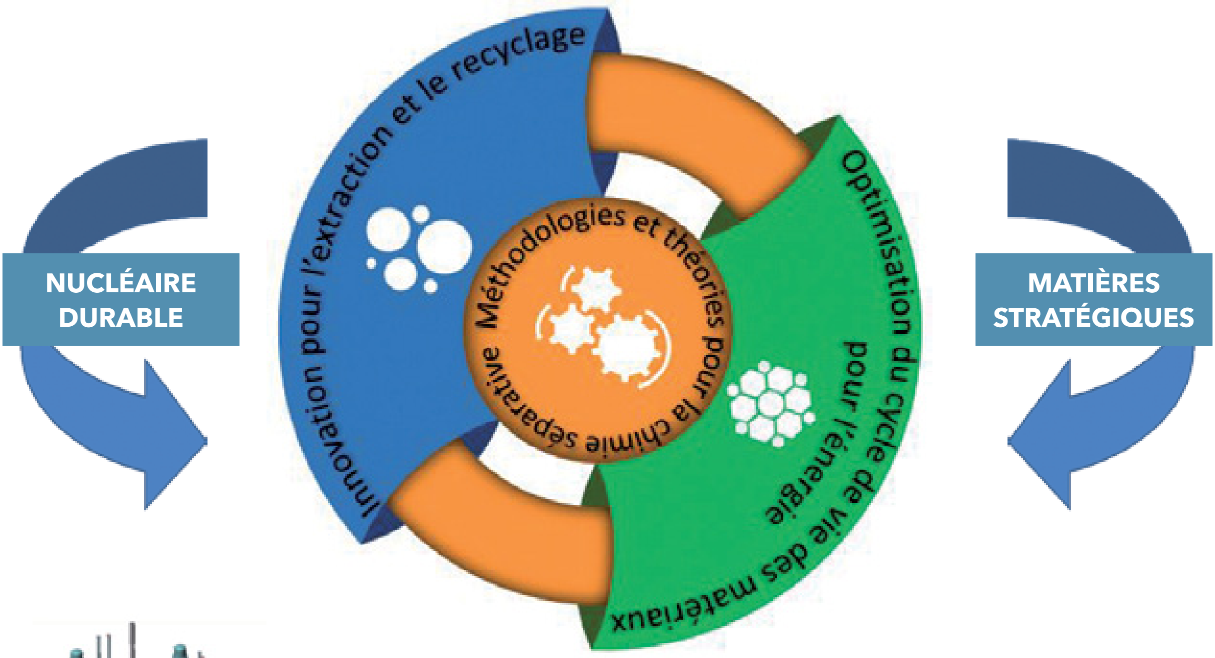
INSTITUT DE CHIMIE SÉPARATIVE DE MARCOULE

CHIMIE ET PHYSICO-CHIMIE DU RECYCLAGE

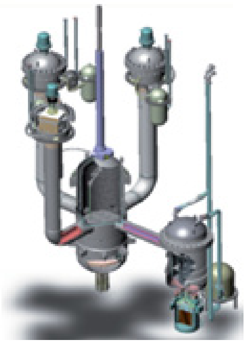
ÉNERGIES DÉCARBONÉES

ÉCONOMIE CIRCULAIRE

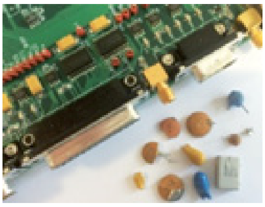


NUCLÉAIRE DURABLE

MATIÈRES STRATÉGIQUES



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.

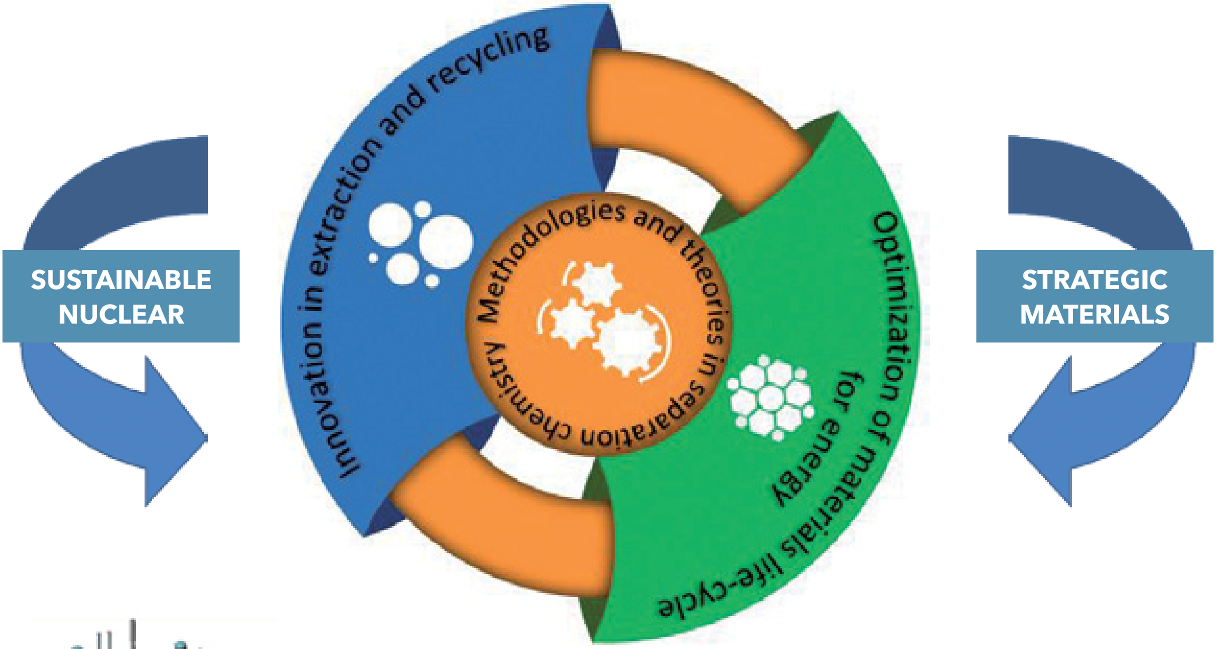


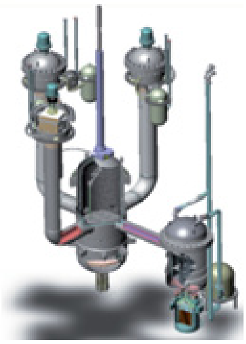
Pour une recherche intégrée aux ambitions du CEA, du Pôle Chimie et de l'I-Site MUSE

CHEMISTRY AND PHYSICAL CHEMISTRY OF RECYCLING

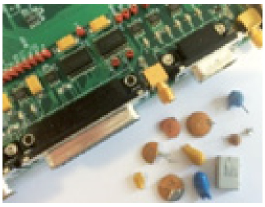
DECARBONATED ENERGY

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 Chemistry Cluster and I-Site MUSE ambitions.

INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCOULE

RAPPORT SCIENTIFIQUE 2017 - 2020
SCIENTIFIC REPORT

Personnel de l'ICSM en avril 2018
ICSM staff

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 et en janvier 2010, les laboratoires ont obtenu l'autorisation de démarrer des expériences incluant quelques grammes d'uranium appauvri et de thorium naturel. En décembre 2020, l'ICSM rassemble une centaine de personnes, dont 45 permanents et 48 scientifiques non permanents (39 doctorants, 9 post-doctorants/ATER/CDD, 1 CDD senior). En outre, plus de 20 étudiants en master rejoignent les huit équipes pendant quelques mois chaque année. Ainsi, le nombre de personnel non permanent a en fait atteint 55% du personnel total, ce qui correspond au niveau de fonctionnement de l'Institut. L'ICSM vise à développer une recherche fondamentale dont l'objectif principal est de «proposer des choix» pour le développement de procédés de chimie de séparation dans les domaines des énergies décarbonées, en intégrant les enjeux d'une énergie nucléaire durable et les défis d'une économie circulaire dans son ensemble comme de réelles opportunités d'innovation et avec une reconnaissance unique en France et une visibilité internationale.

Depuis la première édition 2006 à Montpellier, une école d'été pratique en chimie de séparation se tient chaque année pendant une semaine entière. Depuis 2012, l'Université pratique d'été est organisée en commun avec les équipes associées au sein du laboratoire d'excellence «CheMISyst». Le thème commun des 48 équipes fédérées au sein de cette structure (2012-2022) est la chimie utilisant les interactions dites à longue portée, c'est-à-dire les interactions moléculaires au-delà de la liaison au plus proche voisin.

Les ressources en uranium sont rares, si l'on n'utilise que l'isotope 235 et les déchets liés à la production d'énergie nucléaire sont potentiellement dangereux. L'utilisation de neutrons rapides ainsi que le recyclage multiple du combustible REP permettent d'accroître efficacement les ressources existantes dans l'indépendance nationale, mais seront basés sur l'innovation dans les processus de séparation, qui peuvent être modélisés à l'aide de la théorie prédictive. La compréhension et l'optimisation de la séparation dans le cycle du combustible nucléaire du futur reste un objectif important de l'ICSM. L'élargissement de cet objectif central aux besoins de la chimie du recyclage est crucial pour le développement de technologies énergétiques alternatives : par exemple tous les matériaux développés dans le domaine des batteries, compagnons inévitables des énergies «vertes» intermittentes doivent être recyclés avec une quantité acceptable de dépense énergétique et d'effluents produits. Les matériaux impliqués dans les technologies des énergies renouvelables ont pour la plupart un cycle de vie de l'ordre de 30 ans, proche du délai prévu pour leur mise en œuvre et cela ouvre un immense champ de recherche et de développement pour l'optimisation de leur cycle de vie.

Ce rapport donne ici un aperçu des travaux publiés entre janvier 2017 et décembre 2020. Les huit équipes de recherche travaillent toujours dans le sens des questions scientifiques ouvertes telles que définies et publiées par l'académie française. 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 dans le cas de la flottation par mousse.
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.

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 building was inaugurated in June 2009 and in January 2010, the laboratories were authorised to start experiments including a few grams of depleted uranium and natural thorium. In December 2020, ICSM brings together around hundred people, including 45 permanent staff and 48 non-permanent scientists (39 doctoral students, 9 postdoctoral fellows/ATER/CDD, 1 senior CDD). In addition, more than 20 master students join the eight teams for a few months every year. Thus, the number of non-permanent staff has in fact reached 55% of the total staff, which corresponds to the level of operation of the Institute. ICSM aims to develop a fundamental research whose main objective is to «offer choices» for the development of separation chemistry processes in the decarbonated energies domains, integrating the issues of a sustainable nuclear energy and the challenges of a circular economy in its globality as real opportunities for innovation and with unique recognition in France and international visibility.

A yearly practical summer school in separation chemistry is held yearly for a full week since the first edition 2006 in Montpellier. Since 2012, the Practical summer school is organized in common with the associated teams within the Excellence laboratory "CheMISyst". The common theme of the 48 teams federated in this structure (2012-2022) is chemistry using the so-called Long Range Interactions, i.e. molecular interactions beyond binding to the nearest neighbour[1].

Resources in Uranium are scarce, if only the 235 isotope is used and wastes related to nuclear energy production are potentially dangerous. The use of fast neutrons as well as the multi-recycling of the REP fuel effectively enhances existing resources in national independence, but will be based on innovation in separation processes, that can be modelled using predictive theory. Understanding and optimizing separation in the nuclear fuel cycle of the future remains an important aim of the ICSM. Enlarging this central goal to the needs for chemistry of recycling is crucial for developing alternative energy technologies; for instance; all the materials developed in the domain of batteries, unavoidable companions of intermittent "green" energies must be recycled with an acceptable amount of energy and effluents. Most of the materials involved in renewable energy technologies have a life cycle of around 30 years, close to the time frame for their implementation, and this opens up a huge field of research and development for the optimization of their life cycle.

This report gives here an overview of the work published between January 2017 and December 2020. 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 in the case of foam flotation.
Separation chemistry is the basis of recycling technologies, while recycling is the basis of circular economy which is the only sustainable strategy in a world of limited resources. All scientists, engineers, technicians and students have the common goal to gain the knowledge needed to improve methods in this field.

Stéphane Pellet-Rostaing

Olivier Diat

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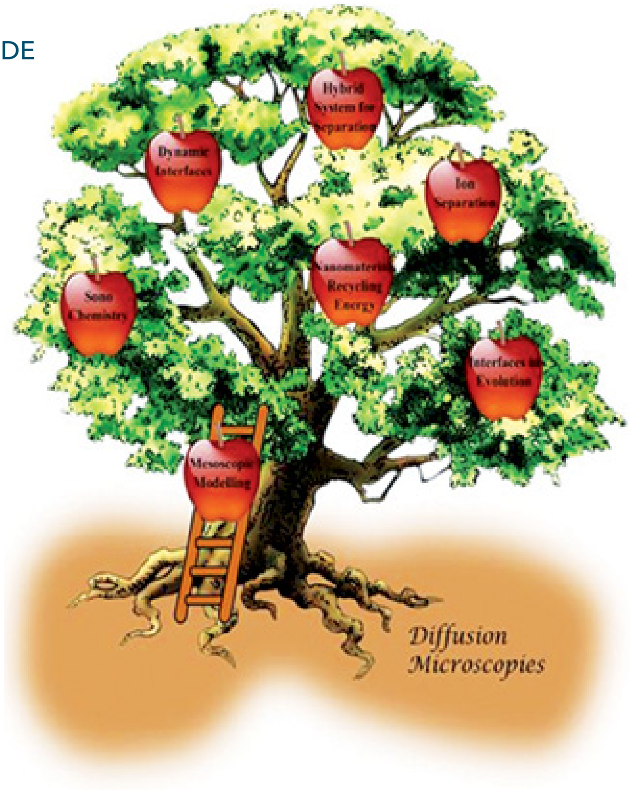
[1] *Special issues devoted to interactions beyond first neighbor appeared in "Current Opinion in Colloids and Interfaces" as special issues in 2015 and 2016*

INSTITUT DE CHIMIE SÉPARATIVE DE MARCOULE



La production d'énergie à partir de combustibles fossiles dont l'impact négatif sur le climat et l'environnement est aujourd'hui inacceptable, accompagné de nouvelles exigences en matière de sécurité des installations et de gestion de leurs déchets, mais également la nécessité d'un recyclage considéré jusqu'à présent comme exceptionnel, mais qui doit devenir la règle universelle et économiquement acceptable, confrontent les scientifiques à une demande sociétale forte pour des solutions maîtrisées en matière de technologies pour les énergies décarbonées, inscrite dans les lois du 13 juillet 2005 et du 18 août 2015. Le « nucléaire durable » du futur, fermant le cycle repose sur des avancées dites « en rupture » *via* une chimie séparative mettant en jeu des fluides complexes mis en oeuvre dans des dispositifs optimisés.

Au-delà du domaine nucléaire, 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 ou certains métalloïdes comme le germanium 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 crée en 2007 est aujourd'hui constituée de huit équipes travaillant en synergie :

> *• Systèmes hybrides pour la séparation (Daniel MEYER)*
> *• Chimie des ions aux interfaces actives (Olivier DIAT)*
> *• Tri ionique par des systèmes moléculaires auto-assemblés (Stéphane PELLET-ROSTAING)*
> *• Sonochimie dans des fluides complexes (Sergueï NIKITENKO)*
> *• Nanomatériaux pour l'énergie et le recyclage (Xavier DESCHANELS)*
> *• Interfaces des matériaux en évolution (Nicolas DACHEUX)*

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

> *• Etude de la matière en mode environnementale (Renaud PODOR)*
> *• Modélisation et chimie théorique (Jean-François DUFRECHE).*

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. Pour l'ICSM, c'est avant tout anticiper et 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 ainsi des challenges majeurs. L'ICSM travaille depuis longtemps 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 efficients. 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, les 5 objectifs ciblés 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 verte et d'ingénierie verte » ne se sont pas avérés assez structurant de notre recherche.

En conséquence, plusieurs axes de réflexion et de coopération 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 le nombre exceptionnel de brevets déposés (une vingtaine entre 2017 et 2020), ne pourrait pas se développer à un niveau de pointe de classe mondiale (comme le montrent les citations dans la littérature internationale) sans les contacts plus étroits entre l'observation et la 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. L'énergie libre de transfert a été systématiquement prise en compte dans cette approche émergente spécifique sous le terme de la «ienaics» avec une certaine similitude avec la neutronique, l'électrochimie et la nanoscience. 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 le domaine de la microscopie à rayons X doux et de la microscopie électronique qui permettent l'observation directe d'agrégats supramoléculaires en solution avec une très haute résolution ou le couplage d'étages ou de cellules spécifiques (humidité relative contrôlée ou température élevée) avec des microscopes électroniques modernes 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 le troisième axe **Optimisation du cycle de vie des matériaux pour l'énergie**. Les interfaces solides/solides et solides/liquides 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).

L'**Institut de Chimie séparative de Marcoule**, créé sans murs en 2007, est dirigé par Stéphane Pellet-Rostaing 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 Balard** et 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 2019 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**.

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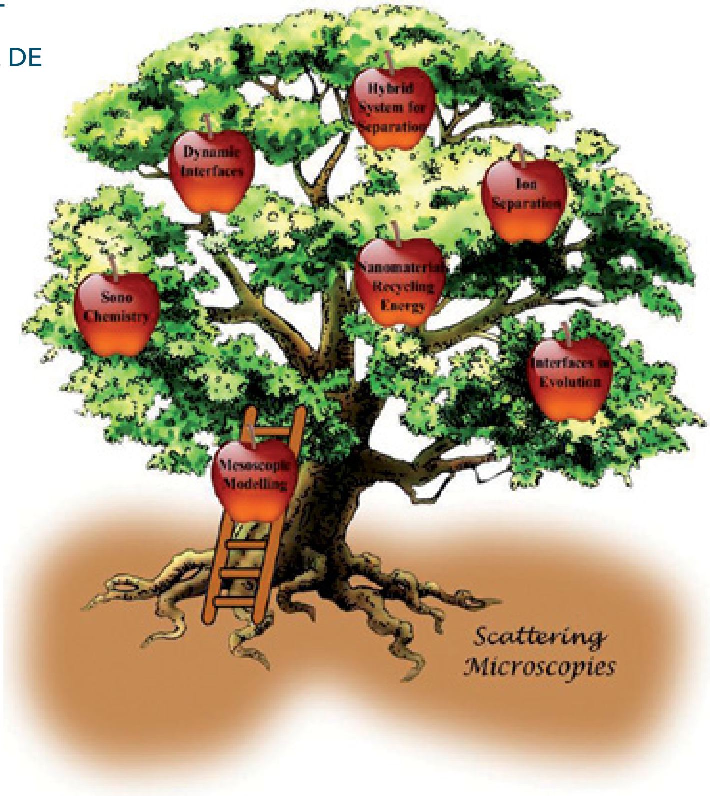

The production of energy from fossil fuels whose negative impact on the climate and the environment is today unacceptable, accompanied by new requirements for the safety of the facilities and the management of their waste, but also the need for a recycling considered until now as exceptional, but which must become the universal and economically acceptable rule, confront the scientists with a strong societal demand for controlled solutions in technologies for the carbon-free energies, inscribed in the laws of July 13th 2005 and August 18, 2015. The «sustainable nuclear power» of the future, closing the cycle relies on so-called «breakthrough» advances via a separation chemistry involving complex fluids implemented in optimized devices.
Beyond the nuclear field, in a world finite in natural resources, closing cycles is part of a controlled extraction/purification process, whether ionic, molecular or colloidal separation. Recycling of so-called «strategic» materials such as rare earths, PGMs or some metalloids such as germanium or antimony is a first challenge in this separation chemistry that belongs to the nanosciences.

Closing cycles of fuels and materials used in energy production does not rest only on progresses on synthetic chemistry of molecules or materials, but also on separation with its two linked side-processes: dissolution and reformation of materials. As long as primary resources are involved, ionic, molecular or colloidal separation are the three processes to be understood and modeled predictively in order to allow growth of the recycling industry, as the core of the circular economy.

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 (Daniel MEYER)*
- *Ions at active interfaces (Olivier DIAT)*
- *Ion separation by self-assembled molecular systems (Stéphane PELLET-ROSTAING)*
- *Sonochemistry in complex fluids (Sergueï NIKITENKO)*
- *Nanomaterials for energy and recycling processes (Xavier DESCHANELS)*
- *Evolving Interfaces in materials (Pr. Nicolas DACHEUX)*

This six teams that are highly specialized are firmly associated to two transverse teams focused 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, humidity:

- *Material study by environmental methods (Renaud PODOR)*
- *Modeling and theoretical chemistry (Pr. Jean-François DUFRECHE).*

In response to an ever-changing societal demand in the face of current and future energy as well as environmental challenges, the research carried out at ICSM contributes to deconstructing the polluting and dangerous picture of chemistry in the field of extraction and purification of recoverable materials. For ICSM, it is above all anticipating and proposing solutions to scientific obstacles allowing a drastic reduction in pollution and environmental footprint of separation processes. This effort must be intensified and rationalized, in particular towards the development of interfaces, 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 characterization methods as well as in mesoscale theory have been increasingly considered. In addition the five objectives followed by ICSM since its creation between «understanding», that is to say demonstrating the predictive power of models based on first principles and «optimizing», that is to say demonstrating the feasibility of new chemical systems in selective extraction, thus including the principles of «green chemistry and engineering» were considered as not sufficiently structuring our research.

During the last period of four years, integration of goals, usage of skills developed in the environmental characterisation methods as well as in the meso-scale theory were more and more considered. Moreover, the distinction made since the creation of the ICSM between "understanding", i.e. demonstrating predictive power of models build on first principles and "optimizing", i.e. demonstrating the feasibility of new chemical systems in selective extraction, including the principles of "green chemistry and green engineering". As a consequence, a first axis of reflexion and cooperation centered on **Innovation in Extraction and Recycling** naturally emerged. As stated above, properly optimize, one first needs to understand and predict. Thus, this large number of innovations also illustrated by the exceptional number of patents (21 between 2015 and 2018) could not grow at cutting-edge world-class level (as shown by citations in international literature) without the closer contacts between observation and theory. In practice, the emerging was possible because of the tools used in the statistical mechanics of interfaces, for example via Gaussian random wavelets. Systematically free energy of transfer was considered in this emerging specific "ienaics" approach with some similarity with neutronics, electrochemistry and nanoscience. This axis of **Methodologies and theory in separation chemistry** grows continuously due to 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. No less importantly, the recent advances in the field of soft X-ray microscopy and electron microscopies which allow the direct observation of supramolecular aggregates in solution with a very high resolution or the coupling specific stages or cells (controlled relative humidity or high temperature) with modern electron microscopes allowing the precise characterization of physico-chemical properties such as self-healing, sintering, dissolution, chemical reactivity through in situ experiments…

No separation process can be made without knowledge of the "durability of materials", i.e. materials that should withstands to extreme constraints and long usage, not only in the life-cycle of the nuclear fuel, but also in this of all materials necessary in the technologies for alternative energies. Life-cycle of all the implemented technology must be investigated and mastered as proposed in the third axis **Optimisation of materials life-cycle for energy**. Solid/solid and solid/liquid interfaces are considered here since the physical and chemical properties of these materials (durability, robustness, ability to confine and filtration…) depend on their synthesis, i.e. from the nature of the precursors (colloid, solution, emulsion…) to the final material (sintered, porous, powder, thin film).

The **Institute for Separation Chemistry of Marcoule** has been created as a virtual laboratory in 2007 and is managed by Stéphane Pellet-Rostaing since 2013. Located 110 km NE of Montpellier and 25 km north of Avignon, ICSM is part of the "**Pôle de Chimie Balard**" and one of the partners of the Excellence laboratory "**Chemisyst**" 2012-2022, devoted to the Long Range chemical interactions (LRI) at work in "systems chemistry". Having effectively started its research activities in January 2010, the Institute was sized to accommodate in 2019 about fifty permanent staff including about 40 researchers, engineers and technicians, about 10 administrative, technical and 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.

**INSTITUT DE
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ICSM – PERMANENTS 2017 - 2020

Equipe DIR

Directeur	PELLET-ROSTAING Stéphane	Gestionnaire	VIDAL Alice
DirecteurAdjoint	*ZEMB Thomas -> 12/18*	Gestionnaire	MENASRIA Aurélie
Directeur Adjoint	DIAT Olivier 01/19 ->	ISI	DIAS Mathilde
Adj. Directeur	ALPE-CONCHY Dominique	ISI	MARCHAL Nicolas 06/18 ->
Assistante	*MARTIN Hélène -> 08/18*	Exploitation	VARON Renaud
Assistante	HAON Véronique 12/20 ->	Exploitation	*CARMINATI Franck -> 07/20*
Secrétaire	*RUSSELLO Vainina ->10/20*	Exploitation	PESCE Claude 01/20 ->

Equipe 1 - LHYS

Chef d'équipe	MEYER Daniel
CR	BOURGEOIS Damien
Chercheur	CARBONI Michaël
MDC	MAYNADIE Jérôme

Equipe 2 – L2IA

Chef d'équipe	DIAT Olivier
Chercheur	BAUDUIN Pierre
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 01/19 ->
MDC	ARRACHART Guilhem
Technicienne	BAUS-LAGARDE Béatrice
Chercheur	DOURDAIN Sandrine
IE	GIUSTI Fabrice 07/18 ->

Equipe 4 - LSFC

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

Equipe 5 - LNER

Chef d'équipe	DESCHANELS Xavier
Chercheur	CAUSSE Jérémy
Chercheur	REBISCOUL Diane
IE	REY Cyrielle
MDC	TOQUER Guillaume
MDC	*CAMBEDOUZOU Julien ->09/18*

Equipe 6 - LIME

Chef d'équipe	DACHEUX Nicolas
MDC	CLAPAREDE Laurent
CR	CLAVIER Nicolas
CR	MESBAH Adel
Chercheur	SZENKNECT Stéphanie

Equipe 7 – L2ME

Chef d'équipe	PODOR Renaud
Ingénieur	BRAU Henri-Pierre
Technicien	CORSO Bruno
IE	LAUTRU Joseph
IE	LE GOFF Xavier
IE	MAYNADIE Sandra
Ingénieur	ODORICO Michaël

Equipe 8 - LMCT

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

CEA
CNRS
UM ENSCM
Autres
Partis

ICSM – NON PERMANENTS 2017 - 2020

EQUIPE DIR

CDD ITA
ROUSSIGNE Elisabeth 02/07/2018-01/06/2021
SCHAPPLER Mireille 02/11/2020-01/05/2021

EQUIPE 1 LHYS

APPRENTI
SIMOES Alizée 01/09/2014-31/08/2017
LAGAE-CAPELLE Eléonore 01/10/2018-30/09/2021

CDD ITA
LASZCZYK Marjorie 13/04/2015-31/05/2017
MASTRETTA Régis 01/12/2016-31/05/2018
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SCALISI Nathalie 26/08/2019-31/12/2020
CHER Sébastien 07/01/2019-06/01/2020

DOCTORANT
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GENESIO Guillaume 01/10/2015-30/09/2018
LACANAU Valentin 01/10/2016-30/09/2019
COGNET Marine 01/10/2016-30/09/2019
RIMSANT Damien 10/2016-10/2019
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

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ICSM ERC

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CDD ITA
KELLER Barbara 02/05/2018-31/10/2018

DOCTORANT
PENISSON Christophe 01/10/2015-30/09/2018

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THEISEN Johannes 16/09/2013-30/06/2018

EQUIPE 2 L2IA

CDD ITA
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FADEL Ophélie 12/11/2014-31/08/2017

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

DOCTORANT
MERHI Tania 01/10/2017-30/11/2020
WANG Jing 16/10/2017-15/12/2020
MALENGA Edward 13/11/2017-13/05/2018
HOHENSCHUTZ Max 03/01/2018-02/01/2021
CHAZAPI Ioanna 21/10/2019-20/01/2023
SKORZEWSKA Klaudia 21/10/2019-20/01/2023
LAMOLINAIRIE Julien 01/10/2020-01/10/2023

POST-DOCTORANT ou CHERCHEUR
MICHEAU Cyril 08/02/2016-07/07/2017
MALINENKO Alla 04/01/2016-03/04/2017

EQUIPE 3 LTSM

APPRENTI
PITON Raphaëlle 01/09/2020-31/08/2022

CDD ITA
LARRIBAU Arthur 03/01/2017-31/12/2017
SUKHBAATAR Tamir 25/11/2019-24/07/2020
TOURE Moussa 01/03/2017-01/03/2019
LE Anh-Hoang 09/09/2019-09/03/2020

POST-DOCTORANT ou CHERCHEUR
MOSSAND Guillaume 30/07/2017-03/06/2019
HAQUIN Victor 02/10/2017-31/12/2018
HERNAN Castro 01/04/2019-30/04/2019
LOPEZ USMA Cesar Augusto 01/05/2018-31/10/2019
MICHEAU Cyril 01/07/2017-01/12/2018
ARRAMBIDE CRUZ Carlos 01/07/2020-30/09/21

DOCTORANT
ARRAMBIDE CRUZ Carlos 01/10/2014-30/09/2017
LOPIAN Tobias 01/12/2014-30/11/2017
SUKHBAATAR Tamir 07/11/2014-06/11/2017
PLEINES Maximilian 02/11/2015-01/11/2018
ARTESE Alexandre 02/11/2016-01/11/2019
WINKLER Robert 02/11/2016-01/11/2019
BEKKAR Fatima 05/12/2018-31/03/2020
FELINES Nicolas 16/10/2017-15/01/2021
LU Zijun Quentin 07/11/2017-06/01/2021
BEN-GHOZI BOUVRANDE Justine 23/10/2018-22/10/2021
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
BEN-GOZHI BOUVRANDE Justine 23/10/2018-22/01/2022
EL MAANGAR Asmae 14/11/2018-31/01/2022
STEMPLINGER Falkner 04/11/2019-03/11/2022
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

EQUIPE 4 LSFC

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

CDD CHERCHEUR
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DOCTORANT
DALODIERE Elodie 22/10/2014-21/10/2017
NOUAILLE Florence 01/02/2014-31/01/2017
SIERRA SALAZAR Andres 01/10/2014-30/09/2017
JI Ran 01/10/2015-30/09/2018
PARIZOT Lauréanne 01/01/2015-31/12/2018
BONATO Laura 16/10/2017-15/10/2020
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

EQUIPE 6 LIME

APPRENTI
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ESTEVENON Paul 10/2016-10/2019
DESFOUGERES Lénaïc 10/2016-10/2019
TRILLAUD Victor 14/10/2016-13/10/2019
QIN Danwen David 01/09/2016-31/08/2020
DALGER Thomas 14/10/2016-13/10/2019
MANAUD Jérémie 02/10/2017-30/11/2020
BERTOLOTTO Solène 10/2017-10/2020
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
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

CDD ITA
SARAVIA Alvaro 03/01/2017-29/10/2018
ZUNINO Morgan 18/06/2018-17/12/2020
DI MASCIO Lara 14/09/2020-13/09/2021
ANZALONE Eddie 14/09/2020-30/12/2021
IMBERT Paul-Henri 14/09/2020-13/09/2021

CEA
CNRS
UM ENSCM
Autres
Partis

EQUIPE 5 LNER

APPRENTI
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BRISCESE Lucas 01/09/2019-01/09/2020

CDD CHERCHEUR
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ALASTUEY Patrizio 11/09/2018-22/12/2018
BECA OVIEDO Andrea 22/05/2018-10/08/2018
SANANES ISRAEL Susan 01/10/2015-30/09/2018
BAUM Markus 02/11/2015-14/12/2018
MONNIER Julien 14/10/2016-13/10/2019
LEBLANC Martin 01/10/2016-01/10/2019
BOUALI Sofiane 01/10/2016-01/10/2019
RUSSO Baptiste 09/10/2017-11/12/2020
BOUBON Rémi 01/10/2017-30/12/2020
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

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LEJEUNE Manuel 28/07/2017-27/07/2018
RUSSO Baptiste – 14/12/2020-13/06/2022
KHODER Hassan 02/11/2020-01/11/2021

EQUIPE 7 L2ME

POST-DOCTORANT ou CHERCHEUR
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DOCTORANT
DELOBEL Florimond 01/12/2015-30/11/2018
MENDONCA Jérôme 02/09/2019-31/08/2022

CDD ITA
CHEVREUX Pierrick 28/08/2017-21/12/2018
GONNET Gautier 19/04/2016-30/06/2017
SALACROUP Johann 11/04/2016-16/12/2018
ARENA Hélène 28/01/2019-27/07/2019

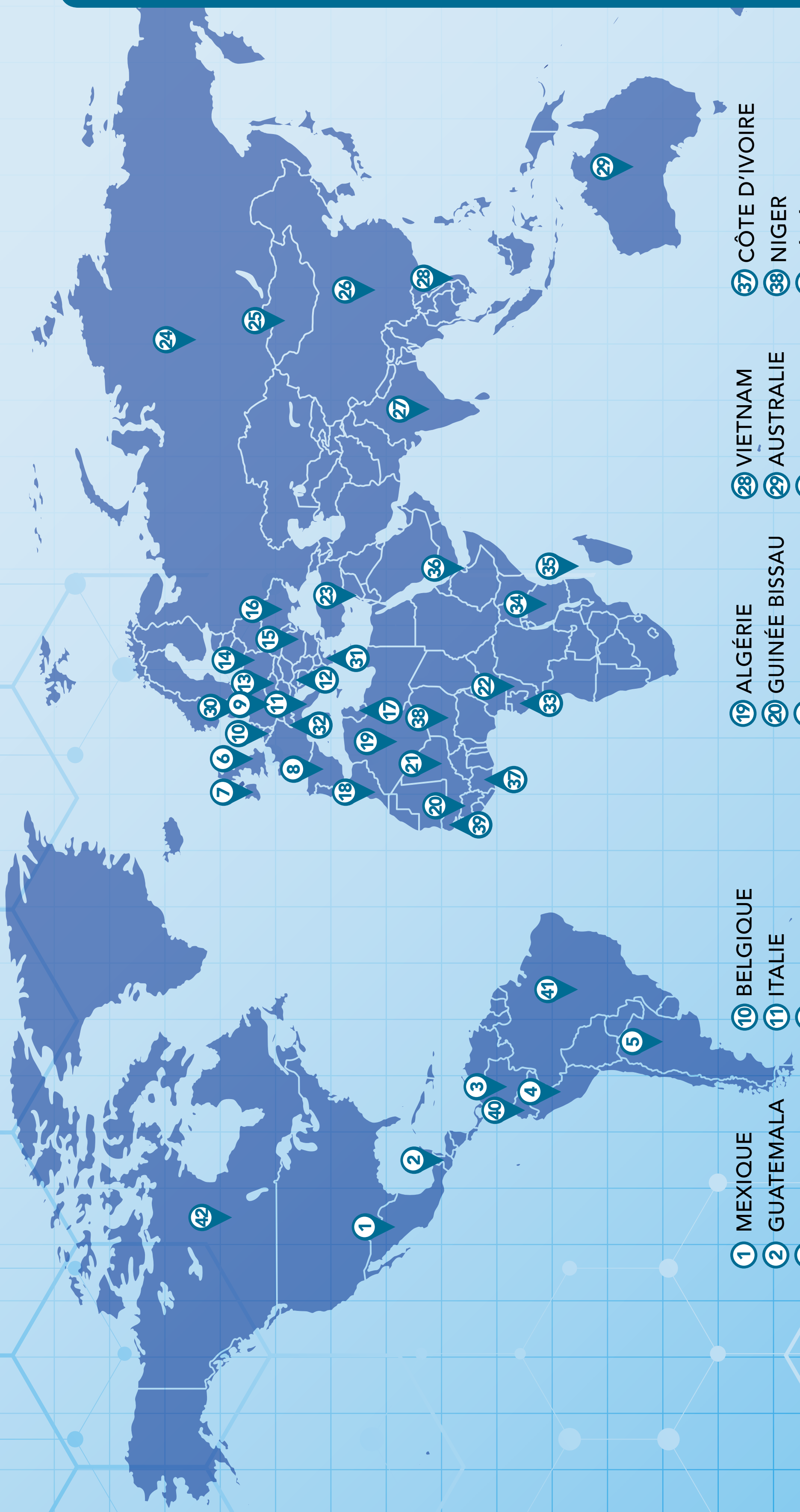
EQUIPE 8 LMCT

DOCTORANT
HOCINE-METAHRI Sarah 01/10/2014-30/09/2017
BLEY Michael 02/11/2015-01/11/2018
COSTE Amaury 01/10/2016-30/09/2019
SPADINA Mario 01/02/2016-31/01/2019
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

POST-DOCTORANT ou CHERCHEUR
PHAM Thanh Tung 20/02/2015-19/03/2017
GOURDIN Simon 20/09/2016-19/09/2017
FOUCAUD Yann 09/12/2019-08/12/2020

ORIGINE GÉOGRAPHIQUE DU PERSONNEL DE L'ICSM

GEOGRAPHICAL ORIGIN OF ICSM STAFF (SINCE 2007)



① MEXIQUE
② GUATEMALA
③ COLOMBIE
④ PÉROU
⑤ ARGENTINE
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⑦ IRLANDE
⑧ ESPAGNE
⑨ ALLEMAGNE

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⑭ POLOGNE
⑮ ROUMANIE
⑯ UKRAINE
⑰ TUNISIE
⑱ MAROC

⑲ ALGÉRIE
⑳ GUINÉE BISSAU
㉑ MALI
㉒ CONGO
㉓ LIBAN
㉔ RUSSIE
㉕ MONGOLIE
㉖ CHINE
㉗ INDE

㉘ VIETNAM
㉙ AUSTRALIE
㉚ DANEMARK
㉛ GRÈCE
㉜ SUISSE
㉝ GABON
㉞ TANZANIE
㉟ COMORES
㊱ DJIBOUTI

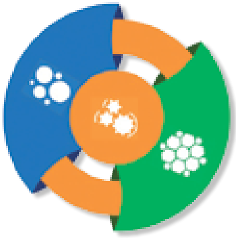
㊲ CÔTE D'IVOIRE
㊳ NIGER
㊴ SÉNÉGAL
㊵ EQUATEUR
㊶ BRÉSIL
㊷ CANADA

ORGANISATION DE CE RAPPORT SCIENTIFIQUE À 4 ANS (2017-2020)

Chacune des huit équipes de recherche rassemble des chercheurs et des ingénieurs sur des compétences spécifiques et qui peuvent sembler très différentes et éloignées à la base. Cependant un grand nombre de résultats sont obtenus au travers de travaux communs leur permettant de publier dans des revues très variées et à participer à un ensemble très éclectiques de conférences internationales.

Au travers de trois axes principaux, les actions de recherche avec des objectifs ciblés que se donnent les chimistes, physico-chimistes créatifs et le personnel en appui à cette recherche sont rassemblées dans ce rapport sous forme de fiches distribuées dans les 3 axes définis dans l'introduction (pages 10-11). Ces axes guident le choix des priorités soutenues financièrement tout en conservant une grande autonomie de réflexion sur des sujets connexes qui pourraient bénéficier de ces recherches.

Axes :



INNOVATION DANS L'EXTRACTION ET LE RECYCLAGE

OPTIMISATION DU CYCLE DE VIE DES MATÉRIAUX POUR L'ÉNERGIE

MÉTHODOLOGIES ET THÉORIES DE LA CHIMIE DE SÉPARATION

Les objectifs ciblés restent :

- Comprendre les mécanismes chimiques qui sous-tendent les processus de séparation chimique et développer des modèles prédictifs
- Optimiser les méthodes de séparation connues, afin d'imaginer, de proposer et de tester des méthodes de séparation optimisées ou innovantes.
- Anticiper le cycle de vie des matériaux utilisés dans le cadre de la production d'énergie nucléaire et alternative
- Développer la «chimie verte» sous toutes ses facettes, y compris la sonochimie.
- Développer des théories et des méthodes de caractérisation et de modélisation.

Les objectifs de recherche s'étendent de la science directement liée à l'énergie nucléaire au recyclage non nucléaire et à la chimie des matériaux, avec une grande partie de la recherche ayant un intérêt «double».

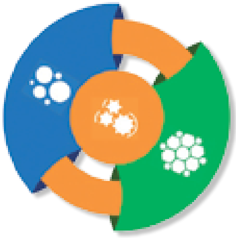
Ensuite, les principaux projets européens/internationaux ainsi que les projets nationaux à travers l'ANR et les projets régionaux à travers le Labex CheMISyst et enfin des processus de valorisation ou pré-maturation sont listés et résumés. Le personnel de l'ICSM est également impliqué dans de nombreuses activités d'enseignement. À la fin de ce rapport sont répertoriées les références bibliographiques des recherches et brevet de l'ICSM couvrant la période 2017-2020.

ORGANIZATION OF THE FOUR-YEAR (2017-2020) ICSM SCIENTIFIC REPORT

Each of the eight active research groups gathers researchers and engineers with specific skills that may seem very different. However, a large number of results are obtained through joined studies allowing them to publish in a wide variety of journals and to participate in a very eclectic set of international conferences.

Through three main axes, the research actions with targeted objectives, that creative chemists, physico-chemists and all staff in support to this research, are gathered in this report in the form of sheets distributed in the 3 axis as defined in the introduction (pages 12-13 pommier). These axes guide the choice of priorities for financial support while maintaining a large autonomy of reflection on related topics that could benefit from this research.

Axis:



INNOVATION IN EXTRACTION AND RECYCLING

OPTIMIZING OF MATERIALS LIFE-CYCLE FOR ENERGY

METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

Focused objectives are still:

- Understand chemical mechanisms underlying processes of chemical separation and develop predictive models
- Optimize known methods for separation, in order to imagine, propose and test optimized or innovative separation methods.
- Anticipate the life-cycle of materials used in the context of nuclear and alternative energy productions
- Develop "Green Chemistry" in all its facets, including sonochemistry.
- Develop Theories and Methods for characterisation and modelling.

Research objectives range from science directly related to nuclear energy to non-nuclear recycling and materials chemistry, with much of the research having a «dual» interest.

Then, the main European/international projects as well as national projects through ANR and regional projects through CheMISyst Labex and finally valorisation or pre-maturation processes are listed and summarized. ICSM staff is also involved in many teaching activities. At the end of this report are listed the bibliographical references of ICSM's research and patents covering the 2017-2020 period.

COLLABORATIONS ACTIVES AVEC DES PARTENAIRES NATIONAUX ET EUROPÉENS

ACTIVE COLLABORATIONS WITH NATIONAL AND EUROPEAN PARTNERS

EN FRANCE

① STRASBOURG
② PARIS
③ RENNES
④ NANCY
⑤ LYON
⑥ GRENOBLE
⑦ AUBERVILLIERS
⑧ LIMOGES
⑨ PERPIGNAN
⑩ MONTPELLIER
⑪ NIMES
⑫ NICE
⑬ SACLAY
⑭ VERSAILLES
⑮ TOURS
⑯ CHAMBERY
⑰ METZ
⑱ CAEN

EN EUROPE (HORS FRANCE) :

① BERLIN
② REGENSBURG
③ KONSTANZ
④ BARCELONE
⑤ STOCKHOLM
⑥ KARLSRUHE
⑦ DRESDEN
⑧ BREMEN
⑨ DARMSTADT
⑩ CYPRUS
⑪ LONDON
⑫ LEUVEN
⑬ LJUBLJANA

LES MISSIONS SCIENTIFIQUES CONTRACTUELLES DE L'ICSM (2015-2020)

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-échelles : 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.

Convention signée le 18-12-2014 par Bernard Bigot (CEA),
Alain Fuchs (CNRS), Pascal Dumy (ENSCM)
et Michel Robert (Université de Montpellier II)

PERSONNEL D'APPUI À LA RECHERCHE ET ÉQUIPEMENTS SCIENTIFIQUES

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 et enfin d'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, protection physique, nettoyage, petits travaux, CEP, …) *(cf. organigramme personnels permanents)*.

Les activités du personnel administratif correspondant à environ 8 ETPT toute tutelle confondue (/ 32 ETPT Recherche, 4 ETPT Enseignement) afin de recevoir et gérer dans les meilleures conditions environ 10 post-doctorants/CDD, 30 doctorants et 50 stagiaires (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) 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. 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 Laboratoire Léon Brillouin (LLB, fermé depuis 2020). 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 Hamburg. 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).


Analyses of solids and surfaces
Transmission Electron Microscopy
Environmental Scanning Electron Microscopy
X-Ray Diffractometer
Thermal Analyses (ATG / TMA)
Atomic Force Microscopy
Surface Analyses
Analyses of liquid or solids
XRF Spectrometer
NMR
Spectrofluorometer
SAXS
Vibrational Spectroscopies
Alpha Spectrometer
ICP-OES
DLS Zetasizer
ICP-MS
Ion Chromatography
Langmuir Trough
DLS / SLS
Analyses of liquids
Glove Boxes
Liquid / Liquid Interfaces
Sonoluminescence Reactor
Furnaces
SHG
Carbon Coater
Other equipments

1/ HYBRID SYSTEMS FOR SEPARATION

L'équipe est constituée au 1er novembre 2020 de :

1 Ingénieur-chercheur CEA/DES, responsable d'équipe (Dr. Daniel Meyer)
1 Chercheur CR-CNRS (Dr. Damien Bourgeois)
1 Enseignant-chercheur MC-UM (Dr. Jérôme Maynadié)
1 Ingénieur-chercheur CEA/DRF (Dr. Michaël Carboni)

Post-doctorants (2017-20) :

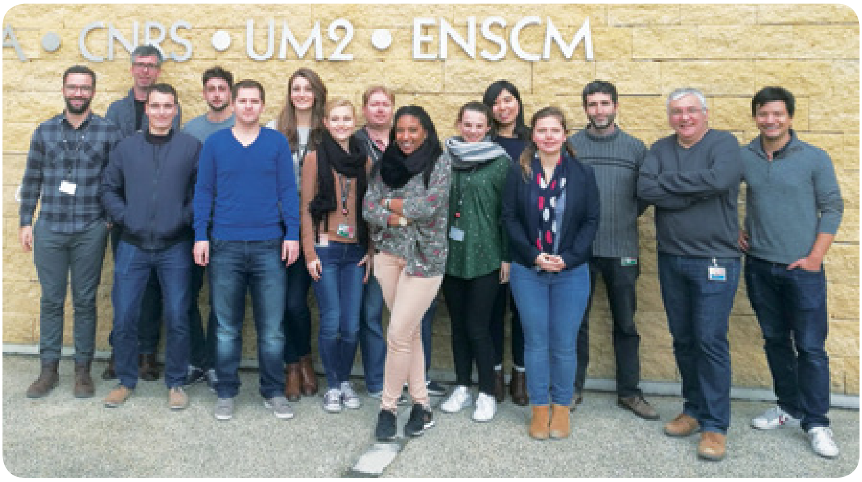
Jingxian Wang (ANR TURBO, 2017-19) : *Solid-liquid exchange between uranium and a synthetic apatite: towards uranium decorporation from bone matrix*

Doctorants (2017-20) :

Ricardo Navarro (thès-e CONACYT, 2013-2017) : *Synthesis and characterization of Metal Organic Frameworks for energy and environmental applications.*
Bertrand Braibant (thèse CEA/DEN, 2013-2017) : *Etude et synthèse de systèmes fluorés pour l'extraction liquide-liquide de métaux stratégiques.*
Guillaume Genesio (thèse UM, 2014-2018) : *Développement de MOFs fonctionnels sur support solide : application à la photochimie.*
Valentin Lacanau (thèse UM, 2015-2019) : *Conception et étude physico-chimique d'amphiphiles auto-assemblés pour l'extraction de métaux et la catalyse en milieu aqueux.*
Damien Rimsant (CEA/DES coll. DMRC, 2016-19) : *Elaboration de matériaux hybrides fonctionnalisés de type MOF pour l'extraction sélective de l'uranium.*
Marine Cognet (thèse UM, 2016-19) : *Elaboration de matériaux hybrides pour le stockage de l'énergie et le recyclage de batteries Li-ion.*
Ali Moussaoui (thèse UM, 2018-21) : *Séparation Liquide/Liquide pilote par la cinétique.*
Fabrice Lorignon (thèse Région / CEA Valo, 2018-21) *: Mise en forme de MOFs sous forme monolithique.*
Aline Chevalier (thèse CEA/DEN, coll. Univ. Strasbourg, 2017-21) : *Extraction liquide-liquide et séparation de métaux à l'aide de bibliothèques dynamiques covalences.*
Elisa Re (thèse CEA/DEN, 2017-21) : *Conception et élaboration de matériaux hybrides à base d'uranium et de thorium.*
Julie Durain (thèse CEA/DEN, 2017-2021) : *Voie alternative courte au multi-recyclage du Pu.*
Elisabeth Makombé (thèse CEA-DES, 2019-23) : *Reformulation solvant et recyclage d'actinides.*
Michael Martin-Romo y Morales (thèse Région / Saint Gobain (CNRS), 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.*

CDD (2017-20) :

Marjorie Laszczyk
(ANR GTM, 2015-17)
Regis Mastretta
(contrat Arcelor Mittal, 2016-18)
Halima Tounkara
(projet CEA Bottom'up, 2017-18)
Sébastien Cher
(contrat Arcelor Mittal, 2019-20)
Nathalie Scalisi
(contrat Sovamep, 2019-20)



The team

L'équipe LHyS a été créée en 2013 à partir du LCPA (Laboratoire de Chimie et Physico-Chimie des Actinides) pour développer de nouvelles activités axées sur l'étude du comportement des métaux dans des systèmes liquides et solides complexes. L'équipe a développé un projet scientifique original basé sur l'intégration des approches solides et liquides utilisées en hydrométallurgie.

L'équipe LHyS contribue aux axes chimie séparative et matériaux de l'ICSM de manière assez équilibrée. Le cadre général est axé sur le cycle des matériaux dans les domaines des énergies «à faible teneur en carbone» et du recyclage des déchets, passant d'une approche fondamentale à une approche plus appliquée.

L'équipe a regroupé la majorité de ses activités sous le concept de chimie circulaire de séparation des métaux. Jusqu'à présent, les approches développées en chimie séparative visent essentiellement le contrôle des étapes unitaires, par des moyens liquides ou solides. La vocation de l'équipe est d'intégrer tous ces développements dans des séquences globales d'extraction-séparation de matériaux fins. Une approche du cycle complet de la matière permet de simplifier les procédés et/ou d'améliorer la valorisation du produit fini. La simplification des procédés vise une meilleure gestion des mélanges, une meilleure flexibilité face à une matière première de composition variable, une réduction du nombre d'étapes, généralement corrélée avec une meilleure maîtrise des déchets générés. Le recyclage ne se limite pas à l'isolement d'un métal purifié, et l'équipe prend également en compte la matière finale : les procédés développés intègrent au mieux la valorisation du métal visé sous forme de produit fini.

L'équipe cherche donc à développer des filières de recyclage courtes, en tenant compte des modèles économiques et écologiques tout en intégrant si nécessaire des considérations de sûreté et de sécurité.

Dans le cadre du cycle du combustible nucléaire, les études réalisées visent à un cycle fermé simplifié, piloté par la sûreté, grâce à une gestion contrôlée de la séparation des actinides associés. Cette approche intègre les aspects de la matière finale par la fabrication directe et contrôlée des matériaux actinides. Dans un contexte plus général de l'industrie des déchets et du recyclage, l'approche développée vise à améliorer la chaîne de valeur par un positionnement pertinent de la chimie de séparation au sein de cette chaîne. En effet, même si elle est inévitable, la chimie doit être réduite à l'essentiel, en tenant compte des critères nécessaires au développement durable.

Dans ce cadre, l'équipe ne cherche pas à développer de nouveaux outils (nouvelles molécules, nouveaux solides, nouvelles méthodologies de synthèse). Néanmoins, la parfaite maîtrise des outils existants nécessite des études de recherche fondamentale visant à comprendre les mécanismes et la nature des forces motrices impliquées.

The LHyS team was created in 2013 from the LCPA (Laboratoire de Chimie et Physico-Chimie des Actinides) to develop new activities focused to study the behaviour of metals in complex liquid and solid systems. The team has developed an original scientific project based on the integration of solid and liquid approaches used in hydrometallurgy.

The LHyS team contributes to the separative chemistry and materials axes of the ICSM in a fairly balanced way. The general framework is focused on the material cycle in the fields of «low carbon» energies and waste recycling from a fundamental to a more applied approach.

The team has grouped the majority of its activities under the concept of circular metal separation chemistry. Up to now, the approaches developed in separative chemistry are essentially aimed at the control of unitary steps, by liquid or solid means. The team's vocation is to integrate all these developments into global extraction-separation-fine material sequences. An approach of the complete material cycle allows to simplify the processes and/or to improve the valorization of the finished product. The simplification of processes aims at a better management of the mixtures, a better flexibility in front of a raw material of variable composition, a reduction of the number of stages, generally correlated with a better control of the generated wastes. Recycling is not restricted to the isolation of a purified metal, and the team also takes into account the final material: the processes developed integrate as well as possible the valorization of the targeted metal in the form of a finished product.

The team therefore seeks to develop short recycling process routes, taking into account economic and ecological models while integrating safety and security considerations if necessary.

In the frame of the nuclear fuel cycle, the studies carried out aim at a simplifying closed cycle driven by safety, thanks to a controlled management of the separation of the related actinides. This approach integrates the final-matter aspects by the direct and controlled manufacturing of actinide materials. In a more general context of the waste and the recycling industry, the approach developed aims at improving the value chain by a relevant positioning of the separative chemistry within this chain. Indeed, even if it is unavoidable, chemistry needs to be reduced to the essential, taking into account the criteria necessary for sustainable development.

Within this framework, the team does not seek to develop new tools (new molecules, new solids, new synthesis methodologies). Nevertheless, the perfect mastery of existing tools requires fundamental research studies aimed at understanding the mechanisms and nature of the driving forces involved.

Main results focus separation:

Studies on phase demixing, the use of fluorinated compounds as well as on three-phase systems have allowed us to progress in our understanding of the relative importance of strong vs weak interactions in the extraction and separation of metals by a liquid-liquid approach.

Based on some fundamental studies already published, the team has developed different hydrometallurgical approaches to recovering Pd from various wastes. We were able to lay the foundations for various process diagrams. In collaboration with different groups, it was possible to demonstrate a direct valuation as catalyst by implementing short recycling routes. Finally, all the fundamental research done in this field lead to a collaboration with the SOVAMEP company to optimize the precious metal recovery.

As the problem of organic pollutants becomes more and more important, we have investigated the possibility of using MOF-type structures for their separation and destruction. Thus Zirconium Metal-organic frameworks (UiO-66, UiO-67 with hydrogenated and fluorinated linkers) have been used for the removal from aqueous solutions of persistent fluorinated pollutants (PFOA and PFOS) as well as aromatic compounds (BTEX). The integration of Ti and Ru by post modification of UiO-67 has allowed not only to extract organic pollutants from aqueous media but also to decompose them photo-chemically.

In contrast to the classical method where a single molecule is designed to extract metal cations under specific conditions, dynamic covalent chemistry provides an approach based on the implementation of an adaptive dynamic covalent library for inducing the generation of the extractant species. In collaboration with the LCS (ISIS), the LHyS team has applied this approach to the liquid–liquid extraction of copper(II) nitrate based on a dynamic library of acylhydrazones constituents that self-build and distribute through the interface of a biphasic system. The addition of copper(II) cations to this library triggers a modification of its composition and the upregulation of the ligand molecules driven by coordination to the metal cations.

Main results focus materials:

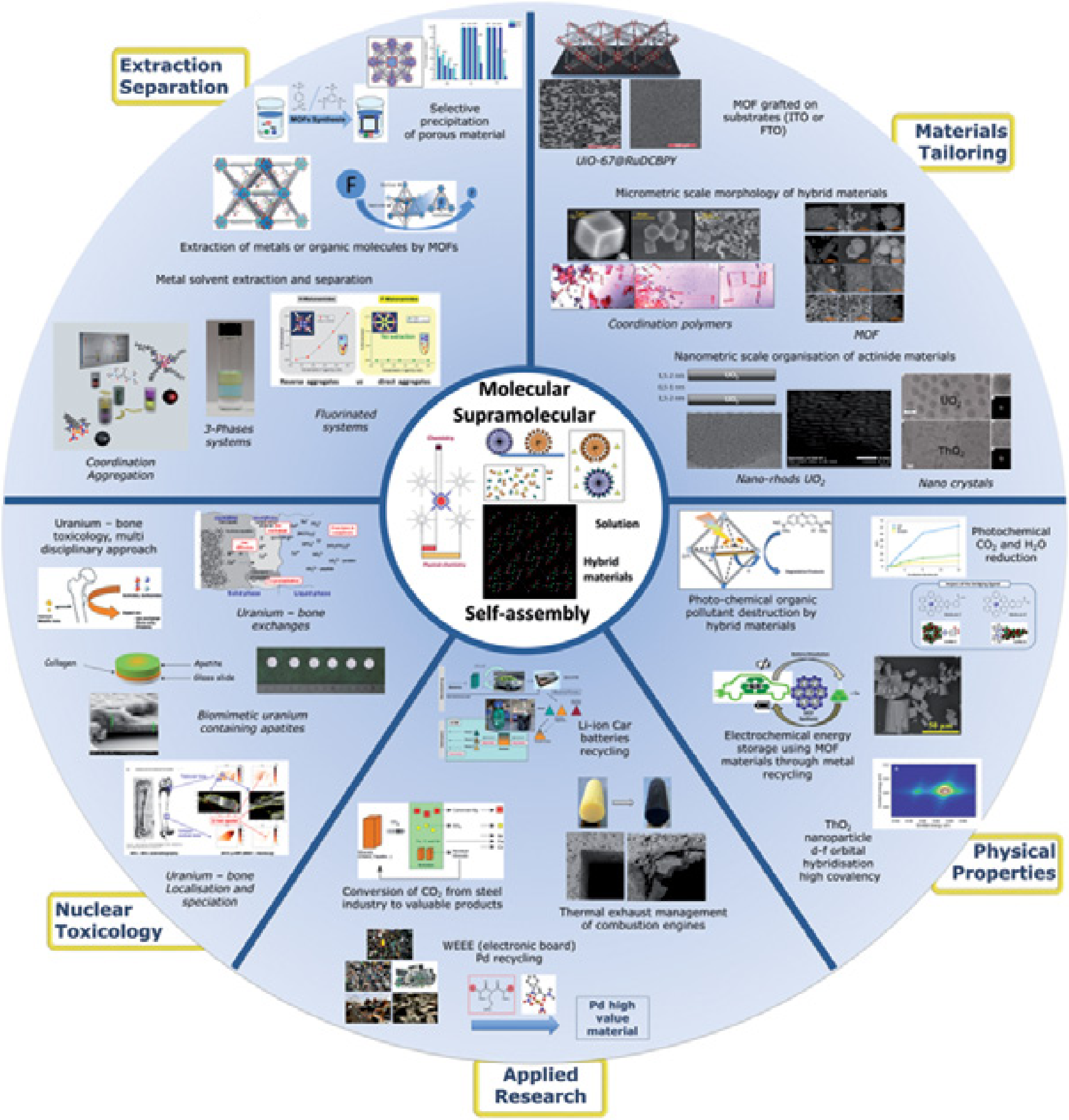
As organized hybrid materials at nanoscale can display unusual properties with respect to the single nano-crystalline counterpart, the team has developed two bottom-up approaches to aim the control of this kind of materials. First, we developed a one-pot approach leading to lamellar nano-sheets materials by the use of a ternary molecular system (dicarboxylic acid, oleylamine, dibenzyl ether). Moreover, in the nano-sheets, the interlamellar distance could be adjusted in accordance with the length of the employed dicarboxylic acid. The second approach, based on functionalization of nanoparticles, has shown that it was possible to use click chemistry as well as electrostatic interactions to build higher order materials by nanoparticles associations.

The literature is currently lacking in efficient, simple and economic shaping procedures for porous materials that do not alter the properties (mainly porosity).

In order to respond to the lack of shaping possibilities of porous materials with broad applicability we have developed, in collaboration with a complementary team, an emulsion approach. Stabilizing Pickering emulsions with metal-organic frameworks (MOFs) is a known way to incorporate this porosity into hierarchically porous materials. Studies generally focus on their final properties and emulsion microstructures are rarely precisely described. Our hypothesis was that characterizing the microstructural and rheological properties of Pickering emulsions stabilized solely by Al-based MOFs (MIL-96) particles would provide insights into how to control their stability and workability for potential industrial applications

Coupling Materials - Separation

Energy storage and its circular economy represent a major societal issue for the years to come. In this field, the LHyS team is strongly interested in the cycle of Li-ion batteries and more particularly that of the active electrode by an approach of hydrometallurgical process integration. This cycle includes its manufacture, its dissolution and the valuation of species in a closed or open cycle mainly based on the use of MOF materials. All of these actions include fundamental and applied studies and implies several external groups national and international (SCARCE project). Based on earlier selective MOF precipitation studies, our team has extended his development on Li-NMC fundamental dissolution studies, electrode materials manufacturing, and several recycling approaches.


Extraction Separation
MOFs Synthesis
Selective precipitation of porous material
F
Extraction of metals or organic molecules by MOFs
Metal solvent extraction and separation
Reverse aggregates vs direct aggregates
Coordination Aggregation
3-Phases systems
Fluorinated systems
Materials Tailoring
MOF grafted on substrates (ITO or FTO)
UiO-67@RuDCBPY
Micrometric scale morphology of hybrid materials
Coordination polymers
MOF
Nanometric scale organisation of actinide materials
UO_2
ThO_2
Nano-rhods UO_2
Nano crystals
Molecular
Supramolecular
Solution
Hybrid materials
Self-assembly
Uranium – bone toxicology, multi disciplinary approach
Uranium – bone exchanges
Collagen
Apatite
Glass slide
Biomimetic uranium containing apatites
Uranium – bone Localisation and speciation
Nuclear Toxicology
Li-ion Car batteries recycling
Conversion of CO_2 from steel industry to valuable products
Thermal exhaust management of combustion engines
WEEE (electronic board) Pd recycling
Pd high value material
Applied Research
Photo-chemical organic pollutant destruction by hybrid materials
Photochemical CO_2 and H_2O reduction
Electrochemical energy storage using MOF materials through metal recycling
ThO_2 nanoparticle d-f orbital hybridisation high covalency
Physical Properties

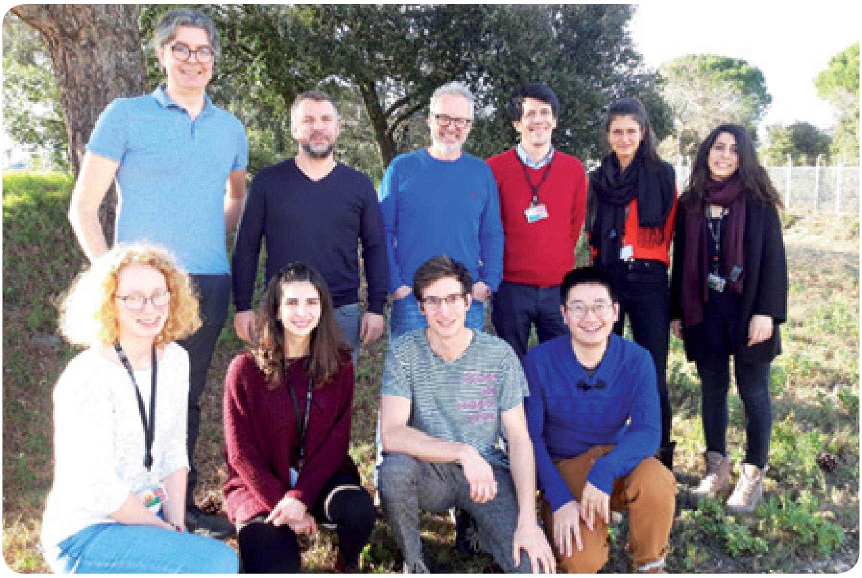
2/ IONS AT INTERFACES

L'équipe est constituée au 1er novembre 2020 de :
1 Chercheur CEA/DRF responsable d'équipe (Dr. Olivier Diat)
1 Ingénieur-chercheur CEA/DRF (Dr. Pierre Bauduin)
1 Enseignant-chercheur ENSCM (Dr. Luc Girard)
1 Ingénieur d'étude CNRS (Alban Jonchère)

Post-doctorants (2017-20) :
Dr. Alla Malinenko (ANR CATASURF, 2016-17) : *Réponse électroacoustique de colloïdes hybrides de POM.*
Dr. Georgy Smolyakov (contrat ADIONICS, coll. avec LTSM et le LHYS, 2016-17): *Extraction liquide/liquide pour désalination de l'eau.*
Cyril Micheau (CEA/DADN, 2016-17) : *Flottation de particules d'argile.*
Donatien Gomes Rodrigues (Labcom Vect'oleo, 2016-17) : *Solubilisation d'antioxydants polaires dans des huiles végétales.*

Doctorants (2017-20) :
Tania Merhi (thèse ENSCM, 2017-20) : *Nano-ions de type dicarbollide en interaction avec des surfaces modèles biologiques.*
Max Hohenschutz (thèse région Occitanie/ Extrachive, 2017-20) : *Nano-ions en interaction avec des surfaces non-ionique.*
Jing Wang (thèse CEA/DEN, 2017-20) : *Etude de l'interface liquide/liquide : expérience et modélisation moléculaire.*
Ioanna Chazappi (thèse CEA, 2019-22) : *Effet de solubilisation avec des nano-ions.*
Klaudia Skorzewska (thèse CEA, 2019-22) : *associations superchaotropes.*
Julien Lamolinairie (co-direction thèse ILL avec Teclis Instrument, 2020-23) : *foam'up.*
Philipp Schmid (co-direction thèse Univ. Regensburg, 2019-22) : *Nanoions and hydrotropes.*
Edouard Malenga (co-encadrement, thèse Univ. Johannesburg, 12 mois, 2017-18) : *Recovery of value from sludge generated during mining of PGMs bearing mineral.*

CDD (2017-20) :
Emile Regnier (ingénieur ANR Foamex, 2019-21)
Ophélie Fadel (ingénieur Labcom Vect'oleo, 2014-17)



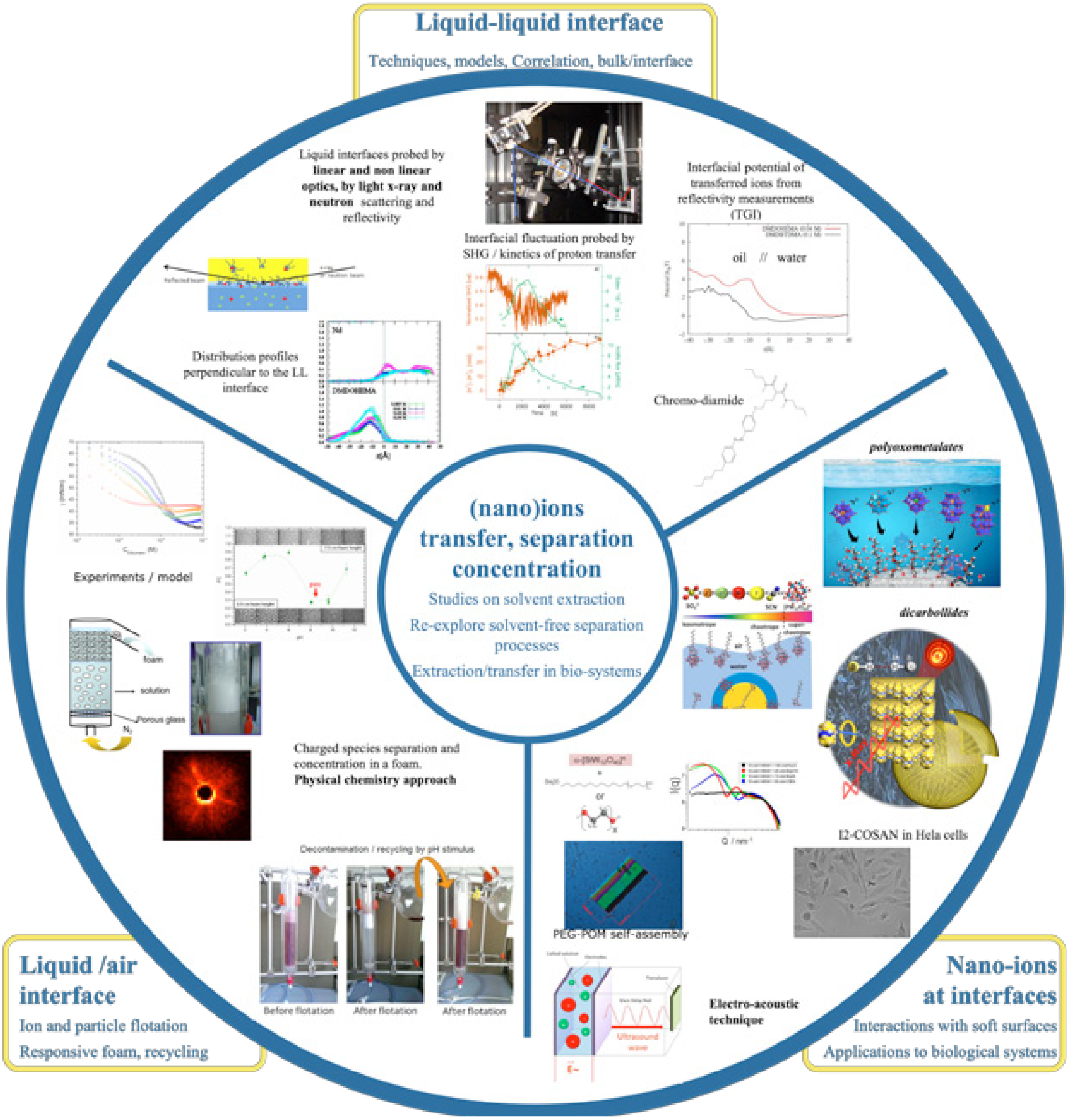
L'extraction liquide/liquide est un procédé de séparation en phases fluides lié au contrôle thermodynamique et cinétique de la distribution des espèces moléculaires à séparer entre des phases liquides non miscibles, usuellement une phase aqueuse et une phase organique. Son optimisation (rendement, coût, réduction de déchets) nécessite de comprendre les phénomènes de diffusion jusqu'aux interfaces, les phénomènes hydratation/déshydratation – solvatation/désolvatation aux interfaces, leur temps de résidence aux interfaces. La recherche dans ce domaine et au sein de l'équipe s'est focalisée sur :
I) la dispersion des espèces ioniques ou non-ioniques et donc leurs spéciations moléculaires ou supramoléculaires dans chacune des phases en étudiant et ajustant la nature du solvant (aqueux or organique) plus ou moins complexe (pure, binaire, ternaire) et sa structuration à différentes échelles,
II) la structuration moléculaire et/ou supramoléculaire de ces solvants à leurs interfaces de contact qui différent de celle du volume.

Déclinée dans le cas des actinides et des lanthanides, une problématique d'importance pour le tri ionique associé au cycle du combustible, cette recherche cognitive s'est étendue au fil des ans à des cas de dépollution, de recyclage, d'extraction de molécules actives tout en prenant en compte un aspect à faible impact environnemental qui requiert la réduction des volumes de solvants ou leur régénération par des étapes simples et peu couteuse, l'optimisation physico-chimique de procédés pour les rendre plus efficace et modulaires c'est-à-dire facilement adaptables, la formulation de solvants verts. L'utilisation de la mousse en est un exemple, une structure fluide métastable avec une interface fluide/air ultradéveloppée pouvant être utilisée pour extraire des solutés de la phase fluide (comme un filet de pêche). Si l'extraction des métaux sous forme cations ainsi que leur sélectivité dans un procédé d'extraction liquide/liquide est classiquement étudié en optimisant i) la structure chimique du ligand pour jouer sur la balance complexation/solubilisation ainsi que ii) le phénomène d'émulsification associé, des progrès peuvent être fait en analysant cette problématique sous l'angle des interfaces et des phénomènes physico-chimiques associés et par la maitrise de l'hydratation des ions ou clusters ioniques en phase aqueuse.

Dans ce rapport, parmi les nombreux sujets en cours qui nous impliquent mais impliquent aussi des collaborations extérieurs nous avons sélectionné des exemples sur lesquels nous sommes porteurs ou plutôt les acteurs principaux : un premier exemple dans l'axe méthodologie et simulation concerne donc l'étude d'interface liquide/liquide comprenant des ligands par une technique d'optique non linéaire et en parallèle utilisant des outils de dynamique moléculaire afin de pouvoir appréhender l'organisation des ions et molécules extractantes autour de l'interface pendant un processus de transfert d'espèces. C'est un travail de thèse en collaboration avec le DMRC/LILA. Un deuxième exemple concerne l'étude de mousses dans l'axe 1, une structure tri-dimensionnelle et labile afin d'extraire des ions ou des particules en limitant la quantité de solvant. Enfin un développement fort de l'équipe après plusieurs années d'études en marge concerne les nano-ions ou ions de taille nanométrique et leurs caractéristiques superchaotropes quand leur densité de charge devient inférieure à 12 é/nm^3. Ces structures moléculaires peuvent en effet jouer le rôle de (co-)tensioactifs, de solubilisants, d'agents structurants de solvant aqueux, d'agent de liaison, d'hydrotropes, de vrais couteaux « suisse » dans la physico-chimie des ions et colloïdes. Cette recherche autour des nano-ions prend du volume dans l'équipe tout en restant focalisé sur des propriétés interfaciales et nous permet d'élargir nos recherches vers des domaines de la biologie et de la médecine du futur.

Liquid/liquid extraction is a separation process related to the thermodynamic and kinetic control of the distribution of the molecular species to be separated between two immiscible liquid phases, usually an aqueous phase and an organic phase. Its optimization (yield, cost, waste reduction) requires among others to understand the diffusion phenomena up to the interfaces, the hydration/dehydration - solvation/de-solvation phenomena at the interfaces, their residence time at the interfaces. Research in this field and within the team has focused on:
I) the dispersion of ionic or non-ionic species and thus their molecular or supramolecular speciation in each phase by studying and adjusting the nature of the more or less complex solvent (pure, binary, ternary) and its structuration at different scales,
II) the molecular and/or supramolecular structuration of these solvents at their interfaces which differs from the volume.

Declined in the case of actinides and lanthanides, an important issue associated with the radioactive fuel cycle, this cognitive research has been extended over the years to depollution of liquids, critical metals recycling, extraction of bioactive molecules. The adding-value can be achieved if the environmental impact is taken into account with the reduction of solvent volumes or their regeneration by simple and inexpensive steps, with the physico-chemical optimization of processes to make them more efficient and modular, i.e. easily adaptable, with the formulation of green solvents. One example is the use of foam, a metastable fluid structure with an ultra-developed fluid/air interface that can be used to extract solutes from the fluid phase (like a fishing net). The extraction of metals in their cationic form as well as their selectivity in a liquid/liquid extraction process is classically studied by optimizing i) the chemical structure of the ligand to play on the complexation/solubilization balance as well as ii) the associated emulsification phenomenon. Progress can be made by analyzing this ion transfer from the point of view of interfaces and associated physico-chemical phenomena and by controlling the hydration of ions or ionic clusters in the aqueous phase.



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

L'équipe est constituée au 1er novembre 2020 de :
1 Directeur de Recherche CNRS responsable d'équipe (Dr. Stéphane Pellet-Rostaing),
1 Ingénieur/chercheur CEA/DRF (Pr. Thomas Zemb)
1 Maître de Conférences UM - HDR (Dr. Guilhem Arrachart)
1 Ingénieur CEA/DRF - HDR (Dr. Sandrine Dourdain)
1 Technicienne CEA/DES (Béatrice Baus-Lagarde)
1 Ingénieur de recherche CNRS (Dr. Fabrice Giusti)

Post-doctorants (2017-20) :
Simon Chapron (ERA-MIN, 2015-2017) : *Ligands pour la récupération de terres rares de mines secondaires*
Fanny Mary (ANR SILEXE, 2015-2016) : *TSIL pour le recyclage de métaux stratégiques*
Georgiy Smolyakov (ADIONICS, coll. L2IA/LHYS, 2016-2018) : *Mécanismes d'extraction par la formulation Flionex*
Manuel Lejeune (POC SYNEXTRACT, coll. LNER, 2017-2018) : *Chromatographie Synergique pour la purification de terres rares*
Guillaume Mossand (CNRS, 2017-2018) : *Extraction de l'uranium de l'eau de l'eau de mer par des résines chélatantes*
Victor Haquin (AREVA 2017-2019) : *Compréhension de l'extraction de l'uranium et de ses impuretés en milieu sulfurique*
Cesar Augusto Lopez (UM LABEX 2018-2020) : *Mécanismes d'extraction en milieux liquides ioniques*
Tamir Sukhbataar (CEFIPRA franco-Indien, 2019-2020) : *« Transformisme » moléculaire et procédés de recyclage de terres rares contenues dans les aimants permanents*

Doctorants (2017-20) :
Tamir Sukhbataar (CTCI AREVA, 2014-2018) : *Approche multi-échelle pour la compréhension de mécanismes d'extraction de l'uranium en milieux liquides ioniques*
Tobias Lopian (ERC, 2014-2017) : *Caractérisation d'une microémulsion pauvre en eau et adaptive à l'extraction de métaux.*
Carlos Arrambide (Contrat Doctoral UM2, 2014-2017) : *Méthodologies de synthèse de résines formo-phenoliques chelatantes : vers une extraction solide-liquide optimisée des métaux stratégiques*
David Bengio (CEA/DEN, 2015-2018) : *Comportement électrochimique des terres rares en milieu liquide ionique (co-direction thèse)*
Alexandre Artese (CEA/DEN thèse phare, 2016-2019) : Caractérisation de ligands bifonctionnels N,P pour la co-extraction U/Pu en milieu nitrique.

Robert Winkler (CEA/DRF, 2016-2019) : *Approche « tout en un » pour la mise en oeuvre de matériaux hybrides à hautes capacités extractantes*
Nicolas Felines (CEA/DES thèse phare, 2017-2020) : *Monoamides énantiopurs pour l'extraction de l'uranium*
Zijun Lu (CEA/DES 2017-2020): *Solution of amphiphilic ion pairs in equilibrium with an aqueous phase: mechanistic study of extraction*
Justine BenGhozi-Bouvrande (CEA/DES 2018-2021) : *Les liquides poreux : un nouveau concept pour l'extraction liquide liquide*
Ruth.Oye-Auke (Contrat Doctoral UM, 2018-2021) : *Méthodologies de synthèse et étude de résines biosourcées thermodurcissables pour la récupération de métaux d'intérêt*
Chen Xing (China Scholarship Council (CSC), 2018-2022) : *Concentration and selective recovery of uranium using nanofiltration processes*
Sahar Belfqueh (Région-BRGM, 208-2021) : *Recyclage et valorisation des terres rares contenues dans des solutions faiblement acides*
Fatima Bekkar (PNE, accueil 18 mois, 2018-2019) : *Synthèse contrôlée de résine chélatantes pour le recyclage*
Elise Guerioni (CEA/DES, 2020-2023) : *Etudes des mécanismes d'extraction de l'uranium en milieu sulfurique par des amines tertiaires à chaînes alkyles ramifiées*
David Lemire (CEA/DES, 2020-2023) : *Ligands chiraux pour la chimie séparative*
Claudine El Khoueiry (SAFAR, CNRSL/Ambassade France) : Thiourées polymérisées pour la décontamination
Julien Couturier (CEREGE - CNRS, 2020-2023) : *Extraction responsable et sélective de métaux critiques à partir de sources secondaires (co-direction thèse)*

L'équipe « Tri Ionique par des Systèmes Moléculaires Auto-assemblés » (LTSM) est aujourd'hui 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) et Stéphane Pellet-Rostaing, Directeur de Recherche CNRS (01/2009). Les orientations de recherche développées au LTSM sont principalement intégrées aux axes « Innovation pour l'extraction et le recyclage », et en connexion étroite avec les axes « Méthodologies et théories en chimie séparative » et « Optimisation du cycle de vie des matériaux pour l'énergie ». 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 dans la compréhension des mécanismes qui gouvernent la séparation. Les publications traitant de l'extraction liquide-liquide se placent exclusivement dans la cadre de la chimie organo-métallique, de la chimie supramoléculaire ou de la physico-chimie des systèmes auto-assemblés. Le LTSM développe une vue générale « iénaïque » des énergies libres de transfert qui est une vision « nanosciences » de l'électrochimie classique, sans champ extérieur mais qui tient compte des interactions faibles au-delà du premier voisin. L'approche « iénaïque » prévoit la conception et la synthèse d'extractants spécifiques originaux (pinces moléculaires, macrocycles, résines) ainsi que l'étude des mécanismes associés gouvernant l'affinité et la sélectivité, et permet en outre de faire des prédictions quantitatives sans paramètres non mesurables. La possibilité d'exalter la complexation par l'auto-association de complexants sous forme de micelles, fibrilles ou cristaux liquides 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, et comme résumé précédemment, le LTSM se situe clairement dans l'approche nanosciences et développe une recherche à caractère fondamental en adéquation avec les orientations initiales de l'Alliance ANCRE et de la SNRI (aujourd'hui Stratégie Europe 2020) dans le cadre 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). La chimie du LTSM doit s'approprier l'évolution des nanosciences : systèmes moléculaires organisés, nanomatériaux et compréhension des forces en jeu à l'échelle nanométrique.

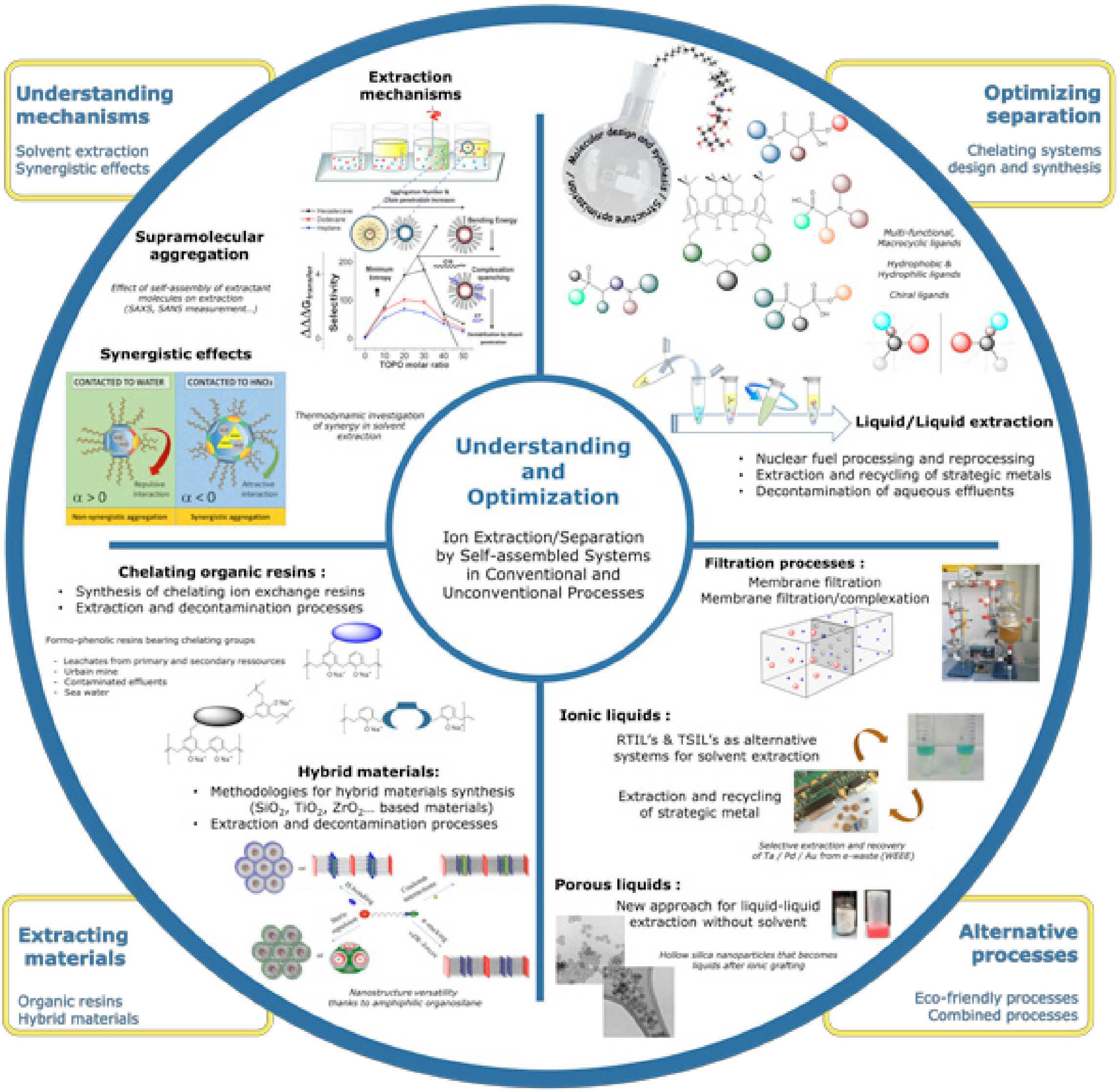
L'implication du LTSM dans les programmes de recherche du CEA à travers leur segmentation (Energie Nucléaire, technologies pour l'Industrie et la communauté scientifique, Socle de la recherche fondamentale), le programme interdisciplinaire du CNRS NEEDS, des collaborations industrielles directes (Morphosis, ADIONICS) ou par l'ANR (CD2I), par l'Europe (ERA-MIN)) ainsi que par des financement de maturation de projets (SATT AxLR), mais aussi des programme européens (ERC REE-Cycle, H2020 REFRAM) et internationaux comme les programmes Franco-Libanais SAFAR ou Franco-Indien CEFIPRA, les programmes de co-financement par la région, ainsi que la coordination du LABEX Chemisyst, celle du Lab'MUSE Chimie et celle du GDR SENA (Franco-Russe) sont à l'origine des projets de recherche commun avec CEA/DES, CEA/DRF, le BRGM, l'Université de Montpellier (ICGM, IEM), l'Université de Savoie (LCME), l'Université de Lorraine (IJL), l'Université de Lyon (IRCE), l'Université Libanaise (Beyrouth), l'IPCE (Moscou), Argonne (USA), le CNEA (Argentine), le CSIR-NML, ou encore les industriels TND, ORANO, Morphosis, Chemec Oy, Tata.
En marge des activités de recherche, le LTSM réalise des contrats de prestation (synthèse à façon, analyses ICP, RMN…) pour le CEA/DEN, le laboratoire PROMES et d'autres industriels (VEOLIA, Cis-Bio).

The group «Ion Separation by Self-assembled Molecular Systems» (LTSM) is today composed of 6 permanent staff, Guilhem Arrachart, Lecturer UM (09/2009), Sandrine Dourdain, Engineer CEA/DRF (07/2010), Beatrice Baus-Lagarde, Technician CEA/DEN (04/2016), Fabrice Giusti, CNRS Research Engineer (07/2018), Thomas Zemb, CEA/DRF Engineer and INSTN Professor (01/2019) and Stéphane Pellet-Rostaing, CNRS Research Director (01/2009). The main strategic lines of research developed at LTSM are mainly integrated into the axes «Innovation for extraction and recycling», and in close connection with the axes «Methodologies and theories in separation chemistry» and «Optimization of the life cycle of materials for energy».

The group values the complementary nature of its skills in synthetic chemistry, analytical chemistry and nanoscience implementing separation-recycling processes via chelating systems for the extraction and purification of metal cations. These molecular systems are implemented in both conventional (liquid/liquid, solid/liquid) and less conventional processes (membranes, non conventional solvents) with an orientation towards understanding the mechanisms governing separation. The two thousand publications per year dealing with liquid-liquid extraction are all within the framework of organometallic chemistry, supramolecular chemistry or the physical chemistry of self-assembled systems. The LTSM is developing an «ienic» general view of free transfer energies: ienic is a «nanosciences» view of classical electrochemistry, without an external field but which takes into account weak interactions beyond the first neighbor. The «ienaic» approach allows the design and synthesis of original specific extractants (molecular tweezers, macrocycles, resins) as well as the study of the associated mechanisms governing affinity and selectivity, which can be the subject of quantitative predictions without non-measurable parameters. This allows the synthesis and implementation of original and specific extracting agents (molecular tweezers, macrocycles, resins) as well as the study of associated mechanisms which govern affinity and selectivity, in particular by taking into account supramolecular cooperative phenomena. The opportunity of enhancing complexation by the self-association of complexing agents in the form of micelles, fibrils or liquid crystals is investigated with the aim of designing disruptive ion separation processes. Beyond the purely nuclear field, these selective effects are studied and implemented in various processes linked to the recycling of materials, associated with energy production and more generally, in the ambitions of sustainable development and energy transition, for example in decontamination or for the selective recycling of strategic metals.
The LTSM is involved in a "colloidal" approach – the triple point where physics, chemistry and technology meet- via a cognitive approach linked to the core orientations of the Alliance ANCRE and SNRI (today 'Europe 2020 Strategy') in the framework of renewable energy and circular economy. This covers the current and future nuclear fuel cycle (upstream and downstream) as well as metals of interest (strategic metals and chemotoxic), from the extraction from ores (uranium, lanthanides, etc.) to the spent nuclear fuel reprocessing (removal of radio-toxic elements) or the recycling of WEEE.

The involvement of LTSM in the CEA research programs through their segmentation (Nuclear Energy Technology for Industry and the scientific community base of basic research), the interdisciplinary program of CNRS NEEDS, industrial collaborations (Morphosis, ADIONICS), through ANR

(CD2I), by Europe (ERA-MIN), European program (ERC REE-Round, H2020 REFRAM), the Franco-Lebanese "SAFAR" or French-Indian CEFIPRA programs, as well as the coordination of the LABEX Chemisyst and the Lab'MUSE CHIMIE and that of the GDR SENA (Franco-Russian) are at the origin of the joint research projects with CEA/DES, CEA/DRF, Montpellier University (ICGM, IEM), Savoie University (LCME), Lorraine University (IJL), Lyon University (ESRD), Lebanese University (Beirut), Regensburg University, ICPE (Moscow), Argonne (USA), CNEA (Argentina), TND, AREVA, Morphosis, Chemec Oy. Alongside the research, LTSM performs service contracts (synthesis, analysis and characterization, expertises ...) to the CEA/DES and other industrial (VEOLIA, ONET-Technology, St Gobain, Cis-Bio).



4/ SONOCHEMISTRY IN COMPLEX FLUIDS

L'équipe est constituée au 1er novembre 2020 de :
1 Directeur de Recherche CNRS responsable d'équipe (Dr. Sergueï Nikitenko)
1 Ingénieur-chercheur CEA/DES (Dr. Rachel Pflieger)
1 Chargé de Recherche CR-CNRS (Dr. Tony Chave)
1 Ingénieur-chercheur CEA/DES (Dr. Matthieu Virot)

Post-doctorants (2017-20) :
Cyril Micheau (projet bottom-up CEA, 2019-20,) : *Etude des colloïdes de plutonium.*

Doctorant (2017-20) :
Elodie Dalodière (thèse soutenue en 2017, codirection ICSM-CEA/DEN/DRCP) *: Synthèse et caractérisation de colloïdes de Pu.*
Andrés Felipe Sierra Salazar (thèse Erasmus Mundus – ICG/IEM/ICSM - University of Messina – University of Delft, 2014-17) : *Waterborne catalytic materials with original design.*
Florence Nouaille (thèse soutenue en 2017, BDI CNRS-AREVA, codirection ICSM- Université de Lille) : *Développement d'un procédé innovant de conversion d'oxyde d'uranium en peroxyde d'uranium.*
Ran Ji (these CEA/DEN/EDDEM 2015-18) : *Study of acoustic cavitation near metal surfaces contaminated by uranium.*
Lauréanne Parizot (thèse soutenue en 2019, Investissements d'Avenir ANDRA, CADET, codirection ICSM - IJLRA): *Etude de la cavitation par impact et par ultrasons pour la dégradation des composés organiques.*
Laura Bonato (thèse CEA/DEN 2017-20) : *Réactivité d'oxydes d'actinides nanostructurés en vue de leur dissolution sous l'effet de la cavitation acoustique.*
Sara El Hakim (thèse UM 2018-21) : *Réactions sonocatalytiques et photocatalytiques en présence de nanocatalyseurs innovants pour l'énergie et l'environnement.*
Manon Cot-Auriol (thèse CEA codir CEA/DES/DMRC, 2019-22) : *Etude de la réactivité de colloïdes d'actinides et de leurs mécanismes de formation.*
Sophie Herr (thèse CEA/DES codirection DMRC, 2019-22) : *Décontamination de sols avec les ultrasons.*

CDD (2017-20) :
Noura Sleiman (IRT-M2P collaboration ICSM-UTINAM, 2019-20) : *Etude de HIFU.*

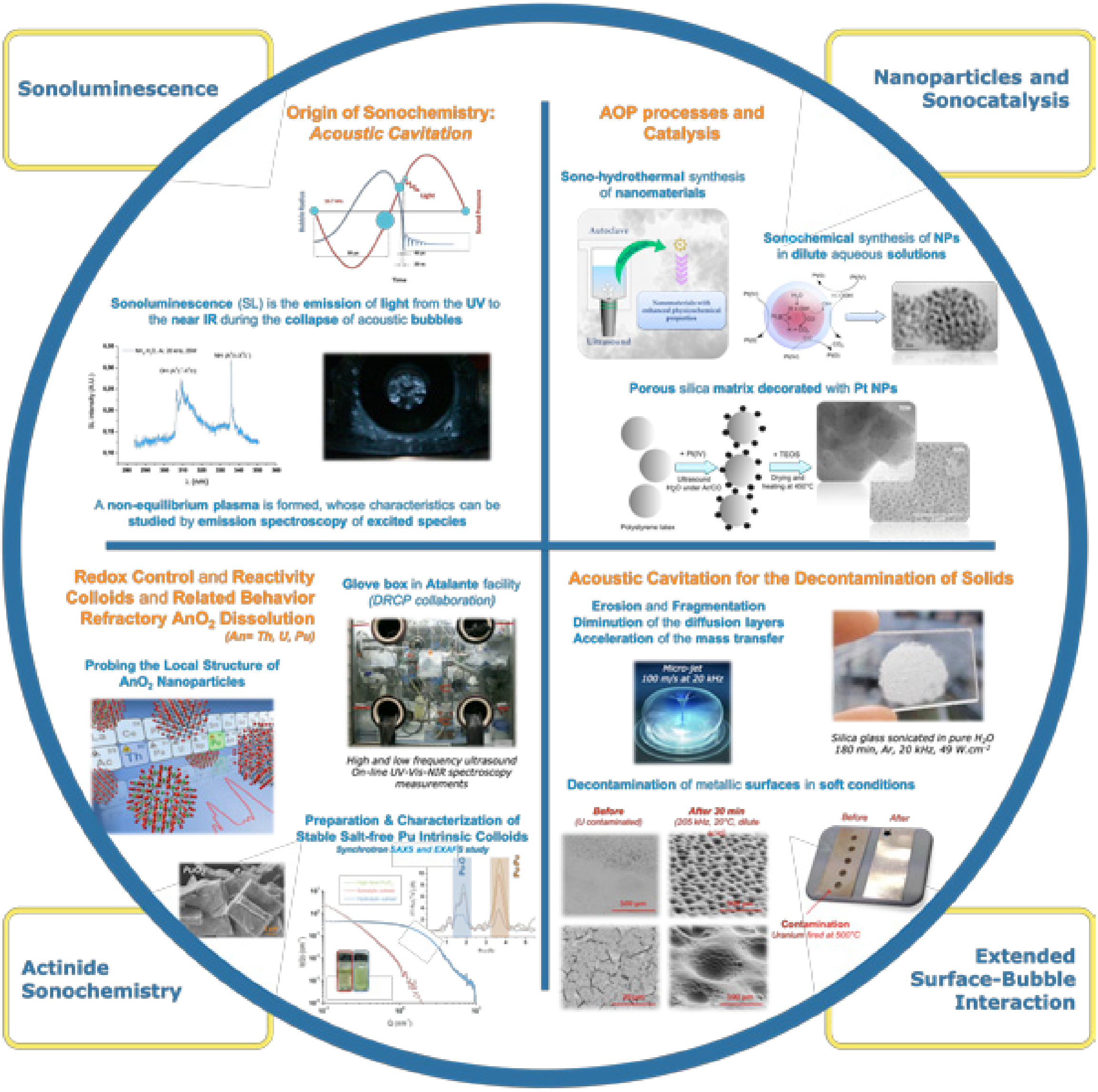
L'objectif principal du laboratoire de sonochimie dans les fluides complexes (LSFC) consiste à mener des études fondamentales sur les mécanismes des réactions sonochimiques (réactions chimiques induites par la propagation d'ondes ultrasonores entre 16 kHz et 1 MHz dans un milieu fluide) en solutions 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 microbulles 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 :
- Spectroscopie de sonoluminescence
- Réactivité sonochimique à l'interface solide-liquide
- Synthèse sonochimique de nanomatériaux et sonocatalyse
- Sonochimie des actinides

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 nonequilibrium 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:
- Multibubble sonoluminescence
- Sonochemical reactivity at solid-liquid interfaces
- Sonochemical synthesis of nanomaterials and sonocatalysis
- Sonochemistry of actinides

Projets (collaborations)
- 2019-22 LINA Projet Région Occitanie
- 2020 Projet PEPS Cellule Energie CNRS (ICSM-IEM)
- 2016-19, Investissements d'Avenir ANDRA, CADET « Cavitation Assistée pour la DEconTamination des eaux » (Institut Jean le Rond d'Alembert)
- Sonoluminescence dans les fluides complexes (LCME, Chambéry ; UTINAM, Besançon, Université de Melbourne, Australie)
- Dissolution sonochimique des oxydes d'actinides (CEA/DES)
- 2015-17, Sonochimie de l'uranium (Comurhex/AREVA; Université de Lille)
- Colloïdes de plutonium(IV) (CEA/DES ; JRC Karlsruhe Allemagne ; ESRF Grenoble ; 2015-2016 projet TALISMAN, 2018-19 projet Bottom-up SONISCOP)
- 2015-17, Synthèse sonochimique de nanomatériaux et applications en catalyse (Erasmus Mundus, ICG ; IEM ; Université de Messine ; Université de Delft ; Université du Cap)
- 2018-19, Synthèse sonochimique de nanoparticules pour les applications biomédicales (TORSKAL)
- 2018-19, Dispersion ultrasonore de fibres naturelles (APM FORENSIA)



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 layers**
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/ NANOMATERIALS FOR ENERGY AND RECYCLING PROCESSES

L'équipe est constituée au 1^{er} novembre 2020 de :
1 Ingénieur-chercheur CEA/DES responsable d'équipe (Dr. Xavier Deschanels)
2 Ingénieur-chercheurs CEA/DES (Dr. Diane Rébiscoul et Dr. Jérémy Causse)
1 Maître de Conférences ENSCM (Dr. Guillaume Toquer)
1 Ingénieur d'étude UM (Cyrielle Rey)

Post-doctorants (2017-20) :

Hélène Arena (ANR CARAPASS, 2016-18) : *Développement d'absorbeurs solaires sélectifs de type nanocomposites SiC-TiC pour centrales solaires à concentration (CSP).*
Manuel Lejeune (POC SYNEXTRACT, coll. LTSM, 2017-18) : *Chromatographie Synergique pour la purification de terres rares.*
Singaravelu Chandra Mohan (CEA/DES, 2019 puis PTC Instrumentation et détection, 2020-21) : *Nanomatériaux comme révélateurs d'irradiation alpha, béta/gamma.*
Hassan Khoder (Fondation maison de la chimie, 2020-21) : *Etude de la dynamique de l'eau au sein de solutions aqueuses confinées dans des matériaux modèles à base de silice.*
Baptiste Russo (2020-22) : *projet Valorisation ABRICeaux.*
Alicia Sommer Marques (2018- 3mois)

Doctorants (2017-20) :

Anna Hautecouverture (CEA/DES, 2020-23) : *Synthèse de solution solide d'oxydes d'actinides par combustion en solution.*
Florian Didier (UM, 2019-22) : *Dépôt électrophorétique de nanoparticules pour des absorbeurs solaires photothermiques.*
Toni Tratnjek (CEA/DES, 2019-22) : *Vers de nouveaux matériaux à porosité hiérachisée pour la capture de produits de fission (Sr, Cs).*
Jun Lin (CEA/DRF, 2018-21) : *Comportement des silices mésoporeuses sous irradiation par des ions de haute énergie.*
Rémi Boubon (CEA/DES PIA ANDRA, 2017-20) : *Etude de l'évolution de l'interface entre les géopolymères et l'alliage Mg-Zr.*

Baptiste Russo (Région/CEA-DES, 2017-20) : *MatéRIaux nanocompoSites pOreux élaborés à partir de balle de riz de Camargue uTilisés comme sOrbants (RISOTO).*
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.*
Julien Monnier (CEA/DES, 2016–19) : *Synthèse d'oxydes d'actinides par combustion des nitrates.*
Martin Leblanc (CEA/DES affectation principale CEA/DEN/DMRC, 2016–19) : *Synthèse d'oxydes d'actinides dédiés à la fabrication de Mox (GEN IV) par dénitration thermique avancée en présence d'additifs organiques.*
Markus Baum (CEA/DES, 2015–18) : *Etude de la chimie de l'eau en présence d'ions dans les silices nanoporeuses.*
Susan Sananes Israel (UM, 2015-18) : *Evolution sous contraintes de silices nanoporeuses greffées par voie CO2 supercritique.*
Sanaa Shehayeb (UM/Université Liban, 2015-17) : *Récepteur solaire photo-thermique obtenu par électrophorèse de nanoparticules à propriétés optiques sélectives.*
Clémentine Mansas (CEA/DEN, 2014-17) : *Extraction sur phases solides à partir de matériaux cœur-couronne : un cœur extractant sélectif, une couronne comme précurseur de matrice de confinement.*

Collaborateurs temporaires :

Anna Coste (Apprenti Licence Pro, CNRS, Coll. L2IA, 2019-20) : *Synthèse et caractérisation par spectroscopie infrarouge de la silice SBA-15.*
Luca Briscese (Apprenti Licence Pro, CNRS, 2019-20) : *Synthèse et étude de silices mésoporeuses fonctionnalisées pour la sorption et le confinement de radionucléides.*
Patricio Alastuey (Doctorant, Universidad Nacional de Tucumán, Sept – Dec. 2018) : *Synthesis of nanostructures transparent ox-ides: study of the effect of doping on their electrical, optoelectronic and photovoltaic properties.*
Alicia Sommer Marquez (Associated Professor, Yachay Tech University, Juin – Aout 2018) : *Encapsulation of photosynthetic plant cells within hierarchical silica monolith enriched with chlorophyll-a by high internal phase emulsion (HIPE) for CO2 adsorption.*
Andrea Beca Oviedo (2018- 3 mois)

Le laboratoire LNER développe plusieurs compétences scientifiques, techniques et d'enseignement pour répondre aux défis posés par la recherche sur les énergies dé-carbonées. 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 mésostructuré – 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 LNER dans la période 2017-2020 sont résumées dans les pages suivantes et peuvent s'inscrire dans les 4 grands thèmes suivants :

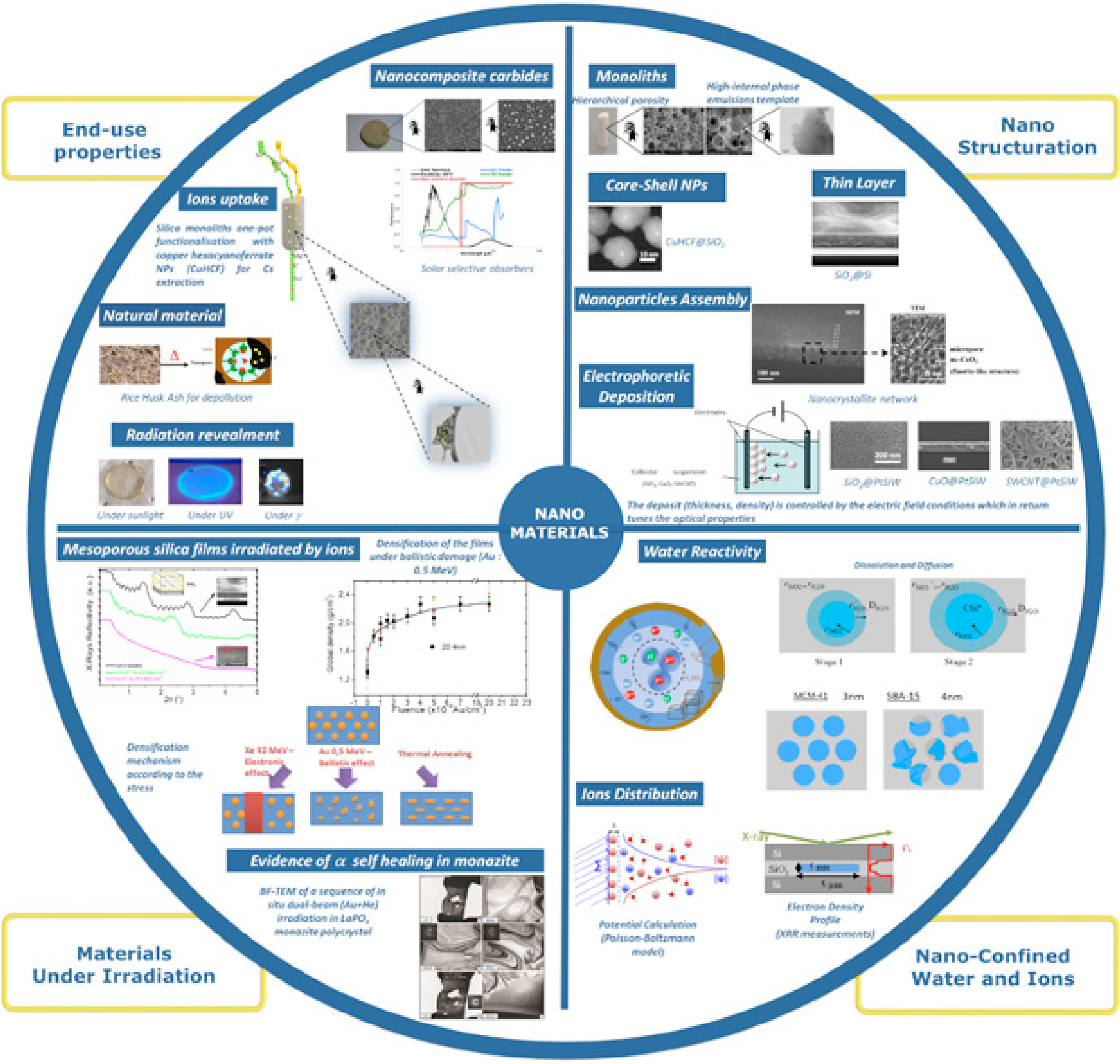
- **Le développement de différentes voies d'élaboration de matériaux nanostructurés : du précurseur (colloïde, solution, émulsion…) au matériau (poudre, couche mince ou massif)**
- **Nanostructuration et optimisation d'une propriété d'usage (Décontamination/dépollution d'effluents, sélectivité optique, révélation de radioactivité alpha/béta….)**
- **Comportement des nanomatériaux sous irradiation**
- **Chimie des ions en milieu confiné**

This team (LNER) 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 LNER 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 part, 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 LNER. 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 allows 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 LNER research topics for the period 2017-2020 are summarised in the following pages and can be divided in 4 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
- Ion chemistry in confined media.



End-use properties

Nano Structuration

Materials Under Irradiation

Nano-Confined Water and Ions

NANO MATERIALS

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

Radiation revealment

Under sunlight

Under UV

Under γ

Monoliths

Hierarchical porosity

High-internal phase emulsions template

Core-Shell NPs

CuHCF@SiO$_2$

Thin Layer

SiO$_2$@Si

Nanoparticles Assembly

Nanocrystallite network

Electrophoretic Deposition

SiO$_2$@PtSiW

CuO@PtSiW

SWCNT@PtSiW

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

Mesoporous silica films irradiated by ions

Densification of the films under ballistic damage (Au : 0.5 MeV)

Densification mechanism according to the stress

Xe 92 MeV – Electronic effect

Au 0,5 MeV – Ballistic effect

Thermal Annealing

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

Water Reactivity

Dissolution and Diffusion

Ions Distribution

Potential Calculation (Poisson-Boltzmann model)

Electron Density Profile (XRR measurements)

6/ EVOLVING INTERFACES IN MATERIALS

L'équipe est constituée au 1^er^ novembre 2020 de :

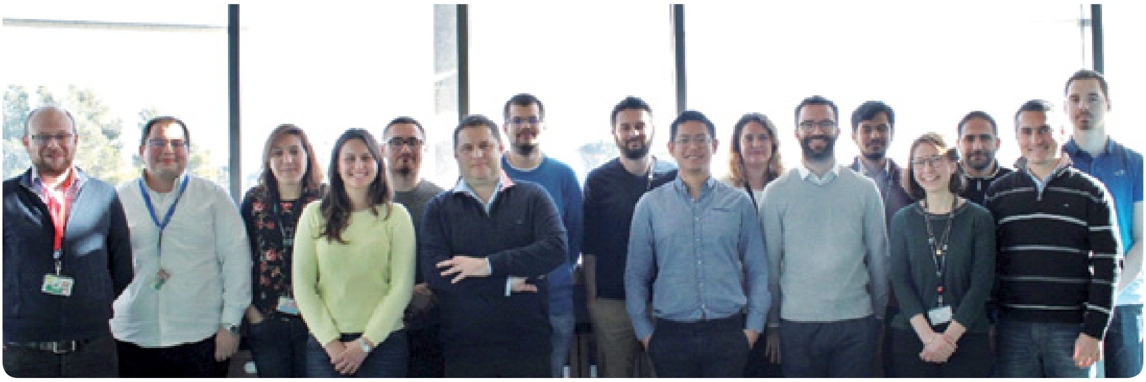
1 Professeur des Universités, responsable d'équipe (Pr. Nicolas Dacheux)
2 Chargés de Recherche CNRS (Dr. N. Clavier ; Dr. Adel Mesbah)
1 Chercheur CEA (Dr. Stéphanie Szenknect)
1 Maître de conférences (Dr. Laurent Claparède)

Post-Doctorants (2017-20) :

Dr. Alvaro Saravia (Valorco2, 2017-2018) : *Etude de la séquestration du* CO_2 *par carbonatation de l'olivine.*
Dr. Delhia Alby (CNRS ICSM/Amphos/Standford/SKB, 2018-2019) : *Coffinitization of* UO_2 *pellets in conditions representative of geologic disposal of spent nuclear fuel.*
Dr. Mohammed Ruwaid Rafiuddin (ANR Xmas, 2018-2020) : *La xénotime pour le conditionnement et stockage des actinides.*
Dr. Ilyes Ben Kacem (Labex Chemisyst, 2018-2019) : *Suivi de l'évolution d'interfaces solide-liquide en cours de dissolution par analyse 3D à l'échelle microscopique par MEB.*

Doctorants affectés à l'ICSM (2017-20) :

Théo Cordara (thèse CEA, coll. DMRC/AREVA, 2014-2017) : *Effet de la présence de produits de fission sur les mécanismes de dissolution de composés modèles à base de dioxyde d'uranium.*
Thomas Dalger (thèse CEA, coll. DMRC, 2016-2019) : *Rôle de l'acide nitreux sur la dissolution des oxydes à base d'uranium (IV) : Mécanisme et suivi operando de l'interface solide/solution.*
Victor Trillaud (thèse CEA, coll. L2ME, 2016-2019)) : *Des systèmes simplifiés aux combustibles modèles : étude in situ du frittage d'oxydes d'actinides et de lanthanides.*
Danwen Qin (thèse CSC, 2016-2020) : *Incorporation of tetravalent actinides in monazite-type ceramics : synthesis, sintering and long-term behavior.*
Jérémie Manaud (thèse ENSCM, coll. LHYS, 2017-2020) : *Conversion hydrothermale d'oxalates d'actinides tétravalents : de la synthèse au frittage des poudres d'oxydes.*
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) : *Etude des mécanismes d'altération des combustibles* MO_X *dans des eaux d'environnement.*
Thomas Barral, (thèse CEA, 2020-2023) : *Etude multiparamétrique de la dissolution d'oxydes mixtes* $(U,Ln)O_2$ *en milieu nitrique : impact de la composition et de la microstructure.*
Sofian Benarib, (thèse CEA, 2020-2023) : *Préparation et frittage direct d'oxydes hydratés d'actinides et de lanthanides.*
Alison Roche (thèse UM, 2020-2023) : *Incorporation d'actinides tétravalents au sein de céramiques de structure monazitique : synthèse, frittage et comportement à long-terme.*



Doctorants non affectés à l'ICSM (2017-20) :

Jean-Charles Alexandre (thèse CEA, coll. CEA-DAM, 2015-2018) : *Etablissement des diagrammes de spéciation du Pu(V) à plusieurs températures pour prédire son comportement dans les eaux de surface.*
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.*
Solène Bertolotto (thèse CEA, coll. DMRC, 2017-2020) : *Etude de la réactivité d'échantillons monocristallins de* UO_2 *vis-à-vis des processus de dissolution en milieu acide nitrique.*
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* $(U,Pu)O_{2-x}$.
Yanis Cherkaski (thèse CEA, coll. DTN, 2015-2018) : *Influence de la microstructure de la thorine yttriée sur sa tenue au sodium, en vue de réaliser des sondes à oxygène dans les réacteurs au sodium de* $IV^{ème}$ *Génération.*
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.*
Lénaïc Desfougères (thèse CEA, coll. DMRC, Mines St-Etienne, 2016-2020) : *Compréhension et modélisation de la conversion thermique d'oxalates d'actinides*
Paul Estévenon (thèse CEA, coll. DMRC, 2016-2019) : *Synthèse et caractérisation de silicates* $MSiO_4$ *(M = Ce, Th, U, Np et Pu).*
Célia Gillet (thèse CEA, coll. DE2D, 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.*
Anne-Laure Ronzani (thèse CEA, coll. CEA-DAM, 2015-2018) : *Etude de bio-indicateurs pour la détection d'activités nucléaires.*

CDD (2017-20) :

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.*
Dr Paul-Henri Imbert (IR CNRS, projet EJP EURAD, 2020-2021) : *Lixiviation d'échantillons frittés de* UO_2 *contenant des produits de fission en conditions d'entreposage direct.*
Morgan Zunino (IE CNRS, projet H2020 GENIORS, 2018-2020) : *Synthèse et frittage d'oxydes mixtes à base d'uranium et d'éléments lanthanides et étude de leur dissolution en conditions de retraitement.*

Le laboratoire d'étude des Interfaces de Matériaux en Evolution (LIME) a pour objectif de décrire et de comprendre les phénomènes siégeant aux interfaces solide/solide et solide/liquide de matériaux d'intérêt pour le nucléaire du futur, aussi bien au cours d'étapes de frittage (densification), que de dissolution ou d'altération (lixiviation) sous contraintes (*Figure 1*).

Les expérimentations relatives aux interfaces solide/solide s'inscrivent dans l'étude du frittage à travers les divers 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 qui étaient accessibles auparavant uniquement par modélisation, mais également d'aboutir à l'obtention de cartes de frittage (taille de grains vs. taux de densification) dans un délai très court. Il en résulte une optimisation des conditions expérimentales en fonction de la microstructure désirée. 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 aux matériaux pour l'amont comme pour l'aval du cycle électronucléaire et doit permettre à terme leur optimisation.

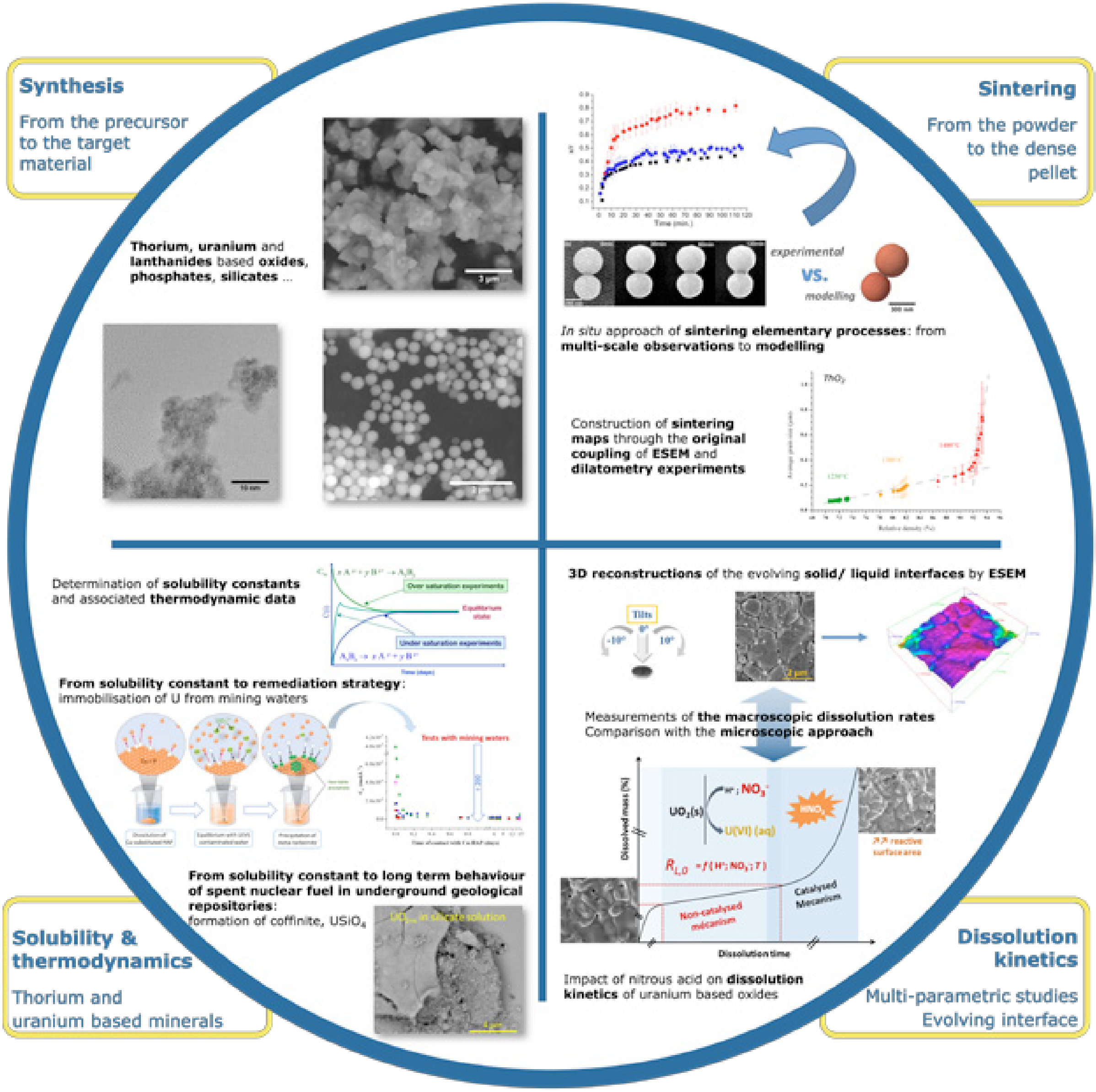


Fig. 1 Représentation de l'approche développée pour étudier les interfaces de matériaux en évolution

Dans ce but, la première étape de l'étude consiste à développer ou à optimiser les conditions de synthèse de combustibles modèles de type oxyde ($U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_2$, $U_{1-x}Ln_xO_{2-x/2}$, $Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Ln_xO_{2-x/2}$, …) en privilégiant l'usage de précurseurs dont la réactivité dans le processus de frittage est améliorée par rapport aux oxydes préparés à haute température. Dans ce cadre, l'utilisation de méthodes de synthèse par voie humide, généralement favorables à l'amélioration de la distribution cationique au sein du solide, a également permis d'étendre le domaine d'existence de telles solutions solides. En parallèle de la préparation de complexes moléculaires d'actinides, un effort particulier a porté sur la précipitation directe d'oxydes hydratés de morphologie contrôlée en conditions hydrothermales (Thèses de Victor Trillaud, 2016-2019, de Jérémie

Manaud, 2017-2020, et de Sofian Benarib, 2020-2023, et CDD de Laura Di Mascio 2020-2021, projet H2020 Geniors). Ces travaux ont notamment permis de préparer des oxydes d'actinides sous la forme de microsphères de taille contrôlée présentant une architecture multi-échelle, ou sous la forme de cristallites nanométriques présentant une forte surface spécifique. Cette maîtrise de la morphologie des poudres d'oxydes nous a récemment conduit à envisager la préparation d'échantillons de composition, d'isotopie et de taille contrôlées pouvant être utilisés comme référence dans le cadre du contrôle des garanties nucléaires internationales opéré par l'AIEA (Thèse de Pierre Asplanato, 2019-2022). En outre, lorsque des précurseurs moléculaires ont été obtenus, leur conversion en oxyde a été examinée par la suite à travers le couplage de plusieurs techniques (analyses thermogravimétriques, diffractions, microscopiques, spectroscopiques). Par ce biais, les intermédiaires réactionnels successivement formés lors de la conversion ainsi que les transformations chimiques et morphologiques de l'échantillon ont été identifiés.

Sur la base de ces résultats, le frittage des oxydes mixtes $U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_2$, $Ce_{1-x}Nd_xO_{2-x/2}$ 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, …). L'histoire d'un solide, soit le lien entre le précurseur utilisé, sa conversion en oxyde, et la microstructure finale du compact densifié a ainsi pu être établie (thèses de Jérémie Manaud, 2017-2020 et de Malvina Massonnet, 2018-2021), par exemple au moyen de cartes de frittage permettant *in fine* de contrôler la microstructure des matériaux céramiques considérés (thèse de Yanis Cherkaski, ICSM-DTN, 2015-2018).

Par ailleurs, des expériences mettant en œuvre l'observation *in situ* des phénomènes de densification ont été menées par microscopie électronique à balayage environnementale à haute température (HT-MEBE). Des données inédites relatives à la cinétique de croissance granulaire ou à la mobilité des joints de grains lors du stade final de la densification ont ainsi été acquises. En outre, les travaux menés dans le cadre de la thèse de Victor Trillaud (ICSM, 2016-2019) sur des composés modèles de morphologie sphérique contrôlée ont conduit à l'acquisition de données expérimentales cinétiques et thermodynamiques originales relatives à la première étape du frittage (élaboration des ponts) des oxydes d'uranium.

L'étude des interfaces solide/liquide s'inscrit principalement dans un contexte de retraitement du combustible nucléaire usé ou de stockage de matrices de conditionnement spécifiques des actinides (thèse de David Qin, China Scholarship Council, 2016-2020 ; post-doctorat de Mohammed Ruwaid Rafiuddin ANR X-MAS, 2018-2020). Plus récemment, ce cadre s'est également étendu au stockage direct de combustibles usés en formation géologique profonde (post-doctorat de Delhia Alby, projet SKB/Amphos21/Univ. Stanford/ICSM, 2018-2019 ; thèse de Théo Montaigne, ICSM/DE2D, 2019-2022) ou à un entreposage de longue durée (CDD de Paul-Henri Imbert, EJP EURAD, 2020-2021).

Concernant les études menées en conditions de retraitement, des tests multiparamétriques de dissolution ont été mis en place. Pour les solutions solides $U_{1-x}Th_xO_2$, la modification du mécanisme de dissolution prépondérant (rédox *vs.* réactions de surface) en fonction de la teneur en uranium (IV) et de l'acidité du milieu de dissolution a été mise en évidence à la fois à l'échelle macroscopique par la variation des paramètres décrivant la cinétique (ordres partiels par rapport à l'activité en proton, énergie d'activation apparente) et à l'échelle microscopique par l'évolution de l'interface solide/solution suivie par MEBE *operando*. Ainsi, des liens étroits ont été démontrés entre la microstructure du matériau et sa résistance à l'altération ou à la corrosion aqueuse. En outre, le rôle potentiellement catalytique d'espèces produites lors de la dissolution de ces solutions-solides en milieu acide nitrique (dont HNO_2) a été étudié (thèse de Thomas Dalger, ICSM/DMRC, 2016-2019). Parallèlement, le passage d'un régime de dissolution non-catalysé à un régime catalysé a été observé pour des échantillons monocristallins de UO_2 (Thèse de Solène Bertolotto, DMRC – ICSM, 2017-2020) permettant de s'affranchir de toute contribution microstructurale. Des observations menées à l'échelle micro et nanoscopiques ont permis de démontrer le rôle prépondérant des défauts structuraux dans l'initiation de la dissolution en milieu acide nitrique et la production d'espèces catalytiques azotées. Enfin, l'existence de faciès de dissolution spécifiques à l'orientation de la face cristallographique exposée à la solution a été mise en évidence.

D'autre part, les études antérieures réalisées au LIME avaient montré que la présence d'éléments lanthanide trivalents au sein de la structure fluorine ($Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$) affectait significativement la durabilité chimique des solides en raison de la fragilisation du réseau cristallin consécutive à la formation des lacunes en oxygène. Le comportement des solutions solides $U_{1-x}Ce_xO_{2-x/2}$ et $U_{1-x}Ln_xO_{2-x/2}$ semble différer des oxydes à base de Th ou de Ce étudiés auparavant, probablement en raison de modifications de la spéciation de l'uranium induite par l'incorporation d'éléments trivalents (thèses de Malvina Massonnet, ICSM – DMRC, 2018-2021 et de Thomas Barral, 2020-2023, projet H2020 Geniors, 2017-2021). De manière analogue, la présence d'éléments platinoïdes au sein de UO_2 a été étudiée dans le cadre des thèses de Théo Cordara (ICSM – DMRC/AREVA, 2014-2017) puis de Thibault Kaczmarek (ICSM – DMRC, 2018-2021). Ces études ont souligné l'existence de phénomènes catalytiques significatifs, liés à la présence de ces éléments au sein du solide.

Un dernier aspect des travaux menés au sein du LIME concerne la caractérisation de phases uranifères ou thorifères d'intérêt aussi bien pour l'amont que pour l'aval du cycle du combustible. Dans ce cadre, la préparation de plusieurs phases uranifères est actuellement réalisée en partenariat avec ORANO et le CEA de Saclay en vue de constituer une banque de données associée à la réponse de ces phases par SLRT (CDD Eddie Anzalone, 2020-2021). Parallèlement, les phases silicatées à base de thorium et d'uranium (IV) font l'objet d'une collaboration internationale (Prof. A. Navrotsky, UC-Davis, Prof. R.C. Ewing, Université de Stanford et X. Guo, Washington State University). Les études ont d'abord porté sur le système thorium – uranium – silicate puis sur la coffinite $USiO_4$, la stetindite $CeSiO_4$ et plusieurs silicates d'actinides (Th, Np, Pu) préparés en conditions hydrothermales (thèse de Paul Estévenon (DRCP/ICSM, 2015-2018). Les données thermodynamiques relatives à la solubilité de ces phases (K_S°, $\Delta_R H^\circ$, $\Delta_R G^\circ$, $\Delta_R S^\circ$) ont également été acquises aussi bien lors des tests de dissolution que par microcalorimétrie. Plusieurs phases phosphatées ont également été étudiées, dont le rhabdophane, la monazite et le xenotime (en tant que matrices de confinement spécifique de certains radionucléides). Initialement réalisé sur les phases purement lanthanidiques, ce travail a logiquement évolué vers l'incorporation d'éléments actinide tétravalents par substitution couplée $2\ Ln^{III} \Leftrightarrow An^{IV} + M^{II}$ (solutions solides monazite/cheralite) ou $Ln^{III} + PO_4 \Leftrightarrow An^{IV} + SiO_4$ (solutions solides monazite/huttonite). Ainsi, des solutions solides incorporant du thorium ont été préparées, pour la première fois par voie humide, dans le cadre de la thèse de David Qin (China Scholarship Council, 2016-2020) puis ont été caractérisées afin d'aboutir à la détermination des données thermodynamiques associées (K_S°, $\Delta_R H^\circ$, $\Delta_R G^\circ$, $\Delta_R S^\circ$). Ce travail est actuellement poursuivi sur des phases incorporant de l'uranium dans le cadre de la thèse d'Alison Roche (2020-2023). Une étude similaire a été menée en parallèle sur le système xénotime/thorite dans le cadre de l'ANR X-MAS (Post-Doctorat de Mohammed Ruwaid Rafiuddin, 2018-2020).

The 'Evolving Interfaces in Materials' group (LIME) aims to describe and understand the various phenomena occurring at the solid/solid and solid/liquid interfaces in the field of the (current and future) nuclear fuel cycles. They are mainly related to the sintering (densification) of ceramic materials as well as to their alteration (leaching or dissolution) under various chemical and/or physical stresses.

The experiments dedicated to the solid/solid interfaces are mainly devoted to the preparation of inorganic powder samples with tailored properties (morphology, size, composition, …) and the study of their sintering. In this framework, coupling of *in situ* and *ex situ* techniques allowed us not only to analyze the different steps of the densification but also to yield original data usually only accessible through modeling. Sintering maps (which represent the variation of the grain size vs. the densification rate) were also obtained, which resulted in an improved monitoring of the final microstructure of ceramics. In the case of the solid/liquid interface, the final goal is also to optimize several properties of some materials in use (or to be used) both in the front- or back-end of the nuclear fuel cycle. Particularly, the approach developed consists in the understanding of the links existing between the chemical composition and/or the morphology of a solid, and its ability to dissolve.

In this aim, the first step of our studies generally dealt with the preparation of mixed oxides as models for nuclear fuels ($Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_{2-y}$, $Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$, …). Wet chemistry routes based on the initial precipitation of crystallized precursors were generally considered for the synthesis in order to improve the reactivity and the sintering capability of the prepared powders, and to homogenize the cationic distribution. The thermal conversion leading to the final oxide form was then examined using various techniques (diffraction, spectroscopy, microscopy, …), which allowed us to identify the reaction intermediates as well as to point out the chemical and morphological transformations of the samples. In parallel to the synthesis of actinides-bearing molecular complexes, a particular attention was paid to the direct precipitation of hydrated oxides with a controlled morphology, especially using hydrothermal conditions. These studies particularly led to the preparation of actinides oxides microspheres with a hierarchical architecture, and of various compositions of $(An^{IV},Ln)O_2$ nanocrystals (An = Th, U). Mastering the morphology of the oxide samples led us to undertake the preparation of reference materials with controlled composition, size and isotopy, that could be used in the frame of the nuclear safeguards control operated by IAEA.

Using this large set of samples, the sintering of $Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_{2-y}$, $C_{e1-x}Nd_xO_{2-x/2}$ and $Th_{1-x}Y_xO_{2-x/2}$ was studied in order to point out the powder-related parameters (specific surface area, homogeneity, amount of residual carbon, …) that can impact significantly the densification process. The thermal history of a solid, which includes the precursor chosen for the preparation, its conversion and the final microstructure of the sintered pellet, was then described. The establishment of sintering maps, which can be used to control *in fine* the microstructure of ceramics, was undertaken for several materials of interest such as $Th_{1-x}Y_xO_{2-x/2}$ solid solutions. Also, *in situ* HT-ESEM observations led to the first experimental data concerning the kinetics and thermodynamics of the first step of UO_2 sintering (elaboration of necks between the grains).

The study of the solid/liquid interface mainly took place in the frame of spent fuel reprocessing and long-term storage of actinides waste forms. More recently, this scope was also extended to the direct storage of spent fuel in an underground repository.

Studies regarding the reprocessing of spent fuel were mainly based on multi-parametric dissolution tests. For $Th_{1-x}U_xO_2$ solid solutions, the modification of the driving dissolution mechanism (i.e. oxidation vs. surface reactions) as a function of the uranium content and the media acidity was evidenced both at the macroscopic and the microscopic scales, using *operando* ESEM observations. As such, links were established between the microstructure of the materials and their chemical durability. Moreover, the catalytic role of chemical species produced during the dissolution of these samples in nitric media (including HNO_2) was studied. In parallel, the transition from a catalyzed to non-catalyzed dissolution regime was observed for UO_2 single crystals, which allowed to avoid any bias coming from the microstructure. Micro- and nanoscale observations led to demonstrate the prevailing influence of point defects in the onset of dissolution, and to point out characteristic dissolution habits depending on the crystallographic orientation of the interface.

Previous works showed that the presence of lanthanide elements within the fluorite-type structure ($Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$) also deeply affected the chemical durability of the solids, mainly through the weakening of the crystal network due to the formation of oxygen vacancies. In comparison, the behavior of $U_{1-x}Ce_xO_{2-x/2}$ and $U_{1-x}Ln_xO_{2-x/2}$ solid solutions clearly differs, probably due to the modification of the uranium redox speciation provoked by the insertion of trivalent elements. In a similar way, the presence of PGM elements within UO_2 was investigated. Such experiments revealed the huge role of catalytic phenomena linked to the presence of PGM elements in the solid and in solution.

A last research topic deals with the characterization of U- and Th-bearing phases of interest for the front- and back-end of the nuclear fuel cycle. In this frame, a collaboration with ORANO and CEA Saclay aims to set up a spectroscopic database specifically linked with TRLS spectra of uranous compounds. In parallel, experiments dedicated to thorium and uranium (IV) silicates are undertaken in the framework of an international collaboration (Prof. A. Navrotsky, UC-Davis, Prof. R.C. Ewing, Stanford University and X. Guo, Washington State University). These studies initially concerned the $Th-U-SiO_4$ system, then were extended to stetindite ($CeSiO_4$) and several actinides silicates (Th, Np, Pu) prepared under hydrothermal conditions. Thermodynamic data of these silicate phases ($K_S°$, $\Delta_RH°$, $\Delta_RG°$, $\Delta_RS°$) were collected, both from dissolution tests and calorimetry measurements. Determination of thermodynamic data was also undertaken for several phosphate-based compounds envisaged as host phases for actinides storage (including rhabdophane, monazite and xenotime).

The natural follow-up to this work then consists in the incorporation of tetravalent actinides through different coupled substitution, i.e. $2\ Ln^{III} \Leftrightarrow An^{IV} + M^{II}$ (monazite/cheralite solid solutions) or $LnIII + PO_4 \Leftrightarrow An^{IV} + SiO_4$ (monazite/huttonite solid solutions). Preparation of these samples was then achieved for the first time with An = Th using a wet-chemistry route, while the synthesis of U-based samples is now under progress. A similar study has also been developed on the xenotime/thorite system within the ANR X-MAS project (2018-2020).

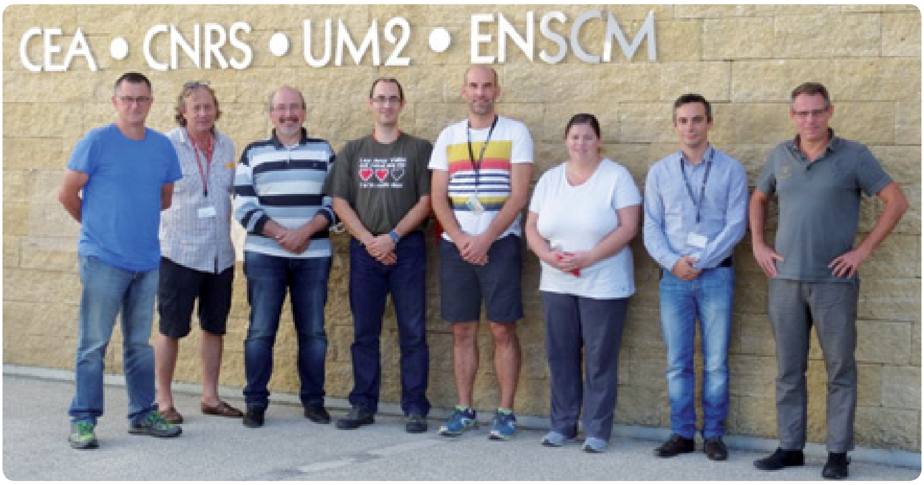
7/ ETUDES DE LA MATIÈRE EN MODE ENVIRONNEMENTAL

L'équipe est constituée au 1^er^ novembre 2020 de :
1 Ingénieur de recherche CNRS responsable d'équipe (Dr. Renaud Podor)
3 Ingénieurs d'études CNRS (Sandra Maynadié, Joseph Lautru, Dr Xavier Le Goff)
2 Ingénieurs CEA (Henri-Pierre Brau, Michael Odorico)
1 Technicien CEA (Bruno Corso)

Post-doctorants (2017-20) :
Ilyes Ben Kacem (these UM – Labex, 2018-19): *Characterization of evolving solid/liquid interfaces during dissolution by 3D analysis at the microscopic scale by SEM.*

Thésards (2017-20) :
Victor Trillaud (thèse CEA, 2016-19) : *Premier stade du frittage du dioxyde d'uranium : une étude in situ par MEBE et MET à haute température.*
Florimond Delobel (thèse financement Institut Saint-Louis, 2015-18) : *Élaboration de carbure de silicium par Spark Plasma Sintering pour des applications en protection balistique.*
Jérome Mendonca (thèse CIFRE NewTEC Scientific à Nimes, 2019-22) : *Développement de micro-fours haute température pour les Microscopes Electroniques à Balayage.*

CDD (2017-20) :
Johan Salacroup (Salarié SATT AxLR, 2016-18) *Développement d'une cellule d'observation in situ de matériaux en cours de dissolution par microscopie électronique à balayage environnementale.*
Pierrick Chevreux (CNRS, 2017-18) *Ingénieur de recherches CNRS Caractérisation des Matériaux.*
Gauthier Gonnet (2016-17) CDD ITA
Helene Arena (2019 6 mois)



Le Laboratoire d'Etudes de la Matière en Mode Environnemental (L2ME) résulte de la fusion, préconisée par l'AERES, des deux laboratoires de Diffraction-Diffusion (LDD) et de Microscopies en Mode Environnemental (LM2E), effective depuis le 1er janvier 2014. Cette fusion des compétences et savoir-faire correspond à une volonté affichée de coupler les informations microscopiques et macroscopiques obtenues par l'ensemble des techniques expérimentales disponibles au sein du L2ME. Il s'agit 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 supramoléculaires 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, permet un 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 (AFM). 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 le démouillage de couches minces de métaux sur différents types de substrats et pour différentes applications (Piles à combustible ; coll. Imperial College London / Surfaces texturées ; Saint Gobain Recherche – UMR 125), l'oxydation d'alliages haute température (applications aéronautiques ; coll. IJL – UMR 7198), 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. Les projets Celdi (soutenu par la SATT AxLR) et FurnaSEM (projet Readynov soutenu par la Région Occitanie) sont actuellement menés pour développer respectivement 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. En parallèle, un projet de reconstruction d'un microscope électronique à transmission (MET) est mené en interne à l'ICSM. Ces actions fortement appliquées sont (ou seront) valorisées dans les années à venir aux travers de collaborations avec des acteurs économiques locaux (société NewTEC, etc) voire au travers de la création d'une startup.

The research group «Study of the Matter in Environmental Conditions » results from the fusion between the LDD (Diffusion and Diffraction group) and the LM2E (Microscopy under Environmental Conditions) group which took place in January 2014. This fusion was driven by the idea to combine the information obtained at the microscopic and at the macroscopic scale using the know-how and competences available in both laboratories. 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.

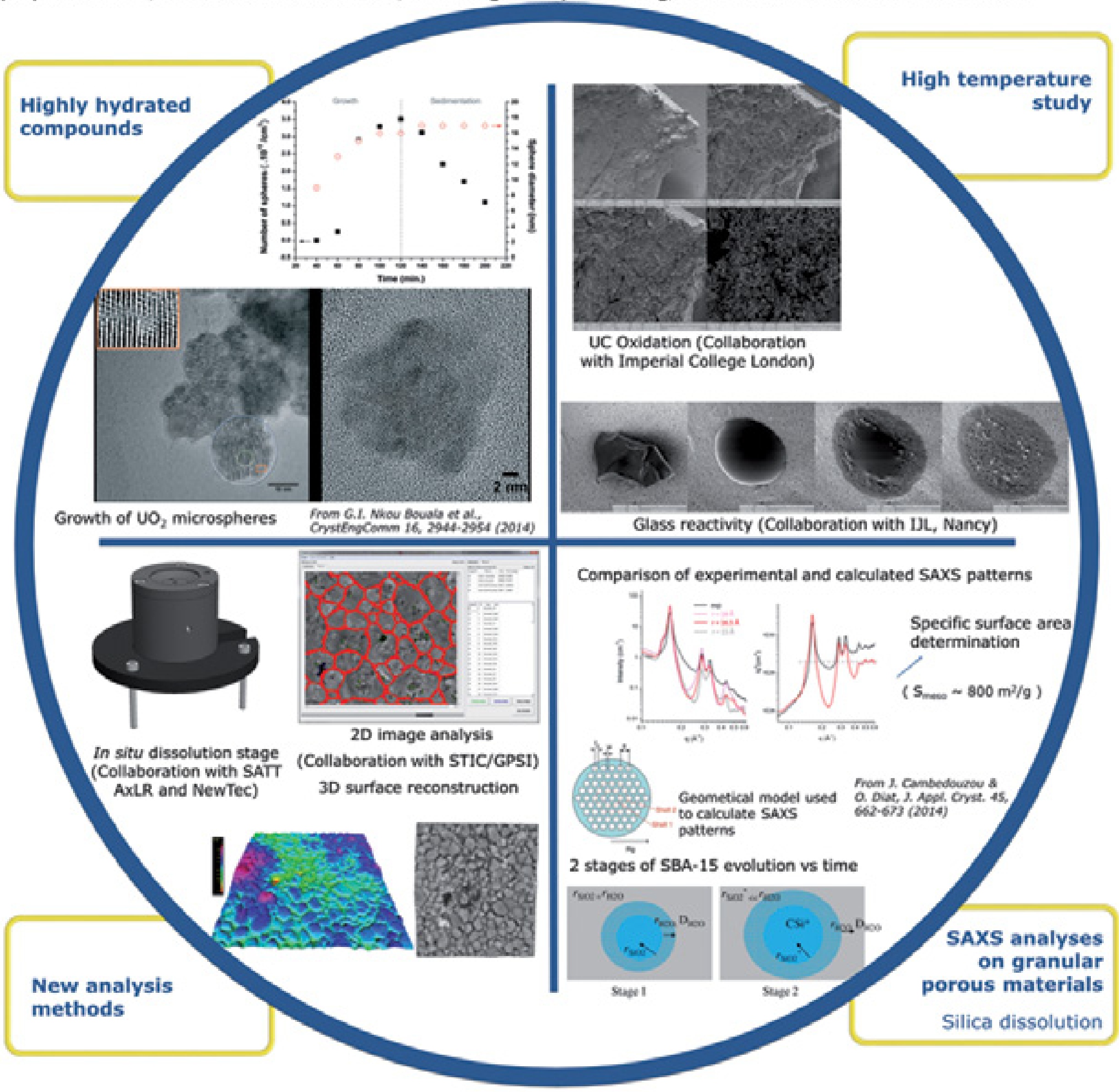
This approach is completed with the instrumental development of specific tools, based on the know-how of the lab team with the aim to answer specific research objectives. These developments can cover small tools (sample holders, etc), stages with dedicated applications or the complete refurbishing of 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[1]. 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. Several other properties such as the dewetting of thin metal films (with application as functional materials or anodes for SOFC – Respective collaboration with Saint Gobain Recherche – UMR 125[2] and Imperial College London), the oxidation of alloys (aeronautic applications – Coll. with IJL – UMR 7198), the oxidation of UC or the aging of materials for SOFC cathodes[3] (Coll. with Imperial College London) have been successfully studied in the framework of national and international academic collaborations.

A second set of result deals with the development of specific tools for the characterization of materials. 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. In parallel, a project aiming to the refurbishing of a TEM and fully funded by ICSM has been successfully conducted. These actions will be further exploited through collaborative development with local industrial partnership (NewTEC company, etc) or through the creation of a company.

Instrumentation / capabilities: **TEM Jeol 200CX, Environmental scanning electron microscope FEI Quantax 200 ESEM-FEG, Scanning electron microscope TESCAN Vega3, Bruker 400 MHz NMR spectrometer, SEM/TEM Specimen preparation Lab, AFM Bruker Multimode 8, Small angle X-ray Scattering, Brucker D8 ADVANCE diffractometer.**



8/ MESOSCOPIC MODELLING AND THEORETICAL CHEMISTRY

L'équipe est constituée au 1er novembre 2020 de :

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)

Post-doctorants (2017-20) :

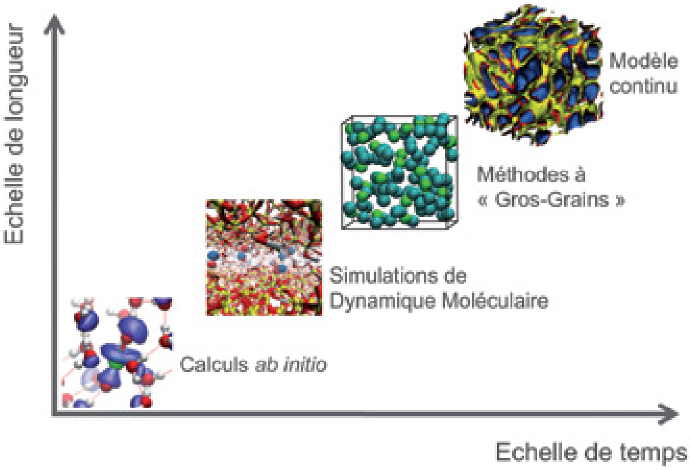
Yann Foucaud (CEA/DES,dec2019-) : *modélisation moléculaire de la SHG.*
Simon Gourdin (DRF, ERC REE-Cycle, 2016-17) : *Extraction des terres rares par des modèles de microémulsions.*
Thanh Tung Pham (CEA/DES, coll. L2IA, 2015-17) : *Modélisation expériences de SHG (génération de seconde harmonique).*

Doctorants (2017-20) :

Thomas Colle (thèse UM, ANR MULTISEPAR, 2020-) : *Modèle de microémulsion: Vers la prédiction des procédés d'extraction liquide-liquide.*
Tristan Kunyu Wang (thèse UM, 2019-) : *Simulation numérique pour les ions aux interfaces : correlations ionique et dépollution des eaux.*
Marin Vatin (thèse CEA, coll. ISEC, 2018-21) : *Approche moléculaire pour prédire le transfert entre phases pour l'extraction.*
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.*
Amaury Coste (thèse UM, ANR DYNAMISTE, 2016-19) : *Etude des solutions concentrées d'alumino-silicates.*
Mario Špadina (thèse CEA et ERC REE-Cycle, coll. Univ. Ljubljana, 2016-19) : *Modélisation par DFT classique de l'agrégation en phase organique pour la séparation.*
Anne-Françoise de Guerny (thèse Labex CalSimLab à LJLL/UMPC, coll. ICSM, 2016-20) : *Calcul mathématique des interactions faibles.*
Michael Bley (thèse CEA, coll. ISEC, 2015-18) : *Modélisation moléculaire de l'activité en solution pour l'extraction liquide-liquide.*
Sarah Hocine (thèse UM MESR, 2014-17) : *Simulation moléculaire d'oxydes pour la séparation.*
Ludovic Jami (thèse Université de Tours en collaboration avec ICSM, 2019-22) : *Transport de molécules actives pour la communication entre insectes.*

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 nanoéchelles).

Les moyens mis en œuvre par l'équipe sont représentés sur les figures qui suivent. La description 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.



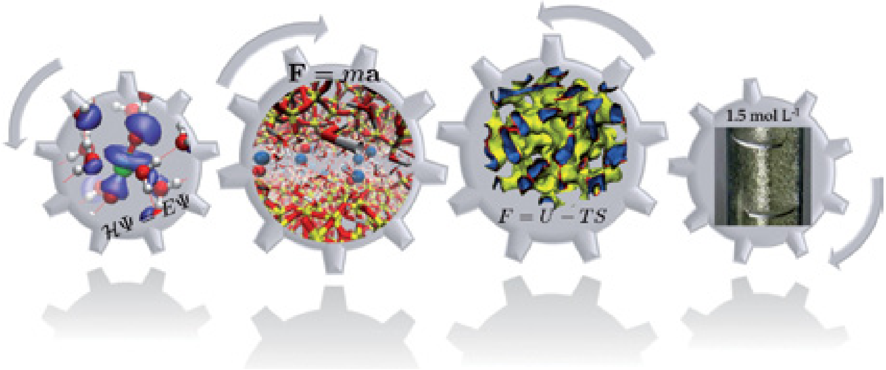
Un tel programme est réalisé dans différents contextes de la chimie séparative et permet de résoudre plusieurs problèmes ouverts :

- Modélisation de l'extraction liquide-liquide. Une approche à gros grains permet de déterminer 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.
- Etude 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 collaboration 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 (présentées dans ce livret dans les pages du laboratoire expérimental correspondant), et aussi une activité méthodologique propre dont la suite présente une sélection.



The main goal of the modeling team consists in studying complex systems, and especially the ones involved in separation chemistry, from a multi-scale approach with a special interest for the models at the intermediate scale (mesoscopic models or nanoscale).

The methodology is presented in the figure. The most fundamental description is the one of quantum mechanics (*ab initio* calculations). It is able to represent elementary events. It is particularly performed in order to study complexation and it can also improve classical models. The latter can be studied from molecular dynamics in order to characterize the material structure, the equilibrium and transport properties, but only at relatively short scales (typically a few nanometers and a few nanosecond – not more). Thus the description of complex systems is possible only thanks to intermediate scale methods (coarse-graining, continuous solvent models, Brownian dynamics, integral equations, classical density functional theories, mode-coupling, interface theory, etc.) implemented in order (I) to describe the physical-chemistry of the processes and (II) to link the result with chemical engineering. The originality of the team comes from the fact that the scale transition is almost systematically studied. The most microscopic scales allow the improvement of the macroscopic models, not only by providing the value of the physical parameters, but also by solely improving the macroscopic fundamental equations.

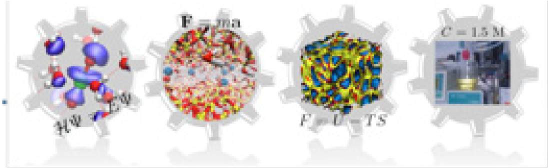
Such a program is applied in different domains and especially to separation chemistry issues:
- Modeling of liquid-liquid extraction. A coarse-graining method allows the calculation of the thermodynamic quantities in the various phases (aqueous and organic solvent phases). This method is developed for more and more complex systems.
- Porous Media, especially the one involved in separation (oxides, porous glasses; etc.). Here the goal consists in getting the maximum information from experiments and in characterizing the relevant underlying mechanisms. We also study clays for the storage of wastes.

At the more fundamental level, we especially study electrolyte theory for transport and equilibrium properties. Some applications with no direct connection with separation chemistry have been made. For example, in nanotechnologies, the role of ionic noise has been studied with connection to experiments involving one-electron transistors. Microemulsions models are also studied in order to model ternary phase diagrams.

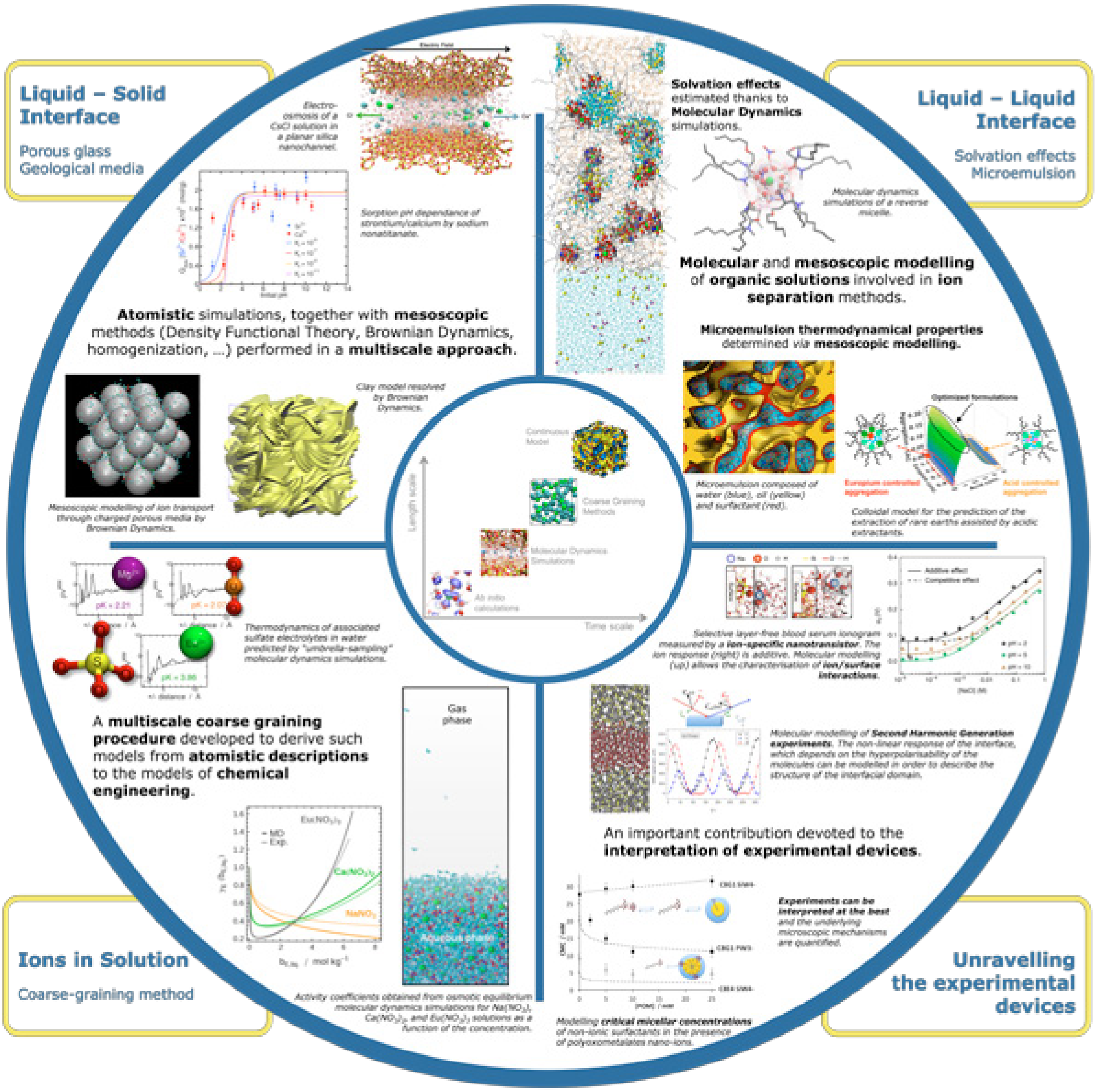
These works have been performed in collaboration with the experimentalists and, in particular, the one of ICSM. The methods at the intermediate scales can be validated from the comparison to the experiments and to molecular modeling results. The final idea would be to propose a global view of processes where every mechanism is integrated in the most adapted level of description, the link between the various models being explicated. Fundamentals of statistical thermodynamics help us to understand that such a project is at least *a priori* possible for the equilibrium processes, but it is much more difficult for dynamical properties, because of the need to uncouple the various time scale, which is not always possible.

Thus, the modeling group has activities in direct connection with ICSM experimentalists (presented in this book in the sections of the corresponding experimental laboratories), but also methodological activities, a part of them being presented in the following pages.

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.

Sorption pH dependance of strontium/calcium by sodium nonatitanate.

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

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

Clay model resolved 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).

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

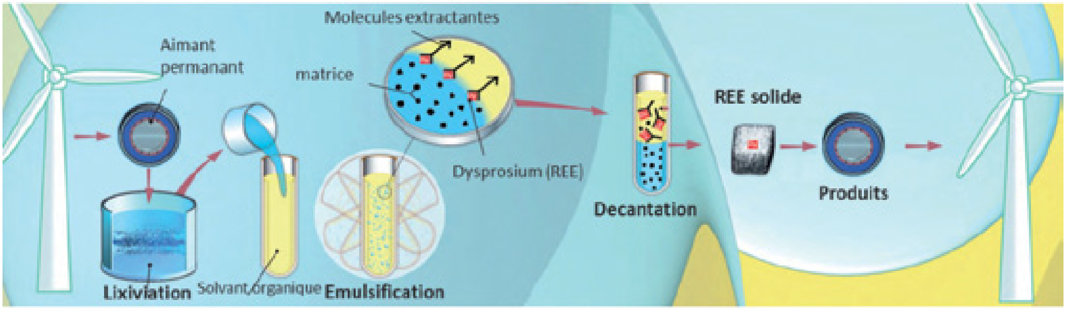
Via the knowledge of the supra-molecular, weak and long-range interactions, for a technological break-through in eco-friendly separation chemistry.

INNOVATION POUR L'EXTRACTION ET LE RECYCLAGE

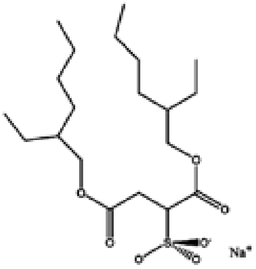
Via la connaissance des interactions supramoléculaires, faibles et à longue distance, pour une rupture technologique sur des procédés écoresponsables en chimie séparative.

EXPLOITING THE AGGREGATION TO OPTIMIZE SEPARATION FORMULATION OF A NEW SYNERGISTIC EXTRACTANT/ SURFACTANT MIXTURE FOR RARE EARTH EXTRACTION

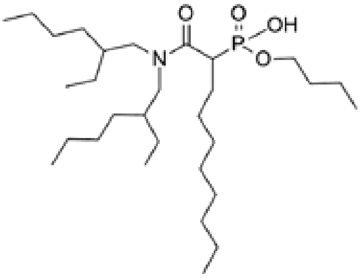
J. Rey, S. Atak, S. Dourdain, G. Arrachart, L. Berthon and S. Pellet-Rostaing



As part of a ERC project REEcycle, we proposed the formulation of a new synergistic extractant system for the extraction rare earth elements from aqueous phosphoric acid solution containing large quantities of impurites currently found in urban mines and secondary deposits. This new synergistic system is original in its concept as it contains in the association of the bifunctional extractant amido-phosphonate, known for its high efficiency for the recovery of uranium from phosphate rocks, with the AOT surfactant molecule known to form reverse micelles in aliphatic diluents.

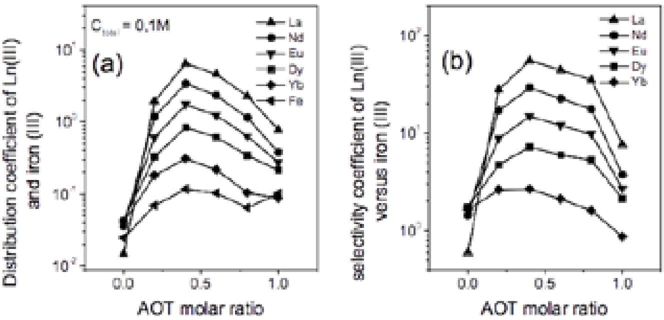


AOT *Bis(2-ethylhexyl) sulfosuccinate sodium*



DEHCNPB *butyl-N,N-di(2-ethylhexyl)carbomoyl-nonylphosphonate*

The mixture was found to extract synergistically rare earth elements with high distribution coefficients (D), and is high Separation Factor (S.F.) toward iron (III) from acid phosphoric solution.



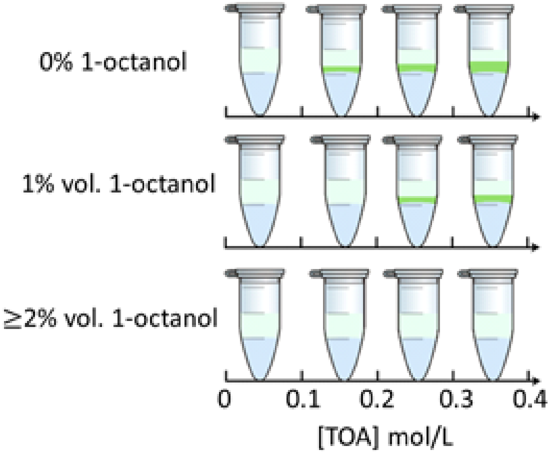
A complete thermodynamic study of its extraction properties was also presented showing this system has the ability to extract REEs from a wide range of phosphoric acid concentration which is often the case in industrial processes.

Rey J., Atak S., Dourdain S., Arrachart G., Berthon L., Pellet-Rostaing S. - **Synergistic Extraction of Rare Earth Elements from Phosphoric Acid Medium using a Mixture of Surfactant AOT and DEHCNPB** - *Solvent Extraction and Ion Exchange* (2017) 35, 321-331.
Rey J., Arrachart G., Dourdain S., Atak S., Pellet-Rostaing S. (2016). - **Procédé liquide-liquide d'extraction de terres rares par association d'un extractant bifonctionnel et d'un tensioactif** - FR. 16 58626.

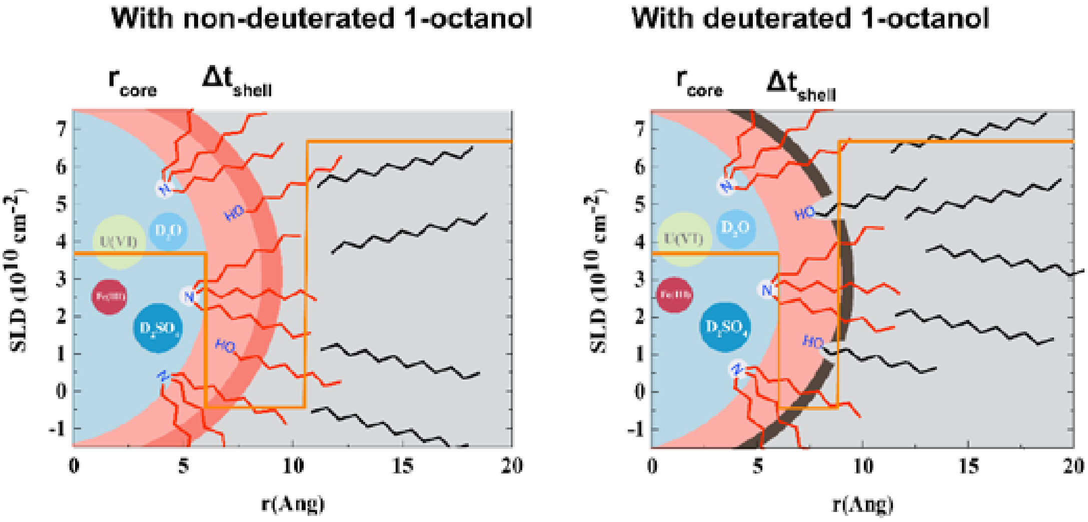
UNDERSTANDING THE EFFECT OF PHASE MODIFIER ON THIRD PHASE APPEARANCE

Zijin Lu, Sandrine Dourdain, and Stephane Pellet-Rostaing

Phase modifiers are often added to solvent extraction processes to avoid the third phase formation. While this important issue was attributed to sticky interactions between reverse aggregates, structural effect of phase modifiers remained ambiguous.



As they are similar to reverse hydrotropes, phase modifiers may act as co-surfactant or as co-solvent in the organic phase in solvent extraction system. We therefore coupled a small-angle scattering approach to surface tension measurements on the TOA-dodecane extraction system, to evaluate by which mechanisms the phase modifier 1-octanol repels the third phase and affects extraction properties. We first confirmed that adding 1-octanol has small influence on extraction efficiency.



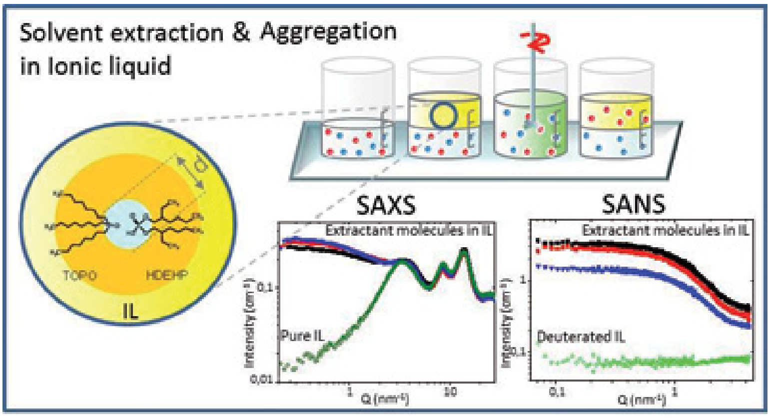
We further varied the scattering contrast of the solution with deuterated 1-octanol, and revealed that 1-octanol locates both in the solvent, acting as a co-solvent and diluting the aggregates, and in an outer-shell of the aggregates. Surface tension measurements demonstrated that instead of penetrating till the core of the aggregates as a co-surfactant, 1-octanol only penetrates their shell, and forms a shielding barrier preventing the aggregates to coalesce.

Lu Z. J., Dourdain S., Pellet-Rostaing S. - **Understanding the Effect of the Phase Modifier n-Octanol on Extraction, Aggregation, and Third-Phase Appearance in Solvent Extraction** - *Langmuir* (2020) 36, 12121-12129.

IONIC LIQUID AS DILUENT IN SOLVENT EXTRACTION: STRUCTURAL ORIGIN OF UNPREDICTABLE EXTRACTION EFFICIENCY

T. Sukhbaatar, C. Lopez, S. Dourdain, R. Turgis, J. Rey, G. Arrachart and S. Pellet-Rostaing

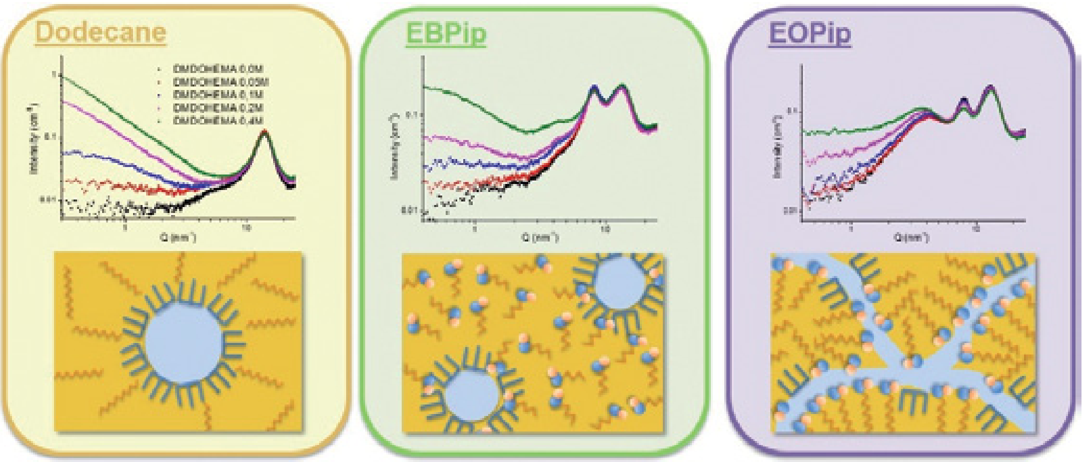
A recent challenge in solvent extraction is today to replace conventional organic solvents (often toxic and volatile), with ionic liquids (IL). Depending on the extraction systems tested, these new solvents can lead to better efficiency than the conventional ones. Although some assumptions based on ions exchanges have been proposed in the literature, the involved mechanisms are still poorly understood. So far, no study was conducted to evaluate the IL effect on the aggregation properties of the extractant molecules, even though ILs are known to modify the curvature radii of surfactant microemulsions.



Investigating the HDEHP/TOPO system in Omim[Ntf2] ionic liquid as diluent, very different extraction properties were observed as a synergistic peak shifted to 50% of TOPO ratio. Aggregates signals similar to the ones observed in conventional diluents were evidenced from SAXS measurements (See Figure). However the strong structural peaks of the IL prevent a proper fit analysis. Therefore the synthesis of fully deuterated IL was proposed, allowing the measurement of SANS spectra with no structural peak.

The IL's deuteration enables full characterization of the aggregates and showed that aggregates are larger in ILs than in the conventional diluent.

Applied on a different system (rare earth extraction with DMDOHEMA in ILs), we also evidenced that the structuration of the ILs influence strongly the aggregates structure and formation, and therefore their extraction efficiency.



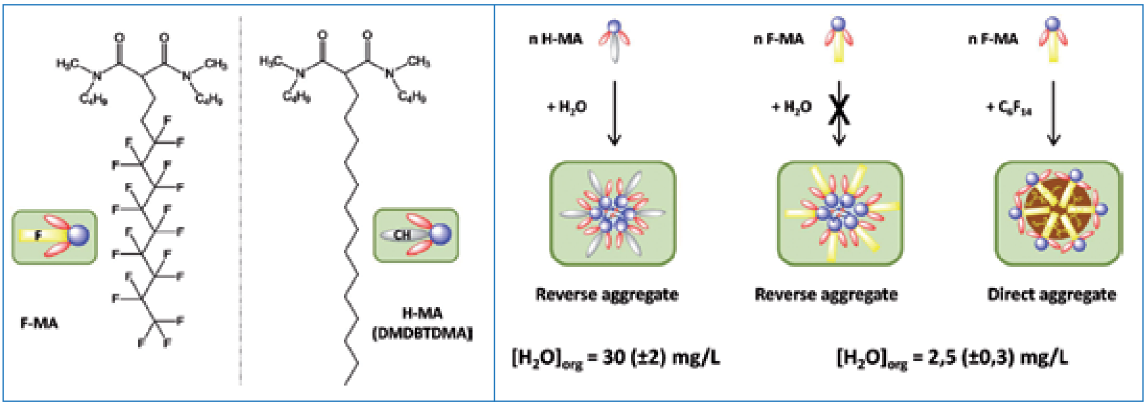
Usma C., Dourdain S., Arrachart G., Pellet-Rostaing S. - **Liquid-Liquid Extraction of Rare Earths Elements by Use of Ionic Liquids** - *Hydroprocess* (2019) 7, 1-9.

LIQUID-LIQUID SYSTEM CHEMISTRY: STRONG-WEAK INTERACTION CORRELATION, THREE PHASES SYSTEMS AND FLUORINATED SYSTEMS

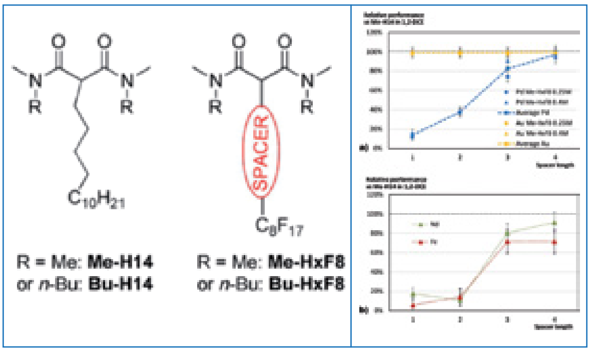
B. Braibant, J. Durain, M.C. Dul, M. Bertrand, S Dourdain, S. Pellet-Rostaing, X. Le Goff, D. Bourgeois, D. Meyer

Better understanding of how a metal ion usually not soluble in an organic phase can be maintained into it by using an extractant is one of the main challenges in the liquid-liquid separation field. One part of this challenge is to elucidate the role of the interactions which can take place 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]

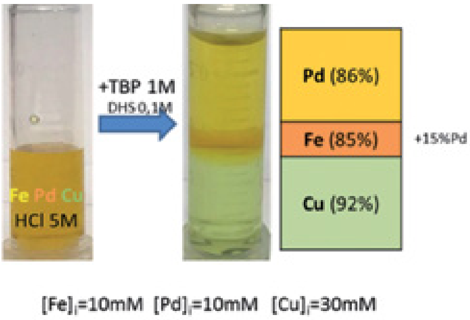
The research done in this field is focused on the formulation of separation solvents and the related molecular topology, weak interactions modulation from H-molecules to Fluorinated molecules [2, 3] and 3 phase systems.[4, 5]



H-molecules vs F-molecules weak interactions



H-molecules vs F-molecules Strong interactions



Future triphasic system

[1] Bourgeois D., El Maangar A. and Dourdain S.- **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] Braibant B., Le Goff X., Bourgeois D., Meyer D. - **Impact of the Long-Range Electronic Effect of a Fluorous Ponytail on Metal Coordination during Solvent Extraction** - *Chem Phys Chem* (2017) 18, 24, 3583

[3] Marie-Claire Dul M-C., Braibant B., Dourdain S., Pellet-Rostaing S., Bourgeois D., Meyer D. - **Perfluoroalkyl- vs alkyl substituted malonamides: Supramolecular effects and consequences for extraction of metalsv**- *Journal of Fluorine Chemistry 200* (2017) 59–65

[4] Braibant B., Bourgeois D., Meyer D. - **Three-liquid-phase extraction in metal recovery from complex mixtures** - *Separation and Purification Technology* (2018) 195, 367

[5] Durain J., Bourgeois B., Bertrand M., and Meyer D. - **Comprehensive Studies on Third Phase Formation: Application to U(VI)/Th(IV) Mixtures Extracted by TBP in N-dodecane** - *Solvent Extraction and ion Exchange* (2019) Vol. 37, NO. 5, 328–346

MOLECULAR TOOLBOX FOR THE EXTRACTION OF STRATEGIC METALS

F. Giusti, G. Arrachart, S. Pellet-Rostaing, M. Whebie, F. Mary, N. Felines

Despite the fact that methods for extraction of strategic metals (such as uranium, rare earth elements…) from an acidic medium (nitric, sulfuric or a phosphoric) are relatively robust processes, more efficient system in terms of extraction efficiency and selectivity with respect to competitors ions remains relevant.

Based on the design of new extracting agent able to extract uranium from a nitric, sulfuric or phosphoric medium, we designed, synthesized and evaluated new bifunctional extractants carrying on one side amine or amide groups and on the other side phosphoric acid or phosphine oxide groups…[1,2]

These bifunctional ligands were found to extract selectively hexavalent uranium U(VI) with high distribution coefficient (D) and selectivity towards competitors in acidic solutions.

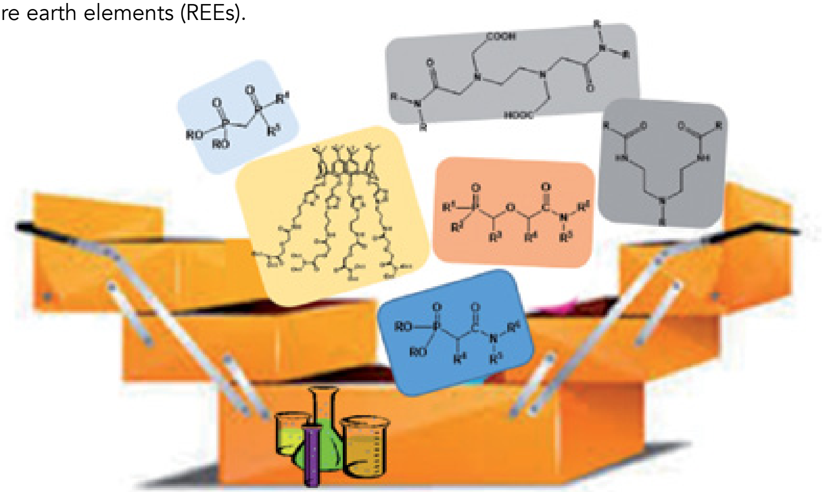
From a similar approach, we synthesized a series of bifunctional molecules with a central oxygen structurally related to glycolamides compounds for the extraction and separation of rare earth elements (REEs).

Beyond the use of bifunctional molecules, the effect of preorganization of ligands on a cavitands platform has been investigated with the functionalization of resorcinarene making the platform useful for the extraction of rare earth elements (REEs)[3] or synthesis of N-Alkyl calix[4] azacrowns for the selective extraction of uranium.[4]

Also, a chromo-extractant has been designed and synthesized to probe the liquid–liquid interface in a neodymium extracting process.[5]

Recently, we designed and synthetized some aminodiamide ligands[6] as well as lipophilic derivatives of polyaminocarboxylic acids respectively for the extraction of uranium and REEs.

We are currently interested in the influence of chirality on extraction performance with the synthesis and design of enantiopure molecules which are involved in hydrometallurgy processes.[7]



Molecular toolbox for liquid-liquid process for the recovery of strategic metals such as uranium or rare earth elements

[1] Leydier A., Arrachart G., Turgis R., Bernier G., Marie C., Miguirditchian M., Pellet-Rostaing S. - **Recovery of uranium (VI) from concentrated phosphoric acid using bifunctional reagents** - *Hydrometallurgy* (2017) 171, 262-266.

[2] Artese A., Dourdain S., Felines N., Arrachart G., Boubals N., Guilbaud P., Pellet-Rostaing S. - **Bifunctional Amidophosphonate Molecules for Uranium Extraction in Nitrate Acidic Media** - *Solvent Extraction and Ion Exchange* (2020) 38, 703-718.

[3] Wehbie M., Arrachart G., Cruz C. A., Karame I., Ghannam L., Pellet-Rostaing S. - **Organization of diglycolamides on resorcinarene cavitand and its effect on the selective extraction and separation of HREEs** - *Separation and Purification Technology* (2017) 187, 311-318.

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[5] Wang J., Arrachart G., Giusti F., Gaelle M. G., Gassin P. M., Jonchere A., Diat O., Girard L. - **Synthesis and Characterization of a Chromo-Extractant to the Probe Liquid-Liquid Interface in a Solvent Extraction Process** - *Journal of Physical Chemistry C* (2020) 124, 10916-10923.

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BIPHASIC EXTRACTION BASED ON DYNAMIC COVALENT CHEMISTRY

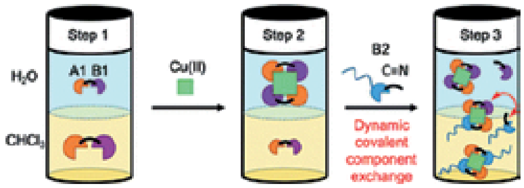
A. Chevalier, D. Meyer
A. Osypenko, J.M. Lehn (ISIS Strasbourg)

In contrast to the classical method where a single molecule is designed to extract metal cations under specific conditions, dynamic covalent chemistry provides an approach based on the implementation of an adaptive dynamic covalent library for inducing the generation of the extractant species.

In collaboration with the LCS (ISIS), the LHyS team has applied this approach to the liquid–liquid extraction of copper(II) nitrate based on a dynamic library of acylhydrazones constituents that self-build and distribute through the interface of a biphasic system.

The addition of copper(II) cations to this library triggers a modification of its composition and the upregulation of the ligand molecules driven by coordination to the metal cations. Among these, one species has proven to be sufficiently lipophilic to play the role of carrier agent and its formation by component exchange enables the partial extraction of the copper(II). The study of different pathways to generate the dynamic covalent library demonstrates the complete reversibility and the adaptability of the system. The detailed analytical investigation of the system provides a means to assess the mechanism of the dynamic extraction process.[1]

The present work laid the foundation of a new liquid-liquid metal extraction-separation approach which opens the possibility of developing a system responding to several metal extraction-separation problems.



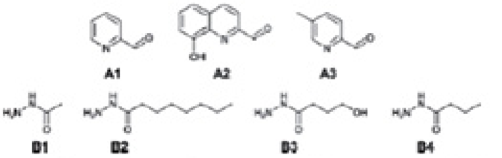
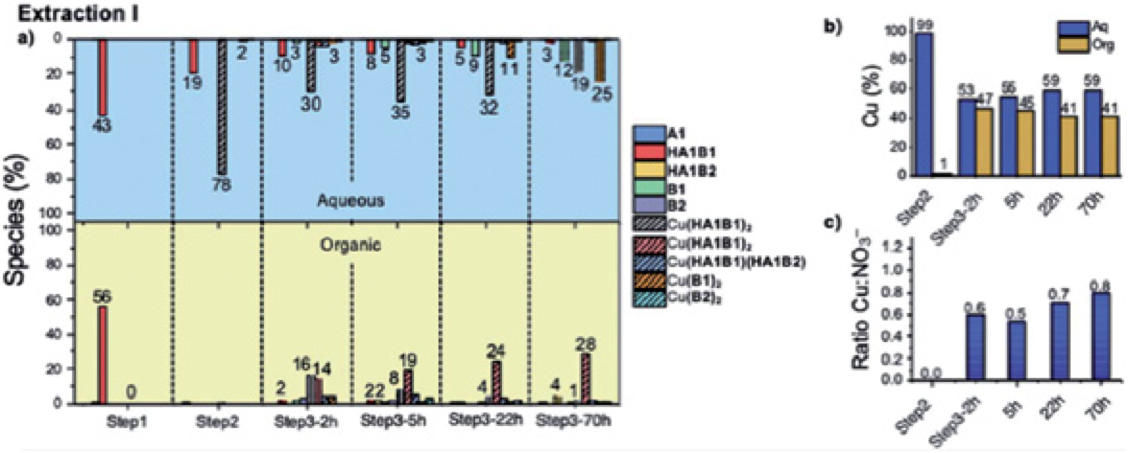


Fig. 1 Reference library of aldehyde A1–A3 and hydrazide B1–B4 components.



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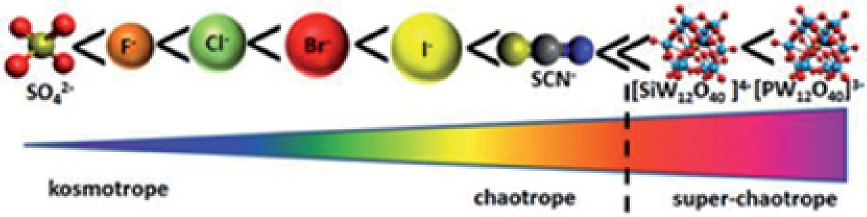
NANO-IONS SPECIFIC EFFECT : SUPERCHAOTROPY

M. Hohenschutz, P. Bauduin, L. Girard, A. Jonchère, T. Merhi, I. Chazzapi, O. Diat

In the frame of studies of ion at liquid interfaces, we have observed that large-size and low-charge density ionic species, such as polyoxometalates (POMs) or (metal-) boron clusters have peculiar behavior compared to classical ions. They have indeed the strong propensity of nano-ions to adsorb at neutral polar interfaces, via non-specific interactions called "super-chaotropy".[1,2] The super-chaotropy scales with the charge density and, to a lesser extent, with the polarizability. It has strong effects on structuring aqueous phases, on solubilization[3] of poorly soluble organic molecules in water, on phase transitions in self-assembly systems in aqueous solution.[4] A simple way for evaluating and classifying nano-ions according to their super-chaotropy was proposed via the cloud point (temperature) variation.[5] The super-chaotropic behavior of nano-ions opens opportunities in separation science, catalysis, and for the design of nanostructured hybrid materials. We can consider that they are at the frontier between ions and (charged-) colloids due to their nm size.

A



B

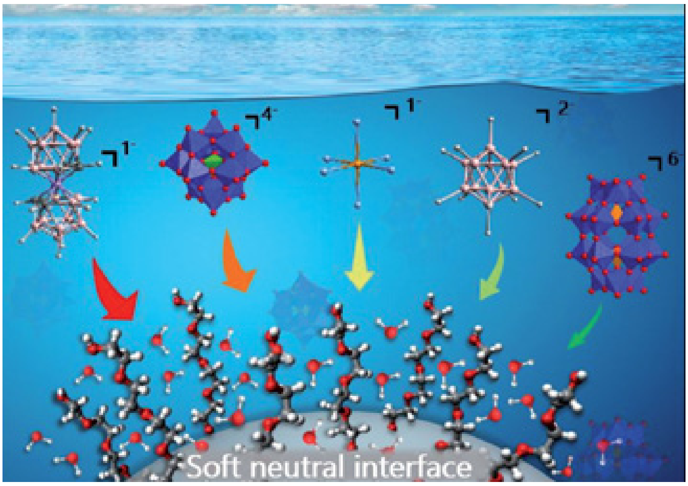


Fig. A) Beyond the Hofmeister series on the "chaotropes" side with Kegging POM as an example. B) Schematic representation of various nanoions (Na-cobalta-bisdicarbolide, Keggin-type silicotungstic acid, Na-hexafluorophosphate, Na-closo-dodecarborate (Na-B$_{12}$H$_{12}$), Dawson-type H$_6$P$_2$W$_{12}$O$_{60}$) in interaction with non-ionic micelles, the strength of the interaction depends on the NIs charge density decrease from right to left.

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[2] Buchecker T., Le Goff X., Naskar B., Pfitzner A., Diat O., Bauduin P. -**Polyoxometalate/Polyethylene Glycol Interactions in Water: From Nanoassemblies in Water to Crystal Formation by Electrostatic Screening**- *Chemistry-a European Journal* (2017) 23, 8434-8442. Buchecker T., Schmid P., Renaudineau S., Diat O., Proust A., Pfitzner A., Bauduin P. -**Polyoxometalates in the Hofmeister series**- *Chemical Communications* (2018) 54, 1833-1836.

[3] Buchecker T., Schmid P., Grillo I., Prevost S., Drechsler M., Diat O., Pfitzner A., Bauduin P. -**Self-Assembly of Short Chain Poly-N-isopropylacrylamid Induced by Superchaotropic Keggin Polyoxometalates: From Globules to Sheets**- *Journal of the American Chemical Society* (2019) 141, 6890-6899. Schmid P., Buchecker T., Touraud D., Diat O., Kunz W., Pfitzner A., Bauduin P. -**Self-assembly of a short amphiphile in water controlled by superchaotropic Polyoxometalates: H4SiW12O40 vs. H3PW12O40**- *Journal of Colloid and Interface Science* (2020) accepted.

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SOLUBILIZATION PROPERTY OF NANOIONS: THE CASE OF METALLA-BIS-(DICARBOLLIDES)

T. Merhi, I. Chazappi, L. Girard, A. Jonchère, P. Bauduin and O. Diat
C. Vinas and F. Teixidor ICMAB (Barcelona, Spain)

Metalla-bis-(dicarbollides), such as the COSAN anion $[Co(C_2B_9H_{11})_2]^-$, have attracted much attention in biology (BNCT for Boron Neutron Capture Therapy or inhibition of cell growth) or in separation science in extraction of radioactive caesium using solvent extraction process. However a deep understanding of their interactions with biological cell-components or with polar organic molecules is still missing. We know from our previous studies that this type of anion can be considered as a nano-ion with a very low charge density ($<3/nm^3$) that can strongly adsorb onto hydrated interfaces. This work[1] was dedicated on the interactions of COSAN with glucose moiety, a neutral and hydrated chemical function that is ubiquitous at biological interfaces. Octyl-glucopyranoside surfactant (C8G1) was chosen as a model as it self-assembles in water into micelles and creates a hydrated glucose-covered interface. Using complementary scattering and spectroscopic techniques, we have deduced from experiments that at low COSAN content and below the critical micellar concentration (CMC) of C8G1, COSAN binds to C8G1 monomers through the hydrophobic effect. Above the CMC of C8G1, COSAN adsorbs onto C8G1 micelles through the superchaotropic effect. At high COSAN concentrations, COSAN disrupts C8G1 micelles and the assemblies become similar to COSAN micelles but with small amount of solubilized C8G1. Therefore, COSAN binds in a versatile way to C8G1 upon either the hydrophobic or the superchoatropic effect depending on their relative concentrations.

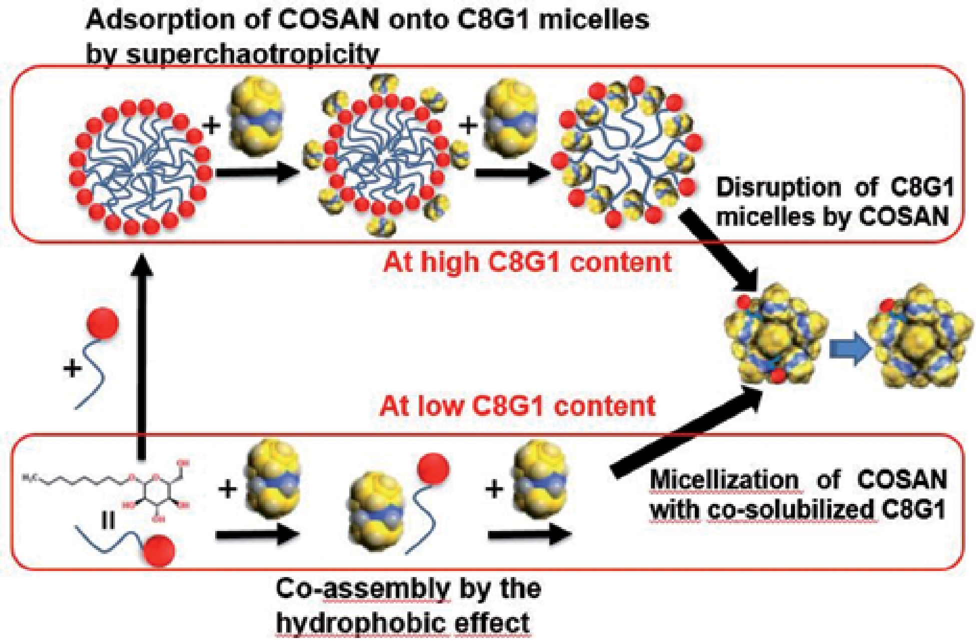

Fig. Sketch of alkyl glucoside surfactant solubilization with COSAN molecules above Surfactant Micellar Concentration (upper sketch) below CMC (lower sketch).

The properties of disruptive effect and/or solubilization of these nano-ions are currently developed either to disperse hydrophobic molecules in water or to separate macromolecules.

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RECYCLING OF END-LIFE PRODUCT THANKS TO IONIC LIQUIDS BASED EXTRACTING SYSTEMS

B. Baus Lagarde, G. Arrachart, S. Pellet-Rostaing
C. Micheau, A.-H. Le (SATT AxLR)

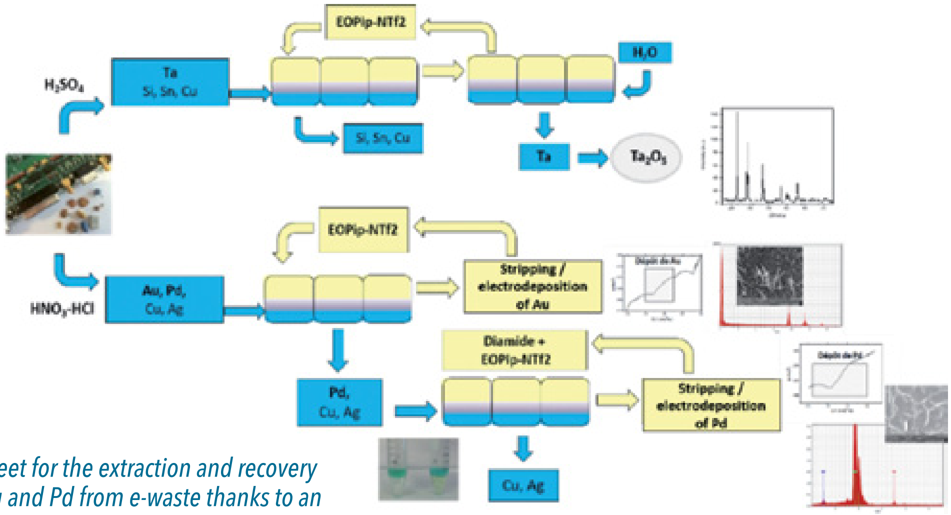
Recycling from end-of-life products including waste electrical and electronic equipment (WEEE, or e-waste) can reduce the environmental footprint by reducing the need for primary raw materials since such "urban mines" are a source of valuable metals. Also due to the growing environmental awareness and the development of green chemistry, intense research studies have been devoted to the development of alternative processes limiting the use of volatiles compounds.

Ionic liquids (ILs) exhibit several properties that make them attractive for the replacement of common organic diluents, among them a wide liquid range, good thermal stability, the ability to solubilize a wide range of solutes, a very low vapor pressure, and non-flammability.

In this context, we develop a novel series of TSILs (task specific ionic liquids) bearing various ketone or phosphonate groups and cations. The extraction behaviour of Ta with these TSILs was investigated in comparison to commonly used extractants such as MIBK or TBP.[1,2]

We also showed that the use of EBPiP-NTf_2 or EOPiP-NTf_2 as extraction media allows the setting of an "eco-friendly" process for extraction and recovery of Ta.[3] High performances can be achieved for the selective extraction of Ta from a leachate of slugs containing metal competitors (Cu, Pd, Au, Si…). The recovery process for Ta and recyclability of the ionic liquid was successfully established which allowed the implementation of the process at a pilot scale.[4]

Recently we were able to extend the feasibility of recovery of other valuable metals such as gold (Au) and palladium (Pd) from waste stream.[5]



Flowsheet for the extraction and recovery of Ta, Au and Pd from e-waste thanks to an IL-based extracting system

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[2] Micheau C., Lejeune M., Arrachart G., Draye M., Turgis R., Michel S., Legeai S., Pellet-Rostaing S. - **Recovery of tantalum from synthetic sulfuric leach solutions by solvent extraction with phosphonate functionalized ionic liquids** - *Hydrometallurgy* (2019) 189.

[3] Micheau C., Arrachart G., Turgis R., Lejeune M., Draye M., Michel S., Legeai S., Pellet-Rostaing S. - **Ionic Liquids as Extraction Media in a Two-Step Eco-Friendly Process for Selective Tantalum Recovery** - *Acs Sustainable Chemistry & Engineering* (2020) 8, 1954-1963.

[4] R. Turgis, G. Arrachart, S. Pellet-Rostaing, M. Draye, S. Legeai, D. Virieux, C. Thomas. - **Processes for extracting and recovering tantalum from acid aqueous phase by an ionic liquid** - WO 2017025547 A1 / FR 3040060 A1 (2017).

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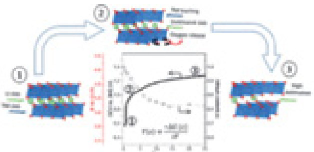
LITHIUM ION BATTERY: ELECTRODE MATERIALS MANUFACTURING AND DISSOLUTION – RECYCLING AND HIGH VALUE PRODUCTS

M. Cognet, M. Joulié, J. Condomines, E. Lagae-Capelle, X. Le Goff, A. Mesbah, N. Dacheux, J. Cambedouzou, J. Maynadié, M. Carboni, D. Meyer
T. Gutel, D. Peralta, A. Boulineau, E. DeVito, R. Gautier (CEA/DRT/DEHT),
S. Madhavi (NTU Singapour)

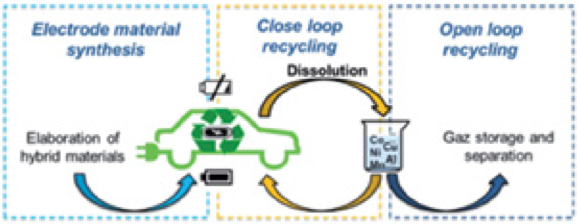
Energy storage and its circular economy represent a major societal issue for the years to come. In this field, the LHyS team is interested in the cycle of Li-ion batteries and more particularly that of the active electrode by an approach of hydrometallurgical process integration. This cycle includes its manufacture, its dissolution and the valuation of species in a closed or open cycle mainly based on the use of MOF materials. All of these actions include fundamental and applied studies and implies several external groups national and international (SCARCE project).

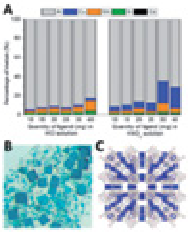
Based on earlier selective MOF precipitation studies, our team has extended his development on LiNMC fundamental dissolution studies[1], electrode materials manufacturing[2], and sereval recycling approaches.[3]



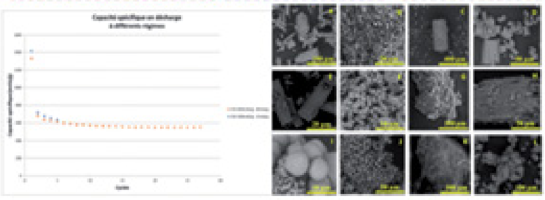
LiNMC dissolution mecanism

Co, Ni, Mn Sulfonate or Fe-phosphate MOF as Electrode materials





Cu, AL MOF for Gaz separation, storage



Reuse of Ni, Mn, Co MOF for electrode materials manufacturing

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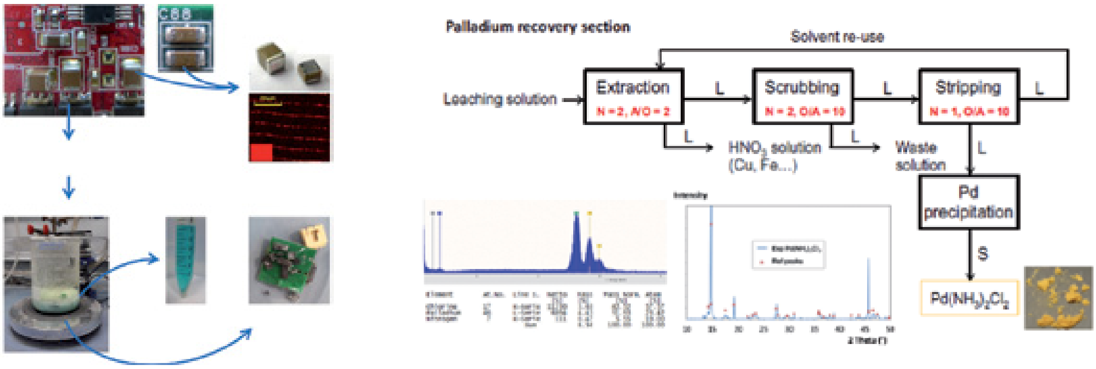
[2] Cognet M., T. Gutel, Peralta D., Maynadié J., Carboni M., Meyer D. - Iron(II)-**Benzene Phosphonate Coordination Polymers as an Efficient Active Material for Negative Electrode of Lithium-Ion Batteries** -*Journal of the electrochemical society* (2017) 164, 12, A2552-A2554.
Cognet M., Gutel T., Gautier R., Le Goff X., Mesbah A., Dacheux N., Carboni M., Meyer D. - **Pillared sulfonate-based metal-organic framework as negative electrode for Li-ion batteries** - *Materials Letters* (2019) 236, 73–76.
[3] Cognet M., Condomines J., Cambedouzou J., Madhavi S., Carboni M., Meyer D. - **An original recycling method for Li-ion batteries through large scale production of Metal Organic Frameworks** - *Journal of Hazardous Materials* (2020) 385, 121603.
Cognet M., Gutel T., Gautier R., Le Goff X., Mesbah A., Dacheux N., Carboni M., Meyer D. - **Pillared sulfonate-based metal-organic framework as negative electrode for Li-ion batteries** - *Materials Letters* (2019) 236, 73–76.
Lagae-Capelle E., Cognet M., Madhavi S., Carboni M., Meyer D. - **Combining Organic and Inorganic Wastes to Form Metal–Organic Frameworks** - *Materials* (2020) 13, 441

PRECIOUS METAL EXTRACTION, SEPARATION, RECOVERY. THE PD CASE: FROM FUNDAMENTAL TO APPLIED RESEARCH

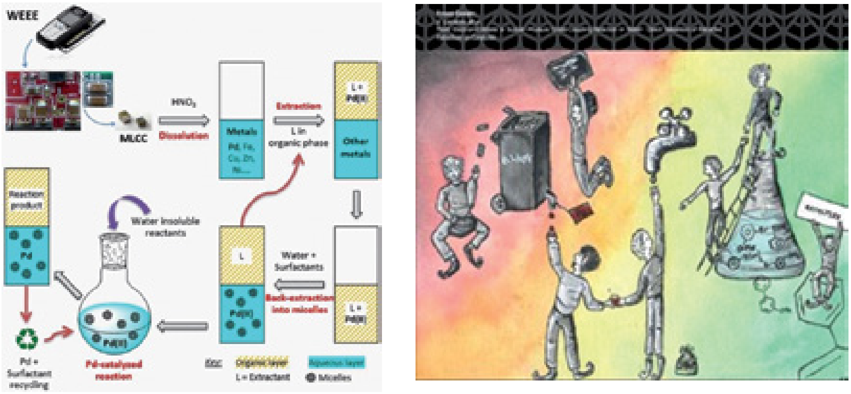
R. Mastretta, V. Lacanau, R. Poirot, D. Bourgeois, D. Meyer
P. Wagner, M. Schmitt, F. Bihel (Univ. Strasbourg)
C. Contino-Pepin, F. Bonneté (IBM Montpellier)

Palladium is a precious metal which is principally employed in autocatalysts. The increasing demand in palladium for this application combined with stable production has recently led to a sharp rise in palladium price as the market remains tight. Palladium price more than doubled over the last three years, and even, in January 2019, reached that of gold. Since then, palladium price regularly reaches ca. 45 k€/kg (1600 $/oz). Palladium market is expected to go further in deficit and production from other secondary resources becomes a key to fulfil palladium needs. Supply from the so-called urban mine appears as a very attractive alternative to traditional mining, especially for Western countries, poorly endowed with natural mineral ores.

In this context and based on more fundamental studies already published, the LHYS team has developed different hydrometallurgical approaches to recovering Pd from various wastes.[1, 2] We were able to lay the foundations for various process diagrams.[3] In collaboration with different groups, it was possible to demonstrate a direct valuation as catalyst by implementing short recycling routes.[4]



Pd recovery from PCB and related process diagram



Direct use in micellar catalysis of Pd recovered from printed circuit board

[1] Mastretta R., Poirot R., Bourgeois D., and Meyer D. - **Palladium Isolation and Purification from Nitrate Media: Efficient Process Based on Malonamides** - *Solvent Extraction and ion Exchange* (2019) 37, 2, 140–156.

[2] Bourgeois D., Lacanau V., Mastretta R., Contino-Pépinand C. and Meyer D. - **A simple process for the recovery of palladium from wastes of printed circuit** - *Hydrometallurgy* (2020) 191, 105241

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[4] Lacanau V., Bonneté F., Wagner P., Schmitt M., Meyer D., Bihel F., Contino-Pépin C. and Bourgeois D. - **From Electronic Waste to Suzuki–Miyaura Cross-Coupling Reaction in Water: Direct Valuation of Recycled Palladium in Catalysis** - *ChemSusChem* (2020) 13, 5224–5230.

FOAM FLOTATION FOR CESIUM EXTRACTION AND CONCENTRATION

P. Bauduin, L. Girard, A. Jonchère, O. Diat

The process called ion flotation allows to concentrate ions or other charged entities from an aqueous solution within a foam that can be produced at the top of an aqueous solution. Foam is created by injecting gas bubbles in the solution that contains surfactant molecules. To maintain a high foam stability in minimizing the solution transport within the foam thanks to an efficient drainage, specific foaming agents have to be used. Multifunctional surfactants such as AKYPOs or ETHOMEENs, both being pH-sensitive and containing ethylene oxide groups are good candidates because they can interact with multi-charged ions without precipitation and keeping their foaming capacity. We have shown in previous studies that monovalent cations are much more depleted from these types of foam films than divalents or even trivalents and thus monovalent cations are difficult to concentrate using this type of process.

In the scope of nuclear incident on the Fukushima power plant in Japan soils remediation contaminated by radioactive cesium became a mission of great importance (DEMETERRES project). Foam flotation can be considered as an economic process for depollute the leaching solution of soils. Nevertheless, as mentioned above it is not well suitable for monovalent cations. However, Prussian blue and its analogues (PBA) nanoparticles represent a class of materials, which is well established for a high selective sorption of heavy and radioactive metallic ions such as cesium and thallium. In a recent study, we have shown that cesium cations can be removed from solution via first their sorption in PBA nanoparticles that can be synthesized in situ the solution and then through the flotation of the nanoparticles, (fig. left) via their sorption within a foam. Size and surface properties of the nanoparticles along with the surfactant chemistry are main parameters determining the efficiency of decontamination process in this procedure. Cesium can be efficiently removed from aqueous solution using this process, down to the ppb level (fig. right).[1,2]

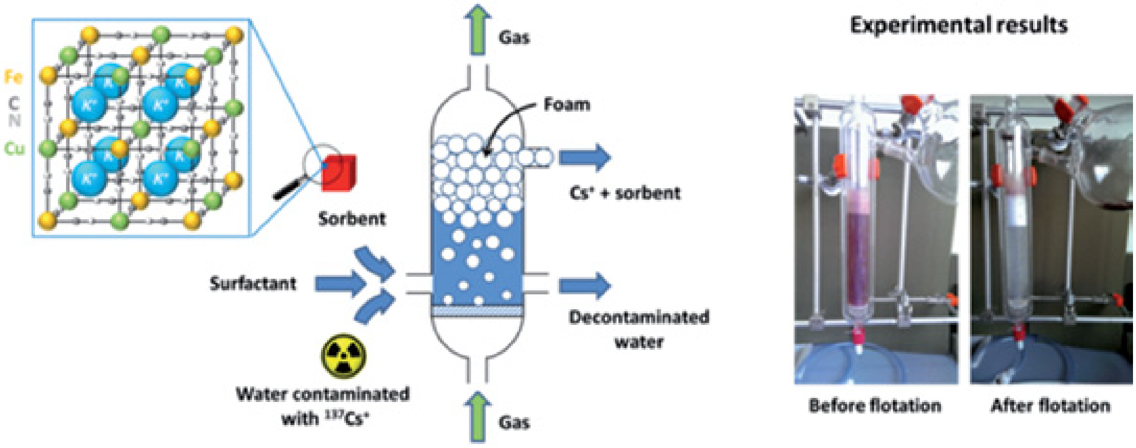

Fig. Left: Schematic representation of foam flotation using a solid sorbent synthesized in-situ (Prussian blue analog nanotiles – PBA-NP). Right: Pictures obtained before and after flotation process showing qualitatively the concentration of PBA-NPs charged with Cs cations.

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[1] Micheau C., Diat O., Bauduin P. -**Ion foam flotation of neodymium: From speciation to extraction**- *Journal of Molecular Liquids* (2018) 253, 217-227.

[2] Micheau C., Dedovets D., Bauduin P., Diat O., Girard L. -**Nanoparticle foam flotation for caesium decontamination using a pH-sensitive surfactant**- *Environmental Science-Nano* (2019) 6, 1576-1584. [Demeterres RSNR and Foamex ANR projects]

SONOCATALYTIC OXIDATION OF ORGANIC COMPOUNDS

T. Chave, S. El Hakim, L. Parizot, S.I. Nikitenko
H. Dutilleul, M.E Galvez, P. Da Costa (UPMC Sorbonne Universités)

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 $OH^\bullet$ 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.

Even if using ultrasonic irradiation with Pt based catalyst gives interesting result, and clearly points out a synergetic effect, the use of scare and expensive materials like platinum should be avoided. This is within this framework a new approach was developed based on the employment of noble free catalyst such as Co_3O_4/TiO_2 for the degradation of EDTA.[1] The *EDTA degradation* was studied under high ultrasonic frequency at 345 kHz in the presence of Ar/O_2 gas mixture at various temperatures (from 20 to 50°C). In all experiments 200 mL of 5 mM EDTA solution were ultrasonically irradiated in presence of 1 g/L of 1 to 6 wt% Co_3O_4/TiO_2 catalysts. The results clearly indicate that the Co_3O_4/TiO_2 catalyst is very stable under these conditions and shows a higher EDTA degradation rate compared to Pt/TiO_2 catalyst. The reaction mechanism is depicted in Fig. 1 and implies the oxidation of EDTA with Co^{3+} catalyst site and reoxidation of Co^{2+} with in situ formed radicals.

Similarly, significant acceleration of EDTA degradation was achieved during sonication in the presence of Ti^0 NPs and $Ar/20\%O_2$ gas mixture. Coating of Ti^0 with TiO_2 nanocrystalline shell reduces sonocatalytic activity. Pristine TiO_2 anatase nanoparticles do not show a sonocatalytic activity in studied system. Suggested mechanism of EDTA sonocatalytic degradation involves two reaction pathways: (i) sonochemical oxidation of EDTA by $OH^\bullet/HO_2^\bullet$ radicals in solution and (ii) EDTA oxidation 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 cavitation bubble/solution interface.[2]

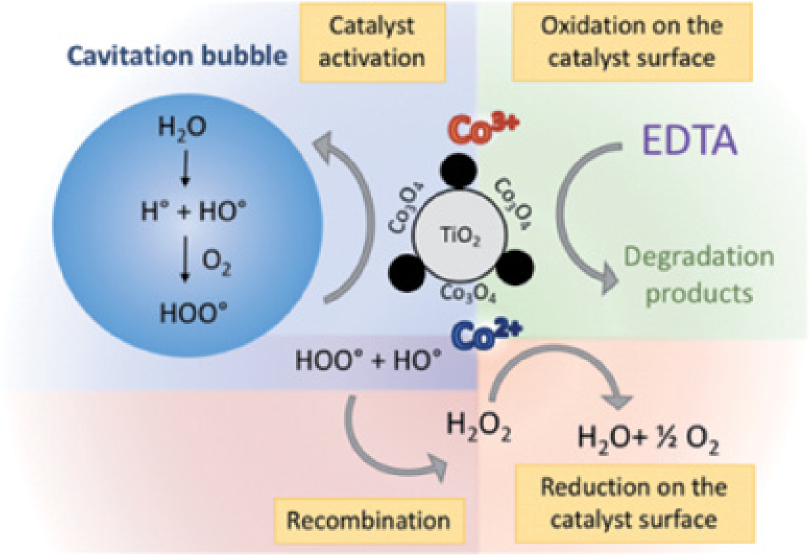

Fig. 1: Mechanism of EDTA sonocatalytic degradation on Co_3O_4/TiO_2 catalyst.

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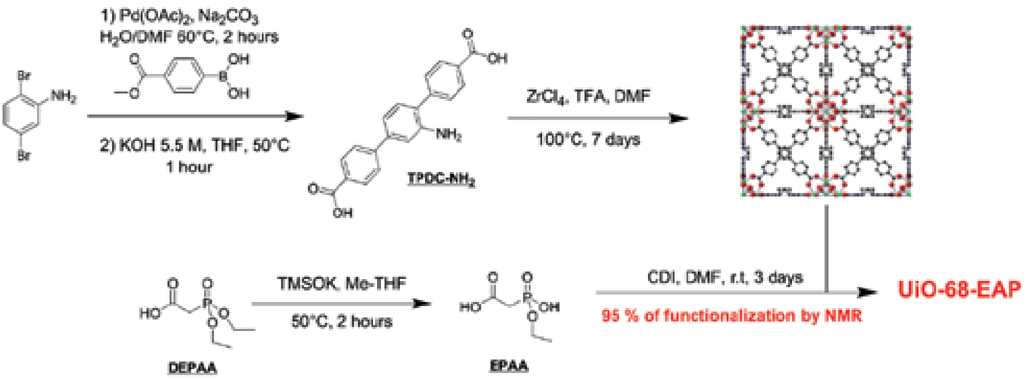
[1] Parizot L., Chave T., Galvez M-E., Dutilleul H., Da Costa P., Nikitenko S. I. - **Sonocatalytic oxidation of EDTA in aqueous solutions over noble metal-free Co_3O_4/TiO_2 catalyst** - *Applied Catalysis B: Environmental* (2019) 241, 570-577.

[2] 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.

MATERIAL SHAPING: MULTISCALE MOF'S FOR EXTRACTION AND SEPARATION OF METALS

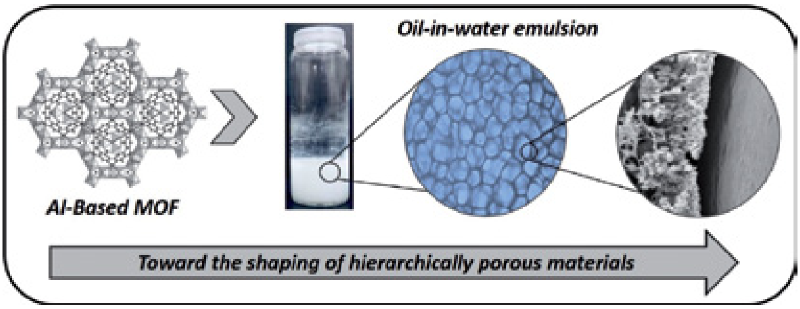
F. Lorignon, M. Carboni, D. Meyer
E. Andreadis, A. Gossard (CEA/DES/ISEC)

A Zr based Metal-Organic Framework functionalized with an amidophosphonate ligand has been synthesized, characterized and tested toward the uranium extraction in sulfuric acid conditions (representative of uranium leaching from ores). [1] A synthetic method has been developed to obtain the material by an efficient post-synthetic modification technique that allows 95% functionalization of active sites of the precursor material (UiO-68-NH_2). *This material has revealed to be stable in aggressive conditions* ([SO_4^{2-}] = 1 M, pH = 2) and to extract uranium up to 25 $mg.g^{-1}$, thus showing for the first time the possibility to use these hybrid materials for such an application.



MOF synthesis for U extraction from aqueous solution

The literature is currently lacking in efficient, simple and economic shaping procedures for porous materials that do not alter the properties (mainly porosity). For a broad applicability in this domain, producing porous materials as handle able materials is crucial. Stabilizing Pickering emulsions with metal-organic frameworks (MOFs) is a known way to incorporate them into hierarchically porous materials. Studies generally focus on their final properties and emulsion microstructures are rarely precisely described. Our hypothesis was that characterizing the microstructural and rheological properties of Pickering emulsions stabilized solely by Al-based MOFs (MIL-96) particles would provide insights into how to control their stability and workability for potential industrial applications. [2,3]



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[1] D. Rinsant, Andreiadis E., Carboni M., Meyer D. - **Uranium extraction from sulfuric acid media with Zr-Metal-Organic Frameworks** - *Materials Letters* (2019) 253, 285–288.

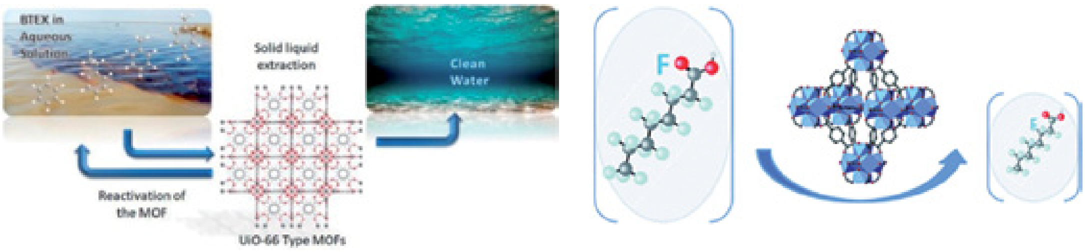
[2] Lorignon F., Gossard A., Carboni M. - **Hierarchically porous monolithic MOFs: An ongoing challenge for industrial-scale effluent treatment** - *Chemical Engineering Journal* (2020) 393, 124765.

[3] Lorignon F., Gossard A., Carboni M., Meyer D. - **Microstructural and rheological investigation of upcycled metal-organic frameworks stabilized Pickering emulsions** - *Journal of Colloid and Interface Science, ASAP* (2021).

EXTRACTION WITH MOF'S OF ORGANIC MOLECULES SEPARATION AND DESTRUCTION

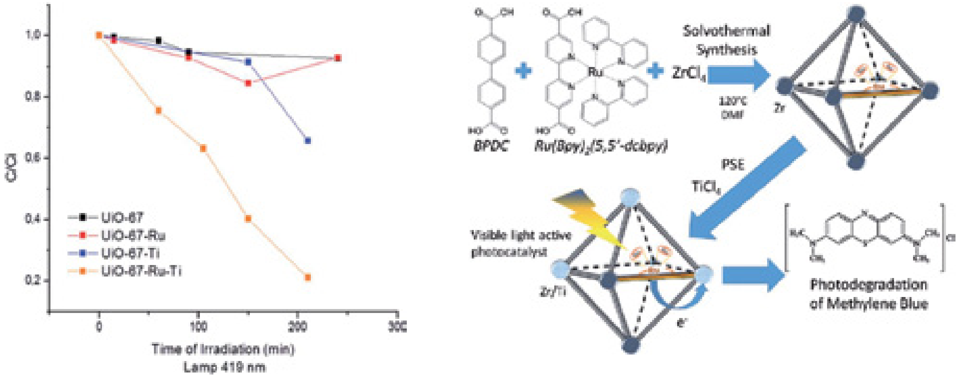
R. Navarro-Amador, L. Cirre, M. Carboni, D. Bourgeois and D. Meyer
K. Sini, Madjid Idouhar (Laboratoire de Chimie Organique Appliquée, Alger)

Zirconium Metal-organic frameworks (UiO-66, UiO-67) have been used for the removal from aqueous solutions of persistent fluorinated pollutants (PFOA and PFOS).[1] The two isostructural materials differ in cavity size, defined by the ligand, bdc (benzene-dicarboxylic acid) or bpdc (biphenyl-dicarboxylic acid) for UiO-66 and UiO-67 respectively. Both materials enable efficient sorption of PFOA and PFOS. UiO-67 shows higher sorption capacities (up to 743 mg.g^{-1} for PFOA and 585 mg.g^{-1} for PFOS) compared to these of UiO-66 (388 and 160 mg.g^{-1} for the sorption of PFOA and PFOS respectively) with a change in the sorption mechanism. UiO-66-F4 has also been tested in this condition to evaluate the influence of a highly hydrophobic material for the sorption of organic pollutants. Same materials have also shown interesting sorption capacities for the BTEX (aromatic pollutants).[2]



Aromatic and fluorinated pollutant extraction from aqueous solution

The efficient use of solar energy is one of the biggest challenges facing scientists; numerous research groups have dedicated their work to offer solutions for this technological purpose to have more ecological and environmentally friendly energy sources and industrial processes. For that matter, the synthesis of a UiO-67 based MOF was made through the combination of two synthetic pathways, first a solvothermal synthesis in the presence of two different linkers, one for the structure and one to work as a light antenna (based on Ru), followed by a process of post-synthetic metal exchange on the coordination node to include a catalyst (Ti).[3] This MOF has been able to remove an organic pollutant from an aqueous solution and to catalyze the degradation of the pollutant under visible light irradiation.



Organic pollutant extraction and light assisted destruction

[1] (a) Sini K., Bourgeois D., Idouhar M., Carboni M. and Meyer D. - **Metal–organic framework sorbents for the removal of perfluorinated compounds in an aqueous environment** – *New J. Chem.* (2018) 42, 17889. (b) K. Sini, Bourgeois D., M. Idouhar, Carboni M. and Meyer D. - **Metal–Organic Frameworks cavity size effect on the extraction of organic pollutants** - *Materials Letter* (2019) 250, 92-95. (c) Brevet en cours

[2] R. Navarro Amador, L. Cirre, Carboni M. and D Meyer - **BTEX removal from aqueous solution with hydrophobic Zr metal organic frameworks** - *Journal of Environmental Management* (2018) 214, 17-22

[3] R. Navarro Amador, Carboni M. and Meyer D. - **Sorption and photodegradation under visible irradiation of an organic pollutant by a heterogeneous UiO-67–Ru–Ti MOF obtained by post-synthetic exchange** - RSC Adv. (2017) 7, 195.

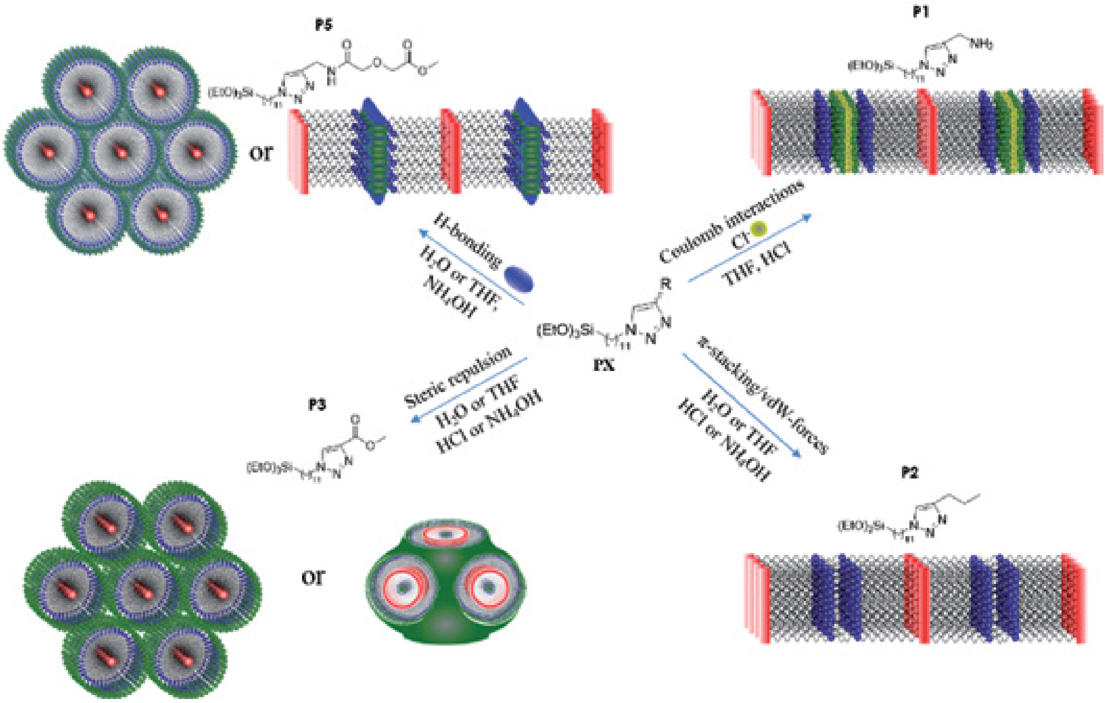
DEVELOPMENT OF A METHODOLOGY FOR THE SYNTHESIS OF HYBRID SILICA WITH HIGH EXTRACTANT CAPACITY

G. Arrachart, S. Pellet-Rostaing, R. Winkler, R. Besnard

In the context of solid-phase extractants, the organically functionalized silica should have a high density of functional groups with a satisfying homogeneity and accessibility. These requirements are usually difficult to obtain with conventional approaches.

The present work aims to establish a critical examination of the self-assembly of amphiphilic organosilane in different condition in order to study the phenomena that influence the self-associative properties of amphiphilic molecules in the controlled preparation of mesoporous materials and nanoparticles with specific chelating properties. Based on their amphiphilic properties, such organosilica precursors could be hydrolyzed to spontaneously give structured materials without requiring further addition of external surfactant. We showed that the structural and morphological versatility offered by this so-called "all-in-one" approach, result in combinatory effects of the addition of TEOS (tetraethylorthosilicate), the role of curvature agent played by a counter-ion and with the change of solvent, including binary mixtures, during the sol-gel process[1,2]

Various silica-based materials bearing functional groups with a densely functionalized surface have been prepared from condensable amphiphile molecules. The availability of such functional groups was established which allowed to engaged such materials in sorption experiments for the valorization of rare earth elements.[3,4]



Overview of material morphologies obtained from the "all in one" approach

[1] Winkler R., Re E., Arrachart G., Pellet-Rostaing S. - **Impact of Solvent Structuring in Water/tert-Butanol Mixtures on the Assembly of Silica Nanoparticles to Aerogels** - *Langmuir* (2019) 35, 7905-7915.

[2] Besnard R., Arrachart G., Cambedouzou J., Pellet-Rostaing S. - **Tuning the morphology of functionalized silica using amphiphilic organosilanes** - *Journal of Sol-Gel Science and Technology* (2017) 81, 452-467.

[3] Besnard R., Winkler R., Arrachart G., Cambedouzou J., Pellet-Rostaing S. - **Ion extraction applications of bilayer-structured hybrid silicas** - *Materials Chemistry Frontiers* (2018) 2, 1031-1039.

[4] Winkler R., Pellet-Rostaing S., Arrachart G. - **Selective Extraction of REEs Thanks to One-Pot Silica Hybrid Materials** - *Applied Sciences-Basel* (2020) 10.

SILICOTITANATES FOR STRONTIUM REMOVAL IN A CONTINUOUS PROCESS

T. Tratnjek, J. Causse, X. Deschanels

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 are promising materials due to the selective capture of Sr with regard to Ca for some compounds from this family like sitinakite for example. Sitinakite is an ionic exchanger with mobile sodium acting as charge compensator in the structure.

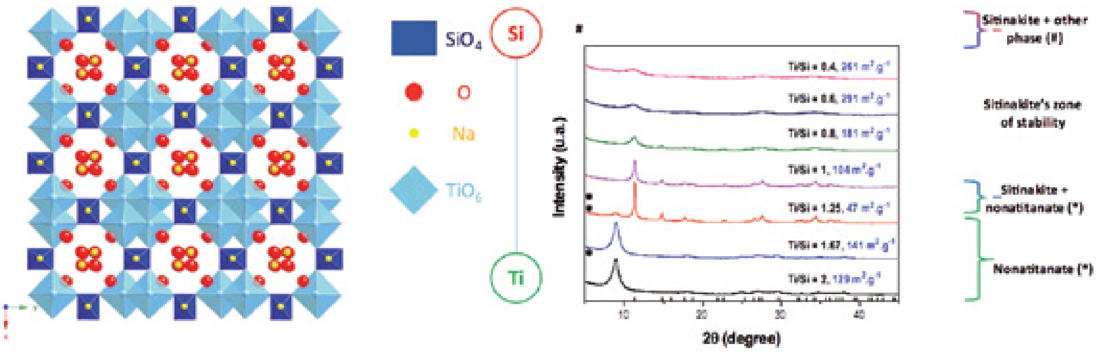


Figure 1: Crystalline structure of Sitinakite (left) - Influence of Ti/Si ratio on the crystalline phase produced and specific surface area (right)

Figure 1 shows crystalline structure of sitinakite with Na located in different chemical environments. While framework site Na in the walls is not particularly accessible, tunnel site Na can easily be exchanged with Sr with quite high selectivity. Ti/Si ratio level variation during hydrothermal synthesis allows covering of different crystalline structures from sodium nonatitanate for high ratio to sitinakite for lower values. If both nonatitanate and sitinakite are able to catch strontium, the selectivity towards calcium is much higher for sitinakite. Moreover, the higher the crystallinity of the phase, the lower the specific surface area, this aspect should also be taken in consideration to analyse the speed of the ionic exchange.

Generally, micro/mesoporous powder, such as sitinakite presented in Figure 1, suits very well with batch processes. However, it is more difficult to use such powder in a continuous mode. Indeed, continuous processes suggest that the liquid outflow goes through the materials with a given speed allowing treatment of larger volumes than in the case of batch processes. This means that the materials should be able to dissipate pressure drops due to the transit of liquid inside the solid. It is therefore possible considering materials with macroporosity with pore size of several tens of micrometers. Ideally, monoliths with hierarchical porosity, i.e. micro/mesopores and macropores will be produced to overcome these problems and design selective materials compatible with continuous processes. The general route followed is a pseudomorphic transformation as shown in Figure 2.

Figure 2: Pseudomorphic transformation general principle used to prepare sitinakite monolithic materials

PHASE SEPARATION OF BINARY MIXTURES AND MICROEMULSIONS INDUCED BY SOFT CENTRIFUGAL FIELDS

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)
S. Marčelja (ANU-Canberra)

Centrifugation is one of the moste common methode to separate emulsions and micropartcles; In the colloidla 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.

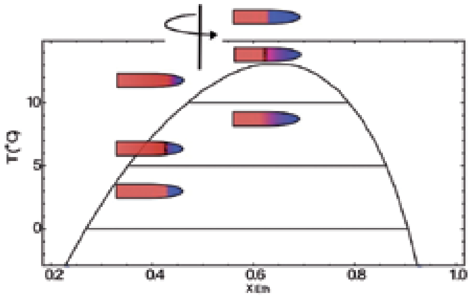


Figure 1: In the model binary system ethanol-dodecane that shows a LCST AT 15C, phase separation induced by centrifugation close and far from the critical point distinguish between reversible near-criticality that appears via a turbid and two-phase separation with a meniscus[1].

Progress in these domain requires understanding of the competition of centrifugal fluids with mixing entropy and fluctuations in structurations at nano-scale. “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 “Boltzmann-Archimedes-Gibbs” theory developed on the nearly regular solution[2] .

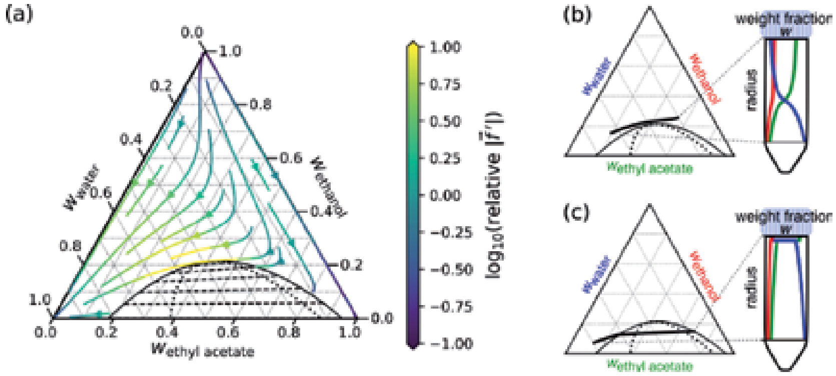
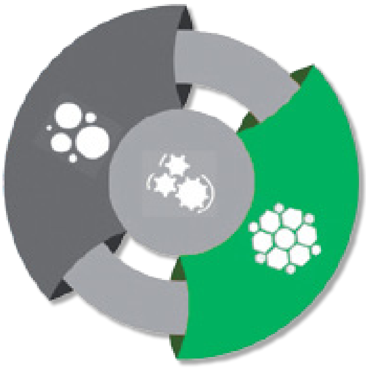


Figure 2.: left: phase diagram water/ethanol/ ethyl acetate system that is used for green extraction in the food and pharmacy are in progress. There is a critical point around 20% Weigth of ethanol at romm temperature; Coloured vector field shows the concentration gardient s appearing under centrifugation: 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) in revision

[2] Stemplinger, S., Zemb, T., Horinek, D., Dufrêche J.-F. **“Centrifuge-induced criticality in ternary systems”,** Submitted (November 2020)



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).

INFLUENCE OF THE GROUNDWATER COMPOSITION ON LONG-TERM RELEASE FROM UO_{2+X} FUEL MATRIX IN GEOLOGICAL REPOSITORY: THE COFFINITIZATION PROCESS

Szenknect Stéphanie, Alby Delhia, Podor Renaud, Mesbah Adel, Dacheux Nicolas
Miserque Frédéric (CEA/ISAS-Saclay)
López García Maria, Duro Lara, Bruno Jordi (Amphos 21, Spain)
Chenxu Wang, Ewing Rodney C. (Stanford Univ, USA); Zetterström Evins Lena (SKB, Sweden)

Most of the highly radioactive spent nuclear fuel (SNF) around the world is supposed to be disposed in deep-mined geological repositories. At the end of the fuel's useful life in a reactor, about 96% of the SNF is still UO_2. Thus, the long-term behavior of UO_2 in SNF must be evaluated under the weathering conditions of geologic disposal for periods of hundreds of thousands of years.

There is ample evidence from nature that many uranium deposits have experienced conditions for which the formation of coffinite, $USiO_4$, has been favored over uraninite, UO_{2+x}, during subsequent alteration events and confirmed by thermodynamic calculations. However, coffinite precipitates in solutions under-saturated with respect to amorphous $UO_2{\cdot}2H_2O$ in silicate solutions with concentrations typical of groundwater and supports the idea that the uraninite to coffinite transformation requires a priori destabilization of uraninite (self-irradiation inducing the solid metamictization, water radiolysis and/or surface oxidation at moderate oxygen fugacity). These findings regarding the thermodynamic stability of coffinite have renewed the interest in considering coffinite as a potential alteration product of SNF in a geological repository and a recent study carried out in collaboration has evidence for the first time the formation of coffinite from UO_2 under conditions typical of near-surface uranium deposits and deep-mined geological repositories for SNF (Fig. 1).[1]

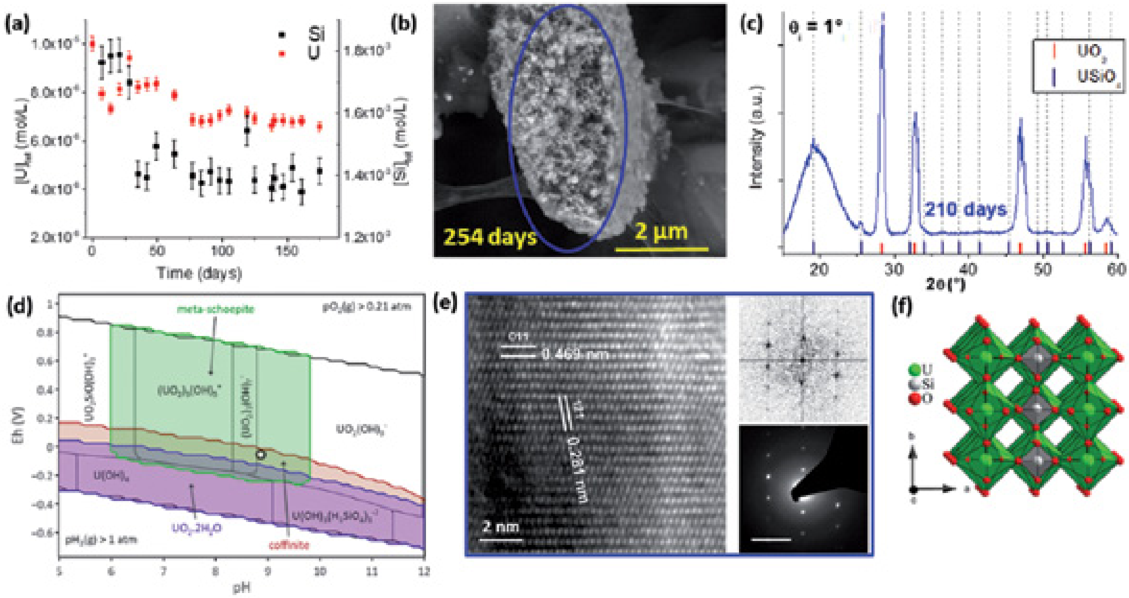


Fig. 1: (a) U and Si elemental concentrations during the leaching of the UO_2 pellet. (b) Environmental-SEM micrograph of the UO_2 pellet after 254 days of leaching showing the presence of neoformed particles. (c) GI-XRD pattern obtained with an incident angle of 1° after 210 days of leaching showing the appearance of the coffinite XRD peaks. (d) Predominance domains of the main U aqueous species and solid phases as a function of the reduction potential, Eh(V) and pH. (e) High-resolution TEM image of the coffinite grain, as indicated by the blue circle in (b) and the XRD pattern of this coffinite grain. (f) Representation of the tetragonal structure of the coffinite.

These results explained the common occurrence of coffinite in sedimentary uranium ore deposits and showed that coffinite should be considered in modelling the long-term behavior of SNF in a geological repository.

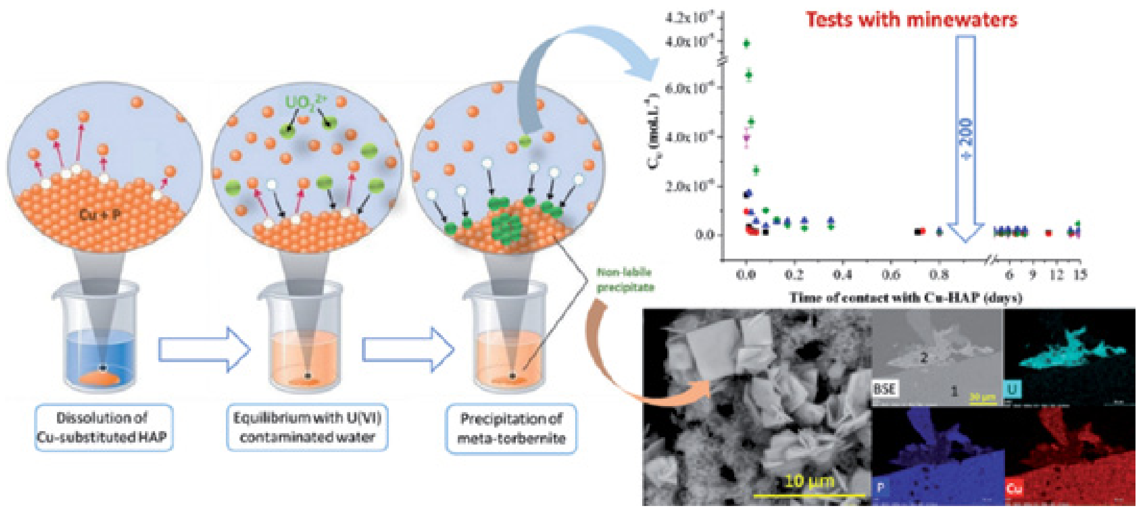
[1] Szenknect, S., Alby, D., Garcia, M.L., Wang, C.X., Podor, R., Miserque, F., Mesbah, A., Duro, L., Evins, L.Z., Dacheux, N., Bruno, J., Ewing, R.C. – **Coffinite formation from UO_{2+x}** – *Scientific Reports* (2020) 10, 12168.

IMMOBILIZATION OF URANIUM IN CONTAMINATED GROUNDWATER THROUGH META-TORBERNITE PRECIPITATION

Szenknect Stéphanie, Mesbah Adel, Clavier Nicolas, Lautru Joseph, Podor Renaud, Dacheux Nicolas
Descostes Michael (Orano-BG Mines)

Uranium ore mining, processing and manufacturing can contribute to groundwater contamination. Uranium is transported in groundwater mainly as dissolved U(VI) species, which can threaten ecosystems in the vicinity of contaminated sites. High costs associated with pump-and-treat remediation strategies and toughening of regulatory requirements regarding sewage discharge have prompted research into more effective methods. In that frame, ICSM and Orano have developed a new method to immobilize U(VI) in a nonlabile uranyl phosphate phase, meta-torbernite $(H_3O)_{0.4}Cu_{0.8}(UO_2)_2(PO_4)_2{\cdot}7.6H_2O$. The low solubility and the stability of this phase under a wide range of environmental conditions was demonstrated through the determination of its thermodynamic properties and geochemical simulations. The ubiquity of meta-torbernite in oxidized secondary U ore deposits, contaminated sediments or mine tailings strengthen this conclusion.

On the other hand, hydroxyapatite (HAP), $Ca_{10}(PO_4)_6OH_2$ has been shown to be effective in sequestering heavy metals, metalloids and radionuclides. The removal mechanism is postulated to occur by coprecipitation or ion exchange. In the method developed by ICSM and Orano, uranyl is immobilized by homogeneous precipitation with dissolved phosphate and copper released from a synthetic copper-substituted HAP forming very low solubility meta-torbernite (Fig.).



Principle of the method developed by ICSM for the immobilization of U(VI) in contaminated water. Evolution of uranium concentration in mine waters contacted with Cu-HAP. SEM micrographs and elemental mapping of the precipitate.

The efficiency of the patented method[1,2] was demonstrated in batch experiments. The synthetic copper-substituted HAP was contacted with mine waters of various pH and compositions. U elemental concentration in solution was found to decrease strongly after 2 hours of contact and U was precipitated as square shaped grains of meta-torbernite (Fig. 1). The results showed the high reactivity of the prepared Cu-substituted HAP, which was attributed to its poor crystallinity and high specific surface area. This material is promising to be used in passive treatment devices such as permeable reactive barriers for water remediation.

[1] Szenknect S., Dacheux N., Mesbah A., Descostes M., Ziouane Y, Maihatchi-Ahamed A. – **Procédé de séparation de l'uranium utilisant une hydroxyapatite dopée au cuivre, procédé de préparation d'une telle hydroxyapatite et hydroxyapatite ainsi préparée** – *FR3055895*.
[2] Szenknect, S., Mesbah, A., Descostes, M., Maihatchi-Ahamed, A., Bonato, L., Massonnet, M., Ziouane, Y., Vors, E., Vercouter, T., Clavier, N., Lautru, J., Dacheux, N. – **Uranium removal from mining water using Cu substituted hydroxyapatite** – *Journal of Hazardous Materials* (2020) 392, 122501

PHENOMENOLOGICAL DESCRIPTION OF THE CORROSION AND ITS IMPACT ON THE DURABILITY OF ENCAPSULATED MAGNESIUM WASTES IN HYDRAULIC BINDERS - DECIMAL

Rémi Boubon, Diane Rébiscoul, Xavier Deschanels

The DECIMAL project (call for projects ANDRA « Optimization of radioactive dismantling waste's management ») takes place in the context of the nuclear waste treatment (see page 168 ANR).

The reprocessing of spent nuclear fuels from french UNGG (Uranium Natural Graphite Gas) nuclear reactors has generated cladding wastes mainly made of magnesium alloys. The CEA strategy is to encapsulate these intermediate-level long-lived wastes into a geopolymer matrix i.e. a porous aluminosilicate filled with an alkaline solution. This solution is a favorable media because it limits the magnesium alloy corrosion and thus the H_2 gas release. Nevertheless, because this H_2 release might be detrimental to the safe storage of conditioned waste packages with respect to the storage requirements supplied by ANDRA. The magnesium alloy reactivity has to be assessed taking into account the irradiation due to the radioactivity of the spent fuel cladding. These data will allow the determination of the durability of the waste package.

In this context, the objective of DECIMAL is to develop a methodology to determine the impact of the reactivity of encapsulated magnesium alloy in a geopolymer matrix on its durability when a corrosion inhibitor is present in the matrix and under irradiation. To reach this goal, three approaches were used: (I) the electrochemical analysis of the corrosion kinetics of the magnesium alloy (CEA/DEN and IRCP) (II) the multiscale characterization of the corrosion products formed during the magnesium alloy corrosion (Ph.D Rémi Boubon, LNER) and (III) the chemo-hydro-mechanical study of the waste package (INSA Rennes).

During the Ph.D of Rémi Boubon, the surface of magnesium alloy during its corrosion was studied in three different configurations: (I) in solutions extracted from bulk geopolymers, (II) inside the geopolymers, and (III) covered by a geopolymer thin film. Through the characterization of the corrosion products by grazing incidence X-ray diffraction (ESRF and ICSM), infrared and Micro-Raman spectroscopies, SEM and STEM coupled to EDX (Fig.a), processes occurring during the corrosion of the magnesium alloy were determined. It was pinpointed that the key parameters driving the nature and the amount of corrosion products are the quantity and the availability of dissolved silica and fluoride species in poral solution.

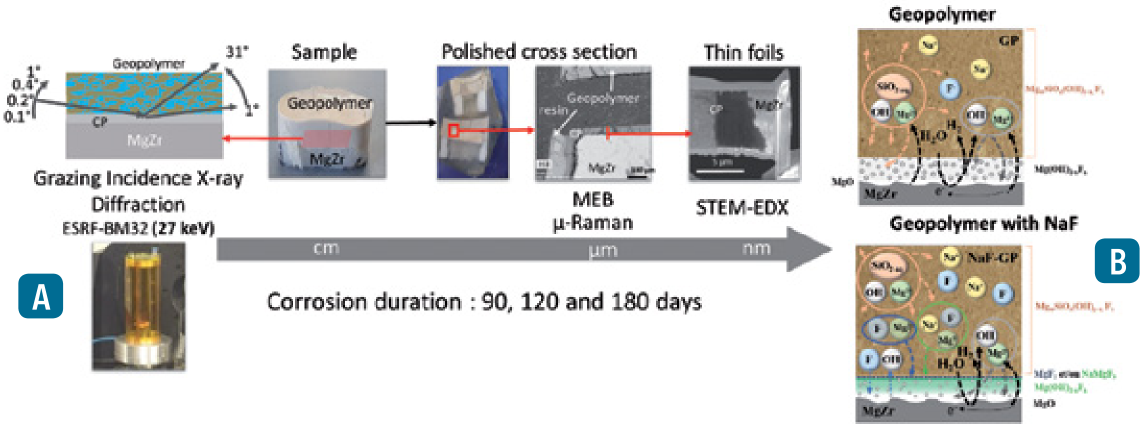


Figure 1: **A** *Multiscale approach used to characterize the magnesium alloy surface within geopolymers with and without corrosion inhibitor NaF during its corrosion and* **B** *schematisation of the associated corrosion processes.*

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[1] R. Boubon, X. Deschanels, M. Cabié, D. Rébiscoul - **Evolution of corrosion products formed during the corrosion of MgZr alloy in poral solutions extracted from Na-Geopolymers used as conditioning matrix for nuclear waste** - *Materials* (2020), 13(21), 4958

MULTIPARAMETRIC STUDY OF THE DISSOLUTION OF FISSION PRODUCTS BEARING ACTINIDE OXIDES

Cordara Théo, Dalger Thomas, Kaczmarek Thibault, Claparède Laurent, Szenknect Stéphanie, Clavier Nicolas, Mesbah Adel, Dacheux Nicolas

The dissolution of spent nuclear fuels (SNF), performed in concentrated nitric acid solution, is a very complex process due to some important chemical and microstructural heterogeneities in the material. In this field, the presence of Fission Products (FP) in various phases present in the SNF can affect the chemical durability of the ceramics during dissolution processes.

In this context, samples of UO_2 (reference material)[1], UO_2 doped with FP incorporated in the fluorite structure (lanthanide elements) or as metallic precipitates (PGM) were prepared by oxalic or hydroxide precipitation then sintered at high temperature. For this large panel of materials, the final microstructure was representative for SNF.

The multiparametric study of the dissolution (macroscopic approach) was developed by varying independently several parameters affecting the normalized dissolution rates (R_L). Not surprisingly, the increase of the nitric acid concentration or temperature led to the decrease of the chemical durability of the prepared materials. Chemical composition and heterogeneity were found to act as first-order parameters. Indeed, the incorporation of lanthanide elements induced a significant increase of the R_L values. However, it remained lower compared to that induced by the presence of PGM, which were associated to the stronger effect. Additionally, significant modification of the preponderant mechanism of dissolution occurred for nitric acid concentration higher than 0.5 M. The dissolution of sintered $Th_{0.25}U_{0.75}O_2$ pellets in various acidic media showed that the increase of the RL values observed after the steady state period was assigned to the simultaneous increase of the specific surface area of the material and of the HNO_2 concentration in solution, which acted as an important oxidative species regarding to uranium (IV).[3]

Simultaneously, operando monitoring of evolving solid/solution interface was developed in order to improve our overall understanding of the dissolution mechanisms involved for the different systems. This work was particularly focused on the description of the evolution of pellets microstructure. The study on the dissolution of UO_2 doped with lanthanide elements revealed preferential dissolution zones located at the grain boundaries. This phenomenon was assigned to the possible accumulation of lanthanides in such zones, leading to the decrease of the chemical durability. The dissolution of UO_2 + 3 mol% PGM ceramics in 0.1 M HNO_3 at 60°C also exhibited preferential dissolution zones located near the metal particles. This could be connected to the existence of nitrogen species at the UO_2/PGM interphase, which are able to catalyze the oxidative dissolution of the ceramics (Fig. 1).[4]

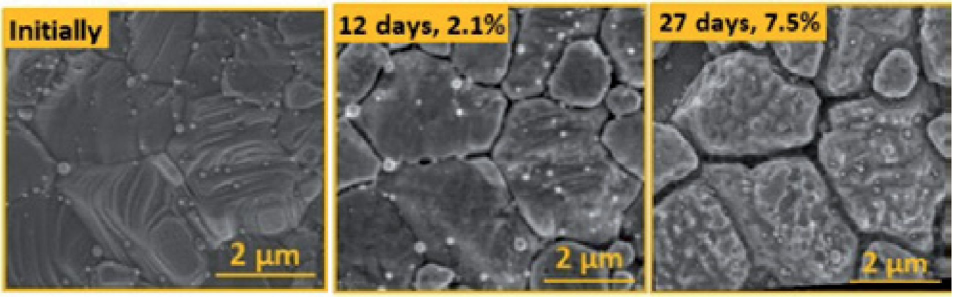


Fig. 1. Microstructural evolution observed during the dissolution of sintered UO_2+PGM in 0.1M HNO_3 at 60 ° C.

[1] Cordara T., Szenknect S., Claparede L., Podor R., Mesbah A., Lavalette C., Dacheux N. – **Kinetics of dissolution of UO2 in nitric acid solutions : A multiparametric study of the non-catalyser reaction** – *Journal of Nuclear Materials* (2017) 496, 251-264.

[2] Cordara T., Bertolotto S., Claparede L., Szenknect S., Mesbah A., Podor R., Lavalette C., Dacheux N. - **Impact of platinum group metals (Ru, Pd, Rh) on the dissolution of UO2** – *Journal of Nuclear Materials* (2020) 528, 151836.

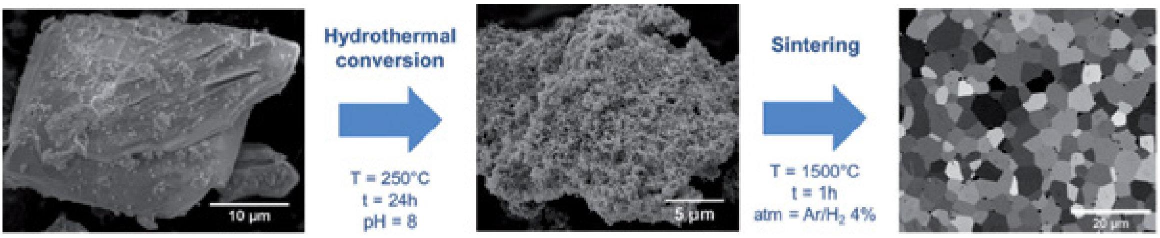
[3] Dalger T., Szenknect S., Tocino F., Claparede L., Mesbah A., Moisy P., Dacheux N. - **Kinetics of dissolution of Th0.25U0.75O2 sintered pellets in various acidic conditions** – *Journal of Nuclear Materials* (2018) 510, 109-122.

[4] Cordara T., Szenknect S., Podor R., Trillaud V., Claparede L., Le Goff X., Mesbah A., Lavalette C., Dacheux N. – **Microstructural evolution of UO2 pellets containing metallic particles of Ru, Rh and Pd during dissolution in nitric acid solution: 3D-ESEM monitoring** – *Hydrometallurgy* (2019) 188, 182-193.

HYDROTHERMAL CONVERSION OF ACTINIDE OXALATES

Clavier Nicolas, Manaud Jérémie, Maynadié Jérôme, Mesbah Adel, Dacheux Nicolas
Martin Philippe (ISEC CEA-Marcoule)

In the frame of the development of future nuclear reactors (so-called generation III and IV), innovative methods for oxide fuels preparation have been developed for years. They are frequently based on wet-chemistry routes, involving the precipitation of crystallized precursors, such as oxalates. Despite the advantages of these methods, the resulting oxide powders suffer from some drawbacks, including powders morphology poorly adapted to shaping and sintering, as well as presence of residual traces of carbon in the final samples. In order to avoid these potential issues and to get the rid of the thermal conversion step, we investigated the use of hydrothermal conditions to convert tetravalent actinides bearing oxalates and directly achieve the dioxide precipitation in solution.



From $U(C_2O_4)_2.6H_2O$ precursor to UO_2 pellet : fabrication of a model fuel through hydrothermal conversion of uranium(IV) oxalate.

The conditions of formation of An(IV) hydrated dioxides (i.e. temperature and duration of the hydrothermal treatment and pH of the initial solution) were first determined for thorium, which constitutes a reference system exempt from redox reactions.[1] In this case, pH values typically above 1 were considered to recover a solid phase. Also, due to the high stability of the thorium oxalate precursor, hydrothermal treatments of more than 5 hours at a temperature above 220°C were required. For uranium (IV)-based compounds[2], the lowest temperatures explored (typically from 180 to 200°C) at pH ≤ 1 led to stabilize UO_{2+x}/U_4O_9 mixtures exhibiting a global O/U ratio of 2.38 ± 0.10 according to the results of HERFD-XANES experiments. Higher temperatures (220-250°C) led the O/U ratio to decrease. Additionally, increasing the temperature of the hydrothermal treatment efficiently improved the elimination of residual carbon species, down to less than 200 ppm. Hydrothermal conversion of $U(C_2O_4)_2.6H_2O$ also led to the drastic modification of the powders morphology. With this aim, pH tuning was used to shift from bipyramidal aggregates (up to pH = 1), microspheres (2 ≤ pH ≤ 5) then to nanometric powders (pH > 5). Finally, a kinetics study showed that uranium oxides were obtained within only few hours. The samples early collected during the treatment were found to be strongly oxidized (O/U = 2.65 ± 0.14) which suggested the existence of U(VI)-bearing amorphous secondary phase which tended to reduce through time. Hydrothermal conversion then probably proceeded as a two-step mechanism composed by the oxidative decomposition of uranium (IV) oxalate followed by the reduction of uranium by organic moieties and its hydrolysis.

Then, a preliminary study dedicated to sintering revealed the good densification ability of the oxides produced. The sintering map of different uranium oxide samples presenting various morphologies was established. It paves the way to the control of the microstructure of final pellets. Finally, the hydrothermal conversion of oxalates has been also extended to $U_{1-x}Th_xO_2$ and $U_{1-x}Ce_xO_2$ solid solutions, cerium being used herein as a plutonium surrogate.

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ELABORATION AND STUDY OF UO_x REFERENCE MATERIALS FOR NUCLEAR SAFEGUARDS

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Pointurier Fabien, Fauré Anne-Laure (CEA-Dam, Bruyères le Châtel, France)
Dzigal Naïda, Sangely Laure (IAEA - Safeguards Analytical Services, Austria)

Particles analyses aiming to measure the isotopic composition of nuclear materials are currently a key tool for safeguards verification by the International Atomic Energy Agency (IAEA). Detection and measurement of the isotopic composition of nanometer- to micrometer-sized particles provide precious information on the activities implemented in any facility. For this purpose, analytical methods based on mass spectrometry techniques, such as Secondary Ions Mass Spectrometry (SIMS), have been developed and are applied by a few specialized laboratories in support of the IAEA's nuclear safeguards program. However, 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, so as to be used for optimization and qualification of analytical methods and instruments.

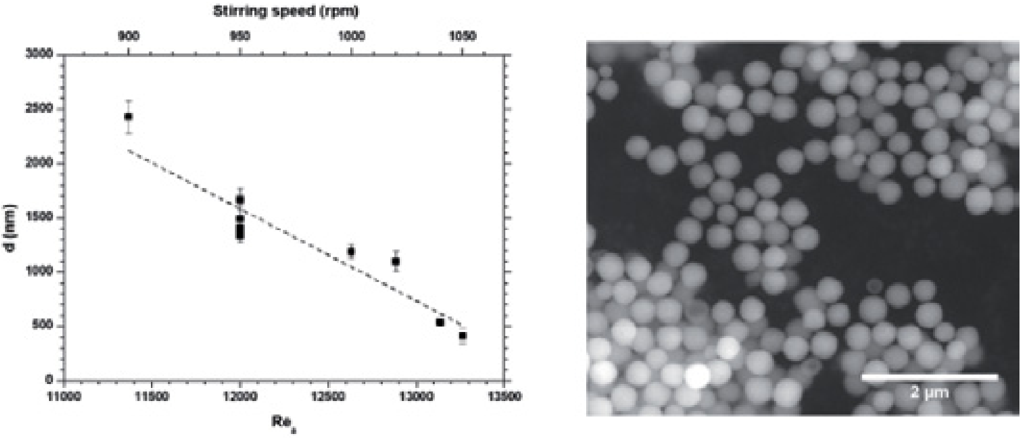

Fig. 1. Variation of the diameter of the UO_x particles produced by hydrothermal conversion of U(IV) aspartate versus stirring speed in the reactor, and SEM observations of the particles produced from $Re_a = 12000$. [1]

With the aim to develop an original and versatile wet chemistry route to UO_x reference materials, we first investigated the hydrothermal conversion of U(IV) aspartate. [1] A multiparametric study was undertaken in order to evidence the impact of pH, aspartic acid concentration, or mechanical stirring, on the formation of samples with controlled size and morphology. On the one hand, acid concentration was found to be the most critical parameter, as microspheres were only obtained for pH values close to 2. On the other hand, the size dispersion of the particles produced could be improved by using a large excess of aspartic acid during the initial precipitation step. Finally, the addition of a mechanical stirring during the hydrothermal treatment step allowed us to control more accurately the size of the particles produced in the range of 300 nm - 2.5 µm (see fig). Further heat treatment of these microspheres at 600°C under various atmosphere led to tune the oxides stoichiometry from UO_{2+x} to U_3O_8 and to produce anhydrous and carbon-free dense particles without altering their initial morphology. The chemical durability of these particles is also under study to evaluate their stability when stored as a suspension.

Finally, preliminary tests were performed on these reference materials for nuclear safeguards. In this aim, UO_2 microspheres were deposited on carbon planchets after dispersion and dilution with ethanol. The number of particles deposited, the spacing between them, and the absence of uranium background between the particles was found to be satisfying. Also, first LG-SIMS experiments aiming to determine the isotopic composition of uranium led to very good results, the behaviour of the particles under the SIMS beam being comparable to typical field sample particles.

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RADIATION EFFECTS IN INNOVATIVE MATERIALS FOR NUCLEAR WASTE PACKAGING

X. Deschanels, Y. Lou, S. Dourdain, C. Rey, J. Causse, G. Toquer, A. Mesbah, D. Rébiscoul
A.M. Seydoux-Guillaume (Université Clermont Auvergne, Clermont-Ferrand, France)
S. Peuget (DES/DE2D/LMPA CEA Marcoule)

An important task of nuclear industry is to find suitable and sustainable ways to dispose nuclear wastes. The final waste-form is subjected to intense irradiations, which are the consequence of the disintegrations (alpha, beta gamma) associated with the presence of radionuclides. To simulate these damage, we have used external irradiations. These last years, two class of materials have been studied at ICSM by these techniques.

The first concerns phosphate minerals, i.e monazite and xenotime, which are promising minerals for the immobilization of Pu and minor actinides. These minerals have a general formula REEPO$_4$ (REE = Ln, Sc Y). The monazite mineral is encountered for the light rare-earth elements (LREE) with larger ionic radii (i.e. for Ln = La – Gd). It crystallizes in the monoclinic P21/n structure type, whereas xenotime occurs for heavier and smaller elements (Y and Ln = Tb to Lu) and crystallizes in the zircon structure type (ZrSiO$_4$) in the tetragonal system (I41/amd). Previous results[1] have demonstrated the ability of monazite structure to maintain a crystalline state despite high radiation damage levels. However, the low critical temperature (180°C), above which amorphization cannot be achieved in monazite under ion irradiation, does not explain the strong radiation resistant to amorphization of actinide-doped monazite (natural or synthetic samples). For that, synthetic polycrystals of LaPO$_4$-monazite were irradiated sequentially and simultaneously, at room temperature on the JANNuS-Orsay/SCALP platform, with alpha particles (He$^+$: 160 keV) and gold (Au^{2+}: 1.5 MeV) ions, allowing respectively the simulation of the effect of the recoil nucleus and the α-particle obtained during an α-decay. Our results demonstrate the existence of the defect recovery mechanism, called α-healing, acting in this structure due to electronic energy deposition of alpha particles, which explains the better damage resistance to amorphization and swelling of actinide doped samples.[2] A similar result was observed for synthetic xenotime mineral[3] (ErPO$_4$) for a higher level of electronic energy deposition.

The second concerns the use of mesoporous silica materials for the management of the nuclear wastes. The so-called "separation-conditioning" strategy, which consists of implementing a functionalized silica porous matrix for the radionuclide sorption, is an interesting alternative. Such matrix could even act as a long term conditioning matrix, after porosity closure, in order to ensure a durable confinement. During its working process and with the presence of radionuclide, the mesoporous structure will be exposed to self-irradiation. This is why it's important to know the structure evolution under such conditions. For this purpose, mesoporous silica thin films deposited on Si-substrate (e~100nm) were irradiated by swift ions, especially Au ions. Porous characteristics of such films were obtained from the X-rays reflectivity measurements (XRR). Ballistic processes lead to a total compaction of the mesoporous structure for a dose of about ~10 keV/nm^3 (~0.5 dpa)[4]. Molecular dynamic simulation results are in good agreement with experimental work, which confirms the ballistic damage hypothesis[5]. Works are in progress in the frame of the ANR project AUTOMACT to have a deeper understanding of this compaction process.

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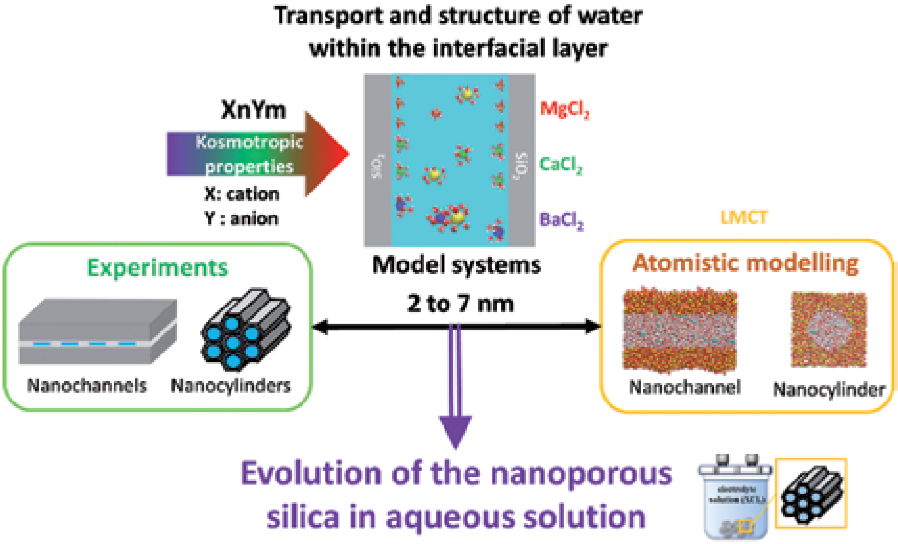
HOW WATER AND IONS PROPERTIES IN NANOCONFINEMENT IMPACT THE EVOLUTION OF MESOPOROUS MATERIALS

Diane Rébiscoul, Markus Baum, Hassan Khoder, Samuel Tardif, Francois Rieutord, Kunyu Wang, Bertrand Siboulet, Jean-Francois Dufrêche

The prediction and the understanding of material behavior regarding their interactions with aqueous solution in the fields of construction, geochemistry, membranes, nuclear wastes… require the use of modelling that is based on thermodynamic models and rate laws. However, most of these materials are completely or partially nanoporous such as cements, geopolymers, biominerals, clay materials, secondary minerals, amorphous nanoporous glass alteration layers…They consist of a set of confined media having a complex form, filled with water and ions. Under these conditions, these thermodynamic models and rate laws lack validation. Indeed, the processes occurring in nanoconfinement such as ion sorption, phase precipitation, pore wall dissolution and the recondensation of dissolved species or electrolyte diffusion differ from that of dense and planar materials in contact with aqueous solution. Since this nanoporosity accounts for a considerable proportion of the total porosity of many of these systems, there is an important impact on their macroscopic behavior.

The main objective of this topic is to gain some fundamental insight on the processes occurring in silica nanoconfinement. To reach this goal, we used an innovative approach, consisting in the use of electrolyte solutions having ions with various kosmotropic properties XCl_2 (X = Ba, Ca, Mg) confined in model systems. This includes two parallel and planar silica surfaces spaced of few nm (nanochannels) and concave silica surfaces oriented or not (highly ordered mesoporous silica materials) (PhD M. Baum). Using various characterization techniques such as hard X-ray reflectivity, small angle X-ray scattering, quasi-elastic neutron scattering, infrared spectroscopy and atomistic modelling (ICSM/LMCT), the water and ion behavior in this model confined silica systems[1] were determined and related to the processes driving the evolution of silica mesoporous materials in aqueous solutions (Fig.). Some of this work is a part of a Ph.D (Markus Baum)[2] and of a post-doctoral position (Hassan Khoder) funded by the *Fondation de la Maison de la Chimie.*



Scientific approach used to study the water and ions properties in nanoconfinement.

[1] Baum M., Rébiscoul D., Tardif S., Tas N.,.Mercury L., Rieutord F. - **X-Ray Reflectivity Analysis of SiO2 Nanochannels Filled with Water and Ions: A New Method for the Determination of the Spatial Distribution of Ions Inside Confined Media**, *Procedia Earth and Planetary Science* (2017) 17 682.

[2] Baum M., Rebiscoul D., Juranyi F., Rieutord F. – **Structural and Dynamical Properties of Water Confined in Highly Ordered Mesoporous Silica in the Presence of Electrolytes** – *Journal of Physical Chemistry C* (2018) 122 (34), 19857. Baum M., Rébiscoul D., Rey C., Juranyi F., Rieutord F. - **Dynamical and Structural Properties of Water in Silica Nanoconfinement: Impact of Pore Size, Ion Nature, and Electrolyte Concentration** - *Langmuir* (2019) 35, 10780. Baum M., Rieutord F., Rébiscoul D. - **Underlying Processes driving the Evolution of Nanoporous Silica in Water and Electrolyte Solutions** - *Journal of Physical Chemistry C* (2020) 124, 27, 14531.

SONOCHEMISTRY IN UNDERSTANDING NATURAL NANO-COMPOSITES FORMATION

R. Pflieger
M-A. Courty, J-M Martinez, E. Hernandez, E. Oliviero, C. Grison, F. Pelissier (Institut PROMES, Perpignan)

The project LINA lead by Mare-Agnès Courty from PROMES institute and supported by Region Occitanie aims at understanding the long-term transfer of nanoparticles produced by ionisation in the atmosphere to bee hives via pollen, nectar, propolis, water and their transformations by honey bees into polymer nanocomposites. The latter are either stored in the hive or eliminated, depending on their toxicity. The project is multidisciplinary, including historical aspects, communication, physical characterization and many others.

The sonochemical approach is used at ICSM, complementary to other plasma techniques at PROMES, to compare *natural nanocomposites* with those formed as by-products of sonolysis, and thus help understand *their formation by the honey bees generating ultrasounds.*

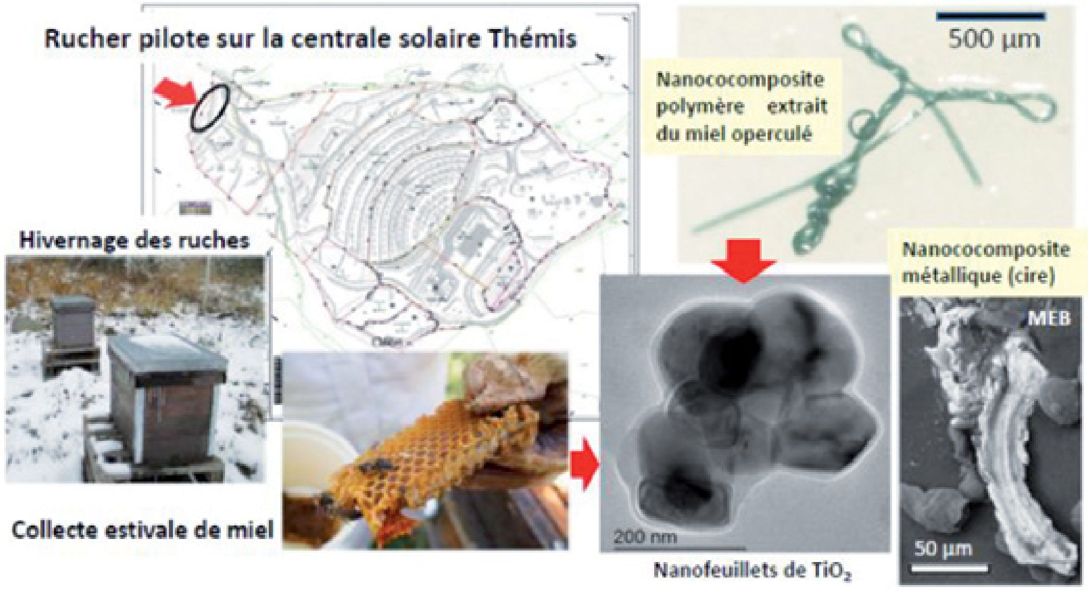


Fig. 1: Honey bee hives in the project, and observed natural nanocomposites produced by the bees (courtesy MA Courty).

SONOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF ACTINIDE OXIDE NANOPARTICLES

M. Virot, C. Micheau, L. Bonato, A. Mesbah, E. Dalodière, X. Le Goff, M. Odorico, O. Diat, T. Chave, N. Dacheux, V. Morosini, S. Dourdain., S. I. Nikitenko
T. Dumas, P. Moisy, L. Venault (ISEC CEA-Marcoule)
T. Wiss, O. Dieste Blanco (Joint Research Centre, Karlsruhe, Germany)
C., Hennig, Prieur, A. Rossberg (Helmholtz-Zentrum Dresden, Germany)
D. K. Shuh, T. P. Tyliszcak (LBNL Berkeley, USA)
D. Menut, P. L. Solari (SOLEIL, Gif-sur-Yvette)

Actinide research at the nanoscale is gaining fundamental interest due to environmental and industrial issues. The knowledge of the local structure and speciation of actinide nanoparticles (NPs), which possibly exhibit specific physico-chemical properties in comparison to bulk materials, would help in a better and reliable description of their behaviour and reactivity. The extended sonication of PuO_2 powder under reducing atmosphere has been found to yield very stable intrinsic *Pu(IV) colloidal suspensions.*[1] Complementary techniques (Vis-NIR absorption, XAS, NEXAFS and HR-TEM) allowed us to describe these colloids as stable suspensions of core-shell NPs composed of a crystalline PuO_2 core covered by hydrolyzed Pu(IV) moieties responsible for their high stability.[1]

A combination of synchrotron small angle X-ray scattering (SAXS) with X-ray absorption spectroscopy (XAS) has been used recently to characterize these two kinds of stable Pu intrinsic colloids.[2] The multi-scale structural properties of these colloidal suspensions were found to be strongly influenced by the synthesis route – spherical NPs of ca. 2.0 nm and elongated structures measuring 5.7 nm of thickness and >30 nm long for hydrolytic and sonolytic approaches respectively. This difference results from the synthesis mechanism and can be attributed to NP aggregation in the absence of capping-ions. The results obtained by both SAXS and XAS approaches converge in the description of Pu(IV) intrinsic colloids as core–shell NPs made up of a PuO_2 core covered with a disordered Pu–O shell characterized by a splitting of Pu–O and Pu–Pu distances and an associated strong increase of associated DWF parameters correlated with the NP shrinking.[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 An(IV) local structure investigated by EXAFS spectroscopy.[3] Particularly, the probed An(IV) first oxygen shell evidences an analogous behaviour for both Pu and Th oxides. This observation confirms that the often observed and controversial 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 PuO_{2+x} species.[3]

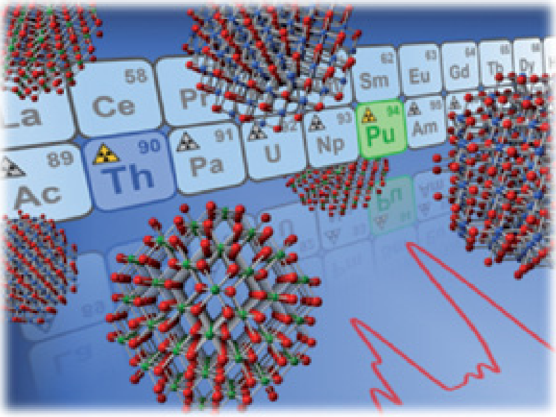


Fig. 1 : Scheme used as a cover picture for Nanoscale Advances and representing the study of AnO_2 NPs.

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[1] Dalodière E., Virot M., Morosini V., Chave T., Dumas T., Hennig C., Wiss T., Dieste Blanco O., Shuh D. K., Tyliszcak T., Venault L., Moisy P., Nikitenko S. I. **Insights into the sonochemical synthesis and properties of salt-free intrinsic plutonium colloids** - *Scientific Reports* (2017) 43514.

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[3] Bonato L. Virot M., Dumas T., Mesbah A., Dalodière, E., Dieste Blanco O., Wiss T., Le Goff X., Odorico M., Prieur D., Rossberg A., Venault L., Dacheux N., Moisy P., Nikitenko S. I. **Probing the local structure of nanoscale actinide oxides: a comparison between PuO_2 and ThO_2 nanoparticles rules out PuO_2+x hypothesis** - *Nanoscale Advances 1* (2020) 214-224.

SONOCHEMICAL DISSOLUTION OF REFRACTORY ACTINIDE OXIDES

M. Virot, L. Bonato, X. Le Goff, A. Mesbah, N. Dacheux, S. I. Nikitenko
T. Dumas, P. Moisy (ISEC CEA-Marcoule)

In heterogeneous systems, acoustic cavitation goes with strong physical effects such as erosion of surfaces, grain fracture, depassivation, increase of mass transfer and decrease of diffusion layers. The additional chemical transformation of the sonicated media coupled to the specific activation of surfaces could be promising for current and future nuclear fuel reprocessing. Within this frame, the behavior of *refractory actinide oxides is investigated under ultrasound irradiation* in collaboration with DES/ISEC/DMRC department (Atalante facility, Marcoule).

The influence of the sample morphology and experimental conditions towards the sonochemical dissolution of nanoscale ThO_2 samples in sulfuric acid media has been studied. Significant sonochemical dissolution rates and yields were observed at 20 kHz under Ar/O_2 atmosphere in dilute 0.5 M H_2SO_4 at room temperature, contrasting with the generally reported high refractory behavior for ThO_2. The dissolution of ThO_2 combines the physical effects driven by the acoustic cavitation phenomenon, the complexing affinity of Th(IV) in sulfuric medium and the sonochemical generation of H_2O_2. *These sonochemical conditions further allow the observation of the partial conversion of ThO_2 into a scarce Th(IV) peroxo sulfate with 1D morphology* resulting from one or both following processes: dissolution/reprecipitation or formation of an intermediate Th(IV) surface complex (see figure).

In a recent study, the preparation and structural characterization of this original Th peroxo sulfate has been carried out in silent conditions. This dihydrate compound crystallizes at room temperature in the form of stable 1D polymeric microfibres. A combination of laboratory and synchrotron techniques allowed to solve the structure of the $Th(O_2)(SO_4)(H_2O)_2$ compound, which crystallizes in a new structure type in the space group Pna21 of the orthorhombic crystal system. In this structure, the peroxide ligand particularly coordinates to the Th cations in an unusual $\mu_3-\eta^2:\eta^2:\eta^2$ bridging mode, forming an infinite 1D chain decorated with sulfato ligands exhibiting simultaneously monodentate and bidentate coordination modes.

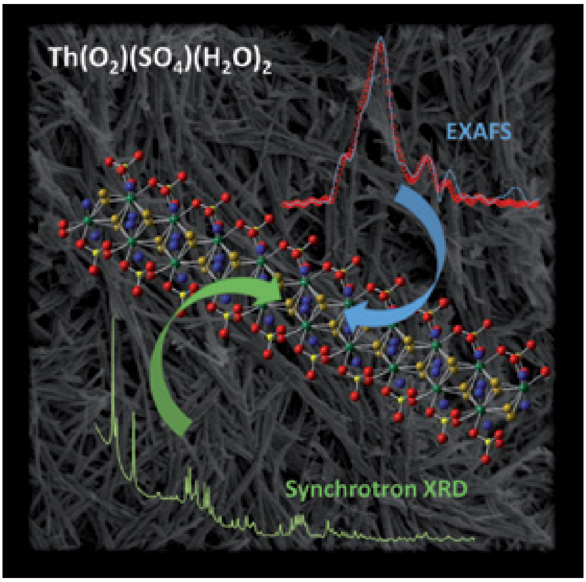


Fig. 1: Frontispiece of Chem Eur J journal showing in the back the 1D polymeric microfibers. $Th(O_2)(SO_4)(H_2O)_2$ compound crystallizes in the space group Pna21 of the orthorhombic crystal system.
Peroxide ligands coordinate Th cations in an unusual coordination mode.
Within this frame, the behavior of refractory actinide oxides is investigated under ultrasound irradiation in collaboration with DES/ISEC/DMRC department (Atalante facility, Marcoule).

[1] Bonato L., Virot M., Le Goff X., Moisy P., Nikitenko S. I. - **Sonochemical dissolution of nanoscale ThO_2 and partial conversion into a thorium peroxo sulfate** - *Ultrasonics Sonochemistry* (2020) 69, 105235.

[2] Bonato L., Virot M., Dumas T., Mesbah A., Lecante P., Prieur D., Le Goff X., Hennig C., Dacheux N., Moisy P., Nikitenko S. I. **Deciphering the Crystal Structure of a Scarce 1D PolymericThorium PeroxoSulfate** - *Chemistry: A European Journal* (2019) 25, 9580-9585.

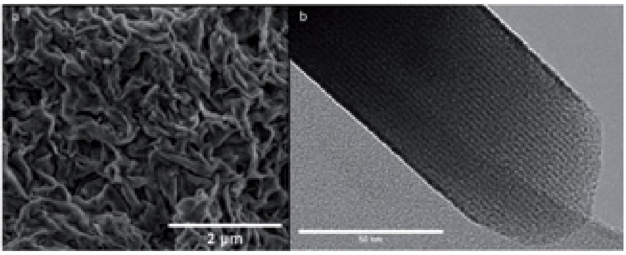
DEVELOPMENT OF ACTINIDES OXIDES NANO-HYBRID MATERIALS

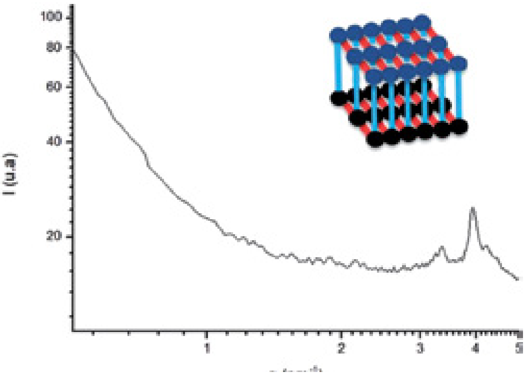
E. Ré, J. Monier, J. Maynadié, X. Le Goff, D. Meyer

This project deals with *the conception of new nano-structured hybrid materials* based on nanocrystals of actinide oxides, which can display unusual properties with respect to the single nano-crystalline counterpart. In this way, we are focused our attention on the development of *two bottom-up synthesis strategies.*

First, we developed a *one-pot approach*. Using a ternary molecular system (dicarboxylic acid, oleylamine, dibenzyl ether), it is possible to obtained nano-sheets displaying lamellar structuration presenting UOx nano-lamellae around 1 nm (figure 1). Moreover, in the nano-sheets, the interlamellar distance could be adjusted in accordance with the length of the employed dicarboxylic acid.[1]

The second strategy is based on the *self-assembly of functionalized nanoparticles*. This strategy starts with the well-known synthesis of metal-oxide nanocrystals (UO_2, ThO_2 or MO_x) stabilized with oleic acid. Then, the surface of the pre-synthesized nanoparticles is modified using capping agents having reactive pendant functionality (alkyne, azide, ionic moiety). To obtain the final material, the crosslinking of modified nanocrystals could be operated through a click-chemistry step catalyzed by Cu(I) or electrostatic interactions. The final goal consists in the formation and the characterization of heterometallic nano-hybrid superlattices.





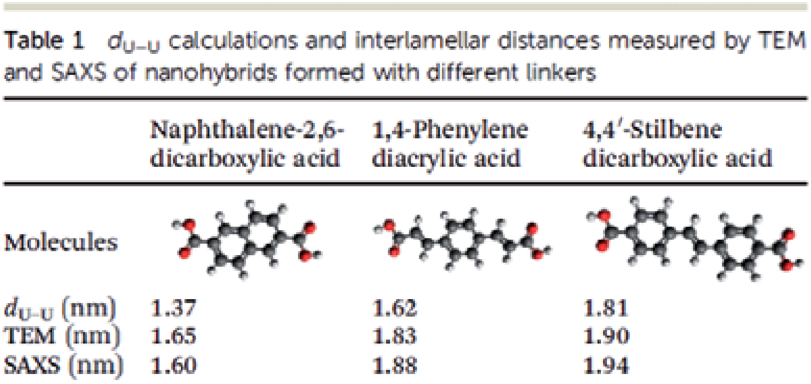


Table 1 d_{U-U} calculations and interlamellar distances measured by TEM and SAXS of nanohybrids formed with different linkers

	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

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[1] Ré E., Le Goff X., Toquer G., Maynadié J. and Meyer D. - **Linker-assisted structuration of tunable uranium-based hybrid lamellar nanomaterials** - *New J. Chem.* (2020) 44, 8463

PHOSPHATE BASED MATRICES FOR THE SPECIFIC CONDITIONING OF ACTINIDES

Qin Danwen, Rafiuddin Mohammed Ruwaid, Mesbah Adel, Szenknect Stéphanie, Clavier Nicolas, Dacheux Nicolas.
Shelyug Anna, Sergey Ushakov, Navrotsky Alexandra (UC Davis)

For long, phosphates based ceramics ($REEPO_4$) appeared as promising candidates for the specific conditioning of tetravalent and trivalent actinides as well as for plutonium excess coming from dismantled nuclear weapons. Such interests come not only from the easy way of fabrication of such materials, but also from their good resistance to radiation damage, interesting sintering capability and high chemical durability. These materials are known to be widespread minerals with a general formula $REEPO_4$ (REE = Ln, Sc Y). Monazite is encountered for light rare-earth elements (LREE) with larger ionic radii (i.e. for Ln = La – Gd) and crystallizes with the monoclinic $P2_1/n$ structure type. Xenotime is formed for heavier and smaller elements (Y and Ln = Tb to Lu) and crystallizes with the zircon structure type ($ZrSiO_4$) in the tetragonal system ($I4_1/amd$). The incorporation of actinides within these structures goes through different substitution mechanisms (Fig. 1).

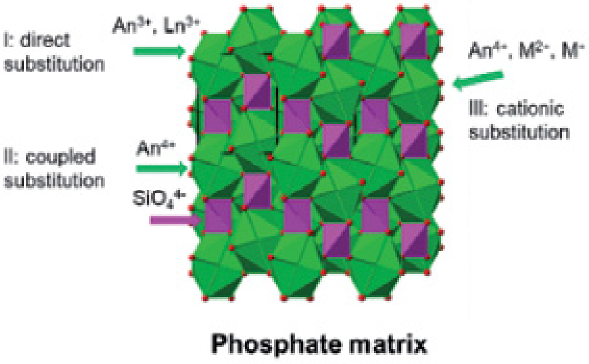

Fig. 1: Substitutions in phosphate matrices

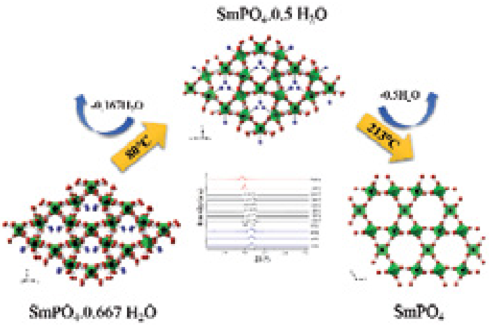

Fig. 2. Dehydration of $SmPO_4.0.667\ H_2O$

These materials are often synthesized by solid-state routes which may lead to heterogeneous samples. Moreover, these protocols usually require successive grinding steps which can be considered as an important drawback when handling radioactive materials. We recently developed various wet chemistry routes, which appeared to be promising in order to prepare pure and homogeneous compounds. The synthesis of the target materials operated directly by precipitation or/and by hydrothermal methods. Also, another path to obtain these materials consisted in synthesizing low temperature precursors, such as rhabdophane[1] and churchite[2] for LREE and HREE, respectively.

As a recent progress, the dehydration process of the rhabdophane structure was toughly characterized leading to the identification of three different successive forms as viewed in Fig. 2 for $SmPO_4.0.667\ H_2O$.

In addition, the incorporation of thorium in the monazite structure, leading to $Ln_{1-2x}Ca_xTh_xPO_4.nH_2O$ (Ln = Pr, Nd)[3] was successfully achieved by wet chemistry route. The development of a multiparametric study allowed the determination of the appropriate conditions required to form pure samples and then the monitoring of their evolution toward anhydrous monazite-cheralite solid solution[4]. More recently, pure solid solutions of $Th_{1-x}Er_x(SiO_4)_{1-x}(PO_4)_x$ were obtained and their thermal stability was explored in the in the frame of the ANR X-MAS project. These results pave the way for the study of uranium (IV) based materials, which requires particular attention due to its potential oxidation when heating.

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[1] Mesbah A., Clavier N., Elkaim E., Szenknect S., Dacheux N. – **In pursuit of the rhabdophane crystal structure: from the hydrated monoclinic $LnPO_4.0.667H_2O$ to the hexagonal $LnPO_4$ (Ln = Nd, Sm, Gd, Eu and Dy)** – *Journal of Solid State Chemistry* (2017) 249, 221-227.

[2] Subramani T., Rafiuddin M.R., Shelyug A., Ushakov S., Mesbah A., Clavier N., Qin D., Szenknect S., Elkaim E., Dacheux N., Navrotsky A. – **Synthesis, Crystal Structure, and Enthalpies of Formation of Churchite-type $REPO_4{\cdot}2H_2O$ (RE = Gd to Lu) Materials** – *Crystal Growth & Design* (2019) 19, 4641-4649.

[3] Qin D., Mesbah A., Gausse C., Szenknect S., Dacheux N., Clavier N. – **Incorporation of thorium in the rhabdophane structure: Synthesis and characterization of $Pr_{1-2x}Ca_xTh_xPO_4{\cdot}nH_2O$ solid solutions** – *Journal of Nuclear Materials* (2017) 492, 88-96.

[4] Qin D., Mesbah A., Clavier N., Szenknect S., Dacheux N. – **From Th-Rhabdophane to Monazite-Cheralite Solid Solutions: Thermal Behavior of $Nd_{1-2x}Th_xCa_xPO_4{\cdot}nH_2O$ (x = 0–0.15)** – *Crystal Growth & Design* (2019) 19, 2794-2801.

PHOSPHATE BASED COMPOUNDS FOR THE CONDITIONING OF ACTINIDES: SINTERING AND CHEMICAL DURABILITY

Qin Danwen, Clavier Nicolas, Stéphanie Szenknect, Adel Mesbah, Nicolas Dacheux.
Shelyug Anna, Sergey Ushakov, Navrotsky Alexandra (UC Davis)

A milestone towards the use of phosphate based ceramics as specific matrices for the conditioning and final disposal of actinides consists in the evaluation of their resistance to radiation damage, to their sintering capability and to their chemical durability. In this frame, an approach based on the direct sintering of low temperature precursors leading to the targeted final ceramics in a unique step was developed. Simultaneously, sintering maps of $Nd_{1-2x}Ca_xTh_xPO_4$ solid solutions (Monazite-Cheralite structure type) were established. The obtained results showed no significant grain growth at 1200°C, densification appearing to be the predominant mechanism. Conversely, the complete densification quickly operated at 1400°C and was followed by an important grain growth. However, the Th-Ca coupled substitution inhibited both densification and grain growth mechanisms, leading the maximum grain size (D_{50}) to decrease by one order of magnitude. Concomitantly, the activation energy associated with the densification ranged from 361 ± 90 to 530 ± 90 kJ.mol^{-1}, depending on the chemical composition considered.[1]

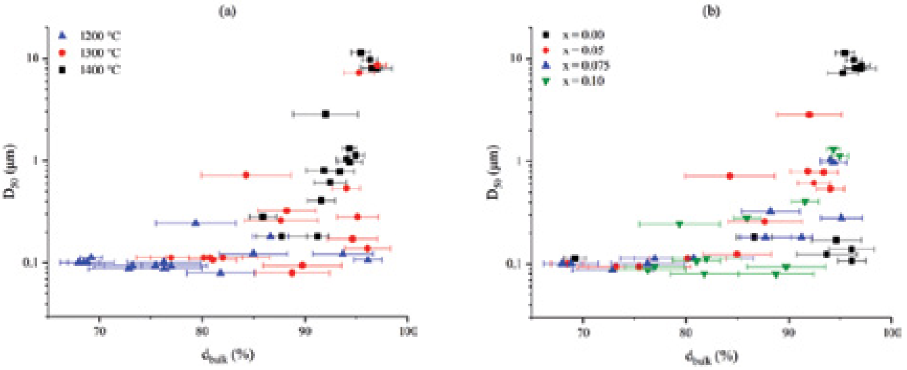

Fig. 1. Sintering map obtained for $Nd_{1-2x}Ca_xThxPO_4$ ceramics. All the samples are gathered depending on their sintering temperature (a) or on their chemical composition (b).

The fully characterized powdered or sintered $Nd_{1-2x}Ca_xTh_xPO_4$ samples were subject to leaching / dissolution experiments under various conditions. From a kinetic point of view, the normalized dissolution rate $R_{L,0}$ of the $Nd_{0.8}Ca_{0.1}Th_{0.1}PO_4$ monazite/cheralite was about 3×10^{-5}g.m^{-2}.d^{-1} at 25°C in 1M HNO_3. All the obtained values were found to be lower than those reported for other ceramics, such as britholite and zirconolite. The apparent activation energy associated with the dissolution reaction, E_A, equaled 46 ± 7 kJ.mol^{-1} and the logarithm of associated apparent normalized dissolution rate constant, k', reached (3.5 ± 1.0) × 10^3 g.m^{-2}.d^{-1}. Moreover, when saturation conditions were reached, Th-rhabdophane $Nd_{0.8}Ca_{0.1}Th_{0.1}PO_4.nH_2O$ or monazite-cheralite $Nd_{0.8}Ca_{0.1}Th_{0.1}PO_4$ were suspected to act as the solubility-controlling neoformed phase. The associated solubility product was found to $K_{s,0}° = 10^{-31.3 \pm 0.1}$. Also thermodynamic data associated to the formation of both phases from elements were determined. The $\Delta_f G$, $\Delta_f H$ and $\Delta_f S$ values (Th-rhabdophane / monazite-cheralite) were equal to - 2097 ± 9 and - 1868 ± 9 kJ.mol^{-1}, - 2205 ± 8 and - 1980 ± 9 kJ.mol^{-1}, - 360 ± 58 and - 376 ± 58 J.mol^{-1}.K^{-1} for Th-rhabdophane and Th-monazite-cheralite, respectively .

In addition of these ongoing studies, irradiation are planned in the frameworks of the ANR JCJC XMAS and of the NEEDS DEPHO in order to examine the resistance of these materials to radiation damage and the potential consequences on their chemical durability.

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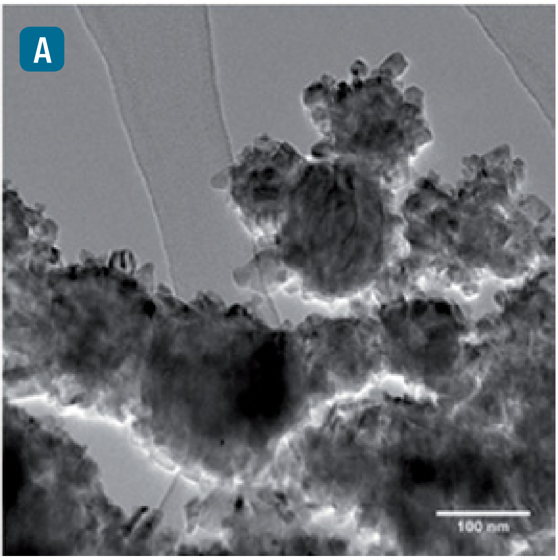
[1] Qin D., Mesbah A., Lautru J., Szenknect S., Dacheux N., Clavier N. – **Reaction sintering of rhabdophane into monazite-cheralite $Nd_{1-2x}Th_xCa_xPO_4$ (x = 0 – 0.1) ceramics** – *Journal of the European Ceramic Society* (2020) 40, 911-922.

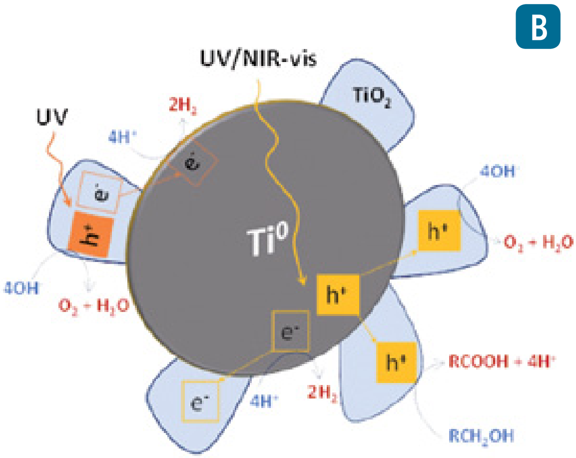
SONOCHEMICAL SYNTHESIS OF NANOMATERIALS FOR ENERGY AND ENVIRONMENT

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[1]. Ti^0 is composed of quasi-spherical particles (30-150 nm) of metallic titanium coated with a metastable titanium suboxide Ti$_3$O.[2] *SHT treatment at 150-214 °C leads to the oxidation of Ti$_3$O and partial oxidation of Ti^0 followed by formation of nanocrystalline shell (10-20 nm) composed of TiO$_2$ anatase* (see fig.).

It was shown that Ti@TiO$_2$ NPs exhibit strong photothermal effect in the photocatalytic process of hydrogen production from aqueous solutions of glycerol.[1,2] Apparent activation energy equal to $E_{act} = 32 \pm 2$ kJ mol^{-1} indicates that the thermal effect is related to the diffusion of reaction intermediates at catalyst surface rather than to the activation of chemical bonds. Effective electron–hole separation between Ti core and nanocrystalline TiO$_2$ anatase shell in Ti@TiO$_2$ NPs was confirmed by photoluminescence spectroscopy. Kinetic study highlights the importance of TiO$_2$ nanocrystalline shell for efficient H$_2$ generation. Electrochemical impedance spectroscopy points out more efficient electron transfer for Ti@TiO$_2$ nanoparticles in correlation with photocatalytic data.





TEM image of Ti@TiO$_2$ NPs **A** *and graphical sketch of suggested mechanism of H$_2$ photocatalytic formation* **B** .

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[1] Nikitenko S.I., Chave T., Le Goff X. - **Insights into the photothermal hydrogen production from glycerol aqueous solutions over noble metal-free Ti@TiO$_2$ core-shell nanoparticles** - *Part. Part. Syst. Char.* (2018) 35, 1800265.
[2] El Hakim S., Chave T., Nada A.A., Roualdes S., Nikitenko S.I. - **Tailoring noble metal-free Ti@TiO$_2$ photocatalyst for boosting photothermal hydrogen production** – *Appl. Cat. A: General* (2021) submitted.

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

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C. Mahé, C. Lepeytre (ISEC CEA-Marcoule)
M. Hamel (DRT/LIST CEA-Saclay)

Carbon Dots (CDs) are luminescent nanoparticles quite recently discovered. 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 and more particularly the interaction with either nuclear radiation or ions in solution. In both cases, the main idea is to use these luminescent materials to detect either radiation or pollutants in water.

For example, the presence of ions in solution can lead to some CDs luminescence quenching making easier the detection of these ions. It is particularly true in the case of Hg ions whose quenching effect on CDs decorated with amino and carboxylic groups on the surface is high for low concentrations (Fig.1).

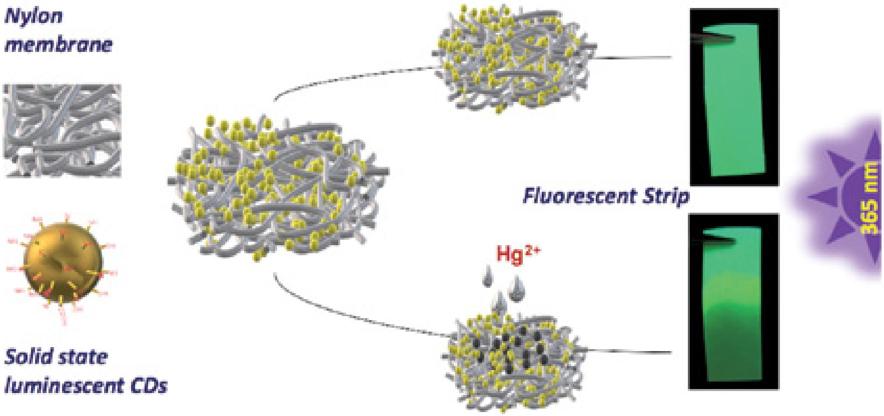


Figure 1: Development of fluorescent strips functionalised with CDs for mercury detection. The presence of Hg ions close to CDs cancels its luminescence (quenching). Limit of detection: 50µmol/L

On the other hand, CDs luminescence can also be produced by nuclear radiations allowing development of a new class of scintillators (Fig. 2). This emerging topic is very promising due to the quite unique properties of CDs. First studies on this topic showed that the materials response and therefore its luminescence is very dependent to CDs core structure (amorphous/graphitic) and to the nature of the surface group. Until now, only hydrophobic nitrogen doped CDs exhibit luminescence under specific ^{90}Sr β radiation. This could be a powerful result regarding the fact that only a few solid state scintillators allow specific detection of β radiations.

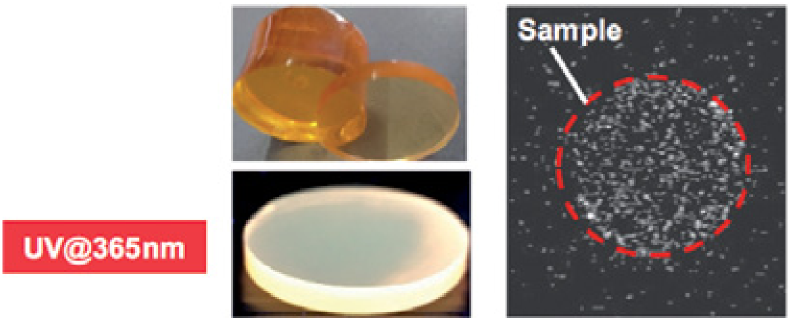


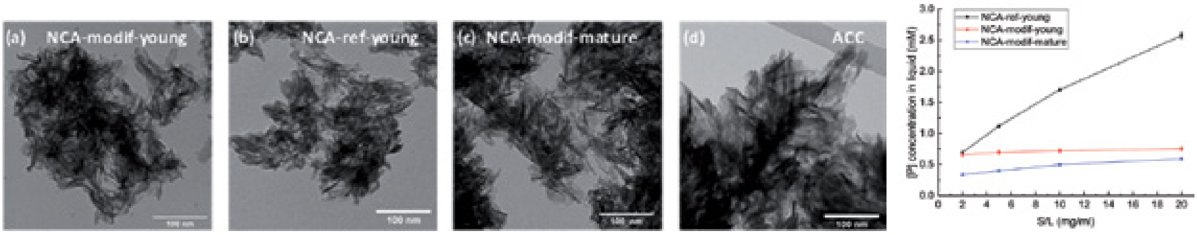
Figure 2: Polyvinyltoluene functionalised with CDs and its luminescence under UV and β radiation. Luminescence under β radiation was collected in a blackbox with an ultrasensitive CCD camera

BIOLOGY AND METAL EXCHANGE: PROTEINS AND BIOMIMETIC BONES

J. Wang, D. Bourgeois, D. Meyer
P. Delangle, C. Vidaud (DRF CEA-Grenoble)
G. Carle (Univ. Nice)
A. Hagège (ISA Lyon)

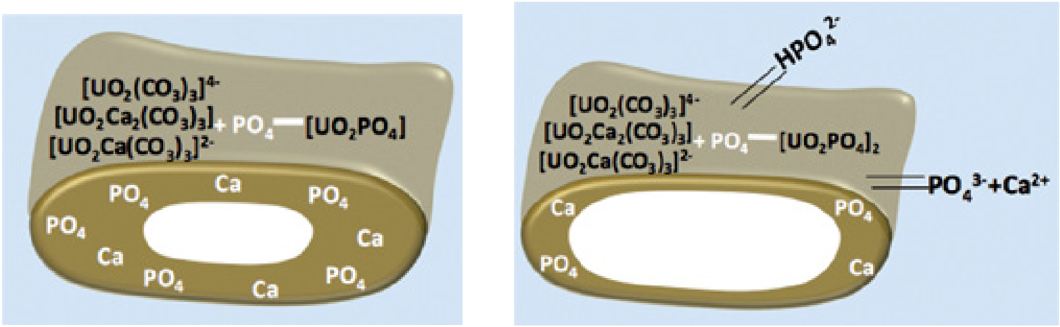
Whatever its entry route into the body, the uranyl cation (UO_2^{2+}) is sent through the blood to its target organs: kidneys, for rapid elimination, and skeleton, for long term sequestration. *The accumulation of uranyl in bones leads to an increased bone resorption and/or and inhibition of bone formation.* To limit this accumulation, and favour excretion as a soluble form, several molecules with decorporating properties were evaluated. But today none of these presents a real efficency, and the conception of new molecules deserves a prior understanding of chemical, biochemical and cellular mechanisms which lead to the accumulation of UO_2^{2+} into the skeleton.

Deciphering the mechanisms of metal exchanges between blood plasma and bone requires the reproduction of this complex physicochemical system: bone mineral is a poorly crystalline non-stoichiometric apatite, in equilibrium with blood plasma, a supersaturated calcium phosphate solution. Careful control of synthesis of nanocrystalline apatites possessing similar structural features as bone mineral, followed by preliminary contact with adequate buffered solution enabled the set up of in vitro experiments that can account for solid/liquid exchange in biomimetic conditions. The interaction between uranium(VI) and bone mineral was studied according to this model, and results obtained are in full agreement with available biological data, and demonstrate that existing information using crystalline apatites is nont relevant. *Uranium accumulation* in bone *is* thus not *the result* of the precipitation of a uranium phosphate phase, but is due to *simple diffusion into the surface amorphous layer*, which can be described as a physical sorption using Langmuir model.[1]



TEM images of miscellaneous synthetic biomimetic apatites and related P and Ca exchange

This approach led us to the proposition of a detailed mechanism for the uranium(VI) exchange with bone matrix. The chemical model was employed for the evaluation of various uranium(VI) chelating peptides, in order to evaluate their ability to remove uranium(VI) embedded in the bone mineral matrix after contamination.



Young bone *Mature bone*

Proposed uranium(VI) exchange process model with young and mature bone mineral matrix.

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[1] Wang J., Bourgeois D., Meyer D. - **Mimicking bone–metal exchanges with synthetic nanocrystalline apatites** - *Mater. Adv.* (2020) 1,3292-3301

RICE HUSK ASH (RHA): A CONVENIENT MATERIAL FOR CIRCULAR ECONOMY

B. Russo, D. Rébiscoul, J. Causse, C. Rey, X. Deschanels
A. Ayral (Inst. Européen Membranes, Montpellier)

ICSM is located in south of France, at about 100 kms from Camargue region, a wetland where most of the French rice is produced. In the rice life cycle, there is a step called shelling where the inedible part is removed from the comestible part of the grain. This inedible part is known as Rice Husk (RH) and represents around 20% of the total mass of a paddy rice grain, which is the name of an unhusked grain. 17000 tons of RH are produced every year without any satisfying industrial outlets until now.

Our group aims to develop an eco-friendly sorbent, directly produced from this biomass by product, in order to facilitate industrial outflows treatment or to handle metallic pollution present in several rivers located in old mining sites around ICSM (Carnoulès, St Laurent-le-Minier, …). RH can be considered as a convenient sorbent precursor due to the presence of a large amount of natural silica (≈ 20 wt%), cellulose, hemicellulose and lignin in the structure. It is therefore possible to prepare nanocomposite RHA materials of either pure silica or mix of carbon and silica after a simple thermal treatment under either oxidative (air) or inert atmosphere (N_2, Ar). In the latter case, C/SiO_2 nanocomposites are potential candidates to depollute outflows with both mineral and organics contaminants.

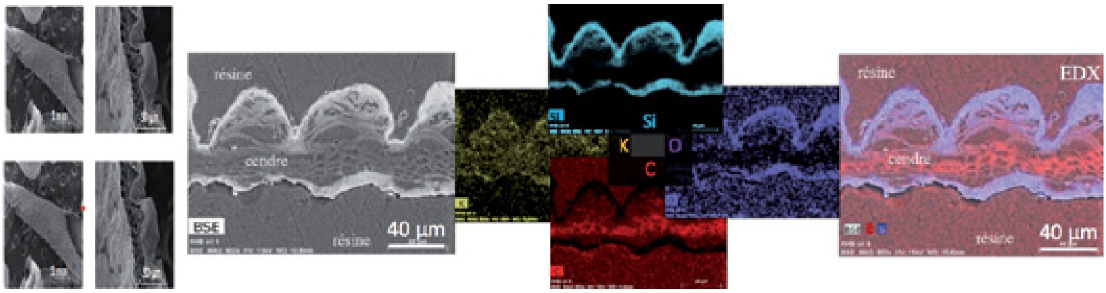


Figure 1: SEM images showing morphology of RHA calcined at 500°C under Argon atmosphere and the repartition of silica, carbon, oxygen and potassium in its microstructure

Figure 1 shows the presence of a large part of potassium in the whole range of RHA. This potassium, as well as calcium, comes from the soil where the rice grows. Our recent studies proved that the presence of potassium in RHA is mandatory to remove metallic ions from polluted outflows. The mechanism responsible for this removal is ion exchange between metallic ions and K and Ca from the RHA.

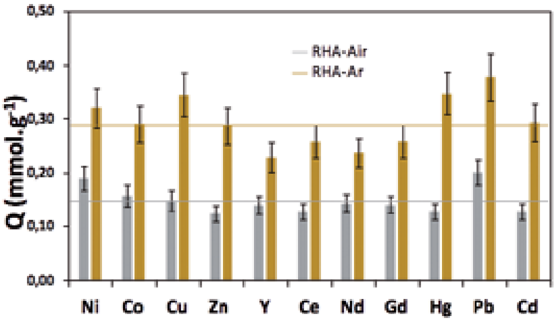


Figure 2: Sorption capacity for RHAs with different metal ions.

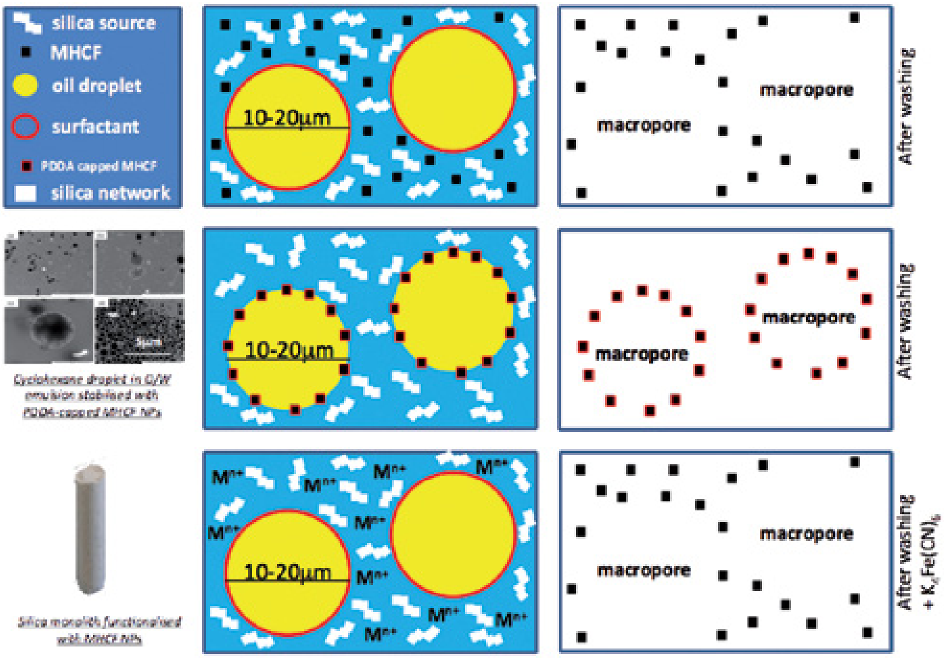
Figure 2 shows that most of metallic ions are exchanged with K and Ca from RHA. It is noteworthy that pollutants often encountered in old mining sites like Hg, Pb and Cd are caught in RHAs. In the case of SiO_2/C nanocomposites prepared under Ar atmosphere, more K is accessible for ion exchange due to a kind of template effect induced by the presence of carbonaceous phase during heating treatment.

A PREMAT funding from Occitanie Region allows now to consider a transfer from the lab to pre-industrial scale (2020-2022). This step will be used to study economic considerations such as business plan and to make the RHA more adapted to continuous treatment of liquid outflows through shaping of the powder.

TEMPLATING NANOMATERIALS WITH EMULSIONS DROPLETS SIZE MATTERS

J. Causse, A. Sommer-Marquez, C. Mansas, N. Talha

The use of soft matter to control long distance mesostructure in nanomaterials is deeply investigated since the discovery of mesoporous silica. Soft matter can therefore be designed under various forms like thin films, bilayers, vesicles, surfactant solutions or emulsions in order to give specific properties to the final material. Emulsions are very handy because this complex fluid can favour versatile properties whether water-in-oil or oil-in-water emulsions are considered or if micro- or macro- emulsions are used. Indeed, emulsions are dispersions of a liquid phase in another immiscible liquid phase with various different possibilities. Depending on the droplet size, their stability varies from days to months and is convenient for texturing nanomaterials. However, changing this droplet size results in changing the size of the reactor. Indeed, while microemulsions are convenient for preparing nanoparticles of all kinds (spherical, core-shell, porous…), macroemulsions can be used to develop inorganic macroporous materials due to quite high oil droplet size (several micrometers). ICSM/LNER develops a part of its research activities on this topic. For the moment, emulsion templated nanomaterials have been used for preparing nanomaterials with energy field of interest and more particularly nuclear decontamination or CO_2 sequestration.[1] While nanodroplets of water-in-oil microemulsions have been used as template to shape core-shell nanoparticles able to entrap Cesium[2], silica monoliths with hierarchical porosity have been prepared from High-Internal Phase oil-in_water Emulsions (HIPE). While in the first case droplets are used as nanoreactor, in the latter case micrometer sized droplets are used to generate macroporosity of the materials. Several ways of functionalisation with Metal Hexacyanoferrates (MHCF) are developed as explained in Figure. These synthetic routes lead to different types of monoliths with regard to the chosen method. MHCF can either be generated in the aqueous phase or at the oil/water interface to promote Pickering emulsions, stabilised in this case with a particle of interest.



Scheme summarizing the multiple synthetic routes developed by ICSM/LNER to achieve silica monoliths functionalised with MHCF NPs.

[1] A. Vaca-Oviedo, J. Causse, A. Sommer-Márquez, **MRS Advances**, 5, 727-733, (2020)
[2] Mansas, C., Grandjean, X., Deschanels, X., Causse, J., Ph-D, University of Montpellier, 2017.

SYNTHESIS OF URANIUM OXIDE COMPOUNDS BY SOL-GEL PROCESSES

Zijie Lu, Diane Rébiscoul, Thomas Zemb, Cyrielle Rey, Julien Monnier, Xavier Deschanels

In the framework of generation IV development for nuclear reactors, two different routes involving a sol-gel process are investigated to obtain actinide mixed oxides.

Conversion of actinides nitrate by Solution Combustion Synthesis

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. In a first step of the process during the thermal treatment leading to the dehydration of these precursors a gel is obtained, and finally the ignition occurs at very low temperature (~200°C) to produce a white powder composed of metal oxide[1] (Figure 1). Solid solutions of $U_yLn_{1-y}O_{2+X}$ (Ce, Gd…) were successfully synthesized by this technique at temperature about 200°C lower than that of a classical denitration reaction. The process conditions (heating rate, excess of fuel…) influence the characteristics of the final product, i.e. crystallinity of the powders, amount of residual carbon, size of the crystallites, and oxygen stoichiometry.

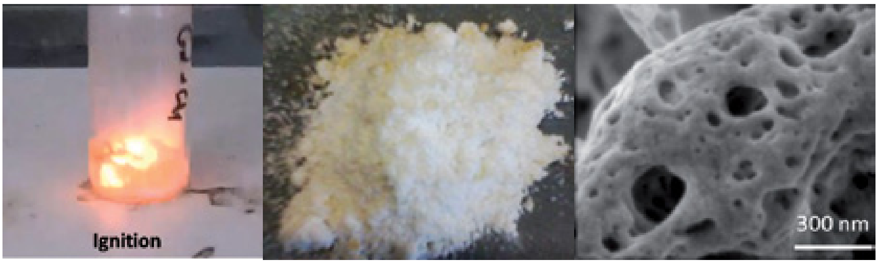


Figure 1 : Example of actinide surrogate powders Gd_20_3 obtained by SCS of Gadolinium nitrate/Glycine

Study of colloidal sol-gel transition for the elaboration of UO_2/ThO_2 materials with controlled and organized mesoporosity (PhD. Zijie Lu).

UO_2/ThO_2 materials having an ordered micro/mesoporosity are prepared either as model materials to study the impact of the pore size on their dissolution in the context of spent nuclear fuel reprocessing and direct repository, or to prepare homogeneous UO_2/AmO_2 and ThO_2/AmO_2 nuclear fuel. To this end, a colloidal sol-gel method was developed using templating agents capable of complexing actinides.[2,3] With this method, the size, the form and the interactions of the polynuclear species/colloids are controlled in the sols[2] (Figure 2) to prepare structured microporous actinide oxide materials.

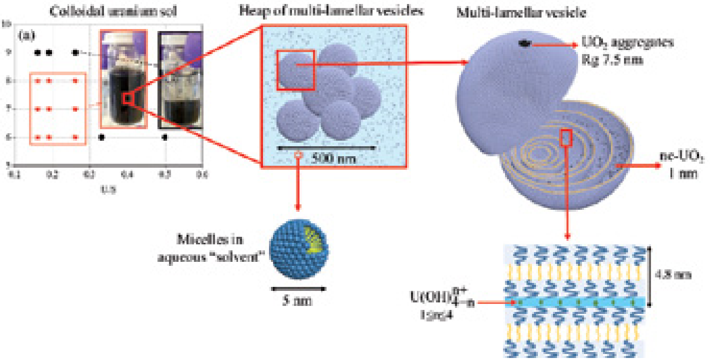


Figure 2: Description of metastable sol of UO_2 nanoparticles supported by multi-lamellar vesicles of carboxylate based surfactant.[2]

[1] Monnier, J., C. Rey, S. C. Mohan, J. Causse, E. Welcomme and X. Deschanels - **Conversion of actinide nitrate surrogates into oxide using combustion synthesis process: A facile approach** - *Journal of Nuclear Materials* (2019) 525: 14-21.

[2] Leblanc, M., Causse, J.,Lu, Z., Rébiscoul, D. - **Stable uranium sols as precursors for the elaboration of nanostructured nc-UO2 materials** - *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2017) 522, 18-27.

[3] Lu, Z., Lautru, J., Zemb, T., Rébiscoul D. - **Colloidal sol of UO2 nanoparticles supported by multi-lamellar vesicles of carboxylate based surfactant** - *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* (2020) 603 125207.

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).

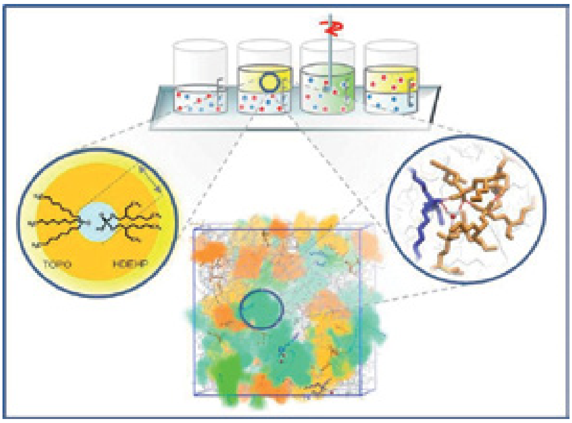
MÉTHODOLOGIES ET THÉORIES POUR LA CHIMIE SÉPARATIVE

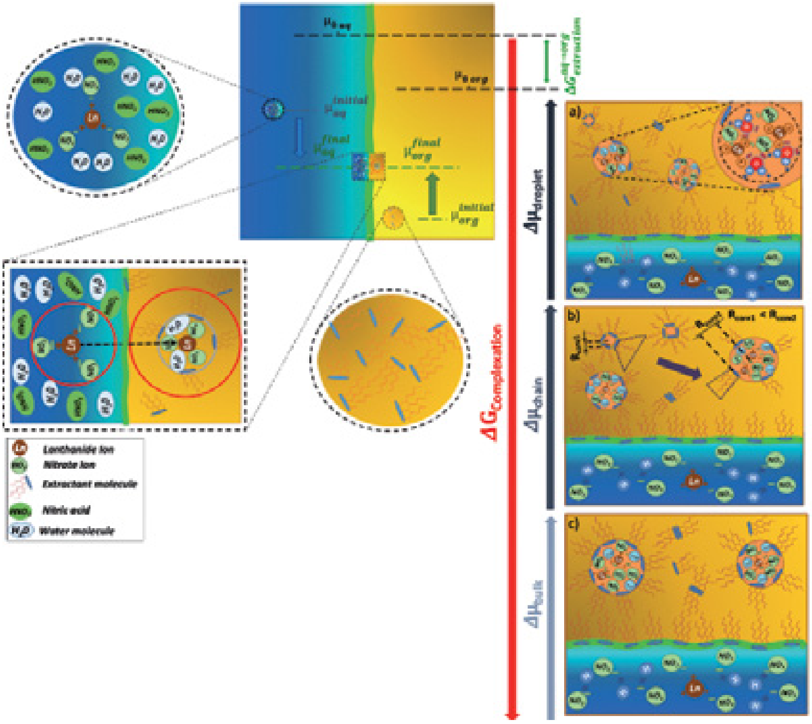
Via le perfectionnement d'outils expérimentaux (microscopies, diffusion du rayonnement, spectroscopies) et la modélisation prédictive multi-échelle (supramoléculaire et colloïdale).

UNDERSTANDING EXTRACTION THANKS TO AGGREGATION

O. Pecheur, J. Rey, Z. LU, A. Artese, A. El Maangar, D. Bourgeois, S. Dourdain, S. Pellet-Rostaing, J-F. Dufrêche, and T. Zemb

Coupled experimental and thermodynamic studies demonstrated the need to take into account weak interactions in the understanding of solvent extraction processes. This well-established industrial technology now beneficiates of a supramolecular approach, complementary to the traditional analysis based on coordination chemistry. In this approach, we focus on the integration of a colloidal approach in the analysis of solvent extraction systems: organic phases employed are complex fluids, in which extracting molecules self-assemble into reverse aggregates.





Via analytical tools employed towards characterization of the organic phases, we emphasized on various examples how aggregation drives extraction. All experimental data is discussed in light of theoretical approaches which propose adequate thermodynamic models and shed light on the importance of entropy on the phenomena.

Acid and diluent effects, synergism and origin of third phase formation have been successfully rationalized thanks to this approach.

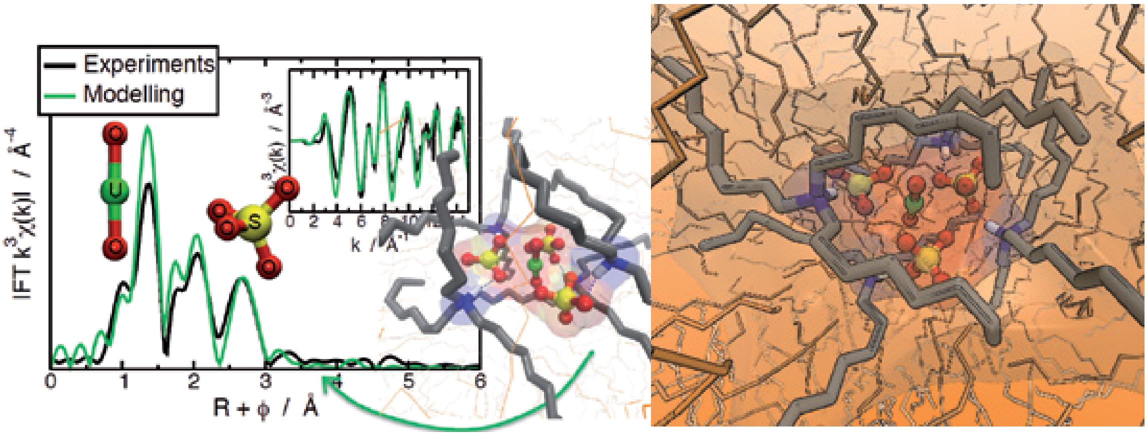
[1] Rey J., Bley M., Dufreche J. F., Gourdin S., Pellet-Rostaing S., Zemb T., Dourdain S. - **Thermodynamic Description of Synergy in Solvent Extraction: II Thermodynamic Balance of Driving Forces Implied in Synergistic Extraction** - *Langmuir* (2017) 33, 13168-13179.
[2] Bourgeois D., El Maangar A., Dourdain S. - **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.
[3] Lu Z. J., Dourdain S., Pellet-Rostaing S. - **Understanding the Effect of the Phase Modifier n-Octanol on Extraction, Aggregation, and Third-Phase Appearance in Solvent Extraction** - *Langmuir* (2020) 36, 12121-12129.

PROBING THE EXISTENCE OF URANYL TRISULFATE STRUCTURES IN THE AMEX SOLVENT EXTRACTION PROCESS

T. Sukhbaatar, M. Duvail, S. Dourdain, G. Arrachart and S. Pellet-Rostaing
T. Dumas, P. Guilbaud (DES/ISEC/DMRC CEA MARCOULE)

Amine Extraction (AMEX process) is the industrial process exploited for the production and purification of uranium. Using tertiary amines as selective extracting agent, it enables the selective extraction of uranyl cations from sulfuric acid leach liquors, which is further exploited yearly to produce 10 % of global electricity consumption. Considering its extensive application, AMEX process is still broadly studied for optimisation and comprehension. However, the core mechanisms of this solvent extraction system remain poorly understood.

Knowledge of the complexe microstructure in solvent extraction phases is mandatory for a full comprehension of ionic separation. Coupling EXAFS with MD simulations for uranyl extraction in sulfuric media with tertiary amine extractants enabled unravelling of unprecedented uranyl tri-sulfate structure.



This behavior confirms the importance of weak association, on molecular organization of an organic phase but also on uranyl coordination sphere as previously demonstrated by other solvent extraction systems. EXAFS analysis showed that octan-1-ol and water do not penetrate the first coordination sphere. However, this raises an interest on the potential role of second sphere molecules (water, octan-1-ol or diluent) on supramolecular and molecular architectures as well as their secondary impact on first coordination spheres.

This study paves the way for better understanding of weak association and diluent effects on molecular and supramolecular structures, which are at the origin of aggregate's thermodynamics in organic phases, and therefore of mechanisms in solvent extraction processes.

Sukhbaatar T., Duvail M., Dumas T., Dourdain S., Arrachart G., Solari P. L., Guilbaud P., Pellet-Rostaing S. – **Probing the Existence of Uranyl Trisulfate Structures in the AMEX Solvent Extraction Process.** – *Chemical Communications* (2019) 55, 7583-7586.

LIQUID/LIQUID INTERFACE OR INTERPHASE IN A SOLVENT EXTRACTION PROCESS

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Philippe Guilbaud (ISEC CEA-Marcoule)
Pierre-Marie Gassin, Gaelle Martin-Gassin (ICGM, Montpellier)

Ion separation using liquid-liquid extraction (LL) or solvent extraction is a key process used in various industrial hydrometallurgy applications, particularly for the nuclear fuel reprocessing. In order to better understand the ion transfer between an aqueous and an organic phase in this type of process it is important to understand i) the speciation of the different ionic and molecular species in each of the two phases in contact and which defines the differences in chemical potential between the two phases but also ii) all the phenomena of molecular and supramolecular interactions at the interface which are at the origin of the potential barriers that can influence the kinetics of ion transfer. Numerous results of volume phase experiments exist and can now be interpreted structurally from molecular dynamics simulations. However, this same experimental/simulation correlated approach at the interface containing ligands and in equilibrium with adjacent volumes has been little explored. Thanks to a collaboration between L2IA and LTSM teams and a laboratory from Montpellier, we first synthesized a diamide extractant containing a chromophore (MAD, figure A) in order to be able to exalt the nonlinear optical signal in a second harmonic generation experiment, which has been proved to be a relevant technique for probing buried fluid interfaces. The different physicochemical and extracting properties of this molecule were studied as well as its response in nonlinear optics (see figure B).[1] In parallel, with LMCT and the LILA team at CEA/DES/ISEC molecular dynamics simulation boxes were built on a reference diamide but also with the new chromophore ligand (see figure C) allowing us to visualize as a function of time the equilibrium of ligand distributions between the organic phase and the LL interface. The objective of comparing the experimental and simulated SHG signal from the simulation boxes has not been still achieved because the SHG response of this new ligand proved to be more complex by revealing a chiral response dependent on the interfacial concentration of the ligand. Nevertheless, it was possible to suggest that for a more amphiphilic extractant and therefore more capable of surface organization and aggregation in solution, a depletion layer close to the interface could generate a potential barrier, source of an ionic transfer more kinetic than diffusive.

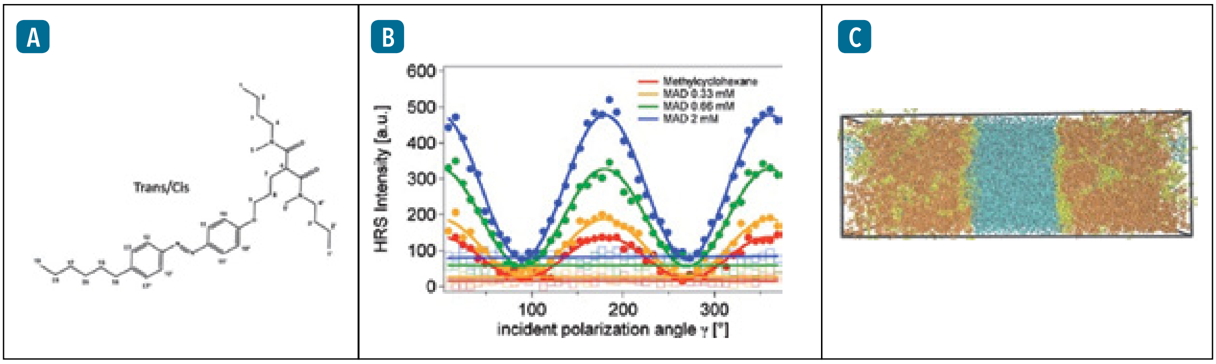

fig. **A** *Chemical structure of synthesized chromodiamide (MAD).*
B *Hyper Raleigh Scattering signal from MAD versus the incident polarization and concentration.*
C *Molecular dynamic simulation box of water/ MAD containing methyl-cyclohexane (0.4M).*

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[1] Wang J., Arrachart G., Giusti F., Gaelle M. G., Gassin P. M., Jonchere A., Diat O., Girard L. - **Synthesis and Characterization of a Chromo-Extractant to the Probe Liquid-Liquid Interface in a Solvent Extraction Process** - *Journal of Physical Chemistry C* (2020) 124, 10916-10923.

CELDI : A NEW TOOL FOR THE DIRECT STUDY OF MATERIALS' CORROSION AND DISSOLUTION

Salacroup Johann, Podor Renaud, Brau Henri-Pierre, Ravaux Johann, Szekneckt Stéphanie
Candeias Antoine (Newtech, Nimes)

In numerous scientific fields such as life, materials and Earth sciences, or quality controls of industrial processes, there is a growing interest for the direct observation - at the submicroscopic scale - of processes occurring at solid / liquid and solid / gas interfaces. So far, only few experimental cells were designed to address this challenging issue. Most of them are devoted to a specific use in Transmission Electron Microscopy (TEM) and are not suitable for observation of large (or thick) samples and the other cells designed to be used in a Scanning Electron Microscope (SEM) chamber do not allow fluid flow.

To address this issue, a dedicated device was developed according to the following requirements: 1) The sample holder must be suitable for large samples. 2) The device must allow the renewal of the fluid through a continuous flow. 3) The device should be sufficiently efficient and secure to be used in any type of conventional SEM. 4) The device should be easy to implement and user friendly. An easy-to-use tool (Fig. 1) was recently tested and patented. This project has been supported by the SATT AxLR. It will be commercialized by the NewTEC company located in Nimes during the first months of 2019.

For the proof of concept, it was used to perform in situ experiments during which series of images was recorded with a SEM, using the back scattered electron detector, high vacuum in the SEM chamber and e-beam acceleration voltage of 30kV. Several images recorded in situ during the dissolution of a $Ce_{0.2}Nd_{0.8}O_2$ ceramic are reported on Fig. 2a. The time between two images can be as low as 20s and the achieved resolution is in the order of a few tens of nanometers. From the image series, local parameters that are characteristic of the material's dissolution can be easily extracted (Fig. 2b). The growth of NaCl crystals was also observed directly from a supersaturated solution. Experiments that last many hours were performed: the liquid system that is inside the stage always remained isolated from the SEM chamber during the complete experiment. 1M acidic and 1M basic liquids can be used.

The CelDi tool will be useful for the study of the dissolution and corrosion of materials. It also offers interesting opportunities for the direct observation of coating formation from liquids and gases. It will be possible to integrate a specific and fast BSE detector in combination with the stage, and work is under progress to develop automatized image processing through dedicated software.

Fig. 1: Artist view of the CelDi tool and pictures of the tool that has been built.

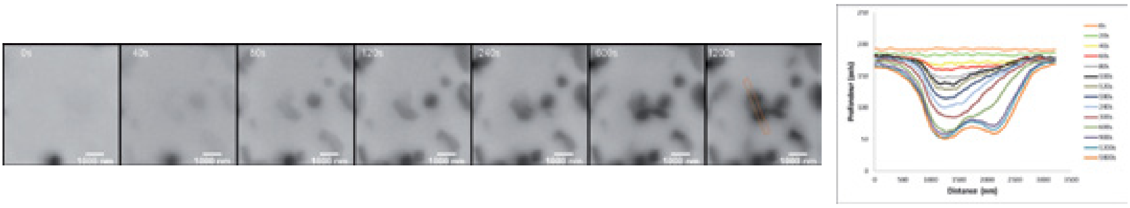
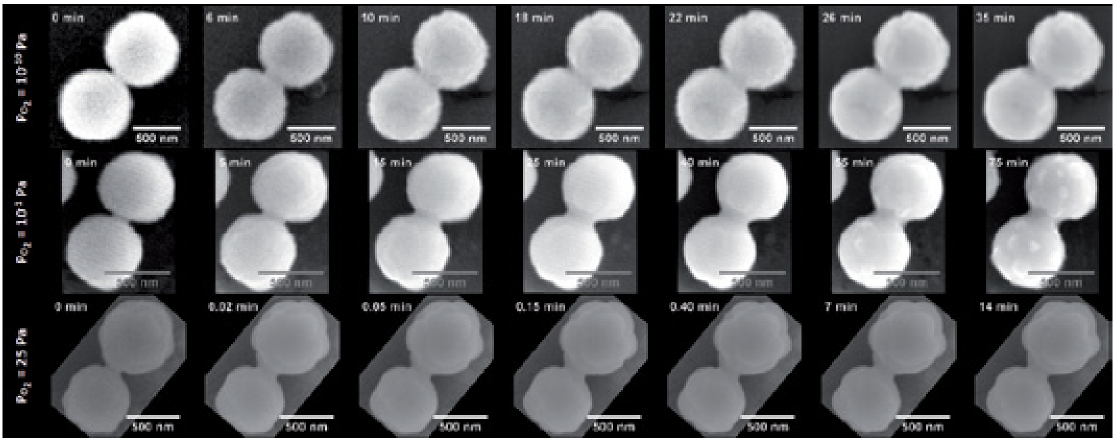


Fig. 2. a) Image series recorded during the dissolution of a $Ce_{0.2}Nd_{0.8}O_2$ ceramic in HCl 0.1M for 1200s.
c) Height profile series extracted from the image series along the orange line drawn in the picture '1200s'.

IN SITU HT-ESEM STUDY OF UO_{2+X} SINTERING FIRST STEP

Clavier Nicolas, Trillaud Victor, Dacheux Nicolas, Podor Renaud

As a key-step for the elaboration of nuclear fuels, the sintering of UO2 has been studied for years. If grain growth processes were investigated thanks to experimental works and calculations, the elaboration of necks during the first step of sintering was generally assessed only through numerical models, frequently based on simple configuration (two spherical single crystals in contact – see fig.). In order to complement such numerical approaches and to collect original and quantitative data to be implemented in the models, the elaboration of necks during the sintering of UO_{2+x} microspheres was experimentally observed *in situ* by High Temperature Environmental Scanning Electron Microscopy (HT-ESEM) under various atmospheres.



In situ HT-ESEM observation of UO_{2+x} microspheres sintering at 1000°C under various pO_2. [2]

In this aim, we first developed an original synthesis protocol yielding size-controlled UO_2 spherical particles through the hydrothermal treatment of U(IV) aspartate. [1] The kinetics associated with the evolution of neck radius, contact angles and centers displacement during the sintering of two microspheres were then evaluated by *in situ* observations in the 800-1200°C range. As UO_2 sintering is well-known to be strongly impacted by atmosphere, different experiments were performed with variable pO_2 to determine its impact on the kinetics of neck formation. It first allowed to evaluate the activation energy attached to the first step of sintering in the different conditions tested. When the dioxygen partial pressure led to stabilize UO_{2+x} oxides, the values obtained were found to increase with x, typically in the 200-400 $kJ.mol^{-1}$ range. [2] Under air atmosphere, the stabilization of U_3O_8 allowed us to provide the first evaluation of activation energy for the first step of sintering, which was close to that obtained for UO_{2+x} with low values of x, and then significantly lower than that obtained for stoichiometric UO2.00 and U_4O_9. Finally, according to the Herring scaling law, the main diffusion mechanism driving the first step of the sintering was found to be volume diffusion, independently from the stoichiometry of the uranium oxides.

Finally, a preliminary study on heterogeneous UO_2/CeO_2 systems (acting as model compouds for MOx fuels) revealed a drastic modification of the morphological evolution of the two grains, induced by the complexification of the diffusion mechanisms involved (including the preferential diffusion of uranium in CeO_2). Conversely, first tests conducted on homogeneous $(U,Ce)O_2$ solid solutions evidenced the classic behaviour described by the models. The stoichiometry of the samples involved in the sintering of actinide dioxides, but also their homogeneity, then must be carefully considered in order to build up predictive numerical models.

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[1] Trillaud V., Maynadié J., Manaud J., Hidalgo J., Meyer D., Podor R., Dacheux N., Clavier N. - **Synthesis of size-controlled UO_2 microspheres from the hydrothermal conversion of U(IV) aspartate** - *CrystEngComm* (2018) 20, 7749-7760.

[2] Trillaud V., Podor R., Gossé S., Mesbah A., Dacheux N., Clavier N. - **Early stages of UO_{2+x} sintering by in situ High-Temperature Environmental Scanning Electron Microscopy** - *J. Europ. Ceram. Soc.* (2020) 40, 5891-5899.

DEVELOPMENT OF NEW METHODS TO STUDY THE DISSOLUTION / CORROSION OF MATERIALS

*Podor Renaud, Szekneckt Stéphanie, Le Goff Xavier, Odorico Michael,
Claparède Laurent, Cordara Théo, Dacheux Nicolas*

The understanding of chemical durability of spent nuclear fuels is a key issue to improve their reprocessing. The influence of well identified parameters such as temperature, acidity and the composition of the dissolution medium were already examined using batch experiments leading to a multiparametric expression of the macroscopic dissolution rate. However, the effect of other parameters associated with the microstructure of the dense material, such as crystallite size, grain size, porosity and homogeneity on the dissolution process are less studied, mainly due to the fact that their impact leads to local modifications of the dissolution rate, which are hardly evidenced without specific methods. The use of surface characterization techniques as atomic force microscopy (AFM), environmental scanning electron microscopy (ESEM), grazing incidence X-Ray Reflectivity (GI-XRR), and light optical microscopy methods, allows tracking the microstructural evolution of the solid/solution interface, identifying various rate contributors and even determining local dissolution rates.[1]

In this context, a specific effort was made at ICSM in order to take advantage of the capabilities of AFM and ESEM. The microstructural evolution of the surface of a ceramic was monitored in operando by recording series of images of a unique zone from the beginning to the end of the dissolution test. Both techniques allows recording 3D views of the sample surface, by direct imaging using AFM and by computing tilted image series for the ESEM. The series of local 3D images of the sample surface are used to characterize precisely the local volumes of dissolved matter and to evaluate local dissolution rates[2,3] (Fig. 1 and Fig. 2).

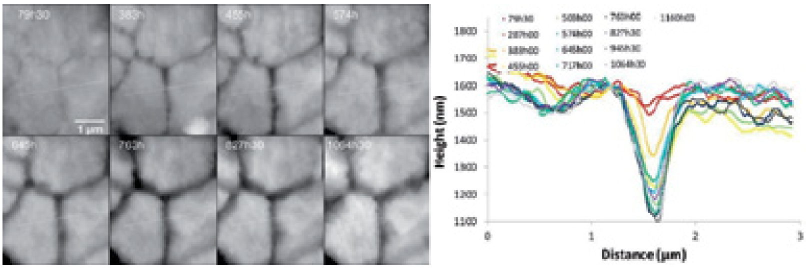

Fig. 1: ESEM observation of UO2 dissolution in 0.1M HNO3 at 60°C. Height profiles determined on the same ROI for stack of height maps recorded at 20 kX magnification.

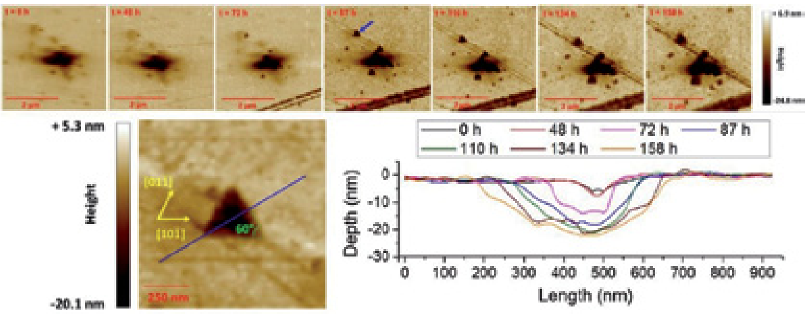

Fig. 2. AFM images of an unique ROI at the surface of (111) UO2. Geometric details of a triangular etch pit. The blue line corresponds to the position of the depth profile drawn perpendicularly to the [1 10] side of the triangle and evolution of the depth profile during dissolution.

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[1] Podor R. et al. - **3D-SEM height maps series to monitor materials corrosion and dissolution** – *Materials Characterization* (2019) 150, 220–228

[2] Cordara T. et al. - **Microstructural evolution of UO2 pellets containing metallic particles of Ru, Rh and Pd during dissolution in nitric acid solution: 3D-ESEM monitoring** – *Hydrometallurgy* (2019) 188, 182–193.

[3] Bertolotto S. et al. - **Effect of surface orientation on dissolution rate and surface dynamics of UO2 single crystals in nitric acid**– *Corrosion Science* (2020) 176, 109020.

IN SITU ESEM STUDY OF THE DEWETTING OF THIN FILMS

R. Podor, J. Lautru
J. Jupille, R. Lazzari (Inst. Des Nanosciences de Paris, Jussieu)
J. Teisseire, P. Jacquet, I. Gozhyk (SVI UMR CNRS/Saint-Gobain, Aubervilliers)

During the last few years, an increasing research effort has been dedicated to the solid-state dewetting of metallic thin films. It is identified as a potential way to produce at will metallic structures for numerous applications but it can also be an unexpected process for specific applications. However, for each application, the control of the morphology obtained through dewetting is crucial. In this respect, the understanding of the physical phenomena driving dewetting in polycristalline films has been greatly improved. The role of grains has been underlined, new diffusion pathways have been identified and the role of crystalline orientation in anisotropic materials has been explored. In the different studies that have been performed, the dewetting of metallic thin layers has been investigated through in situ and real time HT-ESEM.

- Solid-state dewetting of polycrystalline silver thin films was investigated in different annealing atmospheres: secondary vacuum or oxygen-rich (partial pressure 400 Pa) environment (Fig. 1). A model where oxygen plays a key role is proposed to explain the very different observed morphologies; oxygen favours hole creation and isotropic hole propagation as well as grain selection. But, whatever the atmosphere, dewetting does not proceed through the propagation of a rim but instead involves the growth of specific grains and shrinkage of others.[1]
- Periodic arrays of anisotropic silver nanoparticles having peculiar optical properties were fabricated at a macroscopic scale.[2] The dewetting process was described using HT-ESEM image series (Fig 2a-d). A period-dependent optimum in film thickness for the quality of spatial organization is found and discussed in terms of thermodynamics and, for the first time, in terms of the role of grains in the dewetting process (Fig. 2e).

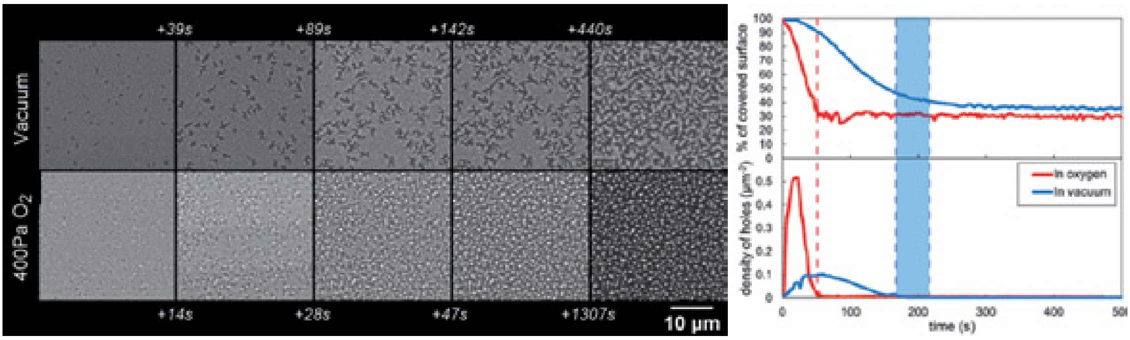


Fig. 1. (a) Snapshots of a 40 nm silver layer dewetting in vacuum and 400Pa O2 at 350 °C. (b) Data extracted from image series.

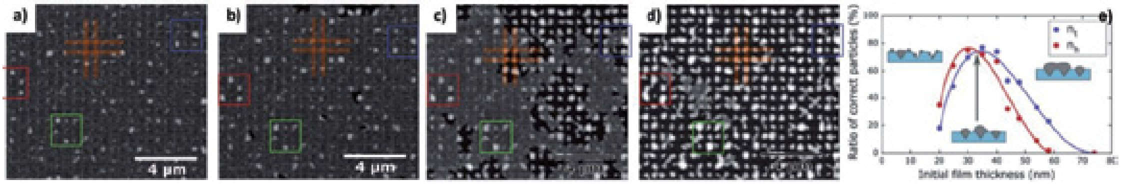


Fig. 2. Selection of grains during dewetting on patterned surfaces (P = 600 nm, square lat-tice): SEM images during a) induction stages and b–d) hole propagation step. As underlined by colored square boxes, notice in image (a) that pits are already decorated by larger grains during induction. The orange cross points at the underlying mesh. e) Quality of the obtained array of particles as a function of the thin film thickness.

[1] Jacquet P., Podor R., Ravaux J., Lautru J., Teisseire J., Gozhyk I., Jupille J., Lazzari R. - **On the solid-state dewetting of polycrystalline thin films: Capillary versus grain growth approach** - *Acta Materialia* (2018) 143, 281-290.

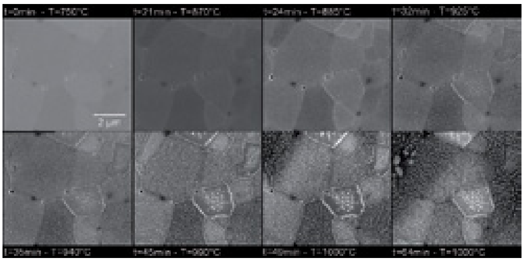
[2] Jacquet P., Bouteille B., Dezert R., Lautru J., Podor R., Baron A., Teisseir J., Jupille J., Lazzari R., Gozhyk I. - **Periodic Arrays of Diamond-Shaped Silver Nanoparticles: From Scalable Fabrication by Template-Assisted Solid-State Dewetting to Tunable Optical Properties** - *Advanced Functional Materials* (2019) 29.

DEGRADATION OF MATERIALS FOR SOFC

R. Podor
B. Song, N. P. Brandon, S. J. Skinner, S. J. Cooper, M. Niania, T. B. Britton, J. A. Kilner (Imperial College London, UK)*

Solid oxide fuel cells (SOFC) convert gaseous fuels, e.g. H2, into electricity through an electrochemical process. SOFC materials (both anode and cathode) require a very precise balance of material properties in order to function at operating temperatures (~600 – 800°C). A number of systems fulfil the requirements, but there are numerous challenges these materials face during manufacture and operation.

In $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite systems used for SOFC cathodes, the A-site is occupied by lanthanum and strontium. Due to the particular crystal-chemistry of these materials, surface precipitation of SrO is favored and this yields to a continuous degradation of the cathodic material. Continuous surface precipitation was observed on polished $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ ceramics using high temperature environmental scanning electron microscopy (HT-ESEM) up to 1000°C.[1] By performing experiments under different atmospheres (Fig. 1). The surface precipitation phenomenon has been clearly observed: the initiation of the SrO precipitation and the density of the precipitates depend on the grain orientations. When comparing the EBSD maps with the HT-ESEM images (Fig. 2a), it is obvious that the precipitation process and grain growth are directly linked with the grain orientations and presence of twinning inside the grains (Fig. 2bcd). From these new data sets, an original description of the surface precipitation has been proposed.



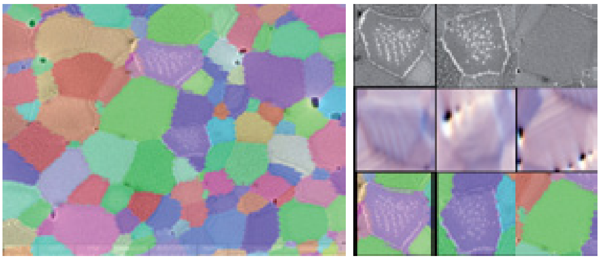


Fig. 1. HT-ESEM micrographs of a SrO precipitation on a polished $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ surface observed at high temperature in the ESEM under 300Pa of water vapor.
Fig. 2a) EBSD data matched with HT-ESEM data. 2bcd) Correlations between the HT-ESEM, Argus and EBSD images determined for 3 specific grains.

The isothermal dewetting behaviour of 40 nm Ni thin film on the yttria-stabilized zirconia substrate has been investigated in the HT-ESEM (Fig. 2) to simulate the anode material degradation in SOFC.[2] The material degradation was quantified though the determination of Triple Phase Boundary density. The coupling of morphological statistics and electrochemical performance degradation enabled qualitative discussion of the observed processes.

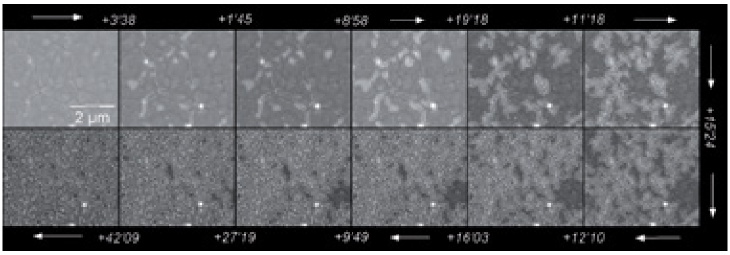


Fig. 3. Snapshots of a 40 nm silver layer dewetting in the controlled gas mixture at 575°C.

[1] Niania M., Podor R., Ben Britton T., Li C., Cooper S. J., Svetkov N., Skinner S., Kilner J. - **In situ study of strontium segregation in La0.6Sr0.4Co0.2Fe0.8O3-delta in ambient atmospheres using high-temperature environmental scanning electron microscopy** - *Journal of Materials Chemistry A* (2018) 6, 14120-14135.
[2] Song B., Bertei A., Wang X., Cooper S. J., Ruiz-Trejo E., Chowdhury R., Podor R., Brandon N. P. - **Unveiling the mechanisms of solid-state dewetting in Solid Oxide Cells with novel 2D electrodes** - *Journal of Power Sources* (2019) 420, 124-133.

OPERANDO MONITORING OF THE SOLID/LIQUID INTERFACE DURING THE DISSOLUTION OF UO_2 SINGLE CRYSTALS

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Bertolotto Solène, Lalleman Sophie, Magnaldo Alastair (CEA/DES/ISEC/DMRC, France)
Raison Philippe (JRC-Karlsruhe, Germany)

In France, spent nuclear fuels (SNF) are recycled in order to recover reusable uranium and plutonium. The head-end step of the reprocessing process is the dissolution of the SNF, which is performed in hot concentrated nitric acid. The dissolution mechanism of UO_2 in nitric acid solutions involves the oxidation of uranium (IV) into uranium (VI) at the solid/solution interface.

Micrometric single crystals appear as the simplest interface to obtain reliable dissolution rates of UO_2 in nitric acid media. From a geometric point of view, oriented and polished single crystal presents large and flat solid/solution interface. This interface can be considered to be free of steps, pores, grain boundaries or cracks, which allows managing properly hydrodynamic conditions in both catalysed and non-catalysed regimes. In this work, the evolution of the topography of oriented surfaces was monitored by environmental scanning electron microscopy (ESEM)[1] and by atomic force microscopy (AFM). Besides, dissolution rates corresponding to the three crystallographic orientations were determined under controlled hydrodynamic conditions in both catalysed and non-catalysed regimes.[2]

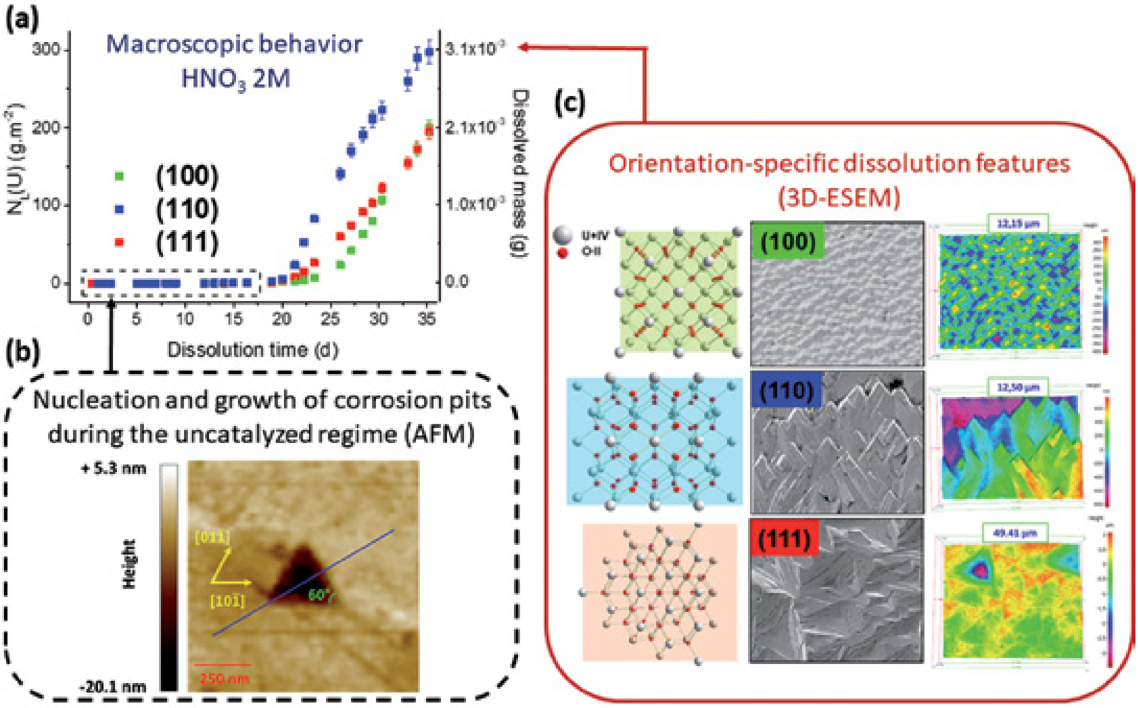


Fig. 1: (a) Evolutions of the normalised weight loss, NL(U) and of the dissolved mass during the dissolution of oriented UO2 single crystals in 2 M HNO3 at 25°C. (b) AFM images of a triangular corrosion pits formed at the (111)-oriented surface during the first kinetic regime. (c) ESEM images and 3D reconstructions of the interface of the oriented single crystals at the end of the dissolution experiment.

The density of defects should be considered as a first order parameter to estimate the duration of the initial slow dissolution step and ultimately to improve our estimation of the dissolution rates at the macroscopic scale.

[1] Podor, R., Le Goff, X., Cordara, T., Odorico, M., Favrichon, J., Claparede, L., Szenknect, S., Dacheux, N. – **3D-SEM height maps series to monitor materials corrosion and dissolution** – *Materials Characterization* (2019) 150, 220-228.

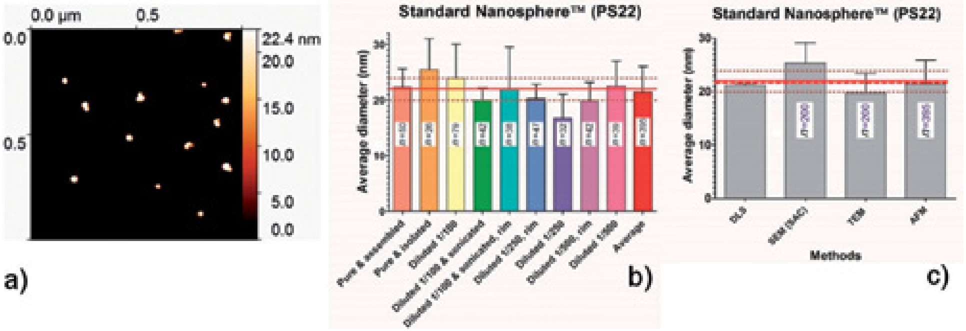
[2] Bertolotto, S., Szenknect, S., Lalleman, S., Magnaldo, A., Raison, P., Odorico, M., Podor, R., Dacheux, N. – **Effect of surface orientation on dissolution rate and surface dynamics of UO2 single crystals in nitric acid** – *Corrosion Science* (2020) 176, 109020.

NANOPARTICLES, NANOSTRUCTURES AND NANODEFECTS IMAGING WITH AFM

Odorico Michael, Podor Renaud, Bonato Laura, Virot Matthieu, Nikitenko Serguei I.
Mir Anamul H., Peuget Sylvain, Pellequer Jean-Luc (ISEC CEA-Marcoule)

In numerous scientific fields such as life, materials and earth sciences, there is a need for a precise description of the materials features at the nanometric scale. Atomic Force Microscopy (AFM) is one of the dedicated techniques for probing material morphology and topography down to the atomic scale. This technique has been used at ICSM to characterize nanoparticles, nanostructures and nanodefects.

- Nanosphere standard particles (PS22) given at a reference diameter of 22±2 nm were precisely characterized by AFM and several other techniques during an inter-comparison experiment with the goal to measure sizes of several nanoparticles (Fig. 1a-c).[1]
- AFM was used to emphasize the evolution of the nanoscale architecture of ThO_2 samples during a heat treatment.[2] The absence of nanostructure is evident for Th oxalate precursors, confirming the temperature dependence of the ThO_2 nanostructure.
- Several types of local defects generated by electron and particle irradiations at high energies and doses were characterized by AFM.



1: Nanosphere standard particles a) AFM view, b) AFM analyses, c) other techniques analyses

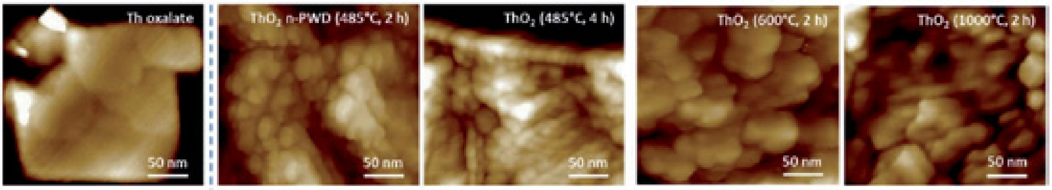


Fig. 2: AFM images showing the nanoscale architecture of ThO_2 samples during heat treatment.

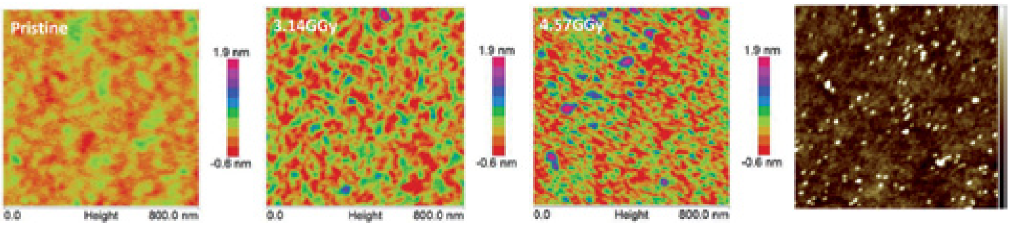


Fig. 3. a) AFM images obtained on the surfaces of pristine (left), 3.14 GGy (center) and 4.57 GGy (right) sample (2.3 MeV electrons irradiation). b) AFM image of ion tracks on the surface of the BS3 glass irradiated with 109 MeV U ions up to $7x10^{10}$ $ions.cm^{-2}$. [3].

[1] Teulon J.M. et al. - **On the operational aspects of measuring nanoparticle sizes** - Nanomaterials (2019) 9, 18.
[2] Bonato L. et al. - **Probing the local structure of nanoscale actinide oxides: A comparison between PuO2 and ThO2 nanoparticles rules out PuO2+x hypothesis**- Nanoscale Advances (2020) 2, 214-224.
[3] Mir A.H., Peuget S. - **Using external ion irradiations for simulating self-irradiation damage in nuclear waste glasses: State of the art, recommendations and prospects**- Journal of Nuclear Materials 539 (2020) 15224618.

COLLOIDAL PHYSICAL CHEMISTRY TOWARDS ELECTROPHORETIC DEPOSITION (EPD)

S. Shehayeb, P. Alastuey, F. Didier, X. Deschanels, G. Toquer

This theme deals with the electrophoretic deposition (EPD) which is known to be an important tool for the fabrication of wide range of materials[1] but this time extended to the nanoscale. This final target is to control, through a bottom-up approach, the formation of nanostructured material associated with selective optical properties designed for photothermal solar collectors. These studies are focused first on stable charged colloidal dispersions which are electrodeposited on substrate with tunable thickness, density and morphology. In this way, we use a home-made cell dedicated of the accurate control of an electric field coupled with a three electrodes system in order to control independently the electric field from the current. Nanoparticle electrophoretic deposition (NEPD) methods are developed here to understand the mechanisms and the yield rate deposition of thin film[2] based on nanoparticles (SiO2,,CuO, SWCNT, MWCNT). The coating on the working electrode surface is based on the migration of charged particles in a polar medium under an electric field. This step implies necessary some physical-chemical conditions in order to reach an efficient electrophoretic mobility characterized by laser Doppler velocimetry and also a quite monodisperse system (studied by SAXS and/or DLS). Nanoparticles at the vicinity of the working electrode are expected to be sufficiently fixed due to short range attractive Van der Waals interactions. Further, nanoparticles form thin films (see figure 1) and the rate of deposition depends mainly on the nanoparticle concentration, deposition time and electric field magnitude. Different kinds of coating are obtained by varying different EPD parameters (voltage type and range, deposition time) to control the final thickness film and also the morphology, which are the main keys to tune and optimize the final optical properties.[3] During NEPD, the electric field strength is the driven force promoting particle packing, affecting thereby the film density and the final thickness but the post-deposition drying process seems also to be a crucial step for the film adhesion. The density and the morphology (thickness and roughness) of the films (see figure 2) are analyzed through energy-dispersive X-ray spectroscopy coupled with the X-film software and scanning electron microscopy respectively.[3] Selective optical properties of films are then analyzed by reflectance spectra of the UV-Vis-NIR and by Fourier transform InfraRed (FTIR) spectroscopy.[4] The calculated efficiency of the tandem material is also enhanced by adding an anti-reflective layer.[5] Advances in the understanding of deposition mechanisms are crucial to finally select the most promising coatings acting as an efficient solar absorber.

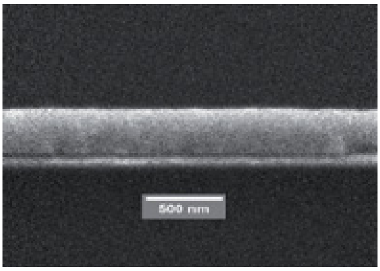


Figure 1 : CuO film cross-section (SEM)

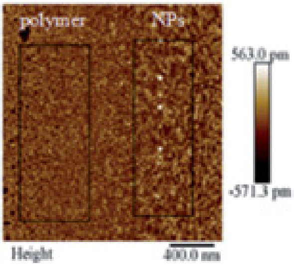


Figure 2 : composite film top-view (AFM)

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SONOCHEMISTRY OF ACTINIDES IN HOMOGENEOUS SOLUTIONS

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Sonochemistry has attracted considerable attention due to the mild and efficient reaction conditions it enables. The observed effects are generally attributed to acoustic cavitation, which is the nucleation, growth, and rapid implosive collapse of gas and vapor-filled micro-bubbles. This phenomenon enables the generation of in-situ redox species with controlled kinetics and therefore suggests the possible application of ultrasound in actinide chemistry. The adjustment of the An oxidation state during recycling processes is important for their recovery and separation necessarily performed with very high yields. In collaboration within ISEC (Atalante facility, Marcoule), the behaviors of Pu ions is investigated in various aqueous solutions under low and high frequency ultrasound.

Pu(V) is currently gaining much attention due to its potential contribution in the environmental migration of An. However, the preparation of concentrated and pure Pu(V) solutions is quite difficult and often hindered by its great instability towards disproportionation, thus limiting the accessibility to physical and chemical property data. The rapid and facile *ultrasound preparation of stable Pu(V)* solutions free from the admixtures of the other Pu oxidation states has been recently demonstrated (Fig 1.).[1] The mechanism deals with the sonochemical reduction of Pu(VI) in weakly acidic perchloric solutions with the in-situ generated H_2O_2 which kinetics can be dramatically enhanced under high frequency and Ar/O_2 atmosphere. The solutions were found to be stable for more than one month, which allowed accurate structural and magnetic property characterizations by XAFS, NMR and DFT calculations. Another recent study showed that the sonication of Pu(III) under Ar/O_2 atmosphere in mild and acidic aqueous solution leads to the observation of a green solution exhibiting an UV-Vis spectra (Fig 1) that has, up to our knowledge, never been reported in the literature.[2,3] Characterizations made with Vis-NIR, XAFS and Raman spectroscopies demonstrated the *formation of a polynuclear Pu(IV) peroxo complex* which formation can be attributed to the sonochemical generation of H_2O_2 which allows the controlled oxidation of Pu(III) to Pu(IV).

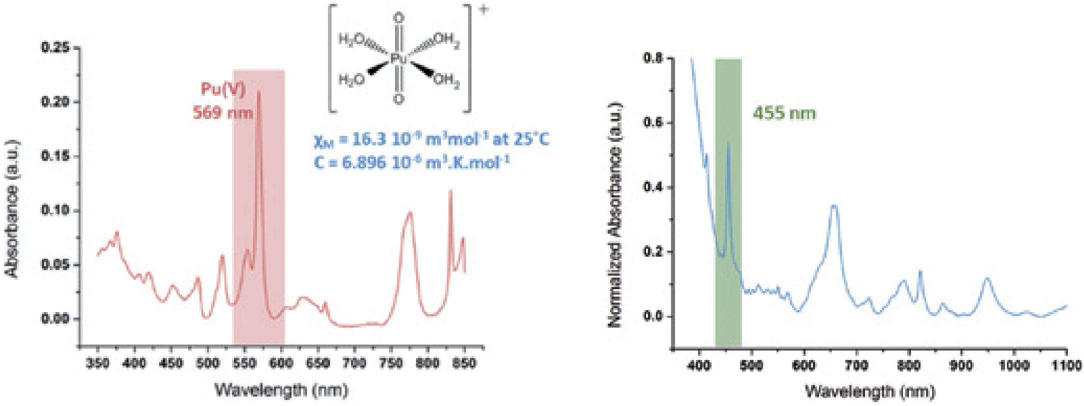

Fig. 1: (left) Vis spectrum of Pu(V) prepared at 203 kHz, Ar/O_2, 21°C (inset: proposed structure for Pu(V)). (right) Vis-NIR spectrum of Pu(IV) peroxo complexe obtained by sonication of a Pu(III) solution.

[1] Dalodière E., Virot M., Dumas T., Guillaumont D., Illy M.-C., Berthon C., Guerin L., Rossberg A., Venault L., Moisy P., Nikitenko S. I. - **Structural and magnetic susceptibility characterization of Pu(V) aqua ion using sonochemistry as a facile synthesis method** - *Inorganic Chemistry Frontiers*, 5 (2018) 100-111.

[2] Thèse E. Dalodière - **Sonochimie du plutonium : synthèse et spéciation en solution et à l'état colloïdal** - *Université de Montpellier* (2017).

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STUDY OF CAVITATION PRODUCED IN NON-CLASSICAL CONDITIONS

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H. Dutilleul, M.E Galvez, P. Da Costa (UPMC, Jussieu)

The acoustic cavitation generated by ultrasound is a renowned approach applied in various field of research ranging from the synthesis of nanomaterials to the treatment of wastewaters. Recently a new way to produce cavitation bubble, based on shock, has merged and is now under investigations and compared to ultrasonic cavitation. This innovative approach generates cavitation by mechanical impact of a piston on the water surface in a low pressure reactor as depicted in Figure. [1]

The characterization of this reactor indicate that impact cavitation is different from ultrasonic cavitation mainly because of the multi-frequency pressure wave produced by the shock with pressure ranging from 20 mbar at the initial stage and up to 50 bars at the impact.
The most appropriate model to describe this phenomenon is the Water Hammer which gives a relation between the pressure at the impact, the speed of the piston and the fraction of gas thanks to the Joukovski's equation. Obtained results verify this linear relation in our domain of study.

Moreover, the bubble visualization by fast camera gives us information onto the large diversity of bubble radius ranging from 0.01 to 2.8 mm depending on the height of the piston and initial pressure.
Besides this physical aspect, the chemical activity generated within this shock induced reactor was assessed by the measurement of $HO^{\bullet}$ radicals using terephtalic acid dosimetry. Formation of $HO^{\bullet}$ radicals was observed and even if the radical formation rates are fold lower than the ones obtained under ultrasonic irradiation, these results confirm the occurrence of the *cavitation phenomenon under mechanical impact* and for the first time the in situ generation of active species. [2]

Moreover, the impact intensity observed during each impact leads to very strong mechanical effects that would certainly be of great interest to enhance heterogeneous systems implying powdered catalysts for instance.

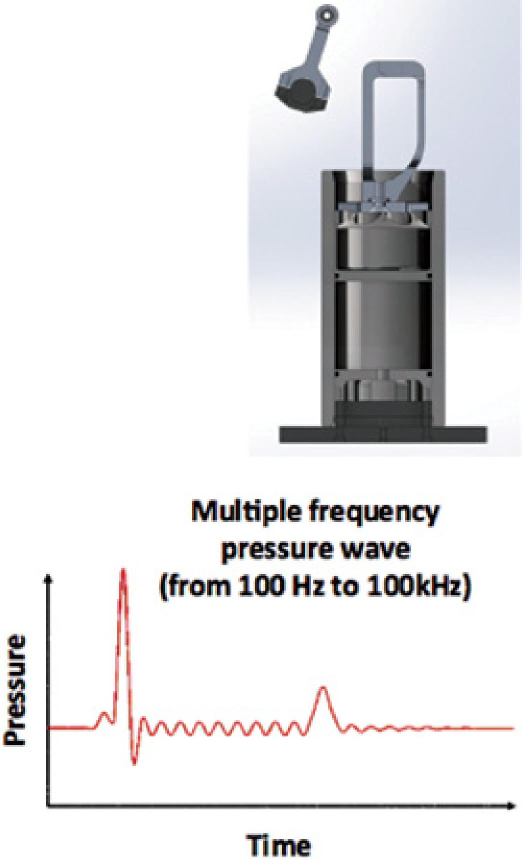

Fig: Schematic representation of the shock induced reactor and the generated pressure wave within the liquid.

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CHARACTERISATION OF THE PLASMA FORMED DURING ACOUSTIC CAVITATION IN WATER

R. Pflieger, R. Ji, T. Ouerhani, M. Virot, S.I. Nikitenko
T. Belmonte (Institut Jean Lamour, Nancy)

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 reactions, in particular through the formation of radicals (e.g. $H^\bullet$ and $HO^\bullet$ in water). Hence, a better understanding 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.[1] For instance, emissions of NH* and OH* in ammonia solutions saturated with Ar correspond to vibrational temperatures of 8000 K (± 1000K) at 20 kHz (low frequency) and 12000 K (± 2000K) at 359 kHz (high frequency, HF).[2] Frequencies in between, so to say intermediate ones (~100 kHz), are poorly characterized. Spectroscopy of SL (see Fig.) showed that they present intermediate properties and share for instance the ability of HF bubbles to dissociate O_2 and N_2 molecules.[3]

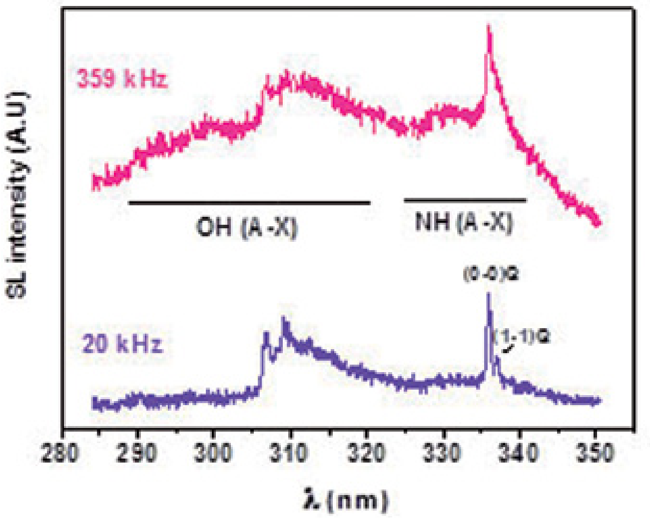

Fig : Sonoluminescence spectra of argon-saturated 0.1M $NH_3 \bullet H_2O$ solution at 20 kHz and 359 kHz.

Acquisition of spectra with higher spectral resolution and their simulation with existing spectroscopy softwares allowed us to underline the lacks of existing software. In particular they are not adapted to high pressure plasmas like the one formed in cavitation bubbles.[1] In such a case, more broadening sources of the emissions lines have to be taken into account, in particular broadening by neighboring charged species (so-called Stark effects). The development of an approach to *better characterize such high-pressure plasmas* is the core of a collaboration with the Jean Lamour Institute in Nancy.[4]

[1] Nikitenko S. I., Pflieger R. - **Toward a new paradigm for sonochemistry: Short review on nonequilibrium plasma observations by means of MBSL spectroscopy in aqueous solutions** - *Ultrasonics Sonochemistry* (2017) 35, 623-630.
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[3] Ji R., Pflieger R., Virot M., Nikitenko S. I. - **Multibubble Sonochemistry and Sonoluminescence at 100 kHz: The Missing Link between Low- and High-Frequency Ultrasound** - *Journal of Physical Chemistry B* (2018) 122, 6989-6994.
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METALLIC SURFACE MANIPULATION BY CAVITATION

R. Ji, M. Virot, R. Pflieger, R. Podor, X. Le Goff, S. I. Nikitenko

Surface treatment under high-power ultrasound is widely used for degreasing, biological decontamination, scaling, and more simply for cleaning. Chemical effects arising from acoustic cavitation in combination with non-conventional activation of surfaces may help dispersing contaminants bound to surfaces in solutions. In comparison to conventional procedures, the microscopic size of acoustic bubbles generated during sonication allows the *decontamination of surfaces* with irregular shapes and complex geometries. Holes, cracks, folds, and machining areas may be treated without addition of concentrated chemicals avoiding restrictive, laborious and often dangerous handling of materials. In nuclear industry, ultrasound-assisted decontamination of surfaces can be of particular interest for dismantling and decommissioning ending life nuclear facilities. The reductions of effluent volumes and time processing coupled to a decrease in the activity level of the generated wastes is an important challenge with financial and environmental potential benefits.

Sonochemical decontamination of metallic surfaces has been investigated in the sonochemistry group for several years. A sonochemical set-up has been developed to treat solid surfaces as a function of various parameters including the nature of the solution, ultrasonic frequency, gaseous atmosphere, emitter/sample distance, etc. Various metallic surfaces are studied in the lab using lanthanide (as surrogates) and actinide oxides as pollutants. Decontamination of surfaces can be carried out in dilute solutions at near ambient temperature and pressure. Fig. 1 shows a metallic surface contaminated with a uranyl solution and treated at high-frequency ultrasound (205 kHz) in dilute acid solution. The surface was rolled (like a snail) to simulate a complex geometry. Alpha spectrometry experiments confirmed the complete decontamination of the sample, which occur through the ultrasonically-controlled dissolution of the surface.[1] After treatment, microscopy pictures (SEM on Fig. 1) allowed the observation of an original pitted surface evidencing the complete removal of the contamination.[2] Such results are very promising towards dismantling and decommissioning of technological wastes. It is important to emphasize that technological opportunities related to industrial ultrasound propagation are nowadays huge (high volumes with batch or continuous processing, coupling of ultrasonic frequencies or techniques, indirect sonication, etc.). Such application for surface treatment at the large scale can therefore be considered as a viable alternative.

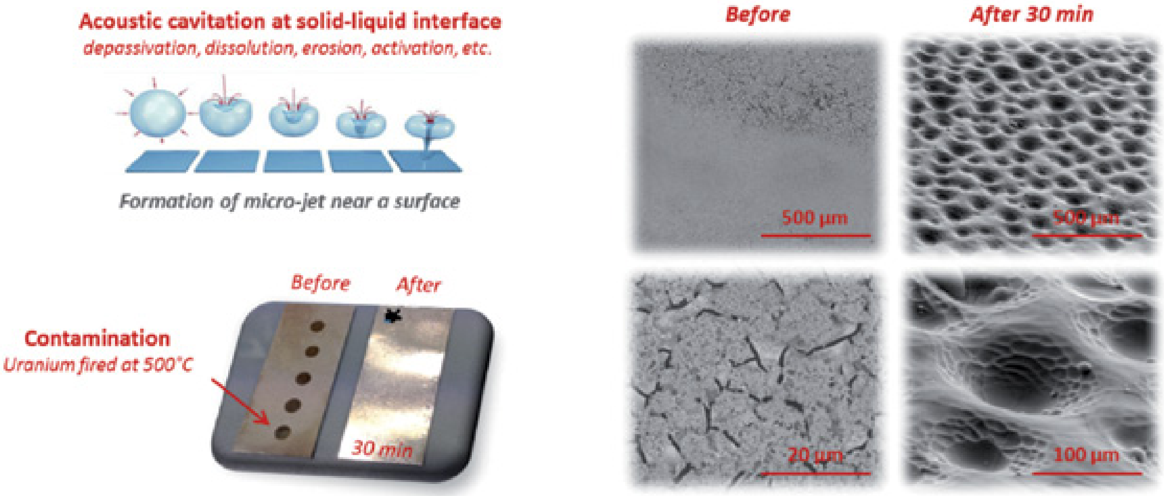

Fig. 1: Anticlockwise direction shows a scheme representative of the formation of a micro-jet near a solid surface; a picture of a U-contaminated metallic surface previously rolled to simulate a complex surface before and after 30 min sonication (205 kHz); and SEM pictures of a contaminated metallic surface before treatment (the surface is almost completely covered by contamination) and after 30 min sonication.

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EXPERIMENTS ON VERY LARGE RESEARCH FACILITIES (MARS/SOLEIL AND ROBL/ESRF)

M. Virot, T. Dumas, O. Diat, S. Dourdain, P. Moisy, S. I. Nikitenko
ROBL/ESRF and MARS/SOLEIL beamlines

The sonochemistry group is highly involved in the characterization of solid and liquid radioactive samples with very large research facilities (synchrotron radiation sources). In collaboration with DES/ISEC/DMRC department, our group frequently apply for proposals to access very large instruments and we developed a strong collaboration with MARS and ROBL beamlines from synchrotrons SOLEIL and ESRF, respectively. We particularly use X-ray absorption spectroscopy (EXAFS/XANES), small-angle X-ray scattering (SAXS) and high-resolution X-ray diffraction for the characterization of intrinsic Pu(IV) colloids exhibiting PuO_2-like structure and actinide compounds.[1-5]

Recently, researchers from ICSM, DES/ISEC/DMRC and MARS/SOLEIL beamline developed an analytical bench allowing SAXS measurements on radioactive samples. The high photon flux and high energy combined with the low spectral width of the incident beam allow a high signal definition in a wider Q range in comparison to classical X-ray sources.[4] This analytical bench allowed the characterization of the multi-scale properties of Pu(IV) colloidal suspensions by combining quasi-simultaneous SAXS and XAS measurements: the local structure, size, morphology and nature of interactions occuring between particles can be probed quasi-simultaneously.[4] Fig. 1 shows the analytical bench in SAXS/XAS configuration with SAXS diagrams obtained on colloids.

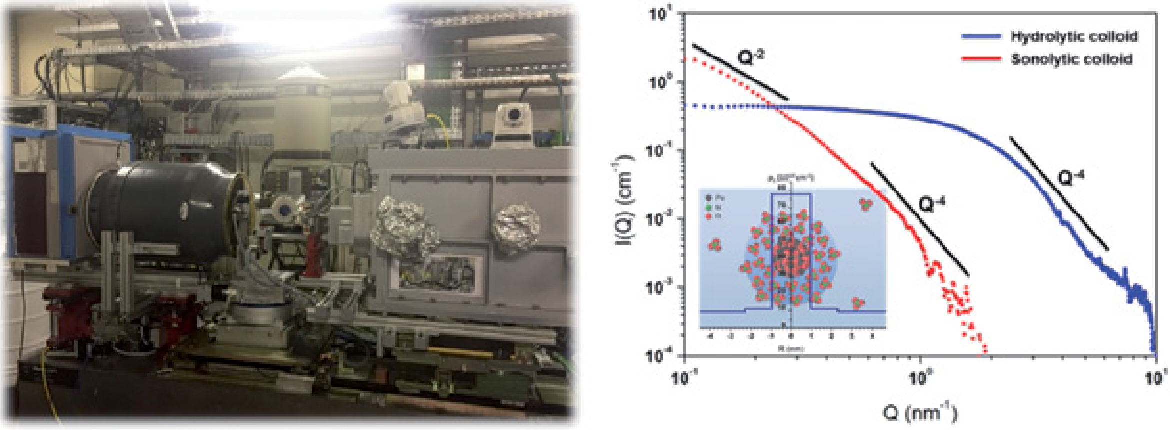

Fig. 1 : (left) picture of the SAXS bench coupled to fluorescence EXAFS spectroscopy on MARS Beamline. (right) SAXS diagrams of 10 mM hydrolytic (blue line) and 0.8 mM sonolytic (red line) intrinsic Pu(IV) colloids. Black lines indicate the slope power laws. The oscillation at $Q = 4$ nm^{-1} is an artefact attributed to the scattering of the Kapton windows of the sample holder. Insert shows a core/shell model applied to characterize hydrolytic colloids.

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[2] Dalodiere E., Virot M., Dumas T., Guillaumont D., Illy M. C., Berthon C., Guerin L., Rossberg A., Venault L., Moisy P., Nikitenko S. I. - **Structural and magnetic susceptibility characterization of Pu(V) aqua ion using sonochemistry as a facile synthesis method** - *Inorganic Chemistry Frontiers* (2018) 5, 100-111.

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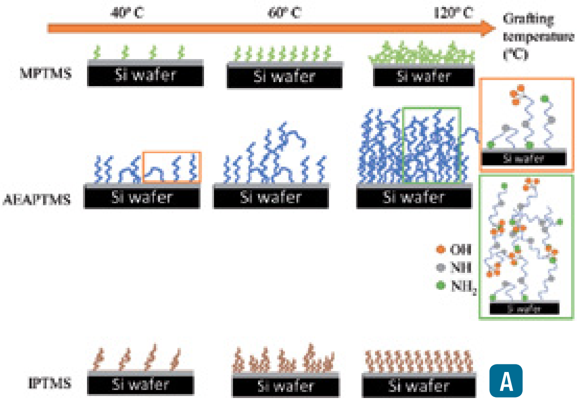
USE OF SUPERCRITICAL CO_2 AS SOLVENT FOR NANOMATERIALS PREPARATION

Susan Sananes Israel, Diane Rébiscoul, Guillaume Toquer, Jérémy Causse

Supercritical carbon dioxide (SC CO_2) is used to functionalize the surface of silica for the preparation of materials with possible applications for selective ion extraction. The scientific approach is to determine the grafted layers characteristics depending on the functional headgroups (SH, NH_2, I, $PO(OH)_2$) on the planar silica surface[1] (Figure 1A) and in nanoconfinement.[2] For the latter, several silica model nanoconfinements such as silica nanochannels (Figure 1B)[2] and highly ordered mesoporous silica are used. Furthermore, their chemical durabilities for decontamination application are assessed by characterizing the evolution of the functionalized silica materials in various aqueous solutions.



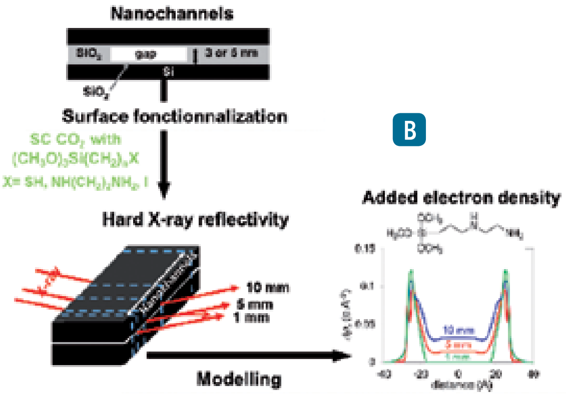


Figure 1: A Schematic representations of the morphologies of grafted layers of MPTMS, AEAPTMS and IPTES as a function of the grafting temperature. [1]

Figure 1: B Scientific approach used to determine the impact of the silica surface nanoconfinement on the microstructure of alkoxysilane layers grafted.[2]

Keeping in mind that systems in supercritical solvent are always difficult to characterize, due to the fact that autoclave cells have to be used in pressure and temperature conditions above critical point (31°C, 73 bars for CO_2), our team has developed specific cells allowing SAXS measurements in this unconventional solvent. At this moment, these cells have been used to assess aggregation and size of ligands designed for extraction of metal of interest from solid matrices through collaborations with Montpellier University or CEA/DEN/DE2D/LPSD (Laboratoire des Procédés Supercritiques et Décontamination).

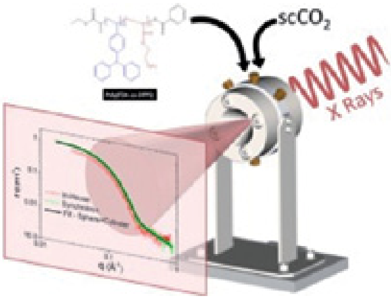


Figure 2: In-situ SAXS cell for a use in supercritical CO2 (scCO2) solvent.

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[2] Rebiscoul D., Israel S. S., Tardif S., Larrey V., Ayral A., Rieutord F. - **Impact of Silica Surface Nanoconfinement on the Microstructure of Alkoxysilane Layers Grafted by Supercritical Carbon Dioxide** - *Journal of Physical Chemistry C* (2019) 123, 12305-12312.

A NEW TOOL FOR THE CALCULATION OF ACTIVITY OF SOLUTIONS BY SIMULATING OSMOTIC EQUILIBRIA

M. Bley, M. Duvail, J.-F. Dufrêche
Ph. Guilbaud (DES/DMRC-CEA Marcoule)

Understanding solvent-extraction-based purification and recycling approaches requires detailed information on different thermodynamic equilibrium properties of phases. Here, a new theoretical method is presented for predicting osmotic equilibria and activities, where a bulk liquid phase and its corresponding vapor phase are simulated by means of molecular dynamics using explicit polarization.

This multi-scale approach based on the thermodynamic interpretation of the time-averaged density profiles from MD simulations of vapor-liquid interfaces is in principle similar to the experimental isopiestic approach for aqueous solutions.
This method has been first applied to aqueous solutions of dysprosium nitrate [$Dy(NO_3)_3$] at different concentrations in order to determine the activity coefficients of the solutes (Fig. 1).[1]

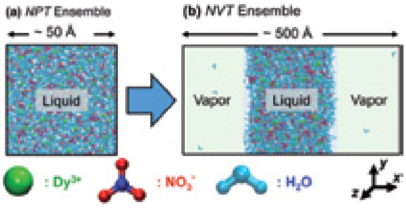

Figure 1: Representation of the MD simulations of (a) a bulk liquid phase and (b) a simulation box representing a liquid-vapor interface.

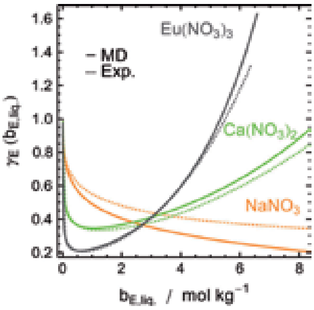

Figure 2: Experimental (dashed lines) and simulated (solid lines) salt activity coefficients for aqueous solutions of $NaNO_3$, $Ca(NO_3)_2$, and $Eu(NO_3)_3$.

Then, using the same approach osmotic and activity coefficients of three aqueous electrolyte solutions with cations of similar ionic radius, but different charges ($NaNO_3$, $Ca(NO_3)_2$, and $Eu(NO_3)_3$), have been described by molecular dynamics with the help of the osmotic equilibrium method up to high concentration.[2] The densities of the liquid bulk calculated and the osmotic and activity coefficients obtained for the three different nitrate salts are in very good agreement with the experimental results (Fig. 2).
Such an approach has been then extended for simulating phase diagrams of binary water/ethanol mixtures.[3] MD simulations of water/ethanol mixtures have been conducted at different ethanol concentrations (Fig. 3). The activities in the liquid phase have been calculated at a given composition, providing a good agreement with the experimental data. An azeotropic point was calculated for an excess concentration at 87 wt% of ethanol compared to the experimental value of 95.5 wt% (Fig. 4).

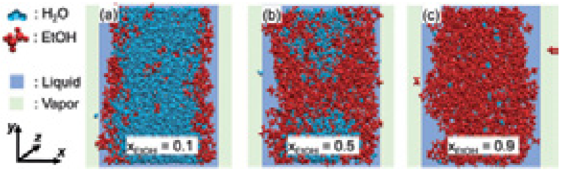

Figure 3: Snapshots representing the liquid phase in contact with vapor phases for different ethanol mole fractions.

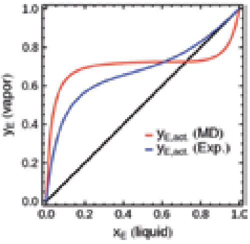

Figure 4: Ethanol gas phase mole fraction yE as a function of the ethanol mole fraction in the liquid phase xE.

This fundamental description of such an approach based on osmotic equilibrium between a solution and the adjacent vapor phase will provide helpful tools for interpreting interfacial phenomena systems.

[1] Bley M., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Simulating Osmotic Equilibria: A New Tool to Calculate Activity Coefficients in Concentrated Aqueous Salt Solutions** – *Journal of Physical Chemistry B* (2017) 121, 9647-9658.
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[3] Bley M., Duvail M., Guilbaud Ph., Penisson Ch., Theisen J., Gabriel J.-Ch., Dufrêche J.-F. – **Molecular Simulation of Binary Phase Diagrams From the Osmotic Equilibrium Method: Vapour Pressure and Activity in Water-Ethanol Mixtures**. – *Molecular Physics* (2018) 116, 2009-2021.

STRUCTURES OF SOLUTIONS RESOLVED AT MOLECULAR AND SUPRAMOLECULAR SCALES: DEVELOPMENTS OF POLARIZABLE FORCE FIELDS FOR MOLECULAR DYNAMICS

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Th. Dumas, A. Paquet, Ph. Guilbaud (DES/DMRC- CEA Marcoule)
A. Poulesquen (DES/DE2D-CEA Marcoule)

Molecular dynamics (MD) simulations coupled with experiments, such as EXAFS and SWAXS techniques, are methods of choice to access the structural, dynamic, and thermodynamic properties of ions in solutions. However, force fields for molecular dynamics have to be developed as accurately as possible in order to reproduce all the experimental solvation properties.

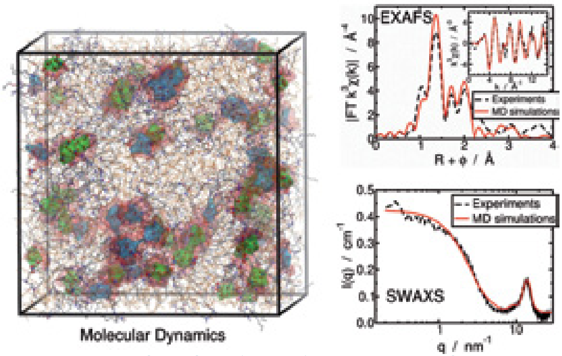

Figure 1: Combined MD/EXAFS/SWAXS approach.

Such an approach coupling both MD simulations with WAXS experiments has also been used for studying concentrated NaOH aqueous solutions from diluted systems to 10 mol L^{-1}.[4] A new polarizable force field has been therefore developed for describing the OH– anion in aqueous solutions by means of classical MD simulations. This new OH– polarizable force field gives an accurate description of the molecular structures of alkali media (Fig. 2).

Combining molecular dynamics with scattering techniques such as EXAFS and SWAXS points out its efficiency for providing realistic pictures of electrolyte salts solvation that is a first needed step to access their thermodynamical properties.

Recently, we proposed a new polarizable force field for describing the UO_2^{2+} solvation by means of classical molecular dynamics in both aqueous[1] and solvent extraction phases.[2,3] This new force field, improved compared to our previous one, provides accurate structural properties.

The transferability of the UO_2^{2+} force field has also been tested on solvent extraction phases containing uranyl nitrate salts with DMDOHEMA molecules in n-heptane[2] and also in the framework of the AMEX process.[3] The good agreements between MD simulations and SWAXS and EXAFS experiments comfort us on the reliability of the force field developed here for describing the solvation structure of the UO_2^{2+} cation in solvent extraction phases at both the molecular (EXAFS) and supramolecular (SWAXS) scales (Fig. 1).

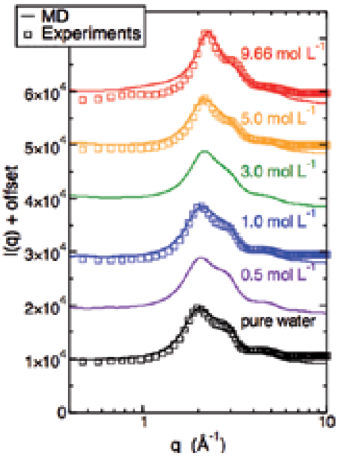

Figure 2: Theoretical (lines) and experimental (square) WAXS intensities for concentrated NaOH solutions.

[1] Lahrouch F., Chamayou A.-C., Creff G., Duvail M., Hennig Ch., Lozano Rodriguez M. J., Den Auwer Ch., Di Giorgio Ch. – **A Combined Spectroscopic/Molecular Dynamic Study for Investigating a Methyl-Carboxylated PEI as a Potential Uranium Decorporation Agent.** – *Inorganic Chemistry* (2017) 56, 1300-1308.

[2] Duvail M., Dumas Th., Paquet A., Coste A., Berthon L., Guilbaud Ph. – **UO_2^{2+} Structure in Solvent Extraction Phases Resolved at Molecular and Supramolecular Scales: A Combined Molecular Dynamics, EXAFS and SWAXS Approach.** – *Physical Chemistry Chemical Physics* (2019) 21(15), 7894-7906.

[3] Sukhbaatar T., Duvail M., Dumas Th., Dourdain S., Arrachart G., Solari P. L., Guilbaud Ph., Pellet-Rostaing S. – **Probing the Existence of Uranyl Trisulfate Structures in the AMEX Solvent Extraction Process.** – *Chemical Communications* (2019) 55, 7583-7586

[4] Coste A., Poulesquen A., Diat O., Dufrêche J.-F., Duvail M. – **Investigation of the Structure of Concentrated NaOH Aqueous Solutions by Combining Molecular Dynamics and Wide-Angle X-ray Scattering.** – *The Journal of Physical Chemistry B* (2019) 123(24), 5121-5130.

ORGANIC PHASES MODELING FOR THE LIQUID-LIQUID EXTRACTION: A MOLECULAR APPROACH

M. Duvail, S. Van Damme, Y. Chen, S. Stemplinger, J.-F. Dufrêche
Ph. Guilbaud (DES/DMRC-CEA Marcoule)

Most of efficient methods known for separating ions are based on equilibria between complex fluids, typically between aqueous and organized organic phases. Understanding the thermodynamics in both phases is therefore a crucial issue in order to optimize the separation processes. Although the aqueous solutions are nowadays well described, a lack remains in understanding the thermodynamics properties of ions in organic phases. Indeed, it is well known that ions migrate from the aqueous to the organic phase thanks to surfactant or extractant molecules in the organic phase, and then are captured in reverse micelles or aggregates. Modeling such processes remains quite difficult since many phenomena are involved: complexation, solvation, electrostatic interactions, polarization forces, etc.

The main goal of this study is to understand the various effects (solvation, electrostatic and van der Waals forces, entropy, curvature) that drive the transfer of lanthanide salts ($Ln(NO_3)_3$) from an aqueous phase to an organic organized phase thanks to the DMDOHEMA molecule.

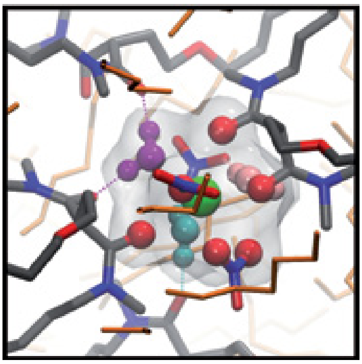

Figure 1: Snapshot obtained from MD simulations representing an aggregate of $La(NO_3)_3L_4(H_2O)_3$ in n-heptane with different types of water molecules. For the illustration, La^{3+} is colored in green, oxygen atoms are in red, nitrogen atoms are in blue, carbon atoms are in black, and hydrogen atoms are in white. n-Heptane molecules are colored in orange.

First, we focused on association pathways of water molecules in reverse micelles containing lanthanum nitrate $La(NO_3)_3$ salts and DMDOHEMA extractant molecules in *n*-heptane.[1] In order to investigate quantitatively the stability of such aggregates as a function of the number of water molecules, umbrella sampling molecular dynamics (MD) simulations have been performed. This work demonstrates that the stability of such aggregates in the organic phase, composed of a polar core and an apolar ring, is clearly a compromise between the curvature properties of the ligand molecules (number of ligands and the shape) and the structural properties inside the polar core (Fig. 1).

Then, in order to quantify these curvature properties, umbrella-sampling MD simulations of aggregates in explicit (described at the molecular level) and implicit (described by its dielectric constant) solvents have been performed.[2] This pointed out that it is crucial to take into account explicitly the solvent in order calculate accurate physico-chemical properties.[3]
Furthermore, coupling both molecular and mesoscopic modeling based on the microemulsion theory proved that such aggregates behave like microemulsions (Fig. 2).
The combination between small size of the polar core and high rigidity of the interface may explain the strong stability of such aggregates in organic phases, and therefore, why such extractant is used in the liquid–liquid separation processes.

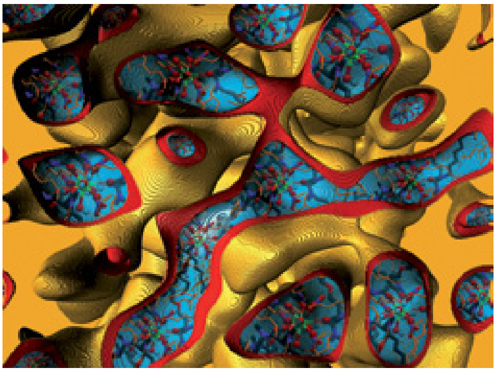

Figure 2: Representation of the microemulsion coupled with MD simulations. For the illustration, water is blue, oil is yellow and the surfactant is red.

[1] Chen Y., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Stability of Reverse Micelles in Rare-Earth Separation: a Chemical Model Based on a Molecular Approach.** – *Physical Chemistry Chemical Physics* (2017) 19, 7094-7100.
[2] Duvail M., Van Damme S., Guilbaud Ph., Chen Y., Zemb Th., Dufrêche J.-F. – **The Role of Curvature Effects in Liquid–Liquid Extraction: Assessing Organic Phase Mesoscopic Properties From MD Simulations.** – *Soft Matter* (2017) 13, 5518-5526.
[3] Stemplinger S., Duvail M., Dufrêche J.-F. – **Unravelling Curvature Properties in Liquid-Liquid Extraction: Eu^{3+} with DMDOHEMA in *n*-Alkanes.** – *Physical Chemistry Chemical Physics* (2020) Submitted

THERMODYNAMICS OF SOLVENT EXTRACTION PHASES

M. Vatin, M. Duvail, J.-F. Dufrêche, Th. Zemb
M. Coquil, M. C. Charbonnel, N. Boubals, Ph. Guilbaud (DES/DMRC-CEA Marcoule)

Separation processes performed for recycling of heavy metals commonly use liquid-liquid extraction for which ions are selectively transferred from an aqueous to an organized organic phase where the ions are typically contained into aggregates. Modelling such processes remains quite difficult since many phenomena occur at different length sizes: complexation, solvation, electrostatic interactions, polarisation forces, etc.[1] Therefore, modelling such processes makes necessary the calculation of the aggregate's free energies. An important term to consider is the free energy of the carbon chains which impose the spontaneous and stretched curvature of the surfactant film.[2]

In this context, we studied how surface phenomena change the interface geometry in diphasic liquid-liquid systems. Without any curvature effect on surface tension, planar, cylindrical, and spherical structures are successively predicted as a function of the total composition and elongation of the simulation box, in accordance with molecular dynamics simulations for a water/n-heptane system (Fig. 1).[3] We pointed out that, taking into account the spontaneous curvature (typically using the Helfrich's formalism) allows for considering new systems, like spherical shells, frustration, or multiples droplets.

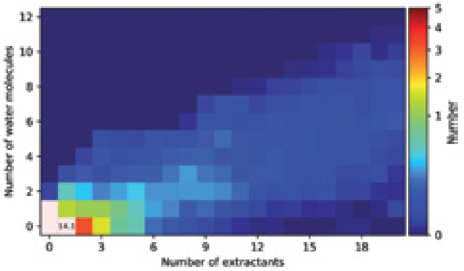

Figure 2: Time average distribution of species as a function of the composition in organic phase: number of extractants and water molecules. Colors correspond to the number of aggregates for a given composition.

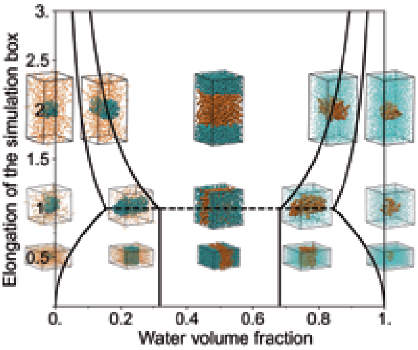

Figure 1: Phase diagram of the equilibrium surface of a water/oil mixture as a function of the water volume fraction and the elongation of the simulation box.

In an attempt of better understanding the role of extractant molecules in the supramolecular properties of solvent extraction phases, aggregation of malonamide extractants diluted in such phases has been studied by molecular dynamics simulations.[4] Using association criteria based on the distances between the molecules present in solution, and the graphs theory, this robust procedure allows calculating distributions of aggregates exactly as a function of their compositions.

Besides, it also allows computing easily fundamental structural and physico-chemical quantities such as average number of water molecules involved in aggregates, equilibrium constants, enthalpies of formation, and aggregation numbers. Finally, increasing the accuracy of the equilibrium constants by hard sphere activity coefficients, we developed a model allowing to estimate critical micelle concentration, and give interpretations on aggregation and osmotic measurements.

[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* (2020) Submitted

[2] Dufrêche J.-F., Zemb Th. – **Bending: from Thin Interfaces to Molecular Films in Microemulsions.** – *Current Opinion in Colloid & Interface Science* (2021) 23, 1178-1187.

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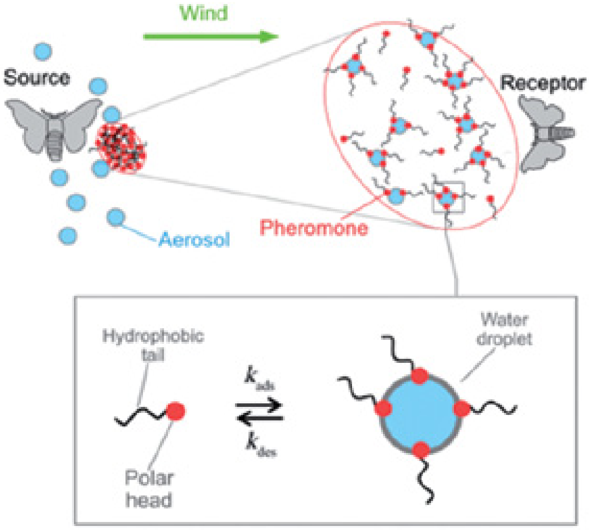
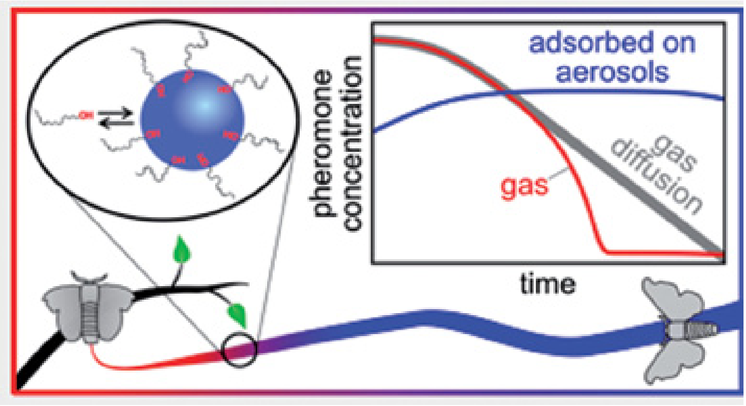
HOW ADSORPTION OF PHEROMONES CONTROL THEIR TRANSPORT

L. Jami, Th. Zemb, J-F. Dufrêche
J. Casas (Université de Tours)

The mystery of long-term and long-distance communication between insects involving quantities of the order of 10 ng and distances up to 10 km is difficult to reconcile with known sensitivity of molecular detection in insect physiology that cannot go below a few molecules per minute and with the mass balance that point towards at least hundred times less incoming flux. We made the working hypothesis that the pheromone adsorbs on the surface of atmospheric aerosols: the efficient transport is no more of individual molecular, but by aerosol surface adsorbed paquet transport containing hundred to thousand molecules.





We developed general transport theory for pheromone molecules in an atmosphere containing aerosols.[1] Many pheromones are hydrophobic molecules containing polar groups. They are low volatile and have some properties similar to those of hydrotropes.[2] Pheromones therefore form a non-soluble film at the water–air interface of aerosols.

Partitioning of pheromones between the gas and the aerosol surface over time is studied for various climate conditions (available aerosol surface) and adsorption affinities (energy of adsorption). We show that, for adsorption energy above 30 k_BT per molecule, transport of pheromones on aerosols dominates over molecular transport typically 10 s after pheromone emission, even when few adsorbing aerosols are present.

This newly understood communication path for airborne chemicals leads to distinctive features including enhanced signal sensibility and increased persistence of pheromone concentration in the air due to slow diffusion of aerosols. Each aerosol droplet has the ability to adsorb thousands of pheromones to the surface, keeping a "history" of the atmospheric content between emission and reception. It also explains why female insects concentrate emission in atmospheric conditions close to the dew point and why truffle dogs show better performance in humid air.

[1] Jami L., Zemb Th., Casas J., Dufrêche J.-F. – **How Adsoprtion of Pheromones Controls Their Transport.** – *ACS Central science* (2020) 6, 1628-1638
[2] Lu Z. J., Dourdain S., Pellet-Rostaing S. – **Understanding the Effect of the Phase Modifier n-Octanol on Extraction, Aggregation, and Third-Phase Appearance in Solvent Extraction** – *Langmuir* (2020) 36, 12121-12129.

MICROEMULSIONS: UNIFICATION OF ULTRA-FLEXIBLE, FLEXIBLE AND RIGID CASES

Th. Zemb, M. Duvail, J.-F. Dufrêche
M. Gradzielski, P. Malo de Molina, M. Simon (TU-Berlin)
Ishi Talmon (Technion, Haifa)

Microemulsions are dispersions of two fluids stabilized by a layer of surfactants. They are optically inactive and differ from mini and macro-emulsions by their thermodynamics stability. They are ubiquitous in important application, not only in the nuclear fuel cycle, but also in the food, agriculture, pharmacy and home care domains. There are more than thousand scientific papers and hundred patents a year dealing with some kind of microemulsions. There are three classes of microemulsions, depending on the flexibility of the surfactant film: the rigid, the flexible and the ultra-flexible microemulsions. These are distinguished by the order of magnitude of the ratio of bending and solvation forces versus thermal free energy.[1] The rigid ones, most used in pharmaceutical applications and inorganic nanoparticle stabilization are shown with their topology on the figure 1A on the left below. The second one is shown on figure 1B on the right together with explicit modelling by Gaussian random waves taking into account thermally excited bending.

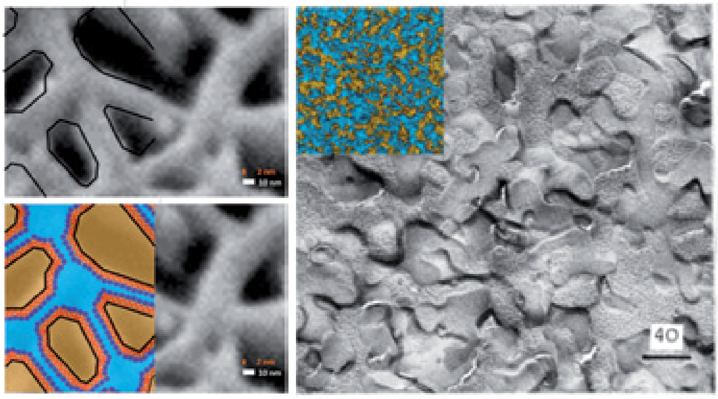
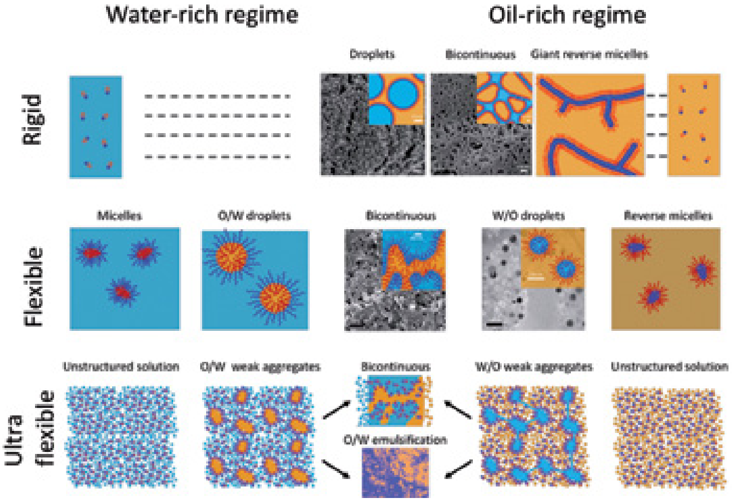


Figure 1: (A, left) the low-water regime in cationic surfactant/water/oil ternary microemulsions: bending rigidity imposes the presence of thin connected water channels of high conductivity that vanishes upon addition of water. (B, right): the bicontinuous flexible case obtained with typical alkyl ethyl oxide ethers with similar chain and head volume: spontaneous curvature is low and induces a randomly bending of the surfactant film at any polar/apolar volume ratio.



Depending on the solvent to water relative rations, all nanostructures shown on the left can be obtained w/o droplets, bicontinuous and w/o.[2]
The variation of topology and hence solubilizing power is crucial for formulation and allows to optimize performance in applications[3], as well as designing the best surfactant mix and couple of solvents used, at peculiar points in the ternary phase prism.

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[1] Dufrêche J.-F., Zemb T. – **Bending: from Thin Interfaces to Molecular Films in Microemulsions.** – *Current Opinion in Colloid & Interface Science* (2020) 49, 133-147

[2] 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* (2020) Under Revision.

[3] Duvail M., van Damme S., Guilbaud Ph., Chen Y., Zemb Th., Dufrêche J.-F. – **The Role of Curvature Effects in Liquid–Liquid Extraction: Assessing Organic Phase Mesoscopic Properties From MD Simulations.** – *Soft Matter* (2017) 13, 5518-5526.

COALESCENCE : CONNECTING SCALES

L. Hilaire, B. Siboulet, J.-F. Dufrêche
S. Charton (DES/ISEC/DMRC CEA MARCOULE)

Coalescence is the dynamic phenomenon by which two immiscible phases, one distributed in drops in the other, reach their state of equilibrium. This state of equilibrium is reached when the drops have disappeared and the two phases are separated by a flat interface. There are many industrial applications concerned by coalescence: liquid-liquid extraction, petrochemicals, cosmetics and nutrition. Coalescence is the succession of three phases: approach, drainage and rupture.

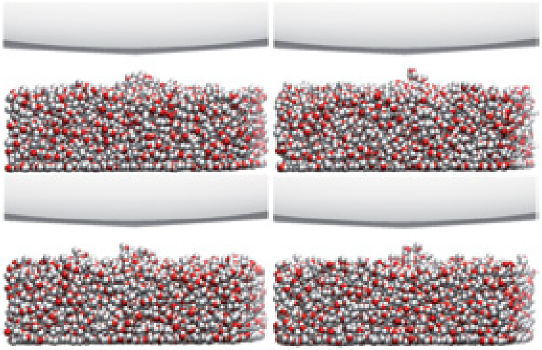

Figure 1: Water surface fluctuations in the vicinity of a spherical ti

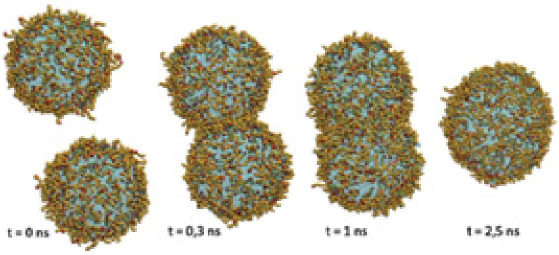

Figure 2: two water-octanol droplets coalescing

Various methods for studying coalescence: TFB (Thin Film Balance), SFA (Surface Force Apparatus), AFM (Atomic Force microscopy). Coalescence is also the subject of modelling. Among the continuous modeling, there are the methods of continuous fluid dynamics (CFD, Computational Fluid Dynamics) and the Lattice Boltzmann method (LBM). To simulate coalescence at the atomic level, classical molecular dynamics (DM) are to be performed.

DM is relevant for the study of the ultimate phases of coalescence: drainage and rupture. Indeed, it produces densities, surface tensions, viscosities, in all possible configurations, temperature, geometry (flat, spherical, ...), concentration (surfactants, solubilized ions, ...). The limitation of the DM is only due to the size of the systems.

The ultimate steps of coalescence are initiated at the molecular level. They result from the interaction between small groups of molecules that come close together. We have therefore tested the relevance of DM on experimental data of this type. The aim was to simulate the interaction between an AFM tip and a liquid surface. DM validates semi-analytical models of such systems, while pointing out their limits, due to the fluctuations or non-continuous nature of liquids at nanoscopic scales[1].

Coalescence, even if it is possible to simulate it at the atomic level, remains a stochastic phenomenon. It must be described by probability laws. For this purpose, we simulate the coalescence of heptane drops in air and water, water in air and heptane. These simulations must be repeated to produce a stochastic description. From indistinguishable initial conditions, we observe variable coalescence times, which illustrates the random nature of coalescence. Such a project requires significant computing resources, which we owe to GENCI's HPC resources.

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[1] Hilaire L., Siboulet B., Charton S., Ledesma-Alonso R., Legendre D., Tordjeman P., Dufrêche J.-F. – **Deformation of a Liquid Near an AFM Tip: Molecular Dynamics Approach Deformation of a Liquid Near an AFM Tip: Molecular Dynamics Approach** – *Langmuir* (2020) 36, 8993-9004

IONS AT LIQUID-SOLID INTERFACES

B. Siboulet, J.-F. Dufrêche, S. Hocine, M. Duvail et à la ligne K. Bohinc (University of Ljubljana)

The determination of adsorption selectivities and ion distributions at solid interfaces is a fundamental and applied topic of interest, concerning separation, energy, energy storage or catalysis. We approach this topic through atomic simulation and mesoscopic models, always making our simulations converge with available experiments.[1]

The information on these distributions is generally indirect (electrokinetic phenomena, titration), but there is a direct method, the X-Standing Wave Reflectivity (XRSW). Although direct and selective, it is largely based on models, such as the old Gouy-Chapman-Stern model. Better resolved and selective, molecular dynamics is the ideal tool to associate with XRSW experiments.[2]

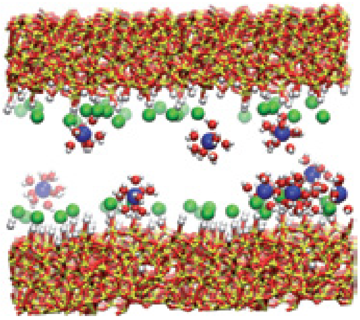


Figure 1: Simulation of $BaCl^2$ at 1 mol/L in a silica nanochannel

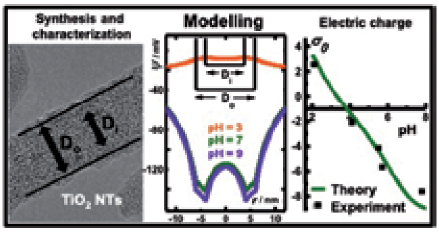


Figure 2: Potential and surface charge of a TiO^2 nanotube

Amorphous structures such as silica present to solvated ions a variety of adsorption sites. The simulations show that it is possible to determine a simple criterion on the adsorption sites that determines the selectivity of each one and to explain the charge inversion phenomena.[3] The condensation of ions in the Stern layer can be studied by molecular dynamics. We have determined the Free Energy Potentials (FEP) between the ions and the surface. These potentials make it possible to distinguish the ions in contact with surface contact from the others, which is the central point of the description of the charged solid-liquid interfaces. The Stern layer appears not as a continuous layer but as a set of ion pairs.We have drawn various conclusions from our simulations~: the observed specificity of ions adsorption is justified by the simulation; the high activation energies for desorption/adsorption indicate the need for long simulations; the treatment of these systems with localized surface charges requires three-dimensional models (existing mesoscopic models are one-dimensional); the surface conductivity formula developed by Bikerman is applicable only at low concentrations; there can be no stagnant layer on a charged interface.[4]

Interface modeling is not limited to atomic simulations. We have developed a model based on the functional theory of classical density coupled with the load control method in terms of mass action law. Applied to Titanate nanotubes, it allows to understand the experimental data, to represent the electrical potential profile, and provides indications on the charging properties under different physical conditions (pH, ionic concentration).[5]

[1] Hartkamp R., Biance A.-L., Fu L., Dufrêche J.-F., Bonhomme O., Joly L. – **Measuring Surface Charge: Why Experimental Characterization and Molecular Modeling Should Be Coupled** – *Current Opinion in Colloid & Interface Science* (2018) 37, 101–114. https://doi.org/10.1016/j.cocis.2018.08.001.

[2] Malloggi F., ben Jabrallah S., Girard L., Siboulet B., Wang K., Fontaine P., Daillant J. – **X-ray Standing Waves and Molecular Dynamics Studies of Ion Surface Interactions in Water at a Charged Silica Interface** – *Journal of Physical Chemistry* C (2019) 123, 30294–30304.

[3] Döpke M. F., Lützenkirchen J., Moultos O. A., Siboulet B., Dufrêche J.-F., Padding J. T., Hartkamp R. – **Preferential Adsorption in Mixed Electrolytes Confined by Charged Amorphous Silica** – *The Journal of Physical Chemistry C* (2019) 123, 16711–16720.

[4] Siboulet B., Hocine S., Hartkamp R., Dufrêche J.-F. – **Scrutinizing Electro-Osmosis and Surface Conductivity with Molecular Dynamics** – *The Journal of Physical Chemistry C* (2017) 121 (12), 6756–6769

[5] Spadina M., Gourdin-Bertin S., Drazic G., Selmani A., Dufrêche J.-F., Bohinc K. – **Charge Properties of TiO_2 Nanotubes in $NaNO_3$ Aqueous Solution** – *ACS Applied Materials & Interfaces* (2018) 10 (15), 13130–13142. https://doi.org/10.1021/acsami.7b18737.

IONS AT INTERFACES FOR NANOTECHNOLOGY

N. Clément (Univ. Lille), B. Siboulet, J.-F. Dufrêche

Despite being ubiquitous in the fields of chemistry and biology, the ion-specific effects of electrolytes pose major challenges for researchers. A lack of understanding about ion-specific surface interactions has hampered the development and application of materials for bio-chemical sensor applications.

Here[1], we show that scaling a silicon nanotransistor sensor down to ~25 nm provides a unique opportunity to understand and exploit ion-specific surface interactions, yielding a surface that is highly sensitive to cations and inert to pH.

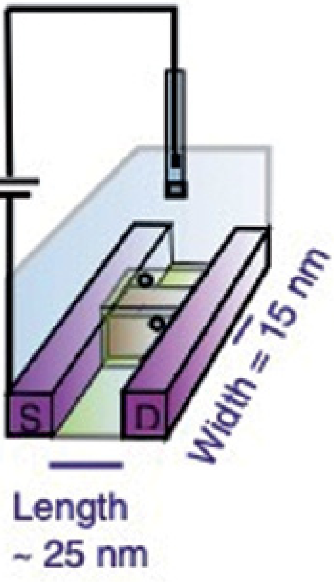


Figure 2: Schematic diagram of a 0D nanotransistor

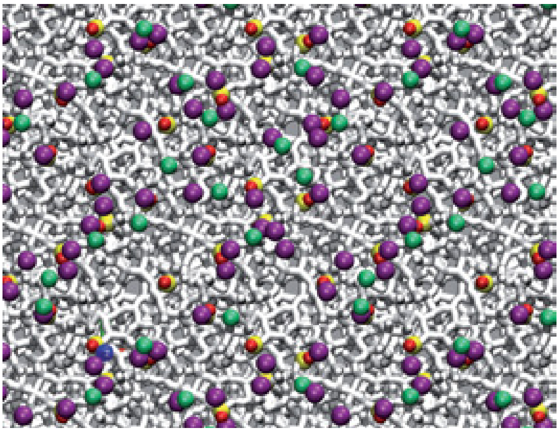


Figure 1 Ions binding on amorphous silica. Binding a single ion is detected by the nanotransistor.

The unprecedented sensitivity of these devices to Na^+ and divalent ions can be attributed to an overscreening effect via molecular dynamics. The surface potential of multi-ion solutions is well described by the sum of the electrochemical potentials of each cation, enabling selective measurements of a target ion concentration without requiring a selective organic layer. We use these features to construct a blood serum ionogram for Na^+, K^+, Ca^{2+} and Mg^{2+}, in an important step towards the development of a versatile, durable and mobile chemical or blood diagnostic tool. Combination of molecular simulations and classical DFT calculations show that the sensibility of the captor is magnified by the small size of the device. A specific response is obtained and the final device compares well with the existing sensors but with a much lower size.

Electrical potential fluctuations can be measured in nanotransistors at the interface of electrolyte solutions. These potential fluctuations can also be simulated at the atomic level by molecular dynamics. Ionic adsorption and desorption are the cause of the electrical potential fluctuations measured by the nanotransistor.

[1] Sivakumarasamy R., Hartkamp R., Siboulet B., Dufrêche J. -F., Nishiguchi K., Fujiwara A., Clement N. – **Selective Layer-Free Blood Serum Ionogram Based on Ion-Specific Interactions with a Nanotransistor.** – *Nature Materials* (2018) 17, 464-470.

SPONTANEOUS EMULSIFICATION : ULTRA-FLEXIBLE MICROMEULSION COEXIST WITH STRUCTURED WATER-POOR EMULSION DROPLETS

Th. Zemb, O. Diat
D. Horinek, W. Kunz (Université de Regenburg)
S. Prevost, I. Grillo (ILL)
S. Marcelja (ANU-Canberra)

In ternary solutions containing two slightly miscible solvents and a hydrotrope, mesostructures appear close to the phase boundary. Near the critical point, hetero-phase fluctuations dominate while on the water-rich side, "pre-ouzo" aggregates of 30_300 solvent molecules are present on the water-rich side while three dimensional w/o networks shown in the figure to the right predominate in the solvent-rich corner of the triangular phase diagram.[1] [2]

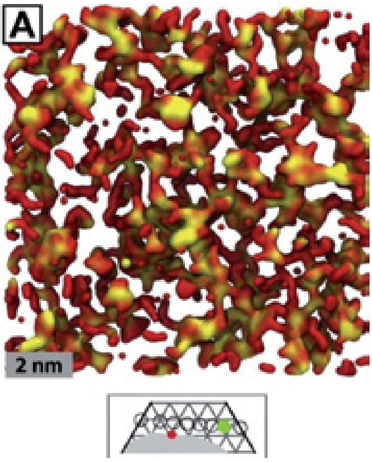


Figure 1: molecular dynamics snapshot showing the network morphology of ethanol ,water and octanol hydoxy-groups at the composition point shown in green on the ternary phase diagram, water-ethanol-octanol

When water is added on the water-rich side with 10 to 40 percent of ethanol to ternary solutions containing pre-ouzo aggregates, spontaneous emulsification known as ouzo-effect is produced we have investigated this. We have made the first real-time studies of emulsification and shown that emulsion and ultra-flexible microemulsions in dynamic equilibrium coexist once formed. The emulsions formed contain a significant amount of water and are structured solutions. The extremely common dispersive liquid-liquid emulsion method (DLLME) used in analytics since 15 years may be explained from this knowledge of the link for nano-scale and meso-scale self-assembly.

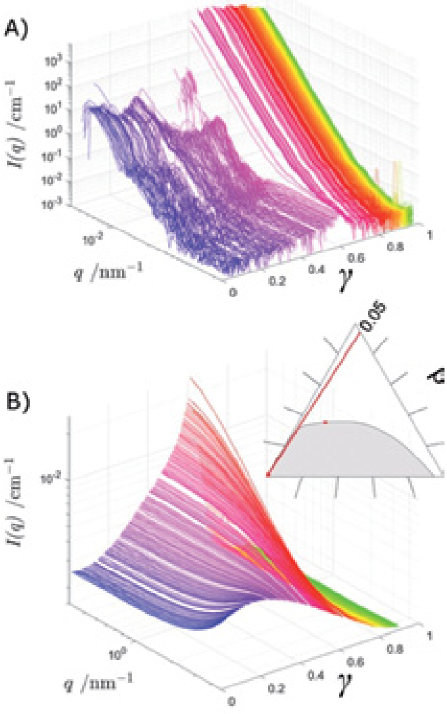


Figure 2: water is added progressively to an initial solution containing 5% of octanol and ethanol. A) shows the ultra-small angle X-ray scattering versus time and B° shows the middle-q range SAXS (on ID02 at ESRF): the low-q date measures the spontaneous emulsion droplet size and number per volume, while SAXS demonstrates the existence of small "pre-ouzo" aggregates in the large aqueous fraction of the sample.

[1] Schöttl S., Lopian T., Prévost S., Touraud D., Grillo I. , Diat O., Zemb T., Horinek D. - **Combined MD/SAS analysis of organization on a nanometer-scale in ternary solvent solutions containing a hydrotrope** – *Journal of colloid and Interface Science* (2019) 540 pp. 623-633

[2] Prévost S., Krickl S. , Marcelja, S. ; Kunz W., Zemb T., Grillo I. - **Spontaneous Ouzo emulsions coexist with pre-ouzo ultra-flexible microemulsions** - *Langmuir 2020* (accepted, in press)

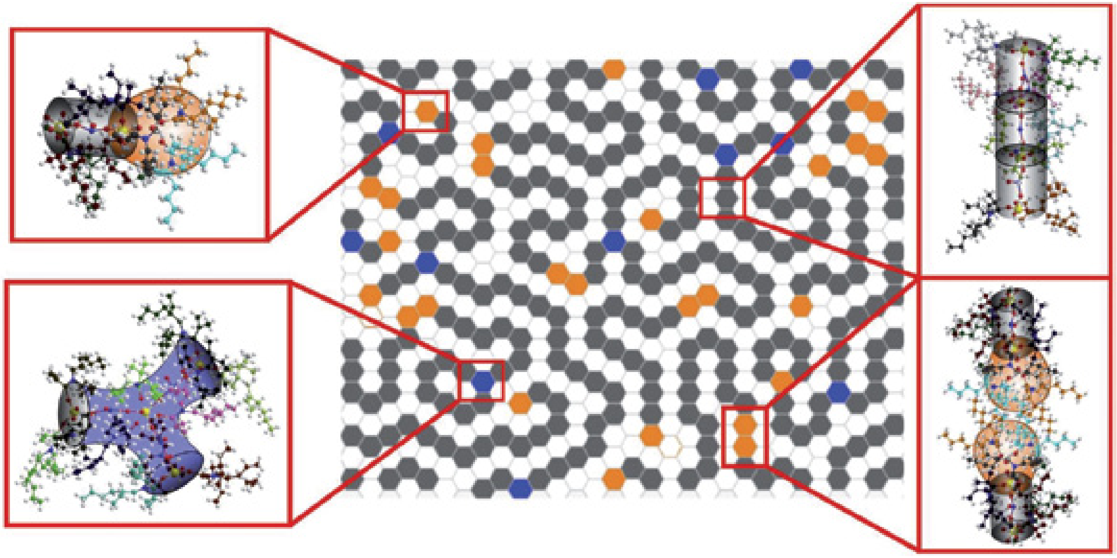
A MINIMAL THERMODYNAMIC MODEL PREDICTING DIRECT AND REVERSE GIANT MICELLE VISCOSITY

Th. Zemb, M. Pleines
Jean Duhamet (ISEC, CEA-Marcoule)
W. Kunz (Université de Regensburg)

The viscosity increase of the organic phase observed when liquid-liquid-extraction processes are intensified causes designing safe difficulties for processes on industrial scale. When acidity or "load" in uranium for example increases, most extractant formulations used in applications exhibit strong increase of viscosity is extracted in the organic phase. We have tackled this problem using as a model system, the family of N,N-dialkylamides with different topologies of the hydrocarbon chain in presence of uranyl experimentally. SWAXS experiments done in Marcoule have detected for the first time the peak due to U-U distance in the solvent phase.

We have developed a minimal model at nano-scale based on the "microphase" concept introduced in biochemistry by Charles Tanford, 40 years ago and never used in the context of chemical engineering. The coexisting microphases are contact-points, end-caps and rigid w/o cylinder (see fig.). Using only measurable parameters such as spontaneous curvature and chain flexibility allows to rationalize all the experimental values observed and does show predictive power : qualitative trends in viscosity variation observed when cation content is increased, and this is dependent on the packing parameter of the extractant used. This model explains why some molecules behave "better" than others and the moderate effect of diluent formulation.[1]

Surprisingly, the model also applies in the o/w case: in the domain of the and body care, the viscosity increase linked to additives such as salts or fragrances has to be increased as much as possible with low solute concentration. Instead of an increase that should be avoided, a viscosity peak is obtained and searched for: our model initially tailored for hydrometallurgy appeared to be robust enough to predict the variation of the viscosity peak as well with other organic additives.[2] Moreover, aqueous phase instability is important when detergents are combined in formulation for laundry. In the case of widely used surfactants in home washing machines with different chemical "branching" of the chains, the same model explains for the first time quantitatively the variation of temperature of usage in detergency for molecules that are isomers in branching of the alkyl chain only.



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[1] Pleines M., Hahn M., Duhamet J., Zemb T. - **A minimal model leading towards a new formulation principle for extracting microemulsions** - *EPJ Nuclear sciences and technology* (2020) 2-18.
[2] Pleines M., Kunz W., Zemb T., Benczedi D., Fieber W. - **Molecular factors governing the viscosity peak of giant micelles in the presence of salt and fragrances** - *Journal of Colloid and Interface Science* (2019) 537, 682-693.

INTERNATIONAL PROJECTS

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«REE-CYCLE-PROJECT» (2013-2018): RARE EARTH EXTRACTION AND RECYCLING WITH LOW HARMFUL EMISSIONS

P.I.: Thomas Zemb (Marcoule), co-P.I. : Jean-Christophe P. Gabriel (Grenoble)
Scientific Advisor: Helmuth Möhwald

Aim of the project: recycling rare earth elements (REE) is a matter of strategic independence for Europe, hence to urgently find processes taking better account of environmental and economic issues. Currently THERE IS NO SUCH INDUSTRIAL PROCESS AVAILABLE[1] and there is no waste recycling for rare earth elements at all. Moreover, 97% of the mining operations are performed in China, hence representing a major Damocles' Sword for the rest of the world's economy.

Our objective was on one hand to develop the fundamental understanding involved in the processing complex fluids (both experimental and theoretical) and on the other hand to use predictive modelling, accelerated determination of phase diagrams as well as free energies of transfer in order to be able to develop new, cost effective and environmentally friendly REE recycling processes.

This was achieved

- by enabling, for the first time ever, a fast and efficient measurement of free energy of mass transfer of five to ten elements between an aqueous solution and a water-poor microemulsion. Thus, it will be possible to explore and master an extensive number of process formulations
- by developing predictive models of ion liquid-liquid separation including the effect of long-range interactions between metal cations and micelles;
- by using the experimental results and prediction tools developed, we will design an advanced & environmentally friendly process formulations;
- by enhancing the extraction kinetics and selectivity, by implementing a new, innovative and selectively triggered triggering cation exchange process step.

Furthermore, this new understanding of mechanisms involved in selective ion transfer should be applicable to optimize knowledge-based processes that are economically, ecologically and sociologically acceptable to other unresolved problems such as heavy metals, hormones, or drug contamination in drinkable water as well as open new recycling possibilities. It will pave the way to economic recovery of metals from a very rapidly growing "mine", i.e. the diverse metal containing "wastes" generated by used Li-ion batteries, super-capacitors, wind turbines, supported catalysts and fuel cells.

The group actively involved in the REE-CYCLE project (as November 2016) J. Theisen, M. Bley, S. Gourdin, Alla Malinennko, J.-F. Dufrêche, M. Spadina, O. Diat, S. Pellet-Rostaing, M. Duvail, C. Penisson, R. Laucournet, D. Meyer, J. Duhamet, A. Leprou, S. Charton, D. Alpe-Conchyand in the first row: Helmuth Möhwald, Thomas Zemb (Principal investigator) and Jean-Christophe P. Gabriel (co-Principal Investigator)

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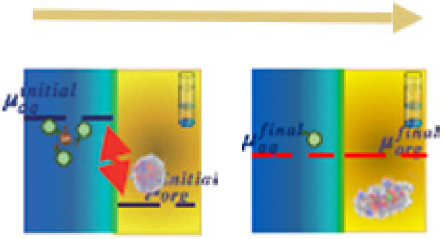
[1] European Union's 7th Framework Program (FP/2007-2013)/ERC Grant Agreement N° [320915] "REE-CYCLE" from proposal submitted by Thomas Zemb and Jean-Christophe Gabriel in February 2012.

IEANICS: COMPETING MOLECULAR FORCES AT COLLOIDAL SCALE EXPLAIN LIQ-LIQ EXTRACTION (WP2)

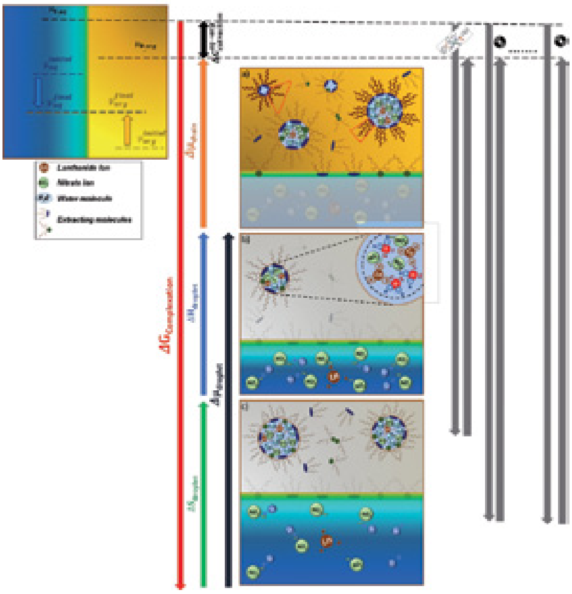
T. Zemb, A. El Maangar, Mario Spadina, Sandrine Dourdain, Damien Bourgeois and J-F. Dufrêche
S. Marcelja (ANU- Canberra)



The knowledge-based control of the transfer of species between liquid phases that is at the basis for extraction and recycling of metals is controlled by the gradients in chemical potential, just as the electrical current exchanged by semi-conductors depends on the electric potential. At the beginning of an extraction experiment, the gradient flows from the aqueous phase to the solvent phase, with a kinetic obstacle at the interphase (shown in green in the figure on the left). Diffuse aggregates similar to reverse micelles are the "container" for all polar extracted species.

While the supra-molecular and coordination chemistry approach used in more than thousand papers per year considers the free energy of transfer to result from multiple competing complexation reactions shown in grey arrows that require hundreds of adjustable parameters to adjust in order to be compatible with experimental plan results. The "ienaics" approach introduced in 2014 considers the three mechanisms competing at the nano-scale[1]: beyond the complexation term shown in red, the droplet term shown in black related to nanometric aggregates of polar species and finally the "chain" term related to solvent nanostructure reorganization, shown in orange[2].

Nowadays, the ienaics decomposition of the free energy of transfer has allowed giving a first explanation of synergy, the link between volatility of solvent and extraction, the optimization of plant design using formulations close but not too close to instability zones in phase diagrams. The success of the integrated ienaics approach is spreading fast to other separation technologies: adding solvent "modifiers"[3], using polymeric membranes, ionic liquids and even chemical analysis via spontaneous emulsification, or extraction from the atmosphere by aerosols[4].



[1] Rey J., Bley M., Dufreche J. F., Gourdin S., Pellet-Rostaing S., Zemb T., Dourdain S. - **Thermodynamic Description of Synergy in Solvent Extraction: II Thermodynamic Balance of Driving Forces Implied in Synergistic Extraction** - *Langmuir* (2017) 33, 13168-13179.

[2] Bourgeois D., El Maangar A., Dourdain S. - **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.

[3] Lu Z. J., Dourdain S., Pellet-Rostaing S. - **Understanding the Effect of the Phase Modifier n-Octanol on Extraction, Aggregation, and Third-Phase Appearance in Solvent Extraction** - *Langmuir* (2020) 36, 12121-12129.

[4] Spadina M., Dufrêche J-F., Marcelja S., Pellet-Rostaing S., Zemb T. -**Molecular forces competing in liquid-liquid extraction** - *Langmuir feature invited paper* (submitted)

SUPRAMOLECULAR AND MESOSCALE MODELING OF LIQUID-LIQUID EXTRACTION OF RARE EARTH SALTS (WP2)

A. Karmakar, M. Bley, S. Gourdin-Bertin, M. Duvail, Th. Zemb, J.-F. Dufrêche

The recycling of rare earth elements and the understanding of nuclear waste management based on liquid-liquid extraction systems is important for the success of present and future technologies. It is crucial to identify and to understand the motors of selectivity and efficiency of such hydrometallurgical approaches. One essential aspect is the understanding of the aggregation processes in organic solvent phases in contact with an aqueous electrolyte solution.

In an attempt of understanding the relation between the extraction and the complexation free energies in the case of lanthanide salt ($Eu(NO_3)_3$)– containing spherical reverse micelles, a minimal thermodynamics model combining supramolecular chemistry and mesoscale has been developed[1], where we took into account the fundamental property of weak aggregation: the aggregates are equilibrated by constant exchange of ligands, so the polydispersity in the aggregates is described using general theories of surfactant self-assembly. This multi-scale approach allows for reducing largely the number of parallel apparent equilibria currently used for dimensioning extraction devices (Fig. 1).

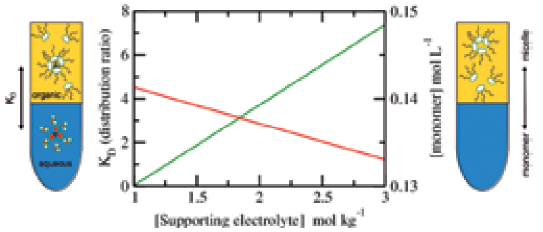


Figure 1: Distribution coefficient and concentration of free monomer in the organic solution as a function of the concentration of supporting electrolyte present in the aqueous phase.

Then, this thermodynamics model has been improved taking into account the variation of the organic phase microstructure[2]. We consider here that the extraction of metals in the form of salts is triggered by complexation and quenched by the associated necessary reorganization of the structured solvent phase. The free energy and corresponding microstructures of the water-poor microemulsions are modelled in the frame of the Gaussian random fields (GRF) model (Fig. 2).

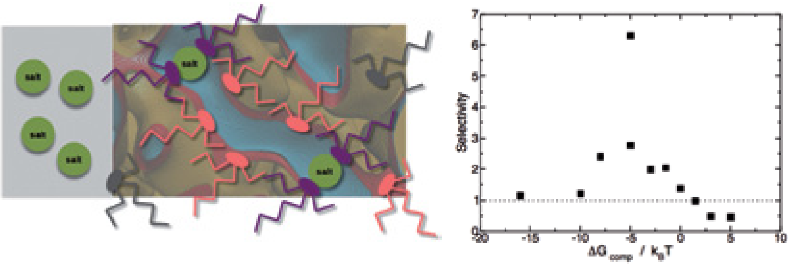


Figure 2: (Left) Schematic representation of the minimal model developed taking into account the variation of the microstructure. (Right) Apparent selectivity between a small and a big salt as a function of the Gibbs energy of complexation calculated for a concentration of extractant of 1 mol L^{-1}.

The curvature frustration energy significantly contributes to the free energy of extraction. The practical case of lanthanide extraction by TBP molecules has been studied. We showed that the structuration of a microemulsion has only a limited impact on the extraction yield. We also highlighted that selectivity between a hydrated and a non-hydrated species is concentration dependent, and cannot be considered as constant as a function of the extractant concentration.

[1] Karmakar A., Duvail M., Bley M., Zemb Th., Dufrêche J.-F. – **Combined Supramolecular and Mesoscale Modelling of Liquid–Liquid Extraction of Rare Earth Salts.** – *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2018) 555, 713-727.

[2] 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* (2020) Accepted.

COLLOIDAL MODEL FOR THE PREDICTION OF NUCLEAR WASTE/RARE EARTH EXTRACTION PROCESSES (WP2)

M. Špadina, S. Gourdin-Bertin, Th. Zemb, J.-F. Dufrêche, K. Bohinc (Univ. of Ljubljana, Slovenia)

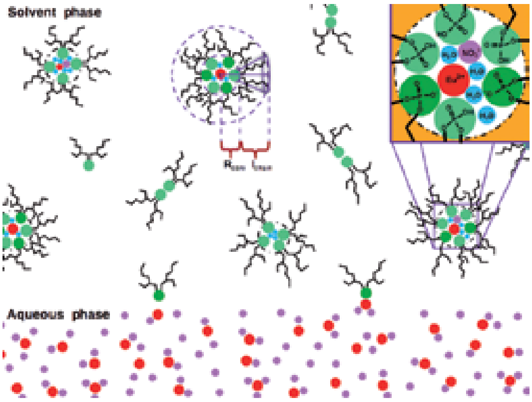


Figure 1: Colloidal modelling of solvent extraction

We develop a colloidal model for the prediction of solvent extraction. We consider a rare earth extraction system for which the solvent phase is similar to water-poor micro-emulsions. All physical molecular quantities used in the calculation can be measured separately. The model takes into account competition complexation, mixing entropy of complexed species, differences of salt concentrations between the two phases, and the surfactant nature of extractant molecules. We consider the practical case where rare earths are extracted from iron nitrates in the presence of acids. The solvent wetting of the reverse aggregates is taken into account via the spontaneous packing. All the water-in-oil reverse aggregates are supposed to be spherical on average.

The model captures several features observed in practice: reverse aggregates with different water and extractant content coexist dynamically with monomeric extractant molecules at and above a critical aggregate concentration (CAC). The CAC decreases upon the addition of electrolytes in the aqueous phase. The free energy of transfer of an ion to the organic phase is lower than the driving complexation. The commonly observed log–log relation used to determine the apparent stoichiometry of complexation is valid as a guideline but should be used with care. The results point to the fact that stoichiometry, as well as the probabilities of a particular aggregate, is dependent on the composition of the entire system, namely the extractant and the target solutes' concentrations. For every chemical species involved in the calculation, the model is able to predict the exact equilibrium concentration in both the aqueous and the solvent phases at a given thermodynamic temperature[1].

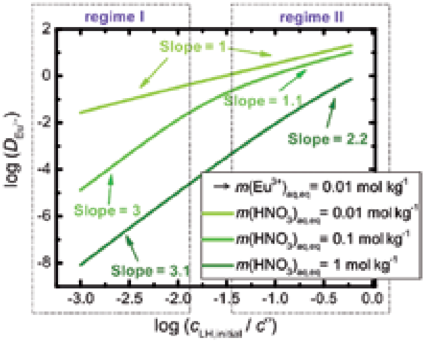


Figure 2: Distribution coefficients as functions of extractant for different conditions. The figure exhibits the difficulty to apply a slope method to get stoichiometries of complexes in solvent extraction

For acidic extractant (HDEHP), multiple extraction regimes were identified. Each of these regimes is controlled by the formation of different species in the solvent phase, ranging from multiple metal cation filled aggregates (at the low acid concentrations in the aqueous phase), to the pure acid filled aggregates (at the high acid concentrations in the aqueous phase). Contrary to the current paradigm of simple stoichiometry behind liquid–liquid extraction, there is a severe polydispersity of aggregates completely different in compositions, but similar in the free energy. This variety of structures on the nanoscale is responsible for the synergistic transfer of ions to the organic phase. Synergy can be understood as a reciprocal effect of chelation: it enhances extraction because it increases the configurational entropy of an extracted ion.

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[1] Špadina M., Bohinc K., Zemb Th., Dufrêche J.-F. –**Multicomponent Model for the Prediction of Nuclear Waste/Rare-Earth Extraction ProcesseExtraction. –** *Langmuir* (2018) 34, 10434-10447.
Špadina M., Bohinc K., Zemb Th., Dufrêche J.-F. – **Colloidal Model for the Prediction of the Extraction of Rare Earths Assisted by the Acidic Extractant** – *Langmuir* (2019) 35 (8), 3215-3230.
Špadina M., Bohinc K., Zemb Th., Dufrêche J.-F. – **Synergistic Solvent Extraction Is Driven by Entropy** – ACS Nano (2019) 13 (12), 13745-13758.

COMPOSITION-DEPENDANT VALLEY OF STABILITY OF THE WEAK DIFFUSE AGGREGATES AT THE ORIGIN OF METAL EXTRACTION (WP2)

With Magali Duvail, Simon Gourdin, Bertrand Siboulet, Michael Bley, Thomas Zemb, J.-F. Dufrêche

The aim of WKP 2 is to develop predictive models for the relation between free energy of supramolecular complexation that is the driving force for extraction and stripping and the observed free energy of transfer between an aqueous and a liquid phase. Classical methods imply dozens of parameter for the seventeen different classes of extraction mechanisms used industrially. Separating colloidal from supra-molecular scale requires to abandon the notion of stoechimetry of complexes, and treat all solvent solution as dispersed media with known area of polar/apolar contact and curvature.

We have first established predictive models for the stability polar aggregate volume in different regions of the ternary phase diagrams[1] (Duvail, Dufrêche, Arleth, & Zemb, 2013). This required to move from a molecular modelling to meso-scale modelling of polar core, head-group distributions and solvent via Gaussian random waves (figure 1), for which an expression of the entropy is now available[2]. Then, the fixed stoechiometry of each aggregate by a map of probability of presence with tow coordinates : the number of water molecules per aggregate and the number of extrctant per aggregate. Up to now, this calculation could only be made explicitely when approximating all agregates as spherical unconnected polar cores [3] (figure 2).

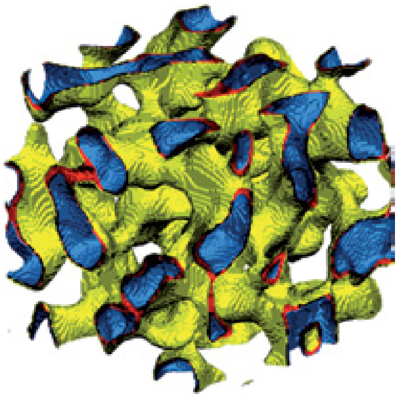

Figure 1: a concentrated solution of extractants represented at the meso-scale. "Hydrophobic" domains (solvent, chains of extractants, modifiers are shown in yellow), ions, water, acids are shown in yellow; polar heads of extractants are shown in red and all water-soluble species are shown as a homogenous blue volume. The snapshot in thermodynamic equilibrium shown on the left has a scale of 10 nm.

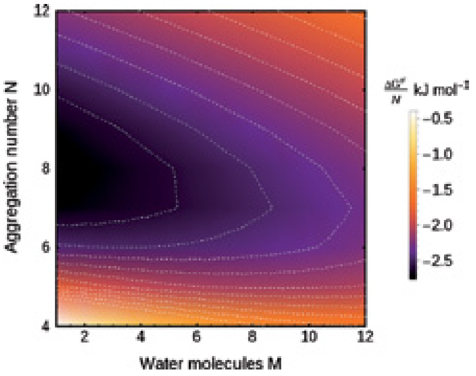

Figure 2: a typical probability map for w/o weak aggregates. The color gives the free energy of aggregation in kJ/Mole for any aggregate with four molecules or more determining an "inside" volume containing polar head-groups as well as M water molecules. All aggregates are supposed to be spherical and the curvature energy given by the intrinsic flexibility of the interface in a given more or less "penetrating" solvent wetting the chains protruding from the aggregate[4].

[1] Duvail, M., Arleth, L., Zemb, T., & Dufrêche, J.-F. **Predicting for thermodynamic instabilities in water/oil/surfactant microemulsions: A mesoscopic modelling approach**. The Journal of Chemical Physics, (2015) 140, 164711.

[2] Marčelja, S. **Entropy of level-cut random Gaussian structures at different volume fractions**. (2017) Physical Review E, 96(4). Page 042147

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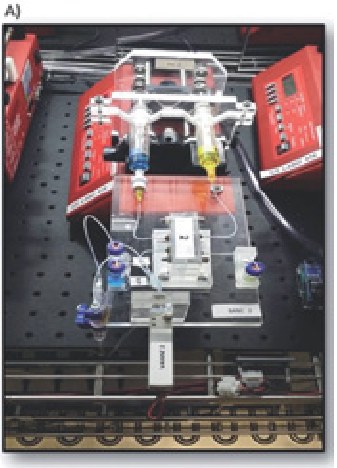
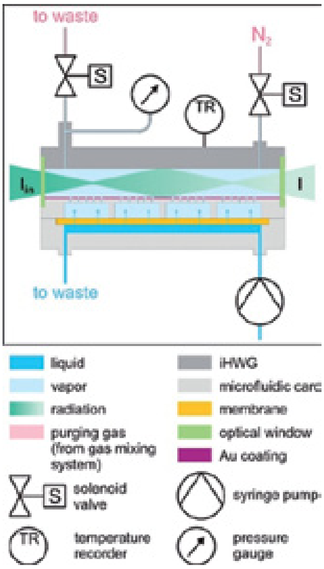
AN INSTRUMENTED MILLI-FLUIDIC DEVICE FOR ON-LINE MEASUREMENT OF ELECTROLYTE EQUILIBRIA AND SOLVENT ACTIVITY DURING LIQUID-LIQUID EXTRACTION (WP1)

Johannes Theisen, Christophe Penisson, Jean-Christophe Gabriel (Grenoble);
Jean Duhamet and Thomas Zemb (Marcoule) and in collaboration with Boris Mizaikoff (Ulm University.)

Quantitative determination the free energy of transfer of species between water and solvent by microfluidics require to measure in situ at entry and at exit of the microfluidic device (as shown on the left) of the concentration of ions and of the solvent activity. The latter is measured by integrated hollow waveguide FTIR.[1] Electrolyte concentrations (as rare earths and iron cations) are obtained via X-ray fluorescence, a non-destructive method that allows routinely determining concentrations as mM/l present on a surface that is illuminated by a collimated X-ray source. We have developed special algorithm of the collected data containing superposed adsorption lines that take into account the conservation of total number of species between input and output. This allows, for the first time, to determine the cation distribution factor and hence free energy of transfer with of un-precedented precision of less than 1 kJ/Mole [2].
The device (figure 1) is able to detect variations down to the percent of typical solvent activity (via Gibbs-Duhem relations).[3,4] Molecular dynamics studies can reproduce the effect of vapor pressure depletion.[5]





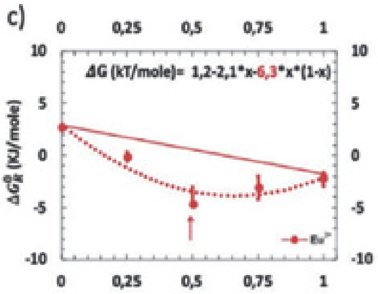


Figure 2 (left side): principle of operation of the on-line measurement of solvent activity by IR adsorption (middle): Absorbance signal obtained for 100% ethanol and 0% ethanol (right side): the detection of the optimal synergy ratio of two surfactants (x axis) as function of the free energy of transfer. Industrial use of mixed extractants is possible for DG between -2 and -5 since the free energy is the logarithm of the extracted rare earth concentration at the optimal ratio, the efficiency is close to -5, i.e. hundred times more than it would be without the synergy that has been detected via milli-fluidic methodology.

[1] Theisen J., Christophe P., Zemb T., Gabriel J. C., Mizaikoff B., Wilk A., Kokoric V. - **Apparatus for the measurement of chemical activity coefficients of gas phase species in thermodynamic equilibrium with liquid phase** - EP 17 198247. dépôt le 2017-10-25

[2] El Maangar A., Theisen J., Penisson C., Zemb T., Gabriel J. C. P. - **A microfluidic study of synergic liquid-liquid extraction of rare earth elements** - *Physical Chemistry Chemical Physics* (2020) 22, 5449-5462.

[3] Kokoric V., Theisen J., Wilk A., Penisson C., Bernard G., Mizaikoff B., Gabriel JCP. - **Determining the Partial Pressure of Volatile Components via Substrate-Integrated Hollow Waveguide Infrared Spectroscopy with Integrated Microfluidics** - *Anal. Chem.* (2018) 90, 4445−4451.

[4] Penisson, C., Wilk, A., Theisen, J., Kokoric, V., Mizaikoff, B., Gabriel, J.C.P., **Water activity measurement of NaCl/H2O mixtures via substrate-integrated hollow waveguide infrared spectroscopy with integrated microfluidics**. *Biotech, Biomaterials, and Biomedical: TechConnect Briefs* 198-201 (2018), CRC Press, ISBN 978-0-9988782-4-9. Proceeding of Nanotech 2018, May 13-16, 2018 Anaheim, CA, USA.

[5] Bley M., Duvail M., Guilbaud P., Penisson C., Theisen J., Gabriel J. C., Dufreche J. F. - **Molecular simulation of binary phase diagrams from the osmotic equilibrium method: vapour pressure and activity in water-ethanol mixtures** - *Molecular Physics* (2018) 116, 2009-2021.

THE LASER INTERFACE FORCE MACHINE: IDENTIFYING NANOMETRIC ELECTRO-ACOUSTIC SURFACE WAVE ON MILLIMETRIC DROPLETS (WP5)

Johannes Theisen, Julien Rey, Maximilian Pleines, Jean-Christophe P. Gabriel and Thomas Zemb in collaboration with Mario Corti, Paola Brocca and Laura Cantu (University Milano).

We have designed and operated as a proof of concept the first optical device allowing to measure nanometric surface waves occurring via electroacoustic at the surface of a droplet containing extractants molecules and a solvent (diluent). The solvent droplet is typically 1 mm size and floats in an aqueous reservoir at fixed pH and containing rare earths and background salt. Surface wave amplitudes can be detected with as low amplitudes than one nanometer, with frequencies close to 100 Hz. If the droplet was on the size of earth, these waves would have an amplitude of the order of the terrestrial tide. The surface layer oscillations that can be detected since the LIFM breakthrough have the same amplitude than that monomolecular films that assemble at the surface of droplets. This break-through was made possible by a newly developed device based on confocal Fabry-Perot for measuring nanometer amplitude resonance surface waves on an extractant emulsion droplet. The device is a combination of Fabry-Perot confocal interferometry used in variable frequency mode under electrical excitation. The figure 1 below shows the millimeter-sized droplet of oil-soluble complexing agent extractant used as interferometer.

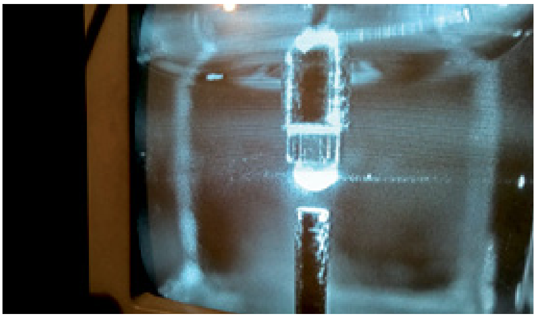
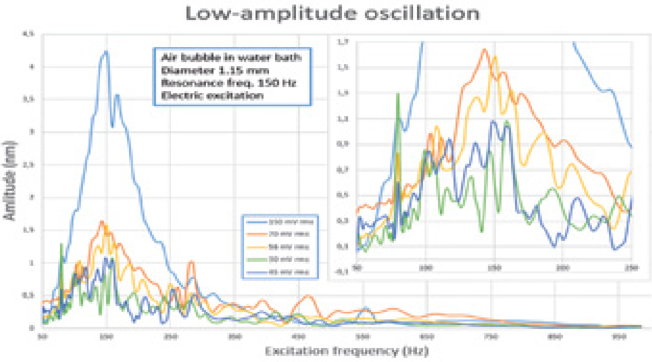


Figure 1: A droplet of typically 1 mm diameter containing a concentrated solution of surface-active extractant is contacted with a solution of high concentration of lanthanide nitrates in nitric acid. The beam crosses the aqueous phase in which some mixed aggregates of slightly water-soluble complexant produce ion oligomers: in the oil droplet, large colloidal aggregates produce scattering. Fabry-Perot confocal interferometry is done in the reflection mode, close to the drop equator, under excitation of a vertical electric field of 5 V/cm in the vertical direction, sweeping in the range 50-250 Hz.

Figure 2: Surface modes of droplets, shown as nanometer amplitude versus electrical excitation frequency. Single shot signal-to-noise ratio = 2 validated for a field of 45 mV/1.5mm = 30 V/m, yielding amplitude of 0.7 nanometre for the surface waves that can be detected in a single shot without accumulation ?



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[1] Corti M., Raudino A., Cantu L., Theisen J., Pleines M., Zemb T. - **Nanometric Surface Oscillation Spectroscopy of Water-Poor Microemulsions** - *Langmuir* (2018) 34, 8154-8162.

Raw data set are obtained -as shown in figure 2- as an amplitude of the surface wave known from the laser wavelength used as well as the local intensity of part of the falling on a photodiode and selected via a lock-in amplifier. The first experiment performed with this new ultra-sensitive instrument was to investigate the surface waves produced when "recognized" Europium ions are present in the water reservoir and the droplet is covered by an extractant molecule. The unexpected formation of a thin solid crust (few mm) of third phase with lyotropic liquid crystal has been detected.[1]

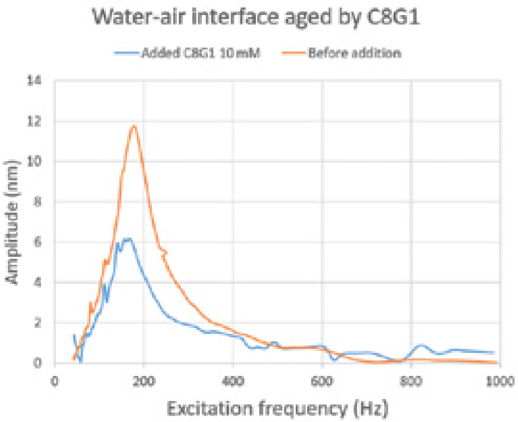


Figure 3: Sensitivity to the presence of a common protein membrane solubilizer (octylglucoside) on the surface of a bubble: one molecule per nm² induces a downshift of the resonance with an increase of relaxation producing FWHM broadening from Q = 0.6 to Q' = 0.75 (10 mM C8G1) ; curve in orange : no octylglucoside, and in blue : with octylglucoside.

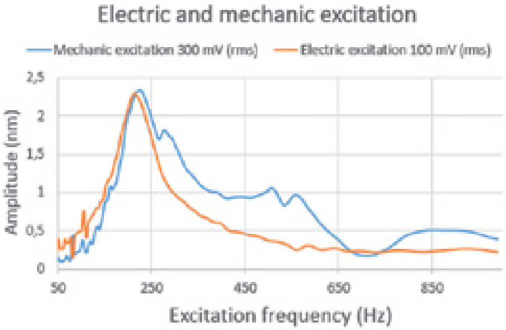


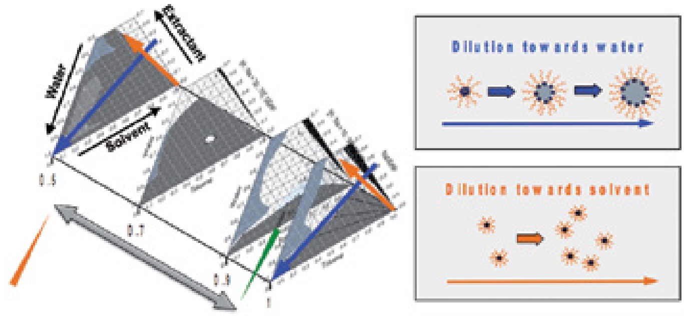
Figure 4: Reciprocity of Onsager coefficients: the same bubble is excited either with electrical excitation produced by the electrodes, or by mechanic excitation via a piezo-electric device located in the bottom of the cell. The main excited mode is the same, but other modes are excited also by echo of the sound on the sample reservoir. Measurement of the hydrostatic pressure and the electrical field of same frequency responsible of the same surface wave amplitude would provide unique information about the energy needed to produce the waves, and therefore the first direct verification (and exploitation) of Onsager reciprocity principle.

Figure 5: Multi-disciplinarity of the team leaders associated in ***the Rare Earth recycling without harmful emissions project :***
(l-r): Jean Duhamet (chemical engineering), Helmuth Môhwald (physical chemistry of interfaces), Stéphane Pellet-Rostaing (functional self-assembled separation chemistry) , Jean-François Dufrêche (statistical physical chemistry), Thomas Zemb (colloidal physical chemistry), Dominique Alpe-Conchy (administration and human resources), Jean-Christophe P. Gabriel (material science and analytical chemistry).

THE FOUR REGIMES OF ELECTRICAL CONDUCTIVITIES IN WATER-POOR MICROEMULSIONS (WP4)

Tobias Lopian, S. Dourdain, Th. Zemb, (ICSM)-, W. Kunz (Université de Regensburg)

The conductivity of ternary water-poor microemulsion is not generally understood. At low water/surfactant ratio, typically below four the conductivity is extremely low, but increases or decreases with concentration. With higher water content, dynamic as well as static percolation behavior were suggested to explain the behavior of the most studied system (AOT/water/NaCl/isooctane). IN intermediate water/surfactant ratio, an anti-percolation is observed upon dilution of water, i.e. a step decrease of conductivity of a factor of more than ten corresponding to a moderate increase of water. No general map in a phase prims being available, the generality of these various sometimes counter-intuitive behaviour was questionable.

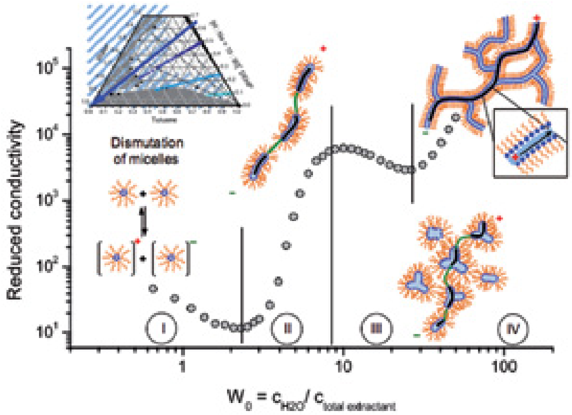


$$Z = \frac{w(NaDEHP)}{w(NaDEHP) + w(HDEHP)}$$

Figure 1: full phase prism, varying not only the three components, but also the H+/Na+ ratio of counter-ions that controls the spontaneous curvature. The analog of AOT, i.e. diethylhexylphosphate (X+DHEP-) very commonly used in hydrometallurgic processes was chosen as model system

The knowledge of all stable single-phase zones in the phase prism as shown in figure 1 allows not only the classical dilution lines with water and oil, but also to establish conductivity behavior while keeping all parameters constants, just varying the surface charge per nm^2, i.e. the spontaneous curvature[1] (fig.1). Confronting conductivity behaviour observed along these different liens allows to identify and understand the condition of appearance of the four regimes of conductivity[2] that were previously suspected fig.2

Figure 2.: Location versus the thermodynamic variable (water/ surfactant) of the four regimes of conductivity and sketch of the corresponing nanostructures (I) dismutation, (II) dynamic percolation, (III) curvature-frustrated intermediate and (IV) static percolation, depending on the water/detergent ratio as well as available surface in m^2/g .



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[1] Lopian T., Dourdain S., Kunz W., Zemb T. - **A formulator's cut of the phase prism for optimizing selective metal extraction** - *Colloids and Surfaces a-Physicochemical and Engineering Aspects* (2018) 557, 2-8.
[2] Tobias Lopian, phD thesis manuscript , Montpellier and Regensburg (November 2017)

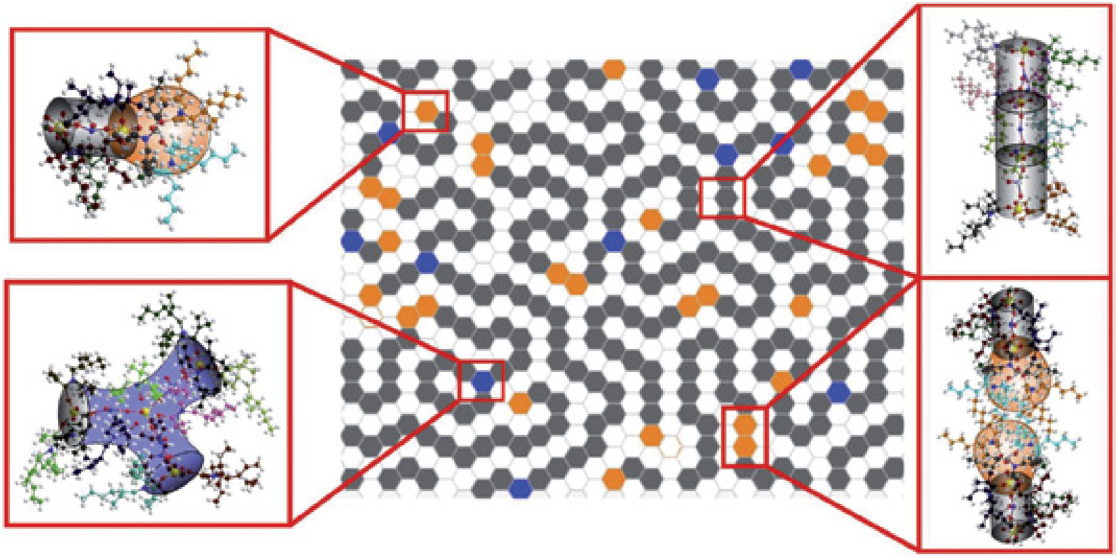
A MINIMAL THERMODYNAMIC MODEL PREDICTING DIRECT AND REVERSE GIANT MICELLE VISCOSITY (WP4)

Maximilian Pleines, Th. Zemb, (ICSM)
Jean Duhamet (ISEC, CEA-Marcoule)
W. Kunz (Université de Regensburg)

The viscosity increase of the organic phase observed when liquid-liquid-extraction processes are intensified causes designing safe difficulties for processes on industrial scale. When acidity or "load" in uranium for example increases, most extractant formulations used in applications exhibit strong increase of viscosity is extracted in the organic phase. We have tackled this problem using as a model system, the family of N,N-dialkylamides with different topologies of the hydrocarbon chain in presence of uranyl experimentally. SWAXS experiments done in Marcoule have detected for the first time the peak due to U-U distance in the solvent phase.

We have developed a minimal model at nano-scale based on the "microphase" concept introduced in biochemistry by Charles Tanford, 40 years ago and never used in the context of chemical engineering. The coexisting microphases are contact-points, end-caps and rigid w/o cylinder (see fig.). Using only measurable parameters such as spontaneous curvature and chain flexibility allows to rationalize all the experimental values observed and does show predictive power : qualitative trends in viscosity variation observed when cation content is increased, and this is dependent on the packing parameter of the extractant used. This model explains why some molecules behave "better" than others and the moderate effect of diluent formulation.[1]

Surprisingly, the model also applies in the o/w case: in the domain of the and body care, the viscosity increase linked to additives such as salts or fragrances has to be increased as much as possible with low solute concentration. Instead of an increase that should be avoided, a viscosity peak is obtained and searched for: our model initially tailored for hydrometallurgy appeared to be robust enough to predict the variation of the viscosity peak as well with other organic additives.[2] Moreover, aqueous phase instability is important when detergents are combined in formulation for laundry. In the case of widely used surfactants in home washing machines with different chemical "branching" of the chains, the same model explains for the first time quantitatively the variation of temperature of usage in detergency for molecules that are isomers in branching of the alkyl chain only.[3]



[1] Pleines M., Hahn M., Duhamet J., Zemb T. - **A minimal model leading towards a new formulation principle for extracting microemulsions** - *EPJ Nuclear sciences and technology* (2020) 2-18.
[2] Pleines M., Kunz W., Zemb T., Benczedi D., Fieber W. - **Molecular factors governing the viscosity peak of giant micelles in the presence of salt and fragrances** - *Journal of Colloid and Interface Science* (2019) 537, 682-693.
[3] Pleines M., Kunz W., Zemb T., Benczedi D., Fieber W. - **Molecular factors governing the viscosity peak of giant micelles in the presence of salt and fragrances** - *Journal of Colloid and Interface Science* (2019) 537, 682-693.

EN MÉMOIRE DU PROFESSEUR HELMUT MÖHWALD

Helmuth Möhwald, Pr Dr honoris causa de Montpellier, Prix Humbold Gay Lussac en Chimie Séparative, était membre du Comité d'Orientation Scientifique de Balard et a présidé le dernier «visiting committee» du CEA consacré à la Chimie en 2009.

Retraité de sa fonction de Directeur-fondateur de l'Institut Max Planck «Colloïdes et Interfaces» de Potsdam depuis février 2017, Helmuth Möhwald était actif à temps partiel à Marcoule et à Grenoble sur le projet Européen de recyclage de terres rares «REE-cycle» (action transverse CEA-DRF/DEN/DRT). Il était membre du conseil scientifique du labex Chemisyst de Montpellier ainsi que du Labex CSC de Strasbourg.

Ses travaux personnels dans l'auto-assemblage sur des surfaces, de l'ordre de 500 articles et cinquante brevets, sont cités plus de dix mille fois par an dans le Web of Science. La partie « engineering » de ses travaux porte sur la lubrification dans l'espace et le transport des radicaux en cristaux liquides. Il restera dans l'Histoire des Nanosciences comme ayant été l'unificateur des équations d'état en 2D et 3D des mélanges de lipides et de polymères. On lui doit aussi la méthode de dépôt de monocouches de charges alternées sur des surfaces (Layer-by-Layer) qui ont conduit à de nombreuses applications allant de la pharmaco-technique à la protection auto-réparatrice contre la corrosion.
Il a été un éditeur-fondateur de la revue ACS-nano, qui s'est hissée très vite dans les dix meilleurs journaux généralistes et le trio de tête en nanosciences. Depuis 2009, il venait régulièrement comme lauréat Humboldt-Gay Lussac et ensuite comme conseiller scientifique actif à l'ICSM pour travailler sur la modélisation d'expériences d'extraction liquide-liquide par microémulsions et diriger des étudiants à l'ICSM à Marcoule, la dernière fois en novembre 2017.

La «life-time Awards colloïdes et interfaces», qui est attribuée tous les trois ans sur nomination ouverte internationale, a été votée en décembre dernier et lui a été remise lors du congrès mondial IACIS à titre posthume à Rotterdam en mai dernier.

«RECYCLING PROJECT» (2014-2017)
LABORATOIRE INTERNATIONAL ASSOCIE CNRS-MPG

Scientists participant to the LIA « RECYCLING » 2014-2017:

- *in Potsdam: Helmuth Möhwald (deceased March 2018), Peter Fratzl (from 2016), Hans Riegler, Luca Bertinetti*
- *in Marcoule and Saclay: Thomas Zemb, Olivier Diat, Michael Odorico, Sophie Charton, Damien Féron, Florence Lequien*
- *PhD students involved:*
  - *Marie Jehannin (co-tutelle Montpellier-Potsdam, 2012-2015): Oxalic precipitation in coalescing droplets: study of the role of coalescence on mixing and nucleation of ceramic precursors*
  - *Virginie Soulié (co-tutelle Montpellier-Potsdam, 2012-2015): Drying of droplets containing soidum chloride and consequences for further corrosion mechanisms on steel*
  - *Aurelio Barbetta (co-tutelle Montpellier-Potsdam, 2013-2017, Labex Chemisyst F/G stipendium): Thermodynamics of water absorption in model structured molecular systems including analogues of hemicelluloses, crystalline cellulose and lignin*
- *Engineers and technicians: Joseph Lautru (Marcoule) and Anne Heilig (Potsdam)*

The RECYCLING project between CNRS/INC and MPG/MPIKG has as original goal linking spectrometry and chemical reactivity in complex fluids induced by ultra-sound, and its application to control movement of ions in colloidal solutions and porous nanomaterials (2009-2012). Special attention is now more focused on separation chemistry to fluids containing metals as ions, nano- or microparticles, with the general aim of applications related to separation and recycling and material life-time extension. The central contractual scientific objectives of the LEA "RECYCLING" for the four years period 2014-2017 are focused on five topics:

1. Droplet coalescence under reactive conditions: we aim to develop quantitative characterization and predictive modeling based on first principles during the contact of two sessile droplets containing surface active and reactive species, coupling of Marangoni effects, bulk flow reactivity producing mechanical turbulence.

2. Metallic corrosion development during drying-wetting cycles by aerosols containing sodium chloride: nanoscience approach to the thermodynamics and hydrodynamics on the three phase contact line between soluble ionic solid, under-saturated solution and partially oxidized metal.

3. Develop atomic force microscopy at an active oil-solvent interface, i.e. with respect to hydrometallurgy, i.e. when cations are selectively exchanged between an aqueous and organic solvent containing oil-soluble ion specific species.

4. Make use of the ion specific ultra-sound adsorption to excite oil/water interfaces and trigger transfer of ionic or colloidal species. The experiment will involve non linear optical caracterisation of reflection at liquid-liquid interface and ellipsometry. The theory will involve evaluation of the potential wave associated to the macroscopic interface, as well for ions as for nanoparticles crossing the interface. The key initial observation was that ultrasound can be used to enhance the phase transfer between oil and water phase and thus also to dissolve ions1.

5. Study the specific salt effects on interaction between wood cell wall i.e. cellulose-crystalline material in contact with a ternary gel lignin-soluble cellulose and water. This includes direct measurement of osmotic pressure due to concentration gradients of metal ion with respect to the solution in which wood cell wall is immersed (or atmosphere at controlled humidity). This study covers in the unified approach free energy of chemical, colloidal and mechanical energy as introduced by Fratzl and Bertinetti in terms of "master equation". This has a wide domain of application as knowledge-based treatments of wood against (or in favor) of swelling/deswelling under osmotic stress and material life-time improvement.

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[1] Key initial reference originating from initial LEA CNRS-MPG « SONO »: G. Toquer, T. Zemb, D.G. Shchukin, H. Möhwald: **"Ionic Physisorption of Bubbles induced by pulsed Ultrasound"** PCCP 12 (2010) 14553

RECYCLING TASK 1

COALESCENCE OF DROPLETS IN REACTIVE CONDITIONS

M. Jehannin (DTEC/ICSM), H. Riegler, S. Charton, Th. Zemb

Surprisingly, two droplets of completely miscible liquids can remain separated for some seconds up to minutes after their contact. This non-coalescence behavior can be explained by a surface tension gradient between the liquids of the two drops. The gradient creates a Marangoni flow which competes with the capillary forces and may delay the coalescence of the droplets. Yet, coalescence and non-coalescence of inert sessile droplets is well understood. However, when reactants are dissolved in both droplets, the system gets more complicated. Indeed, the reaction modifies locally the chemical concentrations, thus influencing the surface tension gradient and the Marangoni flow. This research study on coalescence of reacting droplets is led in a coupled way, both at CEA Marcoule (DEN/DTCD), for which this topic is a key issue for a recently patented process, and at MPIKG (Max Planck Institute of Colloids and Interfaces), which studied coalescence of sessile inert drops. The interplay between a precipitation reaction and the immediate coalescence of sessile drops is investigated. We have found that the combination of a Marangoni flow with a fast reactive process could lead to a periodic pattern of alternating black and colorless stripes. Moreover, the stripe formation is reversible, depending on the surface tension gradient that can be set by adding an surface-active molecule[1].

Two drops, one containing cerium nitrate and the second one containing oxalic acid, are deposited on a silica surface at some distance from each other. In the range of concentrations used, cerium nitrate and oxalic acid are soluble in the solvent, whereas the reaction product, namely cerium oxalate, is insoluble in aqueous solution. Three behaviors were observed (Figure 2). At low oxalic excess, light scattering precipitates are obtained, at high oxalic excess, a transparent domain of precipitates is observed above the high surface tension drop. At intermediate cerium nitrate concentration, a periodic arrangement of the two states is observed.

Marangoni flow is known to occur in the surface layer of the high surface tension drop. The exact thickness of this layer is not known yet. We attempted to address this point by studying the location of the precipitation process. Assuming the reaction height represents the width of the Marangoni layer, we probe, using confocal microscopy, on in-situ coalesced droplets, the vertical position of the first detected crystal. Growth rates (typically minutes) are slow as compared to the coalescence and nucleation processes (typically seconds). The transparent and scattering light areas, recorded by the top view camera (illustrated by Figure 1, top) are due to nanoparticles having different light diffraction properties.

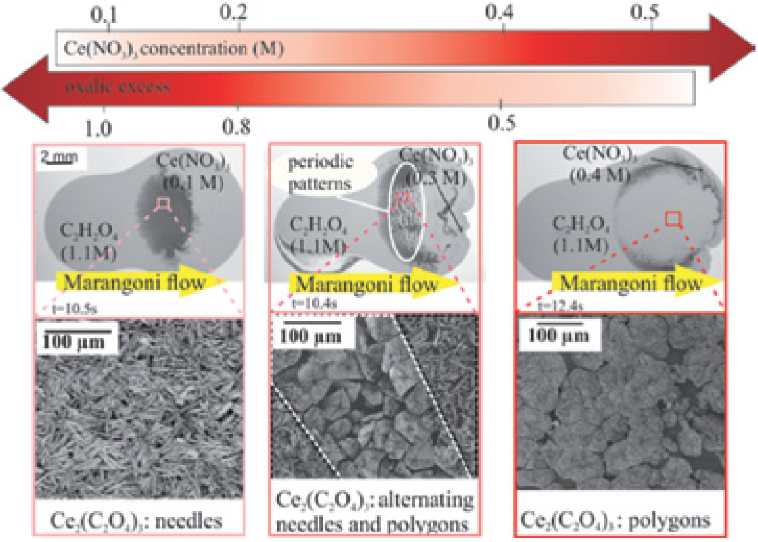

Figure 1 : Top: Coalescence of sessile drops for different initial concentration of cerium nitrate at a constant surface tension difference ($\Delta\gamma$=3mN/m). The Marangoni flow is directed from the oxalic acid drop over the cerium nitrate one. Three behaviors are observed. Bottom: SEM images of the corresponding resulting cerium oxalate morphologies, namely: needles (left), polygons (right) and, for intermediate oxalic excess, alternation of both morphologies (middle).

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[1] Jehannin, M.; Charton, S.; Möhwald, H.; Karpitschka, S.; Riegler, H.and Zemb, Th., **«Periodic precipitaion patterns during coalescence of reacting sessile droplets"** . (2015) *Langmuir,* 31,11484-11490

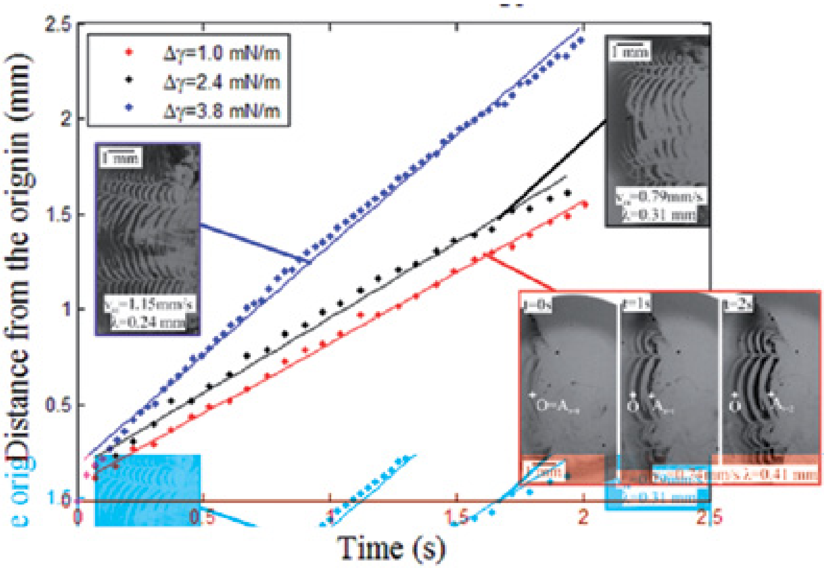

Figure 2 : Distance from the origin evolution in time during fringes formation at different surface tension gradient $\Delta\gamma$. The oxalic excess (0,6M) and the average contact angle ($\theta a=9+0.5°$) are identical for all experiments. The Marangoni flow speed, vM, increases with the surface tension gradient whereas the wavelength of the periodic pattern, λ, decreases.

Now that we elucidated the nature of the fringes, we aim to identify the phenomena responsible for their formation. It is likely that this oscillatory behavior is due to a competition or a feedback between at least two mechanisms, which could be the convection and/or the diffusion (i.e. transport mechanisms) and/or the chemical reaction. Preliminary results indicate that, for a given contact angle, the higher the surface tension difference, the higher the Marangoni flow speed, and the lower the wavelength (Figure 3). The knowledge of the parameters mainly influencing the fringes characteristics is the first step of the development of a numerical model, which would enable sensitivity analysis.

To conclude, the coalescence of droplets is investigated in reacting conditions. In our case study, sessile drops containing cerium nitrate and oxalic acid, the coalescence can lead to three precipitation behaviors depending on the initial oxalic excess. Surprisingly, at intermediate oxalic excess periodic patterns are created. Whatever the behavior, the produced solid particles (after drying) are observed to have identical crystallographic structures but different morphologies, namely polygons or needle morphologies. The periodic patterns correspond to alternating polygons and needles. Currently, we aim to understand the periodic pattern formation by identifying the controlling parameters. This work will enable the development a theoretical model for the coalescence of reactive droplets: an efficient way towards that goal is to investigate the effect of differences in surface tension between droplets as well as the effect of moving form binary solutions to ternary complex fluids, such as ultra-flexible microemulsions[2].

[2] Jehannin, M.; Charton, S.; Corso, B. Möhwald, H.; Riegler, H.and Zemb, Th., «**Structured solvent effects on precipitation of organized cerium oxalate microparticles** (2017) *Colloid & Polymer Science*, vol 295}({10}), pp.1817–1826

SALT-INDUCED MARANGONI FLOW IN EVAPORATING SESSILE DROPLETS

V. Soulié (DEN/DPC/ICSM), H. Riegler, Ph. Prené, D. Feron, H. Moewald, Th. Zemb

The evaporation behavior of a sessile drop is rather complicated because of the subtle issues arising from its description such as the non-uniform evaporative flux. The evaporation at the contact line region is enhanced, which induces a capillary flow towards the edge (leading to the «coffee-ring» effect [1]). For complex fluids the evaporation behavior becomes even more complex, because the non-uniform evaporative flux will lead to an inhomogeneous distribution of the fluid constituents within the drop. This can induce a surface tension gradient, which in turn may lead to a Marangoni flow [2] in addition to the capillary flow.

We study the evaporation of sessile drops from aqueous sodium chloride solutions on solid planar surfaces. The diverging evaporative flux locally enriches NaCl at the droplet edge *(Figure 1.a)*. Since chaotrope salts are depleted from the air-water interface, the surface tension locally increases in the edge region. This can lead to a Marangoni flow in the same direction as the capillary flow, i.e. towards the contact line. Diffusive dilution resulting from the salt concentration gradient will reduce the evaporation-induced gradient *(Figure 1.b)*. We investigate how the flows within the drop and, in particular the Marangoni flow along its surface, are related and affected by: (I) the initial NaCl concentration, (II) the contact angle, (III) the drop size and (IV) the evaporation rate. To this end the shape and the contact angle of the drop are analyzed by simultaneous optical imaging from the top and the side [3], and the liquid flow is studied by particle tracking velocimetry (PTV) with polystyrene particles.

We find that the flow behavior is strongly affected by the initial NaCl concentration. At low initial NaCl concentrations, PTV experiments reveal only a flow towards the contact line. This may arise from the capillary flow compensating for the local evaporative losses, possibly increased by a Marangoni flow component. Thus, capillary and Marangoni flows both favor the formation of a coffee-stain deposit *(Figure 1.b)*. However, above 10^{-3}M NaCl, the surface tension gradient respectively Marangoni flow leads to such a strong flow towards the drop edge, that the capillary pressure in this region increases. Therefore, the compensating capillary flow is now directed inward and we observe a convection roll near the drop edge. This circulating flow can lead to a more uniform salt deposition or a wider coffee-ring, depending on the initial NaCl concentration *(Figure 1.c)*. Experiments reveal that the flow patterns are also affected by the ambient vapor pressure, the drop size and contact angle.

To conclude, the flow behavior of an evaporating drop of a saline solution is dominated by a solely outward flow (combination of Marangoni and capillary forces) at low salt concentrations. At high salt concentrations, the flow behavior changes drastically and is governed by compensating Marangoni and capillary flows that lead to convection rolls[1].

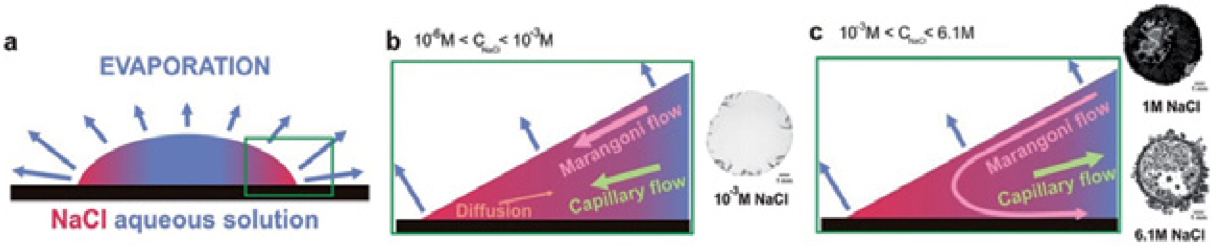

Figure 1: (a) Evaporation behavior of a sessile droplet from aqueous sodium chloride solutions. Locally varying evaporation rate and resulting concentration gradient: below (b) or above (c) 10^{-3}M NaCl. Typical microscopy images of the final deposit patterns from droplets of 10^{-3}, 1 and 6.1M NaCl on silica wafers at T = 25°C and RH = 0%.

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[1] Soulie, V.; Karpitschka, S.; Lequien, F.; Prene, P.; Zemb, T.; Moehwald, H.; Riegler, H., **«The evaporation behavior of sessile droplets from aqueous saline solutions.»** Phys Chem Chem Phys 2015, 17 (34), 22296-22303.

PITTING CORROSION OF IRON UNDER A SESSILE DROPLET FROM AQUEOUS SALINE SOLUTIONS

V. Soulié (DEN/DPC and CEA/ICSM), H. Riegler, Ph. Prené, D. Feron, H. Möhwald, Th. Zemb

The corrosion process induced by evaporation of sessile droplets from aqueous sodium chloride solutionson planar iron surfaces was quantitatively investigated. The spatial distribution of the salt inside the evaporating sessile droplet, which is influenced by the initial salt concentration in the droplet bulk, is correlated to the localization of the anodic and cathodic reactions at the electrolyte-metal interface over the footprint droplet area. At low salt concentration the inverse of the classical well-accepted Evans model is observed: the anode area is established near the three-phase contact line region. Increasing salt concentration leads to a more uniform pitted sessile droplet: we observed locally anodic and cathodic areas over the droplet surface at the metal-electrolyte interface, where local variations in chloride concentrations takes place if the salt concentration reaches a threshold value, experimentally determined by an optical set-up *(figure 1)*.

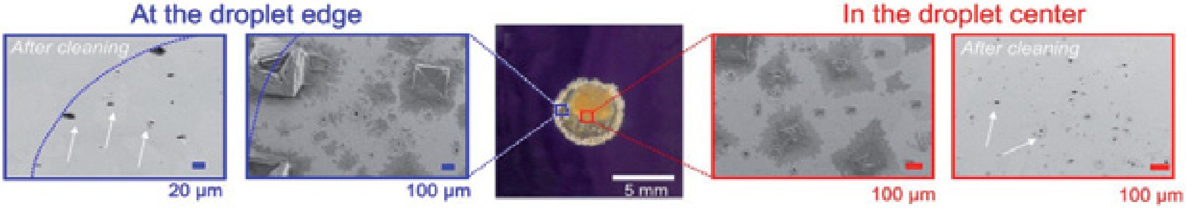

Figure 1: Microscopy image of an iron surface, onto which an aqueous sessile droplet from 1M NaCl (10 µl, contact angle 15.2°) was deposited, after complete evaporation with a relative humidity RH of 40% at T = 23°C. The two insets show SEM micrographs of two different locations on iron corroded under evaporating NaCl sessile droplets: at the droplet edge and in the droplet centre. The white arrows indicate the presence of pit[1]

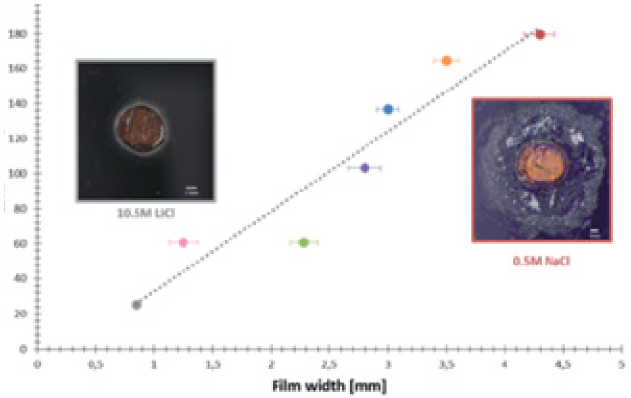

Figure 2: The corrosion rate induced by a sessile droplet from aqueous electrolyte solution deposited on an iron substrate depends to the width of the peripheral film. The measured film width is obtained after 1 day of experiment. Microscopy images of the dried system after on eday experiment from aqueous sessile droplet of 10.5M LiCl and 0.5M NaCl.

Focussing more on the corrosion influence of a sessile droplet[2], we established the presence of corrosion products and some pits demonstrate that pitting corrosion takes place if the salt concentration reches a threshold value, experimentally determined by an optical set-up. Finally, investigation of salt containing chaotropic or cosmotropic species show extremely different corrosion rates, as shown on figure 5 below.

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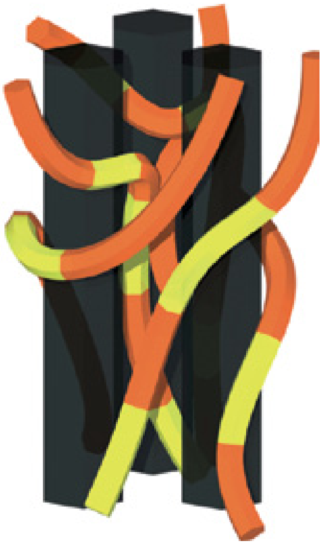
[1] Soulié, V.; Lequien, F.; Ferreira-Gomès, F.; Moine, G., Féron, D.; Prené, Ph.; Moehwald, H.; Zemb, Th. And Riegler, H.; , «**Salt-Induced Iron Corrosion under Evaporating Sessile Droplets of Aqueous Sodium Chloride Solutions**. (2017) MATERIALS AND CORROSION (2017) Volume: 68 Issue: 9 Pages: 927-934

[2] Lequien, F.; Soulie, V.; Moine, G.; Lequien A. ; Feron D ;Prené Ph. ; Moehwald Ph. ; Riegler H. & Zemb, T.
Corrosion influence on the evaporation of sessile droplet ; COLLOIDS AND SURFACES A vol :546 pp 59-66

RECYCLING TASK 5

HYDRATION FORCE IN WOOD AS A MULTI-SCALE MATERIAL: MODELLING OF WOOD FIBRES SWELLING/ DESWELLING BY ATMOSPHERIC HUMIDITY

L. Bertinetti, A. Barbetta, P. Fratzl, Th. Zemb
Collaboration ICSM with Biomaterials Dept MPIKG-Potsdam



Plants use the orientation of cellulose microfibrils to create cell walls with anisotropic properties related to specific functions. A well-known example is wood, that consists of parallel, hollow, cylindrical cells. The so-called "wood material" is a complex, highly anisotropic and hierarchically organized nanocomposite. It is characterized by hydrated stiff crystalline cellulose nanofibres parallel to each others (black on drawing) embedded in a matrix of a much softer, less anisotropic, gel of hemicelluloses, lignin (orange/ yellow hydrocarbons) and water. This matrix is hygroscopic and swells with increasing relative humidity providing a source of internal stress while the cellulose fibrils passively reorient following the stress applied to them. We use a unified approach of the equation of state of colloidal composite under hydration and dessication cycles, in the form of the master equation combining mechanical, colloidal and chemical free energy change during hydration form a reservoir of osmotic pressure Π:

$$\mathrm{d}G_m(D) + \mathrm{d}G_c(D) + \mathrm{d}G_e(D) = v_m \Pi(RH)\mathrm{d}N$$

The resulting general equation of sate relies on only one single parameter: only one single free parameter: the binding "contact point" free energy of hemicelluloses, seen as chemical "snapping" on crystals[1]. The results of the model, compared with experimental sorption data and with small angle X-rays scattering data, seem to capture the main features of the wood swelling by water with and without treatment for preservation done by chemical reactions of impregnation.

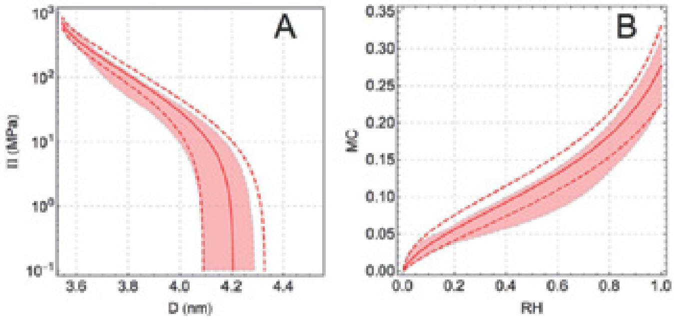


Figure 2: The EOS of wood cell wall (A) in the physical chemistry form of osmotic pressure versus spacing between cellulose crystals and (B) in the form used in material science and chemical engineering: Moisture content versus relative humidity. Dashed lines represent variations associated to uncertaineties in measured values entering the model and shaded areas concern domain of variation observed for this variable material of biological origin.

We have used the same methodology by adding the different interactions as derivatives of the free energy to derive inversely form the deswelling and further re-swelling during the impregnation of salts the energy of adsorption of the choatropic ion responsible for swelling after impregnation: we found a typical value of 8kJ/mol for the case of sodium iodide[2].

[1] L. Bertinetti, L.; Zemb, T.; Fratzl, P. ,- **Chemical, colloidal and mechanical contributions to the state of water in the wood cell wall** - *IOP New Journal of physics* (2016) 18, 083048

[2] Barbetta A., Bertinetti L., Zemb T. - **Composition dependent Equation of State of cellulose based plant tissues in the presence of electrolytes** - *Colloids and Surfaces a-Physicochemical and Engineering Aspects* (2017) 532, 314-322.

«NISI PROJECT» (2018-2021)
INTERNATIONAL RESEARCH PROJECT CNRS-MPG-UNIVERSITY OF REGENSBURG

From January 1, 2018, a collaboration between Marcoule/Montpellier, Potsdam associated with -Regensburg has evolved to the French-German International Research Project "NISI". This program is indeed built around Nano-Ions in interaction with Soft Interfaces.

P.I., Olivier Diat (ICSM), co-P.I., Emanuel Schneck (MPI Potsdam) & Dominik Horinek (Univ. Regensburg)

- *Participant (ICSM): Thomas Zemb, Stéphane Pellet-Rostaing Pierre Bauduin, Luc Girard, Damien Bourgeois, Daniel Meyer, Jean-Francois Dufrêche, Sandrine Dourdain, Bertrand Siboulet, Magli Duvail, Tania Merhi (PhD), Jing Wang (PhD) and Max Hohenschutz (PhD)*
- *Participant (MPI): Peter Fratzl and Ernesto Scoppola (Post-Doc)*
- *Participant (Univ. Regensburg): Werner Kunz and Didier Touraud*

We were working for some years on the understanding of ionic or polar species transfers between two immiscible fluid phases, an aqueous phase and an organic phase. From these studies we have been able to show in some cases a complex equilibrium between the adsorption of nanometric ionic clusters and the release of adsorbed water molecules at the interface. It is known for a long time that ions according to their sizes, charge densities and polarizabilities have specific effects on the activity of water and other species in aqueous solution and that these effects can have important consequences on apolar molecules solubilisation in aqueous phase, on the self-aggregation of surface-active molecules, on the stabilization and on the interaction between soft interfaces (mono- or bi-layers).

In this MPG/CNRS cooperation action, we will focus on the polar/apolar interface and the interactions between these interfaces, these effects are often averaged in the form of a short-range repulsive hydration force with a characteristic length of a few Angströms. However, when these ions are of the order of a nanometre, these effects may appear more complex because they are exalted by an increase of the polarizability effects and sometimes by the presence of additional hydrogen bound interaction between the counter-ion themselves. These are specific to these ionic clusters or nano-ions.

TASK 1)
HEAVY IONS AT LIQUID-LIQUID INTERFACE (WORK STARTED WITH E. SCOPPOLA/ MPI POTSDAM)

We had developed an experimental approach combining X-ray AND neutron reflectivity measurements to determine simultaneously the distribution profile of ions and organic species around water/oil interfaces. The objective was to characterize the structure of a liquid/liquid interface for an understanding of the ions transfer for solvent extraction applications and more specifically to determine the surface potential of ions. This is indeed a crucial information that can be simulated via molecular dynamics approaches and that has to be taken into account to characterize the efficiency of ions transfer. Within this task, we had as objective the development of a simultaneous neutron reflectivity and gamma fluorescence experiment in time-of-light mode at Laue Langevin Institute, so with the use of a single radiation, here neutron, this latter being very suitable to determine the distribution of organic species such as ions extractants molecules in fluid phases. This program required first the development of a specific analytic tool to analyse both signals. However, we did not get sufficient of beamtime in order to optimise the collection of both types of data, from reflectivity and fluorescence the former requiring a high flux and the second requiring an tunable diaphragm to avoid saturation of the detector and an optimized signal over noise ratio. This is a set-up that we did not succeed to achieved before Ernesto Scoppola leaves. Then with the lack of competent and disponible scientists and beamtime we have had to give up this objective. However, we have shown that extractant molecules and ions pairs in interactions with these ligand's molecules form some polarized aggregates at the interface and create some interphases with nanometric extensions in the normal direction. Then, we have reoriented this task in order to see if these observations can be simulated using molecular dynamics methods. A first step without ions and in comparison with experiments was necessary to validate this approach. We have indeed succeed to simulate the equilibrium between lipophilic extractant adsorbed at the water/oil interface and aggregated in the oily phase (see figure).

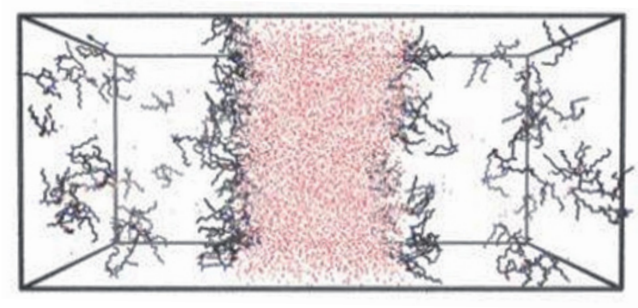


Figure: Snapshot of a 2-phase water(red)/heptane(not displayed) molecular dynamics simulated box with a DMDOHEMA diamide (black) at 0.5M, showing an excess of extractant at water/oil interface and a distribution of extrcatnt in oil under monomeric and aggregated forms.

Scientists involved: J. Wang, A. Jonchère, E. Scoppola, L. Girard, P. Guilbaud, M. Duvail and O. Diat

TASK 2)
INTERACTION BETWEEN NANOIONS AND MODEL 2D SELF-ASSEMBLIES

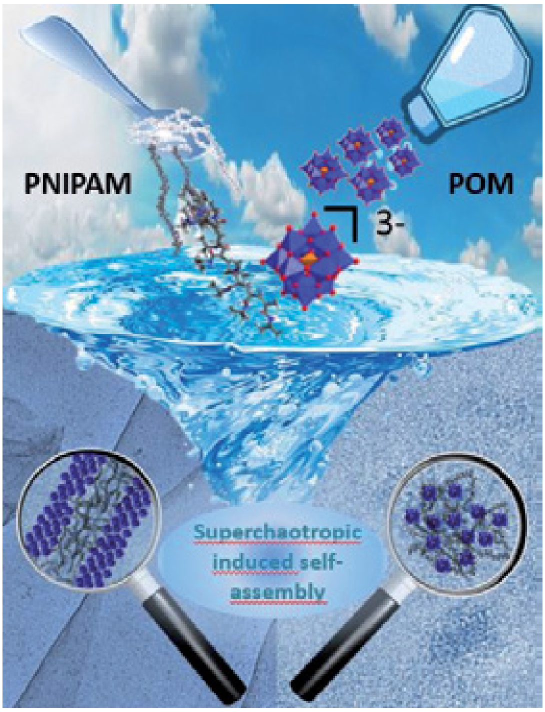
Preliminary researches were carried out in our group to study the impact of nano-ion adsorption onto 2D self-assembled structures made from phospholipidic and other integrated molecules and first results showed some antagonist effects: When nanoions adsorb onto a surface then lateral interaction act on the bilayer's flexibility and fluctuations with either a reinforcement of the bilayer stabilization and liquid crystal 3D structure in case of mesophases or with defects formation and the destructuration of the self-assembly structures The objective is to make a link between experiments results and simulations using ucrreznt models derived from the approach developed by Schwierz and Horinek. We wanted to focus mainly on dicarbollide anions and their interactions with biological functions and support with some cancer therapy applications. Thus we extended this study to a compressed Langmuir monolayer containing glycolipids over a subphase containing various concentration of COSAN and also other types of nano-ions such as polyoxometalates. Varying the headgroup chemistry (one or two galactoside functions) and the alkyl chain saturation, we observed different behaviour of nano-ion in interaction with the subsurface of the glycolipids and this as a function of the surface pressure. Using synchrotron techniques, we found superchaotrope nano-ions interact preferentially with species in gas or in the liquid expended phases than with the solid phase whose crystalline structure is not affected. Lower the charge density of the nano-ions and weaker the interaction between the sugar head groups, stronger is the interaction between the nano-ions and the glycolipids.

Scientists involved: T. Merhi, P. Bauduin, O. Diat, E. Schneck, D. Horinek and J-F. Dufreche

TASK 3)
INTERACTION BETWEEN NANO-IONS AND OLIGOMER OR POLYMER

Polyoxometalates (POMs) are anionic metal-oxygen clusters consisting of oxo-linked MOx polyhedra of early transition metals in their highest oxidation state. Their electronic versatility and the blend of p-bock elements, transitions metals and differently bound oxygen atoms (terminal and bridging) induce special properties resulting in a broad field for applications such as catalysis, material science, biology and medicine. For most of these applications the understanding of the interactions between inorganic POM clusters and organic entities is essential and much effort has been made to the design and building of POM-organic hybrid assemblies. The design of POM-organic composite materials is based on two approaches: an electrostatic coupling between an anionic POM with an organic cation and a covalent coupling with the POMs chemically grafted to organic moieties. We developed a third one based on the super-chaotropic property of such ionic clusters that allows to self-organize POM in 3D structures without any specific solvent, only water. This approach is rather pertinent for the preparation of catalytic supports and this is the objective the common PhD project that we have with this team of Regensburg University.

Within this task, we have shown for the first time that short chain poly(N-isopropylacrylamide) PNIPAM, one of the most famous thermo-responsive polymers, self-assembles in water to form (I) discrete nm-globules and (II) micrometric sheets with nm-thickness upon addition of the well-known Keggin-type polyoxometalate (POM) H3PW12O40 (PW). The type of self-assembly is controlled by PW concentration: at low PW concentrations, PW adsorbs on PNIPAM chains to form globules consisting of homogeneously distributed PWs in PNIPAM droplets of several nm in size. Upon further addition of PW, a phase transition from globules to micrometric sheets is observed for PNIPAMs above a polymer critical chain length. The thickness of the sheets is controlled by the PNIPAM chain length. The PNIPAM sheets are electrostatically stabilized PWs accumulated on each side of the sheets. The shortest PNIPAM chain with 18 repeating units produces PNIPAM/PW globules with 5-20 nm size but no sheets. The PW/PNIPAM self-assembly arises from a solvent mediated mechanism associated to the partial dehydration of PW and of the PNIPAM, which is related to the general propensity of POMs to adsorb on neutral hydrated surfaces. This effect, known as superchaotropy, is further highlighted by the significant increase in the lower critical solubilization temperature (LCST) of PNIPAM observed upon the addition of PW in the mM range. The influence of the POM nature on the self-assembly of PNIPAM was also investigated by using $H_4SiW_{12}O_{40}$ (SiW) and $H_3PMo_{12}O_{40}$ (PMo), *i.e.* changing the POM's charge density or polarizability in order to get deeper understanding on the role of electrostatics and polarizability in the PNIPAM self-assembly process. We show here that the superchaotropic behavior of POMs with PNIPAM polymers enables the formation and the shape control of supramolecular organic-inorganic hybrids.



Ref: Buchecker T., Schmid P., Grillo I., Prevost S., Drechsler M., Diat O., Pfitzner A., Bauduin P. - **Self-Assembly of Short Chain Poly-N-isopropylacrylamid Induced by Superchaotropic Keggin Polyoxometalates: From Globules to Sheets** - *Journal of the American Chemical Society* (2019) 141, 6890-6899.

Scientists involved: A. Pfitzner, T. Buchecker, P. Schmid, I. Grillo, S. Prevost, D. Horinek, JF. Dufreche, P. Bauduin, O. Diat

«PROJET SCARCE» (2018-2021)
SINGAPORE CEA ALLIANCE FOR RESEARCH IN CIRCULAR ECONOMY

En août 2018 a été signé un contrat signé entre le CEA et Nanyang Technological University (NTU) à Singapour pour une durée initiale de 3 ans. L'objectif est de développer des technologies avancées pour le tri, le démantèlement, la dissolution, la séparation et la réutilisation de matériaux issus de l'industrie électrique/électronique et en particulier catégorisés sous 4 axes ou « Research Thrust » (RT) et dans lesquels 2 équipes de l'ICSM interviennent :

- Le recyclage des batteries lithium-ion - (RT1)
- Le développement d'un recyclage durable des panneaux solaires à base de silicium - (RT2)
- Le développement de processus écologiques et peu coûteux pour la récupération des cartes de circuits imprimés (PCB) - (RT3)
- Le recyclage des plastiques toxiques mis en œuvre dans les appareils électroniques - (RT4)

Il s'agit de mettre en œuvre chaque procédé validé à l'échelle d'un pilote de laboratoire (1-10 kg/h) pour chacun des types de déchets.

L'ICSM intervient dans 2 des RTs, avec le LHYS en RT1 et la valorisation des métaux extrait des déchets de batteries [1-4] et le LTSM dans RT3 avec la récupération de métaux dont le Pd présent dans les cartes électroniques.

https://research.ntu.edu.sg/scarce/Pages/Home.aspx

NANYANG
TECHNOLOGICAL
UNIVERSITY
SINGAPORE

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[1] Cognet M., Cambedouzou J., Madhavi S., Carboni M., Meyer D. - **Targeted removal of aluminium and copper in Li-ion battery waste solutions by selective precipitation as valuable porous materials** - *Materials Letters* (2020) 268.

[2] Cognet M., Condomines J., Cambedouzou J., Madhavi S., Carboni M., Meyer D. - **An original recycling method for Li-ion batteries through large scale production of Metal Organic Frameworks** - *Journal of Hazardous Materials* (2020) 385.

[3] Lagae-Capelle E., Cognet M., Madhavi S., Carboni M., Meyer D. - **Combining Organic and Inorganic Wastes to Form Metal**-Organic Frameworks - *Materials* (2020) 13.

[4] Wu Z. R., Soh T., Chan J. J., Meng S. Z., Meyer D., Srinivasan M., Tay C. Y. - **Repurposing of Fruit Peel Waste as a Green Reductant for Recycling of Spent Lithium-Ion Batteries** - *Environmental Science & Technology* (2020) 54, 9681-9692.

«SOLID/LIQUID INTERFACE CHEMISTRY, GENIORS PROJECT»

GEN IV INTEGRATED OXIDE FUELS RECYCLING STRATEGIES

GENIORS

The main objectives of the Work Package of the GENIORS project[1] in which ICSM is involved, i.e. *solid/liquid interface chemistry,* is to better understand the phenomena occurring at the solid/liquid interfaces during spent nuclear fuel reprocessing in order to support potential processes. It is divided in two main topics.

The first task is devoted to the dissolution step. It is examined not only considering the direct interactions between the chemical species coming from the solid and the solution, but also through the development of catalytic reactions at the interface. This task is devoted to the better understanding (then control) of the mechanisms occurring at the solid/liquid interface during dissolution. Several kinds of actinide oxide based solid solutions, including $(U,Ce)O_2$, $(U,Ln)O_2$, are prepared by wet chemistry routes then finally submitted to various dissolution tests. Then, the effects of structural, microstructural and morphological parameters, coming from the "material history" are particularly examined with the help of multiparametric dissolution tests. For both solid solutions, the particular role of redox reactions on the overall dissolution mechanism is examined by combining macroscopic and microscopic approaches (including ESEM, AFM, XRR and Raman spectroscopy).

The second task is focused on the uptake of actinides from solution by precipitation in new kinds of precursors then on the final conversion to oxide based samples by heating (i.e. wet chemistry routes). In this field, various precursors of $(U,Ce)O_2$ and $(U,Ln)O_2$ are prepared by using novel types of ligands yielding to original metal-organic architectures with designed morphology. Their conversion into the final oxides are followed by a large panel of techniques including HT-ESEM (Environmental Scanning Electron Microscopy). Shaping then sintering of these precursors leading to the final oxides by heating are then studied by conventional techniques (dilatometry, HT-ESEM, density measurements). The same methodology is also applied for $(U,Ce)O_2$ and $(U,Ln)O_2$ samples prepared by direct conversion of the precursors to oxides under weak hydrothermal conditions or by denitration process.

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[1] **www.geniors.eu**

TO DEVELOP AN EFFECTIVE EXTRACTION AND SEPARATION TECHNOLOGY TO SELECTIVELY EXTRACT RARE EARTH ELEMENTS FROM WEEE (2018 – 2021)

Partners:
ICSM-UMR 5257 (Marcoule, France); Academic
Terra Nova Development (Isbergues, France); Industrial
CSIR-National Metallurgical Laboratory (Jamshedpur, India); Academic
Tata Consultancy Services Limited (Pune, India); Industrial

Rare earth are ubiquitous, have applications in primarily in clean energy, automobiles and digital technologies. Although public attention has shifted elsewhere, ensuring a secure future supply of rare earths remains an urgent policy challenge for governments and industry. Rare earth markets are small: the total market value for separated REEs was between $3 billion and $5 billion in 2013, and annual world production would fit into one large bulk carrier. Nonetheless, REE's importance for advanced materials across a range of high-tech industries – and especially their key role in boosting energy and resource efficiency – makes them too crucial to ignore. Under a business-as-usual scenario, rare earths supply will remain precarious; and a repeat of the 2010/11 supply crisis remains a distinct possibility in the medium term. Excessive price volatility and uncertainty over future availability could slow the diffusion of best available technologies, e.g., for offshore wind turbines, fluorescent light bulbs in homes, offices and stores; in the hard drives of laptops; and in mobile phones, electric vehicles, washing machines, airplanes, batteries, and many other everyday products. As the world moves towards a cleaner, greener future, the uses for these metals are likely to increase rapidly. Overall world total reserves are 130 thousand metric tonnes and China dominates overall rare earth production. It is estimated that the demand will grow by 50 % in coming 10 years. Some of the rare earth element are at the verge of criticality and are at supply risk. Thus recycling of rare earth becomes a necessity.

The current project proposal is focused on the development of suitable process scheme for the utilization of waste for the recovery of valuable rare earth metal ions. "Selective Leaching" has been targeted in the current proposal, so that rare earth ions (Nd, Dy, Pr) or (Er, Tb, Eu, Y) present in the magnet or lamps respectively comes in the aqueous solution. For the individual separation of rare earth ions from aqueous solution, suitable solvent-extractant combination has to be designed with the help of molecular modeling techniques. To compare the performance of developed combination of extractant, separation studies will also be carried out by using commercially available extractants. Therefore, the idea of the project is to give complete "Extraction" and "Separation" scheme for the recovery of rare earths from scrap magnets and fluorescent lamps, so that it can be tried on the larger scale:

a). Development of process parameters for selective leaching of rare earths metals from WEEE (Waste Electrical and Electronic Equipments - Nd-FeB magnet and fluorescent lamps).
b). Design of suitable solvent-extractant combination (e.g. task specific ionic liquids) using molecular modeling techniques.
c). Synthesis and characterization of recommended solvent-extractant combination or task specific ionic liquids for separating rare earth ions (Nd, Pr, Dy) or (Y, Eu, Tb, Er).
d). Optimization of process parameters for the separation of rare earth ions (Nd, Pr, Dy) or (Eu, Tb, Er) by solvent extraction using commercially available extractants.
e). Conduct large scale trial of the complete process developed for scrap magnets and fluorescent lamps.

N° IFC/7130-WEEE

BEHAVIOUR OF SPENT NUCLEAR FUEL (SNF) PELLETS UNDER INTERIM STORAGE CONDITIONS

IN EUROPEAN JOINT PROGRAMME ON RADIOACTIVE WASTE MANAGE-MENT (EURAD)

In the EURAD project, the Laboratory of Evolving Interfaces in Materials (LIME) is involved in the Work Package *Spent fuel characterization and evolution until disposal (and more precisely in the subtask on the behaviour of Spent Nuclear Fuel (SNF) pellets under interim storage conditions).* In this WP, our goal is to better understand the behaviour of UO_2 based model compounds during leaching tests representative for long-term interim storage in nuclear pools. Especially, the impact of various Fission Products on the chemical durability and on the surface reactivity of the sintered materials is 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 micro-/macro- dual methodology in order to examine the role of several families of FP on the behaviour of the sintered samples during leaching tests. It includes not only the analysis of the released elements in the solution, but also the monitoring of the solid/liquid interface during multiparametric leaching/alteration tests, this latter being possible by coupling various techniques such as AFM, ESEM, GI-XRD. A particular attention is focused on the evaluation of some potential modifications in terms of reactive surface area during the leaching tests as well as on the quantification of the dissolved preferential zones (grain boundaries, triple junctions, pores, …) through the development of 3D reconstructions performed on leached/altered materials.

In the same WP, we are also involved in the preparation of a large panel of sintered uranium-lanthanide oxide based samples for CEMHTI – Orléans. The aim of this second task is to follow the consequences of the incorporation of lanthanide elements in terms of defects formed within the material. The characterization of the samples specifically involves positron annihilation spectroscopy (PAS) in order to probe, as instance, the potential vacancy defects induced by such incorporation in the fluorite structure.

ANR ICSM
2017 - 2020

AGENCE NATIONALE DE LA RECHERCHE

ANR

VECT'OLEO PROJECT ANR-14-LAB4-0005

(SEPT. 2014 – SEPT. 2019)

« LABORATOIRE DE STRUCTURATION DES CORPS GRAS NATURELS POUR LA VECTORISATION DE COMPOS2S BIOACTIFS VEGETAUX EN NUTRITION TOPIQUE ET ORALE »

Dr Olivier Diat

Partners:
ICSM-L2IA (Coordinator)
OLEOS SA, Mauguio

The extraction of active principles contained in plant substrates and their concentrations in natural oils are the basis of the technological concept developed by OLEOS, offering a new generation of cosmetic active ingredients. These ingredients include for example antioxidants and are relatively fragile compounds outside their native environment. However, their formulation in Oléoactifs® results in a remarkable stability of these active principles for several months at room temperature. The principle is based on the theory of «polar paradox of antioxidants». There is a large interest to add in a vegetable oil polar antioxidants that can organize and act in synergy with the non-polar antioxidants. This concept also enhances biological synergism in vivo in particular for the skin, between the properties of fatty acids and micronutrients oil and those of different bioactive extracts. But to date, this technology is limited by two major obstacles: 1 / the concentration of polar compounds using lipo-extractable oil is limited. 2 / the supra-molecular organizations of the various extracted compounds within the oil are not known and therefore the results of the oil- extraction remain empirical and difficult to be controlled at the industrial level. However, the oleo-extraction or the conception of structured vegetable oils is today a promising industrial challenge for green eco-ingredients, with no chemical or synthetic process and more bio-available and easily formulated than hydro-alcoholic based extracts.

At the end of the project, we demonstrated that there was an interest in adding polar antioxidants to vegetable oil that can be organized in a pre-structured oil and can act in synergy with non-polar antioxidants. This concept also enhances the in vivo biological synergy, particularly within the skin, between the properties of the fatty acids, the micronutrients of the oil and those of the various bioactive extracts.

In the framework of Labcom we analyzed the different formulations proposed by Oleos and we were able to provide them the necessary knowledge to understand the efficiencies of their formulation and associated processes. Through proposed model systems, we have been able to draw concepts derived from the physico-chemistry of self-assembled systems and to associate them with dynamic simulation at the molecular level. This allowed to propose some answers to a certain number of questions around the supramolecular organization which determines the success of their development. We were able to develop spectroscopic techniques that we had never used before, but that can and would bring many indicators of effectiveness for the future. The labCom had a strong impact on the scientific development of Oleos with a high improvement of the structured oils knowledge, an optimization of the oleo-eco-extraction concept and process, a molecular insight of an Oléoactifs® and finally the development of specific analytical tools for the quality control and the R&D in the cosmetic area.

SILEXE PROJET ANR-13-CDII-0010

(JUNE 2014 – DEC. 2017)

"STRATEGIC METAL RECYCLING IN IONIC LIQUIDS BY EXTRACTION AND ELECTRODEPOSITION PROCESS"


Dr Stéphane Pellet-Rostaing

Partners:
ICSM-LTSM (coordinator)
LCME Chambery
IJL Metz
TND (Industriel, Isebergue)

The SILEXE project brings the expertise of three academic laboratories and one industrial partner internationally recognized in the field of ion separation (ICSM-UMR 5257), ionic liquids (LCME-EA 1651), electrochemistry (IJL-UMR 7198) and metal recycling from e-cards (TerraNova). SILEXE will investigate Room Temperature Ionic Liquids (RTILs) as unusual media for strategic metal recycling, especially indium, tantalum and gold, through the use of a selective extraction (or back-extraction)/electrodeposition process starting from lipophilic or hydrophilic ligands and Task Specific Ionic Liquids (TSILs) as extractants. A successful recycling of the assessed critical metals is very important regarding increase of resource efficiency, avoidance of possible scarcities and reduction of the overall environmental impacts linked with the life cycles of the strategic metals. Furthermore the positive contribution of the recycling sector to employment and to adding value should be taken into account. Excepted from rare earths contained in the low-energy lamps for which an industrial process has recently emerged (Solvay process), until today for some metals like tantalum in dissipative applications (cell phones), lithium (batteries), gallium, indium and germanium (up-to-date just very small and dissipative amounts in post-consumer materials), there are no running recycling technologies at commercial scales and only first steps in small (pilot) plants are initiated. However, the supply of strategic metals has a clear impact on industrial defense and security of countries that would lack them. In this context, we propose to develop an efficient process for the extraction and purification of the strategic metal In, Ta and Au. RTILs containing chelating ligands or TSILs having strong affinity with the targeted metal will be used as extracting media. The pure metal will be recovered using selective electrodeposition process. Several studies on metal separation by liquid/liquid extraction techniques involving chelating agents in Ioni Liquids, or in Task Specific Ionic Liquids are already described in the literature. It appeared thus interesting to extend the study of metal recovering by extraction and electrodeposition in ionic liquids with potentially more selective synthesized ligands and/or new task specific ionic liquids binding chelating sites. Because they play a crucial role in the ligand-metal binding, the experimental conditions of temperature, acidity, concentrations in solution combined with the ionic liquid properties, especially the nature of the anionic species (hard/soft, BF4-, NTf2-, …) will be as many of parameters which will have to be considered in order to optimise the liquid/liquid separation. Extraction from aqueous phase to hydrophobic ionic liquid containing the ligand (or a mixture of ligands for a potential synergistic effect) or the TSILs or extraction from aqueous phase directly performed in TSILs will particularly be considered. Another strategy will be envisaged, based on a preliminary extraction step from aqueous phase in conventional alcane type solvent followed by a de-extraction process from the organic phase containing the metal-ligand complex to a hydrophilic ionic liquid or task specific ionic liquid. Based on the preliminary results obtained in SILEXE, modulated techniques (selective extraction/electrodeposition and/or de-extraction/electrodeposition ligand/TSIL, lipophilic/hydrophilic ionic liquid, initial aqueous phase containing the targeted metal, ionic strength…), could be extend to the purification of other strategic metals (Ga, Nb…).

CADET PROJECT ANR-ANDRA-RTSCNADAA160014
(MARCH 2016 – SEPT. 2019)
"CAVITATION-ASSISTED DECONTAMINATION"

ICSM : Dr Serguei Nikitenko

Partners:
ICSM-LSFC
Institute Jean Le Rond d'Alembert (D'ALEMBERT) UMR 7190 (Coordinator)

The decommissioning of nuclear facilities has become a topic of great interest because of the large number of facilities which were built many years ago and which will have to be retired from service in the near future. As a result of this activity, a wide range of solid and liquid wastes arise. Aqueous solutions of complexing organic acids (EDTA, oxalic acid, citric acid, ascorbic acid) are frequently applied to enhance radionuclide removal from the contaminated surfaces. The removal of radionuclides from this secondary waste requires appropriate process to destroy the complexing organic matter. This project addresses the problem of minimization of organic contaminants in secondary liquid radioactive waste formed during the decontamination of nuclear devices. The minimization of the generation and spread of radioactivity, and the minimization of the volume of radioactive wastes to levels «as low as reasonably achievable» (ALARA) has both safety and economic significance. The feasibility of scaling-up to industrialization should also be considered taking into account that the decontamination technique should not be labor-intensive, difficult to handle, or difficult to automate.

CADET PIA-project based on cavitation techniques meets these requirements. Indeed, cavitation-based treatment does not require large amounts of side reagents due to in situ generation of strong oxidizers enable organics mineralization. Cavitation processing can be easily automated thus providing maximal level of safety for personal. In this fundamental collaborative project, the aim is to provide the evidence for the activity of coupled cavitations (acoustic and shock induced (spalling)) for organic acids oxidation in waste water produced during decontamination of nuclear facilities and to generate better understanding on developing fields in sonochemical degradation technology. All possible effects brought about by the addition of catalysts with ultrasonic irradiation or shock induced cavitation to remove organic compounds formed complexes with radionuclides from wastewater streams will be studied.

Thus, three main objectives were identified and will be developed in 4 tasks. The first objective is to provide a new cavitation-based process for wasted-water treatment generated during decontamination of nuclear facilities. For this, 2 types of cavitation generation, spalling and ultrasound, based on D'ALEMBERT and ICSM background will be used respectively. The second objective is to confront the two approaches in order to optimize the process also in coupling the cavitation with heterogeneous catalysts. The third objective is to optimize the catalysts according to specific conditions of processing, such as the presence of local shock waves and shearing forces as well as significant concentration of organic acids with a strong complexing ability.

TURBO PROJECT ANR-16-CE34-0003

(OCT. 2016-OCT. 2018)

"TOXICITY OF URANIUM: MULTI-LEVEL APPROACH OF BIOMINERALIZATION PROCESS IN BONE"

ICSM : Dr Damien Bourgeois

Partners:
CEA-TIRO-BIAM (coordinator)
Univ. Nice Sophia Antipolis
CEA/INAC/SCIB, Grenoble
ICSM/LHYS

Uranium chemical toxicity is a subject of concern for the general population as various anthropic activities have led to a substantial increase of the uranium background concentration in the environment. If the actual trend is to reduce nuclear energy in Western Europe, other countries like Russia, China or India have been substantially investing in the development of new nuclear power-plants. Thus the use of uranium will certainly remain a concern for the future generations, worldwide. Most experimental studies related to the health effects of uranium were dedicated to its radiotoxicity and its acute chemical toxicity (nephrotoxicity). Some animal studies and few epidemiological studies also considered chronical exposure, but the data are still too sparse to derive a toxicological threshold associated with long-term effects. Moreover, although the skeleton is well known to be the main site of uranium long-term accumulation, the chemical effects of uranium on bone health remain an open question. Bone is a complex organ composed of an organo-mineral matrix, undergoing constant remodeling thanks to a tightly regulated cellular system. Therefore the question of how uranium interacts with the physiological environment and accumulates in bone matrix can only be answered using a multi-level and multidisciplinary approach, which relies on both molecular and cellular understanding. Recently, we (the consortium of this project) demonstrated that uranium is transported in the blood as complexes with proteins involved in bone metabolism. In addition, we showed that this actinide element affects the main functions of bone cells in vitro, i.e. construction and resorption. The present project represents the first comprehensive mechanistic investigation of uranium interaction with the bone matrix. We propose to study the exchange mechanisms between uranium and bone in vitro and ex vivo, at three different levels: the molecular level, with synthetic biomimetic bone matrices and peptides modeling relevant biological binding sites in proteins; the biochemical level, with bone matrix proteins and circulating proteins; and the cellular level, involving osteoblast/osteocyte and osteoclast functions. This innovative global approach using a multi-level strategy will lead to a better understanding of the mechanisms involved in bio-mineralization of uranium and will help to design and assess new detoxification (also called decorporation) agents for this metal. Moreover, the interdisciplinary procedures developed in this study are of general interest and will bring added value regarding other toxic metals which also accumulate in bone.

CARAPASS PROJECT ANR-16-CE08-0026

(NOV. 2016 - OCT 2020)

“CARBIDE & CARBONITRIDE NANOCOMPOSITE BASED PHOTO-THERMAL SOLAR ABSORBERS”

ICSM : Dr Xavier Deschanels

Partners:
IEM Montpellier, UMR5635 (coordinator)
IEM Montpellier
SPCTS Limoges
PROMES Odeillo
CRM2 Nancy
ICSM - LNER

A common industrial challenge to improve the efficiency of the solar-to-electricity conversion for concentrating solar power (CSP) is to operate at high temperatures (900-1000°C). Research and development efforts on over recent years have therefore focused on the materials that compose the solar absorber which plays the key role in the overall CSP system performance. Silicon carbide (SiC) exhibits a chemical inertness, a high temperature oxidation resistance and a robustness compatible with the operating conditions of further CSP systems. However, despite a good sunlight absorption, SiC has a high thermal emittance, leading to a poor optical selectivity. Promising properties for absorber materials can be found in transition metal carbides and nitrides of column IV according to their refractivity, their inherent spectral selectivity and a lower thermal emittance compared to SiC. However, their major limitation is their tendency to be oxidized in the targeted temperature range. By entering the scope of the Challenge 3 –Stimuler le renouveau industriel– (theme –Matériaux et procédés– and more particularly the priority 14), the CARAPASS project proposes to prepare nanocomposites of the type MX/SiC (M = Ti, Zr, Hf; X = C_xN_{1-x}, $0 \leq x \leq 1$) by combining SiC and transition metal carbide and/or nitride in the same materials with the goal to combine optical selectivity, thermomechanical properties, chemical inertness and oxidation resistance to fit the requirements of the next generation of high temperature absorber materials. These materials are prepared as dense monoliths to maintain their mechanical strength and robustness at high temperature. The four year CARAPASS collaborative research project brings together specialists in materials synthesis, materials characterization, and computational approaches. It is built from five French research institutes, IEM, ICSM, SPCTS, PROMES and CRM^2, with complementary expertises in chemistry, in processing, in characterization of materials - especially for CSP - and in modeling which have already collaborated in the past. To reach our objectives, the project is based on the promising results obtained by IEM and ICSM with TiC/SiC nanocomposites. CARAPASS is subdivided into five interconnected scientific tasks. The first task is focused on the preparation of nanocomposite powders using two chemical routes already investigated by IEM and ICSM. The second task consists in preparing dense materials following three strategies based on pressing, casting and Spark Plasma Sintering processes to be characterized in tasks 3 and 4. Physical and chemical characterization of nanocomposites is the topic of the task 3. In addition to standard material science techniques available in each institute, the thermostructural, mechanical and thermal properties of the nanocomposite monoliths will be evaluated before and after thermal aging. The task 4 studies the optical characterization of the nanocomposites to demonstrate the selective behavior of nanocomposites The optical properties will also be measured after accelerated aging. A theoretical work will be done in task 5 to provide for each selected chemical composition the IR spectra and the visible-UV optical spectra using density functional theory and the GW approximation. The present project is built to elaborate materials that are expected to lead to benefits for the advancement of science, industry and society and should allow France to be in place on this growing thematic at international scale.

DYNAMISTE PROJET ANR-15-CE07-0013
(OCTOBER 2015 – MARCH 2020)
DYNAMICS OF ALUMINO-SILICATES FLUIDS

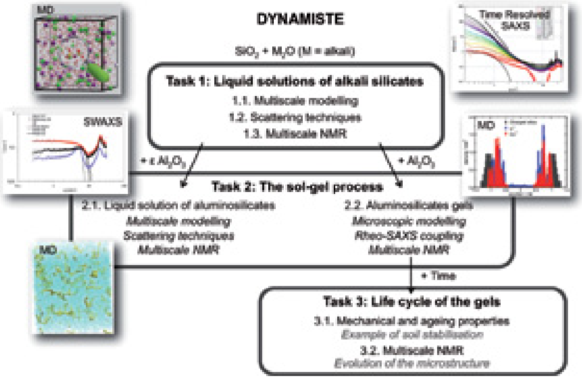
Dr Magali Duvail

Partners:
ICSM-LMCT (coordinator)
CEA-DES-DE2D Marcoule
Laboratoire Charles Coulomb Montpellier
Wöllner GmbH & Co.KG (Ludwigshafen, Germany)

DYNAMISTE aims at developing experimental and theoretical tools in order to optimize industrial processes in which alkali solutions of aluminosilicates are involved in an attempt of developing sustainable and clean industry. This project gathers three academic laboratories recognized for their expertise in the physical chemistry of condensed matter, the Institut de Chimie Séparative de Marcoule with competency in "green chemistry" science, a CEA department for the waste retreatment and conditioning and specialist for the characterization and formulation of cement-based materials, and a CNRS team at the Laboratoire Charles Coulomb expert in multi-scale NMR technics, in collaboration with the German industrial partner Wöllner GmbH & Co.KG, who is one of the leaders in production of alkali silicate solutions.

Thanks to their environmental acceptability and their adaptability over a wide range of applications, alkali solutions of aluminosilicates are increasingly used. During the last 10 years, they have increased their important role as inorganic and water based binders, notably for the production of mineral based, ecological materials for the building and construction industry. Alkali-silicate solutions became more and more important for the alkali activation in geopolymer application, which is considered as green chemistry. Sodium aluminosilicate gel are also used for so-called "ground stabilization" and as "sealing layers" in order to avoid the inflow of groundwater in construction pits or the reinforcement of sandy ground. Although such solutions are increasingly used in the industry, there remain outstanding questions regarding their stabilities, and more precisely concerning the gelation process that is driven by the composition of the solution. It is therefore crucial to provide realistic description of such fluids, which remains quite not well known, and has to be confirmed experimentally and theoretically.

This project relies on a synergic approach coupling both experiments and modeling. In order to access all the spatio-temporal phenomena of such systems, the experimental part consists in studies based on (i) rheology techniques coupled with scattering techniques: Dynamic light scattering (DLS), small and wide angle x-ray and (or) neutron scattering and diffraction (SWAXS, SANS and XRD), and on (ii) multi-scale NMR approaches (from Å to few tens μm). In the meantime, the theoretical part is based on multi-scale methods coupling molecular dynamics and coarse-grained simulations, allowing for accessing the structural and dynamical properties of these fluids at both the molecular and supramolecular scales.



Organization of DYNAMISTE.

These experimental and theoretical developments applied in the context of the soil stabilization will be transferable and adaptable to further important industrial application systems, such as dispersion of clays, geopolymer binders, ecological mineral paints and concrete acceleration.

FOAMEX PROJECT ANR-17-CE08-0016

(FEV. 2018 – FEV. 2022)

« MOUSSES DE LIXIVIATION POUR L'EXTRACTION DE MÉTAUX DES DÉCHETS ÉLECTRONIQUES »

Dr Olivier Diat

Partners:
ESPCI (Coordinateur)
ICSM-L2IA
BRGM
EXTRACTHIVE (start-up)

The recovery of metals from WEEE, Waste from Electrical and Electronic Equipment, is becoming a major challenge to preserve natural metal resources while treating a large amount of waste. Available recycling processes present several drawbacks : pyrometallurgy, based on a smelting process, is highly energy consuming, generates large amounts of off-gases and there are only a few installations in EU requiring non ecological transportation of wastes. Hydrometallurgy, which consists in leaching the metal wastes to extract metal ions in solution, is more suitable for small and local installations, but it generates very large volumes of effluents which need to be treated. The goal of this project is to use foams as a leaching medium to extract and concentrate metal ions from shredded PCBs (Printed circuit boards), the most valuable WEEE. Foams contain 90% of air and 10% of liquids, therefore this idea would help decreasing the amount of effluents. Moreover we expect to improve the efficiency of standard leaching methods due to a better dispersion of waste particle in the foam channels. We expect that our project, by reducing the amount of effluents generated during leaching, will contribute to solving some of the issues of current hydrometallurgy methods and which prevent their industrial development at very large scale. This project will be an opportunity for the start up Extracthive to develop an expertise on foam processes for recycling metals from WEEE, which then may be applied to other types of waste such as batteries and therefore to reach new clients.

AUTOMACT PROJECT ANR-18-CE05-0016

(SEP. 2018- AUG. 2022)

«SOLID FIXATION AND AUTO-CONDITIONING OF ACTINIDE ELEMENTS COMING FROM CONTAMINATED LIQUID OUTFLOWS»

Dr Xavier Deschanels

Partners:
CIMAP GANIL Caen
IRAMIS Saclay
ICG Montpellier
ICSM/LNER (coordinator)

The objective of this basic research project (PRC) is to develop a new strategy for the treatment of radioactive effluents based on the use of a porous functionalized support. This support would allow at the same time the separation of the RadioNucleide (RN) using a selective organic function, and their encapsulation after collapse of the porosity by a «soft» way (sol-gel, heating under stress, irradiation effect). This new concept would result in obtaining a primary wasteform matrix. Mesoporous silicas will be used as model support materials, because the nanometric size of their pores allows easy closure. Furthermore, the silica has a chemical composition close to high-level nuclear waste packaging materials (glass). This new so-called separation / conditioning strategy would constitute a significant simplification of the number of step, compared to «traditional» processes for the treatment of radioactive effluents. Such traditionnal processes usually require a concentration step of radioactivity (evaporation, precipitation, etc.), followed by of a embedding step. It could be adapted to any type of liquid effluents, aqueous or organic, containing radionuclides emitter alpha, beta, gamma. This process could be interesting for the treatment of effluents produced in nuclear installations (STEL ...), but also for the treatment of effluents from dismantling sites because of its compactness. In this project we will focus our study on the treatment of effluents containing actinides, which have a significant radiotoxicity linked to the alpha decays induced . This mode of disintegration could be beneficial for the collapse of the mesoporous structure , leading directly to a «primary wasteform matrix». The closure of the porosity under self-irradiation will therefore be particularly studied, with the realization of materials doped with short-life actinides (244Cm, 238Pu). Another innovative aspect of the AUTOMACT project will be the search and grafting of selective actinide ligands. For that, tributyl phosphate, which is used in the Purex process for the separation of uranium and plutonium, is a potential candidate. The purpose of this project is therefore to propose a new all-in-one RN separation / conditioning route using specific materials allowing both decontamination operations and their simple evolution towards a primary containment matrix.

MULTISEPAR PROJECT ANR-15-CE07-0013-01

(FEB. 2019 – AUG. 2022)

«MODELISATION MULTI-ÉCHELLE DES PHASES ORGANIQUES POUR L'EXTRACTION LIQUID-LIQUIDE »

Pr Jean-Francois Dufrêche

Partners:
ICSM-LMCT (coordinator)
DEN/DMRC CEA Marcoule
Laboratoire Phenix, Sorbonne Université, Paris

The ANR MULTISEPAR project aims to model rare earth (lanthanide) separation processes used in hydrometallurgy and for recycling. More specifically, it will focus on the solvent phase of liquid-liquid extraction processes, the modelling of which being currently at a very early stage. The multi-scale approach will be based on three complementary levels of description. First, at the atomic level, molecular dynamics simulations will calculate the structure and speciation in these solvent phases. The molecular interaction potential that we will use here has recently been validated from ab initio simulations by comparison with spectroscopy experiments. An umbrella sampling methodology will calculate the forces between solutes. The purpose of this step will be both the determination of the physico-chemical ingredients required for solvent phase modelling and also the calculation of the mesoscopic properties used by the other more macroscopic description scales. In another level of descriptions, mesoscopic Brownian simulations will be performed to calculate the effects at greater distance. Based on molecular simulation data (effective interaction potential and mobilities), either Brownian dynamics simulations or Multiparticle Collision dynamics simulations will be used to access the largest scales. The solutes activity coefficients and the stability of the solvent phase can thus be calculated. At the dynamic level, solute transport (diffusion and electrical conductivity) as well as viscosity will also be studied because they drive many industrial processes. As both experiments and molecular simulations show that in some cases solutes decompose poorly into independent particles but rather form a continuous network of hydrophilic parts in the solvent phase, we will also propose a second mesoscopic model to describe these solvent phases, this time based on a microemulsion model. Using a Gaussian random field methodology, we will propose a code representing the Gibbs energy of the solvent phase, which will make it possible to predict both the structure and the extraction properties. The fundamental quantities of this level of description will be here the properties of curvature (spontaneous curvature and rigidity) due to the extractants which will be deduced from the molecular simulations. The study of extraction as a function of the concentrations in the aqueous phase and of the extractant concentration will validate this methodology. We believe that this calculation will be a success if this microemulsion model can represent extraction equilibria with a much smaller set of parameters than traditional models based on multiple chemical equilibria between species. Thus, this project on lanthanide extraction could lead to a model that will be implemented in chemical engineering codes describing this process. We hope that through this multiscale project and the extensive use of numerical computing resources a new image of extraction mechanism will emerge from molecular modelling and that it will be able to bridge the gap to the macroscopic descriptions of this method of separation chemistry.

DECIMAL PROJECT PIA ANDRA

(OCT. 2017 – SEPT 2021)

"PHENOMENOLOGICAL DESCRIPTION OF THE CORROSION AND ITS IMPACT ON THE DURABILITY OF ENCAPSULATED MAGNESIUM WASTES IN HYDRAULIC BINDERS"


Dr Diane Rebiscoul

Partenaires:
CEA/DEN (coordinateur)
INSA Rennes
IRCP-ENSCP
ORANO
ICSM - LNER

The DECIMAL project (call for projects ANDRA « Optimization of radioactive dismantling waste's management ») takes place in the context of the nuclear waste treatment. This fundamental research project, involves four research groups (CEA, ICSM, INSA and IRCP), an industrial partner (ORANO) and also the CEA as nuclear waste producer.

The reprocessing of spent nuclear fuels from French UNGG (Uranium Natural Graphite Gas) nuclear reactors has generated cladding wastes mainly made of magnesium alloys. The CEA strategy is to encapsulate these intermediate-level long-lived wastes into a geopolymer matrix. Thus, the durability of the geopolymer/ magnesium alloy with respect to the storage requirements supplied by ANDRA has to be studied.
Indeed, the reactivity of the magnesium wastes with water in repository implies that the metal can corrode resulting in a dihydrogen gas release that is detrimental to the safe storage of conditioned waste packages. This reactivity may also be affected by the irradiation due to the radioactivity of the spent fuel cladding.

Regarding this context, the objective of this project is to develop a methodology to characterize the impact of the reactivity of encapsulated magnesium alloy in a geopolymer matrix, on its durability, and to understand the processes occurring during the evolution of the metal/matrix interface during aging with or without irradiation. The DECIMAL project proposes a dual approach to study the reactivity of the MgZr alloy: the electrochemical analysis of the kinetics of corrosion of the MgZr alloy encapsulated in geopolymers in the presence or absence of passivating agent and the characterization of the metal/matrix interface (Ph.D Rémi Boubon at LNER). The impact of the reactivity of Mg on the matrix will be considered as chemo-hydro-mechanical proprerties. This methodology will allow the determination of the corrosion processes occurring between the metal and the matrix, their evolution with time and under irradiation.

X-MAS^2 PROJECT ANR-17-CE06-0004

(DEC. 2017 - NOV 2020)

"XENOTIME: A MATERIAL FOR ACTINIDES SPECIFIC STORAGE"

Dr Adel Mesbah

Partner:
ICSM-LIME, CEA Marcoule

For safer and clean nuclear energy, X-MAS^2 project intends to develop promising phosphate matrices dedicated to the long term storage of high level nuclear wastes. This project will consider the xenotime phase having a general formula of $LnPO_4$ (Ln = Tb–Lu) and crystallizes in the zircon structure type. In the case if the trivalent actinides or their lanthanide surrogates the incorporation goes through the formation of solid solutions of $Ln_{1-x}An_xPO_4$. Whereas with tetravalent actinides (Th, U), two different mechanisms will be explored leading to the formation of $Ca_xAn_xLn_{1-2x}PO_4$ et $An_xLn_{1-x}(SiO_4)_x(PO_4)_{1-x}$ compounds. For the first time such materials will be synthesized by wet chemistry methods allowing the formation of pure and homogeneous phases and will be thoroughly characterized. Afterward, their thermal behavior, sintering ability and also their chemical durability will be evaluated in order to propose efficient matrices for the conditioning of high level nuclear wastes.

RECALL PROJECT ANR-20-CEES04

(OCT. 2020 – MARS 2024)

« SUSTAINABLE RECOVERY OF VALUABLE METALS IN BAUXITE RESIDUE »

Dr Stéphane Pellet-Rostaing

Partners:
CEREGE (Coordinateur)
ICSM-LTSM
AMSE
HYMAG'IN (start-up)
ALTEO (Industriel)

The RECALL project, supported by the French Institute of Circular Economy (INEC), aims at recovering selectively critical metals and valorize the iron from bauxite residue with the overall goal of reducing the pressure on natural mineral resources. To reduce the environmental footprint of the extractions, this interdisciplinary and intersectorial project aims at developing sustainable processes (in aqueous media at relatively low temperature and without solvents and strong mineral acids) as an alternative to traditional pyro- and hydrometallurgy processes and to value the economic impact of this technological change in terms of social welfare where potential environmental and health impacts are taken into account. This interdisciplinary project is built on 5 hypothesis: (i) environmentally friendly extraction processes rely in part on selective leaching in mild conditions compared with current technologies that uses significant energy to decompose the entire matrix. (ii) Selectivity can be achieved by coupling a good knowledge of waste composition and the speciation (chemical form) of the targeted critical metals and the choice of the appropriate extractant and extraction methodology. (iii) The use of biological molecules can selectively leach targeted critical elements at reasonable extent. (iv) Iron and critical metals can be co-valorized to reduce the quantity of waste generated by the alumina extraction industry and generate economic value. (v) New processes, can lead to an increase of social well-being compared to traditional approaches. Beyond a potential impact (negative or positive) on the private profit of the industrial implementing new technologies, the valuation of social well-being associated with new processes will be a crucial information for policy makers and citizens. In social well-being is included externalities associated with the process and other sources of economic inefficiency impacting welfare at the aggregate (society wide) level.

LABEX CHEMISYST

PÔLE
chimie
Balard

FROM LABEX CHEMISYST TO MUSE'LAB CHEMISTRY

Till 2019, the four Balard institutes of chemistry from Montpellier University Scientific, ICGM, IBMM, IEM and ICSM plus a team of "soft matter" physicists, of the Laboratory Charles Coulomb (UM) and the Centre of Materials of l'Ecole des Mines were associated around a laboratory of excellence, a Labex, entitled **CheMISyst**. This association was devoted to molecular and interfacial chemistry with a focus on the non-covalent long-range forces driving self-assembly. The related research was dedicated to the study and development of chemical systems, from thermodynamic and structural viewpoints, with strong input from modern analytical chemistry and with a focus on long-range non-covalent self-organization of fluids and solids at nanometer to micrometer scales. The objective was to achieve "systems" capable of selectively recognizing, encapsulating, transporting or transforming ions and molecules in various media. This includes interfacial chemistry, which deals with the study of the properties of ions and molecules confined at the surface of a solid or at the interface of two fluids.

The main topics underlying all the studies were: i) the identification of the forces at the origin of the molecular and supramolecular properties; ii) the understanding of self-assembly and its consequences on the macroscopic properties of molecular systems and materials; iii) the development of predictive models. It was organized around 4 clusters:

CLUSTER 1:
Molecular and interfacial systems for task specific materials
CLUSTER 2:
Chemical systems of self-assembled biomolecules
CLUSTER 3:
Chemical systems for separation and recycling
CLUSTER 4:
Cooperation, synergism and diversity in intermolecular interactions

In 2017, the reorganization of the Montpellier university around the "Montpellier University of Excellence" a new association, an I-SITE that gathers the forces of 19 institutions towards a common ambition: create in Montpellier a thematic research-intensive university that will be internationally recognized for its impact in the fields of agriculture, environment and health. For all its consortium members, this university strives to act as the academic partner they can establish strong ties with, and on which they can fully rely. Through the project construction named MUSE and in perspective of the end of the Labex project Chemisyst planed in 2021, the four institutes of the "Pôle de Chimie Balard" targeted the development of their own structure towards a **Lab'MUSE** staring in 2019 and taking into account a chemistry for man and his environment, i.e. a chemistry thought out differently, accompanying changes in concepts and practices for a controlled management of resources, a protected environment and sustainable health.

Whether it is a question of nutrition, environmental protection or health, it is absolutely necessary to design products that are effective, resistant but non-toxic, degradable after use, and environmentally friendly. With the permanent concern for a chemistry that respects the principles of «green chemistry» and «green engineering» for a judicious and sustainable development, the concept of adaptive molecular systems whose properties are governed by the principles of «cooperation, synergy and diversity of intermolecular interactions» makes the originality of Montpellier's chemistry. Whatever the required application, the aim is to understand and then to control how a set of molecules or supramolecular entities interact (communicate and behave collectively) to create complex systems with properties far beyond those of the individual constituents. This change of paradigm should contribute to this «green revolution», based on transdisciplinary cooperation for which chemistry must be a source of progress for :

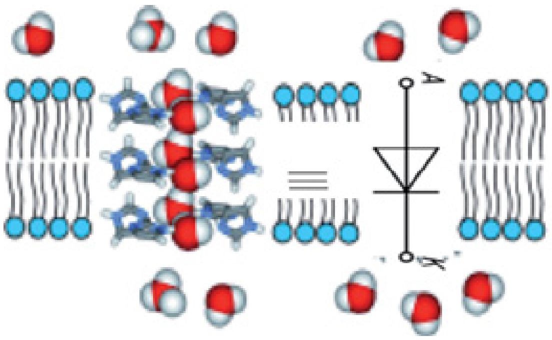
- Promoting an innovative agriculture to contribute to food security and environmental quality and thus meet the challenges of modern agronomy. The aim here is to design active molecules and systems for environmentally friendly agriculture, to study and synthesize plant molecules useful for human health, to recover agricultural waste and to use biomass as a raw material.
- Promoting a transition to an environmentally friendly society to provide complementary solutions to the restoration and protection of the environment but also to eliminate and/or recycle wastes (primary or secondary). The aim here is to design systems capable of producing or storing clean energy, develop processes for the synthesis of molecules that are more environmentally friendly, develop processes for the treatment of contaminated effluents, and implement processes for the reasoned recycling of recoverable materials.
- Improving human health in changing environments by gaining a thorough understanding of physio-pathological mechanisms at the molecular level, designing active molecules, delivery systems, targeting, transport for targeted treatments, drawing inspiration from nature and using living organisms for healing.

« diEAU » : CANAUX À EAU SYNTHÉTIQUES POLARISÉS EN SYSTÈMES LIPIDIQUES : VERS UNE DIODE À EAU

	NOM	PRENOM	INSTITUT
Responsable	BARBOIU	Mihail	IEM
Co-responsable 1	BONNETE	Françoise	IBMM
Co-responsable 1	ZEMB	Thomas	ICSM
Doctorant	KOCSIS	Isvan	

Date de démarrage du projet	Octobre 2014
Date de fin du projet	Octobre 2017

La pression osmotique peut être assimilée à une différence de potentiel chimique. Alors que des transistors et des diodes servent l'électronique, peut-on imaginer des systèmes analogues afin de contrôler technologiquement, cette force à la fois immuable et omniprésente dans le vivant ? La conception de canaux synthétiques mimant le fonctionnement des protéines-canal naturelles sera entreprise dans ce projet par une nouvelle approche multidisciplinaire incluant l'expertise chimique et la maîtrise de l'organisation supramoléculaire de ces canaux artificiels ainsi que la capacité à cristalliser ces systèmes dans leur état fonctionnel au sein de la membrane. Une des clés du projet sera de former des canaux permettant d'orienter le passage de l'eau (grâce à son dipôle) si possible de façon variable et commutable et ainsi créer par analogie une « diode à eau ». Des molécules bolaformes développées par l'IEM connues pour leur capacité à s'auto-organiser et à transporter spécifiquement des molécules d'eau ou des ions seront insérés dans des membranes dont les lipides et les tensioactifs constitutifs développés par l'IBMM seront choisis afin d'une part de favoriser leur activité de canal synthétique et d'autre part leur cristallisation. Une bibliothèque de composés bolaformes étant à disposition, il s'agit maintenant d'appréhender les structures formées, en déterminant le diagramme de phases liquide-cristallines de nos systèmes « amphiphile-eau » à la façon de Luzzatti et al. ; les canaux cristallisés sont appelés «punctuated planes» (illustration Dubois et al.). Il resterait alors à maîtriser la mesure des potentiels chimiques de l'eau : ceci peut être fait par cristallisation en phase cubique comme décrit par Landau et Pebay-Peyroula. L'expérience accumulée dans ce domaine peut donc aider à mieux comprendre et résoudre les aspects qualitatifs de l'intégration des canaux artificiels mis au point à l'IEM. Alors que la cristallisation en phase méso des protéines membranaires est souvent perçue comme un art difficile, la cristallisation de telles structures en systèmes membranaires peut être conduite de manière rationnelle à l'aide d'outils amphiphiles adaptés. Elle devra être effectuée selon les règles de l'art actuellement utilisées avec de plus en plus de succès pour cristalliser les protéines membranaires en systèmes membranaires. Elle nécessite l'utilisation de lipides et de tensioactifs capables d'assurer une intégration de ces systèmes canal dans les membranes et de faciliter leur interaction et leur cristallisation dans la membrane. L'IBMM possède cette expertise à travers son expérience de la synthèse d'outils amphiphiles pour la manipulation et la cristallisation de protéines membranaires. En rassemblant des chercheurs de trois instituts du Labex, IBMM, ICSM et IEM capables ensembles a) de fabriquer des canaux mimant l'activité des protéines de type porine, b) de concevoir, fabriquer et manipuler des matrices membranaires capables d'accueillir ces canaux artificiels et de les cristalliser, c) de rationaliser le processus d'auto- assemblage de ces canaux artificiels et d) d'évaluer la pression osmotique et l'activité de l'eau, nous pensons que les ingrédients seront réunis pour effectuer des avancées significatives dans un domaine crucial de la recherche fondamentale sur les canaux artificiels pouvant conduire rapidement à des technologies appliquées dans le domaine des membranes d'ultrafiltration et de séparation des ions.

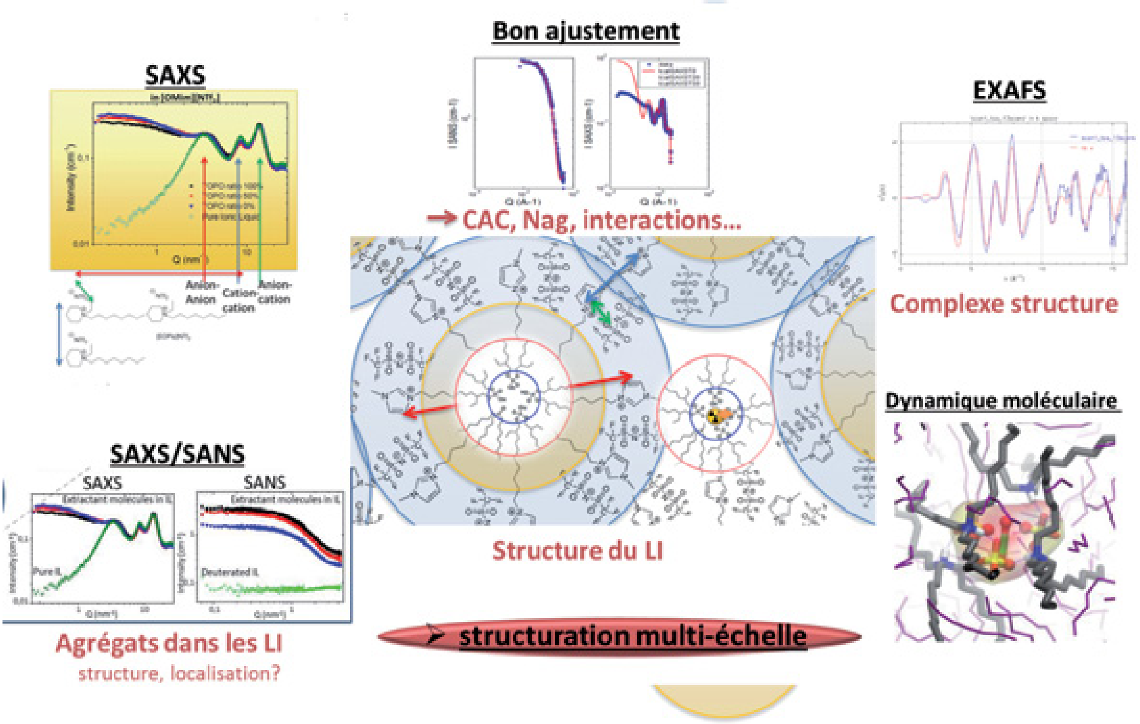


« MERLIN » : EXTRACTION MECHANISMS IN IONIC LIQUID MEDIUM FOR THE EXTRACTION OF METALS OF INTEREST

	NOM	*PRENOM*	*INSTITUT*
Responsable	*DOURDAIN*	*Sandrine*	*ICSM*
Co-responsable 1	*ARRACHART*	*Guilhem*	*ICSM*
Co-responsable 1	*CAMBEDOUZOU*	*Julian*	*IEMM*
Post-Doctorant	*AUGUSTO LOPEZ*	*Cesar*	*ICSM*

Date de démarrage du projet	*1er mai 2018*
Date de fin du projet	*1er novembre 2019*

As part of an approach applied to the recycling of metals of interest, this fundamental study aims at better understanding the extraction performances in ionic liquid media. The objective of this post doctorate is to study and compare the effect of different ionic liquids on the supramolecular aggregation of extraction phases and to put them in relation with their extraction properties. This study will focus on extracting systems already well known and characterized in our laboratory for conventional diluents in the context of the extraction of metals of interest as rare earths. The effect of these new diluents on the extraction performances will be characterized by ICP measurement, X-ray fluorescence, NMR, acid and Karl Fisher titration. These will then be connected to the aggregation properties of extracting molecules determined by scattering measurements of X-ray and neutron at small angles, and by physico-chemical measurements such as surface tensiometry.

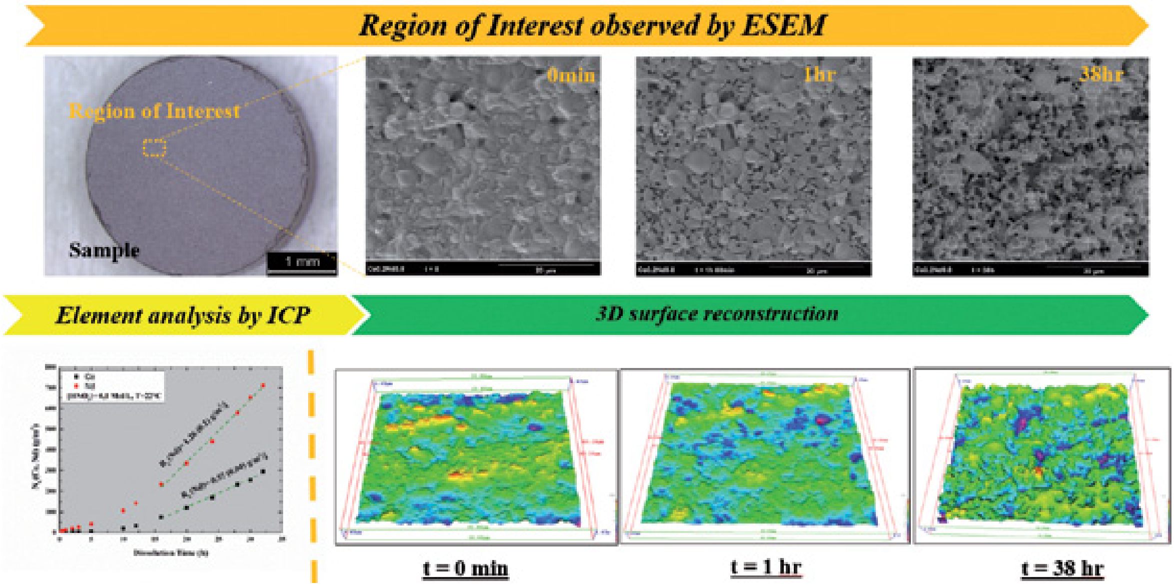


« DISSO3D » : CHARACTERIZATION OF EVOLVING SOLID/LIQUID INTERFACES DURING DISSOLUTION BY 3D ANALYSIS AT THE MICROSCOPIC SCALE BY SEM

	NOM	**PRENOM**	**INSTITUT**
Responsable	PODOR	Renaud	ICSM
Co-responsable 1	DACHEUX	Nicolas	ICSM
Co-responsable 2	SZENKNECT	Stéphanie	ICSM
Post-Doctorant	BEN KACEM	Ilyes	ICSM

Date de démarrage du projet	*8 janvier 2018*
Date de fin du projet	*7 juillet 2019*

This proposal aims to develop a new methodology for the characterization of solid-liquid interfaces during the dissolution process, mainly focused on the 3D reconstruction of surfaces on the basis of tilted SEM image series. The 3D images will be recorded regularly during the sample dissolution in order to determine accurately the local quantities of dissolved matter. The studied materials will be model compounds that are of interest in several application fields: catalysis, solid oxide fuel cells, surrogates for the nuclear fuel. They will be chosen in the CeO_2-Nd_2O_3 binary system. This system allows preparing materials with variable crystal structures and microstructures, depending of the sample composition in order to adapt the dissolution kinetics to the sample observation techniques. In parallel with the methodological developments, numerical modelling based on image processing will be developed to link the local dissolved volumes (mainly related with the preferential dissolution) with the dissolution rates measured at the macroscopic scale.

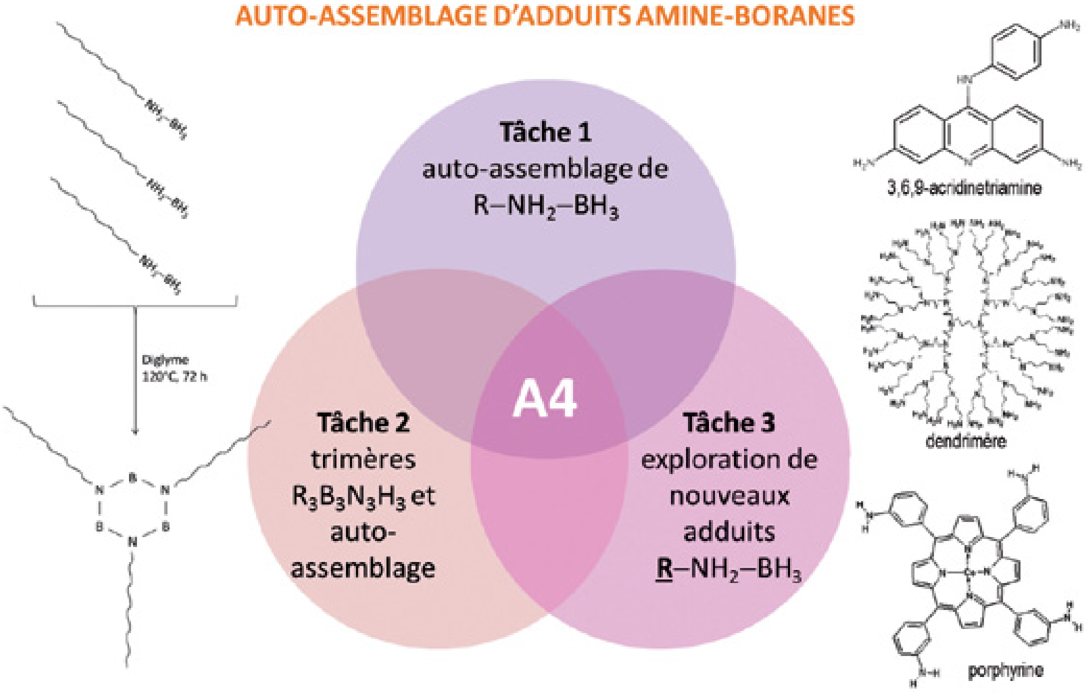


« A4 » : SELF-ASSEMBLY OF AMMONIUM BORANE HYBRID ALKANES IN ORGANIC SOLVENTS

	NOM	PRENOM	INSTITUT
Responsable	*DEMIRCI*	*Umit*	*IEMM*
Co-responsable 1	*ALAUZUN*	*Johan*	*ICGM*
Co-responsable 2	*DOURDAIN*	*Sandrine*	*ICSM*
Post-Doctorant	*ANTIGONI*	*Theodoratu*	

Date de démarrage du projet	*1er mars 2018*
Date de fin du projet	*1er octobre 2019*

The A4 project aims at developing molecules having $-NH_2-BH_3$ groups (with protic hydrogens together with hydridic hydrogens, *i.e.* $H^{\delta}+$ *versus* $H^{\delta}-$) within the context of the supramolecular chemistry. Our idea is to study the interactions $H^{\delta}+\cdots H^{\delta}-$ between the different hydrogens that can exist in the amine-borane adducts. Indeed, such interactions could lead to self-assembling/-organization of systems in solution. Our idea is also to better understand the dynamics behind the assembled/organized systems, and then to elaborate new materials. The consortium involves 3 partners, IEMM, ICGM and ICSM, with complementary expertise in chemistry of amine-/hydrazine-boranes, organic synthesis, and characterization of self-assembling.



« RAMELI » : MOLECULAR DYNAMICS TO RATIONALIZE STRUCTURAL EFFECTS ON EXTRACTION MECHANISMS IN IONIC LIQUID

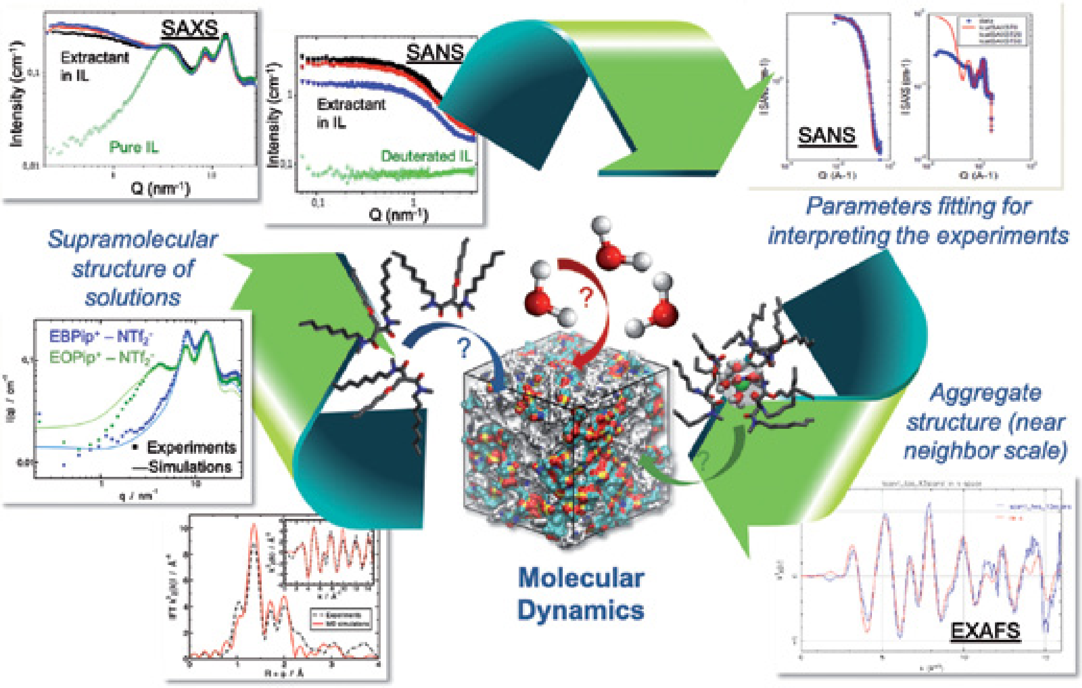
	NOM	PRENOM	INSTITUT
Responsable	*DUVAIL*	*Magali*	*ICSM*
Co-responsable 1	*DOURDAIN*	*Sandrine*	*ICSM*
Post-Doctorant			*ICSM*

Date de démarrage du projet	*1^er^ février 2021*
Date de fin du projet	*31 août 2022*

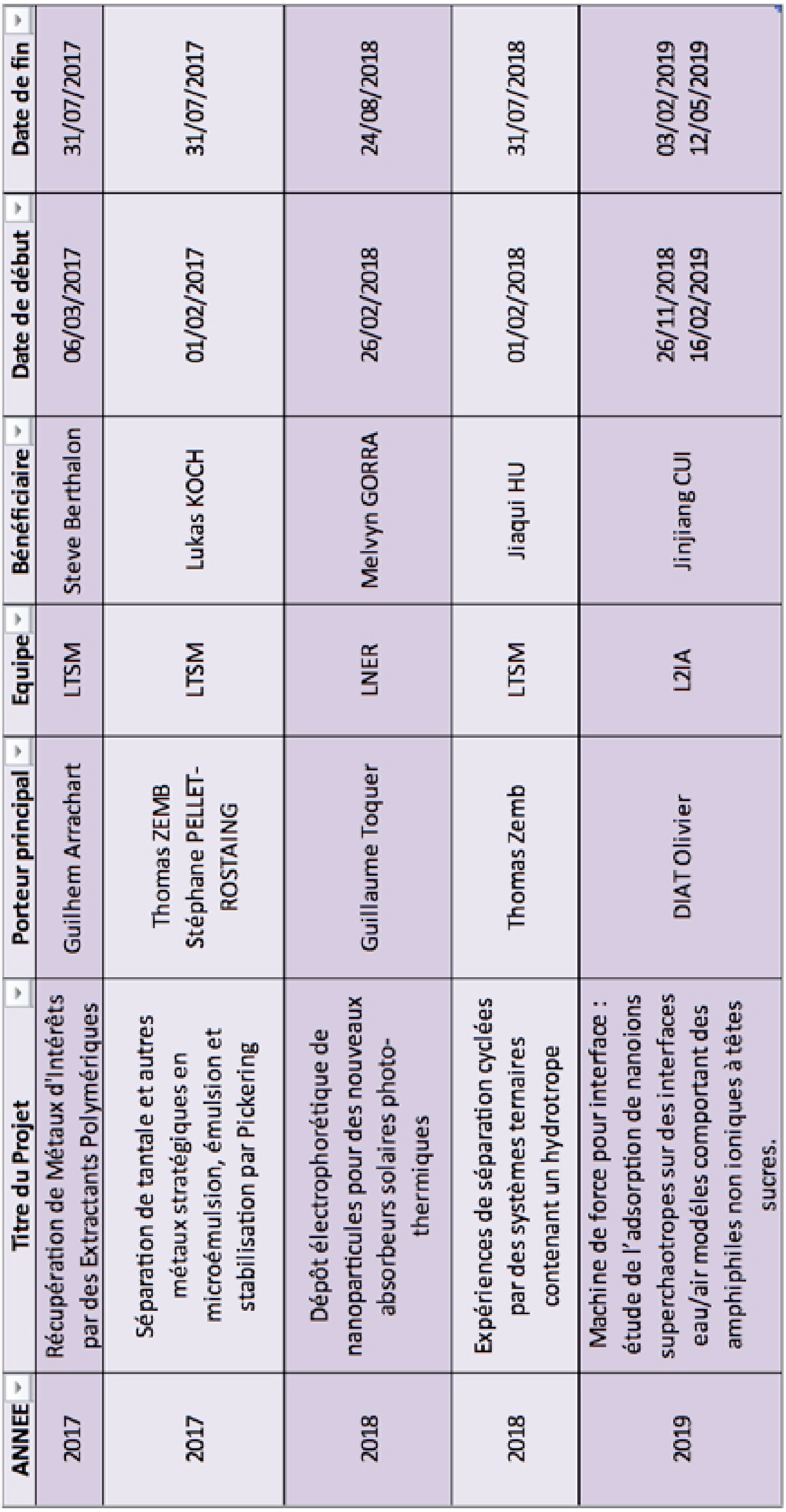
As part of an approach applied to the recycling of metals of interest, an essential challenge in liquid-liquid extraction today consists in replacing conventional organic solvents by non-conventional diluents, typically ecofriendly solvents like ionic liquids. This study will be based on studies performed at ICSM in an attempt of developing extraction processes in ionic liquids, which demonstrated that the best extraction performances in ionic liquid media are not only due to different complexation mechanisms, but also to different structural properties. The objective of this project is to understand the mechanisms occurring in liquid-liquid extraction processes performed in ionic liquid media by developing multi-scale theoretical approaches based on molecular dynamics. It will allow a better understanding of the thermodynamic properties of aggregates in ionic liquid media in order to rationalize the phenomena associated with the transfer of ions involved in liquid-liquid extraction processes.

• Scientific driving question, in the context of system chemistry:

The objectives of this project will provide insights on the structuring and the mechanisms of aggregation of the extracting molecules in ionic liquid media by understanding the effect of the solvent structure on the extraction performances. Applied to the extraction of metals of interest, this project will also allow identifying ionic liquids in which the extraction performances will be improved.



STAGES LABEX



ANNEE	Titre du Projet	Porteur principal	Equipe	Bénéficiaire	Date de début	Date de fin
2017	Récupération de Métaux d'Intérêts par des Extractants Polymériques	Guilhem Arrachart	LTSM	Steve Berthalon	06/03/2017	31/07/2017
2017	Séparation de tantale et autres métaux stratégiques en microémulsion, émulsion et stabilisation par Pickering	Thomas ZEMB Stéphane PELLET-ROSTAING	LTSM	Lukas KOCH	01/02/2017	31/07/2017
2018	Dépôt électrophorétique de nanoparticules pour des nouveaux absorbeurs solaires photo-thermiques	Guillaume Toquer	LNER	Melvyn GORRA	26/02/2018	24/08/2018
2018	Expériences de séparation cyclées par des systèmes ternaires contenant un hydrotrope	Thomas Zemb	LTSM	Jiaqui HU	01/02/2018	31/07/2018
2019	Machine de force pour interface : étude de l'adsorption de nanoions superchaotropes sur des interfaces eau/air modéles comportant des amphiphiles non ioniques à têtes sucres.	DIAT Olivier	L2IA	Jinjiang CUI	26/11/2018 16/02/2019	03/02/2019 12/05/2019

TEACHING

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 and training activities in five directions:

1 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. Both master CSMP and 3rd year option of ENSCM have obtained the label of the Institut International pour l'Energie Nucléaire (I2EN) in november, 2019.

2 The active participation of several ICSM members in four main courses of the Institut Franco-Chinois à l'Energie Nucléaire
(IFCEN at the Sun Yat Sen University, Zhuhai, China), a Sino-French engineer school in which ENSCM is one of the five main partners. Several courses including nuclear fuels, analytical strategy of actinides and chemistry related to the front-end and back-end of the nuclear fuel cycle are (will be) given in the 2015-2020 period.

3 The Annual practical separation chemistry summer-school:
Full five day sessions, including 2 days of practical and a session devoted to understanding experimental results on the light of the concepts developed in the lecture part. Sometimes, it can be coupled to another summer-school like this year. This summer school, initially created in 2007 by INSTN for the whole research at CEA-Marcoule, has been specialized for ICSM from 2009. Since 2012, the teachers and students are coming from the Six UMR associated in Chemisyst project (detailed programs are found in the Annex: 7eme Ecole pratique d'été Labex CheMISyst 2018 on "natural chemical systems in presence of electrolytes: the case of wood" & summer school on "Thermodynamics and energetics of soft-matter systems").

4 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 every Thursday (during months of winter-time). These have been replaced by SPOC on "Science and technology for recycling industrial wastes and formulating stable concentrated solutions" since beginning of 2018 (see flyer of announcement in the annex).

5 The European school of SURFACES AND NUCLEAR SCIENCES
was organized by ICSM for its third edition (2012, 2015 and 2018) around the scope of Surfaces and Nuclear. It brought together in a friendly atmosphere more than 21 participants and 18 speakers from different research centers such as the CEA (Saclay, Marcoule, Cadarache), IPN Orsay, ICSM, and ANDRA belonging to the community of researchers and doctoral students studying physico-chemical modifications occurring on solid or liquid surfaces, for problems related or not to nuclear energy (see annex).

MASTER CSMP – 1ST YEAR (MAIN COURSES)

Basis in chemical processes
Nuclear fuel cycle: from ore to reprocessing
IR and Raman spectroscopies
Liquid and solid NMR
Preparation and properties of colloids
Structure determination in solids
Preparation of inorganic materials
Basis in solution Chemistry
Solution chemistry applied to actinides
Basis in radioactivity
Chimiometry
Radiation-matter interactions – Radioprotection
High-temperature chemistry
Radwaste matrices
Coordination chemistry for f elements
Radiochemistry and chemistry at the trace level
Bibliographic training

MASTER CSMP – 2ND YEAR (MAIN COURSES)

Weak interactions and partitioning chemistry
Analytical chemistry for actinides
Processes for waste treatment and conditioning
Processes for partitioning with membranes
Front-end of nuclear fuel cycle: extraction and separation chemistry
Dissolution and radiation damages in ceramics
Modeling for separation and confinement
Safety and Radioprotection
Nuclear fuels: synthesis and refabrication
Liquid-liquid extraction: thermodynamics, kinetics and processes
Long-term behavior: glasses
Molecular and supramolecular chemistry of f and d elements
Bibliographic training).

EUROPEAN SCHOOL OF SURFACES AND NUCLEAR SCIENCES

MARCOULE INSTITUTE FOR SEPARATION CHEMISTRY
14 -18 MAY 2018 PORQUEROLLES, FRANCE

La EUROPEAN SCHOOL OF SURFACES AND NUCLEAR SCIENCES qui correspond à la troisième édition des écoles thématiques Surfaces et Nucléaire I et II (2012 et 2015) a permis de réunir dans une ambiance conviviale plus de 21 participants et 18 intervenants provenant de différents centres de recherche comme le CEA (centres de Saclay, Marcoule, Cadarache), de l'IPN Orsay, de l'ICSM, et de l'ANDRA appartenant à la communauté des chercheurs et des doctorants étudiant les modifications physico-chimiques survenant sur des surfaces solides ou liquides, pour des problématiques liées ou non au nucléaire.

L'objectif scientifique de l'école était de mettre en relation les participants avec des spécialistes des techniques et de doter les participants des bases théoriques leur permettant de concevoir de nouvelles expériences en lien avec leurs besoins. Ces bases ont été illustrées de quelques exemples d'applications dans le domaine du nucléaire. Les participants ont pu aussi obtenir une liste des différentes installations et techniques de caractérisation de surface disponibles en environnement nucléarisé en France et en Europe.

De plus, les participants ont pu se faire connaître via des « présentations flash » et exprimer leurs besoins en termes de caractérisations. Ceci a permis d'ouvrir un espace de discussion avec les spécialistes présents et d'initier des collaborations entre équipes.

A noter la programmation du prochain rendez-vous en 2021 :
EUROPEAN SCHOOL OF SURFACES AND NUCLEAR SCIENCES II.

Organisatrices ICSM: Stéphanie Szenknect - LIME, Sandrine Dourdain - LTSM, Diane Rébiscoul –LNER

ECOLE THÉMATIQUE RÉFLECTIVITÉ DES RAYONS X ET DES NEUTRONS

10 – 12 OCTOBRE 2018

La 2ème édition de cette école organisée à l'ICSM avait pour objectif de former des étudiants aux principes théoriques de la réflectivité, à son utilisation, aux traitements des données ainsi qu'à leur exploitation au travers de cours et de travaux pratiques. Plusieurs cas d'études ont été présentés afin de montrer aux participants toutes les potentialités de cette méthode d'analyse de surface. Cette école a réuni 23 participants dont des doctorants et des jeunes chercheurs travaillant dans le domaine des surfaces et des couches minces et souhaitant utiliser la réflectivité.

Cette édition a été un réel succès comme en témoigne un article rédigé par 3 participants du CNRS et publié sur le site de **l'Association Française de Cristallographie** :

https://www.afc.asso.fr/l-association/afc-news/1400-des-photons-et-des-neutrons-en-incidence-rasante-a-marcoule

Ecole Organisée par l'Institut Européen des Membranes (IEM; CNRS / UM / ENSCM) et l'Institut de Chimie Séparative de Marcoule (ICSM; CEA / CNRS / UM / ENSCM) avec le soutien de la formation permanente du CNRS :

DOURDAIN Sandrine (CEA-ICSM)
REBISCOUL Diane (CEA-ICSM)
VAN DER LEE Arie (CNRS-IEM)

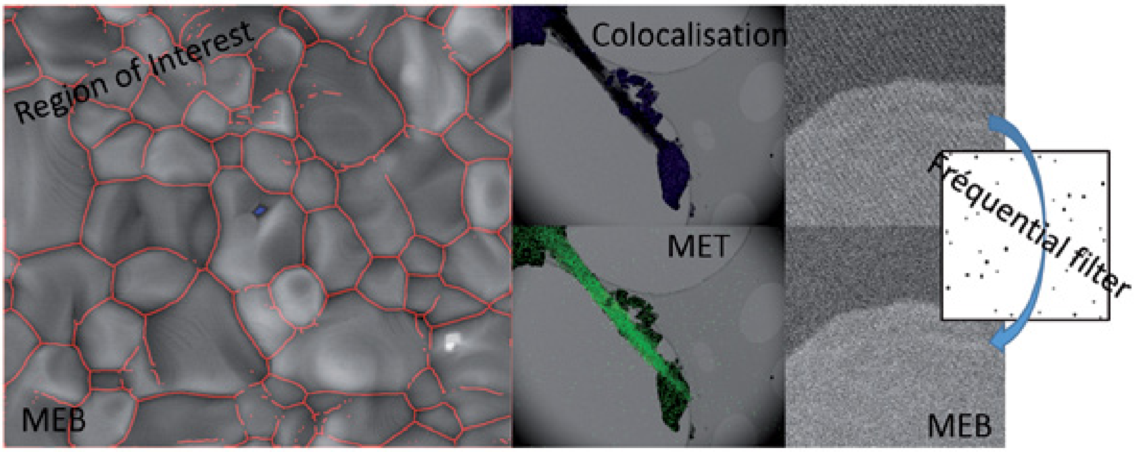
Invités:
Samuel TARDIF (ESRF)
Thomas Zemb (ICSM)

TRAINING: IMAGE ANALYSIS FOR ELECTRON MICROSCOPY

	NOM	PRENOM	INSTITUT
Responsable	LE GOFF	Xavier	ICSM
Co-responsable	BRAU	Henri-Pierre	ICSM

Training	**2017 (1), 2018 (2), 2019(1), 2020(1)**

With the advent of the digital era, nowadays images are multidimensional numerical data that can be processed and analyzed quantitatively to extract more information. ImageJ/Fiji open source software (imagej.net/) is a powerful tool available to process and analyze digital images. Moreover, it also allows the automation of image analysis with custom macros and plugins. With this training, we intend to give a general introduction to ImageJ/Fiji, show how to use it to extract quantitative data and how to write simple macros. We give a set of tools and methods for image segmentation and quick insight of machine –learning into this purpose. This training makes the focus on the analysis of microscopy images but is targeted to all people engaged in research, which wants to start using ImageJ/Fiji for image analysis in general.



Pre-registration is necessary because of the limited number of places in the school.
A short description of research activity and a CV should be sent to softmatter2018@ill.fr
The organising committee will examine your application and inform you in June 2018.

Pre-registration deadline : 20 May 2018
Notification of acceptance : 3 June 2018
Registration deadline : 17 June 2018

Registration fee (including VAT):

- 200€ including lecture material, lunches, social dinner and accommodation (2 nights)
- 150€ including lecture material, lunches and social dinner

Organisers
Leonardo Chiappisi
Thomas Zemb

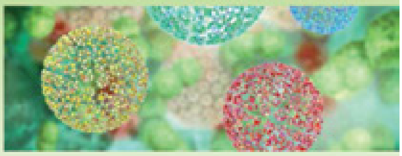
Workshop assistants
Alison Mader
Pauline Charriaux

Email address : softmatter2018@ill.fr

Web site :
https://workshops.ill.fr/e/softmatter2018

Thermodynamics and energetics of soft matter systems

Institut Laue-Langevin, Grenoble, France
from 24 to 26 July 2018



Soft matter pervades into daily life under several forms: biological matter, foams, food products, ink, tires, and many others. In contrast to their very different appearance, all these systems are governed by the same, fundamental physical laws. Aim of the school is providing an overview of the forces governing the behavior of soft matter systems and introducing the most relevant techniques to probe such interactions. The school proposes frontal lectures for doctoral students working in the field of soft matter given by recognized experts from all over Europe. Poster sessions will be opened for discussion on research topic and experimental results between students and invited lecturers.

Tue – 24.7	
9:00 - 9:45	Welcome and Registration *Hall ILL4*
10:00 - 11:30	ESRF Guided Tour *Visitor Center*
12:00 - 13:00	Lunch *ESRF/ILL Canteen*
13:30 - 13:45	School Opening *Chadwick Amphitheatre*
14:00 - 15:30	Lecture 1: **Introduction to colloid and interface Science** *Emanuel Schneck* Introduction to colloid and interface science & its applications. Basic concepts. Van der Waals interactions, the electric double layer, and DLVO theory. Further interaction mechanisms (steric, depletion).
15:30 - 16:00	Coffee Break
16:00- 17:30	Lecture 2: **Fundamentals of self-assembly processes** *Christoph Schalley* Basic Principles in Supra- molecular Chemistry. Non- Covalent Interactions and Host- Guest Complexes. Free energy landscape, polydispersity, cooperativity.
17:30	Poster Session & Discussion with Wine and Cheese *Hall ILL4*

Wen - 25.7	
9:00 - 10:30	Lecture 3: **Methods in Calorimetry and Volumetry** *Giuseppe Lazzara* Free energy and its derivatives: the partial molar quantities. Relevance in colloidal systems and methods to access them. Enthalpy changes in supramolecular aggregates: van't Hoff vs direct methods. Introduction and experimental tips in calorimetry and volumetry. Isothenral titration calorimetry: equilibrium and kinetics. Prediction abilities and case studies.
10:30 - 10:45	Coffee Break
10:45 - 12:15	Lecture 4: **Introduction to colloid and interface Science** *Roland Winter* Methods to probe the energetics, structure and conformational dynamics of biomolecular systems - Introduction to cell membranes, model biomembranes, lipid phase transitions. Proteins and their stability, free energy landscape, folding kinetics, interactions. Methods to probe the thermodynamics, conformation, dynamics and interactions of biomolecules.
12:15 - 14:00	Lunch *ESRF/ILL Canteen*
14:00 - 16:00	ILL/PSCM Guided Tour
16:00 - 17:30	Poster Session & Discussion
17:30 - 20:00	Free Afternoon
20:00	Social Dinner

Thu - 26.7	
9:00 - 10:30	Lecture 5: **Physics of macromolecular systems** *Julian Oberdisse* Conformation of polymer chains, chain statistics, polymer solutions and blends, thermodynamics, phase separation, mechanical properties.
10:30 - 10:45	Coffee Break
10:45 - 12:15	Lecture 6: **Thermodynamics of interfaces** *Antonio Stocco* Thermodynamics of interfaces and adsorption, surface tension, contact angle, wetting. Interaction between surfaces and stabilisation mechanisms (foams, emulsions).
12:15 - 14:00	Lunch *ESRF/ILL Canteen*
14:00 - 15:30	Lecture 7: **Solvation and Solubilization** *Dominik Horinek* Ideal and real mixtures and solutions. Molecules and macromolecules in solution. Free energy of solvation, chemical potentials, activity coefficients: experimental and theoretical approaches. A microscopic view from homogeneous to structured solutions: osmolytes, hydrotropes, surfactants. Concepts from Kirkwood-Buff theory. Solubilization in micro-structured solvents.
16:00	School Closing

7ème Ecole Pratique d'Eté LabEx CheMISyst 2018

Comportement d'un système chimique naturel et fonctionnel en présence d'électrolytes : cas du bois

Date

Du lundi 28 au vendredi 31 août 2018

Présence obligatoire la semaine

Lieu

Ecole des Mines d'Alès, Alès (Gard 30)

Comité scientifique et pédagogique

Thomas ZEMB
Martin IN
Gwenn LE-SAOUT
Nicolas LEMOIGNE
Claire LONGUET
José-Marie LOPEZ-CUESTA
Nicolas LOUVAIN
Aurélie TAGUET

Organisation

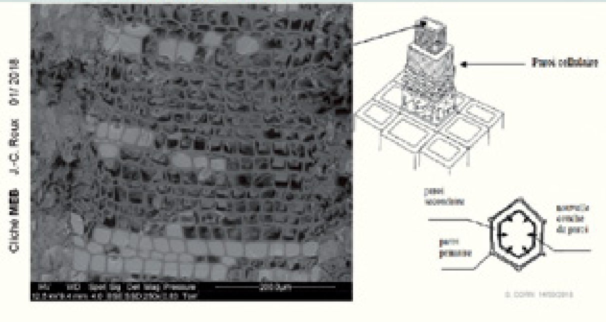
Pauline CHARRIAUX
Chargée de Projets
LabEx CheMISyst
labex@polechimie-balard.fr

Le LabEx CheMISyst organise depuis sept ans, son école d'été ouverte à tous les doctorants, post-doctorants et chercheurs de la communauté du Pôle chimie Balard et du LabEx CheMISyst.

Cette année, l'école d'été organisée du 28 au 31 aout 2018 à Alès, regroupe une partie théorique et une partie pratique sur le thème « Comportement d'un système chimique naturel et fonctionnel en présence d'électrolytes : cas du bois ».

EXEMPLES DE CARACTÉRISATIONS

Bois imprégné (Pin / Polyester insaturé)



Sur le même format que la précédente édition qui fut un réel succès (pédagogie inversée), les participants de l'école prépareront avant et pendant l'école, un exposé de 25 min, par binôme, sur un cours de leur choix parmi ceux proposés. Cette pédagogie active, impliquant les apprenants dans des activités participatives et coopératives, privilégie les échanges avec les conférenciers et les interactions des étudiants entre eux.

L'objectif de ces cours est d'illustrer concrètement l'application des interactions non covalentes et des systèmes chimiques à travers des exemples d'applications issus des travaux de recherche des participants, tout en s'appuyant sur les concepts généraux développés lors de l'école d'été 2017*. Afin d'aider les étudiants dans la préparation de cet exercice original et formateur, des temps seront consacrés à la finalisation des cours, en présence des encadrants.

**Retrouvez les présentations des cours inversés de l'édition 2017 réalisées par les étudiants, sur le site du Pôle chimie Balard (mot de passe d'accès aux fichiers : LC2017).*

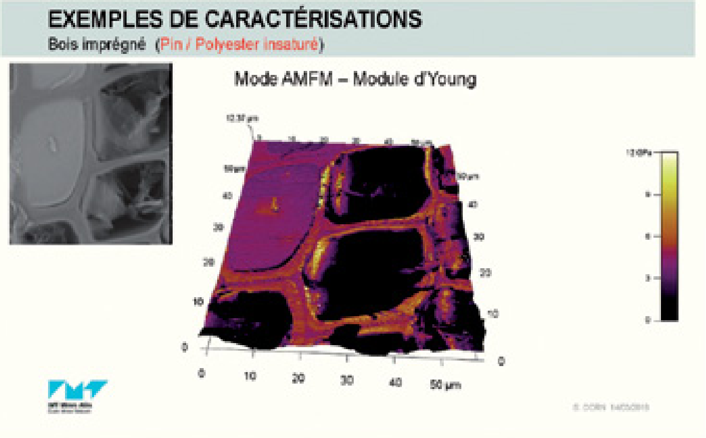
7ème Ecole Pratique d'Eté LabEx CheMISyst 2018

Durant ces cinq jours, les participants effectueront eux-mêmes des expériences lors de travaux pratiques qui donneront ensuite lieu à des communications orales et des discussions concernant les résultats obtenus par chacun. Ces travaux pratiques seront réalisés dans les locaux de l'Ecole des Mines d'Alès.

Enfin, trois conférenciers viendront présenter leurs travaux lors de cette 7ème édition de l'école du LabEx CheMISyst.

Nombre de places disponibles :
20

Public :
Doctorants, post-doctorants et responsables de projets LabEx CheMISyst*
Doctorants inscrits à l'ED SCB
Ensemble de la communauté Balard et du LabEx CheMISyst (chercheurs, enseignants-chercheurs ...)


EXEMPLES DE CARACTÉRISATIONS
Bois imprégné (Pin / Polyester insaturé)

Mode AMFM – Module d'Young

Liste des cours en pédagogie inversée :

(Format : 25 min + 10 min questions / discussions)

1. Pickering emulsions
2. Self-assembly in ionic liquids
3. Kinetics of exchange between phases
4. DLA and RLA
5. How biology makes general interactions specific
6. Screened electrostatic interactions in aqueous extracting systems
7. Characterising, morphology and disorder
8. Rehydration and adhesion
9. Interactions and structuration in mixed solvents

La participation à l'école est gratuite mais obligatoire et valide un crédit à l'ED SCB.

Inscriptions obligatoires en ligne sur le site du Pôle chimie Balard
avant le 14 juin 2018

Document mis à jour le 18/05/2018

Small Online Private Course (SPOC)

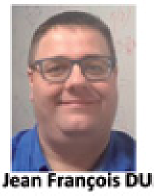
RECYCLING CHEMISTRY:
FROM THEORY TO PRACTICE

Science and technology for recycling industrial wastes and formulation

COURSE CONTENT

Mixing and separating for recycling of metals such as contained in electronic waste requires to master dissolution, formulation of complex fluid, selective extraction and finally re-mixing of electrolytes in order to obtain high performance recycled material with new economic value.
These lectures focus on the scientific basis of recycling and delivery, illustrated by knowledge-based examples of optimized technology involved in effective separation of species between phases.

PEDAGOGIC TEAM



Jean François DUFRÊCHE
ICSM and Université Montpellier

Thomas ZEMB
Scientific Advisor

Florent LEMONT
Program Manager

Marie-Hélène HENGÉ
Course Coordinator

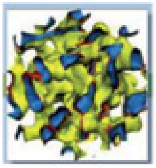
Pedagogic content: ***Pr Thomas Zemb***, *Funding director of the Institute for Separation Chemistry in Marcoule, Professor at the INSTN*
Theoretical parts: ***Pr Jean-François Dufrêche***, *Professor, Montpellier University*
Practical parts, organisation and broadcast: ***Florent Lemont*** *Research Director & Director of the INSTN-Marcoule*

ENTRY REQUIREMENTS

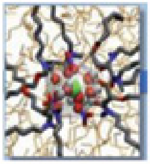
Bachelor level in physical chemistry

- Registration: spoc@icsm.fr
- Opening SPOC: March 1st, 2021
- Estimated effort 3 hours/week

Device scale



Meso-scale



Supramolecular scale

LEARNING METHODS

Entry point on the learning plateform:
- Send your registration request to: spoc@icsm.fr
- You will receive an invitation from « digital learning no reply »
- Follow the access information in the participant's guideline

Smal Online Private Course (SPOC)

LabEx CheMISyst

RECYCLING CHEMISTRY: FROM THERORY TO PRACTICE

Science and technology for recycling industrial wastes and formulation

OUTLINE PROGRAM OF COURSES

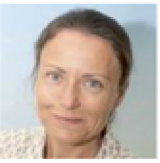
I . Prerequisite concepts

1. Solvents and solubilisation
2. Specific ion effects in solution
3. Specific ion effects at interfaces
4. Deep eutectic solvents
5. Establishing ternary phase diagrams
6. Separation process and operating diagram
7. Chemical potential: a general view at equilibrium
8. Osmotic pressure units and relative humidity
9. Osmolarity of solutes, Raoult and Henry laws
10. Measurement and control of osmotic pressures
11. Osmosis and electrolyte solutions
12. Dynamics in electrolytes solution: a panorama
13. Binary mixtures: water and ionic surfactant
14. Binary mixtures: lipids
15. Electrochemistry of Oxidation state of actinides and lanthanides

II. Scientific basis of recycling chemistry

1. Establishing binary phase diagram
2. Pseudo-phases versus microphases
3. Reading binary phase diagrams
4. Ternary phase diagram: the phase prism and its cuts
5. Ternary phase diagram: curvatures
6. Contacting two liquids for extraction
7. Basis of liquid-liquid extraction: chemistry and molecular forces
8. Definition and measure of the free energy of transfer
9. Steps in free energy as molecular mechanism for transfer
10. Interfacial term: chains and their entropy
11. Basic concepts of liquid formulation
12. Lessons from reading ternary phase diagrams

Werner KUNZ
Regensburg
University



Sophie CHARTON
CEA Marcoule

Helmut CÖLFEN
Konstanz University

Smal Online Private Course (SPOC)

LabEx CheMISyst

RECYCLING CHEMISTRY: FROM THERORY TO PRACTICE

Science and technology for recycling industrial wastes and formulation

III. Implementation in efficient processes

A.FORMULATION FOR SOLUBILISATION

1. Lessons from ternary phase diagrams
2. Basic concepts of liquid formulation
3. Using hydrotropes for solubilisation and oxidation control

B. LIQUID-LIQUID EXTRACTION

1. Liquid–liquid extraction at mesoscale
2. Solubilisation in Ionic liquids
3. Cloud point extraction in practice
4. Macrosocopic modelling: flux and mass balance
5. Devices used in liquid-liquid extraction
6. Apparatus designing
7. Pulsed column functioning

C. FLOTATION AND SEPARATION

1. Liquid gas separation: principles of flotation process

D. *SEPARATION BY CENTRIFUGATION*

1.Brief history of analytical centrifugation
2.Analytical centrifugation
3.Applications
4.Separation of nanoparticles mixtures

E. *SEPARATIONS IN THE NUCLEAR FUEL CYCLE*

1.Marie Curie's fractionated co-cristallisation
2. "Why recycling the spent fuel? "
3. Head of the extraction plant: from used fuel to solution
4. The PUREX process : Separation and purification operations
5. The PUREX process: Technologies of liquid-liquid extraction
6. Recovery of reactants and effluent treatment
7. Oxalic precipitation and metal oxide fabrication
8. Mixing oxides for refrabrication of fuels

Alexander WITTEMANN
Konstanz University

Luc GIRARD
ICSM and ENSCM

Jean DUHAMET
CEA Marcoule

OUTLOOK

Olivier Diat, Stéphane Pellet-Rostaing et Dominique Alpe-Conchy

The current scientific report summarizes the successes obtained in the last four years. With three hundred publications and a number of external citations per year in the range of 2000 (as per web of science), ICSM is in the top five world class Institutes in nanoscience for energy and recycling. The focus of the scientific and technical efforts, initialy defined by several reports of the Academy of Science in the early 2000s, was re-defined for the period 2015-2020 and has to be updated within the new goals assigned to CEA in 2018 for the next contract 2021-2026 associating the CEA, CNRS, University of Montpellier and ENSCM.

One of the reasons of the success is that a significant contribution in the three hundred primary scientific papers in "A" ranked journals, thirty patents and about ten reviews have been written with the co-authorship of colleagues from R/D departments in charge of applications. These activities meet either the demands of industrial partners such as ORANO or a more prospective research (TRL 1-4) for which engineers in R&D departments are associated in common programs with academic scientists and University teachers of ICSM. Moreover, nearly a third of the papers' impact is made in collaboration with international co-signature. 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. For the first time in France since more than 70 years, three international Humboldt prizes have been attributed to works in separation chemistry that were developed in Marcoule: Helmuth Möhwald in 2008, Thomas Zemb in 2010 and Werner Kunz in 2014.

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"). Thus, a cluster of competence and cooperation centred on **"Innovation in Extraction and Recycling"** naturally emerged within the institute, illustrated by the exceptional number of patents (26 between 2015 and 2020) and would not grow at an excellence level (as shown by citations in international literature) without a close link between observation and theory. For example, in solvent extraction, the free energy of ion transfer was thought through a specific "ienaics" approach with some similarities with electron transfer in electronics devices. Thus, within a second 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 explored. No less importantly, the recent advances in electron microscopies which allow the direct 2D observation (and 3D reconstruction) and the complex characterization of physico-chemical properties such as self-healing, sintering, dissolution, chemical reactivity through in situ experiments…

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.

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

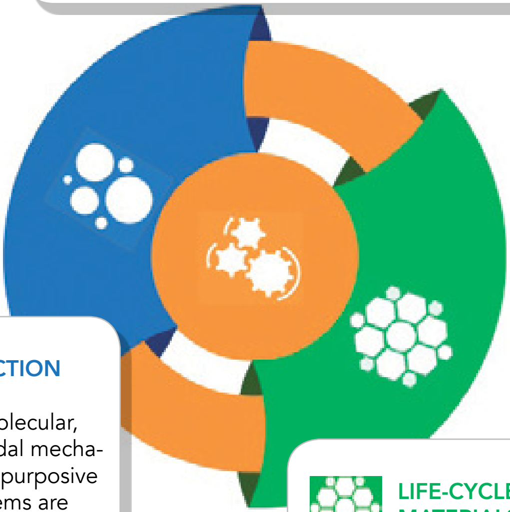
ICSM has to propose an updated version of scientific goals at the end of the current period in December 2020. The question stands: what comes next ? what evolution for 2030 horizon? A plan has been proposed by the direction of ICSM to the scientific council of December 5th, 2018 and this booklet is aimed in the present version to identify strengths and weaknesses of ICSM in order to participate in the effort *via* its 2021-2026 contractual goals of research in energy, using all facets of recycling.

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 (2017-2020)

TRIÉES PAR ANNÉE ET AXES DE RECHERCHE

2020

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LIST OF PATENTS

Patents 2020

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dépôt le 2020-12-02

- S. Pellet-Rostaing ; G. Mossand, A. Leydier, G. Arrachart « **Nouvelles résines formo-phénoliques, leur procédé de préparation et leur utilisation dans l'extraction de l'uranium de l'eau** »
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dépôt le 2018-11-20

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dépôt le 2017-08-07

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  dépôt le 2017

LISTE DES MEMBRES DU CONSEIL SCIENTIFIQUE DE L'ICSM 2018

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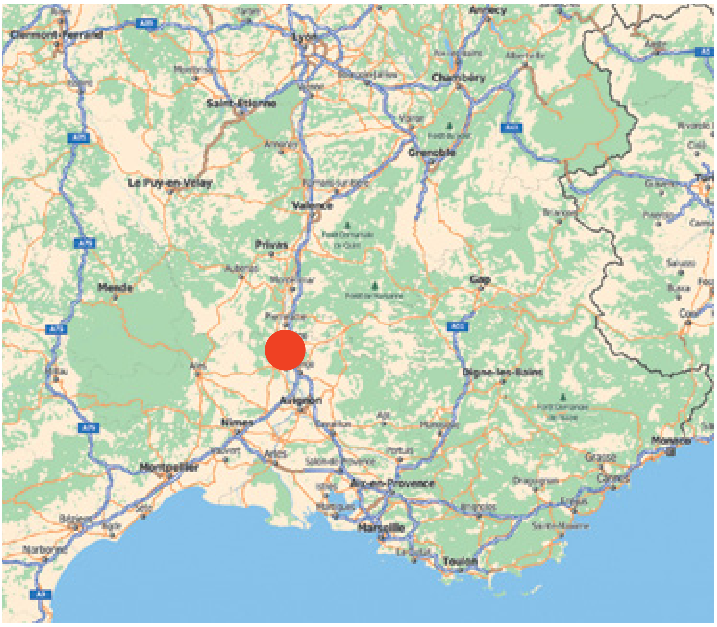
- **Depuis Marseille,** rejoindre l'A7, direction Lyon, sortie 21, Orange-centre. Continuer direction Caderousse (D17) puis direction Marcoule (D131a).

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

- **Depuis la gare TGV Avignon,** rejoindre la N100 en direction de Remoulins/Nîmes, puis prendre à droitela N580 en direction de Bagnols-sur-Cèze jusqu'à la traversée de L'Ardoise et prendre la direction de Marcoule sur la D138a.



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