes chimiques étudiés à l'ICSM. En association avec les équipes en charge de la chimie quantique au sein du Pôle Balard et de la dynamique moléculaire dans les départements de R&D de Marcoule, ce laboratoire de chercheurs théoriciens constitue une équipe transverse travaillant en étroite collaboration avec les autres équipes de l'ICSM.

L'approche de ce groupe est multi-échelle : la matière est décrite par des modèles à des niveaux de descriptions variés, du plus microscopique (description atomique) jusqu'au niveau macroscopique (modèles des sciences de l'ingénieur). Un intérêt tout particulier se manifeste pour le traitement des interactions à l'échelle intermédiaire (échelle mésoscopique ou à solvant continu) car celle-ci constitue l'échelle principale des phénomènes étudiés à l'ICSM. Le lien entre les échelles de description est explicitement réalisé par cette équipe : les paramètres des modèles les plus macroscopiques ne sont pas obligatoirement ajustés car ils peuvent être obtenus à partir des descriptions aux échelles plus petites. Le but final est de proposer une description de la matière pratique suffisamment simple pour faire le lien avec l'échelle pondérale modélisée dans les départements de R&D de Marcoule, en tenant compte des effets microscopiques complexes là où ceux-ci ont un rôle. Une telle approche nécessite de développer des méthodes de chimie théorique et de thermodynamique statistique nouvelles adaptées.

Cette stratégie est particulièrement approfondie pour l'extraction liquide/liquide, pour les phases aqueuses et organiques en contact. Les espèces à extraire sont essentiellement des électrolytes, soit forme d'ions dissociés hydratés, mais aussi de paires d'ions et d'ions complexes, au-delà des lanthanides et actinides motivés essentiellement par les applications dans le cycle du combustible nucléaire du futur, mais incluant les espèces d'intérêt pour les énergies alternatives.

PERSONNEL D'APPUI À LA RECHERCHE, ÉQUIPEMENTS SCIENTIFIQUES ET ÉQUIPES

L'organisation de l'ICSM s'articule donc autour d'une stratégie de recherche structurée en 8 équipes mais aussi d'une équipe de direction avec son administrateur gestionnaire et chef d'installation (CEA/DEN) qui dirige les équipes de gestion et d'appui technique de l'unité (exploitation et sécurité) et son secrétariat, d'une équipe de gestion administrative et financière chargées de l'exécution budgétaire, des opérations de gestion du personnel et de la formation, des achats, des missions et du support de communication de l'unité sur les 4 tutelles. Enfin une équipe d'installation en charge de fonctions multiples (correspondants déchets et effluents, transport, sources radioactives et matières nucléaires, avec l'appui des labos, correspondants des nombreux contrats du centre de Marcoule comme la maintenance, ventilation (en cours de refonte), protection physique (étendue à plusieurs laboratoires), nettoyage, petits travaux, CEP, …) (cf. organigramme personnels permanents) complète la partie direction.

Les activités du personnel administratif correspondent à environ 8 ETPT toute tutelle confondue (pour 32 ETPT Recherche, 4 ETPT Enseignement) afin de recevoir et gérer dans les meilleures conditions environ 10 post-doctorants/CDD, 20 doctorants, une trentaine de stagiaires/apprentis (Master, IUT, BTS) par an. Ces activités couplées à celle de la recherche et de l'enseignement permettent de garantir 1) de la qualité scientifique de la recherche et du respect de l'intégrité scientifique, 2) de la sécurité à tous les niveaux de par le statut de l'unité en tant qu'ICPE chimie déclarée (l'unité possède des matières nucléaires en quantité réduite, 1 kg d'uranium naturel ou appauvri et de thorium) ainsi que des risques chimiques avec, en priorité, les substances CMR. Les formations obligatoires sont assurées pour accéder aux laboratoires et permettre un travail de recherche en toute sécurité en s'engageant de manière responsable et considérant un développement durable, associant maintien de la paix, croissance économique, protection de l'environnement et développement social, dont l'objectif est de satisfaire les besoins actuels de la société et de préparer l'avenir en anticipant les besoins des générations futures.

La gestion des ressources financières (prestations, contrats européens, nationaux PIA et autres financements publiques, des collectivités territoriales, contrats de recherches industriels ou des SATT et autres prestations de type expertises, conseils, services) doit être parfaitement maitrisée afin de mener à bien l'activité de l'ICSM.

Les spécialités de l'ICSM nécessitent l'utilisation d'équipements spécifiques (voir figure) adaptés aux domaines d'expertise en synthèse organique et matériels de purification associés (Chromatographie automatisée, HPLC semi-préparative), synthèse et caractérisation de matériaux inorganiques et hybrides organiques/inorganiques (fours, ATD/ATG, analyses élémentaires, analyseur de surface, dilatométrie, microscope optique 3D) ainsi que d'équipements expérimentaux originaux (réacteurs multifréquences pour la sonochimie, cellules de filtration membranaire, colonnes de flottation, cuve de Langmuir) et d'analyses classiques (UV-Vis, FTIR, chromatographie ionique, GC-MS) ou spécifique (tensiométrie à goutte, DLS, détection acoustique). Les équipements mi-lourds utilisés dans le cadre des missions scientifiques de l'ICSM sont en partie affectés dans les laboratoires de l'Institut, notamment les équipements d'analyses (Diffusion/Diffraction de rayons X, Microscopie Electronique à Balayage Environnemental, RMN 400 MHz liquide et solide, ICP-OES, ICP-MS, spectroscopie Raman, banc d'optique non-linéaire) qui sont pour la plupart mutualisés au sein de la Plate-forme Commune d'Analyses et de Caractérisation (PAC) du pôle de Chimie MUSE. Ils sont en cours de jouvence pour maintenir une excellence dans les recherches de l'institut comme le MEB en 2021, la console RMN en 2024, l'analyseur de surface spécifique (BET) en attente de réception, et bientôt le microscope µ-Raman prévu en 2025 ainsi que le banc de diffusion X aux petits angles. Pour les caractérisations par diffusion de neutrons et de rayons X haute résolution, les équipes effectuent leurs analyses sur les grands instruments de l'Institut Laue-Langevin (ILL) ou au LAEA à Tokaï (Japon) sur le JRR-3 en collaboration avec l'équipe de R. Motokawa. De même, pour celles par rayons X avec du temps de faisceau synchrotron demandé sur les lignes de SOLEIL ou à l'ESRF ou encore au centre HZ à Berlin ou DESY à Hambourg.

Dans le cadre des études menées sur la caractérisation de matériaux sous irradiation ioniques, les expérimentations s'effectuent sur JANNUS (Saclay) et au GANIL (Caen).

1 / SYSTÈMES HYBRIDES POUR LA SÉPARATION (LHYS)

Au 1^er^ décembre 2024 l'équipe était composée de 4 permanents :
1 Chercheur (DR) CNRS, responsable d'équipe (Dr. Damien Bourgeois)
1 Ingénieur-chercheur CEA/DRF (Dr. Michaël Carboni)
1 Enseignant-chercheur (MCF) UM (Dr. Jérôme Maynadié)
1 Ingénieur-chercheur CEA/DES (Dr. Marie Simonnet)

Et sur la période 2021-2024 de non-permanents :

Post-doctorants :
Boushra Mortada (contrat CEA/PTC, 2021-23) : Dépôt 2D de MOF sur surface de verre.
Bastien Jally (Contrat CEA, 2022-2023) : Mise au point de résines imprégnées pour la récupération des platinoïdes.
Jérémy Audevard (PEPR Diadème 2022-26) : Préparation et étude de matériaux poreux pour la séparation de gaz.
Dmytro Nikolaeïvskyi (ANR CAREME, 2024-26) : Préparation de catalyseurs issus du recyclage.

Ingénieurs d'étude ou de recherche en CDD :
Anthony Brunet-Manquat (ANR CAREME, 2022-24) : Préparation de catalyseurs issus du recyclage.
Valentin Pierre (Projet Plan de relance ANR/Sovamep, 2022-24) : Développement de procédés de récupération de métaux précieux.
Marie Moneuse (Eramin 2Boss, 2023-2024) : Etude du recyclage de piles sodium-soufre
Marie Moneuse (Circulades Reculiti, 2025-2026) : Recyclage et valorisation du lithium.

Doctorants :
Elisabeth Makombé (thèse CEA/DES, 2019-23) : Reformulation solvant et recyclage d'actinides.
Michael Martin-Romo y Morales (thèse Région/Saint Gobain, 2020-23) : Valorisation directe de métaux précieux issus du recyclage sous forme de dispositifs pour dépollution.
Tennesse Riant (thèse CEA/DRF, 2020-23) : Comportement de composés lamellaires à pas contrôlé d'oxydes de métaux de transition comme matériaux d'électrodes de batteries.
Raphaël Moneuse (thèse UM, 2020-23) : Séparation des métaux par dynamique adaptative.
Mathéo Henry (thèse CEA/DES ; 2023-2026) Précipitation contrôlée d'actinides en phase organique complexe.
Mawa Khoder (thèse CNRS, projet PIA PREPAC, 2023-2026) : Optimisation de la séparation du ruthénium par la cinétique de transfert.
Raphaëlle Fasola (thèse Région/CEA, 2024-2027) : Récupération et valorisation du vanadium dans les batteries au sodium.
Lucile Golfier (thèse CEA/DES, 2024-2027) : Etude mécanistique de la séparation sélective de l'américium par couplage d'extractants lipophiles et hydrophiles.
Ervin Prozsa (thèse UM, 2024-2027) : Mise en forme de matériaux poreux type MOFs pour la séparation de gaz.

Apprentis :
Sabrine Medjouel (2021-24)
Khady Cissé (2024-2025)
Bastien Girardet (2024-2027)

La compréhension du comportement des métaux dans des phases organiques complexes est au cœur du développement de procédés efficaces de recyclage et de gestion des déchets. Les approches généralement développées en hydrométallurgie visent la plupart du temps à la maitrise d'étapes unitaires, par voie liquide ou solide. L'équipe propose d'intégrer l'ensemble de ces développements dans des enchainements globaux extraction-séparation-fin matière, sous le concept de la chimie séparative circulaire des métaux. Cette simplification des procédés vise à 1) une meilleure gestion des mélanges, 2) une meilleure flexibilité face à une matière première de composition variable, et 3) une diminution du nombre d'étapes, généralement synonyme d'une maitrise des effluents générés. En outre, la notion de recyclage n'est pas restreinte à l'isolement d'un métal purifié, et l'équipe prend en compte la fin matière : les procédés développés intègrent au mieux la valorisation du métal ciblé sous forme de produit fini, pour une application similaire ou différente.

Les études menées au laboratoire sont centrées sur la description et la compréhension des propriétés de systèmes moléculaires et supramoléculaires à base de métaux (d et f). Il s'agit de déterminer le rôle des interactions entre un centre métallique et son environnement proche et lointain dans un processus d'organisation de la matière, puis de mettre à profit cette organisation pour former soit des phases organique complexes spécifiques à un métal, soit des assemblages spécifiques type polymère de coordination. Dans ce cadre, l'équipe ne cherche pas à développer de nouveaux outils (nouvelles molécules, nouveaux solides, nouvelles méthodologies de synthèse), tout en possédant une maitrise parfaite des outils existants, incluant les aspects mécanistiques au niveau moléculaire. Ces études visent le développement de procédés innovants de séparation, dans une approche d'hydrométallurgie raisonnée, ciblant divers métaux d'intérêt avec diverses propriétés physico-chimiques (valence, densité de charge, etc.) tels que les métaux de transition (Pd, Au, Ni, Co, Mn, Ru, Al, Sc), lanthanides ou actinides (U, Th et Pu).

Au niveau fondamental, l'accent est mis sur des problématiques de séparation adaptative, visant à un pilotage contrôlé de procédés pouvant traiter un flux entrant de composition variable. Le développement de systèmes adaptatifs a été envisagé à travers une approche basée sur la mise en œuvre de bibliothèques covalentes dynamiques : contrairement à la méthode conventionnelle pour laquelle une seule molécule est conçue pour extraire les cations métalliques dans des conditions spécifiques, la chimie covalente dynamique permet d'induire la génération de différentes espèces extractantes selon la composition du milieu. En collaboration avec le LCS (ISIS), et dans le prolongement de la thèse d'A. Chevalier (2020), l'équipe LHyS a appliqué cette approche à la distribution du Pd(II) au sein d'un système biphasique. L'ajout d'ions Pd(II) à la bibliothèque déclenche une modification de sa composition par la régulation des molécules extractantes provoquée par la coordination avec le cation métallique (thèse R. Moneuse). La manipulation des flux complexes est également abordée par le contrôle de la séparation, obtenu soit par formulation de phases organiques classiques, soit par une compréhension approfondie de la cinétique de transfert. La thèse d'E. Makombé a mis en évidence un comportement original de la distribution de l'U(VI), ainsi qu'une sélectivité Pu(IV)/U(VI) ajustable par un choix judicieux de la topologie moléculaire des extractants étudiés, principalement des malonamides. Les études actuelles ciblent la séparation Cm(III)/Am(III), avec une étude mécanistique de la séparation sélective de l'Am par couplage d'extractants lipophiles et hydrophiles (thèse L. Golfier). En ce qui concerne le pilotage par la cinétique de transfert, dans le prolongement des études consacrées aux cations Pd(II), Nd(III) et Fe(III) (thèse SA. Moussaoui, 2021), où une augmentation d'un facteur 100 fois du facteur de séparation Pd/Fe a pu être atteinte, les travaux actuels visent la séparation U/Ru (thèse M. Khoder, contrat B. Girardet). Ce dernier travail se focalise également sur le comportement particulier du Ru dans le processus PUREX, avec une étude approfondie du hold-up du Ru dans la phase organique.

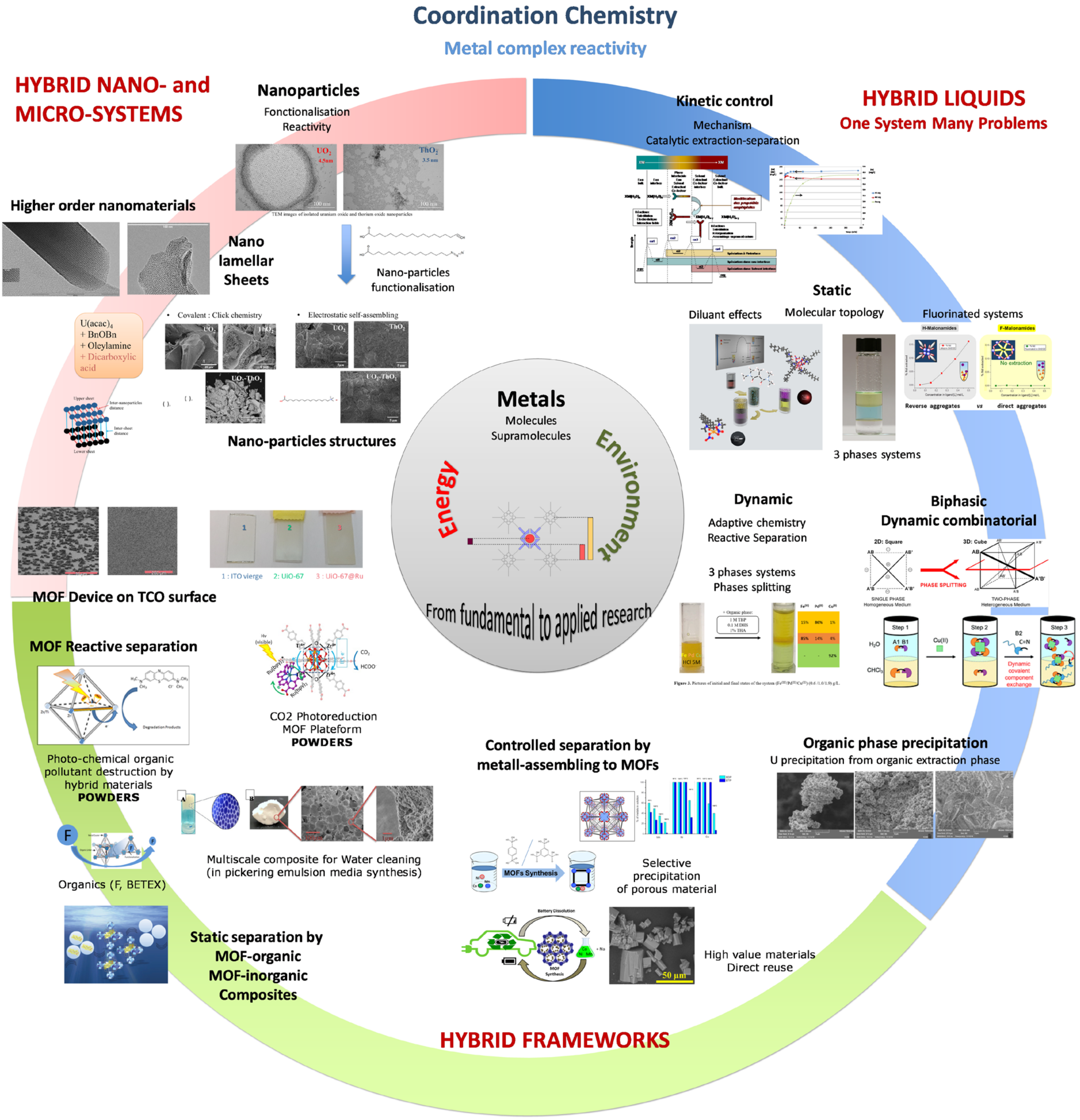
Les systèmes moléculaires étudiés sont ensuite utilisés pour le développement de boucles courtes de recyclage, dans les différentes étapes du cycle de vie des métaux traités à l'ICSM :

En ce qui concerne le cycle du combustible nucléaire, les études visent à la simplification d'un cycle fermé piloté par la sureté, grâce à une gestion contrôlée des mélanges d'actinides. L'approche intègre également la fin matière, par une préparation contrôlée de matériaux d'actinides, purs ou en mélange, et organisés à l'échelle nanométrique. Les études actuelles visent la récupération des actinides majeurs par leur précipitation directe à partir d'une phase organique d'extraction du procédé PUREX, en contournant ainsi les étapes classiques de contre-extraction et de précipitation oxalique (thèse M. Henry). Les matériaux hybrides organisés à l'échelle nanométrique sont obtenus à partir de flux simulés composés d'U(VI) et de Th(IV), ce dernier étant utilisé en tant que substitut du Pu(IV). La sélectivité du procédé vis-à-vis de Zr(IV) et Nd(III) est à l'étude. La conversion des solides obtenus en oxydes d'U et de Th est également étudiée, avec un accent sur la conservation de leurs nano-structures.

Dans le secteur des déchets et du recyclage, l'approche développée vise à améliorer la chaîne de valeur en préparant directement, sans aucune purification, des composés à haute valeur ajoutée, en tenant compte des modèles économiques et écologiques. Diverses applications sont traitées par le biais d'un réseau établi de collaborations universitaires et industrielles :

- Dans le domaine des métaux précieux (ex. Pd, Au), récupérés à partir de déchets électroniques ou industriels, l'équipe LHyS s'intéresse à la synthèse de matériaux pour la catalyse : il a été possible de proposer une voie d'upcycling du Pd par sa valorisation directe en tant que catalyseurs dans le cadre du projet CAREME financé par l'ANR (thèse M. Martin Romo y Morales, contrats A. Brunet-Manquat, D. Nikolaievskyi). Des catalyseurs supportés actifs ont été préparés pour l'oxydation du méthane et l'hydrogénation d'oléfines encombrées. Au cours de ce travail, l'équipe a acquis une expertise précieuse dans la préparation de catalyseurs supportés. En outre, il faut noter que les recherches menées dans ce domaine ont mené à une collaboration renforcée avec la société SOVAMEP, afin d'optimiser la récupération des métaux précieux (Au et Pd, contrat V. Pierre). Collaboration qui s'est récemment matérialisée dans un projet industriel France 2030, impliquant aussi le CEA et le BRGM, exploitant la mise au point de résines sélectives des métaux du groupe platine, qui seront appliquées au traitement d'effluents industriels (contrat B. Jally).

- Dans le domaine du stockage de l'énergie et de son économie circulaire, et en particulier du cycle de vie des électrodes de batteries, l'équipe LHyS propose une approche intégrée basée sur différents procédés hydrométallurgiques : La séparation des espèces est réalisée principalement par l'utilisation de matériaux hybrides tels que les MOFs (Metal-Organic Frameworks). L'approche initialement développée sur des cycles fermés pour les batteries Li-ion (technologie NMC) est actuellement étendue à d'autres technologies telles que Li-S (contrat M. Moneuse) et Na-V (thèse R. Fasola). Ici, d'autres défis se posent car la valeur intrinsèque des matériaux peut être très faible (sulfures, phosphates) et des approches originales de recyclage ou d'upcycling sont considérées. Le travail inclut aussi la fabrication de matériaux actifs à cathode, passant ainsi des déchets aux matériaux actifs. Les études dans le domaine de la synthèse des matériaux d'électrodes ont été enrichies par le développement de matériaux lamellaires polymétalliques organisés à l'échelle nanométrique (thèse T. Riant), qui ont révélé des propriétés intéressantes après des essais de cyclage de batterie. Toutes ces actions comprennent des études fondamentales et appli-



Coordination Chemistry

Metal complex reactivity

HYBRID NANO- and MICRO-SYSTEMS

Nanoparticles

Fonctionalisation
Reactivity

Higher order nanomaterials

Nano lamellar Sheets

Nano-particles functionalisation

U(acac)$_4$
+ BnOBn
+ Oleylamine
+ Dicarboxylic acid

- Covalent : Click chemistry
- Electrostatic self-assembling

Nano-particles structures

1 : ITO vierge 2: UiO-67 3 : UiO-67@Ru

MOF Device on TCO surface

HYBRID LIQUIDS

One System Many Problems

Kinetic control

Mechanism
Catalytic extraction-separation

Static

Diluant effects

Molecular topology

Fluorinated systems

3 phases systems

Dynamic

Adaptive chemistry
Reactive Separation

3 phases systems
Phases splitting

Biphasic
Dynamic combinatorial

Metals

Molecules
Supramolecules

Energy

Environment

From fundamental to applied research

MOF Reactive separation

Photo-chemical organic pollutant destruction by hybrid materials
POWDERS

CO2 Photoreduction
MOF Plateform
POWDERS

Organics (F, BETEX)

Multiscale composite for Water cleaning (in pickering emulsion media synthesis)

Static separation by MOF-organic MOF-inorganic Composites

Controlled separation by metall-assembling to MOFs

Selective precipitation of porous material

High value materials
Direct reuse

Organic phase precipitation

U precipitation from organic extraction phase

HYBRID FRAMEWORKS

quées en collaboration avec plusieurs groupes nationaux et internationaux (projets SCARCE puis SCARCE 2 notamment).

L'expertise de l'équipe LHyS dans la synthèse de matériaux hybrides est également utilisée pour d'autres applications : les MOFs disponibles au laboratoire (Zr, Cu, Al, Fe) sont en cours d'évaluation dans la séparation de gaz, ciblant en particulier le CO_2 ou les gaz nobles (contrat J. Audevard). Aussi, la synthèse de MOFs nouveaux et originaux est en cours d'étude. Finalement, afin de répondre au manque de possibilités de mise en forme de ces matériaux poreux pour un large panel d'utilisations, l'équipe a développé une approche de préparation des matériaux poreux monolithiques hiérarchiquement organisés, basée sur la stabilisation d'émulsions de Pickering à l'aide de MOFs, en collaboration avec une équipe du CEA Marcoule (LPSD) (thèse F. Lorignon). D'autres méthodes de mise en forme des matériaux à base de MOsF sont étudiées en ce moment, tels que l'impression 3D (contrats S. Medjouel & K. Cissé) ou le dépôt sous forme de de couches minces (contrat B. Mortada). L'incorporation de MOFs dans une matrice inorganique, les géopolymères, est également en cours d'étude (PhD E. Prozsa).

1 / HYBRID SYSTEMS FOR THE SEPARATION

Understanding the behaviour of metals in complex organic phases is central to the development of efficient recycling and waste management processes. The approaches generally developed in hydrometallurgy are mostly aimed at mastering single steps, based on either liquid or solid unit operations. The team proposes to integrate all of these developments into global extraction-separation-isolation-purification chains, under the concept of circular separative chemistry of metals. This simplification of the processes aims at 1) a better management of the mixtures, 2) a better flexibility in front of a raw material of variable composition, and 3) a decrease in the number of steps, generally coupled to a better control of the generated effluents. Moreover, the concept of recycling is not restricted to the isolation of a purified metal, and the team takes into account the final material: the developed processes best integrate the recovery of the targeted metal in the form of a finished product, for a similar or different application.

Laboratory studies focus on describing and understanding the properties of metal-based molecular and supramolecular systems (d and f). The central question lies on the determination of the role of interactions between a metal center and its near and distant environment in a process of matter organization. This organization is then used to form either complex organic phases specific to a metal, or specific assemblies such as coordination polymers. In this context, the team does not seek to develop new tools (new molecules, new solids, new synthesis methodologies), but rather to reach a perfect mastery of existing tools, including mechanistic aspects at the molecular level. These studies aim at the development of innovative separation processes, in a sustainable hydrometallurgy approach, targeting various metals of interest with various physico-chemical properties (valence, charge density, etc.) such as transition metals (Pd, Au, Ni, Co, Mn, Ru, Al, Sc), lanthanides or actinides (U, Th and Pu).

At the fundamental level, the focus is set on problems related to adaptive separation, aiming at a controlled management of processes that can handle an incoming flow of variable composition. The development of adaptive systems has been envisaged through an approach based on the implementation of dynamic covalent libraries: Unlike the conventional method for which a single molecule is designed to extract metal cations under specific conditions, dynamic covalent chemistry makes it possible to induce the generation of different extractant species according to the composition of the medium. In collaboration with the LCS (ISIS), and in the continuation of the PhD thesis of A. Chevalier (2020), the LHyS team applied this approach to the distribution of Pd(II) within a biphasic system. The addition of Pd(II) cations to the library triggers a modification of its composition and the regulation of extractant molecules caused by the coordination with the metal cation (PhD thesis R. Moneuse). The handling of complex flows is also approached through the control of the separation, obtained either via formulation of classical organic phases, or via deep understanding of the transfer kinetics. The PhD thesis of E. Makombé revealed an original behavior of U(VI) distribution, as well as adjustable Pu(IV)/U(VI) selectivity, through a judicious choice of the molecular topology of the studied extractants, mainly malonamides. Current studies target the Cm(III)/Am(III) separation, with a mechanistic study of the selective separation of Am by coupling lipophilic and hydrophilic extractants (PhD thesis L. Golfier). Regarding piloting using transfer kinetics, in the continuation of studies dedicated to Pd(II), Nd(III) and Fe(III) (PhD thesis SA. Moussaoui, 2021), where a 100 fold increase in the Pd/Fe separation factor could be attained, the current work targets the U/Ru separation (PhD thesis M. Khoder, contract B. Girardet). Latter work also currently focuses on the peculiar behavior of Ru in the PUREX process, with the Ru hold-up in the organic phase under deep investigation.

The studied molecular systems are then used for the development of short recycling loops, in the different steps of the life cycle of metals treated at ICSM:

Regarding the nuclear fuel cycle, the studies aim at the simplification of a closed cycle driven by safety, through a controlled management of mixtures of actinides. The approach also integrates the final matter aspect, through controlled preparation of actinide materials, pure or in mixture, and organized at the nanoscale. Current studies target the recovery of major actinides by their direct precipitation from organic phase after the extraction stages of the PUREX process, thus bypassing classical back extraction and oxalic precipitation stages (PhD thesis M. Henry). Hybrid materials organized at the nano-scale are obtained from simulated fluxes composed of U(VI) and Th(IV) as a surrogate for Pu(IV). The selectivity of the process regarding Zr(IV) and Nd(III) is under study. The conversion of the obtained solids into U and Th oxides is also investigated, with a focus on their nano-structures.

In the waste and recycling industry, the developed approach aims to improve the value chain by directly preparing, without any purification, compounds with high added value, taking into account economic and ecological models. Various applications are addressed through an established network of academic and industrial collaborations:

- In the field of precious metals (e.g. Pd, Au), recovered from electronic or industrial waste, the LHyS teams addresses the synthesis of materials for catalysis: In collaboration with various groups, it has been possible to propose a short upcycling route of Pd by its direct valorization as various catalysts within the framework of the CAREME project funded by the ANR (PhD thesis M. Martin Romo y Morales, contracts A. Brunet-Manquat, D. Nikolaievskyi). Active supported catalysts have been prepared for methane oxidation and hydrogenation of hindered olefins. During this work, the team gained valuable expertise in the preparation of supported heterogenous catalysts. Also, it should be noted that all the research carried out in this field has led to a close collaboration with the company SOVAMEP to optimize the recovery of precious metals (Au and Pd, contract V. Pierre). collaboration that has been recently extended into a France 2030 industrial projet involving the CEA and the BRGM, after the discovery of platinum group metals selective resins, which will be applied to the processing of industrial effluents (contract B. Jally).
- In the field of energy storage and its circular economy, and in particular active electrodes cycle, the LHyS team proposes an integrated approach based on various hydrometallurgical processes: After classical dissolution, separation of species is performed mainly by the use of hybrid materials such as MOF (Metal-Organic Frameworks). The approach originally developed on closed cycles for Li-ion batteries (NMC technology) is currently being extended to other technologies such as Li-S (contract M. Moneuse) and Na-V (PhD thesis R. Fasola). Here, other challenges arise as intrinsic value of materials can be very low (sulfides, phosphates) and original upcycling approaches are considered. The work includes the manufacture of active cathode materials, thus going from waste to active materials. Studies in the field of synthesis of electrode materials were enriched by the development of lamellar polymetallic materials organized at the nanometer scale (PhD these T. Riant), which revealed interesting properties after battery cycling tests. All these actions include fundamental and applied studies and involve several national and international external groups (SCARCE then SCARCE 2 projects).

The expertise of the LHyS team in the synthesis of hybrid materials is also applied to other applications: MOFs available at the lab (Zr, Cu, Al, Fe based) are being evaluated in gas separation targeting CO_2 or noble gas (contract J. Audevard). Currently, synthesis of new and original MOFs is envisioned. Also, in order to respond to the lack of possibilities of shaping these porous materials with a wide applicability, the team developed, in collaboration with a team of the CEA Marcoule (LPSD), a hierarchically porous material preparation approach based on the stabilization of Pickering emulsions using MOFs (PhD thesis F. Lorignon). Other means of shaping MOF-based materials are being studied in the laboratory, such as 3D printing (S. Medjouel & K. Cissé contracts) or thin-film deposition (contract B. Mortada). The incorporation of MOFs into an inorganic matrix, geopolymers, is also under investigation (PhD E. Prozsa).

2/ LABORATOIRE DES IONS AUX INTERFACES ACTIVES (L2IA)

Au 1er décembre 2024 l'équipe est composée de 5 permanents :
1 chercheur CEA/DRF responsable d'équipe (Dr. Pierre Bauduin)
1 ingénieur-chercheur CEA/DRF (Dr. Olivier Diat)
1 enseignant-chercheur ENSCM (Pr. Luc Girard)
1 ingénieur d'étude CNRS (Alban Jonchère)
1 ingénieur d'étude CNRS (Coralie Pasquier)

Et sur la période 2021-2024 de non-permanents :

Post-doctorants :
Dr. Abderazak Masmoudi (projet CEA/PTC, 2021-22) : Extraction de métaux précieux par flottation ionique.
Dr Hussein Fakhouri (projet ANR Promenix 2023-25) : Nano-ions, an opportunity for the investigation of membrane proteins.
Dr Robert Winkler 2024-24 (Projet ANR Chaopom) : Chaotropic polyoxometalates, from fundamental to applications.

CDD :
Camille Liadouze (ingénieur ANR Foamex, 2021-22) : DEEE/ Extraction par flottation ionique

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Doctorants :
Ioanna Chazapi (thèse CEA, 2019-22) : Effet de solubilisation avec des nano-ions.
Klaudia Skorzewska (thèse CEA, 2019-22) : Flottation superchaotrope.
Julien Lamolinairie (thèse en co-direction avec ILL et Teclis Instrument, 2020-23) : Foam'up.
Philipp Schmid (co-direction thèse Univ. Regensburg, 2019-22): Nanoions and hydrotropes.
Raimoana Frogier (thèse UM, 2021-24) : Nanoions en interaction avec surfaces fonctionnalisées.
Valentin Legrand (thèse UM, 2022-25) : Flottation superchaotrope, extraction du tungstène.
Xiaochuan Ma (Thèse CEA 2023-2026) : Extraction par solvant : Etude des interfaces eau/huile contenant des ligands de type monoamides.
Bastian Müller (thèse CNRS en co-tutelle avec UT Darmstadt 2024-27) : Nano-ions and lipidic membranes.

Apprentis :
Amélie Cartier (BTS, CEA 2021-23) : Physico-chimie des nano-ions en solution
Lorelei Demonet (BTS, CEA 2022-23) : Activation redox de nano-ions par stimulus optique

L'équipe « Ions aux Interfaces Actives » (L2IA) se consacre à l'étude des phénomènes physico-chimiques aux interfaces des systèmes d'extraction. Elle s'intègre pleinement au sein de l'Institut de Chimie Séparative de Marcoule (ICSM) en adoptant une approche de recherche fondamentale, tout en valorisant les savoirs et expertises spécifiques de ses membres. L'équipe puise sa force dans ses compétences multidisciplinaires, couvrant la physicochimie en solution, l'auto-association moléculaire, la chimie colloïdale, la formulation de systèmes complexes et le développement expérimental. Elle s'appuie également sur une maîtrise avancée des techniques de diffusion et de réflectivité des rayonnements X, des neutrons et de la lumière.

Les objectifs scientifiques du L2IA sont multiples :

- **Interface L/L :** Analyser plus finement les phénomènes physico-chimiques aux interfaces des systèmes d'extraction liquide/liquide, en particulier avec des systèmes à base de mono- et diamides, des ligands utilisés dans les procédés de recyclage du combustible nucléaire usé, en utilisant des techniques de réflectivité (X et neutrons), d'optique non-linéaire (génération de seconde harmonique, SHG) et de modélisation. L'objectif est de mieux appréhender les phénomènes de cinétiques d'extraction.
- **Applications nano-ions :** Explorer le potentiel applicatif des ions nanométriques (nano-ions) de faible densité de charge, présentant une propriété superchaotrope mise en évidence par le groupe en 2015. Leur forte propension à s'adsorber aux interfaces neutres en fait de nouveaux outils prometteurs pour accroitre la sélectivité en chimie séparative.
- **Séparation/Lixiviation en mousse :** Développer des procédés innovants de séparation et valorisation des métaux, notamment en combinant nos connaissances sur la formulation des mousses, la flottation ionique et la flottation superchaotrope, permettant d'être sélectif dans la séparation en milieux aqueux et de minimiser l'impact environnemental (pour par exemple la dépollution et la valorisation de sols miniers).
- **Matériaux hybrides structurés par auto-association :** Élaborer des matériaux hybrides organique-inorganique (nano-ion) stimulo-réactifs, en tirant parti des propriétés d'interfaçage (chaotropique) des nano-ions en solution aqueuse pour conférer aux matériaux des structures et fonctionnalités adaptatives. Les nano-ions que nous étudions sont de très bon échangeurs de charge.
- **Mécanisme de chaotropie :** Étudier les fondements mécanistiques de l'effet superchaotrope, en combinant des approches expérimentales, en diversifiant les systèmes d'études (type de nano-ions et substrat organique) et de modélisation pour mieux comprendre, utiliser et développer le potentiel cet effet unique.
- **Solubilisation organique/inorganique :** Explorer de nouvelles voies de solubilisation de composés organique par des nano-ions (inorganiques) dans l'eau, ouvrant ainsi des perspectives pour la formulation de systèmes complexes (et réactifs) sans solvant organique (chimie verte), ou trouver des alternatives aux méthodes usuelles d'extraction de composés hydrophobes ou de protéines (membranaires).

En cohérence avec la politique de recherche et de valorisation de ses tutelles, le L2IA contribue activement à l'émergence de nouveaux concepts de séparation plus respectueux de l'environnement, en s'appuyant sur les avancées de sa recherche fondamentale. Cette démarche s'inscrit dans une volonté de répondre aux enjeux sociétaux contemporains tout s'alignant sur les orientations stratégiques du CEA/DRF, du CNRS et de l'École Supérieure de Chimie de Montpellier.

2/ IONS AT ACTIVE INTERFACES

The 'Ions at Active Interfaces' (L2IA) team is dedicated to the study of physico-chemical phenomena at the interfaces of extraction systems. It is fully integrated into the Institut de Chimie Séparative de Marcoule (ICSM), adopting a fundamental research approach while making the most of the specific knowledge and expertise of its members. The team draws its strength from its multidisciplinary skills, covering physicochemistry in solution, molecular self-association, colloidal chemistry, formulation of complex systems and experimental development. It also has advanced expertise in X-ray, neutron and light scattering and reflectivity techniques.

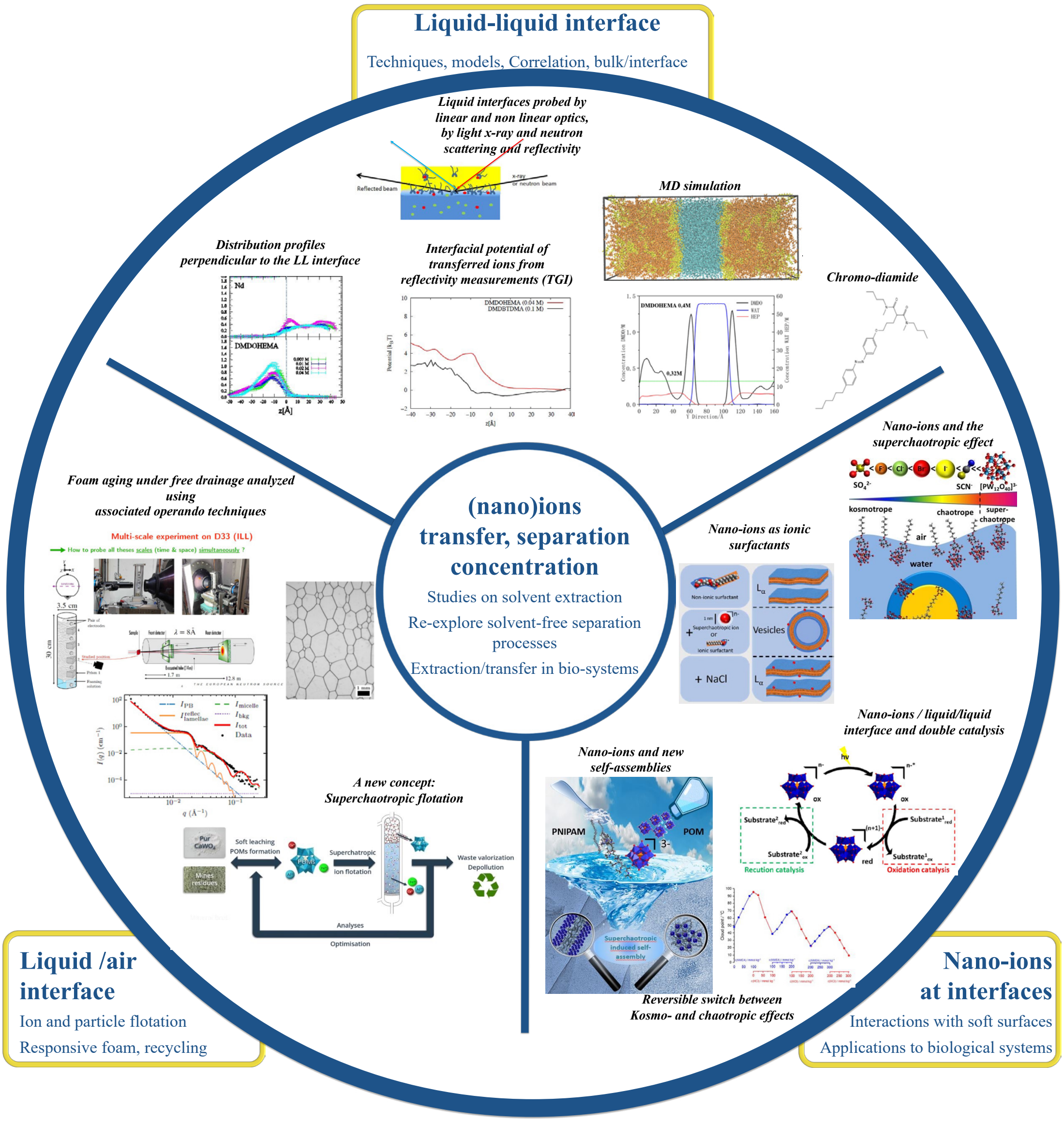
The scientific objectives of the L2IA are multiple:

- **L/L interface:** To analyse in greater detail the physico-chemical phenomena at the interfaces of liquid/liquid extraction systems, in particular with systems based on mono- and diamides, ligands used in spent nuclear fuel recycling processes, using reflectivity techniques (X-rays and neutrons), non-linear optics (second harmonic generation, SHG) and modelling. The aim is to gain a better understanding of extraction kinetics.
- **Nano-ion applications:** Exploring the application potential of nanometric ions (nano-ions) with a low charge density and a superchaotropic property that was demonstrated and studied by the group since 2015. Their strong propensity to adsorb to neutral interfaces makes them promising new tools for increasing selectivity in separative chemistry.
- **Foam Separation/Lixiviation:** Developing innovative processes for separating and upgrading metals, in particular by combining our knowledge

of foam formulation, ionic flotation and superchaotropic flotation, enabling selective separation in aqueous media and minimising environmental impact (for example for the decontamination and upgrading of mining soils).

- **Hybrid materials structured by self-association:** Developing stimulo-reactive organic-inorganic (nano-ion) hybrid materials, taking advantage of the interfacing properties (chaotropic) of nano-ions in aqueous solution to give the materials adaptive structures and functionalities. The nano-ions we are studying are very good charge exchangers.
- **Chaotropic mechanism:** Studying the mechanistic foundations of the superchaotropic effect, by combining experimental approaches, diversifying study systems (type of nano-ions and organic substrate) and modelling to better understand, use and develop the potential of this unique effect.
- **Organic/inorganic solubilisation:** Exploring new ways of solubilising organic compounds by (inorganic) nano-ions in water, opening up prospects for formulating complex (and reactive) systems without organic solvents (green chemistry), or finding alternatives to the usual methods of extracting hydrophobic compounds or (membrane-) proteins.

In line with the research and development policy of its tutelles, the L2IA is actively contributing to the emergence of new, more environmentally-friendly separation concepts, based on advances in its fundamental research.



3/ LABORATOIRE DU TRI IONIQUE PAR LES SYSTEMES MOLECULAIRES AUTO-ASSEMBLES (LTSM)

Sur la période 2020 - 2024 l'équipe était composée de 6 permanents :
1 DR CNRS responsable d'équipe (Stéphane Pellet-Rostaing, depuis 2009),
1 Chercheur CEA/DRF (Thomas Zemb, 2019 – 2024)
1 MDC UM - HDR (Guilhem Arrachart, depuis 2009)
1 Ingénieur CEA/DRF - HDR (Sandrine Dourdain, depuis 2010)
1 Technicienne CEA/DES (Béatrice Baus-Lagarde, depuis 2016)
1 Ingénieur de recherche CNRS (Fabrice Giusti, depuis 2018)

Et sur la période 2021-2024 de non-permanents :

Post-doctorants :
Carlos Arrambide Cruz (CNRS, ANR DECAP 2020-21) : Formulations polymériques pour la décorporation d'uranium.
Evan Lelong (CNRS, ANR RECALL, 2022-24) : Matériaux chélatants pour un procédé solide/liquide d'extraction d'ion dissouts en milieu acide faible.
Lin Jun (CNRS, Reversement CEA 2023-2024) : Effets de diluants et de modificateurs de phase sur l'extraction d'uranium en milieu sulfurique.
Alysson Duarte-Rodriguez (CEA DES, PIA AUDACE, 2024-2026) : Liquides poreux hydrophobes pour l'extraction liquide/liquide.

CDDs :
Tamir Sukhbataar (IR CNRS, CEFIPRA, 2019-2020) : « Transformisme moléculaire » et procédés de recyclage de terres rares contenus dans les aimants permanents.
Frantz Ndebulia Watchou (IE SATT, 2021) : Résines formo-phénoliques biosourcées pour l'extraction d'uranium de l'eau de mer.
Hassan Srour (IE UM, SOLVAY, 2021) : Résines formophénoliques pour l'extraction de lithium de saumures.
Hassan Srour (IE UM, SOLAMAT-MEREX, 2021-22) : Valorisation d'un déchet de l'industrie des lubrifiants.
Evan Lelong (IR, CEA, 2021-22) : Résines formophénoliques pour l'extraction d'uranium de saumures.
Clement Fleury (IE, PEPR Recyclage, 2024-2026) : Formulations à base d'hydrotropes pour le recyclage de terres rares contenus dans des DEEE.
Maud Gautier (IR CEA/DES, 2024-2026) : Effets de diluants et de modificateurs de phase sur l'extraction d'uranium en milieu sulfurique et phosphorique.
Nils Lebrun (AI CNRS, ANR RECALL, 2024-2025) : Matériaux chélatant pour un procédé solide/liquide d'extraction d'ion dissouts en milieu acide faible.

Doctorants :
Justine BenGhozi-Bouvrande (CEA/DES 2018-21) : Les liquides poreux : un nouveau concept pour l'extraction liquide-liquide.
Ruth Oye-Auke (Contrat Doctoral UM, 2018-21) : Méthodologies de synthèse et étude de résines biosourcées thermodurcissables pour la récupération de métaux d'intérêt.
Chen Xing (China Scholarship Council (CSC), 2018-22) : Concentration and selective recovery of uranium using nanofiltration processes.
Sahar Belfqueh (Région-BRGM, 2018-21) : Recyclage et valorisation des terres rares contenues dans des solutions faiblement acides.
Asmae El Maangar (CEA/DES, 2018-21) : L'extraction raisonnée de métaux stratégiques par des hydrotropes.
Simon Stemplinger (CEA/DES, 2019-22) : Théorie de la centrifugation douce dans des fluides structurés formulés à base d'hydrotropes.
Elise Guerinoni (CEA/DES, 2020-23) : Etudes des mécanismes d'extraction de l'uranium en milieu sulfurique par des amines tertiaires à chaînes alkyle ramifiées.
David Le Mire (CEA/DES, 2020-23) : Effect of chirality on the extraction mechanisms of extractatant molecules such as enantiopure monoamides for U/Pu extraction.
Claudine El Khoueiry (SAFAR, CNRSL/Ambassade France, 2020-23) : Synthèse et évaluation de thiourée polymérisée pour le traitement et l'extraction de métaux par procédé solide/liquide.
Julien Couturier (co-direction thèse avec CEREGE - CNRS, 2021-24) : Extraction responsable et sélective de métaux

critiques à partir de sources secondaires.
Lorianne Ginot (CEA focus ECC, 2021-24) : Développement de liquides poreux pour l'extraction des métaux d'intérêt à partir de déchets d'aimants permanents.
Baptiste Bernicot (Contrat Doctoral UM, 2022-25) : DES et NaDES hydrophobes pour l'extraction liquide/liquide.
Marine Thimotée (CEA/DES, 2022-25) : Amino- et amido-phosphonates chiraux pour l'extraction d'actinides.
Eléa Fauvel (CEA/DES, 2024-27) : Développement de ligands lipophiles de type acide aminopolycarboxylique ou acide hydroxamidue pour la séparation des ions.
Aboubacar Bakayogo (CEA/DES, 2024-27) : Solvants eutectiques pour la lixiviation et la séparation d'uranium.

Apprentis :

Raphaelle Piton (2020-22) : EDTA, DTPA et CDTA lipophiles pour l'extraction de terres rares.
Marie Moneuse. (2022-23) : Synthèse et caractérisation d'extractant chiraux.
Bastien Drouot (2023-2025) : Amino- et amido-phosphonates chiraux pour l'extraction d'actinides

L'équipe LTSM au 01/10/2024

Sur la période 2020-2024, l'équipe « Tri Ionique par des Systèmes Moléculaires Auto-assemblés » (LTSM) est constituée de 6 permanents, Guilhem Arrachart, Maître de Conférence UM (09/2009), Sandrine Dourdain, Ingénieur CEA/DRF (07/2010), Béatrice Baus-Lagarde, Technicienne CEA/DES (04/2016), et Fabrice Giusti, Ingénieur de recherche CNRS (07/2018), Thomas Zemb, Ingénieur CEA/DRF et Professeur INSTN (01/2019 – 10/2024) et Stéphane Pellet-Rostaing, Directeur de Recherche CNRS (01/2009). Les orientations de recherche développées au LTSM sont principalement intégrées à l'axe « Innovation pour l'extraction et le recyclage », en connexion étroite avec l'axe « Méthodologies et théories en chimie séparative ». L'équipe valorise la complémentarité de ses compétences en chimie de synthèse, chimie analytique et en nanosciences pour une optimisation raisonnée et maîtrisée des procédés de séparation et de recyclage. Les systèmes moléculaires synthétisés sont mis en œuvre aussi bien dans des procédés classiques (liquide/liquide, solide/liquide) ou moins conventionnels (membranes, solvants non usuels) avec une orientation vers la compréhension des mécanismes qui gouvernent la séparation. Les publications traitant de l'extraction liquide-liquide se placent dans le cadre de la chimie de coordination, de la chimie supramoléculaire ou de la physico-chimie des systèmes auto-assemblés. Le LTSM développe et applique l'approche « iénaïque » qui permet d'estimer les énergies libres de transfert en prenant en compte les interactions faibles au-delà du premier voisin. Ce modèle prédictif permet de rationaliser l'apport de la conception et de la synthèse d'extractants spécifiques originaux (pinces moléculaires, ligands chiraux, macrocycles, liquides ioniques à tâche spécifique, résines) ainsi que l'étude des mécanismes gouvernant l'affinité et la sélectivité. La possibilité d'exalter la complexation par l'auto-association de complexants sous forme de micelles, clusters de pré-nucléation ou agrégats pré-Ouzo est explorée dans le but de concevoir des procédés de tri ionique en rupture. Au-delà du domaine purement nucléaire, ces effets sélectifs sont aussi mis en œuvre dans différents procédés liés au recyclage de matières associées à la production d'énergie et plus généralement, dans les ambitions de développement durable et de transition énergétique, par exemple en décontamination ou pour le recyclage sélectif des métaux stratégiques.

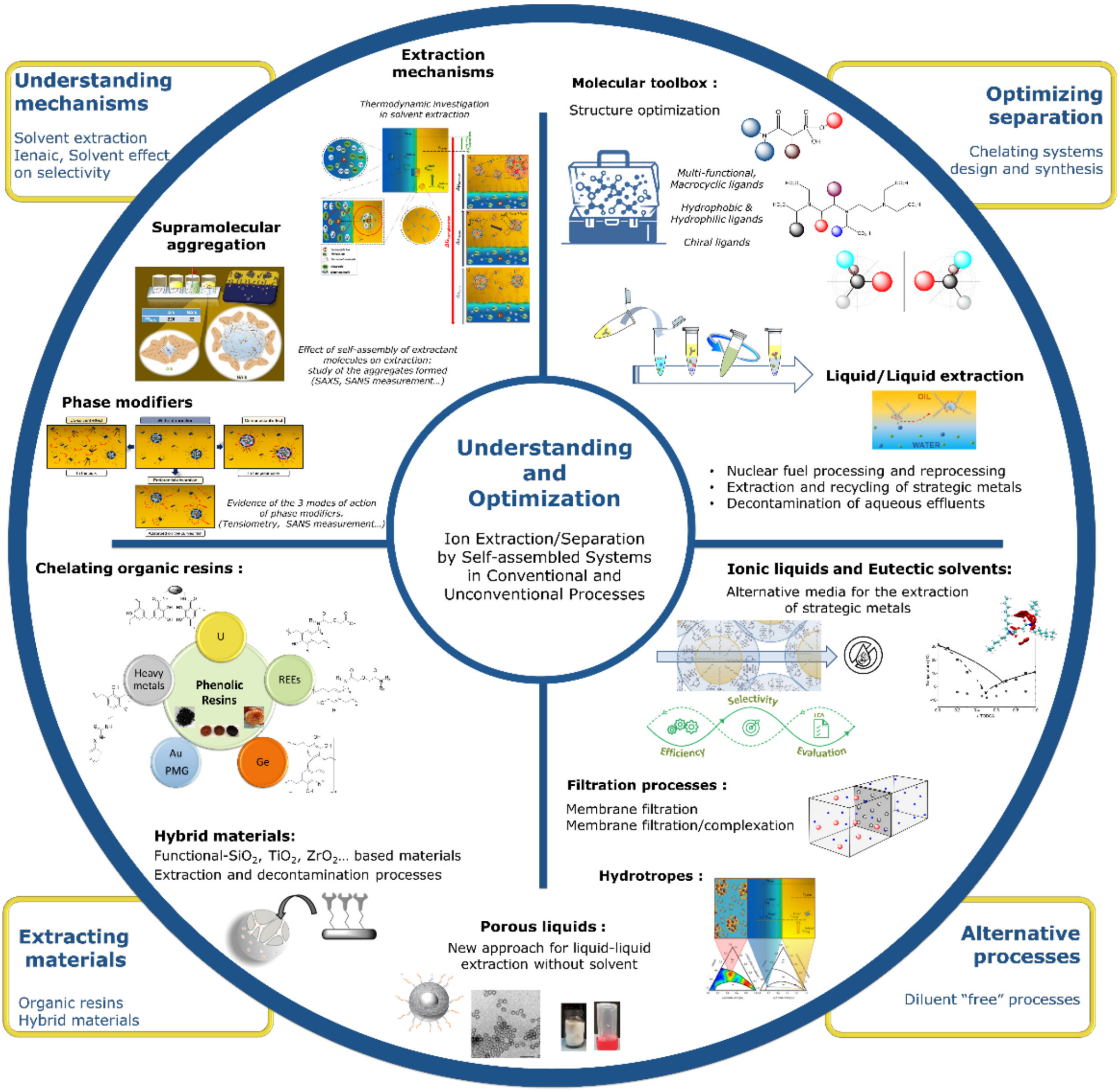
Du point de vue des disciplines abordées, le LTSM se situe clairement dans l'approche nanosciences et s'en approprie les évolutions combinant conception et synthèse de systèmes moléculaires organisés originaux, thermodynamique de la matière molle, nanomatériaux et compréhension des forces en jeu à l'échelle nanométrique. L'équipe développe en l'occurrence une recherche à caractère fondamental en adéquation avec les orientations initiales de l'Alliance ANCRE, les évolutions de la SNR (Stratégie Nationale de la Recherche) en matière de transitions énergétique prévues à travers la SNRE (Stratégie Nationale de la Recherche Energétique) dans le cadre du PIA (Plan d'Investissement d'Avenir) et plus récemment la création de l'Agence de Programmes des Energies Décarbonées (APED) dans les domaines de l'énergie nucléaire, des énergies renouvelables et de l'économie circulaire. Cela couvre aussi bien l'ensemble du cycle du combustible nucléaire (amont et aval du cycle) actuel et futur que celui des métaux d'intérêt (métaux stratégiques et chimio-toxiques), allant de l'extraction des métaux des minerais (uranium, lanthanides, etc.) au retraitement du combustible nucléaire usé (élimination des éléments radiotoxiques) ou au recyclage des déchets de la mine urbaine (DEEE).

L'équipe bénéficie de financements CEA à travers les programmes de recherche de la DES (Cycle du Nucléaire et Recherche Amont) à l'origine du financement de thèses et de projets postdoctoraux/CDD. A l'échelle locale, l'équipe a été soutenue par le financement d'un projet du LabUM chimie et de Contrats Doctoraux UM. Des programmes de maturation (SILEXE, RESULTA et SELECTMAT) ont été financés par la SATT AxLR et un projet de thèse Région Occitanie (RETREAT) a été assuré en partenariat avec le BRGM. Au niveau national, le LTSM s'est engagé dans quatre projets ANR comme partenaires (BMOP4App, RECALL, CARAPASS, DECAP), a reçu l'appuis du CNRS pour le financement d'un projet concernant l'extraction de l'uranium de l'eau de mer (projet ECUM) et participe actuellement à l'axe « métaux stratégiques » du projet PEPR d'accélération « recyclage, recyclabilité et ré-utilisation des matières » ainsi qu'au projet InnovTech du PEPR « SousSol bien commun » par le biais de financements de CDD. Le LTSM est également acteur du programme interdisciplinaire du CNRS NEEDS, ainsi que du financement de projets par des industriels du traitement de déchets (SOLVAY, SOLAMAT-MEREX). Plus récemment (fin 2024), deux projets ont été construits et ont abouti avec les sociétés Novacarb, portant sur l'optimisation du procédé de production de bicarbonate de soude, et BIORET Agri dédié au chaulage d'urines de bovins en vue de récupérer les matières valorisables. Le laboratoire est aussi partenaire de projets financés par le CNRS (PRIME, porté par le CEREGE) et le MAE avec la société MORPHOSIS (porté par CP2M Lyon). En marge de ses activités de recherche, le LTSM réalise des contrats de prestation (synthèse à façon, analyses ICP, RMN…) pour le CEA/DES, d'autres acteurs académiques (Université de Nîmes, CPE Lyon, PROMES) et industriels (Cis-Bio, Extracthive). Enfin, le LTSM répond régulièrement aux appels à projet (« proposal ») des lignes de lumière sur les Synchrotrons SOLEIL, ESRF, ILL… qui lui donne l'opportunité de sonder la matière molle.

Au niveau international, l'équipe a participé à un projet Franco-Indien CEFIPRA, a bénéficié d'un cofinancement par le programme SAFAR d'une thèse en co-direction avec l'Université Libanaise, et reçu l'appuis du China Scholarship Council (CSC) pour le financement d'un projet de doctorat.

Au cours de la période 2020-2024, le LTSM a pérennisé et développé un large tissu de collaborations. Les coopérations « historiques » concernant les activités « cycle du combustible nucléaire » avec les départements de recherche du CEA/DES de Marcoule (DMRC en particulier) et ORANO se sont renforcées notamment par l'accueil dans les laboratoires d'Atalante de doctorants manipulant les actinides dont le Plutonium, et plus largement au niveau national par des collaborations établies avec le CEA de Grenoble et de Saclay. Sur ce plan, il est intéressant de citer les équipes de GéoRessources Nancy (A. Chagne) pour le projet PEPR InnovTech, de CP2M Lyon (S. Daniele) avec WEECYCLING sur la conception de tissus fonctionnels pour l'extraction de métaux précieux ou du CEREGE (C. Levard) dans le cadre de projets portant sur l'extraction de terres rares contenues dans les boues rouges. Le rapprochement avec les équipes du BRGM s'est également accéléré via les projets de thèse co-financés ou à travers le PEPR

RRR (N. Menad, Y. Menard). Par ailleurs, les travaux communs de plus en plus nombreux avec les équipes opérant des lignes de lumière sur les Synchrotrons Soleil et ESRF ont été mis en place ainsi qu'à l'international dans le cadre de collaborations avec le JAEA (R. Motokawa). Sur ce point, des collaborations se poursuivent avec plusieurs institutions étrangères parmi lesquelles le CSIR-NML (A. Kumari), l'Université Libanaise (I. Karamé), l'Université de Regensburg (W. Kunz, D. Horinek), ou encore l'Université d'Aveiro (J. Coutinho, N. Schaeffer).



Thématiques scientifiques abordées par le LTSM

3/ IONS SEPARATION USING SELF-ASSEMBLED MOLECULAR SYSTEMS

Between 2020 and 2024, the "Ionic Sorting by Self-Assembled Molecular Systems" (LTSM) team consisted of six permanent members, Guilhem Arrachart, lecture UM (since 09/2009); Sandrine Dourdain, Engineer CEA/DRF (since 07/2010); Béatrice Baus-Lagarde, Technician CEA/DES (since 04/2016); Fabrice Giusti, CNRS Research Engineer (since 07/2018); Thomas Zemb, Engineer at CEA/DRF and Professor at INSTN (01/2019–10/2024); and Stéphane Pellet-Rostaing, CNRS Research Director (since 01/2009). The team's research activities are mainly aligned with the theme "Innovation for Extraction and Recycling" and are closely connected to the "Methodologies and Theories in Separation Chemistry" axis. LTSM leverages complementary expertises in synthetic chemistry, analytical chemistry, and nanosciences to optimize separation and recycling processes in a rational and controlled manner. The molecular systems developed are used in both conventional processes (liquid/liquid, solid/liquid) and more innovative ones (membranes, unconventional solvents), with a strong emphasis on understanding the underlying separation mechanisms. Publications on liquid-liquid extraction are exclusively focused on coordination chemistry, supramolecular chemistry, and the physical chemistry of self-assembled systems. The team develops and applies the "ienaic approach," a predictive model that estimates free transfer energies by accounting for weak interactions beyond the first coordination shell, thereby guiding the design and synthesis of novel extractants (molecular tweezers, chiral ligands, macrocycles, task-specific ionic liquids, resins) and studying the mechanisms driving affinity and selectivity. The enhancement of complexation via self-association of extractants into micelles, pre-nucleation clusters, or pre-Ouzo aggregates is explored to design disruptive ionic sorting processes. Beyond nuclear applications, such selective effects are also employed in processes related to recycling energy-related materials and, more broadly, in sustainable development and energy transition objectives, including decontamination and selective recycling of strategic metals. From a disciplinary perspective, LTSM is fully embedded in the nanoscience approach, combining the design and synthesis of original organized molecular systems with soft matter thermodynamics, nanomaterials, and the study of nanoscale interactions. The team's fundamental research aligns with the initial vision of the ANCRE Alliance, the evolution of France's National Research Strategy (SNR), its energy transition counterpart (SNRE), and the national "Investments for the Future Program" (PIA), more recently extended by the creation of the Agency for Decarbonized Energy Programs (APED), addressing nuclear energy, renewable energy, and the circular economy. The scope of their work covers the entire nuclear fuel cycle (upstream and downstream), as well as the extraction and recycling of strategic and chemotoxic metals, from mineral ores (e.g., uranium, lanthanides) to the reprocessing of spent nuclear fuel and the recycling of urban mine waste (WEEE). LTSM receives funding from CEA through DES research programs (Nuclear Fuel Cycle and Upstream Research), which support PhD theses and postdoctoral/fixed-term projects; at the local level, support also came from LabUM Chimie, doctoral contracts from UM, and maturation programs (SILEXE, RESULTA, SELECTMAT) funded by SATT AxLR, as well as a PhD project with the Occitanie Region (RETREAT) in partnership with BRGM. Nationally, the team is involved in four ANR projects (BMOP4App, RECALL, CARAPASS, DECAP), received CNRS support for a project on uranium extraction from seawater (ECUM), and contributes to the "strategic metals" axis of the PEPR program "Recycling, Recyclability, and Reuse of Materials" and the PEPR "Subsoil as Common Good" (InnovTech) through fixed-term contract funding. The team is also involved in the CNRS interdisciplinary NEEDS program and has received project funding from waste treatment companies such as SOLVAY and SOLAMAT-MEREX. More recently, in late 2024, two collaborative projects were completed, one with Novacarb on optimizing sodium bicarbonate production, and another with BIORET Agri on the liming of cattle urine to recover valuable materials. The team is also a partner in projects funded by the CNRS (PRIME, led by CEREGE) and the Ministry of Foreign Affairs (MAE), in partnership with the company WEECYCLING (led by CP2M Lyon). In parallel to its research activities, LTSM provides services (custom synthesis, ICP, NMR analyses) for CEA/DES, academic institutions (University of Nîmes, CPE Lyon, PROMES), and industry (Cis-Bio, Extracthive). The team regularly responds to beamline proposals at synchrotrons (SOLEIL, ESRF, ILL), enabling them to explore soft matter at high resolution. Internationally, LTSM participated in a Franco-Indian CEFIPRA project, benefitted from SAFAR program co-funding for a co-supervised PhD with the Lebanese University, and received support from the China Scholarship Council (CSC) for PhD funding. During the 2020–2024 period, LTSM consolidated and expanded a wide network of collaborations, notably with historical partners on nuclear fuel cycle topics, such as CEA/DES Marcoule (especially DMRC) and ORANO, through the hosting of PhD students working on actinides (including plutonium) at the Atalante facilities, and nationally with CEA Grenoble and CEA Saclay. Other notable collaborations include GéoRessources Nancy (A. Chagne) on the PEPR InnovTech project, CP2M Lyon (S. Daniele) and WEECYCLING on functional fabrics for precious metal extraction, and CEREGE (C. Levard) on rare earth extraction from red mud. Collaboration with BRGM has intensified through joint PhD projects and the PEPR RRR (N. Menad, Y. Menard). Increasingly, LTSM is working with synchrotron beamline teams at SOLEIL and ESRF, and internationally with JAEA (R. Motokawa), as well as CSIR-NML (A. Kumari), the Lebanese University (I. Karamé), the University of Regensburg (W. Kunz, D. Horinek), and the University of Aveiro (J. Coutinho, N. Schaeffer).

4/ LABORATOIRE DE SONOCHIMIE EN FLUIDES COMPLEXES (LSFC)

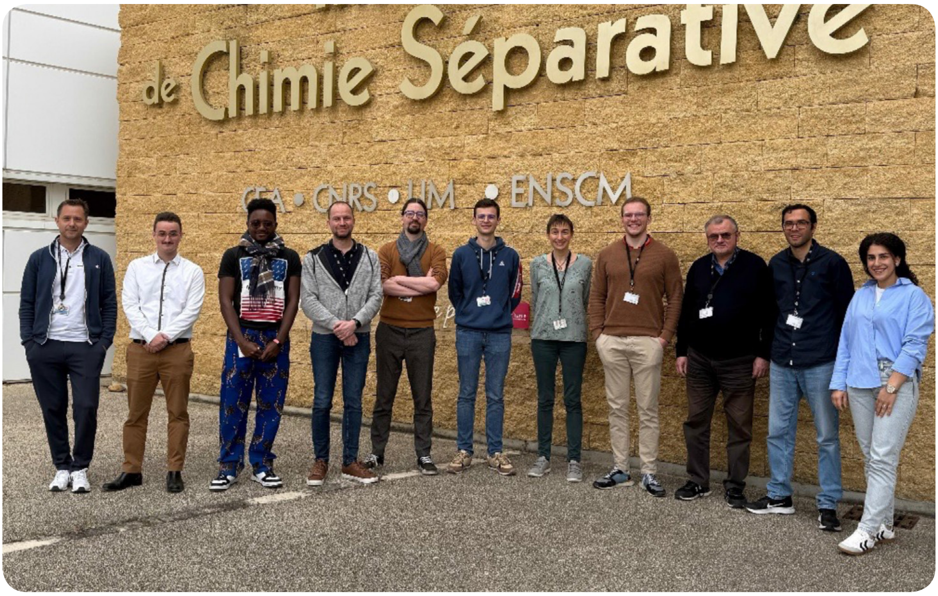
Au 1er décembre 2025 l'équipe est composée de 4 permanents:
1 chargé de recherche CR-CNRS responsable de l'équipe depuis le 01/01/2025 (Dr. Tony Chave)
1 directeur de recherche CNRS responsable d'équipe jusqu'au 31/12/2024 (Dr. Sergueï Nikitenko)
1 ingénieur-chercheur DR CEA/DES (Dr. Rachel Pflieger)
1 ingénieur-chercheur DR CEA/DES (Dr. Matthieu Virot)

Et sur la période 2021-2024 de non-permanents :

Post-doctorants :
Hamed Kalawoun (2024-2026) PEPR Spleen / Ecochem
Simon Bayle 2023-2024 PTC PingPUnc
Baptiste Russo 2023-2024 (CEA DE2D/LMPA)

Doctorants :
Sara El Hakim (thèse UM 2018-2022) : Réactions sonocatalytiques et photocatalytiques en présence de nanocatalyseurs innovants pour l'énergie et l'environnement.
Manon Cot-Auriol (thèse CEA codir CEA/DES/DMRC, 2019-2023) : Etude de la réactivité de colloïdes d'actinides et de leurs mécanismes de formation.
Sophie Herr (thèse CEA/DES collaboration DMRC, 2019-23) : Apport de la cavitation acoustique dans le traitement des sols contaminés au Cs ou pollués aux métaux lourds.
Julien Margate (thèse CEA/DES 2021-2024) : Préparation, caractérisation structurale et réactivité de peroxydes d'actinides.
Rita Salameh (thèse Région Occitanie - CEA/DES, collaboration DMRC, 2022-2025) : Dépollution de terres modèles par lixiviation assistée par sonification.
David-William's Nzodom Djozing (thèse UM 2022-25) : Synthèse sonohydrothermale de nanomatériaux.
Valentin Parent (thèse CNRS PEPR ECOCHEM 2025-2028) : Etude de l'oxydation sonocatalytique de composés organiques

Apprentis :
Alix Clerget (Alternance BUT3Collaboration ICSM/UTINAM Besançon 2024-2025) : Utilisation des ultrasons dans la synthèse et l'incorporation de graphène dans des dépôts électrolytiques d'argent



L'objectif principal du laboratoire de sonochimie dans les fluides complexes (LSFC) consiste à mener des études fondamentales sur les mécanismes des réactions sonochimiques (réactions chimiques induites par la propagation d'ondes ultrasonores entre 16 kHz et 1 MHz dans un milieu fluide) en solutions homogènes et dans des systèmes hétérogènes solide-liquide. Les effets observés en sonochimie ne résultent pas d'une interaction directe entre les ondes ultrasonores et les ions ou molécules mais sont étroitement liés au phénomène de cavitation acoustique : la nucléation, croissance et implosion rapide de micro-bulles de gaz ou de vapeur de solvant dans les liquides soumis à un champ ultrasonore. Le temps d'implosion est de l'ordre de la microseconde et le phénomène résultant induit des conditions locales de température et de pression extrêmes, estimées à plusieurs milliers de degrés et plusieurs centaines d'atmosphères, couplées à des vitesses de refroidissement de l'ordre de 10^{10} $K.s^{-1}$. De récentes études démontrent la formation d'un plasma hors-équilibre dans les bulles au moment de l'implosion. Cette concentration locale d'énergie constitue l'origine des phénomènes d'émission de lumière par les bulles de cavitation – la sonoluminescence, mais également de l'activité chimique en solution et de l'évolution des systèmes en phase hétérogène. En résumé, chaque bulle de cavitation peut être considérée comme un microréacteur chimique à plasma qui ne nécessite pas d'ajout de réactifs spécifiques et ne génère pas de déchets supplémentaires, respectant ainsi les principes de la chimie «verte».

Les thématiques du LSFC:
- Etude fondamentale de la sonochimie et des mécanismes sonochimiques
- Synthèse de matériaux par voie sonochimique et sonocatalyse pour l'environnement et l'énergie
- Chimie et sonochimie des actinides
- Dépollution et décontamination des systèmes hétérogènes solide-liquide

4/ SONOCHEMISTRY IN COMPLEX FLUIDS

The main objective of the laboratory of sonochemistry in complex fluids (LSFC) is to carry out a fundamental research on the sonochemical reactions (chemical reactions induced by power ultrasound at 16 kHz – 1 MHz frequency range) in homogeneous solutions and heterogeneous solid-liquid systems. The effects observed in sonochemistry are not based on direct interaction between the ultrasonic waves and ions or molecules but rather on the phenomenon of acoustic cavitation: the nucleation, growth, and quick implosion of microbubbles of gas or vapor produced in liquids subjected to an ultrasonic field. Transient implosion of cavitation bubbles induces extreme local conditions of temperature and pressure, estimated at thousands of degrees and several hundred atmospheres, coupled with extremely high cooling rate of the order of 10^{10} $K{\cdot}s^{-1}$. Our recent studies revealed the formation of a non-equilibrium plasma inside imploding bubbles. This local concentration of energy is the origin of the light emission known as sonoluminescence, but also the origin of chemical activity in solutions as well as of the evolution of heterogeneous systems. In summary, each cavitation bubble can be considered as a plasma-chemical microreactor that does not require the addition of specific reagents and generates no additional waste, thus respecting the principles of green chemistry.

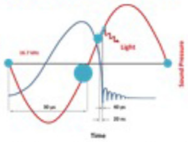
The specific topics of LSFC:
- Fundamental study of sonochemistry and sonochemical mechanisms Sonochemical synthesis of nanomaterials and sonocatalysis for the environment and energy
- Chemistry and sonochemistry of actinides
- Depollution and decontamination of heterogeneous solid-liquid systems

Projets (collaborations)
- 2019-23 LINA Projet Région Occitanie
- 2022 Projet PTC PING-PuNC
- 2024 Projet NEEDS Janus
- 2024 Projet NEEDS SeaWater
- 2024 Projet Bottom-up SODA
- Sonoluminescence dans les fluides complexes (LCME, Chambéry ; UTINAM, Besançon ; Institut Jean Lamour, Nancy ; Université de Melbourne, Australie)
- Dissolution sonochimique des oxydes d'actinides (CEA/DES)C
- Collaboration pérenne avec DMRC (BAG sonochimie au L18, installation ATALANTE)
- Colloïdes de plutonium(IV) (CEA/DES ; JRC Karlsruhe Allemagne)
- Synthèse sonochimique de nanoparticules pour les applications biomédicales (TORSKAL brevet en 2022)
- Projet RESEM VOBUSURF (IRT-M2P) (partenaire, projet porté par Utinam Besançon)
- 2022 – 2027, PEPR ECOCHEM (partenaire principal)
- Dégradation sonochimique de PFAS (depuis 2022) VALGO, France
- Thèse de N. Zahir codirigée « Innovative catalytic materials for green hydrogen production (2022-2026) » Hydrogen Research Institute, Université du Québec à Trois-Rivieres, Canada
- Thèse de M. Munoz coencadrée « Synthèse et caractérisations de cluster de plutonium » (DMRC/LILA 2023-2026)

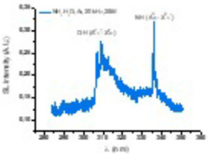
Sonoluminescence

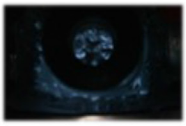
Nanoparticles and Sonocatalysis

Origin of Sonochemistry: *Acoustic Cavitation*



Sonoluminescence (SL) is the **emission** of **light** from the **UV** to the **near IR** during the **collapse** of acoustic **bubbles**

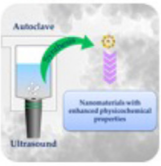




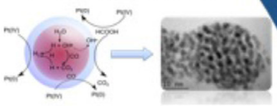
A **non-equilibrium plasma** is formed, whose characteristics can be **studied by emission spectroscopy** of **excited species**

AOP processes and Catalysis

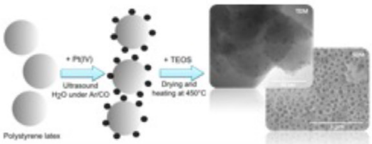
Sono-hydrothermal synthesis **of nanomaterials**



Sonochemical synthesis of **NPs** in **dilute aqueous solutions**



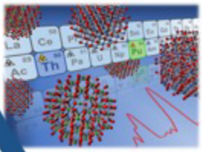
Porous silica matrix decorated with **Pt NPs**



Redox Control and Reactivity Colloids and Related Behavior Refractory AnO_2 Dissolution

(An= Th, U, Pu)

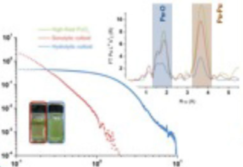
Probing the Local Structure of AnO_2 Nanoparticles



Glove box in **Atalante** facility
(DRCP collaboration)

High and low frequency ultrasound
On-line UV-Vis-NIR spectroscopy measurements

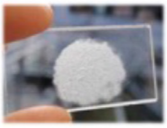
Preparation & Characterization of Stable Salt-free Pu Intrinsic Colloids
Synchrotron SAXS and EXAFS study



Actinide Sonochemistry

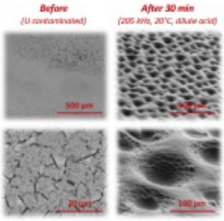
Acoustic Cavitation for the Decontamination of Solids

Erosion and **Fragmentation**
Diminution of the **diffusion layer**
Acceleration of the **mass transfer**



Silica glass sonicated in pure H_2O
180 min, Ar, 20 kHz, 49 W.cm⁻²

Decontamination of metallic **surfaces** in **soft conditions**



Extended Surface-Bubble Interaction

5/ NANOMATÉRIAUX ADAPTATIFS POUR L'ENERGIE

Au 1er décembre 2024 l'équipe est composée de 4 permanents:
1 Directeur de Recherche CEA/DES responsable d'équipe (Dr. Xavier Deschanels)
1 Ingénieur-chercheur CEA/DES (Dr. Vanessa Proust)
1 Enseignant-chercheur ENSCM (Dr. Guillaume Toquer)
1 Ingénieur d'étude UM (Cyrielle Rey)

Et sur la période 2021-2024 de non-permanents :

Post-doctorants :

Singaravelu Chandra Mohan (PTC Nanoreval, 2020-21, puis dispositif MAGELLAN 2022-2023) : EXCIDOTS

Hassan Khoder (Fondation maison de la chimie, 2020-22) : Etude de la dynamique de l'eau au sein de solutions aqueuses confinées dans des matériaux modèles à base de silice.

Baptiste Russo (CNRS, 2020-22) : Projet Valorisation ABRICeaux.

Clémentine Mansas (ANR AUTOMACT, 2021-22) : Functionalized mesoporous silicas - Application to waste conditioning.

Jun Lin (ANR AUTOMACT, 2022-2023) : Pu-doped mesoporous silica for the treatment of contaminated liquid effluents.

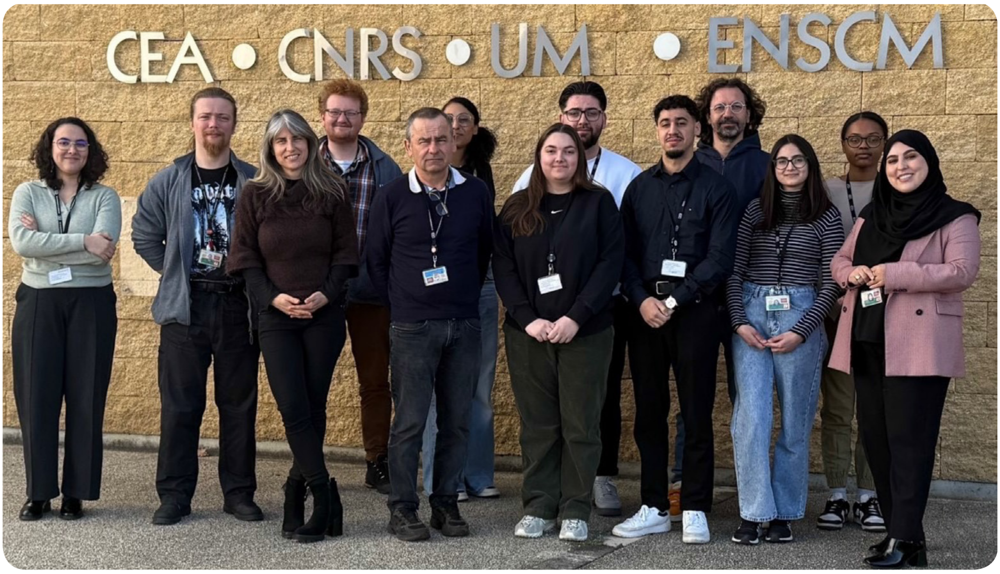
Doctorants :

Martin Zijie Lu (CSC Chine, 2017-21) : Study of colloidal sol-gel transition for the elaboration of actinides oxides materials with controlled and organized mesoporosity.

Toni Tratnjek (CEA/DES, 2019-22) : Vers de nouveaux matériaux à porosité hiérarchisée pour la capture de produits de fission (Sr, Cs).

Florian Didier (UM, 2019-22) : Dépôt électrophorétique de nanotubes de carbone pour la conception de matériaux solaires sélectifs.

Jun Lin (CEA/DRF, 2018-21) : Comportement des silices mésoporeuses sous irradiation par des ions de haute énergie.



Anna Hautecouverture (CEA/DES, 2020-23) : Synthèse de solution solide d'oxydes d'actinides par combustion en solution.
Ryan Roch (CEA focus DEM, 2021-24) : Développement de capteurs intégrant des carbon-dots pour la détection de rayonnement ionisant.
Pierre De Laharpe (CEA/DES, 2022-25) : Auto-réparation des gels d'altération des verres nucléaires sous irradiation.
Oumaima Zriouil (thèse CEA/DES 2024-2027) : Matériaux de Sitinakite pour le traitement continu des effluents contaminés au Sr.
Aya Azeddioui (thèse ENSCM 2023-2026) : Évolution de la nanoporosité de couches minces sous irradiations ionique et électronique.
Hiba Al Amouri (thèse UM 2022-2025) : Electrophoretic Deposition (EPD) of Anisotropic Nanoparticles: Coupling Between Orientation and Properties.
Jordan Soule (Thèse CEA/DES 2024-27) : Solubilisation de l'U et Pu dans les verres nucléaires et impact sur leur comportement à long terme sous eau.

Apprentis :

Freddy Raffo (Licence PRO, CEA, 2022-23) : Matériaux sitinakite pour la capture du strontium

CDD :

Thomas Bedos-Colombeau (PTC Mosac, 2021) : Modélisation de la stabilité d'oxydes mixtes d'actinides sous-stœchiométriques
Sylvain Madinier (CEA/DES 2024-2025) : Synthèse de matériaux sitinakite

Le laboratoire LNAR développe plusieurs compétences scientifiques, techniques et d'enseignement pour répondre aux défis posés par la recherche sur les énergies décarbonées. Le fil conducteur de l'ensemble des thématiques de recherche du LNER est le développement de matériaux structurés à différentes échelles du point de vue de la compréhension des phénomènes mis en jeu lors des différentes étapes d'élaboration, complété par l'étude des propriétés d'intérêt de ces matériaux. Ainsi, le couple « maîtrise et compréhension de l'élaboration d'un matériau méso-structuré – propriétés physico-chimiques » définit l'ensemble des recherches développées au LNER, à la fois dans un objectif cognitif mais également dans un objectif applicatif, en lien avec les diverses collaborations industrielles (et/ou CEA) existantes ou à venir.

L'ensemble des études menées au sein de cette équipe concerne les composites présentant plusieurs structures, de nature (porosités, phase hybrides, oxydes, carbures, …), de taille (nano, méso et/ou micro), et de forme (ordonnée ou amorphe) contrôlées et présentant une ou plusieurs fonctionnalités (chimie séparative, propriétés optiques renforcées, incorporation d'éléments actinides…). Par ce type de structure hiérarchique, les propriétés physiques (fissuration, tenue à l'irradiation, propriétés optiques), mais aussi chimiques (extraction, altération) de ces matériaux présentent des performances hautement non linéaires par rapport à celles des matériaux massifs, rendant ainsi possible le modelage de ces propriétés en fonction des applications souhaitées. Dans tous les cas, la conception de ces matériaux met en œuvre les avancées de la chimie « douce » (sol-gel, colloïdale, émulsion, hydrothermale, …) afin d'obtenir des réactivités lentes et contrôlées permettant alors une caractérisation précise et parfois « in situ » des différentes étapes réactionnelles et donc une meilleure maîtrise du matériau final.

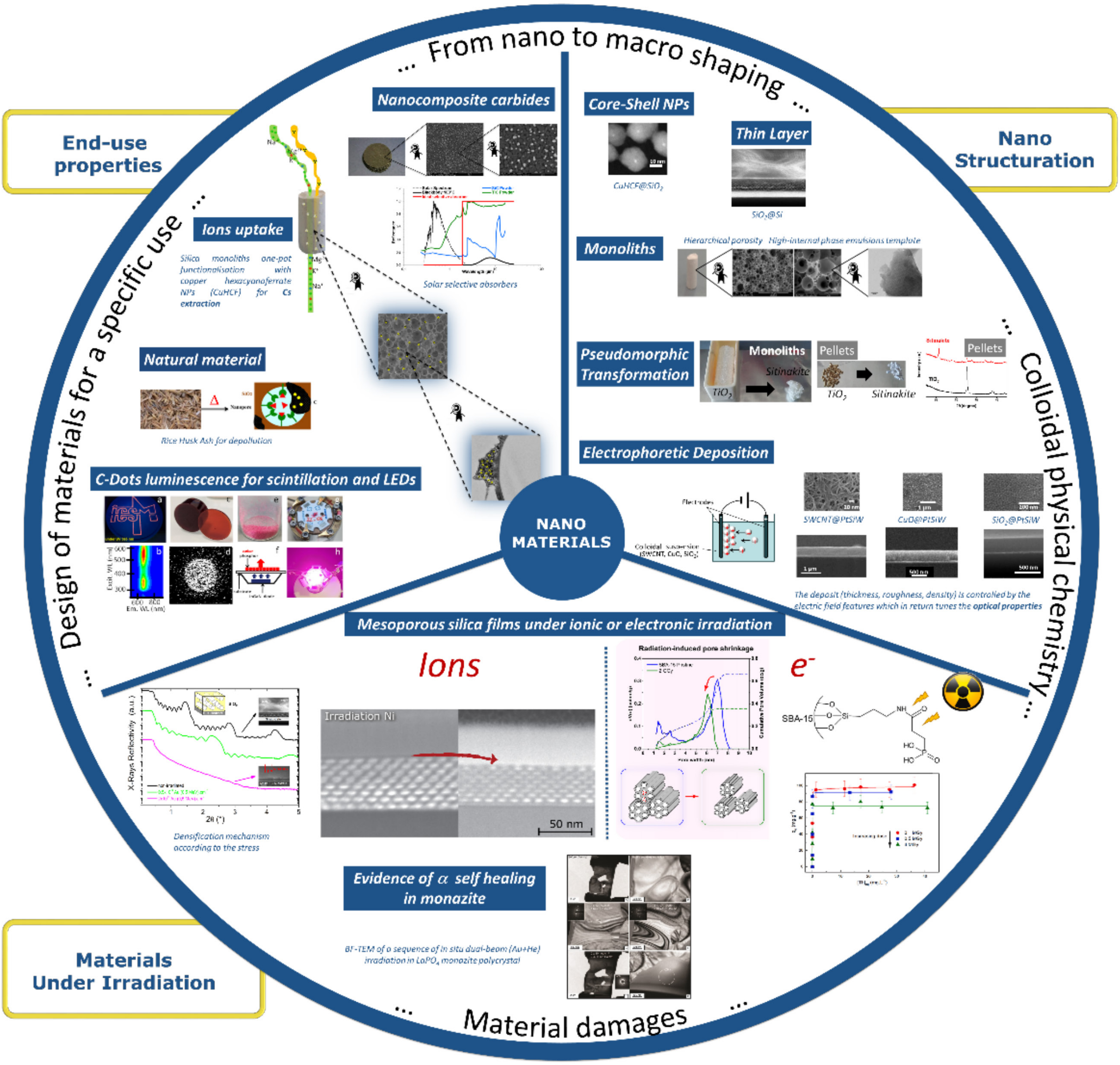
Les thématiques principales développées au LNAR dans la période 2021-2024 sont résumées dans les pages suivantes et peuvent s'inscrire dans les 3 grands thèmes suivants :
- Le développement de différentes voies d'élaboration de matériaux nano-structurés : du précurseur (colloïde, solution, émulsion…) au matériau (poudre, couche mince ou massif)
- Nano-structuration et optimisation d'une propriété d'usage (Décontamination/dépollution d'effluents, sélectivité optique, révélation de radioactivité alpha/béta …)
- Comportement des nanomatériaux sous irradiation.

5/ NANOMATERIALS FOR ENERGY AND RECYCLING PROCESSES

This team (LNAR) presents strong scientific, technical as well as teaching skills to meet challenges arising from research on nanomaterials for low-carbon energy. The common thread of all the LNAR research topics is the development of structured materials at different scales, with the aim of understanding the phenomena involved in the different stages of synthesis, supplemented by studying the properties of interest of these materials. Therefore, both parts, i.e. "control and understanding of mesostructured nanomaterials synthesis" as well as "physico-chemical properties" sets up the outline of all the research activities taking place in the LNAR. This is done for both cognitive goals as well as for applications goals through industrial collaborations (and/or CEA).

The whole research studies led in this laboratory concerns nanocomposites of various kind (porosity, hybrid phases, oxides, carbides…), various sizes (nano-, meso- and/or micro-), various structure (ordered or amorphous), all controlled, with different functions (separative chemistry, optical properties, actinide incorporation). These hierarchical structures allow enhancement not only of the physical properties (cracking, resistance to radiation, optical properties) but also chemical properties (extraction, leaching) of these nanomaterials with regard to bulk materials. In all cases, the synthetic routes use soft chemistry (sol-gel, colloidal precursor, emulsion templates or hydrothermal conditions) in order to work with more controlled slow reaction kinetics allowing fine characterisation, in-situ in some cases, of all different reaction steps. This generally led to a better control of the final shaping of the nanomaterials.

The LNAR research topics for the period 2021-2024 are summarised in the following pages and can be divided in 3 main themes:
- Nanostructured materials synthetic routes: From precursor (colloid, solution, emulsion…) to the final material (powder, thin film, bulk)
- Nanostructuring and optimization of an end user property (Decontamination / depollution of effluents, optical selectivity, alpha / beta radioactivity revelation, etc.)
- Radiation damage in nanomaterials.



End-use properties

Nano Structuration

Materials Under Irradiation

Nanocomposite carbides

Solar selective absorbers

Ions uptake

Silica monoliths one-pot functionalisation with copper hexacyanoferrate NPs (CuHCF) for Cs extraction

Natural material

Rice Husk Ash for depollution

C-Dots luminescence for scintillation and LEDs

Core-Shell NPs

$CuHCF@SiO_2$

Thin Layer

$SiO_2@Si$

Monoliths

Hierarchical porosity High-internal phase emulsions template

Pseudomorphic Transformation

Electrophoretic Deposition

SWCNT@PtSiW CuO@PtSiW SiO_2@PtSiW

The deposit (thickness, roughness, density) is controlled by the electric field features which in return tunes the **optical properties**

Mesoporous silica films under ionic or electronic irradiation

Densification mechanism according to the stress

Evidence of α self healing in monazite

BF-TEM of a sequence of in situ dual-beam (Au+He) irradiation in $LaPO_4$ monazite polycrystal

6/ INTERFACE DE MATÉRIAUX EN ÉVOLUTION (LIME)

Au 1er décembre 2024 l'équipe est composée de 4 permanents :
1 Directeur de Recherche CNRS responsable d'équipe (Dr. Nicolas Clavier)
1 Professeur des Universités, (Pr. Nicolas Dacheux)
1 Chercheur CEA (Dr. Stéphanie Szenknect)
1 Maître de Conférences (Dr. Laurent Claparède)

Et sur la période 2021-2024 de non-permanents :

Post-Doctorant :
Dr Paul-Henri Imbert (CNRS, projet EJP EURAD, 2020-2022) : Lixiviation d'échantillons frittés de UO2 contenant des produits de fission en conditions d'entreposage direct.

CDD :
Eddie Anzalone (IE CNRS, projet CEA, 2020-2021) : Synthèse de phases minérales uranifères.
Lara Di Mascio (IE CNRS, projet CEA, 2020-2021) : Conversion hydrothermale d'oxalates d'actinides.
Thomas Colombeau-Bedos (IE CNRS, 2022) : Développement de sondes à oxygène pour le sodium à base d'électrolyte hafnie dopée.

Doctorants affectés à l'ICSM :
Thomas Barral, (thèse CEA, 2020-2023) : Etude multiparamétrique de la dissolution d'oxydes mixtes (U,Ln)O2 en milieu nitrique : impact de la composition et de la microstructure.
Sofian Benarib, (thèse CEA, 2020-2023) : Apport des méthodes hydrothermales pour la préparation et le frittage direct d'oxydes hydratés d'uranium(IV) et de cérium.
Mohammad Husainy (thèse CEA, 2021-2024) : Spéciation du molybdène dans UO_2 : impact sur la cinétique de dissolution en conditions de retraitement.
Thibault Kaczmarek (thèse CEA, coll. DMRC, 2018-2021) : Impact des éléments platinoïdes et du molybdène dans les mécanismes de dissolution du dioxyde d'uranium.
Malvina Massonnet (thèse CEA, coll. DMRC, 2018-2021) : Impact de la méthode de préparation et des conditions de frittage sur les mécanismes de dissolution des oxydes mixtes $(U,Ce)O_2$.
Théo Montaigne (thèse CEA, coll. DE2D, 2019-2022) : Mécanismes d'altération des combustibles MOX en conditions de stockage géologique.
Alison Roche (thèse UM, 2020-2023) : Incorporation d'actinides tétravalents au sein de céramiques de structure monazitique : synthèse, frittage et comportement à long-terme.
Valentin Legrand (thèse UM, coll. L2IA 2022-2025) : Procédé vert pour la dépollution de sites miniers : Séparation superchaotropique de tungstène par des mousses.
Lorenzo Callejon (thèse CEA 2023-2026) Hétérogénéités structurales et microstructurales : quels impacts sur la cinétique de dissolution ?
Mathias Fulchiron (thèse CNRS 2023-2026) Etude des mécanismes et de la cinétique de dissolution de composés modèles simulant le MOx irradié : comportement spécifique du Rh.
Christin Kraemer (thèse CEA, coll. L2ME, 2023-2026) : Identification des espèces polynucléaires et colloïdales à base d'U(VI) : domaines d'existences, structure et stabilité en conditions environnementales.
Hélène Barbier (thèse CEA, coll. L2ME, 2023-2026) : Voie sol-gel multi-colloïdales pour la préparation de combustibles mixtes.
Dorian Laffont (thèse CEA 2024-2027) : précipitation directe d'oxydes mixtes par conversion hydrothermale réductrice.
Camille Navas (thèse CEA 2024-2027) : Etude de la cinétique et des mécanismes de lixiviation du corium.
Arthur Avallone (thèse CEA 2024-2027) : Etude de la formation de phases d'intérêt pour le corium : la tchernobylite $(U,Zr)SiO_4$ et l'oxyde mixte $(U,Zr)O_2$.

Doctorants non affectés à l'ICSM :
Pierre Asplanato (thèse CEA, coll. CEA-DAM, 2019-2022) : Etude des mécanismes de formation par procédé hydrothermal et d'altération dans différents milieux de particules de référence d'oxydes d'actinides.
Claire Canas (thèse CEA, coll. DTN, 2022-2025) : Mécanismes de corrosion de céramiques électrolytes par le sodium liquide.

Rafael Caprani (thèse CEA, coll. DMRC, HZDR, 2020-2023) : Etude du comportement des produits de fission et de leur impact sur la microstructure des combustibles $(U,Pu)O_{2-x}$.
Marie-Margaux Désagulier (thèse CEA, coll. DMRC, JRC Karlsruhe, 2020-2023) : Elaboration et mesure de propriétés thermodynamiques et structurales d'oxydes mixtes $(U,Pu)O_{2-x}$ à forte teneur en plutonium.
Célia Gillet (thèse CEA, coll. DPME, 2018-2021) : Etudes des effets de synergie entre irradiation et altération par l'eau des verres nucléaires.
Charles Hours (thèse CEA, coll. DMRC, 2019-2022) : Couplage de la simulation de l'évolution de la microstructure de matrices céramiques combustibles et de la modélisation de la dissolution en milieu nitrique.
Lucas Muller (thèse CEA, coll. DMRC, 2022-2025) : Conversion de mélanges U(VI)-Pu(IV) par le peroxyde d'hydrogène en conditions hydrothermales.
Aurélien Perrot (thèse CEA, coll. DPME, 2021-2024) : Etude des produits d'altération à la surface des oxydes mixtes $(U,Pu)O_2$ par imagerie Raman et marquage isotopique.
Matthias Roucayrol (thèse CEA, coll. DMRC, 2023-2026) : Impact des produits de fission sur les propriétés microstructurales et thermophysiques des combustibles $(U,Pu)O_2$.
Fatima Chmali (thèse CEA, coll. DMRC, 2023-2026) : Etude de la préparation de combustible MOx $(U,Pu)O_{2-x}$ par voie hydroxyde.
Michaël Bernar (thèse CEA, coll. DMRC, 2023-2026) : Etude du comportement des produits de fission dans les oxydes mixtes $(U,Pu)O_2$ et de leur impact sur la microstructure du combustible.
Vincent Bosque-Guardia (thèse CEA, coll. DMRC, 2023-2026) : Influence des propriétés microstructurales sur la cinétique de dissolution des oxydes mixtes $(U,Pu)O_2$.

Apprentis :

Kevin Balme (L3 Pro, projet CEA, 2021-2022) : Etude de la stabilité de H_2O_2 en conditions environnementales.
Wassima Zannouh (DUT2, projet AIEA, 2021-2022) : Synthèse et étude de la durabilité de particules d'oxydes d'uranium.
Laura Schuppe (L3 Pro, projet CEA, 2022-2023) : Conversion hydrothermale de carboxylates d'actinides.
Marie Tronyo (L3 Pro, projet AIEA, 2022-2023) : Synthèse de microparticules d'oxydes mixtes à base d'uranium et étude de leur stockage sous forme de suspension.
Valentine Guillard (BUT2-3, projet CEA, 2023-2025) : Altération de combustible modèle simulant les combustibles nucléaires usagés en conditions d'entreposage en piscine en milieu acide borique (projet EURAD).
Ilona Diaz (BUT2-3, projet CEA, 2023-2025) : Etude du comportement à long terme de simulants du combustible nucléaire en conditions de stockage.
Jean Ventaja (BUT2-3, projet AIEA, 2024-2026) : Synthèse et étude de la durabilité de microparticules d'oxydes d'actinides.

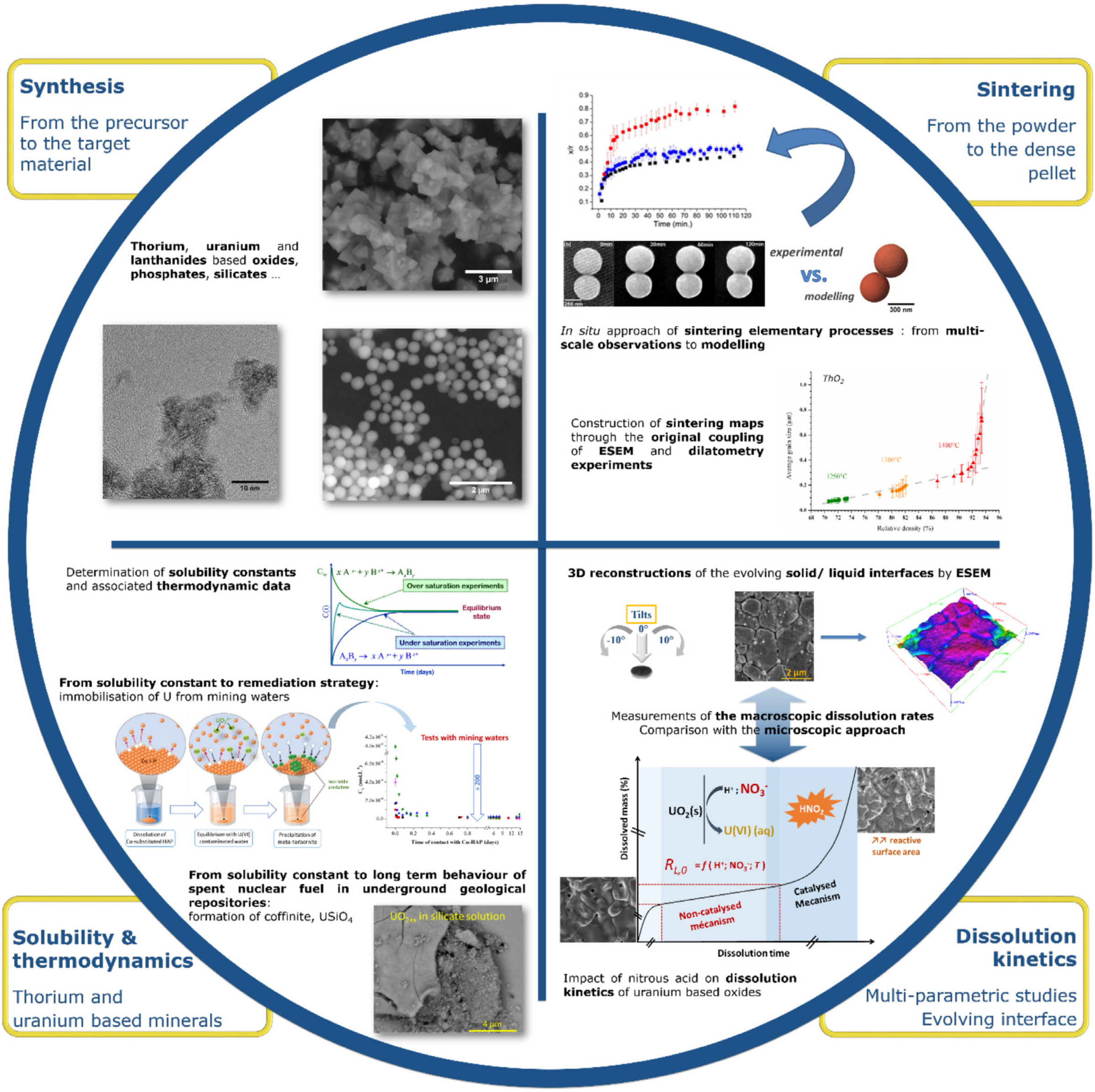


Fig. 1 Représentation de l'approche développée pour étudier les interfaces de matériaux en évolution

Le Laboratoire d'étude des Interfaces de Matériaux en Evolution (LIME) mène des activités de recherche en lien avec l'optimisation du cycle de vie de matériaux, plus particulièrement à travers la compréhension des processus chimiques siégeant aux interfaces solide/solide et solide/liquide. Ces travaux concernent à la fois la description des phénomènes liés aux procédés de synthèse de poudres inorganiques, de leur frittage (densification), et de la dissolution des céramiques obtenues (lixiviation, altération) en présence d'éventuelles contraintes (Figure 1).

Les expérimentations relatives aux interfaces solide/solide s'inscrivent dans le développement de méthodes de synthèses innovantes de poudres céramiques, puis l'investigation des mécanismes intervenant lors de leur frittage à haute température (consolidation de l'objet, grossissement de grains, réduction de la porosité). Ces deux étapes permettent *in fine* de maîtriser les caractéristiques structurales et microstructurales des échantillons d'intérêt, dont l'impact sur différentes propriétés peut alors être examiné de manière séparée. En particulier, l'étude de l'évolution des interfaces solide/liquide vise à appréhender et à comprendre les liens étroits reliant d'une part, la composition et/ou la morphologie d'un solide et d'autre part, sa propension à se dissoudre ou à s'altérer. La démarche expérimentale développée au LIME s'applique en priorité aux matériaux pour l'amont comme pour l'aval des cycles nucléaires actuels et futurs, dont des composés modèles des combustibles neufs et usagés ou de matrices de confinement des actinides, mais également à des thématiques hors nucléaire.

Dans ce but, la première étape de l'étude consiste à développer et mettre en œuvre des méthodes de synthèse originales de combustibles nucléaires modèles ($U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_2$, $U_{1-x}Ln_xO_{2-x/2}$, $U_{1-x}Nd_xO_{2-y}$, $Th_{1-x}Ln_xO_{2-x/2}$, …) en privilégiant l'usage de réactions menant le plus directement possible des ions en solution à la phase oxyde et intégrant les problématiques liées aux procédés de refabrication (utilisation de flux de matières issus d'étapes de recyclage, impact de l'hétérogénéité microstructurale et chimique sur la recyclabilité). La voie hydroxyde, développée et brevetée au laboratoire il y a plusieurs années, a ainsi été optimisée pour différents systèmes chimiques, permettant dorénavant de garantir une amélioration de la distribution cationique au sein du solide, et une réactivité accrue lors du frittage (thèses de C. Canas, 2022-2025, de L. Callejon, 2023-2026, et de F. Chmali, 2023-2026). Un effort important a également porté sur la conversion de différents composés moléculaires d'actinides en conditions hydrothermales conduisant à la précipitation directe d'oxydes hydratés en solution (thèses de S. Benarib, 2020-2023, de L. Muller, 2022-2025, et de D. Laffont, 2024-2027). Ces travaux ont permis de préparer des composés de morphologie et de stœchiométrie en oxygène contrôlées et présentant de faibles teneurs en impuretés, qui ont conduit à poursuivre le développement de ce type de procédés dans une optique d'application industrielle (coll. ORANO – DMRC, CDD L. Di Mascio 2020-2021). Par ailleurs, pour plusieurs des voies étudiées, une collaboration étroite avec les équipes du DMRC a permis d'aller jusqu'à la synthèse de composés à base de plutonium (thèses de L. Muller et de F. Chmali). La maîtrise de la morphologie des poudres d'oxydes nous a également conduits à envisager la préparation d'échantillons de composition, d'isotopie et de taille contrôlées pouvant être utilisés comme matériaux de référence dans le cadre du contrôle des garanties nucléaires internationales opéré par l'AIEA (Thèse de P. Asplanato, 2019-2022, et contrats d'alternance de W. Zannouh, 2021-2022, et M. Tronyo, 2022-2023).

Sur la base de ces résultats, le frittage des oxydes mixtes $U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_2$, $U_{1-x}Nd_xO_{2-y}$ et $Th_{1-x}Y_xO_{2\ x/2}$ a été étudié de manière à identifier les propriétés d'influence de la poudre initiale (surface spécifique, homogénéité, présence de carbone résiduel, …). Le lien entre le précurseur utilisé, sa conversion en oxyde, et les caractéristiques finales du compact densifié a ainsi pu être établi. Une attention particulière a porté sur la microstructure, notamment au moyen de cartes de frittage reliant taille de grains moyenne et densité (thèse de C. Canas). En parallèle, une caractérisation fine par le biais d'expérimentations XAS sur les lignes de lumière Soleil-MARS ou ESRF-ROBL a permis d'établir la spéciation redox des cations (thèses de M. Massonnet, 2018-2021, de Th. Barral, 2020-2023).

L'étude des interfaces solide/liquide s'est historiquement inscrite dans le contexte du retraitement du combustible nucléaire usé. Depuis le début des années 2020, ce cadre s'est étendu au stockage direct de combustibles usés en formation géologique profonde (thèse de Théo Montaigne, ICSM/DPME, 2019-2022 en collaboration avec EDF et l'ANDRA) ou à leur entreposage en piscine de refroidissement sur de longues durées (post-doctorat de Paul-Henri Imbert, EJP EURAD, 2020-2022, thèse d'Aurélien Perrot, ICSM/DPME, 2021-2024 en collaboration avec EDF).

Les études menées en conditions de retraitement reposent sur des tests multiparamétriques de dissolution menés sur des modèles simplifiés de matériaux d'intérêt, souvent multi-élémentaires et/ou multi-phasiques, de manière à étudier indépendamment l'influence de différents facteurs sur la durabilité chimique du solide (hétérogénéité cationique, défauts structuraux/microstructuraux, chimie redox, …).

Ainsi, les solutions solides $U_{1-x}Th_xO_2$ ont pu être utilisées comme simulant des MOx $(U,Pu)O_2$. L'impact de la distribution cationique sur le comportement à la dissolution de solides hétérogènes reproduisant les caractéristiques du combustible réel, a ainsi été mis en évidence à différentes échelles d'observation (thèse de C. Hours, DMRC/ICSM/DEC, 2019-2022, coll. ORANO). L'impact de différentes familles de produits de fission sur le comportement lors de l'étape de retraitement a également été examiné, en premier lieu celui des éléments lanthanide. Le comportement des solutions solides $U_{1-x}Ce_xO_{2-x/2}$ et $U_{1-x}Ln_xO_{2-y}$ s'est avéré différent de celui des oxydes à base de Th étudiés auparavant par l'équipe, notamment en raison de modifications de la spéciation redox de l'uranium induite par l'incorporation d'éléments trivalents (thèses de M. Massonnet, 2018-2021, et de Th. Barral, 2020-2023, projet H2020 GENIORS, 2017-2021). La présence d'éléments platinoïdes et du molybdène au sein de UO2 a été également étudiée dans le cadre des thèses de Thibault Kaczmarek (ICSM/DMRC, 2018-2021) et de Mohammad Husainy (ICSM/DMRC, 2021-2024). Ces études ont souligné l'existence de phénomènes catalytiques significatifs, liés à la présence de ces éléments sous forme métallique au sein du solide, et s'étendent maintenant à la possible revalorisation en aval du retraitement d'éléments d'intérêt économique, dont le rhodium (thèse de M. Fulchiron, 2023-2026, projet PIA4 PREPAC).

L'étude du comportement de composés modèles des combustibles nucléaires usés en conditions d'entreposage sous eau s'est déroulée à travers le projet Européen EURAD. L'approche adoptée dans ces travaux combine des analyses aux échelles microscopique et macroscopique. A l'échelle macroscopique, les tests de lixiviation ont souligné un faible impact de l'incorporation des éléments lanthanide et platinoïde sur la cinétique de dissolution de UO_2. A l'échelle microscopique, le suivi *operando* de l'interface solide/solution au cours des tests de lixiviation a montré la précipitation de phases néoformées dont la nature a été confirmée par des calculs de spéciation (compreignacite, schoepite, …). Le mécanisme de formation d'une autre phase néoformée, la studtite $UO_2(O_2),4H_2O$, a également été étudié, pour illustrer l'impact de H_2O_2 produit par radiolyse alpha et gamma de l'eau au contact de crayons combustibles endommagés (thèse ICSM/DPME A. Perrot, 2021-2024). D'autre part, des expériences d'altération en conditions de stockage profond direct de combustibles MOx MIMAS non irradiés (collaboration CEA Marcoule - DPME) et de matériaux modèles $(U,Ce)O_2$ de microstructures contrôlées préparés à l'ICSM ont été réalisées en parallèle, et ont démontré une excellente analogie de comportement du Ce et du Pu en conditions de dissolution oxydante. Ce travail ouvre de nombreuses perspectives notamment concernant la nature et la stabilité des espèces colloïdales formées (thèse de C. Kraemer, coll. ICSM-L2ME) ou l'étude de phénomènes de sorption à la surface des oxydes.

Un dernier aspect des travaux menés au sein du LIME concerne la caractérisation de phases uranifères formées lors de scénarios d'accidents graves ou considérées comme matrices de conditionnement spécifique en vue d'un stockage profond. Dans le premier cas, un intérêt particulier a porté sur les silicates d'actinides et de zirconium dans le cadre d'une collaboration internationale (Prof. A. Navrotsky, Arizona State University, Prof. X. Guo, Washington State University). Une étape d'optimisation des conditions de synthèse en conditions hydrothermales, puis de purification, ont permis d'aboutir à des composés monophasés (coll. ICSM/DMRC). Les données thermodynamiques relatives à la solubilité de ces phases ($K_S°$, $\Delta_R H°$, $\Delta_R G°$, $\Delta_R S°$) peuvent alors être déterminées par calorimétrie, et les propriétés thermophysiques peuvent être mesurées (thèse A. Avallone, 2024-2027). Ces phases constituent en outre des modèles simplifiés des coriums dont le comportement à long terme peut être évalué (thèse C. Navas, 2024-2027). Dans le second cas, plusieurs phases phosphatées incorporant de l'uranium ont été étudiées dans le cadre de la thèse d'Alison Roche (thèse UM, 2020-2023), dont le rhabdophane et la monazite.

L'équipe développe ainsi une recherche à caractère fondamental présentant des visées applicatives. Elle s'inscrit principalement dans le cadre d'actions visant l'amélioration de procédés du cycle du combustible nucléaire actuel et futur mais relève également de thématiques « non nucléaires » pour lesquelles les étapes de dissolution et de refabrication peuvent constituer des verrous technologiques (coll. ICSM/L2IA dans le cadre de la thèse de V. Legrand, ou projet INNOVTECH dans le cadre du PEPR-Sous-Sols, par exemple). Cette démarche scientifique est clairement pluridisciplinaire, relevant de la science des matériaux (synthèse-frittage-caractérisation), de la chimie des interfaces (solide/solide et solide/liquide), de la chimie en solution et de la radiochimie.

6/ EVOLVING INTERFACES IN MATERIALS

The ‘Evolving Interfaces in Materials’ Group (LIME) conducts research related to optimizing the life cycle of materials, particularly through understanding the chemical processes occurring at the solid/solid and solid/liquid interfaces. This work involves describing phenomena related to the synthesis of inorganic powders, their sintering (densification), and the dissolution of the resulting ceramics (leaching, alteration) in the presence of possible constraints (Figure 1).

Experiments on solid/solid interfaces are part of the development of innovative methods for synthesizing ceramic powders, followed by the investigation of the mechanisms involved in their sintering at high temperature (consolidation of the object, grain growth, reduction of porosity). These two stages ultimately enable the structural and microstructural characteristics of the samples of interest to be controlled, and their impact on different properties can then be examined separately. In particular, the study of the evolution of solid/liquid interfaces aims to understand the close links between the composition and/or morphology of a solid and its propensity to dissolve or alter. The experimental approach developed at LIME is primarily applied to materials of interest for current and future nuclear cycles, including model compounds of new and spent fuels or actinide confinement matrices, but also to non-nuclear topics.

To this end, the first stage of the study consists of developing and implementing original synthesis methods for model nuclear fuels ($U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_2$, $U_{1-x}Ln_xO_{2-x/2}$, $U_{1-x}Nd_xO_{2-y}$, $Th_{1-x}Ln_xO_{2-x/2}$, etc.) with a focus on reactions that lead ions in solution as directly as possible to the oxide phase and that integrate issues related to reprocessing (use of material flows from recycling stages, impact of microstructural and chemical heterogeneity on recycling ability). The hydroxide route, developed and patented in the laboratory several years ago, has thus been optimized for different chemical systems, now guaranteeing improved cation distribution within the solid and increased reactivity during sintering (PhDs by C. Canas, 2022-2025, L. Callejon, 2023-2026, and F. Chmali, 2023-2026). Significant effort has also been devoted to the conversion of various actinide molecular compounds under hydrothermal conditions leading to the direct precipitation of hydrated oxides in solution (PhDs by S. Benarib, 2020-2023, L. Muller, 2022-2025, and D. Laffont, 2024-2027, CEA projects). This work has made it possible to prepare compounds with controlled oxygen morphology and stoichiometry and low impurity levels, which has led to the further development of this type of process with a view to industrial application (collaboration between ORANO and DMRC, CDD L. Di Mascio 2020-2021). In addition, for several of the routes studied, close collaboration with the DMRC teams has led to the synthesis of plutonium-based compounds (PhDs by L. Muller and F. Chmali). Our expertise in controlling the morphology of oxide powders has also led us to consider the preparation of samples with controlled composition, isotopic composition and size that could be used as reference materials in the international nuclear safeguards program operated by the IAEA (PhD by P. Asplanato, 2019-2022, and work-study contracts with W. Zannouh, 2021-2022, and M. Tronyo, 2022-2023).

Based on these results, the sintering of mixed oxides $U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_2$, $U_{1-x}Nd_xO_{2-y}$ and $Hf_{1-x}Y_xO_{2-x/2}$ was studied in order to identify the influencing properties of the initial powder (specific surface area, homogeneity, presence of residual carbon, etc.). The history of the solid, i.e., the link between the precursor used, its conversion to oxide, and the final characteristics of the densified compact, was thus established. Particular attention was paid to the microstructure, notably by means of sintering maps linking average grain size and density (PhD by C. Canas). At the same time, detailed characterization using XAS experiments on the Soleil-MARS or ESRF-ROBL light lines made it possible to establish the redox speciation of cations (PhDs by M. Massonnet, 2018-2021, and Th. Barral, 2020-2023).

The study of solid/liquid interfaces has historically been part of the context of spent nuclear fuel (SNF) reprocessing. Since the early 2020s, this framework has been extended to the direct storage of spent fuel in deep geological formations (thesis by Th. Montaigne, ICSM/DPME, 2019-2022 in collaboration with EDF and ANDRA) or their interim storage in cooling pools (post-doctoral research by P.-H. Imbert, EJP EURAD, 2020-2022, thesis by A. Perrot, ICSM/DPME, 2021-2024 in collaboration with EDF).

Studies conducted under reprocessing conditions are based on multi-parameter dissolution tests carried out on simplified models of the materials of interest, often multi-element and/or multi-phase, in order to evaluate independently the influence of different factors contributing to the embrittlement of the solid (cationic heterogeneity, structural/microstructural defects, redox chemistry, etc.). Thus, $U_{1-x}Th_xO_2$ solid solutions could be used as MO_x $(U,Pu)O_2$ simulants. The impact of cation distribution on the dissolution behavior of heterogeneous solids reproducing the characteristics of real fuel has thus been demonstrated at different observation scales (thesis by C. Hours, DMRC/ICSM/DEC, 2019-2022, ORANO collection). The impact of different families of fission products on the behavior of SNF model compounds during the reprocessing stage was also examined, primarily that of lanthanides. The behavior of the solid solutions $U_{1-x}Ce_xO_{2-x/2}$ and $U_{1-x}Ln_xO_{2-y}$ proved to be particularly different from that of the Th- based oxides previously studied by the team, mainly due to changes in the redox speciation of uranium induced by the incorporation of trivalent elements (PhDs by M. Massonnet, 2018-2021, and Th. Barral, 2020-2023, H2020 GENIORS project, 2017-2021). The presence of platinoid elements and molybdenum in UO_2 has also been studied as part of the theses of Thibault Kaczmarek (ICSM/DMRC, 2018-2021) and Mohammad Husainy (ICSM/DMRC, 2021-2024). These studies have highlighted the existence of significant catalytic phenomena linked to the presence of these metallic elements within the solid, and are now being extended to the possible downstream recovery of elements of economic interest, including rhodium (PhD by M. Fulchiron, 2023-2026, PIA4 PREPAC project).

The study of the behavior of model compounds of spent nuclear fuels under storage conditions was carried out in particular through the European EURAD project. The approach adopted in this work combines analyses at both microscopic and macroscopic scales. On the macroscopic scale, leaching tests showed that the incorporation of lanthanide and platinoid elements had little impact on UO_2 dissolution kinetics. On a microscopic scale, operando monitoring of the solid/solution interface during leaching tests revealed the precipitation of neoformed phases, the nature of which was confirmed by speciation calculations (compreignacite, schoepite, etc.). The formation mechanism of another neoformed phase, studtite $UO_2(O_2)\cdot 4H_2O$, was also studied, to illustrate the impact of H_2O_2 produced by alpha and gamma radiolysis of water in contact with damaged fuel rods (ICSM/DPME PhD, A. Perrot, 2021-2024). Additionally, alteration experiments under direct geologic disposal conditions of non-irradiated MOx MIMAS fuels (CEA Marcoule - DPME collaboration) and $(U,Ce)O_2$ model materials prepared at ICSM were carried out in parallel, showing the excellent analogy between the behavior of Ce and Pu under oxidative dissolution conditions. This work also opens up many prospects, particularly concerning the nature and stability of the colloidal species formed (PhD by C. Kraemer, coll. ICSM-L2ME) and the study of sorption phenomena on the surface of oxides.

A final aspect of the work carried out at LIME concerns the characterization of uranium-bearing phases formed during severe accident scenarios or considered as specific conditioning matrices for deep geological disposal. In the first case, particular interest was focused on actinide and zirconium silicates as part of an international collaboration (Prof. A. Navrotsky, Arizona State University, Prof. X. Guo, Washington State University). A stage of optimization of the synthesis conditions under hydrothermal conditions, followed by purification, led to the production of single-phase compounds (collaboration between ICSM and DMRC). The thermodynamic data relating to the solubility of these phases ($K_S°$, $\Delta_R H°$, $\Delta_R G°$, $\Delta_R S°$) can then be determined by calorimetry, and the thermophysical properties can be measured (thesis A. Avallone, 2024-2027). These phases also constitute simplified models of coriums whose leaching under accidental management conditions can be evaluated (thesis C. Navas, 2024-2027). In the second case, several phosphate phases incorporating uranium have also been studied as part of Alison Roche's PhD (UM thesis, 2020-2023), including rhabdophane and monazite.

The group is thus developing fundamental research with practical applications. It is mainly part of efforts to improve current and future nuclear fuel cycle processes, but also covers "non-nuclear" topics for which the dissolution and remanufacturing stages may constitute technological barriers (ICSM/L2IA collaboration as part of V. Legrand's thesis, or INNOVTECH project as part of the PEPR-Sous-Sols, for example). This scientific approach is clearly multidisciplinary, involving materials science (synthesis-sintering-characterization), interface chemistry (solid/solid and solid/liquid), solution chemistry, and radiochemistry.

7/ ETUDES DE LA MATIÈRE EN MODE ENVIRONNEMENTAL

Au 1er décembre 2024, l'équipe est composée de 8 permanents:
1 ingénieur d'études CNRS responsable d'équipe (Dr Xavier Le Goff)
1 ingénieur de recherche CNRS (Dr. Renaud Podor)
1 ingénier-chercheur CEA/DES (Dr Diane Rebiscoul, mutation du LNER)
2 ingénieurs d'études CNRS (Sandra Maynadié, Joseph Lautru)
1 assistant-ingénieur CNRS (Guilhem Quintard, mutation NOEMI)
1 ingénieur CEA/DES (Henri-Pierre Brau)
1 ingénieur CEA/DRF (Michaël Odorico)

Et sur la période 2021-2024 de non-permanents :

Post-doctorants :
Laëtitia Pinaud (projet PTC liqliqAFM, 2021-22) : Réponse d'une interface liquide/liquide sous une pointe d'AFM.

CDD :
Norma-Maria Pereira-Machado (CNRS, 2022-23)
Mélanie Taron (CNRS, 2022-2026)
Philippe Notez (CNRS 2023-2024)

Thésards :
Jérome Mendonça (thèse CIFRE NewTEC Scientific à Nîmes, 2019-22) : Développement de micro-fours haute température pour les Microscopes Electroniques à Balayage.
Barbier Hélène (thèse CEA 2023-2026) Voie sol-gel multi-colloïdales pour la préparation de combustibles mixtes
Vanèle Audrey Tsapi-Metchop (thèse CEA 2023-2026) : Extraction de lanthanides et d'actinides à l'aide de matériaux fonctionnalisés par une protéine à forte affinité et sélectivité.
Christin Kraemer (thèse CEA 2023-2026) : Identification des espèces polynucléaires et colloïdales à base d'uranium (VI) en solutions aqueuses : domaines d'existence, structure et stabilité en conditions environnementales.
Laxmi Bodapati (thèse UM 2024-2027) : Utilisation de la voie sol-gel multi-colloïdale pour la préparation de matériaux mixtes à base de lanthanides et de métaux de transition.

Apprentis :
Siham Hassak (M1-M2 instrumentation, 2020-22) : Reconstruction d'un microscope électronique à transmission.
Kaïs El Bouaissi Dos Santos (2023-2024) : Conducteur de microscopes (MEB et AFM).
Emile Agniel (2024-2025) : Etude de la réactivité chimique des matières premières lors de l'élaboration de verres écoconçus.
Léane Taccard (2024-2025) : Développement d'outils et de solutions pour accélérer la transition écologique.

Le Laboratoire d'Etudes de la Matière en Mode Environnemental (L2ME) regroupe l'ensemble des techniques liées à la diffusion/diffraction des rayons X, la résonance magnétique nucléaire, la microscopie à champ proche et à la microscopie électronique. Cette combinaison de compétences et savoir-faire correspond à une volonté de coupler les informations microscopiques et macroscopiques obtenues par l'ensemble des techniques expérimentales disponibles au sein du L2ME.

Il est ainsi possible de décrire encore plus précisément le comportement de l'échantillon en maitrisant, lors de l'enregistrement des mesures, les paramètres physiques auxquels est soumis l'échantillon (température, taux d'humidité, nature des gaz, pression…). Le contrôle des paramètres d'environnement échantillon, dans le domaine de la microscopie, permet l'observation directe d'objets usuellement reconnus comme non observables par les techniques d'imageries conventionnelles et ouvre le champ de l'expérimentation *in situ* et l'accès à la détermination de grandeurs physiques originales. En particulier, les avancées récentes en microscopies à rayons X et électroniques permettent d'accéder à l'observation directe des agrégats supra-moléculaires en solution avec des résolutions, spatiale et temporelle, inégalées à ce jour, sans nécessité de mettre en œuvre des techniques de préparation d'échantillons lourdes et génératrices d'artéfacts.

Le couplage de dispositifs dédiés (humidité contrôlée ou haute température) avec des microscopes électroniques de conception récente permet la compréhension fine de certaines propriétés des matériaux (auto-cicatrisation, frittage, démouillage, dissolution, réactivité chimique…). L'expérimentation *in situ*, l'imagerie haute résolution, couplée à l'analyse chimique locale du matériau, donne accès au suivi direct des mécanismes de réarrangement de surface, allant de la description des mécanismes de dissolution des matériaux jusqu'à de réelles expériences de recuit des matériaux *in situ*.

En parallèle, une approche multi-échelle de caractérisation de la matière, du nanomètre au micron, est développée. Elle repose sur une maitrise des mesures dans l'espace réciproque dans une large dynamique d'intensité et de vecteur de diffusion. Ici, diffusion aux petits angles et diffraction utilisant des rayons X durs sont utilisées conjointement pour la caractérisation multi-échelle statistique des matériaux, permettant de contourner les effets dus au choix d'images représentatives. A ce niveau, des grandeurs physico-chimiques allant jusqu'aux potentiels d'interaction, aux interfaces fractales et aux courbures peuvent être déterminées directement, en contrôlant conjointement température et activité du solvant.

Cette approche expérimentale est complétée par une capacité de développement instrumental « à façon » d'outils adaptés qui se base principalement sur les savoir-faire des membres de l'équipe. Il s'agit là de répondre à des besoins de recherche spécifiques exprimés par les chercheurs de l'ICSM. Les développements technologiques peuvent porter non seulement sur de l'instrumentation légère (porte-échantillons, etc…), mi-lourde (cellules dédiées) ou lourde (reconstruction d'un appareil).

Les compétences de l'équipe dans la pratique instrumentale et l'interprétation des spectres de diffusion-diffraction et des images de microscopie permettent des développements méthodologiques originaux. Ces savoir-faire et développements sont partagés avec les équipes de recherches, internes ou externes à l'institut et ils conduisent à l'acquisition de résultats scientifiques inédits. Un premier ensemble de résultats porte sur la caractérisation de matériaux par microscopie électronique à balayage environnementale, et plus particulièrement sur l'étude de leur réponse à des contraintes spécifiques lors d'expériences menées *in situ* (effet de l'humidité relative ou de la température). L'un des résultats marquants obtenus en mode humidité contrôlée est la mise en place d'outils et de méthodes d'analyses originales d'observation et d'analyse des processus de dissolution des matériaux, basées sur la reconstruction 3D des surfaces à partir d'images MEBE mais également par microscopie à force atomique. Ces outils ouvrent la voie à la caractérisation précise de mécanismes locaux de dissolution. Les études menées à haute température ont permis d'accéder à des observations et des informations relatives aux différents stades du frittage des céramiques totalement inédites à ce jour. D'autres propriétés telles que l'évolution microstructurales de films minces (Ce,Gd)O2+ Ag durant un traitement thermique (Coll. IJL, NewTec), l'évolution d'un revêtement Al-Si déposé sur un substrat d'acier (Coll. Krytur, NewTec, Laboratoire de Réactivité de Surface, IJL), l'oxydation de carbure d'uranium ou encore le vieillissement des matériaux pour piles à combustibles (Coll. Imperial College London) ont également été étudiées avec succès dans le cadre de collaboration avec des laboratoires d'autres universités.

Un second ensemble de résultats porte sur le développement d'outils spécifiques de caractérisation des matériaux via des environnements échantillons ou des programmes informatiques. Les projets Celdi (soutenu par la SATT AxLR) et FurnaSEM (projet Readynov soutenu par la Région Occitanie puis Bourse CIFRE) ont menés aux développements d'une cellule d'étude directe de la dissolution / corrosion des matériaux dans la chambre d'un MEB et une série de fours (haute et très haute température) miniatures pour MEB. Le plugin SEraMic (intégré au logiciel ImageJ) permet l'analyse semi-automatique d'images acquises en microscopie électronique. L'équipe se tourne maintenant vers l'application de l'intelligence artificielle en collaboration avec l'université de Lorraine pour optimiser le nombre d'images nécessaires lors de l'analyse et le traitement d'images et de données. En parallèle, le projet de reconstruction d'un microscope électronique à transmission (MET) mené en interne à l'ICSM depuis plusieurs années est maintenant soutenu via un financement ANR LabCOM (NewTEM – 2022-2027). La majorité de ces actions sont fortement appliquées et sont (ou seront) valorisées dans les années à venir aux travers de collaborations avec des acteurs économiques locaux, notamment avec la société NewTEC Scientific.

Un troisième ensemble de résultats couvre des développements méthodologiques portant sur l'étude des colloïdes, de leur caractérisation et de l'utilisation des véhicules tests comme outils de caractérisation pour l'étude des interfaces solides - liquides. Les sujets abordés portent notamment sur la préparation de matériaux à partir de sols multi-colloïdaux ou la caractérisation des colloïdes intrinsèques d'uranium. Ces projets sont menés dans le cadre de trois thèses (2 CEA et UM). L'un des résultats marquant a montré que la préparation d'oxydes mixtes à partir de sols multi-colloidaux permet l'obtention de matériaux dont la distribution élémentaire est homogène à l'échelle nanométrique.

7/ STUDY OF MATTER IN ENVIRONMENTAL CONDITIONS

The Laboratory for the Study of Matter in Environmental Mode (L2ME) combines all the techniques related to scattering/diffraction and electronic microscopy. This combination of skills and know-how corresponds to a desire to couple microscopic and macroscopic information obtained by all the experimental techniques available within the L2ME.The main goal is to describe precisely the behavior of a sample submitted to reactive conditions by controlling relative humidity, temperature, nature of the gases, gas pressure while recording images or performing measurements.

The control of the sample environmental conditions, in the field of electron microscopy, allows observing directly objects that are generally not observable by the conventional imaging techniques. This paves the way to in situ experiments and this can yield to the measurement of physical parameters and activation energies. As an example, recent advances in the field of soft X-ray microscopy and electron microscopies allow the direct observation of supramolecular aggregates in solution with a very high resolution, without any specific sample preparation and with unexpected spatial and time resolutions.

Coupling specific stages or cells (controlled relative humidity or high temperature) with modern electron microscopes allows the precise characterization of physico-chemical properties such as self-healing, sintering, dissolution, chemical reactivity through in situ experiments …

In parallel, a multi-scale approach for matter characterization ranging from the nanometer to the micrometer scale is being developed. It relies on the mastering of measurements in the reciprocal space in a wide dynamics of intensities and scattering vectors. Here, small-angle scattering and diffraction using hard X-rays are jointly used for the statistical multiscale characterization of the materials, allowing us to bypass the problem linked to the selection of representative images. Therefore, physico-chemical data including interaction potentials, fractal interfaces and curvatures can be directly determined by simultaneously controlling temperature and solvent activity.

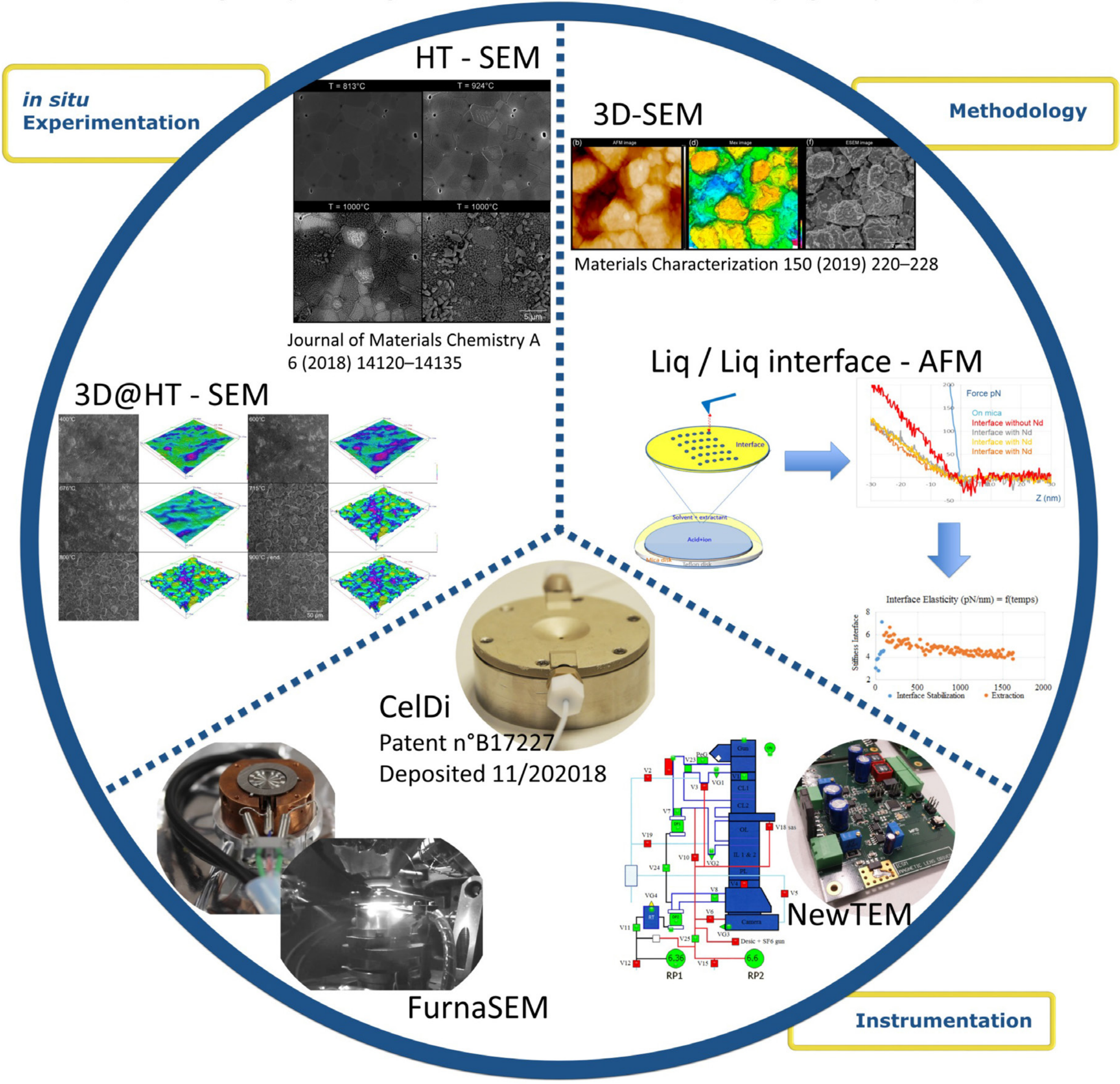
This approach is completed with the instrumental development of specific tools, based on the know-how of the lab team with the aim to answer specific research objectives. These developments can cover small tools (sample holders, etc), stages with dedicated applications or the complete refurbishing of apparatus.

The skills of the team in terms of instrumentation and interpretation of XRD and SAXS spectra, as well as in the recording of electron microscopy images and image processing, allow developing original technical methodologies. The know-how of the L2ME team is shared with other research teams, yielding to the obtaining of original scientific data and results. A first set of results relates to the characterization of materials by environmental scanning electron microscopy, and more particularly to the study of their response when they are submitted to specific constrains during in situ experiments (relative humidity, temperature…). One of the main results obtained during the observation of materials under controlled relative humidity conditions is the development of new strategies for the study of dissolution processes, based on image processing as well as 3D surface reconstruction. These tools pave the way to the precise determination of very local dissolution processes. In parallel, original experimental data – and knowledge - relative to the first stage of sintering have been recorded during experiments performed with the ESEM combined with a high temperature stage. Other properties such as the microstructural evolution of (Ce,Gd)O2+ Ag thin films during heat treatment (Coll. IJL, NewTec), evolution of an Al-Si coating deposited on a steel substrate (Coll. Krytur, NewTec, Laboratoire de Réactivité de Surface, IJL), oxidation of uranium carbide and the ageing of fuel cell materials (Coll. Imperial College London) have also been successfully studied in collaboration with laboratories at other universities.

A second set of result deals with the development of specific tools for the characterisation of materials (sample environments or computer programs). The CelDi (funded by SATT AxLR) project is dedicated to the development of a stage that can be implemented in a SEM to observe directly the dissolution and/or corrosion processes. The FurnaSEM project (funded by Occitanie Region) is devoted to the development of a new series of high temperature furnaces that can be implemented in SEMs. The SEraMic plugin (integrated into the ImageJ software) allows the semi-automatic analysis of images acquired by electron microscopy. The team is now turning to the application of machine learning (deep learning) for the analysis and processing of images and data. In parallel, the project aiming to the refurbishing of a TEM and fully funded by ICSM for several years, is now supported by ANR LabCOM funding (NewTEM). Most of these actions are highly applied and are (or will be) developed in the coming years thanks to collaborations with local economic players, in particular with the company NewTEC Scientific.

A third set of results covers methodological developments relating to the study of colloids, their characterisation and the use of test vehicles as characterisation tools for the study of solid-liquid interfaces. Topics covered include the preparation of materials from multi-colloidal sols and the characterisation of intrinsic uranium colloids. These projects are being carried out as part of three theses (2 CEA and UM). One of the key results showed that the preparation of mixed oxides from multi-colloidal sols produces materials with a homogeneous elemental distribution on the nanometric scale.

Instrumentation / capabilities: Environmental scanning electron microscope Quattro ESEM-FEG, TEM 200CX, Scanning electron microscope Vega3, 400 MHz NMR spectrometer, SEM/TEM Specimen preparation Lab, AFM Multimode 8, Small angle X-ray Scattering, D8 ADVANCE diffractometer (reflectivity, high temperature,…).



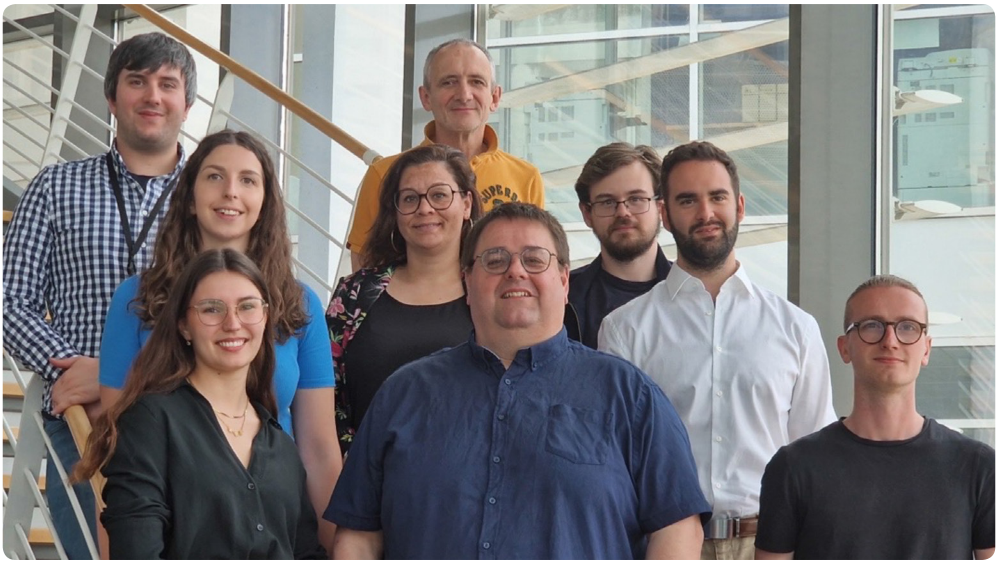
8/ MESOSCOPIC MODELLING AND THEORETICAL CHEMISTRY

L'équipe est constituée au 1er novembre 2024 de 3 permanents :
1 Professeur Université Montpellier, responsable d'équipe (Prof. Jean-François Dufrêche)
1 Chercheure CEA/DRF (Dr. Magali Duvail)
1 Chercheur-Ingénieur CEA/DES (Dr. Bertrand Siboulet)

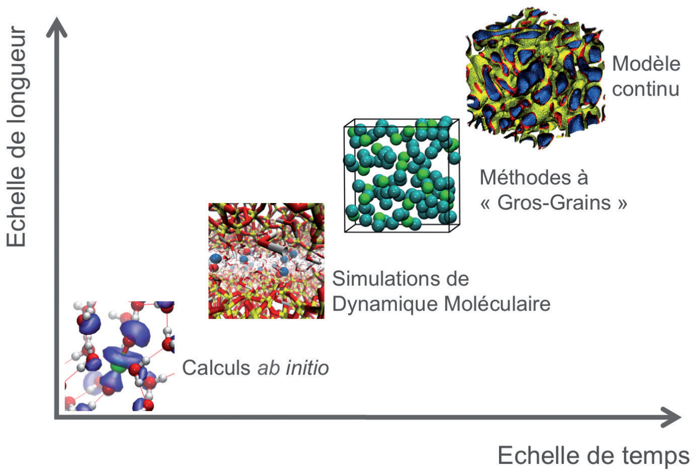
Et sur la période 2021-2024 de non-permanents :

Post-doctorants :
Sébastien Le Crom (LABUM Université Montpellier, 2021-22) : Rationalisation par dynamique moléculaire des effets de structure dans les mécanismes d'extraction en milieu liquide ionique.
Yann Foucaud (CEA/DES, 2019-21) : Modélisation moléculaire de la SHG.

Doctorants (2021-24) :
Jordan Klein (thèse CEA, 2023-) : Modélisation de liquides ioniques pour l'extraction d'ions uranyle.
Gustave Szczepan (thèse CEA, 2023-) : Prédiction de l'apparition de troisièmes phases par une approche multi-échelle.
Geoffroy Rodrik (thèse CEA, 2023-) : Modélisation chimie-physique des oxydes d'uranium à l'interface avec une solution pour la dissolution.
Erwann Guillam (thèse CEA, coll. ISEC, 2022-) : Prédiction moléculaire du transfert d'ions pour l'extraction.
Lara Žiberna (thèse CEA, coll. ISEC, 2022-) : Simulation de l'équilibre et du transport des ions aux interfaces liquide – liquide.
Ludovic Jami (thèse Univ. Tours en collaboration avec ICSM, 2019-22) : Transport de molécules actives pour la communication entre insectes.
Tristan Kunyu Wang (thèse Univ. Montpellier, 2019-22) : Simulation numérique pour les ions aux interfaces : corrélations ionique et dépollution des eaux.
Marin Vatin (thèse CEA, coll. ISEC, 2018-21) : Modélisation multi-échelle de solutions organiques et systèmes interfaciaux pour l'extraction liquide-liquide.
Lolita Hilaire (thèse CEA, coll. ISEC, 2018-21) : Modélisation de la coalescence : connecter les échelles - de l'approche déterministe à l'approche stochastique.
Mathilde Coquil (thèse CEA, coll. ISEC, 2017-21) : Identification des contributions à l'origine de la sélectivité en extraction liquide/liquide.



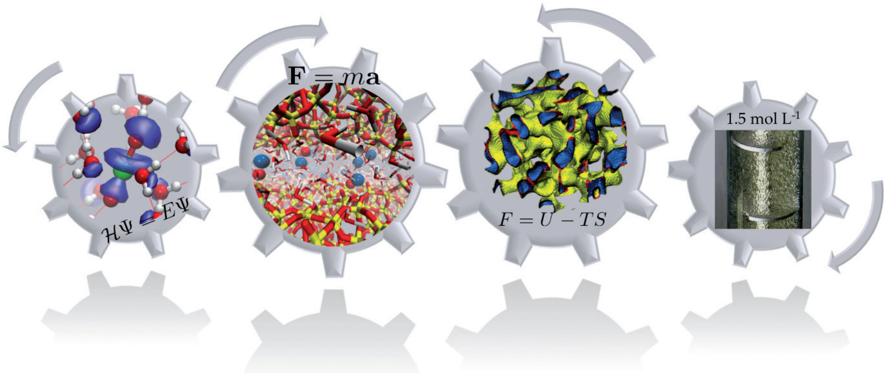
Les objectifs de l'équipe de modélisation consistent à étudier les systèmes complexes, en particulier ceux mis en jeu dans la chimie séparative, par une approche multi-échelle avec un intérêt tout particulier pour les modélisations aux échelles intermédiaires (mésoscopiques ou nano-échelles).
Les moyens mis en œuvre par l'équipe sont représentés sur les figures qui suivent. La des-cription la plus fondamentale est celle de la mécanique quantique (calculs ab initio) capable de représenter l'acte élémentaire. Elle est en particulier étudiée pour déterminer la complexation moléculaire et elle peut aider également à améliorer les modèles classiques. Ceux-ci peuvent être étudiés par la dynamique moléculaire pour caractériser la structure des milieux, leurs propriétés d'équilibre et le transport, mais seulement sur des échelles assez faibles (quelques nanomètres et nanosecondes tout au plus). Les études des milieux complexes reposent donc sur des descriptions à des échelles intermédiaires (modèles à « gros grain », théories à solvant continu, dynamique brownienne, équations intégrales, fonctionnelles de la densité classique, couplage de modes, théorie des interfaces, etc.) qui sont implémentées pour décrire la physico-chimie des processus et faire le lien avec le génie chimique. L'originalité de cette équipe de modélisation vient en particulier du fait que le passage d'échelle est presque systématiquement étudié. Les échelles les plus microscopiques permettent ainsi d'améliorer les modélisations macroscopiques, non seulement en leur fournissant des paramètres, mais aussi en améliorant directement leurs équations fondamentales.



Un tel programme est réalisé dans différents contextes de la chimie séparative et permet de résoudre plusieurs problèmes ouverts :
• Modélisation de l'extraction liquide-liquide. Une approche à gros grains permet de déter-miner les propriétés thermodynamiques dans les différentes phases (aqueuse et organique). Cette méthode est peu à peu développée pour des systèmes de plus en plus complexes.
• Étude des milieux poreux, en particulier ceux utilisés pour la séparation (oxydes, verres poreux, etc.). Le but est ici d'obtenir le maximum d'informations des expériences et de préciser les mécanismes physico-chimiques sous-jacents. Des études sont aussi menées sur les argiles de stockage.
Au niveau fondamental, nous étudions particulièrement la théorie des électrolytes pour les propriétés d'équilibre et de transport. Certaines applications sans lien direct avec la séparation ont été menées. Ainsi, en nanotechnologies, le rôle du bruit ionique a été étudié en relation avec des expériences utilisant des transistors à un électron. Les modèles de microémulsions sont aussi mis en œuvre pour l'étude des diagrammes de phase ternaires de ces milieux.

Toutes ces études sont réalisées en collabora-tion avec les expérimentateurs et, en particulier, ceux de l'ICSM. Les méthodes aux échelles intermédiaires peuvent ainsi être validées par comparaison aux expériences et aux modélisations moléculaires. L'idée à terme est de proposer une vision globale des processus où chaque mécanisme est intégré dans l'échelle de description la plus adaptée et où les liens entre les différents éléments de l'engrenage sont explicités. Les fondements de la thermodynamique statistique nous font comprendre qu'une telle tâche est au moins a priori faisable pour les processus d'équilibre, mais elle est plus délicate pour les phénomènes dynamiques, en raison de la nécessité de découpler les différentes échelles de temps, ce qui n'est pas toujours possible.

Le groupe de modélisation a ainsi à la fois des activités en lien direct avec les expérimentateurs de l'ICSM et aussi une activité méthodologique propre.



8/ MESOSCOPIC MODELLING AND THEORETICAL CHEMISTRY

The main goal of the modeling team is to study complex systems, particularly those involved in separation chemistry, from a multi-scale approach, with a particular focus on models at the intermediate scale (mesoscopic models or nanoscale).

The methodology is presented in the figure. The most fundamental description is that of quantum mechanics (ab initio calculations). It is capable of representing elementary events. It is particularly used to study complexation and can also be used to improve classical models. These can be studied by molecular dynamics to characterize the structure of the media, their equilibrium and transport properties, but only on rather small scales (a few nanometers and nano-seconds at most). Therefore, studies of complex media can only be conducted using intermediate scale methods («coarse-graining» models, continuous solvent theories, Brownian dynamics, integral equations, classical density functionals, mode coupling, interface theory, etc.) that are used (i) to describe the physical chemistry of the processes and (ii) to make the link with chemical engineering. The originality of the team stems from the fact that the scale transition is studied almost systematically. Most microscopic scales enable the improvement of the macroscopic models, not only by providing the values of physical parameters, but also by directly improving the macroscopic fundamental equa-tions.

Such a program is carried out in different contexts of separation chemistry and allows for the resolution of several open issues:

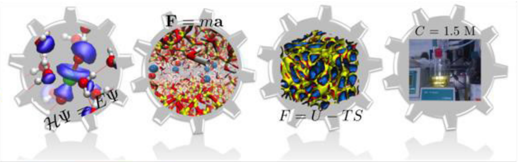
- Liquid-liquid extraction modeling. The thermodynamic quantities in the various phases (aqueous and organic solvent phases) can be calculated using a coarse-graining method. This method is being developed for increasingly complex systems.
- Porous Media, particularly those involved in separation (oxides, porous glasses, etc.). Here, the goal is to elicit as much information as possible from experiments while also characterizing the relevant underlying mechanisms. We also investigate clays for waste storage.

At the most fundamental level, we concentrate on electrolyte theory for transport and equilibrium properties. Some applications that have nothing to do with separation chemistry have been developed. In nanotechnologies, for example, the role of ionic noise has been studied in close connection with experiments involving one-electron transistors. Microemulsion models are also studied in order to model ternary phase diagrams.

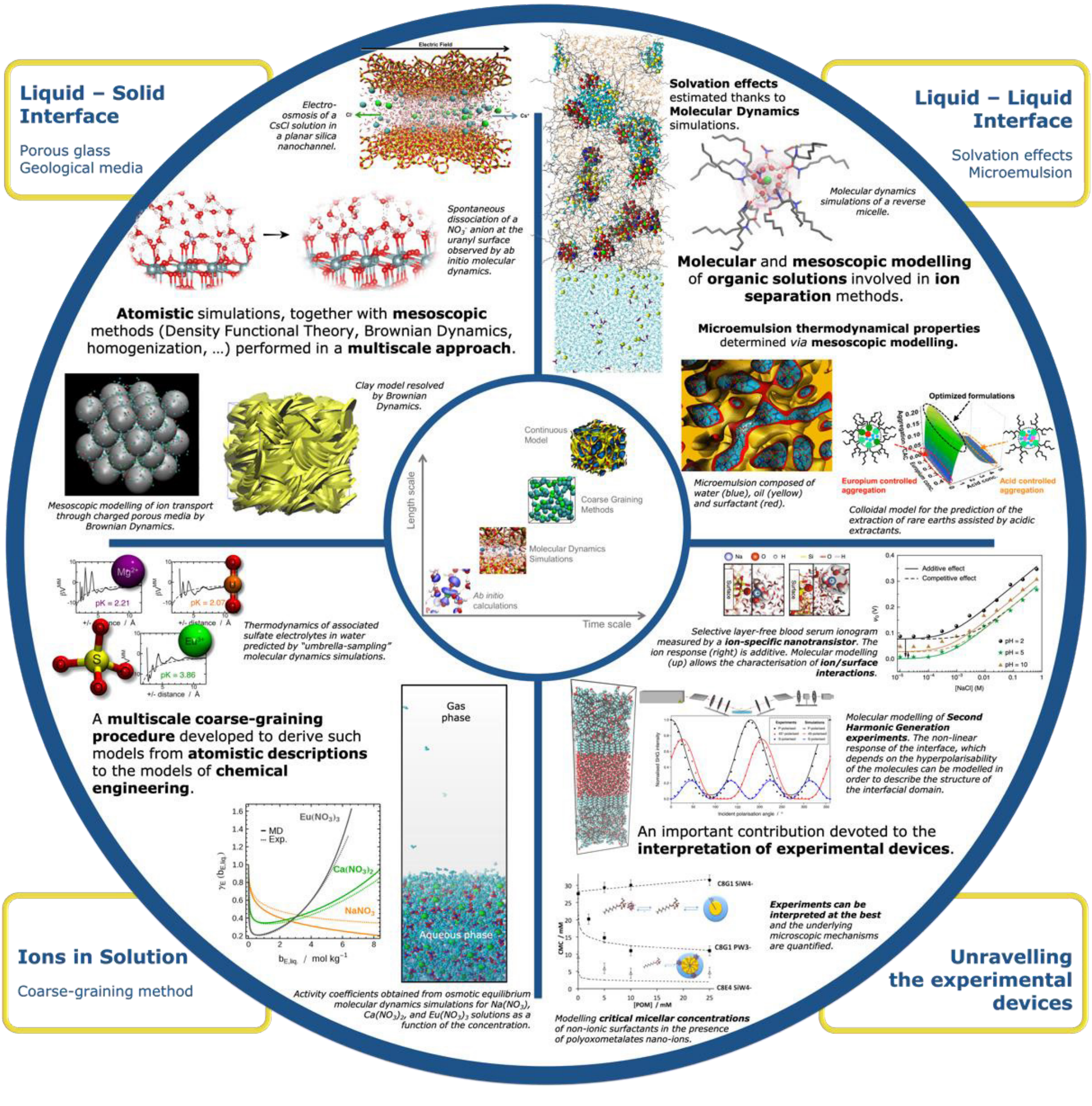
These works have been performed in collaboration with experimentalists, particularly those of ICSM. The methods at the intermediate scales can be validated by comparing them to the experimental results and molecular modeling results. The final idea would be to propose a global view of processes in which every mechanism is integrated into the most appropriate level of description, the link between the various models being explained. The fundamentals of statistical thermodynamics help us in understanding that such a project is at least a priori possible for the equilibrium processes, but it is much more difficult for dynamical properties due to the need to uncouple the various time scales, which is not always possible.

Thus, the modeling group has activities that are directly related to the experimentalists at ICSM, as well as methodological activities on its own.

From atoms and molecules ...



... to the macroscopic world.



Liquid – Solid Interface

Porous glass
Geological media

Electro-osmosis of a CsCl solution in a planar silica nanochannel.

Spontaneous dissociation of a NO_3^- anion at the uranyl surface observed by ab initio molecular dynamics.

Atomistic simulations, together with **mesoscopic** methods (Density Functional Theory, Brownian Dynamics, homogenization, ...) performed in a **multiscale approach**.

Clay model resolved by Brownian Dynamics.

Mesoscopic modelling of ion transport through charged porous media by Brownian Dynamics.

Liquid – Liquid Interface

Solvation effects
Microemulsion

Solvation effects estimated thanks to **Molecular Dynamics** simulations.

Molecular dynamics simulations of a reverse micelle.

Molecular and **mesoscopic modelling** of **organic solutions** involved in **ion separation** methods.

Microemulsion thermodynamical properties determined *via* **mesoscopic modelling.**

Microemulsion composed of water (blue), oil (yellow) and surfactant (red).

Europium controlled aggregation
Acid controlled aggregation

Colloidal model for the prediction of the extraction of rare earths assisted by acidic extractants.

Thermodynamics of associated sulfate electrolytes in water predicted by "umbrella-sampling" molecular dynamics simulations.

A **multiscale coarse-graining procedure** developed to derive such models from **atomistic descriptions** to the models of **chemical engineering**.

Activity coefficients obtained from osmotic equilibrium molecular dynamics simulations for $Na(NO_3)$, $Ca(NO_3)_2$, and $Eu(NO_3)_3$ solutions as a function of the concentration.

Ions in Solution

Coarse-graining method

Selective layer-free blood serum ionogram measured by a ***ion-specific nanotransistor****. The ion response (right) is additive. Molecular modelling (up) allows the characterisation of* ***ion/surface interactions****.*

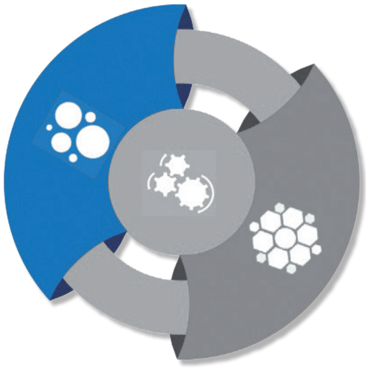
Molecular modelling of ***Second Harmonic Generation experiments****. The non-linear response of the interface, which depends on the hyperpolarisability of the molecules can be modelled in order to describe the structure of the interfacial domain.*

An important contribution devoted to the **interpretation of experimental devices**.

Experiments can be interpreted at the best *and the underlying microscopic mechanisms are quantified.*

Modelling ***critical micellar concentrations*** *of non-ionic surfactants in the presence of polyoxometalates nano-ions.*

Unravelling the experimental devices



INNOVATION IN EXTRACTION AND RECYCLING

INNOVATIONS POUR L'EXTRACTION ET LE RECYCLAGE

INNOVATION IN EXTRACTION AND RECYCLING

Via the knowledge of the supramolecular, weak and long-range interactions, for a technological break-through in eco-friendly separation chemistry.

INNOVATION POUR L'EXTRACTION ET LE RECYCLAGE

Via la connaissance des interactions supramoléculaires, faibles et à longue distance, pour une rupture technologique sur des procédés écoresponsables en chimie séparative.

INNOVATIVE STRATEGIES AND PROCESSES FOR RARE EARTH ELEMENTS RECYCLING USING NON-TOXIC HYDROTROPES

A. El Maangar, C. Fleury, G. Arrachart, T. Zemb and S. Pellet-Rostaing

The recovery of rare earth elements (REEs) from end-of-life materials is both economically and environmentally beneficial. However, the overall recovery rate is low due to the lack of an efficient and clean recovery process. Liquid–liquid extraction and acid leaching are widely used in hydrometallurgical processes for recycling REEs from of NdFeB permanent magnets. A crucial challenge in solvent extraction is to replace conventional organic solvents with less toxic and volatile solvents, to avoid a third phase formation and to extract as much metals as possible with the lowest viscosity.

We showed that the use of hydrotropes as diluents (Figure) decreases the viscosity of solutions by more than a factor of ten, even at high amount of extracted cations. It also increases the extraction efficiency of typical ionic extractants such as anionic phosphates or non-ionic amides and inhibit all types of third-phase transitions that occur when using conventional diluents. In addition, the maximum possible loading is enhanced by a factor of two or three compared to alkanes, allowing more compact design and intensification of extraction processes.

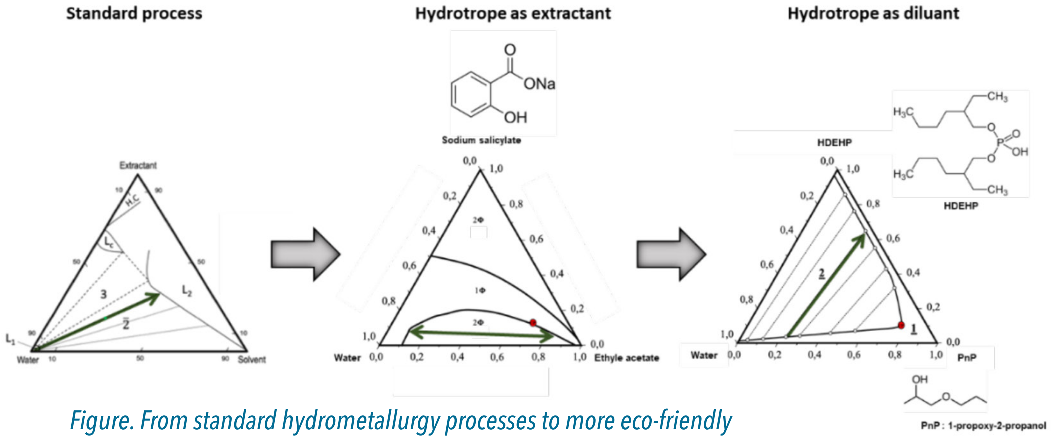


Figure. From standard hydrometallurgy processes to more eco-friendly ternary systems with non-toxic hydrotropes

Based on small-angle X-ray scattering analysis and surface tension measurements, the origin of the gain in Gibb's energy of transfer and of the tunable selectivity in the family of rare earth elements is further identified by three mechanisms: reduction of the term linked to complexation, extraction enhancement by a synergistic effect between the hydrotrope and the complexing molecule, and intra-aggregate entropy of mixing.[1-3]

Hydrotrope-based formulations were also applied for the leaching of NdFeB permanent magnets. The use of conventional mineral acids and their mixtures still presents issues, including the release of toxic gases during the leaching, the handling of a high-concentration acid in an industrial-scale operation, and selectivity concerns. Groundbreaking improvements are still needed to meet the increasingly stringent requirements on the environmental impact of metal waste leaching.

We showed that replacing conventional acids with hydrotrope-based formulations (using a ternary mixture of water, sodium salicylate (NaSal), and an environmentally compatible diluent, ethyl acetate (AcOEt), as the solubilizing system) achieves selective leaching and avoids subsequent liquid/liquid extraction steps. Finally, the compatibility of oxalic acid with the ternary mixture NaSal/H2O/AcOEt allows the sequential precipitation of REEs in the leaching medium, which can then be recycled. This may open a completely new pathway to reducing toxic effluents in hydrometallurgy and recycling.[4-7]

[1] El Maangar A., Fleury C., Pellet-Rostaing S., Zemb T. – **Leaching and recycling of NdFeB permanent magnets using ionic non-toxic hydrotropes instead of extractants** – *Front. Chem. Eng.* (2024) 6, 1–12. hal-04923472v1.

[2] El Maangar A. Degot P., Huber V., Causse J., Berthault P., Touraud D. , Kunz W., Zemb T. – **Pre-nucleation cluster formation upon ethyl acetate addition to an aqueous solution of an anionic hydrotrope** – *J. Mol. Liq.* (2020) 310, 113240. hal-02561827

[3] Bourgeois D., El Maangar A., Dourdain S.– **Importance of weak interactions in the formulation of organic phases for efficient L/L extraction of metals** – *Curr. Opin. Colloid Interface Sci.* (2020), 46, 36-51. hal-03698291v1.

[4] El Maangar, A., Duhamet, J., Pellet-Rostaing, S., Zemb – **Process for liquid/liquid extraction of rare earths or actinides via synergistic combination of a co-solvent hydrotrope with anonic or chelating extractants** – *Patent FR3128706* (A1) / WO2023078989 (A1) (2023). hal-04956611.

[5] El Maangar A., Zemb T., Fleury C., Duhamet J., Dufrêche J.-F., Pellet-Rostaing S.– **Decreasing viscosity and increasing accessible load by replacing classical diluents with a hydrotrope in liquid-liquid extraction** – *Front. Chem. Eng.* (2024) 6, 1–17. hal-04923518v1.

[6] El Maangar, Theisen J., Penisson C., Zemb T., Gabriel J.-C. P. – **A microfluidic study of synergic liquid-liquid extraction of rare earth elements** – *Phys. Chem . Chem. Phys.* (2020) 22(10), 5449–5462. hal-02476112v1.

[7] Maurice A. A., Theisen J., Rai V., Olivier F., El Maangar A., Duhamet J., Zemb T., Gabriel J.-C. P. – **First online X-ray fluorescence characteri-zation of liquid-liquid extraction in microfluidics** – *Nano Select* (2022) 3(2) 425-436. hal-03274989v3.

UNDERSTANDING UNCONVENTIONAL METAL ION TRANSFER MECHANISMS

E. Makombe, S.A. Moussaoui, M. Simonnet, D. Bourgeois – L. Berthon, A. Lélias (DMRC), Y. Ueda, C. Micheau, R. Motokawa (JAEA)

Better understanding how an extractant maintains the otherwise insoluble metal ion in an organic phase is one of the main challenges of the liquid-liquid separation field. Classical solvating extraction systems rely on the coordination of extracted metal as a unique well defined complex, such as $PdCl_2(DOS)_2$ in the case of the well-known extrac-tion of Pd(II) by dioctylsulfide (DOS). However, in some cases, the distribution ratio of the considered metal does not follow a simple law as anticipated from a unique coordination equilibrium. It is therefore challenging to elucidate the role of the interac-tions occurring at the molecular level, especially the relations between first order interactions (such as chemical bonding or electrostatic interactions) and low energy second order interaction (H bonding, polarisation, dipole).[1] Various examples are investi-gated in detail at the LHYS, in particular Pd(II) and U(VI) extraction using diamides, for which the out-come of extraction is strongly impacted by the chemical structure of the extractant, despite unchanged coordinating moiety.

$$-\frac{d[Pd^{2+}]_{aq}}{dt} = k_1[Pd^{2+}]^1_{aq}[THMA]^2_{org}[H^+]^{-1}_{aq}[NO_3]^2_{aq}$$

$$-\frac{d[Pd^{2+}]_{aq}}{dt} = k_2[Pd^{2+}]^1_{aq}[DBMA]^2_{org}[H^+]^{1}_{aq}[NO_3]^2_{aq}$$

Figure 1: Impact of the molecular topology of extractant (diamide) on extraction mechanism

In the case of Pd(II) extraction, the role of H^+ in the extraction mechanism is very intriguing (Fig. 1) with a reverse impact on both kinetics and thermodynamics depending on the extractant structure. A detailed molecular characterization is underway, in collaboration with a team from the Japanese Atomic Energy Agency (JAEA).[2] In the case of U(VI) extrac-tion using THMA, the distribution ratio is strongly impacted by the total U(VI) amount in the system, and increases with an increasing U(VI) quantity, in opposite trend as is usually observed in classical solvent extraction systems (Fig. 2). [3]

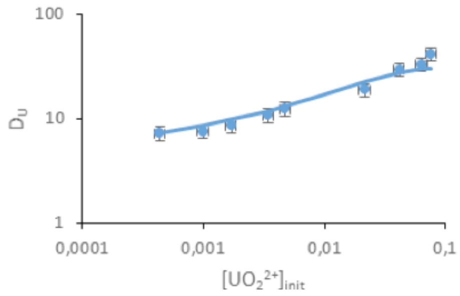


Figure 2: Experimental (squares) and modelled (line) distribution of U(VI) with 0.2 M THMA in toluene, 3 M HNO_3

The rationalization of both systems with THMA in toluene is currently underway, based on an approach relying on the description of the extraction mechanism by several chemical equilibria, involving mixed species encompassing the metallic cation alone, the metallic cation and the acid, or two metal-lic cations in the specific case of U(VI). Simulation of the distribution ratios obtained through the variation of several parameters (e.g. ligand, acid and metal concentrations) using this set of equilibria is mostly successful (e.g. Fig. 2), and revealed:

- In the case of Pd(II), the highest fitted thermo-dynamics constants correspond to two species, $Pd(NO_3)_2L_3$ and $Pd(NO_3)_3HL_2$. Due to the presence of the latter species, the value of the slope analysis strongly depends on the nitric acid concentration at which the study is performed. The coordination complex character-ized using X-ray single crystal diffraction ($Pd(NO_3)_2L$) is not the major species in organic phase.
- In the case of U(VI), more species are observed due to the occurrence of several bimetallic U(VI) complexes encompassing a μ-nitrato bonding ligand. This result was also observed after molecular dynamics simulations. Hence, in that case, both the nitric acid and the U concentrations impact the slope value, explaining some discrepancies observed between our work and the literature.

Complete characterization of the systems using advanced spectroscopic techniques (EXAFS, SANS) is underway, and the impact on the outcome of the extraction of other metal ions present in the system will be investigated.

[1] D. Bourgeois, A. El Maangar, S. Dourdain **«Importance of weak interactions in the formulation of organic phases for efficient liquid/liquid extraction of metals»**, *Current opinion in colloid & interface science*, 2020, 46, 36-51.

[2] C. Micheau, Y. Ueda, R. Motokawa, K. Akutsu-Suyama, N.L. Yamada, M. Yamada, S.A. Moussaoui, E. Makombe, D. Meyer, L. Berthon, D. Bourgeois **«Organization of malonamides from the interface to the organic bulk phase»**, *J. Mol. Liq.*, 2024, 401, 124372.

[3] E. Makombe, D. Bourgeois, L. Berthon, D. Meyer **«Uranium(VI) and thorium(IV) extraction by malonamides: Impact of ligand molecular topology on selectivity»**, *J. Mol. Liq.*, 2022, 368, 120701.

PILOTING THE SEPARATION IN SX SYSTEMS

R. Moneuse, M. Khoder, L. Golfier, S.A. Moussaoui, M. Simonnet, D. Bourgeois, D. Meyer - A. Lelias (DMRC), A. Osypenko, J.M. Lehn (ISIS, Stransbourg Univ.)

One of the challenges for separative chemistry remains the control of flows of metal mixtures of variable composition. Finding the right sequence, formulating the optimal organic phase, working on mixtures without going till ultimate separation, playing with transfer kinetics are examples of the levers the LHyS team has identified and is currently studying.

In the specific case of nuclear spent fuel reprocessing, the recovery valuable elements such as Am(III) is considered, for either FBR fuel or space-craft energy. Am(III) chemistry is very similar to Cm(III) and the Ln(III), making its selective separation a chemical challenge. Current state-of-the-art does not provide any molecule able to separate Am from Cm with sufficient efficiency (separation factor SF>5). It is thus proposed in some processes (e.g. the European AmSel process) to combine hydrophilic ligands to the usual lipophilic extractants to enhance the selectivity. In our lab, we chose to focus on the phenanthroline dicarboxamides compounds (PTdA, Fig. 1) because of their good properties observed for the separation of adjacent Ln(III)[1,2], that should resemble the behavior of adjacent An(III). The on-going research focuses on two key parameters to improve the selectivity: the extraction mechanisms of undesirable co-extracted fission products (namely Sr and Zr) and the improvement of the separation factor by fine-tuning the carboxamide substituents.

It is also possible to rely on a difference in transfer kinetics to improve the separation of elements of interest. For example, the selective recovery of Pd from electronic waste was carried out at the ICSM, based on kinetic control of the process. Some fission products, such as Fe, Ru, Pd, or Zr, appear to have behavior primarily governed by chemical kinetics. In order to best define the operating conditions of an optimised separation process, a detailed knowledge of the phenomena as well as the parameters allowing the transfer is essential. Characterization of Pd(II) transfer kinetics has been completed, and that of Ru(III) is currently under investigation.

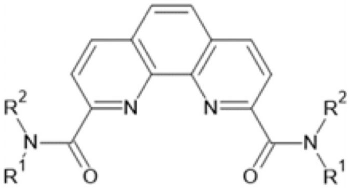


Figure 1: Phenanthroline dicarboxamide (PTdA)

In another approach, completely different from the classical method where a single molecule is designed to extract metal cations under specific conditions, dynamic covalent chemistry has been exploited as a tool to generate the extractant molecules. In collaboration with the LCS (ISIS), the LHyS team has implemented an adaptive dynamic covalent library to the liquid–liquid extraction of metal ions: acylhydrazone constituents self-build and distribute through both phases of the system in the presence of Pd(II) and Cu(II)[3] (Fig. 2). This work laid the foundation of a new liquid-liquid metal extraction-separation approach and opens the possibility to develop a system responding to several metal extraction-separation problems.

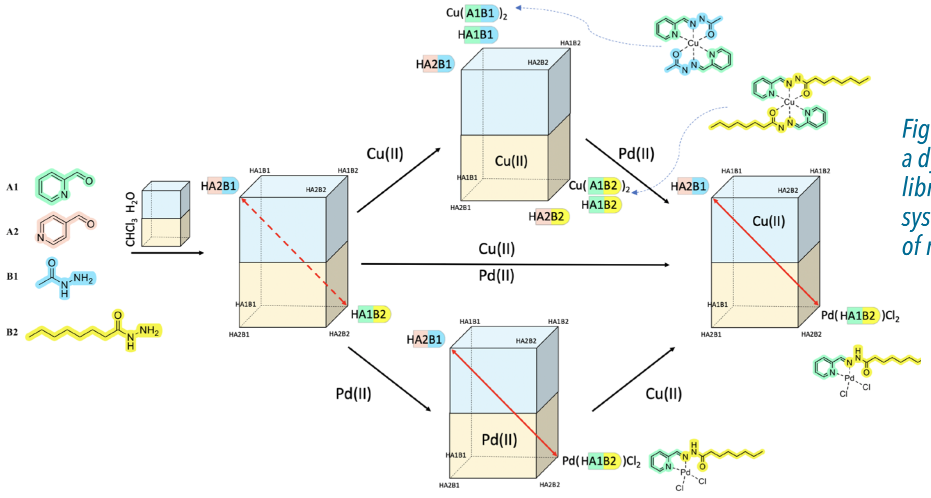


Figure 2: Behavior of a dynamic covalent library in biphasic systems in the presence of metal ions

[1] M. Simonnet, T. Kobayashi, K. Shimojo, K. Yokoyama, T. Yaita **«Study on Phenanthroline Carboxamide for Lanthanide Separation: Influence of Amide Substituents»** *Inorg. Chem.*, 2021, 60, 13409–13418.

[2] M. Simonnet, TY. Sasaki, T. Yaita **«Combining a Lipophilic Phenanthroline Carboxamide and a Hydrophilic Diglycolamide to Increase the Separation Factors of Adjacent Light Lanthanidese»** *Solvent Ext. Ion Exch.*, 2023, 41, 857–867.

[3] R. Moneuse, D. Bourgeois, X. Le Goff, J.M. Lehn, D. Meyer **«Behavior of a Dynamic Covalent Library Driven by Combined Pd(II) and Biphasic Effectors for Metal Transport between Phases»** *Chem. Eur. J.*, 2023, 29, e202302188.

EFFECT OF CHIRALITY ON SOLVENT EXTRACTION PERFORMANCES AND MECHANISMS

N. Félines, D. Lemire, M. Thimotée, C. Marie (DMRC), F. Giusti, S. Dourdain, G. Arrachart and S. Pellet-Rostaing

It is well established that solvent extraction performances result from a combination of the affinity of the ligand towards the targeted element and the ability of the ligand to cluster and trap this element into reverse aggregates. So, it is not trivial to note that most of branched ligands commonly used in hydrometallurgical processes, are mixtures of stereosisomers, namely enantiomers and diastereo-isomers carrying one or several chiral centers (see fig. A). At the opposite of enantiomers, diastereoisomers are not expected to show the same chemical (chelation) and physical chemical (aggregation) properties, thus two main interesting questions could be: i) Does chirality may affect the performances of liquid-liquid extraction ? ii) What is the extent of this effect ? In order to address those concerns, we initiated, in collaboration with the DMRC group (CEA Marcoule), a new project aiming at developping diastereopure ligands and assessing their extracting properties regarding their absolute configuration. As preliminary results, pioneering works reported in N. Felines Ph. D. thesis deal with the synthesis of diastereopure stereoisomers of N,N-bis(2-ethylhexyl)butyramide (DEHBA) and the studies of their extraction properties towards uranium (U) and plutonium (Pu) at low or high acidity in the context of the spent nuclear fuel cycle.[1] Complementary works reported in D. Lemire Ph. D thesis allowed to supply further diastereopure position isomers of DEHBA (see fig. B) designed to provide relevant informations on the involved mechanisms that were investigated by SAXS, EXAFS and UV-vis spectroscopy.[2] The effects of chirality were markedly more noticeable when the chiral center was close to the complexation site, demonstrating the predominance of the regioisomerism effects over those of the chirality. These phenomena could be interpreted by referring to the inner and outer sphere complexes and their respective susceptibility to steric hindrance (see fig. C). Building on the acquired experience in the field, we are now focusing on the syntheses of more complex diastereopure structures, which are amido- and aminophosphonates (see fig. D), commonly used for U extraction performed in nitric or sulfuric media. This work is currently developed in our laboratory by M. Thimotée (Ph. D student).[3]

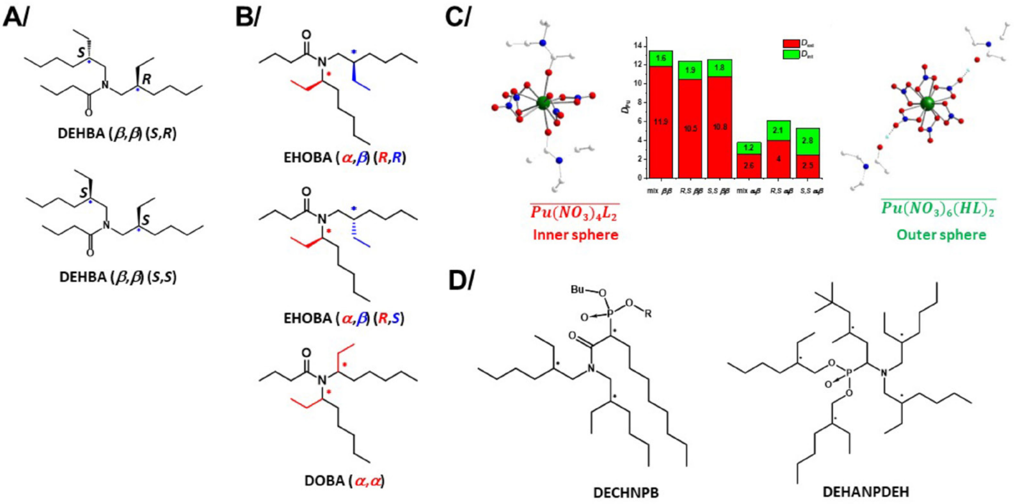


*Figure. Chemical structures of (R,S) and (S,S) DEHBA diastereoisomers (A) and their regiomers (B). Chiral carbons are labeled with *, α and β are the relative positions of the ethyl branching. C) Results yielded after Pu extraction from nitric medium, performed with racemic (mix) and diastereopure stereoisomers and regiomers of DEHBA. Structure and distribution of outer and inner sphere complex for each monoamide. D) Structures of amido-(left) and amino-(right)-phosphonates.*

[1] Félines N., Arrachart G., Giusti F., Beillard A., Marie C., Pellet-Rostaing S. – **Stereochemically enriched extractants for the extraction of actinides** – *New Journal of Chemistry* (2021) 45, 12798-12801. hal-03395204v1

[2] Lemire D., Dumas T., Guillaumont D., Solari P. L., Menut D., Giusti F., Arrachart G., Dourdain S., Pellet-Rostaing S. – **Molecular and Supramolecular Study of Uranium/Plutonium Liquid−Liquid Extraction with N,N-Dialkylamides** – *Inorganic Chemistry* (2024) 63, 18809-18819. hal-04721661v1 ; Lemire D., Dumas T., Marie C., Giusti F., Arrachart G., Dourdain S., Pellet-Rostaing S. – **Stereo- and Regiochemical Effect of N,N-Dialkylamide Extractants on the Speciation of Pu Complexes** – *Eur. J. Inorg. Chem.* (2023) e202300461. hal-04224206v1.

[3] Thimotée M. – Ph. D in preparation (2022-2025).

EVALUATION OF EUTECTIC SOLVENT FOR EXTRACTION APPLICATIONS

B. Bernicot, A. Bakayogo, J. Couturier (CEREGE), N. Schaeffer (Univ Aveiro), S. Dourdain, G. Arrachart and S. Pellet-Rostaing

The use of ionic systems as extracting phases is particularly significant. Among them deep eutectic mixtures (DES) as extractant systems is another innovative approach recently explored by LTSM. These are mixtures of two or more components that form a liquid at room temperature with properties similar to those of ionic liquids. DES can be ionic or non-ionic systems, based solely on interactions between a donor and an acceptor of hydrogen bonds.

In this context we studying the implementation of non-ionic hydrophobic DES (HDES) and their use in the recovery of rare earths, particularly from permanent magnets. This study is studied in close collaboration with Nicolas Schaeffer from the University of Aveiro in Portugal. Thanks to a detailed characterisation study using complementary techniques and a correlation between theoretical and experimental data (in particular FT-IR spectroscopy, small-angle X-ray scattering (SAXS) and molecular dynamics (MD)) to explain the struc-ture and interactions controlling the formation of these new HDES, the mechanisms behind their formation have been exposed, providing guidelines for the future design of new HDES and their use in solvent extraction applications.

The HDESs studied demonstrate highly efficient extraction of rare earths, even at low acid concentrations, thereby significantly reducing acid consumption and the associated environmental impact. This innovation offers clear advantages over conventional organic phases, as it eliminates the need for volatile diluents and phase modifiers, simplifying the process and reducing environmental and health risks. The main results confirm that HDES allows for greater extraction due to the ability to increase the concentration of the extractant without causing third phase problems. A life cycle assessment (LCA) was carried out to objectively compare the environmental impact of the HDES system with that of the conventional extraction system used for rare earth extraction, and a range of seven environmental indicators demonstrated that the HDES system significantly improves the sustainability of the process.

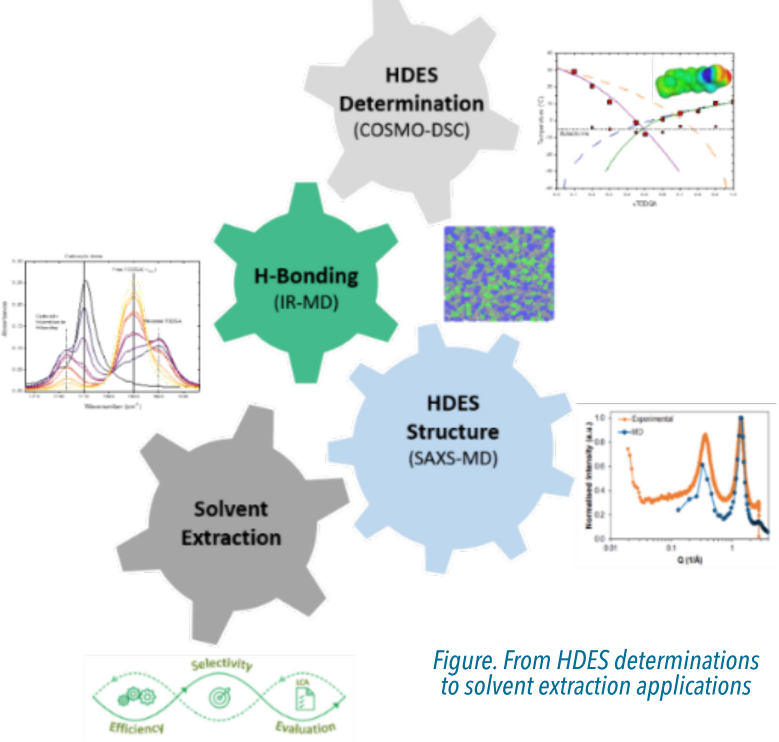


Figure. From HDES determinations to solvent extraction applications

This approach is being extended with the implementation of HDES for uranium extraction and DES for miner-al deposit leaching. Indeed, non-conventional solvents, such as DES, can be used to selectively leach metals of interest. Such systems have been studied as part of the leaching of red mud (bauxite residue), in the ANR RECALL project and as part of a thesis funded by the CNRS, in collaboration with CEREGE.

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FROM IONIC SOLVENT TOWARD DILUENT-FREE SOLVENT EXTRACTION SYSTEMS

C. Micheau, S. Le Crom, Z. Lu, E. Guerinoni, J. Klein, S. Dourdain, F. Giusti, G. Arrachart and S. Pellet-Rostaing

A crucial challenge in solvent extraction is to replace conventional organic solvents with less toxic and volatile solvent as ionic liquids (ILs). Depending on the extraction systems studied, ILs can lead to better efficiency than the conventional ones.[1]

An eco-friendly process was proposed based on ionic liquids such as N-ethyl-N-alkyl-piperidinium bis(trifluoromethylsulfonyl)imide (EOPiP-NTf_2)[2] or functionalized task specific ionic liquids (TSILs) for the extraction and stripping of tantalum from sulfuric acidic medium that may come from e-waste. The study of the key parameters of the IL-based process was investigated including the effect of Ta concentration, H_2SO_4 concentration, equilibration time, temperature, IL partitioning… The recovery of other valuable metals such as Au and Pd from aqua regia leachate of e-waste was also demonstrated and a global flowsheet was proposed including the possibility to recover the metals thank to an electrodeposition process.[3] Having successfully passed initial laboratory tests, this technology is now in the maturation phase.

Rare earth extraction with DMDOHEMA in EOpip Ntf_2 was also studied with a fundamental approach to evaluate the mechanisms of extraction in ionic liquids. It was observed with this extractant, that rare earth extraction is higher in IL that in conventional diluent, without any exchange of the IL anions or cations.[4] This very interesting behavior was investigated in more details with a coupled theoretical and experimental approach (Small Angle X Ray scattering and Molecular Dynamics) to evaluate the role of the IL structure in these better extraction efficiencies.[5]

With a similar approach, we also designed a diluent-free IL system composed of a pure mixture of extractants which was shown to solve many problem of the industrial process used for U extraction: higher efficiency, no third phase, no organic compound evaporation.[6,7,8]

Nowadays, we believe that such ionic solvent, that can concern both ionic liquids or greener deep eutectic solvents are of high potential for extraction of valuable and strategic metals.[9]

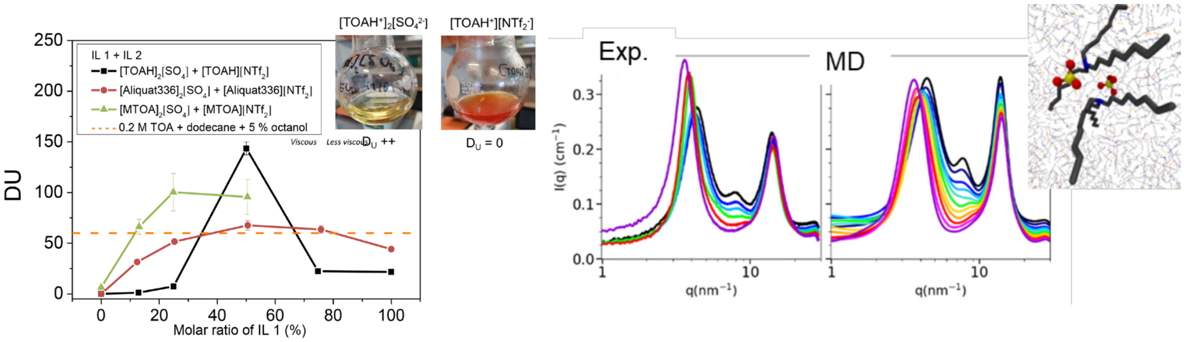

Figure. Coupled SAXS and molecular dynamic to understand structural effects in extraction mechanisms in ILs.

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URANIUM EXTRACTION – FROM THE APPLICATION OF THE IENAIC APPROACH TO INDUSTRIAL APPLICATIONS

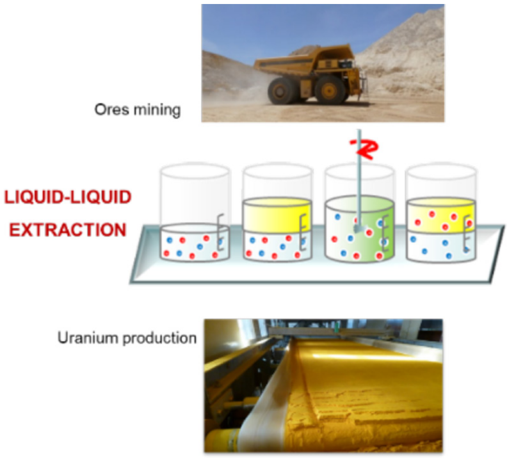
Z. Lu, E. Guerinoni, S. Dourdain, F. Giusti, G. Arrachart and S. Pellet-Rostaing

The AMEX uranium purification process, used in the front-end nuclear fuel cycle, is based on a liquid-liquid extraction method that faces several limitations, such as the non-selective extraction of certain cations, high volatily, and the formation of a third phase. A study, involving the organic synthesis of new extracting molecules and analysis using neutron and X-ray scattering, demonstrated that the branching of alkyl chains in amines directly influences supramolecular organization, which in turn affects extraction efficiency and the formation of the third phase.

These results, obtained through collaboration with JAEA (Japan), were explained using the IENAIC thermodynamic approach.[1-3]

This project also provided a better understanding of the effect of phase modifiers on third-phase formation and their potential role in improving the selectivity of extracted metals.[4] These advancements have attracted the interest of ORANO, which has initiated an R&D collaboration to enhance uranium extraction at two of its mining sites.

In this context, we also designed a diluent-free IL system composed of a pure mixture of extractants which was shown to solve many problem of the industrial process used for U extraction: higher efficiency, no third phase, no organic compound evaporation.[5-7] This global project on uranium production illustrates how fundamental research can contribute to industrial applications.[8]



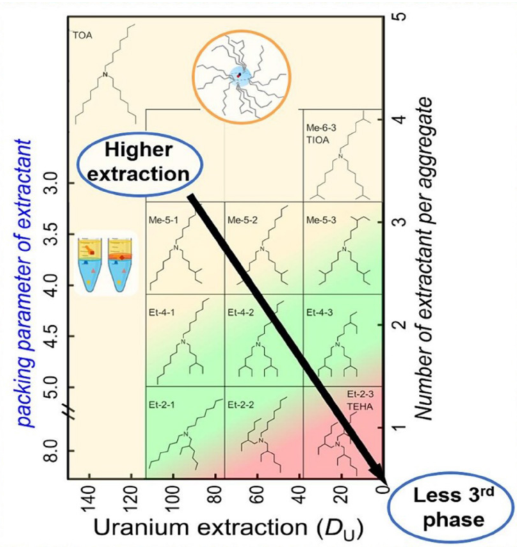


Figure. Uranium purification from ores via liquid-liquid extraction (left) and uranium extraction efficiency as a function of alkyl chain branching quantity and position (right).

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[6] Guerinoni E., Dourdain S.; Lu Z.; Giusti F., Arrachart G., Couturier J., Hartmann D., Pellet-Rostaing S. – **Highly efficient diluent-free solvent extraction of uranium using mixtures of protonated trioctylamine and quaternary ammonium salts. Comparative Life Cycle Assessment with the conventional extractant** – *Hydrometallurgy* (2024) 224, 105257. hal-04668410v1.

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NANO-IONS SPECIFIC EFFECT: SUPERCHAOTROPY

P. Bauduin, L. Girard, A. Jonchère, C. Pasquier et O. Diat

We have found that large-size ionic species with low-charge density, like polyoxometalates (POMs) or (metal-) boron clusters, behave differently from conventional ions regarding their surface properties at liquid interfaces. Indeed, they have a strong pro-pensity to adsorb at neutral polar (hydrated) inter-faces through non-specific interactions, an effect referred to as "super-chaotropy".[1] The super-chaotropy increases as the nano-ions charge densi-ty decreases. The study of the cloud point (tem-per-ature) variation of some non-ionic organic species in water was suggested as a straightforward method for assessing and categorizing nano-ions according to their super-chaotropy.[2] Depending on where they are on the superchaotropicity scale, they interact more or less strongly with non-ionic, polar mole-cules or supramolecular structures in bulk solutions or at interfaces in the sub-millimolar range. Soft-matter research has new avenues to be explored thanks to our understanding of this property. It is indeed possible to induce phase transitions in self-assembling systems, to structure aqueous phases as or with hydrotropes. The superchaotropic behav-ior of nano-ions makes it possible to control molecular co-assembly constituted of non-ionic oligomers or polymers or proteins by changing concentrations and the choice of their counterions.

Physico-chemical properties of non-ionic com-pounds can be strongly altered by nano-ions. For example, the water solubility of sparingly soluble organic molecules or the stability of non-ionic foams can be significantly improved. The used of super-chaotropic behaviour of nano-ions opens then opportunities in separation science, catalysis, and the design of nanostructured hybrid materials. In physi-cal chemistry of solutions, nano-ions close the gap between ions and (charged-) colloids, because of their nm size.

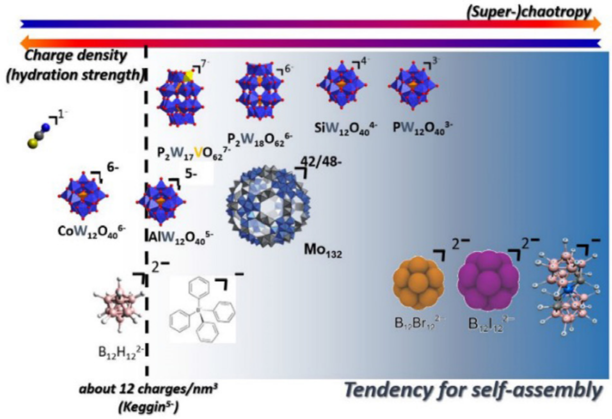

Figure. Various types of inorganic anionic clusters such as the heteropolyoxometalates (Keggin, Dawson, kleperate…), the bisdicarbolide and derivatives, dodecarborate ($B_{12}Y_{12}^{2-}$, Y= H, Br, Cl, I), and organic ones such as tetraphenylborate are distributed as a function of their superchaotropicity and beyond the Hofmeister series on the "chaotropes" side with the thiocyanate, SCN-, on the left upper side.

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SUPERCHAOTROPIC ION FLOTATION

V. Legrand, S. Szenknect, K. Skorzewska, L. Girard, C. Pasquier, A. Jonchère, O. Diat and P. Bauduin

Ions are extracted and separated by foams in the industrial process known as «ion foam flotation.» The classical ion flotation method makes use of ionic foaming agents (surfactants) to selectively remove ions through electrostatic interactions. As explained in previous pages, superchaotropicity is the general property of low charge density nanometric size ions (nano-ions) that adsorb onto neutral hydrated sur-faces. This property could become a driving force in a nano-ions flotation process using non-ionic surfac-tant, converting this process into pure nonelectro-static, a "superchaotropic (SC) ion flotation" and then to be selective against "classical" ions. For example, the large size and low charge density of some polyoxometalates (POMs), compared to classical ions, have this peculiar superchaotropic behavior. A precedent thesis project was carried out to provide a proof-of concept evidence for SC ion flotation process. The need for novel, straightfor-ward, eco-friendly extraction techniques to stop environmental damage in the mining industry led to the selection of molybdenum as targeted species. Indeed, at low pH, molybdate forms low charge density polyoxometalate species such as $Mo_{36}O_{112}^{8-}$, also known as Krebbs anion. $Mo_{36}O_{112}^{8-}$ has a low charge density and present superchaotropic characteristic. For this study, the following chemical system was used: molybdate and polyoxyethylene (10) oleyl ether (BrijO10®) surfactant in aqueous solution. The effects of pH and Mo and surfactant con-centrations on Mo extraction with foam and its spe-ciation were investigated by SAXS and Raman spec-troscopy. The objective was achieved as super-chaotropic flotation of molybdate by a non-ionic surfactant has been shown to be effective. Molybdate could also be selectively separated from tungstate and copper ions and a separation factor of 2 or 3 was achieved without any further optimization. Superchaotropic flotation appears to be an innova-tive method for the extraction and separation of metalate species and was recently extended to tungsten recovery from scheelite mining residues ($CaWO_4$). We have first successfully dissolved scheelite in a H_2SO_4-H_3PO_4 mixture keeping mild conditions to form the phosphotungstate $[PW_{12}O_{40}]^{3-}$ heteropolyoxometalate in solution and preventing the formation of insoluble tungstic acid. A multiparametric study including small angle scat-tering techniques allowed to assess dissolution kinetics under varying temperatures, acid concen-trations, and W:P ratios, optimizing conditions for $[PW_{12}O_{40}]^{3-}$ formation. The W-selective flotation process achieved nearly 100% extraction efficiency, separating superchaotropic species from calcium using non-ionic surfactants. This robust method enables mild leaching and sustainable tungsten recovery from complex ores, even in iron-rich conditions.

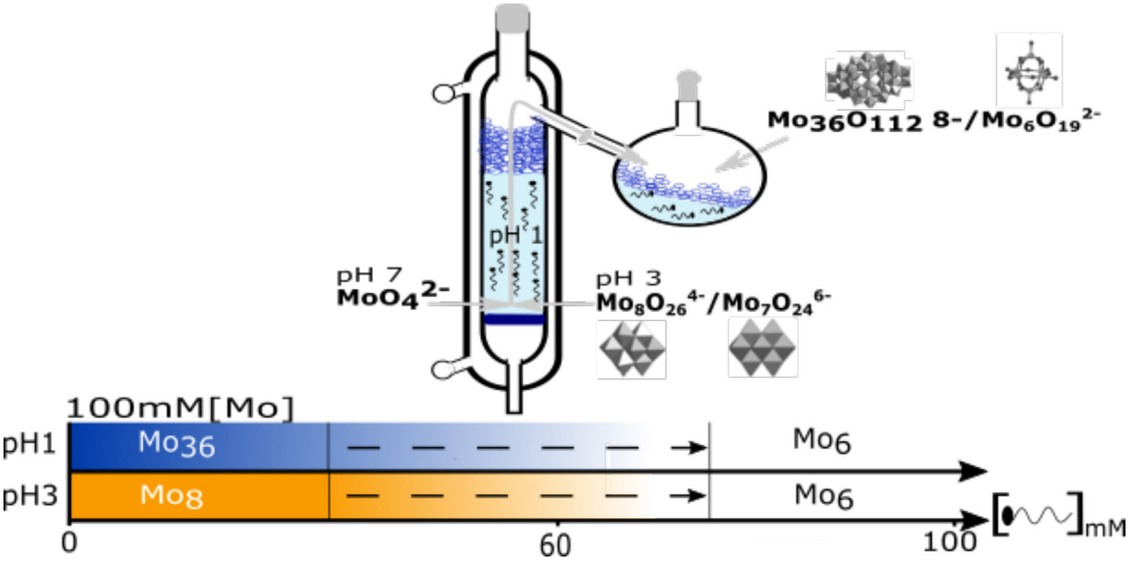

Figure. Extraction process of molybdate species by superchaotropic ion flotation (top). Change in the speciation of molybdate species upon addition of non-ionic surfactant. This change in the speciation is driven by the affinity and stabilization of the superchaotropic nano-ions with non-ionic surfactant.

FROM ELECTRONIC WASTE TO VALUABLE MATERIALS & CATALYSIS

M. Martin Romo Y Morales, D. Nikolaievskyi, A. Brunet-Manquat, D. Bourgeois, J. Maynadié – C. Contino-Pepin, F. Bonneté (Avignon Univ.) P. Wagner, M. Schmitt, F. Bihel (LIT, Strasbourg Univ.), F. Morfin, J.L. Rousset (IRCELyon), H. Kaper (St Gobain)

Catalysis is at the heart of most industrial processes, and extensive R&D efforts are directed towards the development of better performing catalysts. Pre-cious metals such as platinum group metals (PGM) take the lion's share of catalysed reactions because of their unique reactivity. However, their high prices make their applications often limited. One solution is the development of new catalysts based on cheaper transition metals, but complete substitu-tion remains a long-term challenge. Catalysts em-bedding PGM can be regenerated and recycled, and metals of interest recovered, re-purified, and used directly to produce new catalysts. But all these met-als are still coming initially from a natural ore deposit, and whatever the turnover of the recycling processes, stocks in metals decline – about 50% of the pre-cious metals contained in converters end-up in exhaust dust – and have to be supplemented, with-out mentioning new needs. A solution generally put forward in order to overcome the anticipated lack in natural resources is the exploitation of the so-called 'urban mine', i.e. our waste. This solution is especial-ly attractive in developed countries, since these 'consumers' societies generate lots of waste, and are poorly endowed with natural resources. For instance, waste of electric and electronic equipment (e-waste) have been described to contain in aver-age a 100 fold higher concentration in precious metals (gold, palladium…) than natural sources. Nevertheless, today, recycling of e-waste remains low, and only gold-rich fractions are valued, through the complete successive separation of all present metals, which necessitate intensive purification sequences. We recently demonstrated that it is possible to perform palladium-catalyzed reactions employing a pre-catalyst prepared from palladium(II) solutions mimicking those obtained during the processing of e-waste, bypassing all final isolation and purification steps. Such an approach shortens the e-waste processing scheme, and minimizes associated secondary wastes. [1]

Many catalytic processes using palladium rely on heterogeneous catalysts. We have started to address the preparation of palladium-based supported catalysts directly from e-waste, with total oxidation of methane and hydrogenation reactions as possible applications. This project is being developed in the frame a collaborative ANR project (CAREME). The aim of this work is not to develop new catalysts from a technological point of view, but to prepare and characterize palladium-based catalysts starting di-rectly from a waste, employing the shortest possible scheme to bring palladium contained in the waste into active catalyst.

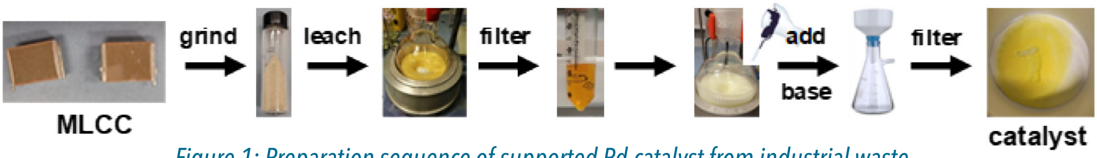

Figure 1: Preparation sequence of supported Pd-catalyst from industrial waste

First encouraging results were obtained on me-thane oxidation reaction, after the development of a suitable impregnation protocol directly from the leachate of industrial Pd-containing waste, which is a strongly acidic solution (Fig. 1). The precipitation-deposition technique is particularly suitable for the preparation of catalysts from acidic media. The impact of various metallic impurities on the catalytic performance was studied. Through variation of the pH, the impurities co-deposited with Pd could be limited and the catalytic performance of catalysts derived from real waste was greatly enhanced (Fig. 2). [2]

This strategy is currently under development at the LHYS, and nice results have been obtained in hy-drogenation reactions after changing the impregna-tion sequence: It is well known that palladium can be very active in hydrogenation reactions, but that this reaction is more sensitive to catalyst poisoning. The catalysts are currently prepared after palladium extraction in an organic phase, followed by deposition after impregnation on the catalyst support (alumina). The extraction allows the Pd to be isolated from the most impurity metals present in leachates except Ag and traces of Bi, depending on the extraction-stripping strategy applied.

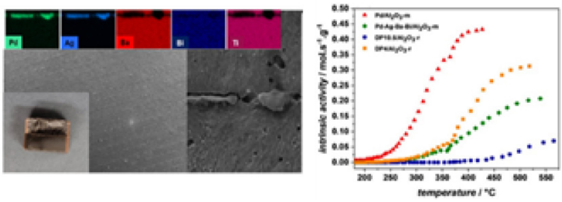

Figure 2: Activity of 1% Pd-Al_2O_3 catalysts prepared from waste in methane oxidation reaction

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ORGANIC RESINS AS SORBENT MATERIALS FOR METAL EXTRACTION

C. El Khoueiry, E. Lelong, G. Mossand, R. Oye Auke, F. Giusti, G. Arrachart, S. Pellet-Rostaing

The extraction of specific target species from industrial sources (such as mining deposits, desalination plants, and urban mining), nuclear effluents, or natural surface waters (including seawater and rivers) represents a critical challenge in the valorisation and recycling of strategic metals, as well as in decontamination processes. A variety of organic solids, notably chelating and ion-exchange materials, has been developed for selective ion separation by solid-liquid processes. The primary goal of this project was to synthesise novel chelating systems and subsequently produce specific resole-type phenolic resins. The covalent introduction of specific ligands into the resin's backbone, in conjunction with their intrinsic robustness, enhances selectivity towards target metals. This improvement is driven by the characteristics of the chelating agents, including their coordination sites and rigidity.

Thus, the objectives were twofold: first, to establish an efficient methodology for the preparation of these organic materials; and second, to deploy these materials in the solid-liquid extraction of selected metals.

Investigations focused more precisely on the synthesis of phenolic resins completely free of formal-dehyde, using nontoxic and potentially bio-based chemicals. By integrating particular ligands into the phenolic precursors, the resulting resin can be employed for the recovery of various strategic metals such as rare earths elements,[1] gold [2] or uranium, [3,4] as well as heavy metals, for instance mercury [5]. Owing to the versatility of this approach, sorbent materials can be implemented in multiple forms, including dense solids and foams. In addition, depending on the configuration of the cross-linked network, water-soluble polymers may also be ob-tained, enabling applications in filtration processes assisted by complexation.

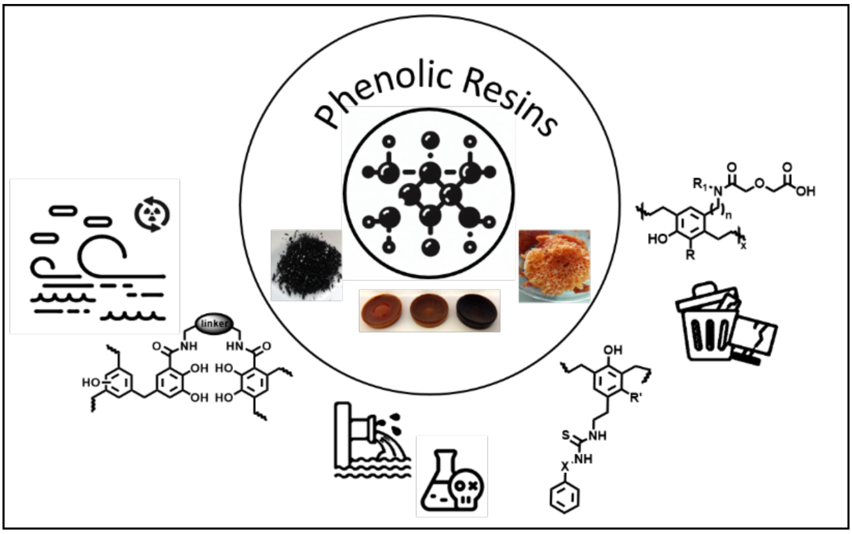

Figure. Application overview of phenolic resins.

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SONOCATALYTIC AND SONOCHEMICAL OXIDATION OF ORGANIC COMPOUNDS

T. Chave, S. El Hakim, R. Pflieger, M. Virot, S.I. Nikitenko

Water remediation and treatment of industrial wastewaters containing organic compounds such as carboxylic acids, dyes or complexing agents are today's topics and worldwide concerns. Several techniques appear promising for the treatment of such kind of aqueous effluents like advanced oxidation process (AOP) or wet air oxidation for more concentrated aqueous effluents. Sonochemistry is a promising approach that can be considered for water treatment since OH• radicals can be generated during water sonolysis. However, despite the extreme local conditions observed during acoustic cavitation phenomenon, and the generation of oxidizing and non-selective species, using ultrasonic irradiation alone is efficient only at low concentration in organic pollutants.

Following our work on the sonocatalytic degradation of EDTA in the presence of Co_3O_4-based catalysts (Thesis L. Parizot 2016-2019 PIA ANDRA), we recently focused in the degradation of the same molecule but in the presence of Ti or Ti@TiO_2 type catalysts prepared under sonohydrothermal conditions and also involved in photocatalysis generation of hydrogen (Thesis S. El Hakim 2018-2022).[1],[2] This study, carried out at high ultrasonic frequency in an Ar/(20%)O_2 atmosphere, showed that the activity of the Ti@TiO_2 catalyst for EDTA oxidation decreased as the TiO_2 layer increased. Thus, in contrast to the photocatalysis experiments, the Ti catalyst passivated under air, shows here the best activity for EDTA degradation and allows the complete defunctionalization of EDTA after 7 hours of ultrasonic treatment at 345 kHz as shown in Figure 1. This result is notable as it is close to that obtained for the Co_3O_4/TiO_2 type catalyst. However, unlike the Co_3O_4 system, which involved the Co^{3+}/Co^{2+} redox couple, suggested mechanism of EDTA sono-catalytic degradation involves two reaction path-ways: (i) sonochemical oxidation of EDTA by $OH•/HO_2•$ radicals in solution and (ii) EDTA oxida-tion at the surface of Ti^0 NPs in the presence of oxygen activated by cavitation event. Ultrasonic activation most probably occurs due to the local heating of Ti^0/O_2 species at the cavitation bub-ble/solution interface.

In addition to this sonocatalysis research, since 2022 we have been working with VALGO/SPUMA company on the degradation of specific contaminants such as PFAS (per- and polyfluoroalkylated substances) by sonolysis alone. Recent studies focused on the sonochemical degradation of these organic pollutants have shown that hydrophobic molecules are preferentially degraded not by radical attack, but by a pyrolysis process that takes place at the bubble-solution interface or even in the bubble core for short, non-amphiphilic chains. Due to the surface-active nature of PFAS, these compounds tend to accumulate at the bubble-solution interface and can thus be degraded by the local heating generated during cavitation bubble implosion (Figure 2). Degradation rates approaching 98-99% can be achieved at high ultrasonic frequencies without the addition of reagents or catalysts to the system. This work suggests that sonochemistry is a promising solution to the problem of degrading these so-called eternal pollutants.

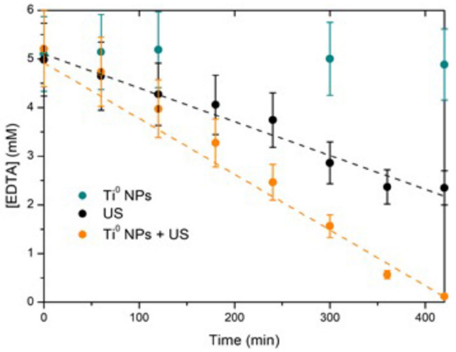


Figure 1. Evolution of EDTA concentration over time in presence of Ti^0 NPs (2 g/L) at 40 °C under Ar/(20%)O_2 with or without 345 kHz ultrasonic irradiation.

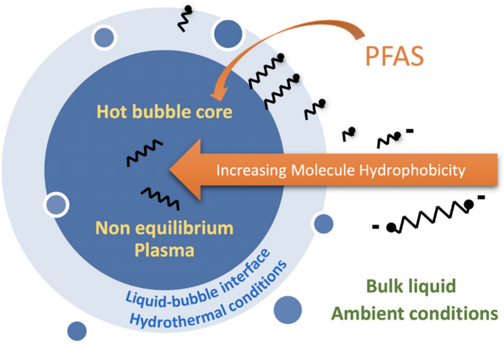
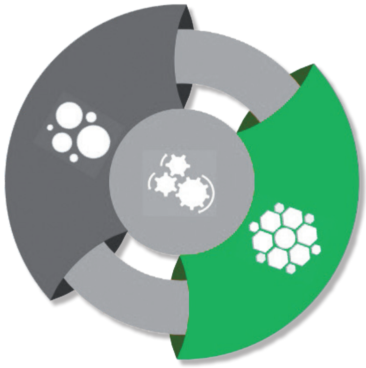


Figure 2. Schematic Representation of the 3 reaction zones of the cavitation bubble and the relative positioning of the organic molecules according to their hydrophilic-hydrophobic properties.

[1] El Hakim S., Chave T., Nikitenko S.I. - **Sonocatalytic degradation of EDTA in the presence of Ti and Ti@TiO_2 nanoparticles** - *Ultrasonics Sonochemistry* (2021) 70, 105336.

[2] El Hakim S., Chave T., Nikitenko S.I. - **Photocatalytic and Sonocatalytic Degradation of EDTA and Rhodamine B over Ti^0 and Ti@TiO_2 Nanoparticles** - *Catalysts.* (2021), 11 (8), 928.



LIFE-CYCLE OPTIMIZATION OF MATERIALS FOR ENERGY

OPTIMISATION DU CYCLE DE VIE DES MATÉRIAUX POUR L'ÉNERGIE

LIFE-CYCLE OPTIMIZATION OF MATERIALS FOR ENERGY

Via the understanding of the chemical and physico-chemical mechanisms linked to the evolution of liquid-solid and solid-solid interfaces in materials for energy production (nuclear and alternative).

OPTIMISATION DU CYCLE DE VIE DES MATÉRIAUX POUR L'ÉNERGIE

Via la compréhension des mécanismes chimiques et physico-chimiques en lien avec l'évolution des interfaces liquide-solide et solide-solide des matériaux pour la production d'énergie (nucléaire et alternative).

SYNTHESIS OF ACTINIDE OXIDE COMPOUNDS BY COMBUSTION SYNTHESIS PROCESS

Anna Hautecouverture, Cyrielle Rey, Julien Monnier, Xavier Deschanels
Paul Estevenon (DES/ISEC/DMRC CEA MARCOULE)

As part of the development of generation IV nuclear reactors, solution combustion synthesis is studied to convert actinide nitrates into a solid solution of actinide mixed oxides[1]. Solution Combustion Synthesis (SCS) involves the self-propagation of an exothermic reaction in a media composed of organic fuels (glycine, citric acid…) and a metal nitrate dissolved in water. After mixing, a thermal treatment leads to the dehydration of the precursors as a gel, finally the ignition occurs at very low temperature (~200°C) to produce the metal oxide powder. The fuel/nitrate ratio is a key parameter that changes the reactivity and flame temperature of the reaction. This ratio determines the characteristics of the powders obtained, namely the residual carbon content, the crystallinity, the specific surface and can induce a phase transition in the final oxide.

In a first stage, this reaction was employed with actinide substitutes. The conversion of $Gd(NO_3)_3$ to Gd_2O_3 with glycine and citric acid as fuel, was successfully obtained at low temperature (~210°C) about 200°C lower than that of a classical denitration reaction. Gd_2O_3 monoclinic phase powders with a high specific surface (10-20 m^2/g), a low amount of residual carbon and a good crystallinity were obtained.

Based on these results, studies on the conversion of actinides/lanthanides nitrates were done to obtain solids solutions of $UCeO_{2+x}$ and $U\text{-}PuO_{2+x}$. For these elements which have several redox states, different phases have been obtained depending on the fuel/nitrate ratio. For example, in the case of the citric acid (CA) and uranyl nitrate (U) system, the fluorine phase was obtained for $0.6<CA/U<0.7$ and a mixture of fluorine phase and U_3O_8 phase in variable proportions for $0.3<CA/U<0.6$ or $0.7<CA/U<1$. The origin of these structural changes has not yet been clearly established, it is likely that they result from a combination of the temperature reached and the gases produced by the thermal decomposition of the precursors (NH_3, CO/CO_2) which set the operating redox conditions. It was also possible to obtain powders of solid solution $U_yPu_{1+y}O_{2+x}$ by SCS reaction for $0.9<y<0$. Post-treatment under a reducing atmosphere was necessary to obtain stoichiometric compounds. The powders obtained have a porous morphology.

Sintering at 1600°C under reducing conditions ($Ar/5\%H_2$) of SCS uranium oxide and uranium-cerium oxide powders was carried out. The pellets have a high density (>90%) and good microstructural characteristics (grain size less than 10 µm).

To conclude, the synthesis by combustion in solution allows an easy conversion of actinide nitrates into oxides. The solid solutions obtained by this route have good chemical homogeneity over a wide range of composition (eg, $U_yPu_{1+y}O_{2+x}$ $0.9<y<0$), a low residual carbon content ($C<0.1\%$ for CA-U sys-tem). These characteristics are interesting for the fabrication of MOx fuels. The sinterability of the powders requires further studies.

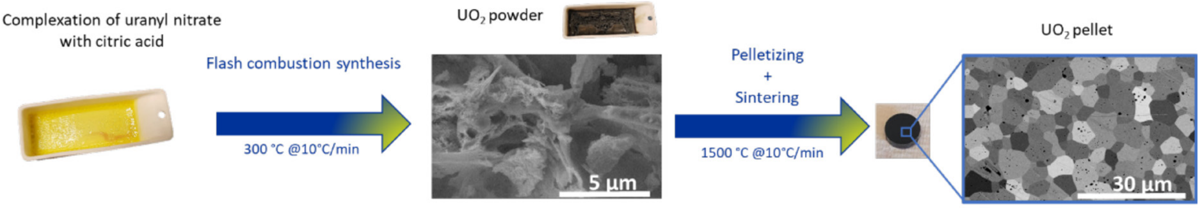


Figure 1. Uranyl nitrate / UO_2 conversion by solution combustion synthesis

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LONG-TERM BEHAVIOUR OF MODEL SPENT FUELS IN WET CONDITIONS

T. Montaigne, A. Perrot, S. Szenknect, L. Claparède, R. Podor, X. Legoff, J. Lautru, N. Dacheux.
In collaboration with CEA DES/ISEC/DPME

The behaviour of model compounds of spent nuclear fuel in interim storage and geological disposal represents a novel research area for the LIME, as evidenced by its involvement in the European projects EURAD and EURAD 2. The stage of storing fuel in cooling pools constitutes a pivotal phase within the fuel cycle. The storage time for MOx $(U,Pu)O_2$ spent fuels is considerably longer than for UOx fuels, owing to their significantly slower cooling rate. During this stage, exposure of the fuel to the pool water is prevented, except in the event of a cladding rupture. A thorough examination of this accident scenario is imperative to mitigate the radiological consequences. In this context, the study carried out at LIME investigates the weathering mechanisms under interim wet storage conditions of several model materials simulating the heterogeneous microstructure of MOx fuel. Specifically, a series of leaching tests were conducted at temperatures of 50°C or 70°C, in the presence of boric acid (2500 ppm, pH =5) and potentially lithine (LiOH) as a pH buffer, over periods reaching up to 1300 days. Concurrently, the evolution of the surface of the materials was monitored operando by MEBE to identify the presence of preferential dissolution zones and the precipitation of secondary phases. The results obtained demonstrated the impact of the presence of platinum group metals and lanthanides fission products on the materials' alteration mechanisms.

While reprocessing of spent fuel is the reference scenario in France, the direct storage of irradiated MOx remains an option under study. However, the mechanisms and kinetics of oxidative dissolution of MOx, as well as the role of species present in the groundwater at the Cigéo site, remain to be eluci-dated. In order to gain a more profound understanding of these mechanisms, experiments were con-ducted on the alteration of non-irradiated MOx fuels (CEA Marcoule - DPME collaboration) and $(U,Ce)O_2$ model materials with a controlled microstructure. First, experiments were conducted on the alteration of $(U,Ce)O_2$ materials in the presence of H_2O_2.[1] Secondly, the specific role of calcium and silicate ions was studied through alteration experiments in solutions of simplified compositions involving the two categories of materials. Figure 1. Studtite precipitation at the surface of UO_2 grains in a heterogeneous $(U,Ce)O_2$ model material.

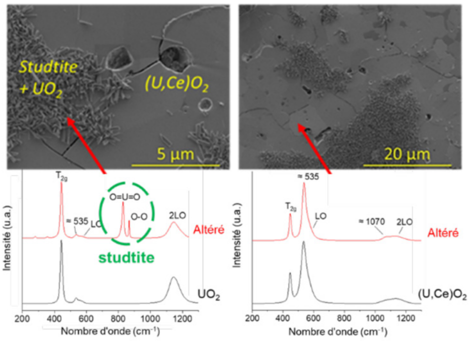

Figure 1. Studtite precipitation at the surface of UO_2 grains in a heterogeneous $(U,Ce)O_2$ model material.

A notable finding of this study is the remarkable analogy observed between the behavior of Ce and Pu under oxidizing dissolution conditions. In the presence of H_2O_2, a significant decrease in the rate of alteration of homogeneous $(U,Ce)O_2$ solid solutions was observed as the cerium content increased. This phenomenon was attributed to the formation of a cerium (IV)-rich passivating layer, as evidenced by XPS analyses of the surface of the altered materials (CEA Saclay - DRMP collaboration). The alteration of the heterogeneous model material in the presence of H_2O_2, the primary product of alpha radiolysis of water, resulted in the precipitation of studtite $(UO_2(O_2)\cdot 4H_2O)$ located exclusively on the surface of the UO_2 matrix and not on the cerium-rich zones (Figure 1). Concurrent findings had previously been obtained with MIMAS MOx.[2]

In order to gain a better understanding of the mechanisms by which studtite is formed on the surface of UO_2, original experiments were designed (Figure 2). Alteration tests on UO_2 in the presence of H_2O_2 were combined with monitoring of the stud-tite precipitation reaction under radiolysis by iso-tope exchange using, on the one hand, labelled solutions of $H_2{}^{18}O$ and, on the other hand, labelled $U^{18}O_2$ synthesised at LIME [3].

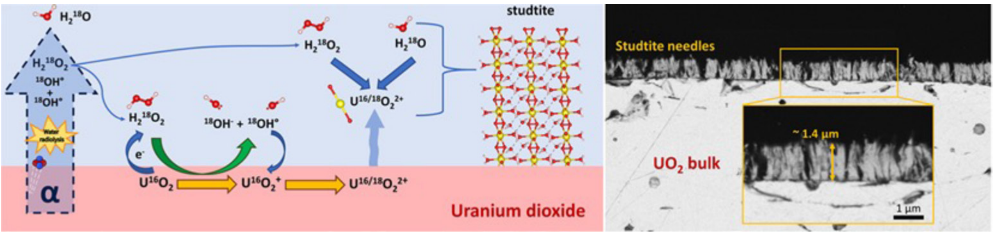

Figure 2. Mechanism of studtite $(UO_2(O_2)\cdot 4H_2O)$ formation at the UO_2-water interface under alpha radiolysis.

[1] Montaigne Th., Szenknect S., Broudic V., Imbert Ph-H., Tocino F., Martin Ch., Miserque F., Jégou Ch., Dacheux N. -**Oxidative dissolution of $(U,Ce)O_2$ materials in aqueous solutions containing H_2O_2**- *npj Materials Degradation* (2023) 7, 34.

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DESIGN AND ADVANCED CHARACTERIZATION OF MODEL COMPOUNDS FOR FRESH & SPENT NUCLEAR FUELS

Th. Barral, L. Callejon, M. Fulchiron, Ch. Hours, M. Husainy, Th. Kaczmarek, M. Massonnet, L. Claparede, S. Szenknect, N. Dacheux, N. Clavier - In collaboration with CEA/DES/DMRC and CEA/DES/DEC

MOx fuels have a heterogeneous microstructure resulting from their manufacturing process. This microstructure is characterized by the coexistence of several solid solutions $(U,Pu)O_2$ with varying plutonium content. After irradiation, the fission reactions undergone during the reactor life lead to an even more complex solid. The various fission products (FP) can be found dissolved in the initial solid solution (particularly lanthanides), but can also form metal precipitates (platinum group elements: Pt, Rh, Rd, etc.) or oxides (Mo, Ba, etc.). Studying the fabrication and the sintering of model compounds is thus of paramount importance in order to (i) high-light the relationships between the powder preparation route, the heat treatment conditions and the final microstructure during the manufacture of fuel materials, and (ii) prepare compounds that reproduce all or part of the characteristics of irradiated fuels.[1]

The fabrication of model compounds of current MOx fuels has been studied using the $(U,Th)O_2$ system, with thorium being used as a Pu(IV) simulant. Heterogeneous pellets were obtained by mixing several homogeneous powders of $U_{1-x}Th_xO_2$, which enabled the preparation of a panel of samples with a matrix-inclusion microstructure, similar to those of real fuels.[1]

$U_{1-x}Ce_xO_{2+\delta}$ solid solutions were also studied in the frame of the H2020 GENIORS project, in particular to highlight the effects of the atmosphere and cerium content on densification and final microstructure of more homogeneous fuels for fast neutron reactors. Dilatometric studies showed that while the cerium content only slightly alters sintering under Ar/H_2 atmosphere, the densification kinetics are signifi-cantly altered under argon, leading to less densified samples with larger grains.[2] These changes were correlated with the variation in the final O/(U+Ce) stoichiometry[3] (HERFD-XANES measurements at Soleil/MARS beamline) and illustrated by the construction of sintering maps.

A similar methodology was also used in the prepara-tion of compounds simulating simplified irradiated fuels. The $U_{1-x}Nd_xO_{2\pm\delta}$ system made it possible to address the incorporation of fission products from the lanthanide family into the structure of UO_2.[4] A reducing sintering atmosphere (Ar/H_2) prevented the oxidation of uranium (IV) at high temperatures, which was observed under argon, leading to the transient formation of U_3O_8. As previously, the use of argon resulted in an average grain size ten times larger than that obtained in a reducing sintering atmosphere, while macroscopic properties such as relative density, porosity, and cation distribution homogeneity remained unchanged. However, detailed characterization of the grain boundaries by TEM showed a slight local enrichment in Nd for samples prepared under Ar/H_2.

Finally, samples with secondary phases typical of certain fission products were prepared. In the case of molybdenum, which is one of the main PFs formed, XRD analyses indicate that Mo has almost negligible solubility in the UO_2 structure. SEM, TEM, and EDX characterizations of the UO_2 + Mo pellets produced reveal that molybdenum is present in the form of nanometric metallic particles with a spherical geometry.[5] The addition of molybdenum also ap-pears to play an inhibitory role in the growth of UO_2 grains during sintering. Similar samples were also obtained with other metal fission product simulants, including Ru, Rh, and Pd.[6]

These studies have therefore improved our understanding of the mechanisms governing the for-mation of the microstructure of samples during the sintering stage, in particular by highlighting the links between the redox chemistry of uranium and grain growth. They have also made it possible to produce samples with microstructures very similar to those of real new or spent nuclear fuels that can be used in further studies including dissolution tests.

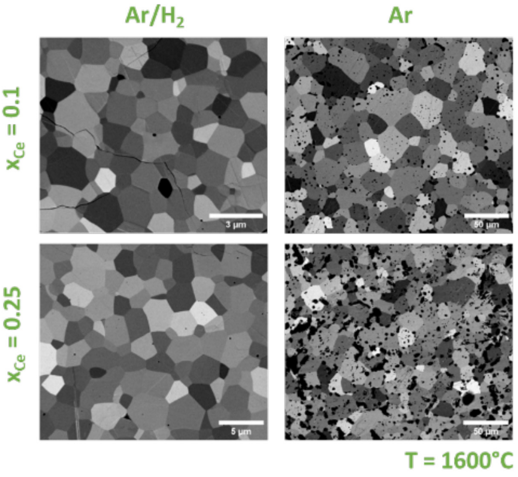

Figure 1. SEM observation of the microstructure of $U_{1-x}Ce_xO_{2+\delta}$ ceramics for different sintering atmosphere.

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[1] Hours C., Claparede L., Reynier-Tronche N., Viallard I., Podor R., Dacheux N. -**Dissolution of $(U,Th)O_2$ heterogeneous mixed oxides**- *Journal of Nuclear Materials* (2023) 586, 154658.

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NUCLEAR GLASSES : WEATHERING GEL BEHAVIOR UNDER IRRADIATION AND OTHER ASPECTS

P. De Laharpe, J. Soule, C. Rey, B. Siboulet, J.M Delaye, H. Arena, G. Jouan (DES/DE2D/LMPA CEA MARCOULE), X. Deschanels

Borosilicate glasses were chosen in France as wasteform for high-level radioactive waste, to be used in the CIGEO deep geological repository. They are designed to accept high loads of radionuclides while maintaining chemical durability. However, due to the considerable time scale at which they must perform (up to several hundred thousand years), longterm weathering is bound to occur, with the two main sources of damage being the self-irradiation of the package and the aqueous corrosion of the glass. Several decades of thorough investigation on simplified and complex compositions have uncovered the central aspects of nuclear glass aqueous alteration. In a typical aluminoborosilicate glass, the most soluble species are diffused out of the glass while the rigid network is hydrolyzed and reorganized in a gel-like altered layer called alteration gel. Over time, the slow maturation of the gel leads to the formation and morphological evolution of a nanometer-scale po-rous network, correlated with changes in water transport properties. Regarding self-irradiation, and despite the intrinsic resistance and self-healing properties of a vitreous network to radiation damage, the accumulation of deposited energy inside nuclear glasses can trigger certain effects when coupled with aqueous alteration. It has already been demonstrated, for instance that a pre-irradiated nuclear glass will be altered faster in the presence of water, accelerating pore formation and progression of the altered layer. Conversely, recent *in-situ* TEM experiments on already-formed gels showed that the porous structure can collapse when irradiated with a Xe ballistic beam. Similar behaviors have been reported across a wide spectrum of projectile energies, investigating the radiation-induced pore collapse in ordered mesopo-rous silica MCM-41 and SBA-15. The similarity between those materials suggest that mesoporous silica could serve as model materials to better understand this latter phenomenon occurring in gels. Hence, among several parameters that require investigation to bridge the two situations, both the influence of hydration prior to, and during irradiation, of mesoporous silica have been studied in the past two years[1], during the PhD of P. de Laharpe.

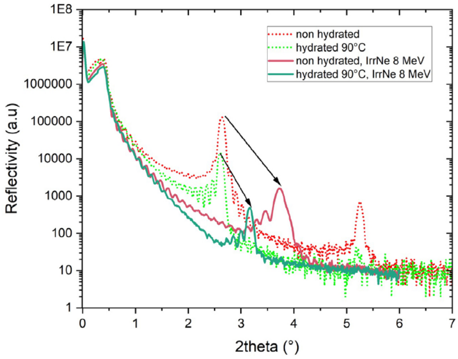

Figure 1. XRR profiles of MCM41-type thin films irradiated with Ne, 8 MeV at 1,8.1014 ions.cm^{-2}

In a first set of experiments, high-temperature (pH=7, 90°C in saturated conditions) leaching of mesoporous silica was performed before careful washing and drying. Structures were characterized in XR Reflectivity and FTIR, and samples were irradiated in the electronic regime with swift heavy ions (Ne, 8 MeV) at various fluences, along with non-hydrated ones. XRR profiles of hydrated samples compared to non-hydrated ones, clearly displayed a slower collapse of the porous structure (Figure 1). This was further confirmed by characterization of some of the samples in gas adsorption ellipsometry, indicating that the leached structure can sustain more damage before collapsing. Experiments elucidating the influence of water presence are conducted in Molecular Dynamics. Indeed, displacement cascades can reliably reproduce the ballistic damage of low-energy projectiles, whereas real-world irradiation experiments are performed in vacuum and a sealing screen would stop the projectile. Irradiations are simulated as follows (Figure 2):
i) A unit cell of mesoporous silica is simulated with periodic boundary conditions, in presence or absence of water. ii) Si atoms are randomly picked, changed to heavier atoms, accelerated to 1.2 keV (the energy is chosen to fit the dimensions of the simulation box) and retransformed to Si at the end of the simulation. iii) When 100 such displacement cascades have been simulated, a free-volume relaxation simulation is performed to let the porous network adjust to the structural damage. In a dry cell a mechanism similar to sintering is induced by the cascades, leading to a rapid pore closure consistent with experimental data. While these experiments are still being computed, early results suggest that new mechanisms take place when pores are (even partially) filled with water, such as radiation-assisted dissolution or hydration swelling, yielding volume changes significantly different from the dry situation.

The solubility of actinides (U, Pu) in nuclear glasses is another subject studied in the laboratory as part of J. Soule's thesis, which has just started. The aim of this work is to verify the containment qualities of a U- and Purich glass, produced from aqueous solutions generated by R&D studies at the Atalante facility, compatible with final disposal at CIGEO.

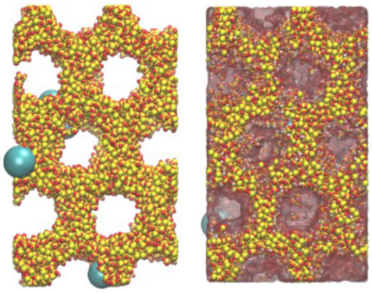

Figure 2. Left: the dry cell after a serie of 100 projectiles (-3.2% vol.). Right: the wet cell after a series of 100 projectiles (+1.7% vol.)

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[1] Laharpe, Pierre de, Xavier Deschanels, Jun Lin, Sylvain Peuget, Helene Arena, Melanie Taron, et Clara Grygiel. « **Exploring the combined effects of water immersion and ion irradiation on mesopo-rous silica** ». MATERIALS LETTERS (2024) 371 :136791

RADIATION EFFECTS IN MESOPOROUS MATERIALS

Jun Lin, Cyrielle Rey, Guillaume Toquer, Jérémy Causse, Sandrine Dourdain, Aya Azeddioui, Pierre de Laharpe, Xavier. Deschanels

The behavior of mesoporous materials under radiative stress raises special issues that have yet to be fully explored. These materials have in common with nano-materials a very high interfacial surface area, and a radius of curvature of the interfaces in the nanometer range, which can lead to accelerated damage or, conversely, to self-repair the damage area. Several studies have shown that nanomaterials exhibit increased resistance under these extreme irradiation conditions. It is likely that this is linked to the "annihilation" of irradiation defects on the material's interfaces, which constitute favorable zones for their recombination. To give an order of magnitude, a displacement cascade has a characteristic volume of around ten nm^3 , which is comparable to that of a mesoporosity. To address this question, thin films of mesoporous silicas less than 100 nm thick, deposited on a silicon substrate, with pores around 4 nm in diameter, were irradiated with ions C-0.98MeV/A, Ca-9.17MeV/A, Ar-0.98 MeV/A, Ni-0.57 MeV/A, Xe-0.71 MeV/A, Au-0.5 MeV. These films exhibit an organized porous network, enabling their damage to be monitored by X-ray reflectivity. Mesoporous silica pellets of the SBA15 type (dpore~7nm) were also irradiated with electrons of energy between 0.5 and 2MeV. In this case, damage and related pore volume variation were measured by gas adsorption (BET, BJH method) and SAXS. Despite the very different conditions used for these irradiations, densification of the pore network was observed in all cases[1]. For thin films[2], this process starts at a deposited energy of around $3x10^{21}$ keV/cm^3 and can reach complete densification at an energy of 3x1022 keV/cm^3. Densification is observed at comparable energies for pellets irradiated with electrons[3,4]. These different irradiation conditions correspond to quite distinct physical energy deposition processes: ballistic effects inducing a high atomic displacement rate in the case of Au irradiation, electronic effects inducing the formation of a cylinder of defects in the wake of the ion in the case of irradiation with high-energy ions, and finally radiolytic effects in the case of electron irradiation. At present, there is no global mechanism to explain these evolutions, and this point remains to be investigated.

Internal irradiations associated with the use of Pu doped mesoporous silica completed this study. This study was developed within the framework of ANR Automact. To achieve this, SBA15 mesoporous silicas were grafted with phosphonic ligands[5]. These samples were brought into contact with an aqueous solution containing 120 ppm plutonium at pH~0.3. After a few hours of exchange, equilibrium was reached, leading to approximately 10% mass Pu binding to silica. These tests were carried out with two Pu solutions, one containing mainly ^{239}Pu and the other ^{238}Pu. The material obtained after sorption of ^{238}Pu is used to study the impact of irradiation damage, given the relatively short half-life of this isotope, while the other material (doped with ^{239}Pu) is used as a referen

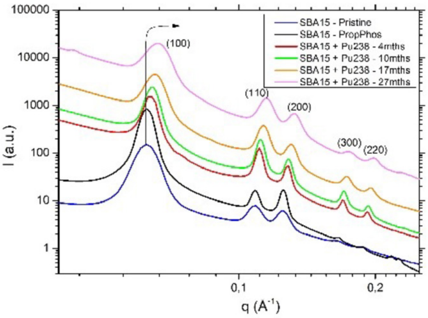

Figure 1. SAXS measurements carried out at different times after 4 to 27 months of ageing highlight the shift in structure peaks corresponding to densification of around 10% by volume after 27 months.

These samples were then analyzed using the small-angle X-ray scattering (SAXS) technique on the Mars line of the Soleil synchrotron at different timescales (0-4-10-17-27 months). The results show a reduction of around 10% in the unit volume of the silica hexagonal pattern for the sample doped with ^{238}Pu, compared with less than 1% for its counterpart doped with 239Pu (Figure 1). This result suggests the possibility of closing the mesoporosity of a silica and, ultimately, encapsulating a radionuclide by radiative effect (Figure 2).

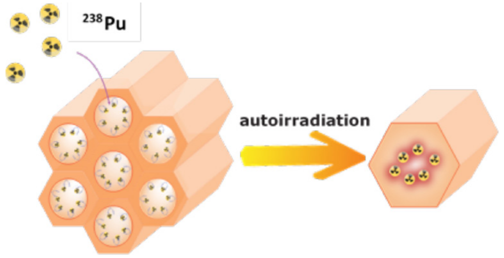

Figure 2. Schematic diagram of self-irradiation densification of ^{238}Pu-doped SBA15 mesoporous silica.

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FROM ACTINIDE SILICATES TO PHASES OF INTEREST OF CORIUM

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Each step in the nuclear fuel cycle (including the front-end and back-end phases) involves chemical processes governed by thermodynamics. Understanding the behavior of actinides in these processes relies on thermodynamic calculations which require well-constrained thermodynamic data. However, thermodynamic data are lacking for many phases containing actinides. In order to determine consistent sets of thermodynamic data, the ICSM, in collaboration with UC Davis and then with Washing-ton State University, developed a methodology based on the preparation of single-phase samples, followed by the combination of solubility measurements with molten oxide solution calorimetry to access thermodynamic data.

This methodology has been successfully applied to several silicate phases containing actinides (Figure 1), for which optimized hydrothermal synthesis conditions were first determined by varying several experimental parameters : pH of the starting mixture, ligand concentrations (including carbonate ions), reagent concentrations, temperature and duration of thermal/hydrothermal treatment, redox conditions, etc… For thorium, two sets of optimized conditions allowed the formation of $ThSiO_4$ (in an acidic medium without complexing agents and in a weakly basic medium in the presence of large amounts of carbonate ions). For uranium, only weakly basic carbonate media allowed the formation of $USiO_4$ coffinite.

For cerium, the conditions for the formation of pure $CeSiO_4$ were only achieved starting from Ce(III) (in solution or as a solid precursor of Ce(III)) under very strict conditions in terms of pH, concentrations and temperature. This made it possible to determine the associated thermodynamic data[1]. The four optimized protocols were applied to the plutonium system in the hot laboratories of the ATALANTE facility.

As the synthesis conditions for the formation of $PuSiO_4$ are very similar to those obtained for $CeSiO_4$ [1], it can be concluded that cerium is the best substitute for plutonium in silicate-rich environments.

At the same time, the optimal conditions for the synthesis of hafnon HfSiO4 and zircon $ZrSiO_4$ were defined. These studies showed that the conditions for the formation of $ZrSiO_4$, $CeSiO_4$ and $USiO_4$ are largely incompatible. However, solid solutions of chernobylite $(Zr,U)SiO_4$ have been reported in the lava formed after the Chernobyl NPP accident[2]. In order to verify the stability of the solid solutions $(Zr,U)SiO_4$ and $(Zr,Ce)SiO_4$, the conditions of zircon synthesis were applied. This resulted in the preparation of pure solid solutions with concentrations up to 60% of each substitutional element (Ce,U)[3,4]. These materials are now of strong interest for the determination of several thermochemical and thermophysical properties and for the better description of the ternary phase diagrams ZrO_2-UO_2-SiO_2 and ZrO_2-CeO_2-SiO_2.

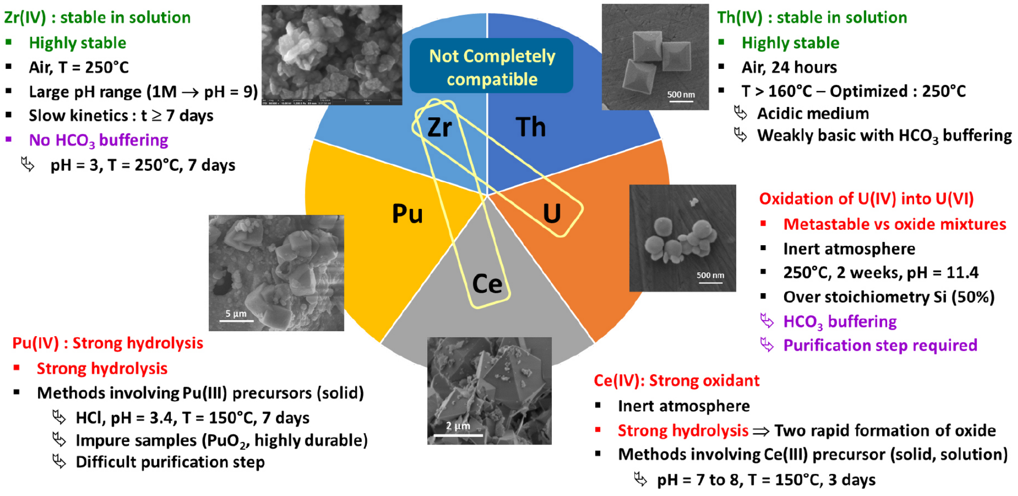

Figure 1. Optimized conditions of formation and morphology of $MSiO_4$ samples (M = Zr, Ce, Th, U, Pu).

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HYDROTHERMAL CONVERSION OF AN CARBOXYLATES

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In collaboration with CEA/DAM/SRCE, CEA/DES/DMRC, IAEA/Safeguards Analytical Services and Orano

Innovative methods for oxide fuels preparation are frequently based on wet-chemistry routes, involving the precipitation then the calcination of crystallized precursors. Despite the advantages of these methods, the resulting oxide powders suffer from some drawbacks, including morphology poorly adapted to sintering, and residual traces of carbon in the final samples. In order to avoid these potential issues and to get rid of the thermal conversion step, we investigated the use of hydrothermal conditions to convert tetravalent actinides bearing carboxylates and directly achieve actinide dioxide precipitation from solution.

While our initial work focused on the hydrothermal conversion of simple An(IV) oxalates (with An(IV) = Th or U), the study was extended to $U_{1-x}Ce_xO_2$ solid solutions, with Ce being used as a substitute for plutonium[1]. At 250°C, the conversion of mixed U(IV)/Ce(III) oxalates is quantitative between pH = 2 and 10, with the acidity of the medium influencing the morphology of the oxides. The conversion is also congruent and complete after 2 hours of treatment, with the cationic homogeneity of the oxides remaining unchanged thereafter. The hydrothermal conversion mechanism is complex, involving several redox reactions and inducing a change in the valence of uranium, which corresponds to oxidative dissolution followed by reductive precipitation.

From this observation, the hydrothermal conversion of a solution containing uranium(VI) and oxalate ions was undertaken as a simplified model of the U(VI)-M(IV) system. We demonstrated that hydrothermal conditions allowed, under defined conditions, complete reduction of uranyl ions to $UO_{2+\delta}$ by oxalates[2]. This reaction was monitored in situ by X-ray absorption spectroscopy on the FAME beamline at ESRF, using an original device. Hydrothermal conversion of actinide oxalates into oxides is then an extremely versatile tool that can be implemented in a large variety of chemical systems. Additionally, the first studies dedicated to the sintering of the powders obtained revealed a good densification ability[3]. The sintering map of different uranium oxide samples presenting various morphologies was established and paves the way to the control of the microstructure of final pellets.

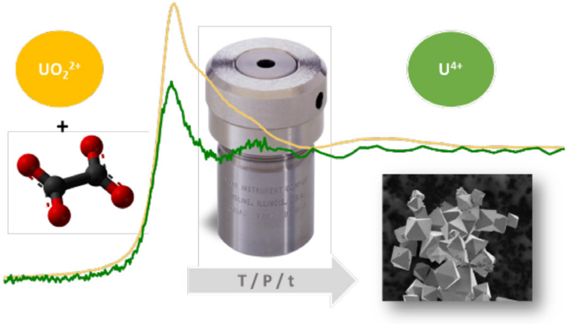

Figure 1. Hydrothermal conversion of uranyl oxalate into UO_{2+x} unraveled by in situ XANES.

Similar methodology was used to study the hydrothermal conversion of An(IV) aspartates (An(IV) = Th, U), with the aim to develop an original and versatile wet chemistry route to AnOx reference materials, to be used in isotopic measurements of nuclear materials. Indeed, the detec-tion and the measurement of the isotopic composition of nanometer- to micrometer-sized particles provide are currently a key tool for safe-guards verification by the International Atomic Energy Agency (IAEA). Because of the low number and extremely small size of the particles of interest, particles analyses are always an analytical challenge, which requires reference materials representative of the analyzed samples. Such materials are typically actinide oxide particles with well-known sizes, densities and isotopic compositions, which could be used for optimization and qualification of analytical methods and instruments.
With this aim, uraniumthorium mixed oxide microspheres were synthesized through the hydrothermal conversion of aspartate precursors[4]. This latter was performed at T = 160°C and led to mixed dioxide micro-particles with controlled spherical morphology and size, up to 5 mol.% in thorium. In order to remove impurities, densify the microparticles, and control the chemical form of the final compounds, heat treatments were performed under various atmospheres. Nearly stoichiometric $(U,Th)O_2$ dioxides were obtained under reducing conditions (Ar-4%H2) while U_3O_8-based samples were formed under air, with thorium incorporated in the structure up to 2 mol.%. Last, the homogeneity of the cation distributions was evaluated by LG-SIMS analyses of individual particles. It led to consistent results, which paves the way to use these mixed oxide particles in the field of nuclear safeguards. The chemical durability of these particles was also studied to evaluate their stability when stored as a suspension[5].

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SEPARATE EFFECT STUDIES OF MODEL SPENT NUCLEAR FUELS REPROCESSING

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In collaboration with CEA DES/ISEC/DMRC

Spent nuclear fuel contains multiple fission products with a complex multiphase microstructure. In order to better understand its behavior during reprocessing, an approach using different model compounds (Figure 1) has been implemented to discriminate the impact of different parameters related to both the solid and the solution.

In fission products, platinum group elements (Ru, Rh, Pd) and molybdenum can impact reprocessing in nitric acid. These fission products occur as metal precipitates in the UO_2 matrix. Part of the research explores how these elements influence fuel dissolution during reprocessing. Model compounds based on UO_2, containing 3% of these elements, were prepared and subjected to dissolution experiments in more or less aggressive nitric environments. The results highlighted a change in the dissolution mechanisms, thus affecting the speed and process of UO_2 dissolution[1]. Molybdenum, in particular, plays a key role due to its complex speciation in irradiated fuel. Experiments show that its oxidation state (0, +4, +6) significantly influences dissolution, with important implications for the optimization of the PUREX process. Model compounds with different molybdenum phases have been used to identify phase-specific dissolution mechanisms and to evaluate their effect on the chemical durability of the fuel.

The incorporation of trivalent lanthanides into the UO_2 matrix has also been studied to understand their effect on dissolution in nitric media. $U_{1-x}Ln_xO_{2\pm y}$ compounds have been studied, showing that the presence of lanthanides slightly increases the dissolution rate compared to the results obtained on $Th_{1-x}U_xO_2$[3]. The sintering conditions, and in particular the atmosphere used (Ar or Ar/H_2), influence the microstructure and oxygen stoichiometry of the compounds prepared and, consequently, the dissolution kinetics. Operando monitoring revealed that dissolution is mainly concentrated at the grain boundaries in pellets sintered under a reducing atmosphere, while it is more homogeneous in those sintered under an inert atmosphere[4]. Similar behavior was observed for $U_{1-x}Ce_xO_{2\pm y}$ compounds.[5]

In fast neutron reactors (FNR-Na), MOX fuels exhibit microstructural heterogeneity marked by plutonium-rich zones that are resistant to dissolution. Another line of research examined the evolution of these heterogeneities during dissolution experiments using thorium as a plutonium simulant. The results show selective dissolution of uranium-rich zones and the formation of insoluble residues from thorium-rich zones, complicating reprocessing[6]. In addition, monitoring the evolution of the solid/solution interface during alteration made it possible to quantify the evolution of the reactive surface, which is specific to compounds with heterogeneities.

This research thus provides a better understanding of dissolution mechanisms, which is crucial for improving the reprocessing and recycling of different types of spent nuclear fuel.

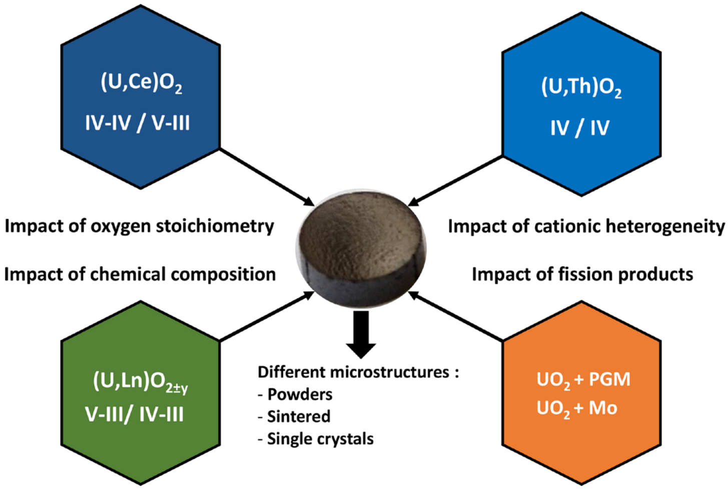

Figure 1. Diagram showing the different systems studied as part of the study on spent fuel reprocessing.

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SONOCHEMICAL DECONTAMINATION OF SOLID SYSTEMS

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N. Sleiman, L. Hallez, J.-Y. Hihn (Utinam, Besançon; IRT M2P)

For the past ten years, the LSFC has been studying the behavior of massive materials (oxides, Mg, Al, stainless steel, glass, c-Si, etc.) under the effect of acoustic cavitation. In the nuclear field, the decontamination of metal surfaces is of great interest for the dismantling of nuclear installations and equipment that have reached the end of their life. The development of a device allowing the study of the behavior of massive materials under ultrasonic irradiation has demonstrated that metal surfaces artificially polluted by Ce, Sr, or U can be efficiently decontaminated in dilute solutions at ambient temperature and pressure. Decontamination factors were quantified and are sufficient for potential applications on a larger scale.[1]

The evolution of the Mg surface under US irradiation was studied at different frequencies, including at 3.6 MHz in focused configuration (HIFU), in the framework of a collaboration with UTINAM supported by IRT-M2P.[2] The use of frequency wobbling that makes it possible to either enhance or quench cavitation allowed to distinguish the contributions of cavitation-induced erosion and wave propagation.

The contribution of ultrasound in decontamination is also verified for dispersed solids such as soils, and is studied within the framework of a collaboration with CEA/DES/DMRC/STDC/LPSD. As part of her thesis, Sophie HERR (2019-2023) studied the decontamination under US of a simplified simulant of contaminated soils from Fukushima (a vermiculite artificially contaminated with Cs). In this type of clay, cesium is trapped between the layers of vermiculite, and decontamination generally requires combining ion exchange (using high concentrations of Mg^{2+}) and high temperatures (hydrothermal conditions).[3]

It has been shown that ultrasound can improve desorption kinetics by an order of magnitude, as well as increase desorption yields.

This ultrasound-washing combination is also effective in accelerating soil decontamination kinetics and increasing yields, at least under carefully selected conditions (Figure 1).[4] First results were obtained by Sophie HERR (2019-2023) on vermiculite contaminated with zinc and nickel: low frequency US (20-50 kHz) appears to create new sorption sites and leads to transfer of the contamination to more available sites. On the other hand, high frequency US (360 kHz) leads to transfer of the contaminant from less accessible fractions to more accessible ones.

Following this study, Rita SALAMEH's (2023-2026) thesis, supported by the Occitanie Region, focuses on the decontamination of real soils contaminated with copper, zinc and nickel.

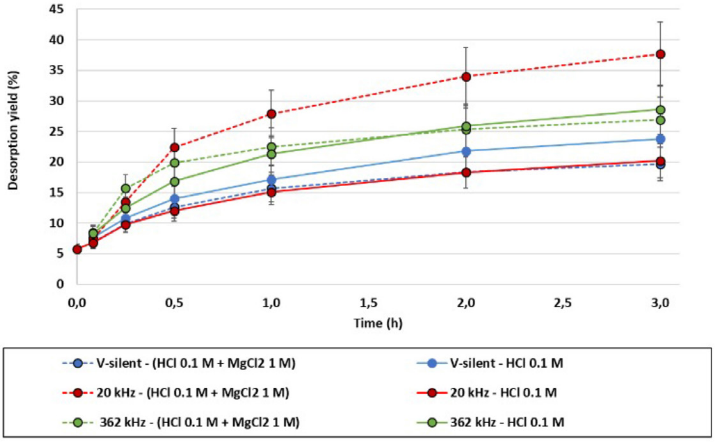

Figure 1. Ni desorption kinetics from polluted vermiculite –vermiculite mass to acid volume ratio set to 20 g.L^{-1}, HCl concentration to 0.1 M and $MgCl_2$ concentration to 1 M. (a) Desorption in silent conditions; (b) desorption at 362 kHz; (c) desorption at 20 kHz.

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SILICOTITANATES FOR STRONTIUM REMOVAL IN A CONTINUOUS PROCESS

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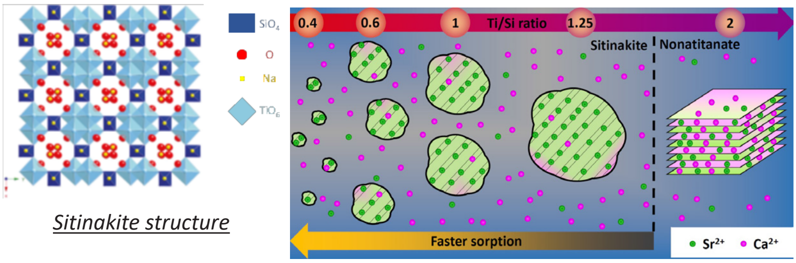
Nuclear fuel reprocessing generates contaminated aqueous outflows after liquid-liquid extraction of uranium and plutonium through Purex process. These outflows contain a wide range of minor actinides and fission products and must be treated. Most of these radionuclides are separated from aqueous medium thanks to a precipitation in alkaline medium but some of them remain in solution, just like ^{137}Cs and ^{90}Sr. While treatment solutions exist in the case of Cs, others must be implemented in the case of Sr. Crystalline silicotitanates such as Sitinakite are promising materials due to the selective capture of Sr with regard to Ca. Sitinakite is an ionic exchanger with mobile sodium acting as charge compensator in the structure (Fig. 1-left).

This crystalline phase is obtained via hydrothermal reaction. During this synthesis, the variation of the Ti/Si ratio leads to a structural change of the species formed. For high values of Ti/Si (around 2), it is the sodium nonatitanate phase that is preferentially formed (Fig1-right). Although this phase is also known to capture Strontium, it does not show any selectivity towards Calcium. For Ti/Si ratios below 1.5, sitinakite is preferentially formed. As shown in Fig1-right, the lower the Ti/Si ratio, the less crys-talline the sitinakite becomes, with smaller grain sizes resulting in higher and higher exchange rates between Strontium and sodium[1].



Sitinakite structure

Figure 1. Left: Sitinakite crystalline structure ($Na_2Ti_2O_3SiO_4{\cdot}2H_2O$). Right:Effect of Ti/Si ratio used during synthesis on the structure of the crystalline phase and on the Strontium uptake.

After exploring the synthesis of sitinakite pow-ders from liquid Si and Ti precursors such as TEOS or TTIP, our team developed an alternative synthesis route using solid precursors such as TiO_2 or SiO_2. This route has led to the formation of sitinakite powders, which are cheaper to synthesize and more feasible on an industrial scale. This work was the subject of a patent[2] and served as the basis for the next step, which concerns the formulation of porous materials that allow for column treatment of strontium-contaminated outflows. For that, the most remarkable route, illustrated in Figure 2, involves the pseudomorphic transformation of a macroporous TiO_2 mono-lith. This monolith is obtained by infiltration of a polyurethane foam, which acts as a sacrificial template. After calcination at 800°C and hydrothermal treatment at 170°C in the presence of tetraethyl orthosilicate (TEOS) and sodium hydroxide, a porous monolith consisting mainly of sitinakite is obtained. This monolith features crystallites around 70 nm in size, and a macroporosity that mirrors that of TiO_2: macropores 300 to 1000 µm in diameter with a wall thickness of around 50µm. However, the use of this material in columns would require an increase in its mechanical properties. A PhD is currently underway in the labora-tory to study the development of sitinakite mono-liths.

Figure 2. Pseudomorphic transformation of TiO_2 monoliths into sitinakite.

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SONOHYDROTHERMAL SYNTHESIS OF NANOMATERIALS FOR ENERGY AND ENVIRONMENT

S. El Hakim, T. Chave, X. Le Goff, S.I. Nikitenko
A.A. Nada, S. Roualdes (Institut Européen des Membranes, Montpellier)

Ultrasonic cavitation can be applied in a wide range of experimental conditions and even during hydrothermal treatment. Ti@TiO_2 core-shell nanoparticles (NPs) have been obtained using simultaneous action of hydrothermal conditions (100-214 °C, autogenic pressure P = 1.0–19.0 bar) and 20 kHz ultrasound, called sonohydrothermal (SHT) treatment, on metallic Ti^0 NPs in pure water. The influence of the 3 hour treatment temperature on the final composition of the material was studied and compared to classical hydrothermal treatment.

Pristine Ti^0 is composed of quasi-spherical particles (30-150 nm) of metallic titanium coated with a meta-stable titanium suboxide Ti_3O which can still be observed for temperature treatment below 150°C.[1] SHT treatment at 150-214°C leads to the oxidation of this Ti_3O and also to the partial oxidation of Ti^0 followed by formation of nanocrystalline shell (10-20 nm) composed of TiO_2 anatase (Figure 1). Rietveld refinement analyses revealed that SHT drastically increase this oxidation rate of Ti_3O and Ti(0) into crystalline TiO_2 compared to hydrothermal conditions without ultrasound.

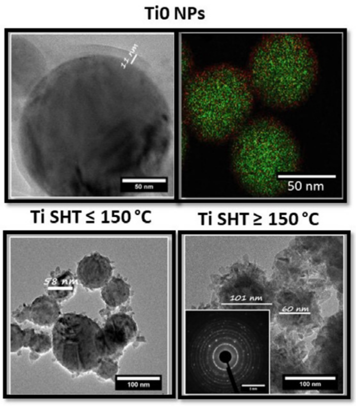

Figure 1. TEM images of Ti@TiO_2 NPs obtained after a SHT treatment for 3 hours at various temperatures compared to pristine material with elemental map-ping showing the presence of oxygen (red dots) at the surface of titanium core (green dots).

Photocatalytic performances of obtained material were then assessed for the hydrogen production in presence of sacrificial reagents. It was shown that Ti@TiO_2 NPs exhibit a strong photothermal effect during the photocatalytic process of hydrogen production from aqueous solutions of glycerol. The effective electron–hole separation between Ti core and nanocrystalline TiO_2 anatase shell in Ti@TiO_2 NPs was confirmed by photoluminescence spec-troscopy. In the same way, kinetic study highlights the importance of TiO_2 nanocrystalline shell for the efficient H_2 generation as shown in Figure 2.[1] Ap-parent activation energy equal to $E_{act} = 32 \pm 2$ kJ mol^{-1} indicates that the thermal effect is more related to the diffusion of reaction intermediates at catalyst surface rather than to the activation of chemical bonds. However, recent studies on the photothermal hydrogen production using the H/D kinetic isotopic effect revealed the involvement of the hole-mediated O-H bond cleavage in the limiting stage of this process at the active site of the photocatalyst.[2]

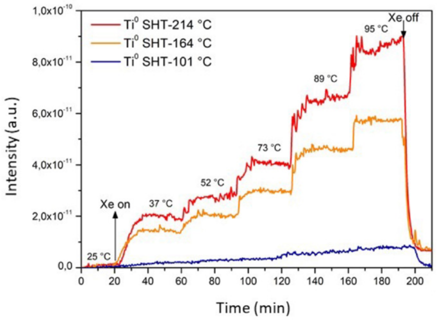

Figure 2. Hydrogen signal evolution during the 0.5 M Glycerol solution photocatalytic treatment (Xe lamp 8.9 W) at various temperatures in the presence of the different Ti@TiO_2 catalysts (0.12 g/L).

Recently, we focused on the sonohydrothermal synthesis of zeolite A from amorphous aluminosilicate gel, and on its phase transformation into sodalite (W. Nzodom's thesis 2022-2025).[3] The results of this work show that the simultaneous coupling of ultrasound and hydrothermal conditions enables zeolite A to be synthesized 10 times faster than under conventional hydrothermal conditions. To our delight, the rate of conversion of zeolite A to sodalite is increased by a factor of 100 compared to autoclave treatment without ultrasound. In the end, this study confirmed the innovative and eco-responsible nature of the sonohydrothermal treatment, which can lead to a considerable reduction both in synthesis time and in the energy required to prepare materials of industrial interest such as zeolites.

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PREPARATION, REACTIVITY AND MULTI-SCALE CHARACTERIZATION OF ACTINIDE OXIDE NANOPARTICLES

M. Virot, T. Dumas, P. Moisy, S. I. Nikitenko

Actinide (An) research at the nanoscale is gaining fundamental interest due to environmental and industrial issues. Much effort is currently dedicated to the preparation of well-defined nanoparticles (NPs) and related nanomaterials that could taylor specific properties in comparison to their bulk analogues. Sonochemistry has been widely used for the preparation of NPs and offers new perspectives in the nuclear domain. The sonication of PuO_2 powder under reducing atmosphere was found to yield very stable intrinsic Pu(IV) colloidal suspensions composed of NPs with a PuO_2-like structure and offering striking similarities and differences with colloids obtained by hydrolysis.[1] This observation started persistent studies dedicated to the characterization of the multiscale properties of PuO_2 NPs (i.e. size, shape, local structure, formation…).

Small angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) were combined on an innovative analytical bench on SOLEIL/MARS synchrotron beamline to characterize Pu(IV) intrinsic colloids.[2] The structural properties of the NPs were found to be strongly influenced by the synthesis route. Both SAXS and XAS approaches converged in the description of Pu colloids as core–shell NPs made up of a PuO_2 core covered with a size-dependent disordered Pu–O shell possibly solvated with counter ions from the medium.[2]

More recently, the synthesis and relevant characterization of PuO_2 and ThO_2 NPs displayed as dispersed colloids, nanopowders or nanostructured oxide powders, allowed to establish a clear relationship between the size of the nanocrystals composing these oxides and their corresponding local structure (XAS).[3] Particularly, an analogous behaviour was noticed for nanosized Pu and Th oxides confirming that the often observed splitting of the Pu-O shell on the Fourier transformed EXAFS signal of PuO_2 samples is attributed to a local structural disorder driven by a NP surface effect rather than to the presence of controversial PuO_{2+x} species.[3]

New insights were recently provided about the formation mechanism of PuO_2 NPs by investigating an unprecedented kinetic isotope effect observed during their hydrolytic synthesis in H_2O or D_2O and attributed to OH/OD zero point energy difference.[4] The signature of a Pu(IV) oxo–hydroxo hexanuclear cluster, appearing as an important intermediate during the formation of the 2 nm PuO_2 NPs (syn-chrotron SAXS/XAS), was further revealed indicating that their formation is controlled by H-transfer reactions occurring during hydroxo to oxo-bridge conversions.

The significant dissolution of refractory ThO_2 NPs was observed under 20 kHz ultrasound ($Ar/(20\%)O_2$) in dilute 0.5 M H_2SO_4. It was showed to result from a combination of physical effects provided by low frequency ultrasound, sulfate complexations and sonochemical generation of H_2O_2. Surprisingly, the extended ultrasonic treatment allowed to observe the partial precipitation of a secondary phase attributed to an unprecedented Th peroxo sulfate, $Th(O_2)(SO_4)(H_2O)_2$ exhibiting 1D morphology. The crystalline structure of this compound was studied and later resolved.[6]

The preparation of U intrinsic colloids was obtained by 20 kHz sonolysis of UO_3 powder in pure H_2O under Ar/(10%) CO at 20 °C. These conditions allowed the partial conversion of powdered UO_3 into a stable colloidal suspension made out of NPs (HR-TEM, XAS) exhibiting a schoepite-like crystallographic structure.[7]

More generally, these results offer new insights about the preparation and thorough characterization of An oxide NPs. The state-of-the-art and recent advances in the topic were recently summarized in two reviews.[8,9]

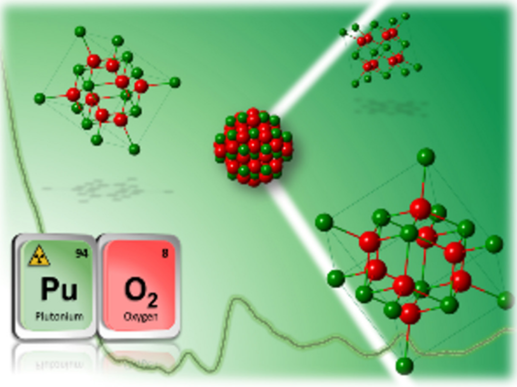

Figure 1. Cover picture used for Nanoscale Advances journal for a Review article

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CARBON DOTS (CDS) LUMINESCENCE: A TOOL FOR DESIGNING NEW MATERIALS

C. M. Singaravelu, R. Roch, C. Rey, X. Deschanels, J. Causse

Carbon Dots (CDs) are luminescent nanoparticles discovered in 2004. They have the advantage of avoiding the use of metals, sometimes rare, in the design of luminescent materials. This generic name gathers carbon nanoparticles with sizes below 10nm. Numerous studies arose these past few years owing to the extreme simplicity of the synthetic routes (hydrothermal, microwaves…) and the wide range of molecular precursors able to lead to CDs. Our group studies these nanoparticles having different goals in mind.

While the development of sensors for ion detection was first successfully investigated for the specific detection of mercury[1], other more promising applications are now investigated. We first focused our work on hydrophobic nitrogendoped CDs emitting in the red light range, i.e. Red Dots. These Red Dots have the particularity of being able to be excited both in the UV range (300-375nm) and in the blue-green light range (450-600nm) (Fig. 1-b). Accord-ing to the literature, the doping of the CDs graphitic core with certain elements (N, S, ...) or the presence of functional groups on the surface can explain this dual excitation. However, the mechanisms are not clearly identified and we recently started to collaborate with modellers capable of simulating the emission spectra of CDs based on their structural design.

This dual excitation allows us to envisage two types of promising applications: β scintillators[2] and LEDs[3]. In the case of β scintillators, the Red Dots are dispersed in a plastic matrix (Polystyrene, PS) sensitive to β radiation (electrons) (Fig 1-c). The PS emits UV light when exposed to β radiation, thus activating the red emission of the Red Dots by a radiative energy transfer mechanism (Fig 1-d). This subject is the topic of Rayan Roch’s thesis, which will be defended in 2025.

In the case of LEDs, the blue excitation property of red dots is used. The most widespread LEDs technology uses an InGaN semiconductor chip that emits in the blue because it is the most energy efficient. The blue light is then converted by a layer of phosphor to produce another richness of light at different wavelengths (white light, red light etc.). Our team is developing phosphors based on Red Dots that can convert part of the blue light into red light and thus produce a pink/purple light that is very useful in the horticultural field for boosting plant growth (Fig 1-e to h). This subject was addressed at LNAR as part of a start-up project that was abandoned for lack of an investor.

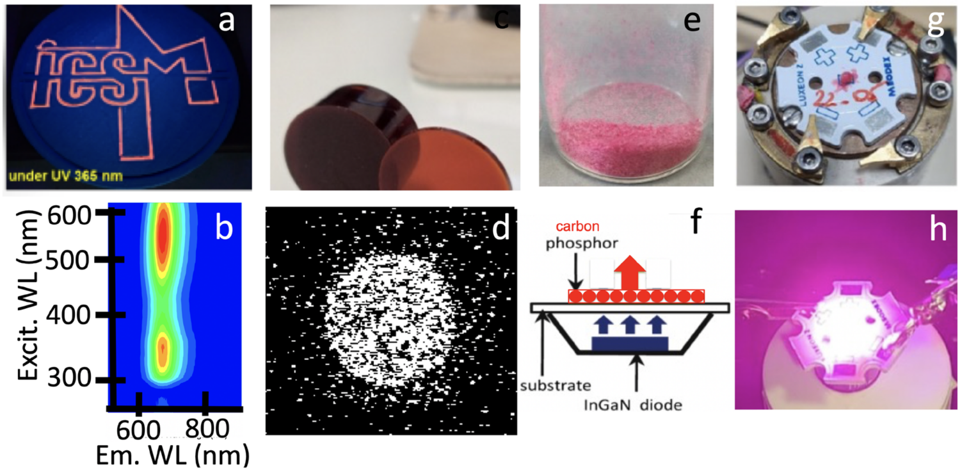

*Figure 1. **a**- ICSM logo made of Red Dots under UV excitation @ 365nm. **b**- Contour 2D diagram showing dual excitation of Red Dots for a single emission in the red region (650nm). **c**- Plastic scintillators made with Red Dots under artificial white light. **d**- Red Dots scintillators under 90Sr (β-@0.5MeV) source excitation. White pixels show visible emission. **e**- Red Dots phosphors. **f**- Scheme of the operating principle of a LED with Excidots phosphors. **g**- LED with an Excidots phosphor layer. **h**- Production of pink/purple light with a LED equipped with an Excidots phosphor layer*

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COLLOIDAL PHYSICAL CHEMISTRY TOWARDS ELECTROPHORETIC DEPOSITION (EPD)

H. Al Amouri, F. Didier, X. Deschanels, G. Toquer

Electrophoretic deposition (EPD) is known as an important tool for the production of wide range of coatings but which is extended to the nanoscale in our studies. The ultimate goal is here to control, via a bottom-up approach, the formation of nanostructured materials associated with selective optical properties designed for photothermal solar collectors. Our studies initially focus on stable charged colloidal dispersions, which are electrodeposited onto substrates of adjustable thickness, density and morphology. Carbon nanotubes (CNTs), deposited by electrophoretic deposition (EPD), have recently been investigated as selective solar absorbers. First, various types of CNTs with different aspect ratios are ultrasonically dispersed in an aqueous solution of pyrocatechol violet (PV) or sodium cholate (SC) as an electrosteric stabilizer. The PV couples to the outer walls of the CNTs via π-π stacking interactions and acts as a dispersing agent as well as a charging agent. PV adsorption isotherms on CNT combined with N_2 physisorption isotherms are performed to optimize the CNT/PV ratio. In this way, Zeta potentials down to -40 mV are obtained for dispersed CNTs, which are deposited on platinized silicon wafers by EPD, forming a thin film. EPD kinetics are then studied as a function of the applied electric field (in the 8–20 V cm^{-1} range) and interpreted by a Sarkar & Nicholson model type (see fig. 1).

X-ray reflectivity is used to characterize coating density around 1.3 g cm^{-3}, and film cohesion is measured by nanoindentation coupled with atomic force microscopy images (see fig. 2). The hemi-spherical reflectance of the samples is measured by spectrophotometers equipped with an integrating sphere and, from the spectra, absorptance (α) and emittance (ε) are calculated[1]. The selectivity of the deposits, based on α and ε values, is then examined as a function of applied electric field and coating thickness. Single-walled CNT deposits exhibit a solar absorption of 0.91 and a thermal emission of 0.05. Thermal annealing experiments reveal that the coatings can withstand up to 300°C while retaining selective properties and losing only 21% of the initial efficiency. The calculated efficiency of the tandem material would be also enhanced by the addition of an anti-reflective layer [2,3]. Progress in understanding deposition mechanisms is crucial to ultimately selecting the most promising coatings acting as efficient solar absorbers.

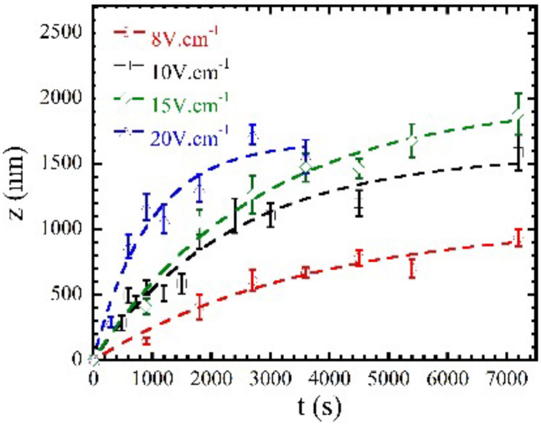

Figure 1. EPD kinetic of SWCNT coating

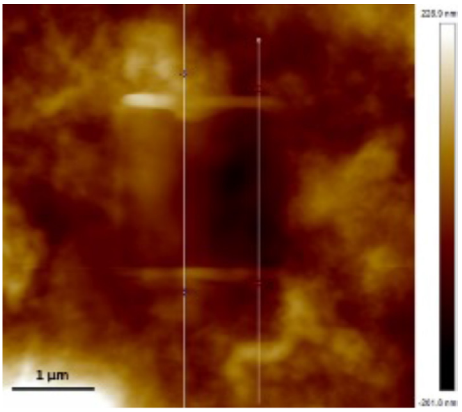

Figure 2. Nano-indentation constraint of 3.10^2 MPa leading to 10% of the film compacting

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FROM ENERGY-TECH WASTE TO VALUABLE MATERIALS & GAS STORAGE

R. Fasola, M. Moneuse, M. Carboni, J. Maynadié, M. Simonnet, D. Bourgeois, S. Madhavi (NTU)

Lithium-ion batteries, particularly those based on Nickel, Cobalt, and Manganese (NMC), have played a crucial role in powering our portable electronic devices and electric vehicles. However, this technological evolution generates a growing problem: the accumulation of battery waste containing valuable metals. Our team is working on this subject with an original approach: developing a recycling process that transforms this waste into valuable materials. We recover metals from used batteries and convert them into porous materials (MOFs) with multiple applications. Our research has demonstrated the potential of these materials as active electrodes for lithiumion batteries, thus enabling a closed-loop recycling cycle. We are also exploring other applications for these materials within the framework of open-loop recycling (Figure 1). Our key strategy: to develop original recycling processes to maximize the valorization of materials throughout their life cycle.

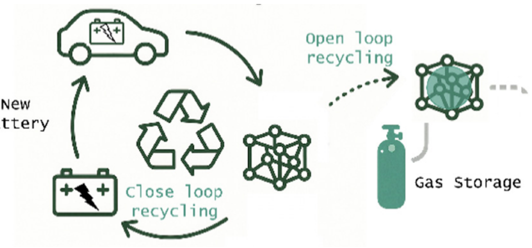

Figure 1: Strategy for the recycling of Li-Ion batteries

More specifically, an NMC-based MOF, obtained from model solutions of battery waste, was tested as an electrode in a coin cell battery. This material revealed a significant capacity of 690 mAh/g and good cyclability, retaining its performance after 50 charge/discharge cycles (Collaboration with LITEN CEA/Grenoble).[1] Development activities for similar, but nano-sized materials (Metal Organic Nanosheets - MONs) have also been proposed for this application.[2]

These promising results have encouraged us to explore the large-scale production of MOFs from battery shreddings. This approach opens also the way to open-loop recycling, allowing the creation of high-value materials for gas storage. These same materials can then be transformed into porous monoliths, facilitating their practical use (Collaboration with DMRC CEA/Marcoule).[3] This strategy, known as upcycling, has also been extended to the recycling of photovoltaic modules by combining metallic and organics wastes (Collaboration with NTU/Singapore).[4]

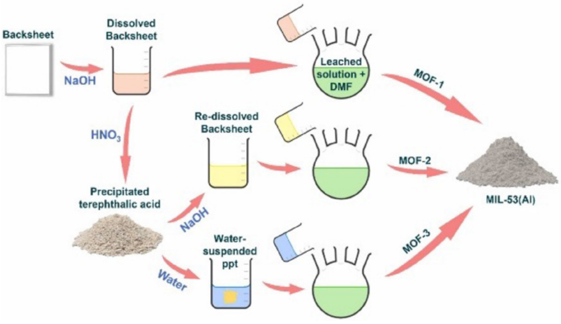

Figure 2: Combining organic and inorganic wastes from photovoltaic modules to form MOFs

We are developing these activities in close collaboration with stakeholders ranging from international to local actors. These methods are being developed within the framework of the SCARCE 2 project, a collaboration between the CEA and NTU (Singapore), at the forefront of environmentally friendly battery recycling.[5,6]

At the European level, we are participating in an ERA-MIN project dedicated to eco-designed batteries. More locally (region), we are involved in the RECULITI project, in collaboration with teams from the Universities of Montpellier and Toulouse, and the SNAM, to propose an original end-of-life solution by mixing recycled batteries and waste from the national aerospace industry. We have also started working on the recovery of vanadium to build a new generation of batteries (region/CEA).

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HIERARCHICALLY POROUS 3D SHAPING OF METAL-ORGANIC FRAMEWORK MATERIALS

E. Prozsa, F. Lorignon, S. Medjouel, D. Pianca, M. Carboni, D. Meyer - A. Gossard (DMRC)

Metal-Organic Frameworks (MOFs) have attracted a lot of attention over the past two decades mainly because their unique set of properties, notably their high porosity and surface area, are useful for gas storage and separation, but these materials are also well suited to the decontamination of liquid effluents. They are synthesized as crystalline solid powders but, for a broad applicability, producing MOFs as handleable materials is crucial. Furthermore, the main challenge for their use in fix bed processes consists in creating and controlling a meso- and macroporous network in the body of the material while ensuring the MOF's micropores remain accessible.1 Different routes have been proposed to shape MOFs in this way, namely various mechanical processes (granulation, pressing, extrusion or spray drying), finely controlled metal-organic gel formation, thin film deposition, and sacrificial templating.

Our strategy was shaping MOF monolith by using Pickering emulsions.[2] The emulsions are stabilized by MOFs solid particles with a high internal phase emulsions (HIPE) (Figure 1). Then, by growing a solid skeleton in the continuous phase to support the global structure and eliminating the internal phase, a macro porous material can be obtained with the pore size defined by the size of the initial droplets of the emulsion.

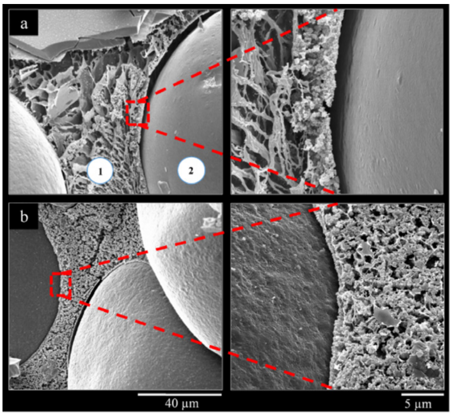

Figure 1. Cryo scanning electron micrographs of emulsions with MOFs concentrations of (a) 1 wt.% and (b) 3.5 wt.%. (1) Continuous aqueous phase concentrated in MOFs and (2) oil droplet.

Controlling the properties of the emulsion was crucial to optimizing the microstructural design of the MOF-functionalized.[3] To avoid pore blockage due to the integration of MOF particles, the proposed method relies on controlling the hydrophilic/hydrophobic balance of the MOF particles through the controlled adsorption of hydrophobic organic molecules by the MOF before emulsion formation. This treatment allows the MOF particles to be positioned at the paraffin-water interface in the emulsion, thereby reducing their integration into the monolith wall during aqueous phase polymerization. The result is a monolith integrating MOFs particles with increased accessibility, even preserving the original porosity and internal surface area properties of the material, and enabling their application in fixed-bed processes. The strategy was validated by the capture of N_2 and CO_2 (Figure 2).[4]

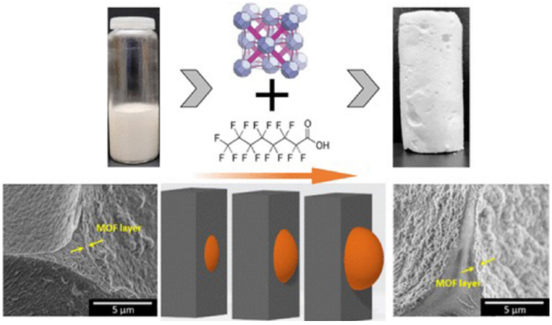

Figure 2. Controlling polyHIPE Surface Properties by Tuning the Hydrophobicity of MOF Particles Stabilizing a Pickering Emulsion

We are also developing method to shape porous MOFs materials by using 3D-printers.[5] Different strategies are ongoing but our first effort has been focused on direct-ink writing (DIW). In this technique, the extruder of the printer will be replaced to support a syringe connected to a peristaltic pump to deposit directly a paste (ink) containing the MOF on the hot bed of the printer conducting to the solidification of the ink. Additive formulation are often composed of solvent/thermosetting polymers/adhesive polymers. Such formulation is close to those that we have used to form monoliths by Pickering emulsion and need a research effort to optimize and characterize the viscosity and other rheological properties of the ink to optimize the deposition. Finally, our recent efforts involve functionalizing geopolymers (alumino-silicate materials) as a novel approach to shaping MOFs.

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DEVELOPMENT OF NEW HYBRID MATERIALS FOR ENERGY

T. Riant, M. Henry, B. Mortada, X. Le Goff, D. Meyer, J. Maynadié, M. Carboni, D. Bourgeois

In the nuclear industry, materials and more particularly those based on actinides are omnipresent. To increase our knowledge of this type of materials, it seems essential to develop new simple and effective synthetic strategies for the production of model materials or precursors of model materials. In this context, actinide-based hybrid materials appear to be good candidates presenting modular physico-chemical properties. This project deals with the conception of new structured actinide-based hybrid materials, which can display unusual properties with respect to the bulk inorganic counterpart. In this way, we are focused our attention on the development of new bottom-up synthesis strategies.

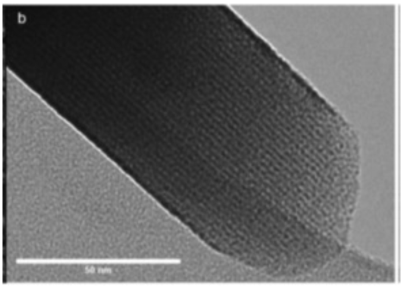

Figure 1. TEM image of actinide-based nano-sheet

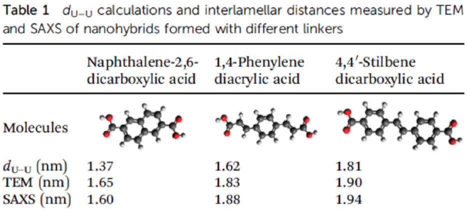

Table 1 d_{U-U} calculations and interlamellar distances measured by TEM and SAXS of nanohybrids formed with different linkers

	Naphthalene-2,6-dicarboxylic acid	1,4-Phenylene diacrylic acid	4,4′-Stilbene dicarboxylic acid
Molecules			
d_{U-U} (nm)	1.37	1.62	1.81
TEM (nm)	1.65	1.83	1.90
SAXS (nm)	1.60	1.88	1.94

Table 1. Table of inter nano-lamellae distances

First, we developed a one-pot approach in order to control the nano-structure of the material.[1] Using a ternary molecular system (dicarboxylic acid, oleyla-mine, dibenzyl ether), it is possible to obtained nano-sheets displaying an intern nanometric structuration in which UOx nano-lamellae (around 1 nm) are separated by organic linkers (Figure 1). In the nano-sheets, the inter-UOx nano-lamellae distance could be adjusted in accordance with the length of the employed dicarboxylic acid linker (Table 1). Moreover, the stacking distance between two nano-sheets could be modulated by adjustment of the synthesis temperature. Using this synthesis methodology, it is possible to modulate the structure of materials at the nanometric scale by adjusting some parameters intrinsic to the reaction. This approach is currently developed in the team for the synthesis of new NMC (Ni/Mn/Co) hybrid materials for Li-ion batteries.[2]

A second strategy, based on the self-assembly of functionalized nanoparticles, is developed.[3] This strategy starts with the well-known synthesis of metal-oxide nanocrystals (UO_2, ThO_2 or MOx) stabilized with oleic acid. This method permits to obtain well-defined monodisperse nanoparticles with an average size of 4.5 nm for UO_2 and 3.5 nm for ThO_2 (Figure 2 top). Then, the surface of the pre-synthesized nanoparticles is modified using capping agents having reactive pendant functionality (alkyne, azide, ionic moiety) without modification of the morphology of the nanoparticles. To obtain the final materials, the crosslinking of modified nanocrystals could be operated through a click-chemistry step catalyzed by Cu(I) or electrostatic interactions (Figure 2 bottom). The final goal consists in the formation and the characterization of heterometallic nano-hybrid superlattices.

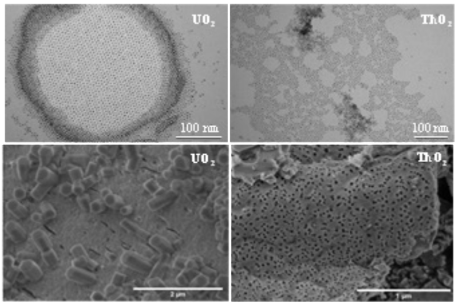

Figure 2. Top: TEM images of UO_2 (left) and ThO_2 (right) nanocrystals / Bottom: SEM images of functionalized nanoparticles self-assemblies (UO_2 (left) and ThO_2 (right)

The third strategy is developed with the goal to produce actinide-based hybrid materials using complex organic phases from liquid-liquid extraction processes.[4] Currently, in the spent fuel cycle, the liquid-liquid extraction step is followed by stripping one. To avoid this latter, it could be interesting to induce direct controlled precipitation in the com-plex organic phase (metal ions + extractant + dodecane), using simple ditopic organic linkers as dicarboxylic acids to promote the formation of coordination polymers or MOF potentially having adjustable properties (structure, morphology, texture, robustness). These materials could be envisaged as new precursors for the preparation of actinide-based oxide materials used in the nuclear fuel cycle.

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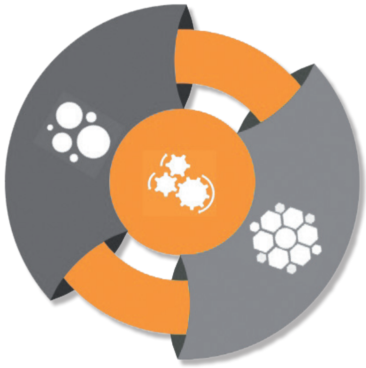
[1] Elisa Re, Xavier Le Goff, Guillaume Toquer, Jerome Maynadie and Daniel Meyer, **"Linker-assisted structuration of tunable uranium-based hybrid lamellar nanomaterials"**; *New J. Chem.*, 2020, 44, 8463.

[2] Tennessee Riant, Diane Rebiscoul, Jérôme Maynadié, and Daniel Meyer, **"Surfactant-assisted lamellar structuration of tunable Co-based hybrid nanosheets"**; *New J. Chem.*, 2023, 43, 20109.

[3] Thèse E. Ré.

[4] Thèse M. Henry.



METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

MÉTHODOLOGIES ET THÉORIES POUR LA CHIMIE SÉPARATIVE

METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

Via the refinement of experimental tools (microscopies, radiation scattering, spectroscopies) and multi-scale predictive modelling (supramolecular, mesoscopic and colloidal).

MÉTHODOLOGIES ET THÉORIES POUR LA CHIMIE SÉPARATIVE

Via le perfectionnement d’outils expérimentaux (microscopies, diffusion du rayonnement, spectroscopies) et la modélisation prédictive multi-échelle (supramoléculaire et colloïdale).

MOLECULAR APPROACHES FOR UNRAVELING THE LIQUID-LIQUID EXTRACTION

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Ph. Guilbaud, T. Dumas, C. Berthon, D. Moreno Martinez (CEA ISEC/DMRC)*

The majority of efficient ion separation methods are based on equilibria between complex fluids, typically aqueous and organized organic phases. Understanding the thermodynamics in both phases is therefore crucial for optimizing separation processes. Although aqueous solutions are now well characterized, understanding the thermodynamic properties of ions in organic phases remains a significant challenge. Ion transfer from the aqueous to the organic phase occurs through interactions with amphiphilic surfactant or extractant molecules present in the organic phase, where the ions are subsequently confined within reverse micelles or aggregates. Accurately modeling these processes is complex, as it involves a wide range of interacting phenomena, including complexation, solvation, electrostatic interactions, van der Waals forces, polarization effects, entropic contributions, interfacial curvature, etc[1].

Here we explore how these phenomena influence ion transfer across both phases. To access the structural, dynamic, and thermodynamic features of ions in solution, molecular dynamics (MD) simulations coupled with experiments, such as EXAFS, SWAXS, and NMR techniques, are preferred[2] (Fig. 1).

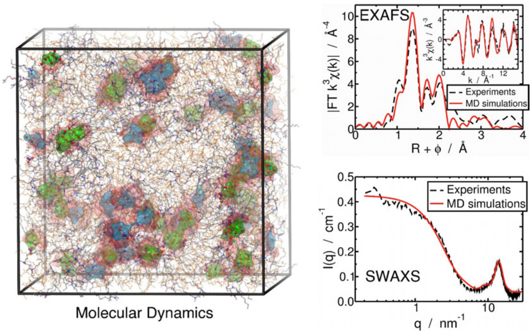

Figure 1. MD simulations coupled with EXAFS and SWAXS spectroscopies

Indeed, it allows for providing realistic pictures of ion solvation, which is a first step needed to access their thermodynamic properties[3].

Weak association and diluent effects on solvent extraction mechanisms have been investigated using MD simulations, revealing that, while such effects can influence the structural properties of the aggregates, particularly within the polar core, they have little effect on the curvature properties[4]. Furthermore, MD simulations were employed to investigate aggregation properties and to better understand the role of extractant molecules in the supramolecular organization of solvent extraction phases[5]. Using association criteria between molecules in solution combined with graph theory, this robust approach enables straightforward calculation of key structural and physicochemical parameters, including equilibrium constants, enthalpies of formation, and aggregation numbers (Fig. 2).

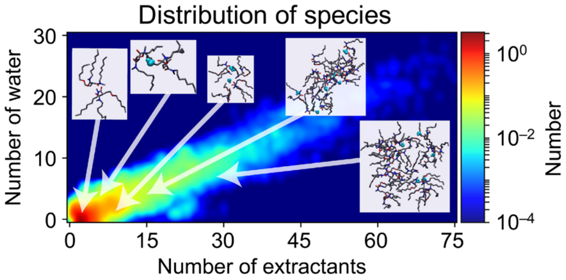

Figure 2. Distribution of water-DMDOHEMA aggregates calculated from MD simulations

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[1] Coquil M., Boubals N., Duvail M., Charbonnel M.-C., Dufrêche J.-F. – **On Interactions in Binary Mixtures Used in Solvent Extraction: Insights From Combined Isothermal Titration Calorimetry Experiments and Molecular Dynamics Simulations** – *Journal of Molecular Liquids* (2022) 345, 116985

[2] Poulin-Ponnelle C., Duvail M., Dumas Th., Berthon C. – **Contribution of Molecular Dynamics in pNMR for the Structural Determination of AnV and AnVI Complexes in Solution** – *Inorganic Chemistry* (2022) 61, 15895–15909

[3] Duvail M., Moreno Martinez D., Žiberna L., Guillam E., Dufrêche J.-F., Guilbaud Ph. – **Modeling Lanthanide Ions in Solution: A Versatile Force Field in Aqueous and Organic Solvents** – *Journal of Chemical Theory and Computation* (2024) 20, 1282–1292

[4] Stemplinger S., Duvail M., Dufrêche J.-F. – **Molecular dynamics simulations of Eu(NO3)3 salt with DMDOHEMA in n-alkanes: Unravelling curvature properties in liquid-liquid extraction** – *Journal of Molecular Liquids* (2022) 348, 118035

[5] Vatin M., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Thermodynamics of Malonamide Aggregation Deduced From Molecular Dynamics Simulations** –*Journal of Physical Chemistry B* (2021) 125, 13, 3409–3418

STRUCTURE AND THE THERMODYNAMICS OF COMPLEX SOLUTIONS

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V. Dru, Ch. Sorel (CEA ISEC/DMRC), I. Billard, M. Plazanet (Univ. Grenoble Alpes)

Understanding solvent extraction-based purification and recycling approaches requires detailed information on different thermodynamic properties of phases to develop a sustainable and clean industry.

The use of non-standard diluents to replace conventional organic solvents is a key challenge in liquid-liquid extraction. Ionic liquids (ILs) provide economic and environmental benefits due to their very low volatility. They also enable much higher extraction performances than traditional solvents. We recently addressed a complete picture of the microscopic mechanisms leading to temperature-induced phase separation in IL-based acidic aqueous biphasic solutions, which represents a breakthrough in the field of metal recycling[1]. Small-angle neutron scattering (SANS) revealed an unusual property of the tributyltetradecylphosphonium chloride ($[P_{4,4,4,14}]Cl$), acid, and water mixture: a lower critical solution temperature (LCST) that leads to phase separation upon heating. This behavior was attributed to increasing disorder in the short aliphatic chains surrounding the IL ions, which allows chloride ions to bind to the micelle surface, thereby enhancing the screening of electrostatic repulsion that normally keeps the micelles in suspension. At the same time, molecular dynamics (MD) simulations and small-angle X-ray scattering (SAXS) were combined to investigate the structure of two piperidinium- and (trifluoromethylsulfonyl)imide-based ILs ($[EBPip^+][NTf_2^-]$ and $[EOPip^+][NTf_2^-]$) that differ in the alkyl chain length of their cation and are used for rare-earth extraction[2]. A detailed analysis of the different contributions to the X-ray scattering data revealed the structural correlations responsible for the low-q peak observed in ILs containing long-chain alkyl cations, as well as the angular correlations between anions at large distances. The decrease in apolar microdomain volume observed for piperidinium-based ILs can be attributed to alkyl chain alignment, which may explain the observed differences in extraction performance[3] (Fig. 1).

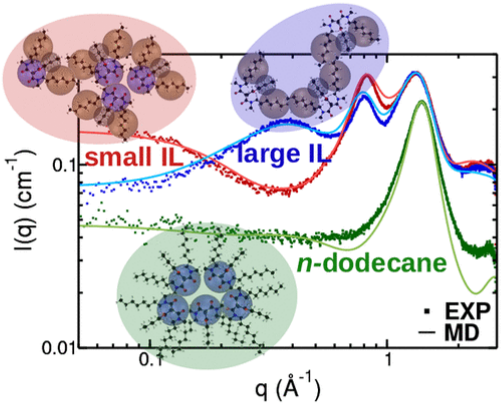

Figure 1. MD simulations combined with SAXS spectroscopy to explain the ILs' supramolecular organization with DMDOHEMA.

This combined approach has also been employed to investigate the influence of structural effects on uranium extraction performance, focusing on novel, high-potential ionic liquids consisting of mixtures of amphiphilic ion pairs without diluents, including protonated trioctylamine sulfate $[TOAH^+]_2[SO_4^{2-}]$ and protonated trioctylamine N-methyl-bis(trifluoromethylsulfonyl)imide $[TOAH^+][NTf_2^-]$. Accurately determining and predicting the thermodynamic properties of electrolytes in solution properties is essential for a comprehensive understanding of the mechanisms involved in processes[4]. For example, binary thermodynamic data for ruthenium(III) nitrosylnitrate have been reported over a wide molality range, from 0 to 18 $mol \cdot kg^{-1}$. However, due to the complex chemistry of this electrolyte, a combination of methods, including the simple solution concept and the Kusik-Meissner-Tester method, has been used to determine the binary data of an electrolyte exhibiting a deviation from the simple behavior when using the simple solution concept[5]. As a result of a mathematical approach, the deviation has been estimated, and the Vdovenko and Ryazanov equation used to compute the density has been corrected, allowing it to be used for mixtures that deviate from the simple behavior.

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[1] Meyer G., Schweins R., Youngs T., Dufrêche J.-F., Billard I, Plazanet M. – **How Temperature Rise Can Induce Phase Separation in Aqueous Biphasic Solutions** – *Journal of Physical Chemistry Letters* (2022) 13, 2731–2736

[2] Le Crom S., Dourdain S., Pellet-Rostaing S., Duvail M. – **Long-Range Organization Study of Piperidinium-Based Ionic Liquids by Polarizable Molecular Dynamics Simulations** – *Journal of Physical Chemistry B* (2022) 126, 3355–3365

[3] Le Crom S., Dourdain S., Pellet-Rostaing S., Duvail M. – **Exploring the Aggregation Behavior of Extractant Molecules in Ionic Liquids: A Coupled Polarizable Molecular Dynamics and SAXS Study** – *Journal of Physical Chemistry B* (2023) 127, 6408–6420

[4] Dufrêche J.-F., Siboulet B., Duvail M. – **Chemical Models for Dense Solutions** – *Faraday Discussions* (2024) 253, 79–99

[5] Dru V., Sorel Ch., Dufrêche J.-F. – **Activity of Ruthenium(III) Nitrosylnitrate Aqueous Solution: Using Ternary Mixtures to Get Binary Data** – *Journal of Molecular Liquids* (2021) 329, 115464

ORGANIC PHASES MESOSCOPIC MODELING FOR SOLVENT EXTRACTION

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D. Horinek (University Regensburg), K. Bohinc (University of Ljubljana), M. Gradzielski (Technische Universität Berlin)

Identifying and understanding the motors of selectivity and efficiency of hydrometallurgical processes based on liquid-liquid extraction is crucial for rare-earth elements recycling and nuclear waste management. One essential aspect is understanding the aggregation processes in organized organic solvent phases in contact with aqueous electrolyte solutions. In such approaches, the organic solvent phases are assumed to behave like microemulsions, which are thermodynamically stable mixtures of oil, water, and surfactant[1].

Despite their importance in chemical engineering and separation science, the forces that drive solute transfer are still poorly understood. Indeed, molecular forces and entropy drive ion phase transfer (Fig. 1).

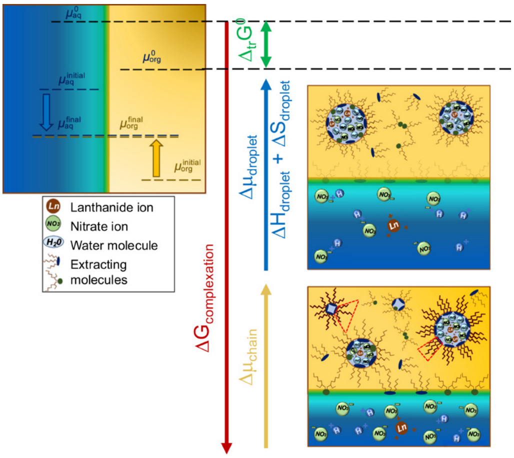

Figure 1. Molecular forces at work in LL extraction

Extraction is thus governed by a combination of high-energy interactions related to short-range forces, such as ion pairing and complexation, and low-energy interactions arising from supramolecular and nanoscale organization, which are similar to long-range solvent-averaged interactions.[2] Modeling such complex systems remains challenging due to the coupling between these interaction domains, especially given that the resulting free energy of extraction is on the order of a few k_BT, ensuring the reversibility of the process. Nonetheless, quantification is possible. The resulting free energy of transfer is rationalized by combining terms representing strong complexation energies, counterbalanced by various entropic effects and the confinement of polar solutes in nanodomains dispersed in the diluent, together with interfacial extractant terms.

Furthermore, rather than assuming a simple complexation reaction with predefined stoichiometries, we developed a minimal thermodynamics model combining supramolecular chemistry and mesoscale, in which metal salt extraction is triggered by complexation and quenched by the associated necessary reorganization of the structured solvent phase, which is assumed to be a microemulsion[3] (Fig. 2).

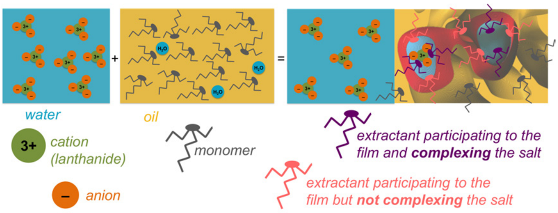

Figure 2. Minimal thermodynamics model

Finally, to obtain coherent descriptions of colloidal equations of state, colloidal interactions such as hydration and depletion forces must be considered. This differs significantly from the standard DLVO paradigm, which combines electrostatics and dispersion forces.[4] For example, based on classical density functional theory, we recently developed a general theoretical description of ternary solutions of small molecules in a centrifugal field that could be used to predict analytical experiments or large-scale industrial separation chemistry.[5,6]

[1] Gradzielski M., Duvail M., Malo de Molina P., Simon M., Talmon Y., Zemb Th. – **Using Microemulsions: Formulation Based on Knowledge of Their Mesostructure** – *Chemical Reviews* (2021) 121, 5671-5740

[2] Špadina M., Dufrêche J.-F., Pellet-Rostaing S., Marčelja S., Zemb Th. – **Molecular Forces in Liquid-Liquid Extraction** – *Langmuir* (2021), 37, 10637–10656

[3] Gourdin-Bertin S., Dufrêche J.-F., Duvail M., Zemb Th. – **Microemulsion as Model to Predict Free Energy of Transfer of Electrolyte in Solvent Extraction** – *Solvent Extraction and Ion Exchange* (2022) 40, 28-63

[4] Zemb Th., Rosenberg R., Marčelja S., Haffke D., Dufrêche J.-F., Kunz W., Horinek D., Cölfen H. – **Phase Separation of Binary Mixtures Induced by Soft Centrifugal Fields** – *Physical Chemistry Chemical Physics* (2021) 23, 8261-8272

[5] Stemplinger S., Prévost S., Zemb Th., Horinek D., Dufrêche J.-F. – **Theory of Ternary Fluids Under Centrifugal Fields** – *Journal of Physical Chemistry B* (2021) 125, 12054-12062

[6] Stemplinger S., Zemb Th., Horinek D., Dufrêche J.-F. – **Aggregating Fluids Under Centrifugal Fields** – *Journal of Molecular Liquids* (2023) 386, 122358

UNDERSTANDING LIQUID–LIQUID INTERFACES: A MOLECULAR PERSPECTIVE

M. Duvail, M. Vatin, L. Ziberna, E. Guillam, J.-F. Dufrêche
Ph. Guilbaud (CEA ISEC/DMRC)

Metal recycling often relies on liquid–liquid extraction, where various ionic metal species are selectively transferred from an aqueous phase to an organic phase through the action of amphiphilic extractant molecules. Therefore, we aim to describe and better understand the mechanisms of ion extraction occurring at liquid–liquid interfaces, with a particular focus on water/oil interfaces relevant to separation chemistry. In recent years, advances in molecular modeling have made it possible to more accurately describe these complex systems. However, simulating ion adsorption and transfer at interfaces, along with their associated kinetics, remains challenging due to the complexity and timescales involved.

We first focused on how surface phenomena influence interfacial geometry in biphasic liquid–liquid systems. In the absence of curvature-dependent surface tension effects, our models predict a progression from planar to cylindrical and then to spherical structures, depending on the overall composition and the elongation of the simulation box, consistent with molecular dynamics (MD) simulations of the water/n-heptane system[1] (Fig. 1).

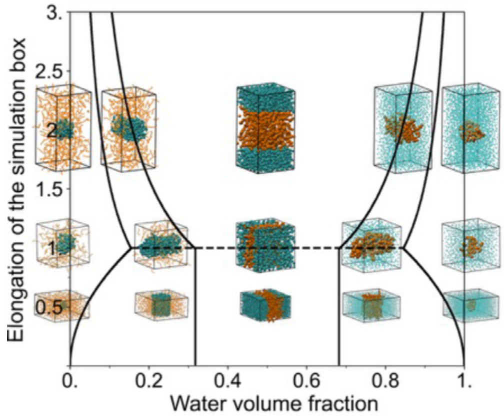

Figure 1. Phase diagram of the equilibrium surface of a water/oil mixture as a function of the water volume fraction and the elongation of the simulation box

By introducing spontaneous curvature through Helfrich's formalism, we extended this framework to more complex morphologies, including spherical shells, frustrated structures, and systems with multiple droplets. This approach offers a powerful lens through which to explore the subtle balance of forces that govern self-assembly in extraction systems.

In addition, we are developing theoretical approaches based on MD simulations to investigate ion transfer mechanisms and predict their thermodynamic and kinetic properties. This modeling effort is closely integrated with experimental data obtained at ICSM in recent years, including surface tension measurements, neutron and X-ray reflectivity, and second-harmonic generation (SHG). Two complementary simulation strategies are being pursued:

- Classical MD simulations to study ion adsorption at interfaces, with the goal of characterizing interfacial organization and its evolution in the presence of ions,
- Biased MD simulations to explore the free energy landscape of ion transfer, thereby gaining insight into the efficiency of different extractant molecules.

These approaches have been applied to systems relevant to solvent extraction, including water/DMDOHEMA/alkane mixtures (Fig. 2), as well as binary and ternary systems composed of water, octanol, a commonly used polar modifier in solvent extraction, and methanol (Fig. 3).

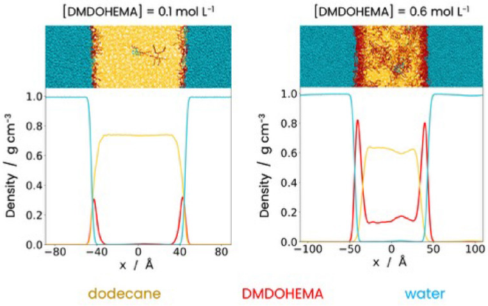

Figure 2. Density profiles calculated from MD simulation, and corresponding simulation boxes

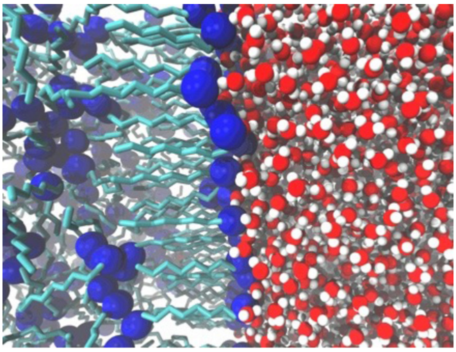

Figure 3. Water / Octanol interface

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[1] Vatin M., Duvail M., Guilbaud Ph, Dufrêche J.-F. – **Liquid/Liquid Interface in Periodic Boundary Condition** – *Physical Chemistry Chemical Physics* (2021) 23, 1178–1187

LIQUID/LIQUID INTERFACE OR INTERPHASE

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P. Guilbaud (ISEC CEA-Marcoule)
P-M. Gassin, G. Martin-Gassin (ICGM, Montpellier)

A crucial step in many commercial hydrometallurgy applications, especially for the reprocessing of nuclear fuel, is ion separation via liquid-liquid extraction (LL) or solvent extraction. In order to better understand the ion transfer between an aqueous and an organic phase in this type of process, it is important to know precisely i) the speciation of the different ionic and molecular species in each of the two phases in contact which defines the differences in chemical potential between the two phases (the ienaics con-cept) and ii) all the molecular and supramolecular interactions at the interface which are at the origin of the potential barriers that can influence the kinetics of ion transfer. Several results from volume phase experiment can now be explained structurally by molecular dynamics simulations. However, there has not been much research done on a similar experimental/simulation coupled method at the interface containing ligands and in equilibrium with neighboring volumes. Recently, as part of a thesis, we resumed studies on the structural analysis of liquid/liquid interfaces using neutron and X-ray reflectivity, as we had carried out in Ernesto Scoppola's thesis, in the presence of diamide-type extractants. In the present case, we have targeted a monoamide-based system, a family of CHON extractants, i.e. comprising only C, H, O and N atoms, in order to allow complete incineration of the effluent waste and recognized selectivity for U(VI) versus Pu(IV), as is tributylphosphate (TBP), widely used in the PUREX process for separating fission products downstream of the cycle. However, unlike TBP or a certain number of diamide-type extractants (used for the selective extraction of lanthanides and D ele-ments), the aggregation in the relatively compact organic phase, often compared to inverted micelles with small aggregation numbers, is much less pronounced and does not generate a 3rd phase with the composition developed in the processes if the aliphatic chains of the ligand are not too long, an extremely positive point for industrial application, particularly in the nuclear industry for criticality issues.

The aim is therefore, as in the work by E. Scoppola, to determine the distribution of ligands and associated charges in the vicinity of the interface and at equilibrium in order to assess the potential barrier that may or may not slow down the ion transfer process. One of the additional difficulties of this study, led by X. Ma and in collaboration with ESRF and ILL is to work in the presence of (depleted) uranium and therefore to follow its distribution at ligand concentrations and under acidic conditions (~3M), conditions close to the processes envisaged.

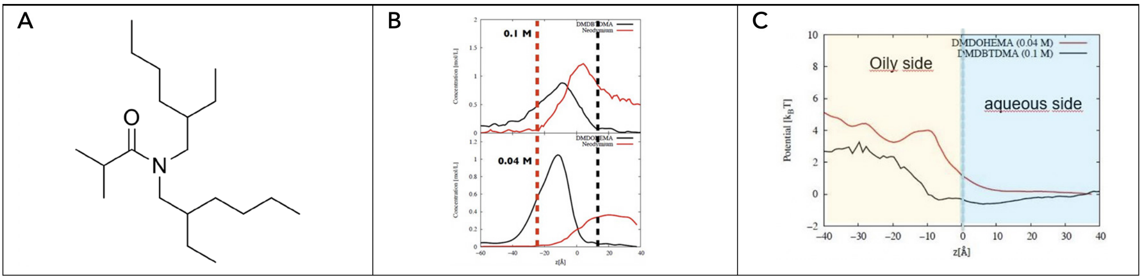

Figure. A) Chemical structure of a selected monoamide (DEHiBA). B) extractant's (for two diamides, DMDO-HEMA-0.04M in dodecane and DMDBTDMA- 0.1 M in dodecane) and Nd-ion (Neodymium) concentration distribution around the water/oil interface. C) Energy barrier in k_BT unit deduced from the ion concentration profile and showing a lower barrier for the DMDBTDMA system and for which the ion transfer is qualified of diffusive.

MULTISCALE MODELLING FOR INTERFACES

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S. Charton (CEA/DES), R. Vuilleumier (Sorbonne Univ. -ENS), J. Casas (Univ. Tours)

Multiscale modeling has been carried out for various experimental systems, either in connection with particular experiments that have been poorly interpreted, or with new applications, particularly in biology. In particular, three important systems have been studied by this approach.

Firstly, we studied the modeling of SHG. [1,2] This experimental method was so far mainly interpreted by macroscopic concepts based on electromagnetism, which are not easy to implement for separation chemistry. For the first time, we were able to propose an ab initio calculation. It appeared that it is the whole modeling of this SHG method that needs to be revised. Indeed, the signal in the case of the simplest interface (water/air) is not mainly a signature of the interface but a quadrupolar volume term (Fig. 1).

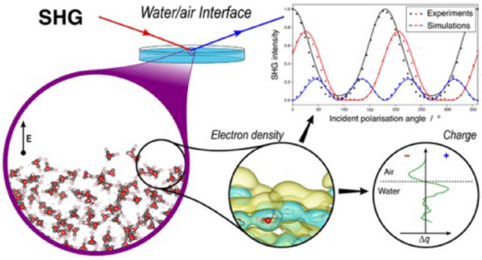

Figure 1. Theoretical approach based on ab initio calculation for the SHG signal interpretation

Moreover, the environment and hydrogen bonds quantitatively change the signal since they invert its sign. This work proposes a new framework to interpret and implement this very important experimental method for interfaces.

Next, coalescence, a very important phenomenon in separation chemistry, was studied.[3,4] The aim was to establish the macroscopic laws (van der Waals interactions, drainage hydrodynamics, stochastic initiation of coalescence) using molecular dynamics. We were able to show, for example, the importance of slip at the liquid-liquid interfaces or the Poisson character of the phenomenon (Fig. 2).

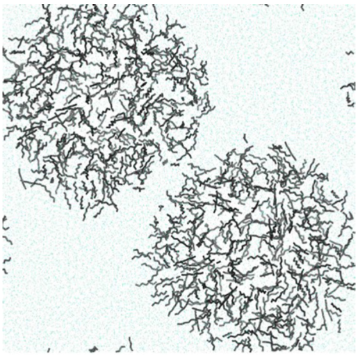

Figure 2. Coalescence of two heptane nanodroplets in water

Finally, the role of aerosols in chemical communication between insects was studied using a similar multi-scale approach (Fig. 3). [5]

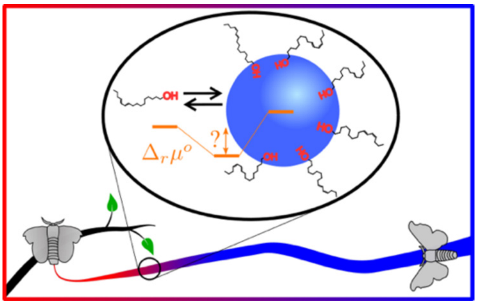

Figure 3. Modeling of bombykol adsorption on an aqueous aerosol

It was shown that physically if aerosols have the capacity to adsorb pheromones, given the characteristic times this phenomenon will take place during communication. The minimum value of the Gibbs energy of adsorption was determined. Molecular dynamics was able to confirm the proposed mesoscopic model and show that in the case of the bombyx, which is the reference moth in this field, aqueous aerosols do not necessarily support individual adsorption but possibly collective adsorption.

[1] Foucaud Y., Siboulet B., Duvail M., Jonchère A., Diat O., Vuilleumier R., Dufrêche J.-F. – **Deciphering Second Harmonic Generation Signals** *Chemical Science* (2021) 12, 15134–15142.

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[4] Hilaire L., Siboulet B., Charton S., Dufrêche J.-F. – **Coalescence Initiation in Liquid-Liquid Systems: A Stochastic Model** – *Langmuir* (2023) 39, 14853–14858

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TEST VEHICULE: A NEW EXPERIMENTAL TOOL TO STUDY PROCESSES OCCURRING AT THE SOLID-LIQUID INTERFACE

D. Rébiscoul, M. Baum, H. Khoder, O. Walker, R. Boubon, K. Wang, B. Siboulet, J.-F. Dufrêche, S. Tardif, F. Rieutord, V. Larrey, J.-M. Zanotti, J. Ollivier, M. Odorico, J. Lautru, R. Podor, X. Le Goff

The physical-chemical processes occurring at the solid-liquid interface such as adsorption, complexa-tion, species transport, dissolution, condensation, precipitation and electrochemical reaction, drive the evolution of bulk or porous materials when their surface are in contact with an aqueous solution. Thus, it is important to describe these processes to *in fine* predict the material surface behavior in solution.

To study the process occurring at the solid-liquid interface, we used since few years, the so-called test vehicule. A test vehicule is defined as the use of a model sample presenting a distinctive signal when it is analyzed with a specific characterization tool. From this distinctive signal, with or without the use of a fitting model, it is possible to have a precise quanti-fication of values characteristic of a process. Several examples are presented on the Figure 1.

Among these examples, the highly ordered silica mesopores such as SBA15 and MCM41, *in situ* characterized by Small Angle X-ray Scattering have allowed the quantification of the kinetics of dissolu-tion of the silica pore wall and the solution diffusion through its microporosity.[6] Another example is the silica nanochannels with a height of 3 or 5 nm made of etched grooves in silica films, coupled to the interface X-ray reflectivity analysis using hard X-rays that directly provides the ion distribution of the nanochannel-confined solution. Using this combination and probing the filling kinetics of the nanochannels with ionic solutions XCl_2 1 M having cations presenting increasing kosmotropic properties (X : Ba < Ca < Mg), we directly evidence the interface, i.e. the interaction existing between ions and the surface and show that the formation of ion pairs may result in dramatic changes of solution properties in extreme confinement.[2]

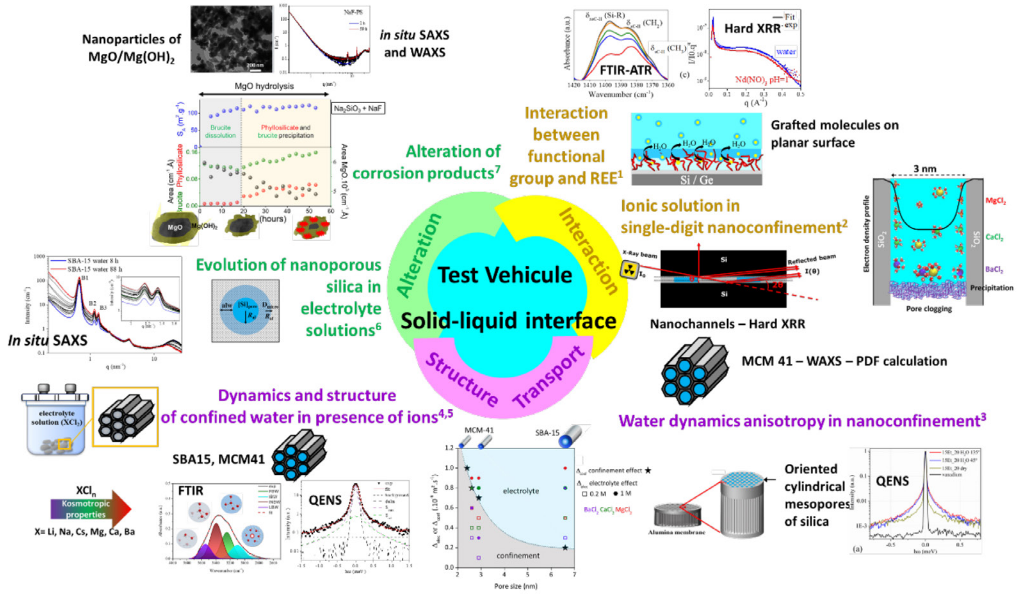

Figure 1. Illustration of test vehicule used for the study of the solid-liquid interface.

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SERAMIC: A SEMI-AUTOMATIC METHOD FOR THE SEGMENTATION OF GRAIN BOUNDARIES

R. Podor, X. Le Goff, J. Lautru, H.P. Brau, N. Clavier

The SEraMic method[1], implemented in the SEraMic plugin for Fiji or ImageJ softwares, has been developed to calculate a segmented image showing the grain boundaries from a ceramic cross-section. This method has been used to accurately and automati-cally determine the grain boundary positions – and further assess the grain size distribution - of monophasic ceramics or metals / alloys t. The only required sample preparation is a mirror polished cross-section. The SEraMic method is based on the recording of at least 6 backscattered electron (BSE) SEM images with different tilt angles ranging between -5° to +5°, of a unique region of interest, which emphasize the orientation contrasts of the grains (Fig. 1). As this latter varies with the incident beam angle with the sample, the set of images contains the information relative to all the grain boundaries. The SEraMic plugin calculates and builds auto-matically the segmented image of the grain boundaries from the set of tilted images (Fig. 2).The SEraMic method is compared with the classical thermal etching methods. It is applied to the determination of grain boundaries for different types of materials (oxides, phosphates, carbides, alloys). The method remains easy to use and accurate when the average grain diameter is higher or equal to 0.25 µm. The plugin has been enhanced by the addition of a component for automatic measurement of inter- and intra-granular porosity, which has been added at the request of users. The Seramic method is currently being compared with artificial intelligence-assisted grain segmentation techniques.

The SEraMic method saves a lot of time (about 90-95%) in the tedious analysis steps of sample preparation (annealing for thermal etching in particular) and determination of the average grain size in ceramics. It is independent of the operator. It allows working on large quantities of grains (from 800 to 2000). Finally, this method will be adapted to work on multiphase materials.

It is currently being used in numerous projects currently underway at ICSM to characterize ceramics or establish sintering maps.

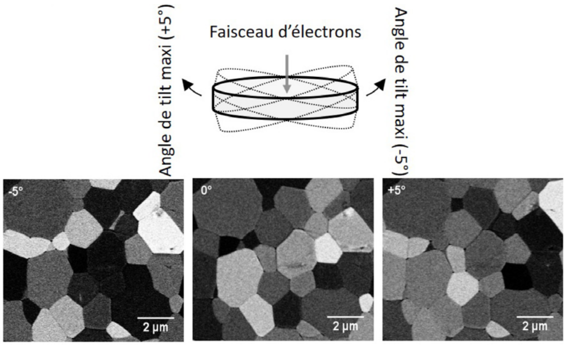

Figure 1. Principle of the SEraMic method: recording of tilted BSE image series.

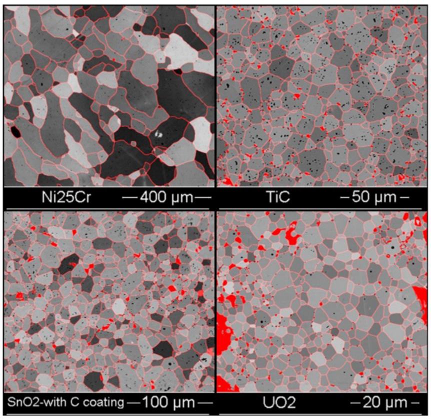

Figure 2. Segmented images for different types of materials using the SEraMic method.

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MULTI-COLLOIDAL SOLS FOR THE PREPARATION OF MIXED OXIDES MATERIALS

D. Rébiscoul, H. Barbier, L. Bodapati, N. Clavier, R. Podor, J. Lautru, X. Le Goff

Mixed oxide materials are of interest in a number of applications including nuclear power with the MOX nuclear fuel (mix of uranium and plutonium oxides) used in nuclear reactors, membranes, catalysis, energy conversion, microelectronics, photolumi-nescence and biotechnology. Innovative soft prepa-ration methods are currently being studied to improve the material homogeneity at a nanometric scale. This is necessary to avoid the formation of metal clusters that can modify the macroscopic properties of materials. This is particularly the case with Pu in nuclear fuel which must be homogene-ously distributed on a sub-micron scale to avoid the hot spot formation.

The colloid self-assembly route have been identified as an interesting route to prepare from aqueous sols, oxide material made of a loose packing of oxide nanoparticles with an ordered distribution. Recently, this process was used to prepared actinide oxide material without generating dust until the shaping stage[1-3]. This method is based on the pH control and the use of a complexing agent to limit the hydrolysis and condensation reactions and thus, to control the size of the colloids of a few nanometers.

Based on this route and as a part of 2 PhD works (H. Barbier, CEA and L. Bodapati, UM) we prepared multi-colloidal sols either by mixing metal salts (f-block elements) either by mixing mono-colloidal sols and study the homogeneity of the resulting mixed oxide materials. By the use of small and wide-angle X-ray scattering to determine the size, nature, shape and colloidal fraction of the colloids as a function of the experimental conditions, the homogeneity of the colloid self-assembling was controlled. As illustrated on the Figure 1 with the use of Th-Ce sols, selecting the well adapted multi-colloidal sol, material presenting an homogenous distribution of the two elements at a nanometric scale was obtained.

These results highlight that multi-colloidal self-assembly route offers large opportunity for the preparation of mixed oxide materials.

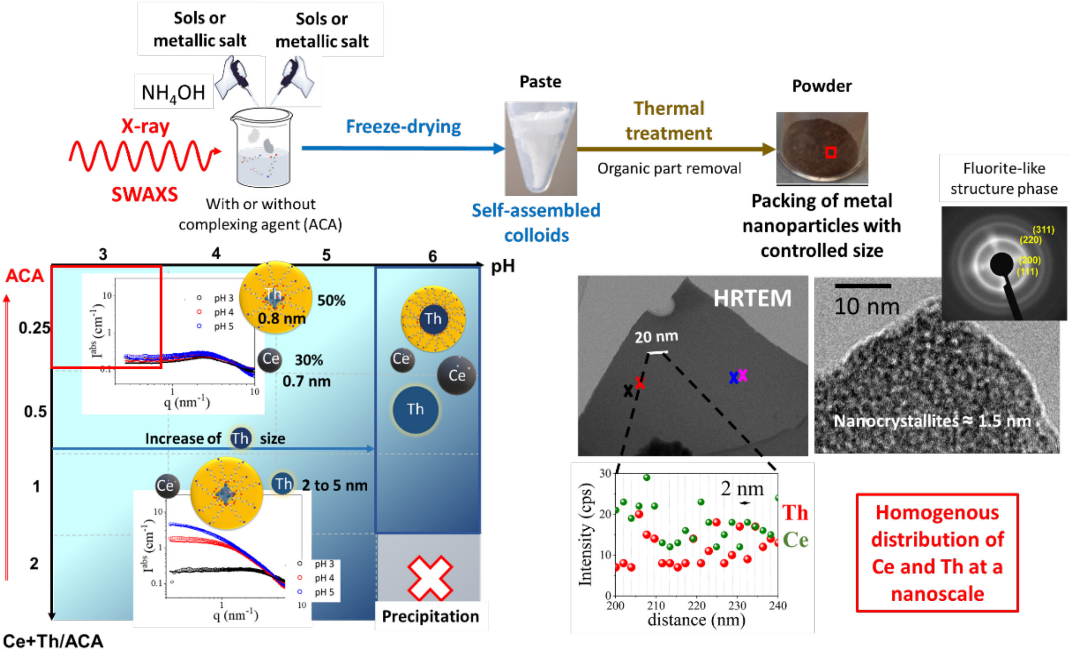

Figure 1. Illustration of the use of multi-colloidal sols for the preparation of Th-Ce mixed oxide material homogenous at a nanometric scale.

[1] Rebiscoul D., Lu Z., Zemb T. FR3131583 - EP4206162.

[2] Rebiscoul D., Lu Z., Zemb T. - FR3131654.

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IN-DEPTH STUDY OF U(VI) INTRINSIC COLLOIDS

D. Rébiscoul, H. Barbier, C; Kramer, L. Bodapati,.N. Clavier, R. Podor, J. Lautru, C. Tamain, X. Legoff, S. Szenknect

The formation of U(VI) intrinsic colloids has a non-negligible impact on the dissemination of actinides in the environment. It is therefore essential to better identify their nature, formation conditions, and stability domains. These specific points are especialy important since the behavior of these elements in environment is generally estimated by geochemical transport modeling. This modeling relies on the accurate prediction of their speciation in various situations based on thermodynamic databases that have to be continuously updated. These databases include some formation constants of few actinide polynuclear species such as uranyl hydroxocarbonates, Th and Pu hydroxydes but do not include many of the others. Indeed, thermodynamic data for polynuclear clusters or colloids are not available in these standard compilations. This limits the accurate prediction of actinide speciation, which requires not only a knowledge of the soluble actinide species under typical geochemical conditions, but also the stable colloidal species containing potentially tens or even hundreds of actinide atoms. To reach this goal, the actinide colloid concentration as well as the number of actinide atoms per colloid have to be determined.

For the first time, as a part of a Master internship (H. Barbier), a PhD (Christin Kraemer) and in collaboration with the LIME, we proposed a simple, reliable and systematic experimental method for accessing these key properties for U(VI) intrinsic colloids in simplified solutions. Based on geochemical simulations, elemental analyses by Inductively Coupled Plasma Optical Emission Spectroscopy and *in situ* Small and Wide Angle X-ray Scattering characterizations, we were able to probe key properties of U(VI) colloids such as their size, volume, concentration and stoichiometry.

As silicate species are ubiquitous in the geosphere, the formation of U(VI) colloids was studied at first in simplified model solutions containing salts of interest such as NaCl and Na_2SiO_3 at weakly alkaline pH. The determination of the colloid properties made it possible to calculate the U(VI) distribution coefficient between intrinsic colloids and solution. This crucial coefficient can be included in thermodynamic databases to calculate in similar environmental conditions, an accurate U(VI) speciation that takes into account the predominant colloidal form.

This new methodology enhance predictive geo-chemical calculation, especially to predict the fraction of U(VI) present as colloids that may migrate into natural waters.

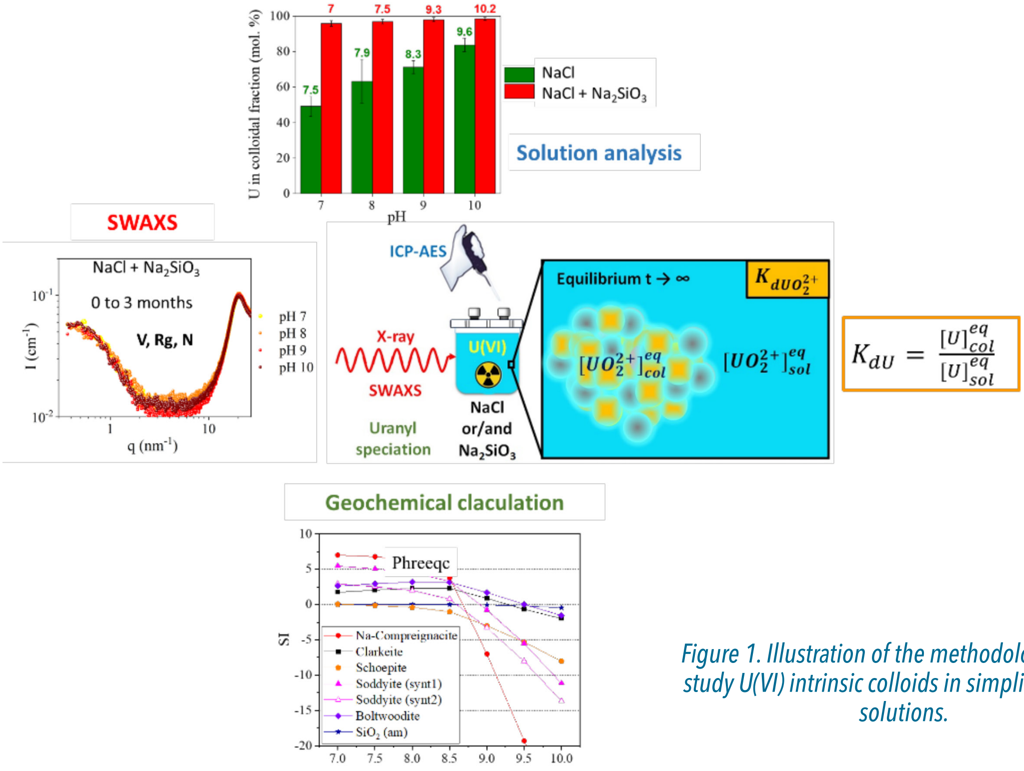

Figure 1. Illustration of the methodology used to study U(VI) intrinsic colloids in simplified model solutions.

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OXIDES INTERFACIAL SYSTEMS AND THEIR ENVIRONMENT

B. Siboulet, K. Wang, J.-F. Dufrêche, D. Rébiscoul, M. Duvail, M. Spadina, H. Khoder, B. Baus-Lagarde

Charged surfaces interaction with ions is still a challenging issue. The interaction can be described through continuous models, or at the atomic level, with molecular dynamics, which includes both anions and cations. Still, analyzing the role of cationanion interaction in adsorption is seldom considered at the atomic level despite the significance for separation.

We conducted a series of studies that provide a more precise description of the interface than is typically found in similar work, including those involving simulations. Our findings for silica surfaces demonstrate that a strong affinity between ions in a dissolved salt enhances ion adsorption at the surface, primarily in the form of ion pairs. The extent of this pair adsorption differs markedly between $BaCl_2$ and $MgCl_2$.

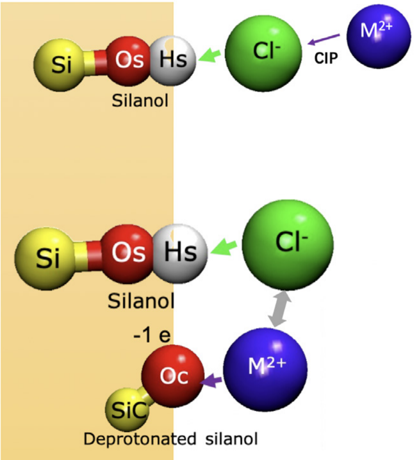

Figure 1. Interaction between ions drives adsorption

This can be analyzed in terms of thermodynamic paths. Experiments involving the insertion of MCl_2 solutions into silica nanochannels, analyzed via X-ray reflectivity (XRR), reveal that fluid mobility within the channel is hindered in the case of $BaCl_2$, unlike with $MgCl_2$ or $CaCl_2$. Simulations[2] clarify whether this behavior stems from ion-surface interactions or interionic interactions in the bulk: it is the bulk association that drives this phenomenon, consistent with observed trends in solubility.

Confined electrolytes are simulated at the classical level[3]. Simulation of ion surface interaction allows to disentangled the individual contributions of electrolytes, nanoscale confinement, and cation–surface interactions. We systematically evaluated how each factor influences water dynamics. Simulations show that monovalent cations interact weakly with the silica surface[4]. This is why water dynamics in their presence are primarily governed by confinement. In contrast, divalent cations exhibit strong interactions with the silica surface, introducing an increased additional influence on water behavior.

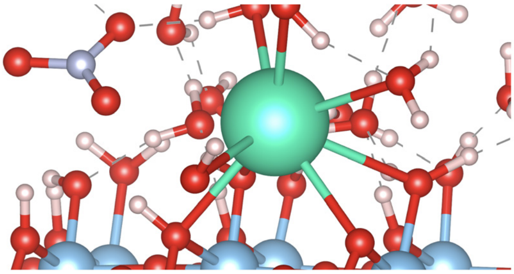

Figure. 2 Adsorption of $CsNO_3$ on TiO_2

Another example is TiO_2 nanotubes that can be used for water decontamination.

We integrated a variety of experimental techniques—ranging from structural analyses to measurements of the properties of aqueous nanotube suspensions—with continuum solvent modeling and quantum DFT-based simulations, in order to evaluate Cs^+ adsorption on TiO_2 nanotubes and to predict the separation behavior of metal ions. The mesoscopic simulation shows that the nanotube are effective for decontamination in the limit of low pH and high concentration.

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CHARACTERISATION OF BUBBLES AND OF THE SONOCHEMICAL PLASMA

R. Pflieger, S. Herr, S.I. Nikitenko
M. Ashokkumar (University of Melbourne)
M. Draye (University Savoie Mont-Blanc)
J.-Y. Hihn, L. Hallez (Institute Utinam)
R. Mettin (University of Göttingen)

Sonoluminescence (SL) is the emission of UV-visible light triggered by the violent collapse of microbubbles generated in liquids submitted to ultrasonic irradiation. This violent collapse leads indeed to extreme conditions in the bubbles (T>5000 K) which are the source for the sonochemical reac-tions, in particular through the formation of radicals (e.g. H and $HO^{\bullet}$ in water). Hence, a better under-standing of the conditions reached in the bubbles would allow an optimization of the sonochemical reactions. These conditions are probed by measuring the SL spectrum by means of a spectrograph coupled to a CCD camera. In well-chosen conditions, SL spectra bear emissions of excited species which can be fitted to estimate characteristic temperatures of the plasma or that can be monitored to follow the evolution of the sonicated system. For example, the study of SL spectra has made it possible to monitor the degradation of ionic liquids under ultrasound (Figure 1, collaboration with the University Savoie Mont-Blanc), and the conditions (in particular, water content) under which this degradation is more or less marked.[1] This approach has also been used to better characterize the very high ultrasonic frequencies (> 3 MHz) in focused geometry [2], which are increasingly used in the medical and surface treatment sectors, as they enable an intense, highly localised effect to be obtained. The effect of cavitation at these very high frequencies can be exacerbated by frequency modulation, as demonstrated in collaboration with the Institute Utinam in Besançon.

The combination of SL measurement with pulsed ultrasound can be used to monitor the dissolution of bubbles and to estimate bubble size distribution from it. A strong effect of the gas nature was observed at 362 kHz, with cavitation bubble sizes of 3.0 µm for Ar, 1.2 µm for He, 3.1 µm for Xe, 2.8 µm for O_2, around 1 µm for N_2 and air.[3] In non-conventional conditions (e.g. under hydrothermal conditions), the presence of cavitation can be probed by acoustic spectroscopy, with the presence of sub- and ultra-harmonics illustrating the strong oscillations of bubbles.[4]

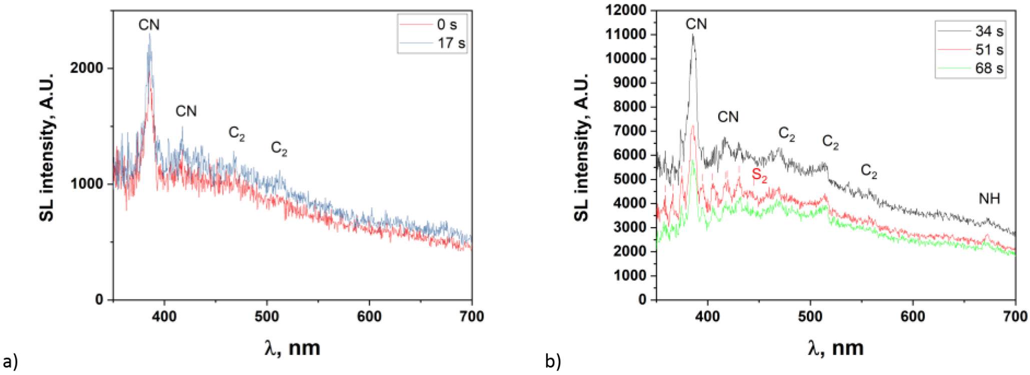

Figure 1 : Appearance of molecular emission bands in the SL spectrum a) after 17 seconds and b) up to 68 seconds of ultrasonic irradiation, indicating the degradation of the water-saturated ionic liquid [BEPip][NTf$_2$] from the first moments of sonolysis at 20 kHz under Ar.

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MULTI-SCALE STRUCTURAL CHARACTERISATION OF FOAM

J. Lamolinairie, A. Jonchère, C. Pasquier, L. Girard, P. Bauduin and O. Diat

To investigate foam structure and because there is currently no one approach that can gather the essential data concurrently over all pertinent length scales, studies have been conducted sequentially, with each technique investigating a separate foam sample. However, because each sample is distinct, the results are not comparable. Additionally, the experimental demonstration of theoretical foam destabilization mechanisms was previously ham-pered by the lack of a comprehensive perspective of the evolution of the foam structure with aging.

The idea was to develop a device capable of probing the same sample of foam with multiple techniques within a single experiment.

The developed device consists of a quartz column – based on the FOAMSCAN model produced by Teclis Scientific within which the foam sample is produced. A wide range of data is then collected from the nano to the centimeter scale through the simultaneous use of three techniques: electronic conductivity, macro-photography and small-angle neutron scattering (SANS). Analysis of the simulta-neous data acquired by the device has enabled the first multi-scale characterization of the structural evolution of foam, significantly improving understanding of the underlying aging processes.

The average thickness of foam films, obtained using SANS data, combined with the repulsion between facing foam films, deduced from the curvature of plateau borders in the image data, has allowed the first quantification of pressure inside the foam. The pressure measured in the foam has been found to differ by a factor of 10 from the pressure measured on a single film, despite the fact that a thin-film pressure balance is typically used to measure pressure on a single film. This finding further demonstrates the unreliability of combining results from various experimental set-ups.[1]

«The ILL's D33 diffractometer was constructed and equipped with not one but two detectors, one closer and one further from the sample, giving it a particularly wide Q-range. With this setup, it is possible to probe the entire structure of foam in a single experiment, from hundreds of nanometers to one nanometer. The neutron beam's comparatively large 15 mm diameter enables non-destructive probing of hundreds of bubbles at once, guaranteeing that the results are statistically significant. Additionally, the ILL's neutron out-put, which is the world's highest continuous neutron flux, has an unparalleled temporal resolution that makes it possible to closely monitor the foam's structural development.

For the device's development, the Partnership for Soft Condensed Matter (PSCM) at ILL was crucial. «At the PSCM, extensive preliminary work was done to characterize foam using all available methods. The PCSM is crucial to ensuring that neutrons are only utilized when their contribution is vital because they are an expensive probe» according to Dr Leonardo Chiappisi.

The new device represents an important milestone in the quest to understand foam and opens new perspectives for the field.

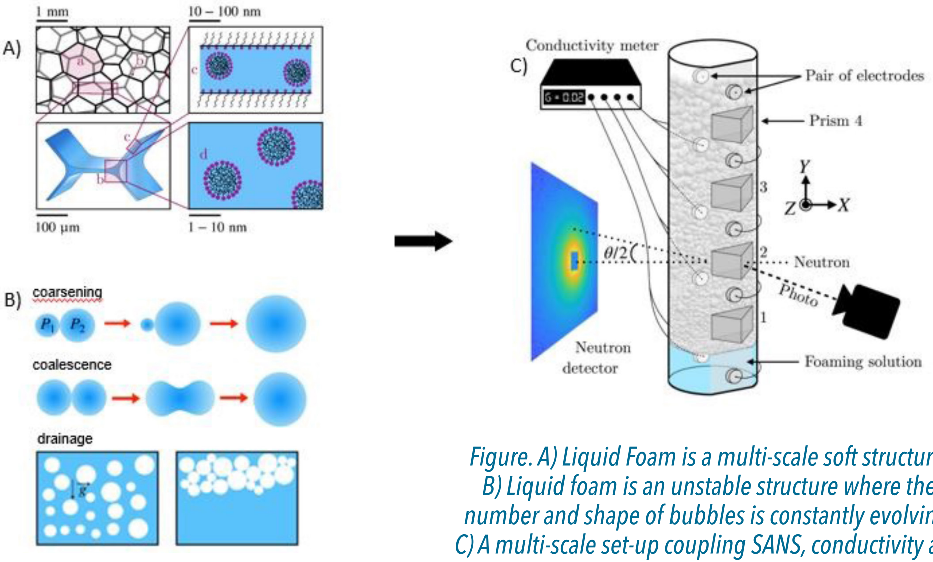

Figure. A) Liquid Foam is a multi-scale soft structure. B) Liquid foam is an unstable structure where the number and shape of bubbles is constantly evolving. C) A multi-scale set-up coupling SANS, conductivity and optical imaging for investigating foam structure.

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[1] Lamolinairie J., Dollet B., Bridot J. L., Bauduin P., Diat O., Chiappisi L. - **Probing foams from the nanometer to the millimeter scale by coupling small-angle neutron scattering, imaging, and electrical conductivity measurements** - *Soft Matter* (2022) 18, 8733-8747.

FURNASEM: A NEW METALLIC FURNACE FOR HT-SEM

J. Mendonça, H.P. Brau, D. Nogues, A. Candeias, R. Podor

In situ high-temperature experimentation in a Scanning Electron Microscope (SEM) is an advanced technique for the study of matter that allows the visualization of the dynamics of microstructural transformations that a material undergoes during heat treatment. The implementation of this technique requires the use of a micro-furnace allowing the heating and observation of the samples. The work carried out with the industrial partner NewTEC Scientific (Readynov FurnaSEM project and Cifre thesis of J. Mendonça) is to design, produce and test a new micro-furnace, called FurnaSEM, capable of heating and cooling rapidly (about 10°C/s) a millimetre-sized sample up to 1300°C, under high vacuum and reduced gas pressure. The design choices for the microfurnace (flat furnace with a sample on top) are based on extensive literature research. The materials used to manufacture the various elements of the microfurnace are chosen according to their physical and chemical properties. The geometry of the furnace and the materials selected are implemented in a digital model, called a digital furnace, and the shape of the parts is optimised by thermal calculations. In parallel, the FurnaSEM microfurnace was manufactured, tested and characterised in a test bench specially developed for this work (Fig. 1). The experimental results validated some of the numerical model results and discussed their limitations (Fig. 2). The technical operational characteristics of the FurnaSEM micro furnace have been precisely established and are in accordance with the specifications. Numerical calculations and measurements in the test bench show that the positioning of a sample on FurnaSEM can generate a temperature jump. Effective solutions to limit this artefact are proposed. The FurnaSEM microfurnace is used to perform *in situ* experiments in a SEM up to 1340°C, under vacuum and gas. All the technical characteristics of FurnaSEM have been validated under operating conditions and many new results have been obtained. [1,2]

A new generation of microfurnaces has been developed based on the coupling of a numerical and experimental approach.[3] Recommendations for the future user on the geometry of the samples and their positioning on the furnace are given on the basis of quantifiable elements.[4]
Finally, the geometry of the furnace can be adjusted on demand using numerical simulations.
The FurnaSEM 1300 furnace is currently marketed by NewTEC Scientific.[5]

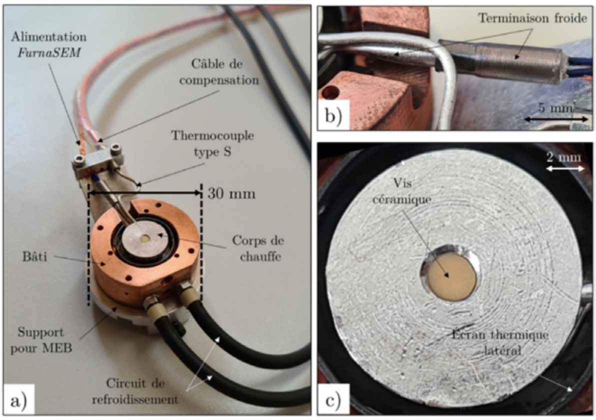

Figure 1. View of the FurnaSEM 1300 furnace.

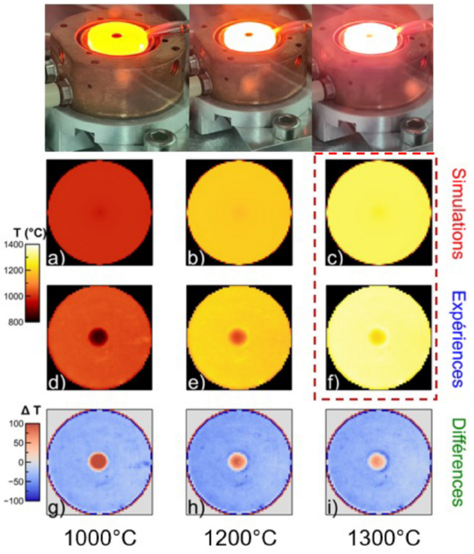

Figure 2. Experimental and numerical views of the FurnaSEM 1300 device under operating conditions at 1000, 1200 and 1300°C.

[1] Podor, R., Mendonça, J., Lautru, J., (...), Mathieu, S., Vilasi, M. – **Evaluation and application of a new scintillator-based heat-resistant back-scattered electron detector during heat treatment in the scanning electron microscope** – *Journal of Microscopy* (2021) 282(1), 45-59.
[2] Trillaud, V., Podor, R., Gossé, S., (...), Dacheux, N., Clavier, N. – **Early stages of UO_{2+x} sintering by *in situ* high-temperature envi-ronmental scanning electron microscopy**– *Journal of the European Ceramic Society* (2020) 40(15), 5891-5899.
[3] J. Mendonça, H.P. Brau, D. Nogues, A. Candeias, R. Podor - **Development of a microfurnace - FurnaSEM - dedicated to in-situ SEM observation up to 1300°C - Part I: Concept, fabrication and validation** - *Review of Scientific Instruments* (2024) 95 53704
[4] J. Mendonça, H.P. Brau, D. Nogues, A. Candeias, R. Podor - **Development of a microfurnace - FurnaSEM - dedicated to in situ SEM observation up to 1300°C - Part II: Study of the thermal response of samples** - *Review of Scientific Instruments* (2024) 95 53705
[5] J. Mendonça, J. Lautru, H.P. Brau, D. Nogues, A. Candeias, R. Podor - **Development of a microfurnace - FurnaSEM - dedicated to in situ SEM observation up to 1300°C - Part III: in-situ high temperature experiments in the Scanning Electron Micro-scope** - *Review of Scientific Instruments* (2024) 95 53706

NEW IMAGING MODES FOR HIGH TEMPERATURE SCANNING ELECTRON MICROSCOPY

R. Podor, J. Lautru, J. Mendonça, H.P. Brau, X. Le Goff, D. Nogues, A. Candeias

The use of the FurnaSEM device opens new opportunities in terms of imaging conditions due to its flat configuration and its fully metallic conception. For example, the working distance between the sample and the objective lens can be reduced (thus improving the signal-to-noise ratio of the images and improving the resolution) or new detectors can be associated with the furnace.

First of all, the working distance between the sample and the objective lens can be minimized. Thus, low voltage images (up to 3kV) could be recorded under residual gas pressure at high temperature. They allow observing surface details of a $(Ce,Gd)O_2$-Ag thin film as low as 30 nm, during thermal treatment at T=350°C (see Fig. 1). Second, the design of a fully metallic furnace makes it possible to reduce the outgassing of the furnace during the heat treatments. This property allows the direct observation of the microstructural evolution of metallic materials and opens new perspectives in the field of metallurgy. Third, the furnace can be tilted relative to the primary electron beam and series of tilted images can be recorded at high temperature. These images are then used to reconstruct a 3D image of the sample surface directly at high temperature. These images can be recorded continuously and allow the topographic variations of a sample during heat treatment to be described quantitatively. This technique have been used to study the surface variations of an Al-Si coating deposited on a steel substrate during a heat treatment (Fig. 2)[1]. Last, a backscattered electron detector that can be used at high temperature, developed by the Czech company Crytur, was adapted to the SEM and used to study phase transformations at high temperatures (Fig. 3)[2]. These methodological developments open up new avenues of study for understanding the behavior of materials at high temperatures (sintering, oxidation, reactivity of glasses, etc.).

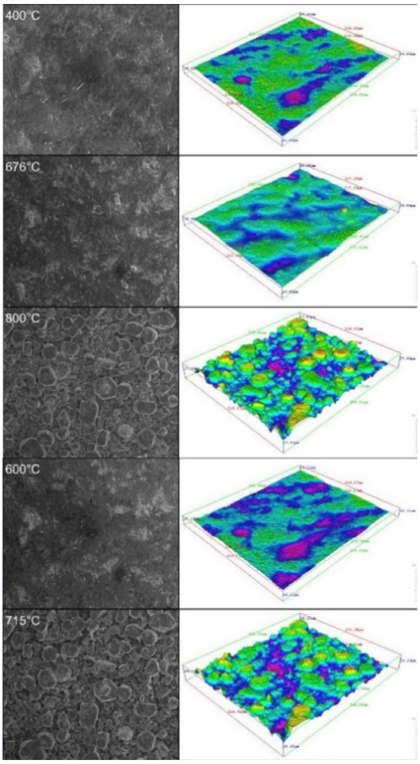

Figure 2. 3D images of Al-Si coating deposited on a steel substrate during a heat treatment.

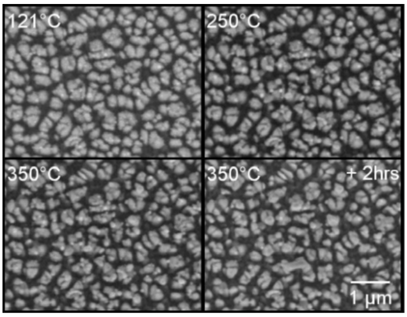

Figure 1. Microstructural evolution of a $(Ce,Gd)O_2$ + Ag thin film during a heat treat-ment observed at $E_0 = 5kV$.

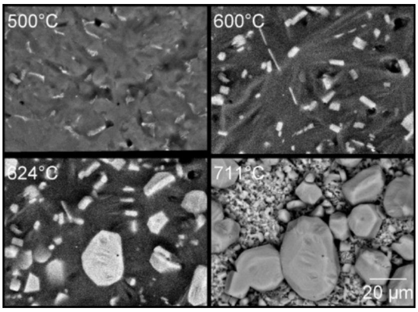

Figure 3. BSE images of Al-Si coating deposited on a steel substrate during a heat treatment.

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[1] Podor, R., Mendonça, J., Lautru, J., (...), Mathieu, S., Vilasi, M. – **Direct Observation of the Surface Topography at High Temperature with SEM**– *Microscopy and Microanalysis* (2020) 26(3), 397-402.

[2] Podor, R., Mendonça, J., Lautru, J., (...), Mathieu, S., Vilasi, M. – **Evaluation and application of a new scintillator-based heat-resistant back-scattered electron detector during heat treatment in the scanning electron microscope** – *Journal of Microscopy* (2021) 282(1), 45-59.

INTERNATIONAL PROJECTS

ERA•MIN

DFG
Deutsche
Forschungsgemeinschaft

eurad 2
European Partnership
on Radioactive Waste Management

cnrs
IRP

CEA / NTU
SCARCE

horizon
europe

EUROPEAN JOINT PROGRAMME ON RADIOACTIVE WASTE MANAGEMENT

With the European Joint Programme on Radioactive Waste Management EURAD-1 a step change in European collaboration was envisaged towards safe radioactive waste management (RWM), covering all phases including predisposal and disposal, through the development of a robust and sustained science, technology and knowledge management programme that supports timely implementation of RWM activities and serves to foster mutual understanding and trust between Joint Programme participants.

In EURAD-1, the Laboratory of Evolving Interfaces in Materials (LIME) was involved in the « spent fuel characterization and evolution until disposal » work-package (WP). In this WP, our goal was to better understand the behaviour of UO$_2$ based model compounds during leaching tests representative of interim storage in nuclear pools. Especially, the impact of various Fission Products (FP) on the chemical durability and on the surface reactivity of the sintered materials was examined. With this aim, we first developed the synthesis of a large variety of sintered UO$_2$ samples doped with FP. Then, we applied a dual approach that includes not only the analysis of the released elements in the solution, but also the monitoring of the solid/ liquid interface during multiparametric leaching tests. This latter was made possible by coupling various techniques such as AFM, ESEM, GI-XRD. A particular attention was devoted to the existence preferential zones (grain boundaries, triple junctions, pores, …) through the development of 3D reconstructions performed on leached/altered materials.

The LIME was also involved in the preparation of a large panel of sintered pellets of uranium-lanthanide oxide that were provided to CEMHTI – Orléans. In this second task, the consequences of the incorpo-ration of lanthanide elements in the UO$_2$ structure were evaluated. The characterization of the samples by CEMTHI partner involves positron annihilation spectroscopy (PAS) in order to probe the potential vacancy defects induced by such incorporation in the fluorite structure.

EURAD-2 builds upon EURAD-1 to further implement a joint strategic programme of research, development and knowledge management activities at the European level, bringing together and comple-menting EU Member States programmes in order to ensure cutting edge knowledge creation and preservation in view of delivering safe, responsible and publicly acceptable solutions for the manage-ment of radioactive waste throughout all programme phases (from "cradle to grave"). In EURAD-2, the LIME is involved in the SAREC WP (Release of **sa**fety **re**levant radionuclides from spent nuclear fuel un-der deep disposal **c**onditions). The main objective of this WP is to improve the quantification and the mechanistic understanding of the release of safety relevant radionuclides covering most representative types of spent nuclear fuel and of the fuel evolution both prior and posterior to contact with groundwa-ter to better predict the radionuclide source term for geologic disposal post-closure safety assessment.Within this WP, the LIME is particularly in-volved in task 4 aiming to discriminate radionuclide contributions from open grain boundaries, closed porosity, rim grains during alteration and secondary phase formation during leaching/dissolution of spent nuclear fuel under condition relevant for deep geological. Once again, model compounds of con-trolled composition and microstructure will be pre-pared and used in specifically designed leaching experiments that couple the monitoring of the evolution of FP release in solution and observations of the altered surface at the microscopic scale.

HORIZON-EURATOM-2023-NRT-01
TOPIC 09
ACTION EURATOM-RIA

NOVEL 2D-3D MATERIALS FOR LANTHANIDE RECOVERY FROM NUCLEAR WASTE (MALAR, N°101164053)

Une approche innovante de récupération des lanthanides dans les déchets nucléaires.

La récupération des lanthanides est généralement complexe et gourmande en ressources. Les matériaux 3D construits à partir de feuilles 2D et d'architectures poreuses offrent de plus grandes surfaces et des propriétés chimiques uniques qui contribuent à la séparation et à la récupération des lanthanides contenus dans les déchets industriels. Le projet MaLaR, financé par l'UE, se propose de développer une approche de récupération sélective des métaux rares dans les déchets nucléaires. Il entend créer de nouveaux matériaux 3D à partir de feuilles 2D afin d'améliorer l'efficacité de la récupération des lanthanides dans le combustible nucléaire usé. Le projet fera appel aux infrastructures de radiochimie de diverses institutions européennes pour développer des matériaux poreux destinés à séparer les actinides et les lanthanides des déchets nucléaires fortement acides. La coordination est assurée par HZDR, qui opère la ligne chaude ROBL de l'ESRF, et regroupe par ailleurs des équipes suédoises (Universités de Umea et d'Uppsala) et roumaines (Université Polytechnique de Bucarest). Au sein du consortium, le LIME s'intéressera plus particulièrement à la spéciation physico-chimique des éléments lanthanides dans différents composés d'uranium, dont les oxydes U_4O_9, U_3O_8, et UO_3, ou les phases hydratées de type studtite ou schoepite. Ces études s'appuieront sur les méthodes de caractérisation synchrotron disponibles à HZDR/ROBL et sur des calculs de structure électronique réalisés à Uppsala. Dans un deuxième temps, la dissolution des composés uranifères dopés en lanthanides sera étudiée, et permettra de fournir des lixiviats pouvant être mis en œuvre dans les expériences de séparation. Le projet entend ainsi fournir des solutions technologiques dédiées à la gestion des déchets nucléaires.

THE EUROPEAN ENERGY RESEARCH ALLIANCE (EERA)
JOINT PROGRAMME ON NUCLEAR MATERIALS (JPNM)

SPECTROSCOPY FOR ELEMENT SENSITIVE ANALYSIS OF NUCLEAR MATERIALS (SESAM)

X-ray absorption and emission spectroscopies (XAS/XES) in hard and tender X-ray regime are nowadays essential element sensitive approaches for post-irradiation and *in-situ* non-destructive ex-aminations of nuclear materials. They were successfully applied to the development of new manufacturing and reprocessing processes, their behaviour in reactor and their stability under storage conditions. The development of beamlines dedicated to actinide and other radioactive elements allows detailed investigations of nuclear materials. However, both the lack of a complementary alternative in the laboratory and the strongly limited synchrotron beamtime availability are narrowing the impact of those advanced analysis methods to only a few materials each year. In addition, high quality experimental and calculated standards are still missing while being mandatory to cope with the increasing complexity of the composition and microstructure of nuclear materials, especially when considering irradiated nuclear fuels and molten salts. The revival of laboratory instruments with performance complementing those of synchrotrons are now a game changer, opening a completely new range of routine XAS/XES applications in radiochemical laboratories. Similarly, new high-end methods (HERFD-XAS, RIXS) are developed at the synchrotron, with unprecedented sensitivity to both the electronic and local structure of elements in chemically or environmentally complex systems.

The goal of the SESAM project is to set up a synergy and common framework between all the major Eu-ropean actors in the fields of XAS/XES and actinide research, to supply the missing experimental and calculated standards via extensive data benchmarking campaign on actinides' oxides and halides. SESAM is also aiming the development of dedicated new instrumentations and methodologies at both laboratory and synchrotron alike to push nuclear materials beyond state of the art.

The consortium managed by the University of Helsinki involved also the Belgian Nuclear Research Centre (SCK CEN), the CEA, the CNRS, the Karlsruhe Institute of Technology (KIT), the Helmholtz Zentrum Dresden-Rossendorf (HZDR), the Delft University of Technology (TU Delft) and the Paul Scherrer Institute (PSI).

E R A•M I N

TOWARD SUSTAINABLE BATTERIES BASED ON SILICON, SULFUR AND BIO-MASS DERIVED CARBON AS 2BOSS PROJECT IN ERAMIN2 EUROPEAN CALL

Closing the circular economy loop by recycling raw materials to create new components is especially important in a fast-expanding and strategic industry like energy storage. Because batteries are a crucial component of portable electronics and electric vehicles, it is important to create efficient and cost-effective recycling methods to keep up with the industry's rapid expansion. Although lithium-ion batteries are currently the most popular technology, they have a number of inherent limitations that prevent their production from being sustainable. These limitations include their moderate specific energy capacity and durability, their heavy reliance on a number of essential raw materials (CRMs) for the EU, and the difficult and expensive recycling of these CRMs due to their dispersion and metal-metal mixing. Toward sustainable batteries based on silicon, sulfur, and carbon obtained from biomass (2BoSS) will concurrently develop an innovative battery technology and the related recycling strategies to enable a circular reuse of raw materials that ensures a sustainable manufacturing.

By focusing on these four key areas, 2BoSS will create environmentally friendly batteries that are appropriate for the circular economy: 1) creation and testing of a silicon-sulfur battery technology that offers optimum performance, reduces the need for CRMs, and permits the circular use of resources. 2) defining and validating efficient recycling techniques that enable raw material separation and reuse; 3) assessing the cost, life cycle, and environmental, health, and safety impacts; and 4) designing high-performance products and scaling up their production.

A battery technology supported by a cobalt-free Li2S-based cathode and a graphite-free silicon-based anode will be optimized and validated by 2BoSS.

The consortium gathers the FUNDACIO INSTITUT DE RECERCA DE L'ENERGIA DE CATALUNYA, the Department of ENVIRONMENT, LAND AND INFRASTRUCTURE ENGINEERING (DIATI) in Turin (Italy), the Commissariat à l'énergie atomique et aux énergies alternatives (CEA / France) with the participation of ICSM/LHYS team and Cleopa Gmbh / Innovation Energy Efficiency in Julich (Germany).

IRP

INTERNATIONAL RESEARCH PROJECT (IRP) I.R.P. CNRS-MPG –UNIVERSITY OF REGENSBURG "NISHI" 2023-28

The development of this new IRP entitled "NISHI" for "Nano-ions at soft and hard interfaces" is built on the base of a previous one, n° 0466 and entitled "NISI" for "Nano-ions at soft interfaces" that was handled between 2018 and 2021.

P.I., Olivier Diat (ICSM/L2IA)
co-P.I. Emanuel Schneck (Physics Department / Softmatter biophysics), Pr. Dr. Regine von Klitzing (Physics Department / Softmatter and interface) at Darmstadt Technical University
co-P.I. Dominik Horinek (Univ. Regensburg)
Others partners: ICSM-LMCT, Pr. W. Kunz and Pr. A. J. Bäumer at university of Regensburg, Dr L. Chiappisi from ILL, Dr B. Dollet at Grenoble Alpes University and Pr E. Leontidis at Cyprus University.

Ions are present in all states of matter and interact through Coulombic forces with their surroundings, influencing complex supramolecular structures and transport across compartments. In aqueous environments, ion–water interactions significantly affect solvent behavior, giving rise to Specific Ion Effects (SIE). These effects, beyond simple electrostatics, vary with ion size, charge density, and polarizability, influencing phenomena such as colloidal stability, foam dynamics, and protein solubilization.

SIE are commonly observed at high salt concentrations and depend on the ion's ability to either salt-out (kosmotropes) or salt-in (chaotropes) molecules. Recent attention has turned to superchaotropic ions—large, low-charge-density ions like polyoxometalates (POMs) and boron clusters—which induce salting-in effects even at very low concentrations (millimolar to sub-millimolar). These ions exhibit surfactant-like or hydrotropic behavior, impacting self-assembly processes and solubilization properties.

This understanding opens up novel avenues in soft matter science and formulation chemistry, allowing the design of less energy-intensive processes and new solvents capable of dissolving lipophilic compounds. Superchaotropic ions bridge the gap between traditional salts and hydrophobic solutes, offering innovative tools for material and biomedical applications.

So, the general outline of this project can be described in 4 tasks:

Task 1: To understand the interaction of superchaotropic nano-ions with a polar or neutral amphiphilic molecules, which necessitates a precise quantification of their hydration thermodynamics. The next stage of this project involves modelling the adsorption and penetration interaction strength within the neutral self-assemblies of these nano-ions as a function of their charge density and as a function of the surface chemistry of the self-assemblies. The following tasks' sensor applications will be researched using the same methodology applied to solid surfaces functionalized by polar molecules.

Task 2: Building novel phase diagrams for ternary systems and examining the solubilisation mechanism of a fourth lipophilic solute will be exciting to develop in this second task as we would like further explore the hydrotropic property of superchaotropic nano-ions and the formation of surfactant-free microemulsions. The thermodynamical approach as well as the supramolecular structure of the nanometric self-clusterings characterizing these systems will be investigated and simulated, as already studied in collaboration with Horinek group on classical hydrotropes such as short alcohols in pre-ouzo systems.

Task 3: Nano-ions interacting with 2D, monolayer fluid interfaces; this task is a continuation of one of the tasks of the previous IRP and that was strongly impacted by the COVID period. It is also closely related to task 1 but on a more experimental activity by first studying the direct interactions of nano-ions (by varying their chemistry) with flat surfaces of neutral (or zwitterionic) amphiphilic molecules whose intra-film lateral interactions will be tuned. This will either be examined at thermodynamic equilibrium (using a Langmuir balance or a thin film pressure balance) or out of thermodynamic equilibrium by looking at foams stabilized by nano-ions. These studies will allow us to investigate a more dynamic aspect of the interactions by determining characteristic exchange and diffusion times, data that are currently missing. Surface rheology will be also addressed in that task. A cotutelle thesis program between Montpellier Univ. and TU Darmstadt has started in September 2024.

Task 4: As a more prospective task, nano-ions such as polyoxometalates or carboranes clusters are also known for their photocatalytic properties that can be exploited in association with sensors. This type of development can follow two approaches, either following strategy based on nano-ions adsorption onto pre-functionalised sensors surface or via the transfer on the sensor substrate of a pre-organised monolayer pre-organised and having concentrated the nano-ions at a liquid/air interface. In both cases, the characterization of the final deposition has to be controlled to be tuned and optimised, using reflectivity techniques and interfacial spectroscopy as well as electrochemical analysis to characterise the required catalytic efficiencies.

These research areas have been combined with those created in the current ANR projects (PROMENIX and CHAOPOM), where the program is already well-established.

Universität Konstanz

PHASE SEPARATION OF BINARY MIXTURES AND MICROEMULSIONS INDUCED BY SOFT CENTRIFUGATION

T. Zemb and J-F.Dufrêche
R. Rosenberg, D. Haffke, H. Cölfen (University of Konstanz)
W. Kunz, D. Horinek (Uni Regensburg), S. Prevost (ILL-Grenoble) and S. Marčelja (ANU-Canberra)

Centrifugation is one of the moste common methode to separate emulsions and micropartcles; In the colloidal domain, when particles and droplets to sediment are well below 100 nm, centrifugation Is not efficient enough to separate in speceis at accepatble cost in energy, time and effluent volume. In this domain for which chromatography is nowadays still the least ineefiient and costly. Ultra-centrifugation would be the method of choice but for preparative separation, but it is only used since the Nobel works of Svedberg a century ago for analytics. The recent udnerstanding of surfactant-free microemulsions has opened the possibility of a technoliogical breackthrough in the form of soft centrifugation < 2000 g) with seprative performance of Ultracentrifugation and extremely fast kinetics, due to the large transient flutuations present near phase boundaries of complex fluids.

Progress in these domain requires understanding of the competition of centrifugal fluids with mixing entropy and fluctuations in structurations at nanoscale. "strange" behaviour sar esignalled sicne fifty years, but there was no predcitive theory availble for sepration beyond the well known centrifugation in nearly-critical fluids. We have detremined experimenatlly and developed a parametre-free general tehory for binary fluids, as well as for regular solutions. In both cases, near-critical instbilities ar eenhanced by centrifugation nera the critial point. Far for the critical point, emuslification in the frorm of "ouzo" droplets is predicted also in ternary fluids that are close to regular solutions. Test of the effects predicted by a parameter free "**B**oltzmann-**A**rchimedes-**G**ibbs" theory developed on the nearly regular solution [2,3].

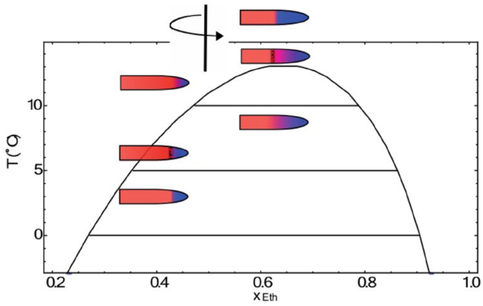

Figure 1: In the model binary system ethanol-dodecane that shows a LCST AT 15C, phase separation induced by centrifugation close to as well as far from the critical point. Centrifuge-induced separation occurs with a meniscus while centrifuge-induced criticality appears as a turbid zone near the middle of the test tube [1].

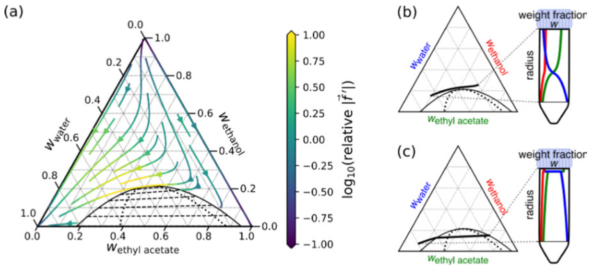

Figure 2.: left: phase diagram water/ethanol/ ethyl acetate system that is used for green extraction in the food and pharmacy are in progress. There is a critical point around 20% Weigth of ethanol at romm temperature; Coloured vector field shows the concentration gradientsappearing under centrifugation: near the critical point, the water/oil ratio fluctuates, while far from the critical point, when composition reches the miscibility gap , spontaneous emulsification is induced by the centrifugation.

[1] Zemb, T., Rosenberg, R., Haffke, D., Kunz, W., Dufrêche, J-F., Horinek, D. and Cölfen, H., **Phase separation of binary fluids in centrifugal fields"** PCCP, 2021, 23 (14), 8261–8272

[2] Stemplinger, S.; Prevost, S.; Zemb, T.; Horinek, D.; Dufreche, J.-F. **Theory of Ternary Fluids under Centrifugal Fields.** J. Phys. Chem. B 2021, 125 (43), 12054–12062.

[3] Stemplinger, S.; Zemb, T.; Horinek, D.; Dufreche, J.-F. **Aggregating fluids under centrifugal fields**. J. Mol. Liq. 2023, 386, 122358.

[4] Cölfen, H.; Rosenberg, R.; Haffke, D.; Stemplinger, S.; Zemb, T.; Horinek, D., **Two Types of Liquid Phase Separation Induced by Soft Centrifugation in Aqueous Ethyl Acetate Using Ethanol as Cosolvent**, RESEARCH, 2023, 6, 26

PROJET SCARCE 2 POUR "SINGAPORE CEA ALLIANCE FOR RESEARCH IN CIRCULAR ECONOMY"

Après le premier projet de collaboration signé en août 2018 entre le CEA et Nanyang Technological University (NTU) à Singapour pour une durée de 3 ans*, un second projet collaboratif a été signé en 2023 dans la continuité du précédent. Ce projet Scarce 2 est divisé en 3 actions : le recyclage des batteries Li-Ion (RT1), des panneaux solaires (RT2) et des cartes électroniques (RT3). L'ICSM (principalement le LHYS) est impliqué dans le RT2 (Co-I de la tache). Avec la croissance de l'industrie solaire photovoltaïque (PV) et l'accumulation de modules PV en fin de vie, il y a une obligation pour une bonne gestion de leur recyclage. Ce projet vise à développer un processus efficace de démontage des panneaux et de récupération des matériaux avec une empreinte carbone plus faible, et à étudier les applications alternatives pour les matériaux récupérés (Si, Ag, In, Ga ...). L'objectif premier de ce projet sera une valorisation complète (>= 90%) des matériaux par voie mécano-chimique à température ambiante pour réduire le coût énergétique tout en minimisant l'empreinte carbone sur l'environnement avec un passage d'une échelle de laboratoire à un démonstrateur de laboratoire de 1 kg/h.

https://www.cea.fr/drf/Pages/Actualites/Vie-de-la-DRF/2023/CEA-NTU-Singapore-partenariats.aspx

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* L'ICSM était intervenu sur la valorisation des métaux extrait des déchets de batteries.

ANR ICSM
2022 - 2024

AGENCE NATIONALE DE LA RECHERCHE
ANR

Project	Acronyme	Title	Period
ANR-17-CE08-0016	**FOAMEX**	*Mousses de lixiviation pour l'extraction de métaux des déchets électroniques*	2018-22
ANR-18-CE05	**AUTOMAC**	*Solid fixation and auto-conditioning of actinide elements coming from contaminated liquid outflows*	2018-22
ANR-15-CE07-0013-01	**MULTISEPAR**	*Modelisation multi-échelle des phases organiques pour l'extraction liquid-liquide*	2019-22
ANR-20-CE04-0007	**RECALL**	*Sustainable recovery of valuable metals in bauxite residue*	2021-25
ANR-21-CE06-00010	**BIOLLPS**	*Molecular forces and liquid-liquid phase separation in solutions of biological macromolecules*	2021-25
ANR-21-CE08-0013	**ALUPLAT**	*Dégradation de revêtements d'aluminure sur superalliages réels et modèles contenant du platine*	2021-25
ANR-21-CE06-0010	**CAREME**	*Catalyse par des métaux issus du recyclage : valorisation directe de déchets*	2021-25
ANR-22-CE29-0023	**ITALLIX**	*Transport d'ions à travers une interface liquide-liquide en vue de processus d'extraction métallique*	2022-26
ANR-22-CE06-0026	**PROMENIx**	*Les nano-ions comme opportunité pour l'étude des protéines membranaires*	2022-26

ICSM responsible	Partners	Link
Olivier Diat	**ESPCI** ICSM-L2IA BRGM EXTRACTHIVE (start-up	*https://anr.fr/Projet-ANR-17-CE08-0016*
Xavier Deschanels	**ICSM-LNER** CIMAP GANIL Caen IRAMIS Saclay ICG Montpellier	*https://anr.fr/Projet-ANR-18-CE05-0015*
Jean-Françcois Dufreche	**ICSM-LMCT** DEN/DMRC CEA Marcoule Laboratoire Phenix, Sorbonne Université, Paris	*https://anr.fr/Projet-ANR-18-CE29-0010*
Stéphane Pellet-Rostaing	**CEREGE** ICSM-LTSM AMSE Aix Marseille School of economics HYMAG'IN (start-up) ALTEO (Industriel)	*https://anr.fr/Projet-ANR-20-CE04-0007*
Thomas Zemb	**IBS Institut de Biologie structurale** ICSM-LTSM ILL Institut Laue Langevin	*https://lyonbiopole.com/r_and_d_project/bio-llps*
Renaud Podor	IJL Institut Jean Lamour **LaSIE Laboratoire des Sciences de l'Ingénieur pour l'Environnement** Pprime Institut, Recherche et Ingénierie en Matériaux, Mécanique et Energétique ICSM / L2ME (responsible Renaud Podor)	*https://anr.fr/Projet-ANR-21-CE08-0013*
Damien Bourgeois	**IRCE Lyon** ICSM-LHYS LIT BRGM Saint Gobain	*https://anr.fr/Projet-ANR-21-CE07-0057*
Jean-Françcois Dufreche	**LIPHY** ICSM-LMCT LEPMI	*https://anr.fr/Projet-ANR-22-CE29-0023*
Pierre Bauduin	I2BC Institut de Biologie Intégrative de la Cellule **ICSM / L2IA** IBS Institut de Biologie Structurale CEA/Institut Joliot/Li2D	*https://anr.fr/Projet-ANR-22-CE06-0026*

Project	Acronyme	Title	Period
ANR-22-CE92-0043	**CHAOPOM**	*Les nano-ions comme opportunité des protéines membranaires*	2022-26
ANR-23-CE42-0024	**HYPOSEL**	*Comprendre les intéractions ioniques spécifiques avec des nanotransistors pour le contôle de l'hyponatremie*	2023-27
ANR-24-CE06-7247	**HYPOSTAR**	*Structures mésoporeuses hybrides fonctionnalisées par des polymères comme nouveaux absorbants polyvalents de micropolluants*	2023-27
ANR-24-CE09-6614	**BMOP4App**	*Nanomatériaux hybrides mésoporeux à base de biphosphonates pontants et d'oxydes métalliques pour la valorisaiton des déchets*	2023-27
ANR-22-LCV1-0006	**LABCOM**	*REFURBISHING OF TRANSMISSION ELECTRON MICROSCOPES*	2023-28
PIA ANDRA	**DECIMAL**	*Phenomenological description of the corrosion and its impact on the durability of encapsulated magnesium wastes in hydraulic binders*	2017-21
PIA France 2030	**PREPAC**	*Procédés de Récupération des Platinoïdes dans l'Aval du Cycle*	2023-27
PIA 4	**ESOP**	*Extraction Par Solvant Pur*	2023-27

ICSM responsible	Partners	Link
Pierre Bauduin	**Institut Lavoisier, UVSQ** ICSM / L2IA Constructor University, Bremen	*https://anr.fr/Projet-ANR-22-CE92-0043*
Jean-Françcois Dufreche	**LAAS Laboratoire d'analyse et d'architecture des systèmes** LIMMS Laboratory for Integrated Micro Mechatronics Systems ICSM / LMCT	*https://anr.fr/Projet-ANR-23-CE42-0024*
Diane Rebiscoul	**ICGM Institut Charles Gerhardt Montpellier** IEM Institut Européen des Membranes ICSM / LMCT LCMCP Sorbonne Université	*https://anr.fr/Projet-ANR-24-CE06-7247*
Guilhem Arrachard	ICGM, Institut Charles Gerhard Montpellier ICSM / LTSM **CP2M, Laboratoire de Catalyse, Polymérisation, Procédés et Matériaux, Lyon**	*https://anr.fr/Projet-ANR-24-CE09-6614*
Renaud Podor	**ICSM/L2ME** NewTEC Scientific	*https://anr.fr/Projet-ANR-22-LCV1-0006*
Diane Rebiscoul	**ICSM-LNER** ISEC, CEA Marcoule INSA Rennes IRCP ORANO (industriel)	*https://cea.hal.science/cea-02338702/file/201800003266_annexe.pdf*
Nicolas Dacheux	**ICSM/LIME** et LHYS, CEA/ISEC CEA Marcoule	
Sandrine Dourdain	ICSM/LTSM, **ISEC/DMRC CEA Marcoule**	

TEACHING
& WORKSHOPS

TEACHING ACTIVITIES LINKED TO ICSM

In cooperation with ENSCM and Ecole doctorale ED 459
And
Institut National des Sciences et Techniques Nucléaires - INSTN – antenne de Marcoule

ICSM develops teaching activities in four directions:

- The master "Chimie Séparative, Matériaux et Procédés", created in 2005 by INSTN/Marcoule and University of Montpellier.
Two years of teaching (M1/M2) associating separation chemistry, radiochemistry, material chemistry and chemical processes engineering with application to the front-end and the back-end of the nuclear fuel cycle (extraction, separation and purification, elaboration, sintering, dissolution, radioactive waste management, decommissioning and so on). The practical is divided in four semesters including main courses, practices, bibliographic studies and two training periods of 4 months (1st year) and 6 months (2nd year). Since 2008, a large part of the teachings is shared with the 3rd year option of ENSCM dedicated the radiochemistry and environment. 10-15 students plus a similar number of students follow the training every year from ENSCM. Teaching was progressively diffused in English (written and/or oral). Teaching is aimed at the diffusion of critical knowledge on chemistry, radiochemistry, interfaces chemistry, conception and synthesis of new materials for nuclear purpose and processes linked to nuclear and alternative energy production *(see the different courses next page)*

- Three ICSM members actively participated in four main courses at the Institut Franco-Chinois de l'Énergie Nucléaire (IFCEN) at Sun Yat-sen University in Zhuhai, China — a Sino-French engineering school in which ENSCM is one of the five main partners (with CEA INSTN, ENSCP, Mines de Nantes and Grenoble INP). These courses, covering topics such as nuclear fuels synthesis, analytical strategies for actinides, and chemistry related to the front-end and back-end of the nuclear fuel cycle, were delivered during the 2015–2025 period.

- The "Thursday Lectures on separation chemistry", as M3/D1 program was aimed for masters and PhD students (credits given by ED459), one lesson more on the experimental side and one more theoretical side which were delivered in the ICSM building have been replaced by SPOC on "Science and technology for recycling industrial wastes and formulating stable concentrated solutions" since beginning of 2018 *(see the flyer of announcement page 142)*

- Several practical-schools, workshops, thematic days, conferences are organized by ICSM staff with help of collaborators and a list is given in the next pages. Some of these organizations becomes even regular ! *(see page 144)*

MASTER CSMP
1ST YEAR (MAIN COURSES)

Fundamentals of radioactivity
Polymers
Solution chemistry applied to actinides
Advanced inorganic materials
Solutions, colloids, interfaces
Liquid NMR spectroscopy and X-ray diffraction
Chemometrics, statistical data analysis, experimental design
Materials characterisation methodology
Coordination chemistry and organic chemistry
Professional projects - project follow-up

Option (2 over 3):
Solution chemistry
Crystallography I
Thermodynamics and phase equilibria

MASTER CSMP
2ND YEAR (MAIN COURSES)

Indicator-scale chemistry - Radiochemistry
Innovative synthesis and extraction processes
Radioprotection / radiation-matter interaction
Liquid-liquid extraction: kinetics and thermodynamics
High-temperature chemistry
Communication and professional integration
Fuel cycle: from mining to waste management
Coordination chemistry of f-elements
2-4 month internship (including bibliography)

Option (2 over 3):
Process Engineering Fundamentals
Hybrid and structured materials
Materials for confinement

SPOC ON SEPARATION CHEMISTRY

2024-2025

Small Online Private Course (SPOC)

SEPARATION CHEMISTRY: FROM THEORY TO PRACTICE

Science and technology for recycling industrial wastes and formulation

COURSE CONTENT

Designing better, safer, more efficient and sober methods for recycling metals such as the one contained in electronic wastes requires to master jointly dissolution, formulation of complex fluid, selective separation and finally re-mixing of solutions in order to obtain recycled material with new economic value.

These lectures focus on the scientific basis of separation methods and are illustrated by knowledge-based examples of optimized technology involved in effective separation of species between phases.

PEDAGOGIC TEAM

Jean François DUFRÊCHE
Université de Montpellier

Luc GIRARD
ENSCM

Florent LEMONT
INSTN

Three course modules
- Introduction to separation chemistry (Chapters I,II)
- Separation for **nuclear** energy (Chapters III, V)
- Separation and recycling of **metals** (Chapters III, IV)

See details on courses contents:
https://www.icsm.fr/index.php?pagendx=4769&project=icsm_engl

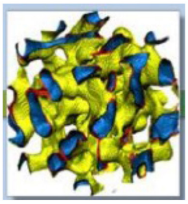
Bachelor level in physical chemistry

Answering successfully to 70 % of the quiz associated to one module (two chapters) allows delivery by INSTN of a certificate of success corresponding to 1 ECTS (20h at ED SCB Montpellier)

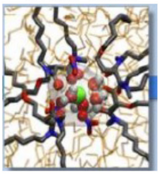
- Registration by mail to : *spoc@icsm.fr*

Publishing: Marie-Hélène HENGÉ

Device scale



Meso-scale



Supramolecular scale

LEARNING METHODS & TOOLS

Entry point on the teaching platform:
- **Send your registration request to: spoc@icsm.fr**
- **You will get an invitation from « digital learning no reply » (check your spams)**
- **Follow the access information in the participant's guideline**
- **Please check the practical information in the first section and the meeting dates and links for the Visio**

Event	Title	Date
ECOLE	*Ecole d'automne de réflectivité des rayons X et des neutrons*	05-08 octobre 2021 (IEMontpellier)
ATELIER	*Atelier CECAM «ion adsorption and electrokinetic transport at interfaces»*	04-06 Mai 2022 (ICSM)
ECOLE	*Ecole thématique de diffusion des rayons X et des neutrons aux petits angles*	15-17 juin 2022 (ICSMarcoule)
ECOLE	*Ecole thématique Surfaces et Nucleaire*	19-22 juin 2022 (Méjannes le Clap)
ECOLE	*Ecole d'été «eau et santé»*	27-30 Juin 2022 (Saint-Martin de Londres, 34)
ECOLE	*14th AFMBioMed international summer school*	21-26 Aout 2023 (ICSM)
ECOLE	*ECIS (European Colloïd and interface Society) summer school*	28 aout-1er septembre 2023 (ICSM)
FORMATION	*Initiation aux traitements d'images avec le logiciel IMAGEJ / FIJI*	26-28 septembre 2023 (ICSM)
JOURNÉE SCIENTIFIQUE (SCF/CRRC)	*Journée Nucléaire & Radiolyse*	03 Juillet 2024 (ICSM)
ATELIER	*Données de base pour la compréhension du comportement du corium*	02 juillet 2024 (ICSM)
ATELIER	*journée micro- / nano-fluidique*	16 septembre 2024 (ICSM)
ECOLE	*4ème Edition de l'école d'Automne Réflectivité des rayons X et des neutrons*	08-11 octobre 2024 (ICSM)
ECOLE	*International school in Sonochemistry ESS - GDR Cavitation*	07-09 juin 2023 (ICSM)
FORMATION	*Journée du GUMP (Groupement des Utilisateurs des Microscopes Philips) à Marcoule*	07-09 novembre 2023 (ICSM)
CONFÉRENCE	*3ème Rencontres Rayonnement Radiochimie*	18-20 Juin 2024 (NIMES)
CONFÉRENCE	*1ère Conférence de Chimie séparative colloïdale*	23-26 juillet 2024 (CEA Cadarache)

Organizers	Participants
S. Dourdain, D. Rébiscoul (ICSM), A. Van der Lee (IEM)	11 partipants
J.-F. Dufrêche (ICSM), R. Hartkamp (Delft univ.) L. Joly (Univ. Lyon) and M. Predota (Czech Rep.)	45 participants
J. Cambedouzou (IEM), S. Dourdain, P. Bauduin, O. Diat (ICSM), A. Gibaud (univ. Le Mans), F. Bonneté (Paris Cité)	24 participants et 6 intervenants
S. Szenknect (LIME), S. Dourdain (LTSM) and D. Rébiscoul (L2ME)	17 participants et 11 intervenants
Labmuse (S. Pellet-Rostaing), pôle de recherche Chimie de Montpellier	16 participants
M. Odorico (ICSM), J.-L. Pellequer (IBS Grenoble)	40 participants
O. Diat et personnel ICSM (L2IA, LTSM, L2ME, LMCT, LSFC)	44 participants
H.-P. Brau, J. Lautru et X. Le Goff (ICSM)	10 participants
M. Virot	6 intervenants
N. Dacheux, S. Szenknect (ICSM) S. David (CNRS/IN2P3) S. Loubiere (CEA) programme NEEDS et GDR SciNEE	
R. Pflieger et D. Rebiscoul	6 intervenants
S. Dourdain et D. Rébiscoul (CEA-ICSM), A. Van der Lee (IEM), G.Vignaud (IRDL, Université Bretagne Sud)	15 participants
S Nikitenko (ICSM) and JY. Hihn (Univ. Franche Comté)	20 participants
R. Podor, J. Lautru, PH. Brau	
ICSM/LSFC, ISEC/DPME , ISEC/DMRC	100 participants
J.-C. Gabriel (CEA), H. Goutte(CEA), F. Lemont (INSTN), S. Sarrade (CEA), Th. Zemb (CEA)	35 participants

OUTLOOK

Stéphane Pellet-Rostaing, Marielle Asou-Pothet et Olivier Diat

This scientific report summarises the achievements made in the fields of recycling and nanoscience for energy over the last four years. With still more than 250 publications but a number of external citations per year of about 2000 (according to web of science), ICSM remains still an active institute in terms of innovation more than 30 patents over this period. This specific scientific activity has also developed strongly on a global scale around the widespread development of the circular economy. The ICSM is still a reference in this field, although facing more challenges to maintain its position at the top due to its competence in this area, which has been capitalized since its founding.

The direction of scientific and technical efforts, initially defined by several reports from the Académie des Sciences in the early 2000s, has been redesigned with a roadmap for the coming years validated by each supervisory body and presenting the research avenues for the HCERES committee. The ICSM remains dynamic and continues to respond to numerous regional, national and European calls for projects through a number of academic and industrial collaborations.

One of the reasons of the success is that a significant contribution in the three hundred primary scientific papers in "A" ranked journals, the sustained rate of patent filings and the important number of co-authorship with colleagues from R/D CEA departments in charge of applications, of international collaboration and with activities that meet either the demands of industrial partners such as ORANO or a more prospective researches (TRL 1-4). Last but not least, more than half of the articles are co-signed by complementary teams within the Institute. To our best knowledge, this is a unique case of pluridisciplinary approach.

Since its creation, the ICSM has always balanced between "understanding" - i.e. demonstrating the predictive capacity of models built on known principles- and "optimizing" - i.e. demonstrating the feasibility of new chemical systems in selective extraction sometimes implemented in breakthrough technological processes (thus including the principles of "green chemistry and green engineering"). As a result, an area of expertise and collaboration within the institute focused on **«Innovation in Extraction and Recycling»** keeps growing, as evidenced by the development of synergism in solvent formulation or water-saving technologies, the application of sonocatalytic and sonochemical oxidation processes for degrading organic waste compounds, to revisit alternative and green solvent or process for extraction applications through deep physical chemical evaluations and to develop more the up-scaling approach from taking waste materials and converting them into something new and valuable. This innovation would not excel without a close link between observation and theory. Within a third cluster of **"Methodologies and theory in separation chemistry"**, a large number of experimental protocols, such as the measure and calculation of "lost" extracting molecules not active in separation, or new separation methods without classical extractant/surfactant are still explored. The development to support recent developments in electron microscopy, which enable direct 2D observation (and 3D reconstruction) and the complex characterization of physico-chemical properties to advance our understanding of self-healing, sintering, dissolution, and chemical reactivity through in situ experiments, is also significant. Interfaces, matter's frontiers, liquid/liquid, liquid/solid or liquid/gas matter, for ion exchange in are difficult to probe because often embedded, of the order of nanometer in thickness and always in evolution but are essential to quantify and characterized in order to understand the kinetic of ion transfers for dissolution, extraction and separation processes. And this is one of our main objectives of research.

No separation process can be made without knowledge of the "durability of materials", i.e. materials that should withstand to extreme constraints and long usage. This is true in the nuclear fuel area and along its life-cycle, but also for all materials used in other decarbonated energies. Life-cycle of all the implemented technology must be investigated and mastered as proposed in the cluster **"Optimisation of materials life-cycle for energy"**. Solid/solid and solid/liquid interfaces are deeply investigated from the initial state of the precursors (dispersed molecular clusters, colloids, emulsions…) to the final state of the final material (sintered, porous, powder, thin film) since the physical and chemical properties of these materials (durability, robustness, extraction, confinement…) depend on their evolution during synthesis and on their life-cycle (for example under irradiation). In order to target the dissolution impact, a specific attention has been placed on chemical or physical heterogeneities within the matter in recent years and the development of new valuable outputs such as carbon dots.

So, to facilitate the understanding of the underlying profound unity within the institute, our research projects are still presented in this booklet under those three clusters.

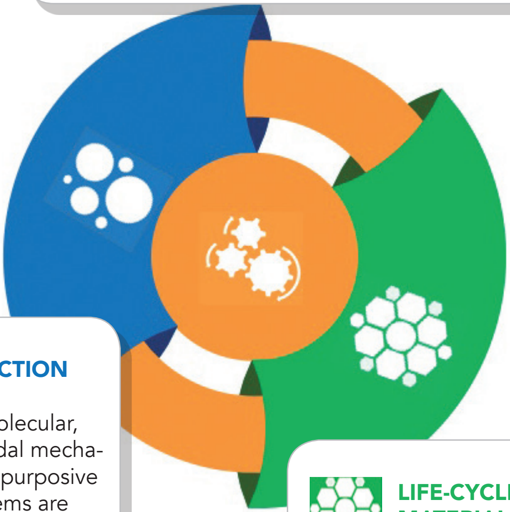
Stéphane Pellet-Rostaing

Olivier Diat

THE CONNECTED CLUSTERS OF INNOVATION AT ICSM

METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

by the use of tools and methodologies already mastered (light reflection, X-ray and neutron scattering, neutrons) or innovative (nonlinear optics, electro-acoustic, advanced electron microscopy), as well as based on statistical physical chemistry.



INNOVATION IN EXTRACTION AND RECYCLING

From the knowledge of molecular, supramolecular and colloïdal mechanisms, the design and the purposive synthesis of chemical systems are devoted to the nuclear fuel cycle and extended to the recycling of strategic metal by taking into account the principles of eco-friendly processes.

LIFE-CYCLE OPTIMIZATION OF MATERIALS FOR ENERGY

by studying the cycle of chemical and/or physico-chemical processes related to the life of materials and associated fluids. It involves understanding and establishing relationships between the structure (nano-organization, microstructure, electronics, composition…) and the reactivity (dissolution, physical stress, irradiation ...) of solid compounds and related.

Multi-scale theories and microscopic observations are methodologies for consolidating innovative separation and recycling progresses as well as material life-time for carbon - free energies based on green chemistry principles.

LIST OF PUBLICATIONS ICSM (2021-2024)

LISTED BY YEAR AND RESEARCH AXIS

2024

Innovation in Extraction and Recycling

[1] Barba-Bon A., El Haitami A., Pasquier C., Niksic-Franjic I., Diat O., Bauduin P., Cantin S., Nau W. M. - **Boron Cluster Anions Dissolve in Lipids Causing Membrane Expansion and Thinning** - *Angewandte Chemie-International Edition* (2024) 63.
[2] Belfqueh S., Chapron S., Giusti F., Pellet-Roastaing S., Seron A., Menad N., Arrachart G. - **Selective recovery of rare earth elements from acetic leachate of NdFeB magnet by solvent extraction** - *Separation and Purification Technology* (2024) 339.
[3] Chazapi I., Merhi T., Pasquier C., Diat O., Almunia C., Bauduin P. - **Controlling Protein Assembly with Superchaotropic Nano-Ions** - *Angewandte Chemie-International Edition* (2024) 63.
[4] Deng Y. Q., Xia D., Bourgeois D., Meyer D., Campidellis S., Isnard H., Francois V., Ronceray R., Reynier B., Gabriel J.-C. - **Maximized Lanthanide Extraction Using Supercritical CO_2 and Fluorinated Organophosphate Extractants** - *ACS Sustainable Resource Management* (2024) 1, 1780-1790.
[5] El Khoueiry C., Giusti F., Lelong E., Arrachart G., Nsouli B., Karame I., Pellet-Rostaing S. - **Thiourea resole polymers for recovery of noble element** - *Hydrometallurgy* (2024) 223.
[6] El Maangar A., Fleury C., Pellet-Rostaing S., Zemb T. - **Leaching and recycling of NdFeB permanent magnets using ionic non-toxic hydrotropes instead of extractants** - *Frontiers in Chemical Engineering* (2024) 6.
[7] Ginot L., Ben Ghozi-Bouvrande J., Prévost S., Pellet-Rostaing S., Dourdain S. - **Lead Extraction in a Functionalized and Permeable Silica-Based Porous Liquid** - *Journal of Physical Chemistry B* (2024) 128, 2550-2558.
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[11] Guerinoni E., Giusti F., Dourdain S., Dufreche J. F., Motokawa R., Ueda Y., Aoyagi N., Zemb T., Pellet-Rostaing S. - **Impact of branching position and degree on uranium extraction by amines: A supramolecular and thermodynamic study** - *Journal of Molecular Liquids* (2024) 403.
[12] Lejeune M., Draye M., Legeai S., Michel S., Arrachart G., Pellet-Rostaing S. - **Easy to scale up synthesis of a high-purity piperidinium based ionic liquid combining both sustainability and cost-effectiveness** - *Journal of Ionic Liquids* (2024) 4.
[13] Lemire D., Dumas T., Guillaumont D., Solari P. L., Menut D., Giusti F., Arrachart G., Dourdain S., Pellet-Rostaing S. - **Molecular and Supramolecular Study of Uranium/Plutonium Liquid-Liquid Extraction with N,N-Dialkylamides** - *Inorganic Chemistry* (2024) 63, 18809-18819.

[14] Micheau C., Ueda Y., Motokawa R., Akutsu-Suyama K., Yamada N. L., Yamada M., Moussaoui S. A., Makombe E., Meyer D., Berthon L., Bourgeois D. - **Organization of**

malonamides from the interface to the organic bulk phase - *Journal of Molecular Liquids* (2024) 401.
[14] Pochat-Cottilloux H., Frances F., Girard L., Rivonkar A., Gossard A. - **Colloidal magnetic gels for the decontamination of limited access metallic surfaces** - *Environmental Technology & Innovation* (2024) 35.
[15] Reaux-Durain J., Mortada B., Bertrand M., Maynadié J., Carboni M., Meyer D., Bourgeois D. - **Back-extraction of major actinides from organic phase through precipitation** - *Comptes Rendus. Chimie* (2024) 27, 1-10.
[16] Regnier E., Hubeau A., Touze S., Guignot S., Meyer D., Diat O., Bourgeois D. - **Copper leaching with aqueous foam for processing of electronic waste** - *Comptes Rendus. Chimie* (2024) 27, 1-9.
[17] Ueda Y., Micheau C., Akutsu-Suyama K., Tokunaga K., Yamada M., Yamada N. L., Bourgeois D., Motokawa R. - **Fluorous and Organic Extraction Systems: A Comparison from the Perspectives of Coordination Structures, Interfaces, and Bulk Extraction Phases** - *Langmuir* (2024) 40, 24257-24271.

Life-Cycle Optimization of Materials for Energy

[1] Benarib S., Munoz M., Kieffer I., Hazemann J. L., Dacheux N., Clavier N. - **Reductive hydrothermal conversion of uranyl oxalates into UO^{2+x} monitored by in situ XANES analyses** - *Dalton Transactions* (2024) 53, 13982-13995.
[2] Couturier J., Oularé P. T., Collin B., Lallemand C., Kieffer I., Longerey J., Chaurand P., Rose J., Borschneck D., Angeletti B., Criquet S., Podor R., Pourkhorsandi H., Arrachart G., Levard C. - **Yttrium speciation variability in bauxite residues of various origins, ages and storage conditions** - *Journal of Hazardous Materials* (2024) 464.
[3] de Laharpe P., Deschanels X., Lin J., Peuget S., Arena H., Taron M., Grygiel C. - **Exploring the combined effects of water immersion and ion irradiation on mesoporous silica** - *Materials Letters* (2024) 371.
[4] Henry M., Rinsant D., Maynadié J., Carboni M. - **Uranium extraction by metal-organic frameworks: advanced materials for new sorption possibilities** - *Dalton Transactions* (2024) 53, 17110-17122.
[5] Hunault L., Pedraza F., Aranda L., Siblani M. M., Cormier J., Podor R., Mathieu S. - **Type I Hot Corrosion Of Platinum-Containing Model γ and γ′ Alloys** - *High Temperature Corrosion of Materials* (2024) 101, 999-1011.
[6] Husainy M., Podor R., Le Goff X., Kaczmarek T., Moisy P., Dacheux N. - **Speciation and chemical behavior of molybdenum in uranium dioxide samples prepared by hydroxide precipitation** - *Journal of Nuclear Materials* (2024) 596.
[7] Kvashnina K., Claret F., Clavier N., Levitskaia T. G., Wainwright H., Yao T. K. - **Long-term, sustainable solutions to radioactive waste management** - *Scientific Reports* (2024) 14.
[8] Roch R., Deschanels X., Singaravelu C. M., André N., Rey C., Causse J. - **Evidence of the contribution of molecular fluorophores to the luminescence of carbon entities formed by solvothermal treatment of trinitropyrene** - *Rsc Advances* (2024) 14, 39858-39866.
[9] Roy J. J., Phuong D., Verma V., Chaudhary R., Carboni M., Meyer D., Cao B., Srinivasan M. - **Direct recycling of Li-ion batteries from cell to pack level: Challenges and prospects on technology, scalability, sustainability, and economics** - *Carbon Energy* (2024) 6.
[10] Singaravelu C. M., Deschanels X., Rey C., Causse J. - **Investigation on Fluorescence Origin and Spectral Heterogeneity in Carbon Dots: A Dynamic Perspective** - *Chemphotochem* (2024) 8.
[11] Strzelecki A. C., Zhao X. D., Estevenon P., Xu H. W., Dacheux N., Ewing R. C., Guo X. F. - **Crystal chemistry and thermodynamic properties of zircon structure-type materials** - *American Mineralogist* (2024) 109, 225-242.

[12] Zhao X. D., Strzelecki A. C., Dacheux N., Qi L., Guo X. F. - **Phonon softening induced phase transition of CeSiO4: a density functional theory study** - *Dalton Transactions* (2024) 53, 6224-6233.

Methodologies and Theories in Separation Chemistry

[1] Aghelmaleki A., Afarideh H., Cairós C., Pflieger R., Mettin R. - **Effect of mechanical stirring on sonoluminescence and sonochemiluminescence** - *Ultrasonics Sonochemistry* (2024) 111.

[2] Bruckschlegel C., Pasquier C., Toquer G., Girard L., Odorico M., Lautru J., Diat O., Bauduin P. - **Toward Distinguishing between the Superchaotropic and Hydrophobic Characters of Nanometric-Sized Ions in Interaction with PEGylated Surfaces** - *Journal of Physical Chemistry Letters* (2024) 15, 4229-4236.

[3] Causse J., Lavaud C., Ravaux J., Lautru J., Podor R. - **Characterization of complex micellar systems by Scattering techniques (SAXS and SANS) and wet-scanning transmission electron microscopy (wet-STEM)** - *Colloids and Surfaces a-Physicochemical and Engineering Aspects* (2024) 682.

[4] Cavalcanti V. O., Roques J., Horlait D., Gilabert E., Riant G., Colombeau-Bedos T., Clavier N., Gentils A. - **Study of helium diffusion in yttria: A multiscale approach based on the density functional theory and kinetic Monte Carlo, with transmission electron microscopy and thermo-desorption spectroscopy** - *Journal of Nuclear Materials* (2024) 597.

[5] Djozing W. N., Valange S., Nikitenko S. I., Chave T. - **Sonohydrothermal synthesis of zeolite A and its phase transformation into sodalite** - *Dalton Transactions* (2024) 53, 16407-16421.

[6] Dufrêche J. F., Siboulet B., Duvail M. - **Chemical models for dense solutions** - *Faraday Discussions* (2024) 253, 79-99.

[152] Dufreche J.-F., Plazanet M., Meyer G., Billard I. - **How NaCl addition destabilizes ionic liquid micellar suspension until phase separation** - *Comptes Rendus. Chimie* (2024) 1, 1-7.

[7] Duvail M., Martinez D. M., Ziberna L., Guillam E., Dufreche J. F., Guilbaud P. - **Modeling Lanthanide Ions in Solution: A Versatile Force Field in Aqueous and Organic Solvents** - *Journal of Chemical Theory and Computation* (2024) 20, 1282-1292.

[8] El Monjid A., Szenknect S., Mesbah A., Hunault M., Menut D., Clavier N., Dacheux N. - **Incorporation of U(IV) in monazite-cheralite ceramics under oxidizing and inert atmospheres** - *Dalton Transactions* (2024) 53, 2252-2264.

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- **Depuis Marseille,** rejoindre l'A7, direction Lyon, sortie 21, Orange-centre. Continuer direction Caderousse (D17) puis direction Marcoule (D131a).

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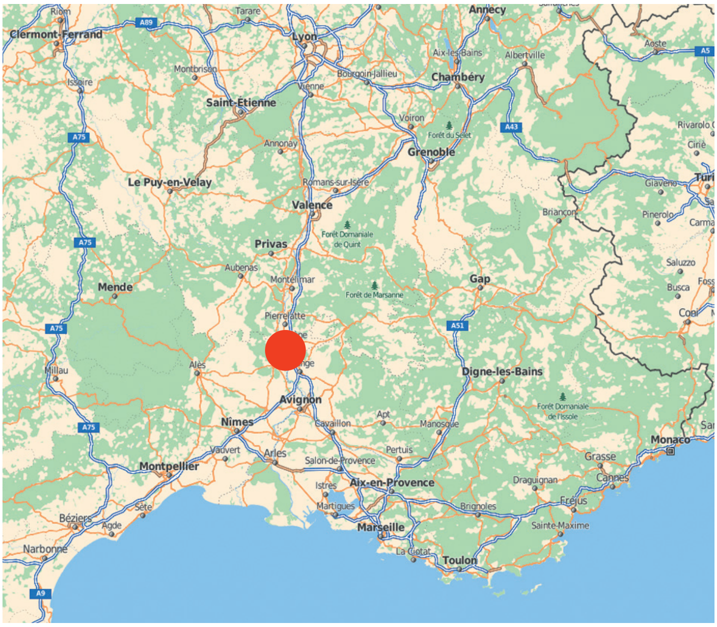

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