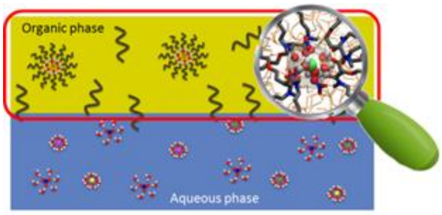
UMR 5257 CEA-CNRS-UM2-ENSCM

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

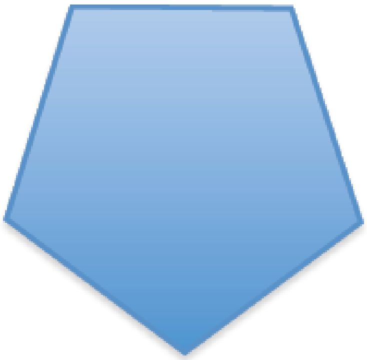
ICSM



Sélectivité par
auto-assemblage

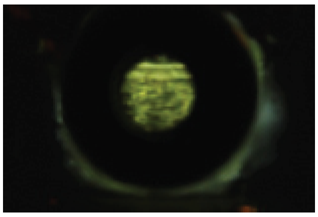
Comprendre la séparation

Optimiser la séparation

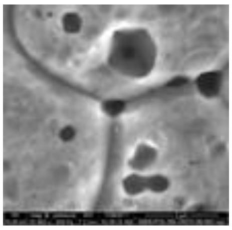


Chimie verte

Anticiper le cycle de vie

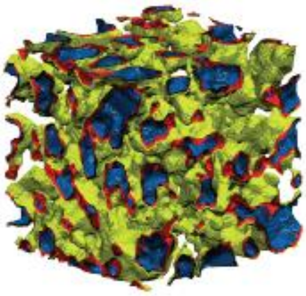


Sonoluminescence
de l'uranyle



Evolution des cristallites
et des joints de grain sous
stress chimique

Méthodes et théorie



Modèle de microémulsion pauvre en eau

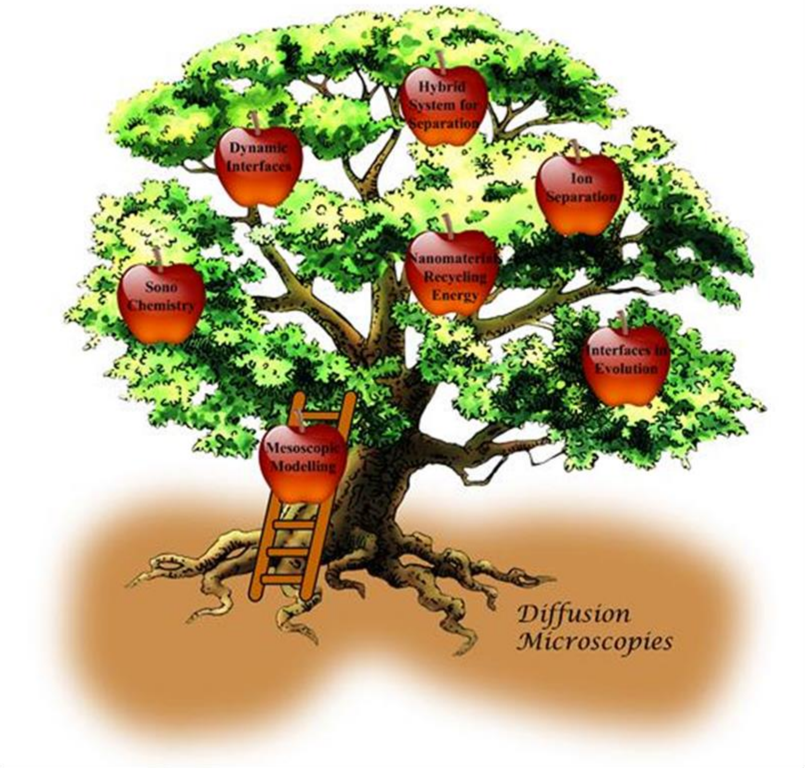
Institut de Chimie Séparative de Marcoule

SCIENTIFIC REPORT 2011 - 2014

Permanent staff at ICSM as in October 2014

Institut de Chimie Séparative de Marcoule

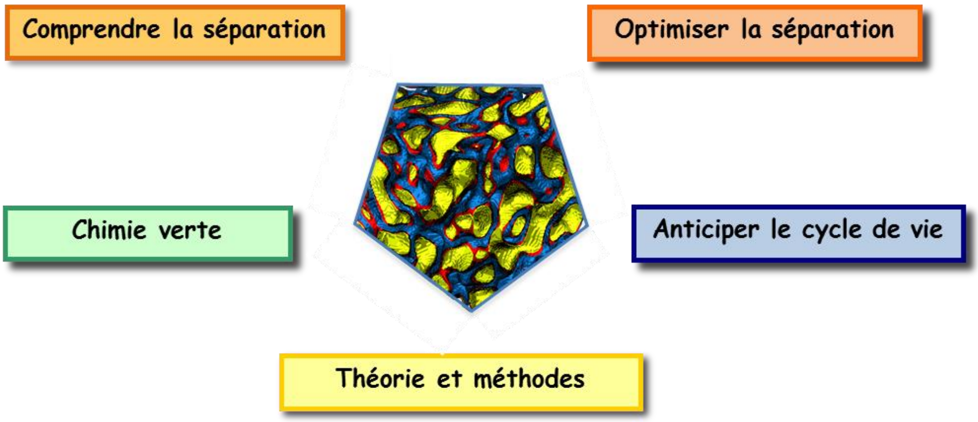
La raréfaction inéluctable des combustibles fossiles, l'impact négatif sur le climat et l'environnement de plus en plus inacceptable de la production d'énergie à partir de ces derniers, de nouvelles exigences en matière de sécurité des installations et de gestion de leurs déchets, la nécessité d'une production croissante d'eau douce dans de nombreuses régions,… confrontent les scientifiques à une demande sociétale forte pour des solutions pratiques et fiables en matière de technologies pour l'énergie. Avant la disponibilité espérée de l'énergie de fusion et en cohérence avec une nécessaire intensification, inscrite récemment dans la loi (13 juillet 2005), de l'utilisation des énergies renouvelables, un « nucléaire durable » -c'est-à-dire utilisant de manière optimale l'isotope 238 de l'uranium- ne se déclinera pas à partir de simples extrapolations de l'existant mais reposera sur des avancées en chimie séparative.



Dans le domaine des énergies alternatives, rendre celles-ci durables dans la même acception revient à fermer efficacement de la même manière les cycles des fluides et des matériaux d'usage dans les autres technologies de l'énergie. Dans un monde fini en ressources naturelles, fermer les cycles relève d'une démarche de tri sélectif, qui est au niveau du chimiste une séparation ionique, moléculaire ou colloïdale. Recycler les terres rares au lieu de les extraire du sol en sont un premier défi d'importance pour cette chimie qui relève des nanosciences, via les aspects colloïdaux qui sont au cœur de nombreux procédés.

Dans le but de développer la recherche fondamentale au service des « utopies nécessaires » de la chimie pour l'énergie, l'unité mixte CEA/CNRS/UM2/ENSCM et ses huit équipes se sont installés dans les laboratoires, opérationnels en 2010, pour y démarrer leurs travaux de recherche :

- *Matériaux hybrides pour la séparation (Daniel MEYER)*
- *Chimie des ions aux interfaces actives (Olivier DIAT)*
- *Tri ionique et isotopique par les systèmes moléculaires auto-assemblés (Stéphane PELLET-ROSTAING)*
- *Sonochimie dans des fluides complexes (Sergueï NIKITENKO)*
- *Nanomatériaux pour l'énergie et le recyclage (Xavier DESCHANELS)*
- *Surfaces de matériaux en évolution (Nicolas DACHEUX)*
- *Microscopies en mode environnementale (Renaud PODOR)*
- *Modélisation mésoscopique et chimie théorique (Jean-François DUFRECHE).*



Comprendre la séparation : il s'agit de caractériser du point de vue structural et thermodynamique les systèmes organisés fonctionnels qui permettent le tri ionique efficace par transfert aux interfaces en allant vers la prédictibilité des transferts entre phases associés, aussi bien dans le cas liquide-liquide que liquide-solide.

Optimiser la séparation : lorsqu'un système de transfert d'espèces pour le recyclage est compris et modélisé à l'échelle de la liaison ainsi qu'aux échelles supramoléculaire et mésoscopique, il faut imaginer, synthétiser, formuler et mettre en œuvre dans des dispositifs de recyclage les mélanges de molécules sélectionnés.

Chimie verte : il s'agit d'intégrer dans la chimie pour l'énergie autant que possible les douze principes de la chimie verte et les douze principes du « green engineering » dans la chimie du recyclage et de l'énergie durable car renouvelable. Un effort particulier est porté sur la sonochimie, science des réactions chimiques induites par les ultrasons.

Anticiper les cycles de vie : il s'agit d'observer dégradation et corrosion de surface qui dépendent -au-delà de leur simple composition- de la voie de synthèse. Ceci permettra d'adapter les matériaux et les fluides d'usage aux dispositifs de recyclage associés à leur cycle. Au-delà des matériaux d'usage, ceci s'applique aux combustibles ou aux matrices de stockage.

Théorie et méthodes d'observation : la quasi-totalité des méthodes de séparation ioniques ou moléculaires dépendent de systèmes auto-assemblés : il faut d'une part les observer en microscopie environnementale et d'autre part, dans l'espace réciproque via la diffusion de rayons X aux petits angles. La théorie doit permettre de modéliser toutes les séparations, notamment en assurant le couplage entre l'échelle supra-moléculaire et l'échelle mésoscopique.

L'**Institut de Chimie séparative de Marcoule**, créé sans murs en 2007, est dirigé par Stéphane Pellet-Rostaing depuis 2013. L'ICSM a été inauguré en juin 2009 et a ouvert ses laboratoires le 20 janvier 2010. Il est 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 « Che**MIS**yst » 2012 - 2020 sur la chimie des systèmes moléculaires et interfaciaux. L'ICSM est dimensionné pour accueillir en 2019 cinquante chercheurs permanents, cinquante non-permanents et une équipe de quatre techniciens ingénieurs exploitants. En octobre 2014, 45 chercheurs permanents sont affectés à l'UMR ICSM dans les huit équipes actives actuellement. Les propositions de stages au niveau master, post-doc et thèses sont accessibles sur le site **www.icsm.fr.**

Foreword

The joint research unit “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 has been inaugurated in June 2009, with laboratories opened in the fall 2009 and has obtained authorisation to start experiments including a few grams of depleted uranium and natural thorium in January 2010. Last take-off was from our theory group, who started in October 2009.

But the unit "Institut de Chimie Séparative de Marcoule" existed as a team scattered in several places in France since 2007. Scientific activity began in the fall of 2007 with progressive joining of ICSM of team leaders, co-workers, technicians and students, today with 45 permanent staff and 46 non-permanent scientists (post-docs and students). Also, about 20 master students join the nine teams for a few months every year.

Our practical summer school in Analytical and separation chemistry is held yearly for a full week including practical sessions since the first edition 2006 in Montpellier. The detailed program of these summer school are reproduced in the Annex, as well as the menu of the Thursday lectures in separation chemistry” Since 2012, the Practical summer school is in common with the associated teams within the Excellence laboratory “CheMISyst”, a project 2012 till 2020 devoted to chemistry using weak 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 allows to multiply existing resources in national independence, but will be based on new separation processes, that can be modelled using predictive theory. Understanding and optimizing separation in the nuclear fuel cycle is the central aim of the ICSM. Enlarging this central goal to the needs for chemistry of recycling, for instance, strategic metals crucial for alternative energy, is the natural extension surfaces of needs and development of science, with a srong link for technology and implementation with our 600 colleagues from R. Departments in Marcoule, as well as the chemists form the “Pôle de Chimie Balard du Languedoc-Roussillon”.

The report here gives an overview of the work published and submitted since January 2011. The eight active research teams still work in the direction of the scientific open questions as defined and published by the French academy in 20072. Separation chemistry, a branch of physical chemistry, is a key part of « green chemistry ». The science required is the emerging « Nanoscience », as defined by Bernard Bigot, then Haut-Commissaire à l’Energie Atomique at the launching of the ICSM as a project in July 2004.

TZemb

Stéphane Pellet-Rostaing
Marcoule, November 24, 2014

Thomas Zemb
Marcoule, November 24, 2014

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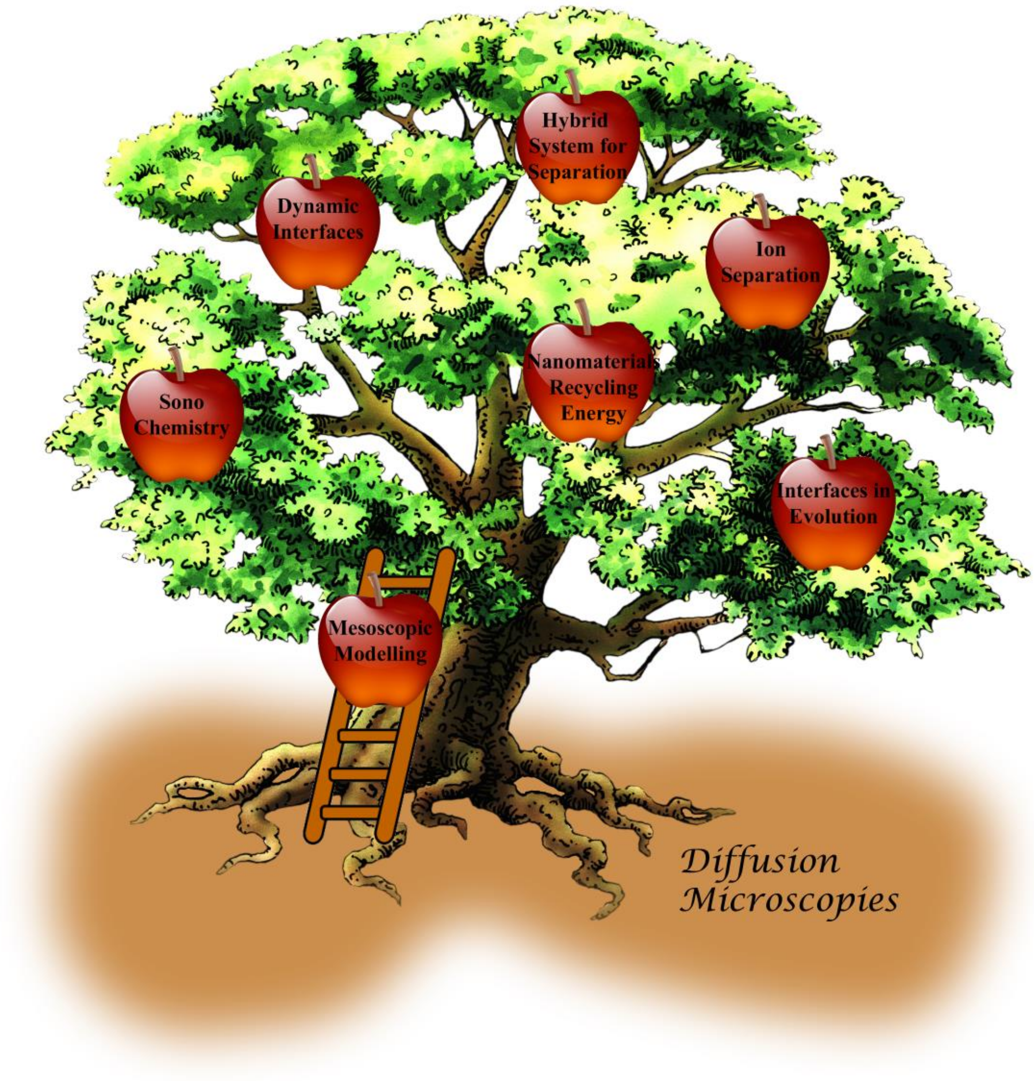
[1] « Long-range Interactions in Nanoscale science », R G French, V A Parsegian et al., Rev. Mod. Physics **82** n°2 (2010) pp. 1887-1944

[2] M. Leroy, M. H. Hengé-Napoli et Th. Zemb, « Complex fluids, divided solids and their interfaces : Open questions addressed at the ICSM for a sustainable nucelar energy » ; CRAS Chimie (2007) 10 , pp. 1042-1049


Hybrid System for Separation
Dynamic Interfaces
Ion Separation
Nanomaterials Recycling Energy
Sono Chemistry
Interfaces in Evolution
Mesoscopic Modelling
Diffusion Microscopies

Organigramme de l'ICSM

ICSM 2014 - Permanents

- **45 fin 2014**
- **dont : 15 CEA/DEN & 8 CEA/DSM**
- **12 CNRS, 7 UM2 & 3 ENSCM**

Direction ICSM

Statut	Nom	Partenaire
Directeur	PELLET-ROSTAING	CNRS
Directeur adj.	ZEMB	CEA/DSM
Adj. Directeur	ALPE-CONCHY	CEA/DEN
Assistante	MARTIN	CEA/DEN
Secrétariat/Gestion	MENASRIA	UM2
Gestionnaire	VIDAL	CNRS
Exploitation	GUILLOT	CEA/DEN
Exploitation	VARON	CEA/DEN
ISI	DIAS	CEA/DEN

Equ. 1 - LHYS

Statut	Nom	Partenaire
Chef d'équipe	MEYER	CEA/DEN
MDC	MAYNADIE	UM2
CR	BOURGEOIS	CNRS
Ingénieur	CARBONI	CEA/DSM

Equ. 2 – L2IA

Statut	Nom	Partenaire
Chef d'équipe	DIAT	CEA/DSM
Chercheur	BAUDUIN	CEA/DSM
MDC	GIRARD	ENSC
IR	JONCHERE	CNRS

Equ. 3 - LTSM

Statut	Nom	Partenaire
Chef d'équipe	PELLET-ROSTAING	CNRS
MDC	ARRACHART	UM2
Chercheur	DOURDAIN	CEA/DSM
Technicienne	DUBOIS	CEA/DEN

Equ. 4 - LSFC

Statut	Nom	Partenaire
Chef d'équipe	NIKITENKO	CNRS
CR	CHAVE	CNRS
Chercheur	PFLIEGER	CEA/DEN
Chercheur	VIROT	CEA/DEN

Equ. 5 - LNER

Statut	Nom	Partenaire
Chef d'équipe	DESCHANELS	CEA/DEN
Chercheur	CAUSSE	CEA/DEN
Chercheur	REBISCOUL	CEA/DEN
MDC	TOQUER	ENSCM
IE	REY	UM2

Equ. 6 - LIME

Statut	Nom	Partenaire
Chef d'équipe	DACHEUX	UM2
CR	CLAVIER	CNRS
Chercheur	SZENKNECT	CEA/DEN
CR	MESBAH	CNRS
MDC	CLAPAREDE	UM2

Equ. 7 – L2ME

Statut	Nom	Partenaire
Chef d'équipe	PODOR	CNRS
MDC	CAMBEDOUZOU	ENSCM
IE	LE GOFF	CNRS
IE	RAVAUX	CNRS
IE	MAYNADIE	CNRS
Ingénieur	BRAU	CEA/DEN
Ingénieur	ODORICO	CEA/DSM
Technicien	CORSO	CEA/DSM

Equ. 8 - LMCT

Statut	Nom	Partenaire
Chef d'équipe	DUFRECHE	UM2
Chercheur	DUVAIL	CEA/DSM
Chercheur	SIBOULET	CEA/DEN

ICSM 2014 – Non-Permanents

ICSM DIR

CDD Administratif

RUSSELLO Vainina 01/09/2014-31/08/2015

EQUIPE 1 LHYS

APPRENTI

SIMOES Alizée 01/09/2014-30/06/2016

CDD Ingénieur Technicien

AGOT Alexia 22/04/2014-21/10/2015
BANGOY Nathalie 10/06/2014-09/12/2015
PEREZ Emilie 09/12/2013-08/06/2015

DOCTORANT

BRAIBANT Bertrand 27/10/2014-26/10/2017
GOUDY Violaine 01/10/2012-24/10/2015
NAVARRO AMADOR Ricardo 03/11/2014-02/11/2017
RUFFRAY Kevin 24/10/2012-15/10/2015

POST-DOCTORANT

MERCEILLE Aurelie 08/11/2013-07/11/2014

EQUIPE 2 L2IA

ATER

GASSIN Pierre Marie 01/09/2013-31/08/2014

CDD Ingénieur de recherche

FADEL Ophélie 12/11/2014-11/11/2015

POST-DOCTORANT

DEDOVETS Dmytro 12/03/2014-11/03/2015
EL OUAZZANI Hasnaa 06/06/2014-18/05/2015
NASKAR Bappaditya 20/09/2013-31/12/2014
LAI Jonathan 01/02/2012-07/03/2014
SINHA Prashant 15/11/2013-23/05/2014

CEA
CNRS
UM ENSCM
Partis

EQUIPE 3 LTSM

CDD Chercheur

TURGIS Raphael 16/06/2014-15/12/2015

DOCTORANT

ARRAMBIDE CRUZ Carlos 01/10/2014-30/09/2017
BESNARD Romain 24/10/2012-01/10/2015
GUILLOT Marie 01/02/2012-31/01/2015
REY Julien 04/11/2013-03/11/2016
SUKHBAATAR Tamir 07/11/2014-06/11/2017
WEHBIE Moheddine 01/06/2013-31/05/2016
LOPIAN Tobias 01/12/2014-30/11/2017

INTERIM

LEYDIER Antoine 21/01/2013-18/07/2014

POST-DOCTORANT

MARY Fanny 10/05/2012-10/05/2014

EQUIPE 4 LSFC

DOCTORANT

DALODIERE Elodie 22/10/2014-21/10/2017
OUERHANI Temim 01/11/2013-31/10/2016

POST-DOCTORANT

MOROSINI Vincent 29/5/2012-28/05/2014

ICSM LNER

APPRENTI

BEX Arnaud 01/09/2012-31/08/2014

DOCTORANT

COULIBALY Moustapha 05/11/2012-04/11/2015
LOU Yu 11/10/2013-10/10/2016
MANSAS Clémentine 03/11/2014-02/11/2017
SHEHAYEB Sanaa 15/01/2015-11/11/2017
SARAVIA Alvaro 06/03/2012-05/03/2015
CHARLOT Aude 15/03/2011-14/03/2014
GOSSARD Alban 03/11/2011-02/11/2014

INTERIM

TALHA Najat 12/05/2014-07/05/2015

POST-DOCTORANT

SOMMER Alicia 12/11/2013-11/05/2015
MOLONEY Micheál 01/10/2013-31/05/2014

EQUIPE 6 LIME

APPRENTI

HIDALGO Julia 25/09/2014-24/09/2015

ATER

CLAPAREDE Laurent 01/09/2013-31/08/2014

DOCTORANT

CORDARA Théo 04/11/2014-03/11/2017
GAUSSE Clémence 04/11/2013-03/11/2016
MARTINEZ Julien 03/10/2011-31/12/2014
TOCINO Florent 01/10/2012-14/10/2015

EQUIPE 7 L2ME

APPRENTI

SALACROUP Yohann 15/10/2012-14/10/2014

DOCTORANT

GOUZE Benoit 15/01/2013-15/01/2016
NARDIN Thibaud 05/11/2012-05/11/2015
NKOU BOUALA Galy 04/11/2013-03/11/2016

POST-DOCTORANT

NICOLE Jimmy 13/03/2012-12/03/2014

EQUIPE 8 LMCT

DOCTORANT

HOCINE-METAHRI Sarah 01/10/2014-30/09/2017
NGUYEN Thanh Nghi 19/10/2012-18/10/2015
VILLARD Arnaud 01/10/2012-30/09/2015

POST-DOCTORANT

CHEN Yushu 10/10/2013-30/09/2015

ICSM ERC

CDD Administratif

LEPROU-TACONET Aline 01/09/2014-31/03/2016

CONSEILLER SCIENTIFIQUE

MÖHWALD Helmut 01/02/2014-01/02/2015

POST-DOCTORANTS

THEISEN Johannes 16/09/2013-30/09/2015
SYLL Ousmane 06/02/2014-30/06/2015

Non Permanents ICSM par équipe - 2014

Organisation of the quadriennal report 2011-2014 of ICSM

The report is organized by scientific topics: each of the eight active research groups gathers a community of researchers and engineers from different expertises, who publish in various domains in the corresponding journals, and who participate at different international meetings.

However, a large fraction of crucial results are obtained and published in common between teams within ICSM, via collaborations associating theoretical and preactical expertise from different teams.

A large fraction with our international contractual partners: ITU Karlsruhe, MPI Potsdam within the Laboratoire Européen Associé LEA “SONO” (2008-2014) and our partners from Jühlich.

Five focussed objectives of the research actions undertaken guide the choice of financially supported priorities within the large autonomy of creative chemists working at ICSM:

Understand Separation	**Understand** chemical mechanisms underlying processes of chemical **separation**
Optimize Separation	**Optimize** known methods for **separation**, in order to imagine, propose and test new separation methods, including supramolecular systems.
Anticipate life-cycle	**Anticipate** the **life-cycle** of materials used in the context of nuclear and alternative energy productions
Green Chemistry	Develop **“Green Chemistry”** in all its facets, including sonochemistry.
Methods and theory	Develop T**heory**, with special attention to mesoscopic modelling, a well as develop M**ethods** of characterisation of fluid and solid samples: small angle scattering as well as environmental electronic microscopy.

Coloured rectangles appearing on each page of report identify the objectives related to each scientific theme. The research objectives spread from science directly related to nuclear energy and to non nuclear recycling and material chemistry, with a large part of research with “dual” interest. At the end of the booklet, references directly relevant to nuclear and non nuclear are given.

Liste des fiches-actions par objectif

Understand Separation - Comprendre la séparation

Optimize Separation - Optimiser la séparation

Anticipate life-cycle - Anticiper le cycle de vie des matériaux

Page

Methods and Theory - Méthodologies et théories de la chimie séparative

Page

Green Chemistry - Chimie Verte

Page

Origine géographique du personnel de l'ICSM

Les Missions Scientifiques contractuelles de l'ICSM (2014-2018)

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 2 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 4$^{\text{ème}}$ 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 son environnement proche et lointain 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 principalement 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.

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'électro-nucléaire, c'est-à-dire comprenant aussi les énergies alternatives.

Thématique 4 - Sonochimie dans des Fluides Complexes (LSFC)

L'origine des effets chimiques des ultrasons (sonochimie) est la cavitation acoustique : nucléation, croissance et implosion de bulles de gaz 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 pressions extrêmes (formation d'un plasma hors équilibre). Ce confinement inertiel dans des fluides peut favoriser des réactions chimiques mais également une émission de lumière, connue comme 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. Ces études ont pour but de mieux comprendre les mécanismes des réactions sonochimiques afin d'optimiser les conditions opératoires, par exemple pour maximiser la production de radicaux et d'espèces excitées.

Chaque bulle de cavitation peut être considérée comme un microréacteur à haute température qui ne nécessite pas l'addition de réactifs spécifiques et ne génère pas de déchets supplémentaires, respectant ainsi les principes de la chimie "verte". L'industrie nucléaire du futur pourrait avoir besoin de cette chimie non productrice de déchets pour développer de nouvelles voies de dissolution, de décontamination ou de traitements de déchets secondaires liés au cycle des nouveaux combustibles. De plus, l'activation des surfaces solides sous irradiation ultrasonore présente beaucoup d'intérêt dans le domaine non-nucléaire lié au développement d'approches innovantes de recyclage des métaux stratégiques.

Une des potentialités de la sonochimie réside en la synthèse de matériaux monodispersés 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 cycles de vie très courts des bulles, 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 l'activation des nanoparticules à l'interface bulle/solution.

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.

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. 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 est 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. Dans le futur, cette stratégie sera particulièrement approfondie pour l'extraction liquide/liquide, pour les phases aqueuses et organiques. 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.

1 – Hybrid Materials for Separation

Personnels actuels de l'équipe

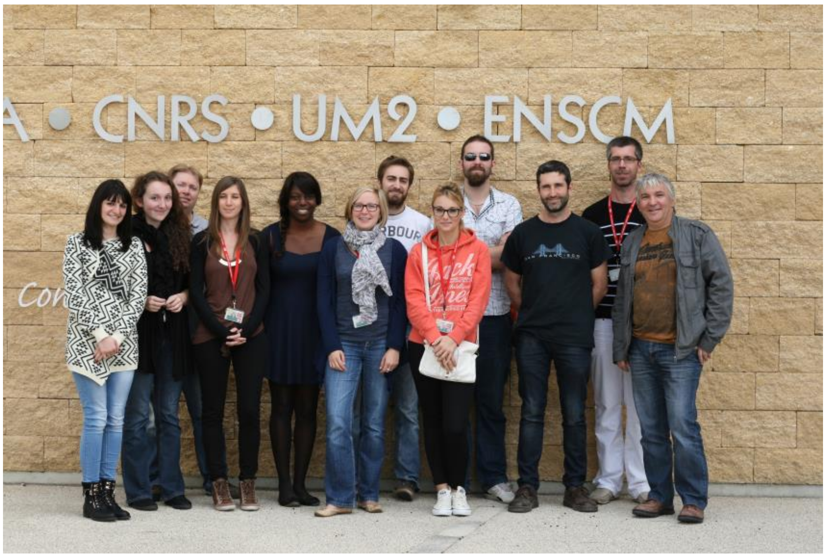
Chercheurs permanents :
Dr. D. Meyer - Responsable équipe CEA/DEN (2007-)
Dr. D. Bourgeois - Chercheur CNRS (2009-)
Dr J. Maynadié - Enseignant-Chercheur UM2 (2009-)
Dr M. Carboni - Chercheur CEA/DSM (2014-)

Post-doctorants :
Dr. A. Merceille (2013-2014) – Etude toxicologique de l'uranium dans les os

Doctorants :
R. Poirot (2011-2014) – Extraction du palladium par un malonamide : comportement et spécificités par rapport aux lanthanides
V. Goudy (2012-) – Synthèse, caractérisation et réactivité de composés moléculaires polymétalliques pour la photochimie et les transferts de charge
K. Ruffray (2012-) – Synthèse et caractérisation de précurseurs polymetalliques type polymères de coordination pour le contrôle des propriétés de matériaux

Ingénieur d'étude :
N. Bangoy (2014-) – Projet VALORCO, réduction des émissions de CO_2

Technicien supérieur :
E. Perez (2014-) – Recyclage de batteries Li-ion
A. Agot (2014-) - Projet ANR GTM, optimisation des catalyseurs de voiture par la Gestion thermique via les Matériaux



Le cadre général de la recherche prévue au laboratoire (initialement LCPA) depuis sa création jusqu'en 2012 était celui de la compréhension fondamentale de la chimie et de la physico-chimie des actinides qui occupent une position particulière dans le tableau périodique.
Depuis 2012, le laboratoire a recentré ses activités de recherche sur le développement et l'étude de liquides complexes et de solides hybrides dans le cadre de la chimie séparative, des matériaux innovants et du stockage de l'énergie. Cette mutation thématique s'est accompagnée d'un changement de nom de l'équipe qui s'appellera Laboratoire des systèmes HYbrides pour la Séparation (LHYS) dès janvier 2015.

En dehors du projet sur les composés moléculaires bimétalliques U/Th - élément-d, les activités de recherche sur les actinides, propres au LCPA, se termineront en 2015. Après 2015, les activités du LHYS sur les actinides se feront essentiellement sur la base de collaborations avec des équipes du CEA ou d'autres organismes (Universités,…). En interne ICSM, le LHYS continuera à développer des précurseurs soit moléculaires ou hybrides (polymère organométallique, polymère de coordination, …) pour la synthèse de matériaux type céramique ou métallique à base d'actinides en collaboration avec le LIME et le L2ME.
Dans chacun des domaines, si les études menées sont en général fondamentales, certaines actions en cours de réalisation le sont avec un objectif clairement appliqué.

Ainsi les thématiques de l'équipe sont les suivantes :
- Matériaux :
    - Polymères de coordination comme précurseur de matériaux « durs »
    - Polymères de coordination pour l'énergie
    - Matériaux biomimétiques de l'os pour des études de toxicologie des métaux
- Séparation des métaux par voie hydrométallurgique
    - Influence des interactions faibles et de la topologie moléculaire en séparation liquide-liquide
    - Séparation par métallo-assemblage vers des produits finis à haute valeur ajoutée
    - Recyclage des métaux stratégiques (liquide-liquide, précipitation)

Matériaux et composés moléculaires

Polymère de coordination

Le LHYS s'intéresse aux polymères de coordination en tant que précurseurs de matériaux comme les oxydes ou les carbures, et en tant que matériaux pour l'énergie (photo-physique, électrochimie et catalyse). Plus particulièrement, l'équipe développe des linkers (ligands bi ou polytopiques) pour synthétiser des polymères de coordination bi- ou polymétalliques à base d'éléments de transition d et f (lanthanides, métaux d).
Comme précurseurs de matériaux, l'objectif est de transférer des structures, compositions, microstructures et morphologies obtenues avec des polymères de coordinations vers des matériaux obtenus à haute température comme les céramiques.
Pour l'énergie, l'objectif est double.
- Premièrement nous visons à développer un moteur photo-physique de séparation de charge permettant la réduction du CO_2 ou de l'eau par le couplage d'un centre photo-actif (Ru, Ir) et d'un catalyseur dans une matrice hybride 3D. Un système mixte contenant un photosensibilisateur à base de Ru et un métal d liés entre eux par un ligand de type polyaromatique a été développé. Dans un premier temps, des ligands et des molécules mono- et bimétalliques ont été synthétisés et caractérisés (spectroscopie, temps de vie,…). Ces systèmes seront dans un deuxième temps intégrés dans un solide moléculaire type polymère de coordination. L'objectif est de comprendre le transfert intramoléculaire d'un photoélectron lorsqu'on passe d'un système moléculaire vers un système polymérique tridimensionnel équivalent. Cette étude s'effectue en collaboration avec le Laboratoire de Chimie des Processus Biologiques du Collège de France dirigé par Marc Fontecave, spécialisé dans les systèmes de photosynthèse artificielle. Un intérêt particulier sera également porté aux propriétés électrochimiques de ces composés.

- Deuxièmement, nous souhaitons mettre en forme des polymères de coordination sous forme de couches très minces à l'interface de matériaux type ITO, FTO afin d'utiliser les photoélectrons générés dans un circuit électrochimique.

Matériaux biomimétiques : Lamelles osseuses

Afin de comprendre la façon dont l'uranium s'intègre dans le tissu osseux et dont il peut éventuellement s'en extraire, tout en se passant d'expérimentation animale, une approche mettant en œuvre des systèmes d'os synthétiques a été développée en collaboration avec le CEA/DSV, KIT-INE (Karlsruhe), l'INSERM de Lyon et l'Université de Nice (Biologie et radiochimie). Différentes méthodes de synthèses ont été développées et ont conduit à l'obtention de différents types de composés synthétiques. Ces composés ont été caractérisés et leur compatibilité avec la croissance de cellules osseuses (ostéoblastes) a été validée. Cette approche permet ainsi d'obtenir un matériau biomimétique contenant une quantité d'uranium contrôlée et d'étudier au niveau chimique, biochimique et cellulaire un système représentatif contenant de l'uranium dans un processus biologique soit d'insertion, soit de décorporation d'uranium du tissu osseux.

Nanoparticules

Après une première collaboration entre l'ITU et l'ICSM qui a permis de mettre au point une approche combinée supramoléculaire et plasma pour l'obtention de couches de nanoparticules d'oxydes d'actinides sur substrats, la synthèse de nanocristaux d'oxydes d'actinides a été mise au point. Ces études réalisées au JRC-ITU (Karlsruhe Allemagne) sur U, Th, Np et Pu seuls et sur des oxydes mixtes U/Th. Ces études ont montré une très grande différence de réactivité et de morphologie entre le système U et le système Th. Le système U/Th mixte a permis d'obtenir des morphologies intermédiaires ente celles obtenues avec de l'U pur et de Th pur. Les nanoparticules de Np sont proches de celles obtenues avec de l'U. Les nanoparticules de Pu montrent un comportement propre. Dans tous les cas, les tailles sont de quelques nanomètres et montrent une très faible dispersion. Les nanoparticules obtenues sont stables et ne s'agglomèrent pas en raison d'une couche organique en surface. Cette activité a pris fin en 2014.

Séparation des métaux par voie hydrométallurgique

Ces études se placent dans le contexte de la détermination des forces fondamentales qui régissent la séparation de métaux soit par précipitation soit par voie liquide-liquide, avec comme vision l'amélioration et/ou le développement de procédés de séparation pour le recyclage. Il est ainsi primordial de comprendre l'origine de la stabilité d'une phase organique contenant des ions métalliques, un système moléculaire extractant et un solvant. Dans le cadre de la compréhension du rôle des interactions faibles dans un processus de solubilisation d'éléments métalliques dans une phase organique complexe, le LHYS a développé deux approches :

Systèmes moléculaires fluorés

Cette étude s'intéresse plus spécifiquement au rôle des interactions de polarisation ainsi que d'entropie interne dans une phase solvant-extractant-métal par substitution d'une partie hydrogénée de l'extractant de type amphiphile, par une partie fluorée tout en gardant le volume moléculaire et la partie polaire constante. Afin de maitriser la topologie moléculaire de l'extractant modifié, des études via différentes approches synthétiques ont été nécessaires pour accéder à des amphiphiles fluorés type diamides, phosphonates, phosphates, mono ou bi caténaires. D'un point de vue application, ces systèmes fluorés peuvent être mis en œuvre dans des systèmes triphasés ou encore en milieu CO_2 supercritique.

Métaux critiques (métaux nobles, terres rares…)

Dans certains procédés étudiés dans le cadre du retraitement du combustible irradié, il a été observé une séparation entre des lanthanides légers et des lanthanides lourds en même temps qu'une co-extraction d'éléments tels que le Pd, le Mo ou le Zr. Une approche alternative à l'étude classique centrée sur les lanthanides consiste à déterminer pourquoi deux éléments ayant des propriétés chimiques très différentes tels que les lanthanides légers et le Pd se comportent de façon similaire en extraction alors que des éléments ayant une chimie proche, les lanthanides légers et lourds, se comportent de façon différente toujours pour un même systeme extractant. Dans ce contexte, le comportement du Pd lors d'une solubilisation, soit via une solution aqueuse ou via un système solide, a été étudié par rapport aux lanthanides.

Précipitation par métallo-assemblage

Ces études s'intéressent au développement d'une approche de séparation des métaux par auto-assemblage spécifique entre un métal et une ou des molécules organiques bi ou polytopiques. Le développement des architectures moléculaires sera partagé avec celui de la partie polymère de coordination. L'idée est de séparer des métaux sur la base de leurs propriétés de coordination (géométrie et transfert de charge) et de s'affranchir de la partie électrostatique et de polarisation du modèle DLVO.

Recherche appliquée

Gestion Thermique des Moteurs par le carbure de silicium (2014-2015)

Cette étude s'intéresse à l'application de la recherche sur le contrôle des matériaux type carbure, par voie moléculaire, dans le domaine des catalyseurs de véhicule à moteur thermique. L'objectif est de créer sur un support (cordiérite) de catalyseur de voiture un réservoir thermique qui empêche les fluctuations de température au niveau des sites réactifs du catalyseur.

Valorisation CO_2 issu de la métallurgie (2014-2016)

Ces études s'inscrivent dans le cadre de la valorisation du CO_2 produit par l'industrie métallurgique. Le procédé de référence est la carbonatation de roches type silicate de magnésium (olivine). Les produits de départ contiennent du fer, nickel et chrome qu'il faut extraire et séparer pour obtenir un carbonate de magnésium pur et valoriser les autres métaux séparés.

Recyclage batteries (2013-2015)

Cette action est une collaboration bilatérale avec VEOLIA/SARPI sur le recyclage des batteries de véhicule électrique. L'objectif est de recycler le maximum de masse (à minima 50%) d'une batterie de véhicule électrique. Ces études s'intéressent essentiellement à la mise en solution et la séparation des métaux d'intérêt.

From coordination polymers to doped rare-earth oxides

T. Demars, J. Maynadié, J. Ravaux, R. Podor, C. Genre,
N. Vigier, D. Meyer

Rare-earth mixed oxides are attractive compounds in a number of technological areas, such as catalysts for various organic reactions, thermal barrier coating materials or components in fuel cells. Doped ceria, for example, are of considerable interest as solid oxide fuel cell (SOFC) anodes and electrolytes, because of their high ionic conductivity. They are also choice components for molecular electronics. Other *f*-metal oxides, namely actinide oxides, are currently used as fuels in nuclear plants and are considered promising materials for new fuels in the fourth generation of nuclear power reactors.

We have developed a synthesis route towards *f*-elements oxides, based on thermal conversion of coordination polymers of controlled structure and morphology.[1] In a first step, mixed metal coordination polymers are prepared as solid solutions. Synthesis by auto-assembly of metal ions and ligand 2,5-dihydroxy-1,4-benzoquinone (DHBQ) leads to mixed coordination polymers. Two ways were developed, an aqueous way and an anhydrous one, leading to species with different structure. In both ways, the proportions of the different metals in the CPs are equal to the proportions of the metal ions introduced in the starting synthesis mixture. Mixed Ln(III)/Ln(III), Ln(III)/Th(IV), Ln(III)/U(IV) and Th(IV)/U(IV) with controlled composition were easily obtained, and powder PXRD measurements proved they are indeed solid solutions.

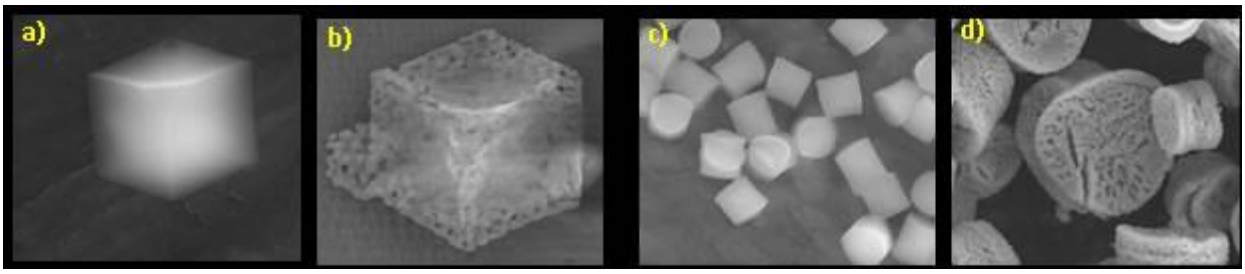


Figure 1: a) and b): a micrometric cube of the coordination polymer $Nd_2(DHBQ)_3.24H_2O$: before and after 900°C heat treatment ; c) and d): a micrometric cylinder of the same compound before and after 900°C heat treatment. The morphology of the mesocrystal is retained upon calcination and conversion to Nd_2O_3.

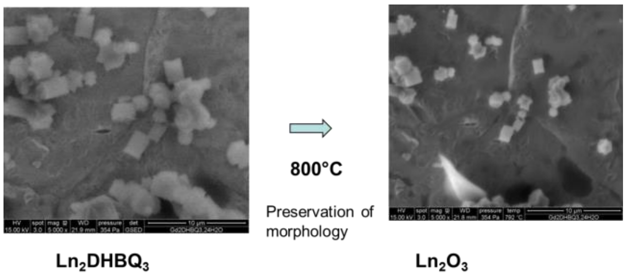


Figure 2: preservation of the morphology during thermal conversion

In a second step, the CPs were heated under air at 900°C and converted to mixed Ln/Ln, Ln/Th, Ln/U and Th/U oxides as solid solutions of controlled composition. We observed that the morphology of the starting PCs is retained upon heating (see Fig. 1), allowing synthesis of mixed oxides with easily tailorable morphology. It is thus possible, through a careful choice of ligands, to transfer control over the composition and morphology of coordination polymers to hard inorganic materials.

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[1], « **From coordination polymers to doped Rare-Earth oxide** », T. Demars, M. Boltoeva, N. Vigier, J. Ravaux, J. Maynadié, C. Genre, D. Meyer, *Eur. J. Inorg. Chem.*, **2012**, 3875-3884

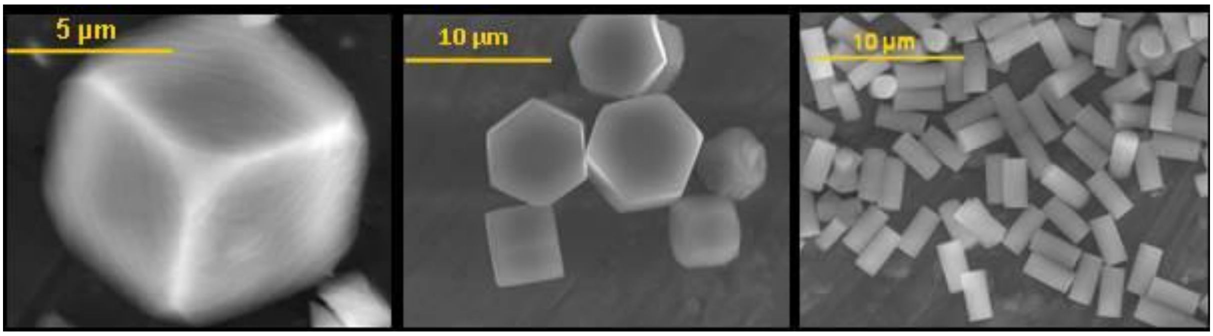
Rare-earth coordination polymers with controlled morphology

T. Demars, J. Ravaux, R. Podor, C. Genre, D. Meyer
T. Sievers, (MPI-Potsdam - Germany)

Metal-organic coordination polymers (CPs) have been subjected to intense scrutiny due both to the diversity of their structures and to their huge potentiality as functional molecular materials for a variety of applications including gas storage, separation chemistry, catalysis, drug delivery, sensors, optical and magnetic devices among. Coordination polymers properties can be highly dependent on crystal and control of particle growth is therefore an important challenge for the design of functional CP-based materials. Thus far, attention has been primarily focused on macro-scale crystalline samples of CPs typically obtained by solvothermal or self-assembly methods. A few reports were devoted to the synthesis of micro- or nano-sized CPs crystals of controlled size and shape, but understanding the growth mechanism of these objects remains a challenge.

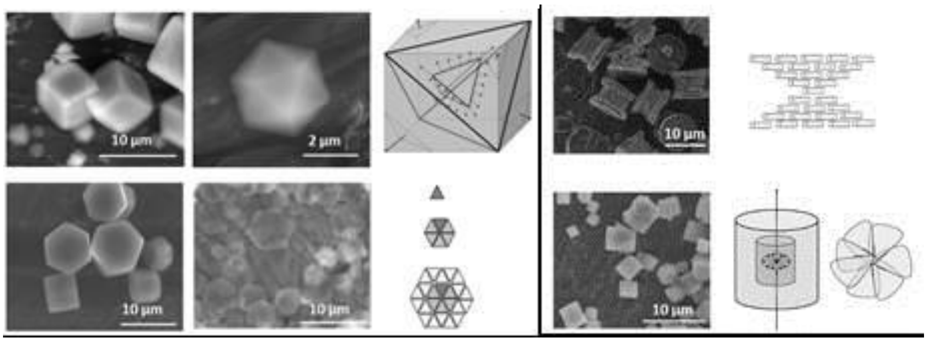
We were able to synthesize well-defined homogenous mesocrystals of the metal-organic framework $[Nd_2(DHBQ)_3(H_2O)_6]\cdot 18H_2O$ by direct precipitation. Mesocrystals with cylindrical, hexagonal, cubic and truncated octahedral shape and tunable size can be obtained easily and with good yields[1] (see pictures). Their morphology can be easily tailored through control of experimental conditions such as solvent, temperature, reactants concentration and reactants addition speed.

The mesocrystals are built from aggregated nano-scale crystalline particles, which assemble differently when the experimental conditions are modified.



Different shapes of coordination polymers obtained by kinetic controlled synthesis.

The study of these objects provides most valuable insight in the understanding of mesocrystals growth mechanisms. The influence of experimental parameters such as temperature, concentration, polarity of the solvent on the growth, nucleation and aggregation of these particles is under investigation.



Shapes and underlying symmetries

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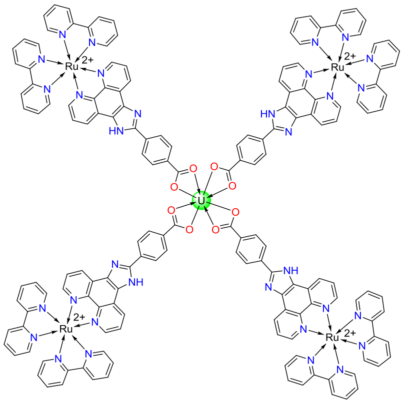
[1] “**Vapour pressure dependence and thermodynamics of cylindrical metal–organic framework mesoparticles: an ESEM study**”, T. Sievers, C. Genre, F. Bonnefond, T. Demars, J. Ravaux, D. Meyer and R. Podor, Phys. Chem. Chem. Phys., **2013**, 15, 16160-16166.

d-f Heterometallic precursors

K. Ruffray, V. Broha, J. Maynadié, X. Le Goff, D. Meyer.

This project, focused on the synthesis of d-f heterometallic materials precursors, is based on two different approaches: supramolecular precursor's thermic conversion, and coordination polymers thermic conversion.

The first approach is a molecular pathway. 1 Ruthenium complexes, initially studied for their photo-induced electronic transfer properties, were adapted to form heterometallic compounds, by adding a carboxylic acid functional group to the ligand to bind an f-element. Once synthesized, those compounds were characterized (NMR, UV-vis. and IR spectroscopy, electrochemistry), and photo-physical properties, like emission and excited state life-time, were investigated. Thermic conversion of these supramolecular precursors, depending on applied parameters, would lead to obtain d-f heterometallic oxides or carbides.



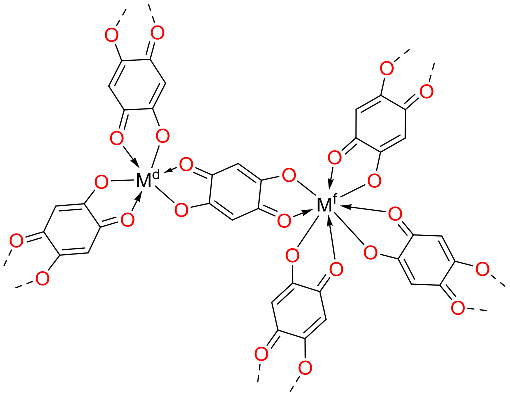
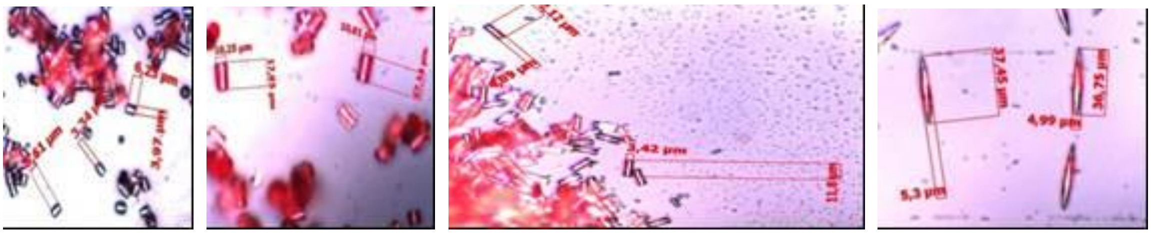


Figure 1 (left): Supramolecular precursor of d-element f-element material
Figure 2 (right): Coordination polymer of DHBQ precursor of an M^d-M^f material
(M^d = Fe, Mo, Ru, Rh, Ni, Pd, Pt ; M^f = Ce, Pr, Nd, Th)

The second approach is an auto-assembly pathway.2 It implies coordination polymers based on 2, 5-dihydroxy-1,4-benzoquinone (DHBQ), already known for f-f or d-d materials. Looking to insert a d-element in the f-metal polymer network, we would obtain a material precursor for d-f heterometallic mixed oxides. Studies on the morphology modification of the objects, along with d-element inside the material, have been started and partially done.



*Figures 2: Images obtained from optical microscopy of cerium polymers obtained with 0% (4*6 µm cylinders), 10% (10*18 µm cylinders), 20% (4*12 µm cylinders) and 40 % (4*37 µm toothpicks) of nickel.*

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[1] **Activation intramoléculaire photo-induite de complexes de métaux f par un photo-sensibilisateur**, K. Ruffray GECOM-CONCOORD 2014, Vers (France).

[2] **Étude des propriétés physico-chimiques des polymères de coordination de la famille des quinones**, V. Broha, Stage Master II CSMP 2014.

Molecules and coordination polymers: Photophysical properties

V. Goudy, J. Maynadié, C. Genre, D. Meyer
*C. Mellot-Draznieck*s*, M. Fontecave (Collège de France)*

Main aims of these studies are to dermine and compare charge transfer and charge separation induced by light irradiation, between a molecular species and the related 3d coordination polymer. It is expected an improvement of the photophysical yield when going from molecule to condensed matter.

As a first step we have developped molecular bimetallic species containing a photosensitive element (Ru or Ir) and a catalyst (d-element) to get the photophysical (spectra, lifetime,…) and electrochemical properties. Several systems containing Ru and Ru-Co were synthetised and some basic characteristics (NMR, UV-Vis, voltammograms,…) were collected 1,2. These bimetallic species are constructed in order to be used as precursor of high ordered matter. The organic bitopic ligand developped for this project has shown a delocalised electronic pi-system based on nitrogen containing aromatic rings (figure 1,2).

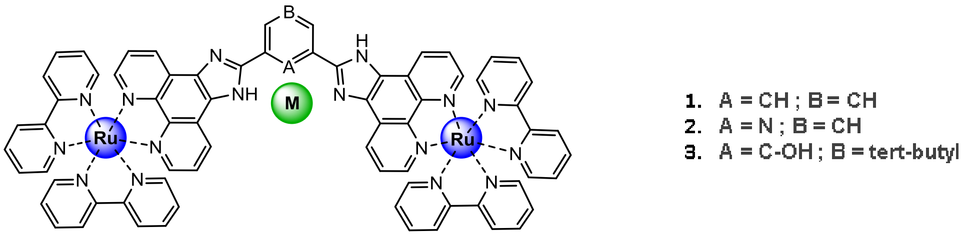

Figure 1: Bimetallic molecular photosystems containing d-elements.M is the catalyst.

A second step will be the transposition in a 2D or 3D molecular hybrid network of the molecular building unit previously developed (figure 2).

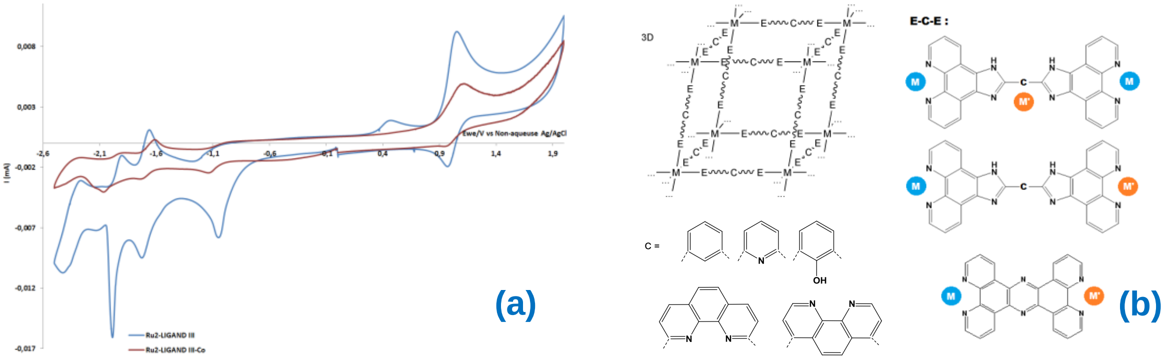

Figure 2: (a) Cyclic voltammograms of Ru(bpy)$_2$(Ligand 3) (blue) and Ru(bpy)$_2$(Ligand 3)-Co(red) in acetonitrile. (b) Schematic view of a n dimensional molecular network: E-C-E is the organic unit, M and M' the metallic elements.

The comparison of the photophysical properties and the electrochemical behavior between the molecules and the molecular network will highlight the cooperative effect when going from single ordered system to a high ordered system.

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[1] Goudy V. « **Synthèse et caractérisation de composés moléculaires pour la photochimie et les transferts de charge »-** Stage Master II CSMP 2012

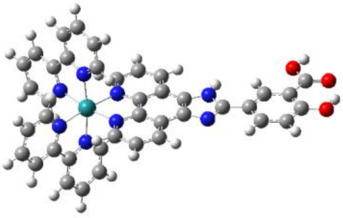
[2] Goudy V. « **Synthèse, caractérisation et réactivité de composés moléculaires polymétalliques pour la photochimie et les transferts de charge »-** Oral GECOM-CONCORD – 18 au 23 Mai 2014

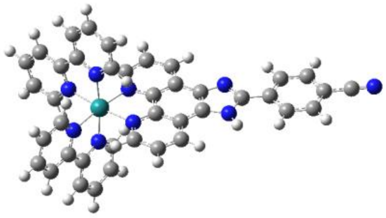
Molecular modelling of photophysical properties

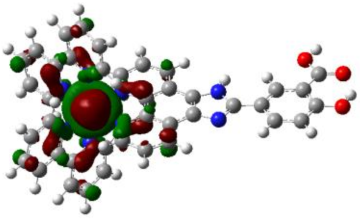
X. Le Goff, V. Goudy, J. Maynadié, D. Meyer

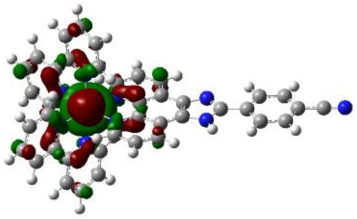
In order to understand the relation between a molecular structure and the photophysical properties of molecular species such as transition metal complexes with a photosensitizer and a catalyst, we have started theoretical studies based on TD DFT approaches.[1]

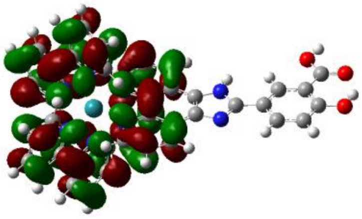
Main goal is to get a correlation between the structure of an organic linker in a bimetallic molecular species and the lifetime of the excited state.

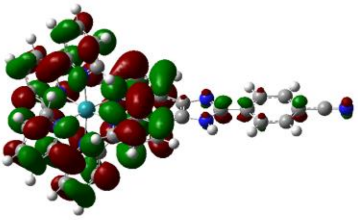

Complexe A


Complexe B

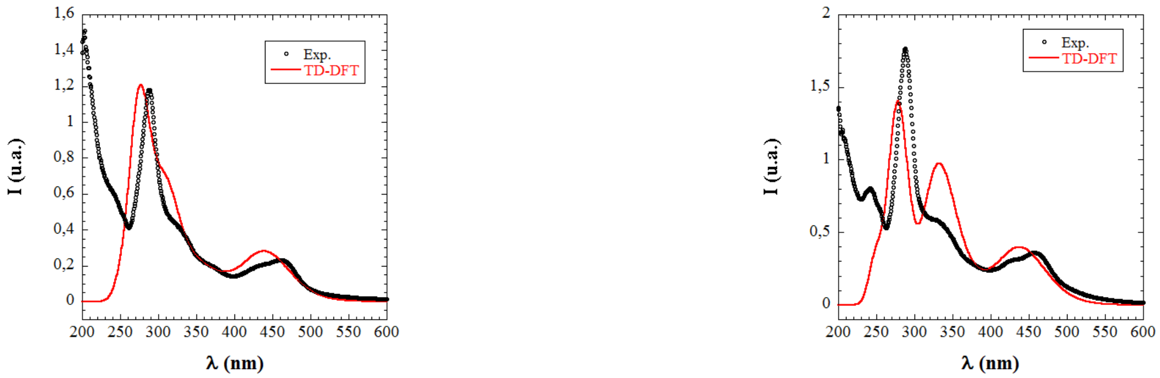

HOMO A


HOMO B


LUMO A


LUMO B

TD-DFT calculation (B3LYP base LANL2DZ)



Comparison experimental and theoretical absorption spectras for complex A and B

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[1] New activity of the LHYS collaboration with LM2E

Light-harvesting hybrid devices for the Photoproduction of chemical energy

R. Navarro, M. Carboni, D. Meyer

The sustainable production and storage of energy is one of the most important scientific and technological challenges facing humanities resources. For that matter, light-driven photochemical reactions, such as water splitting and CO2 reduction with water, can transform sunlight energy into chemical energy. Designing an efficient material that features molecular functional components for light harvesting and catalysis can address the challenges of the field and create a technology breakthrough to convert sunlight into solar fuels, i.e. an alternative energy to battery interesting for its easy storage.

Inorganic-organic hybrid materials (Known as MOFs for Metal-Organic Frameworks) are a class of hybrid materials built from metal ions or clusters bridged by organic linkers with a particular high porosity, stability, and easy tunability. These materials were proven of great interest for diverse applications and particularly for light-harvesting materials. First results are promising and research on this field highly active. However, the use of a solid support is the only chance for these materials to go into further industrial development.

Our interest is to develop a Layer-by-Layer approach for the assembly of a MOF with multiple redox-active and/or chromophoric sites on transparent conductive surface to create a functional device. We do believe that this strategy provides a simple, modular, and straightforward method for depositing functionalized dyes/catalysts to obtain solar fuel with a high efficiency [1].

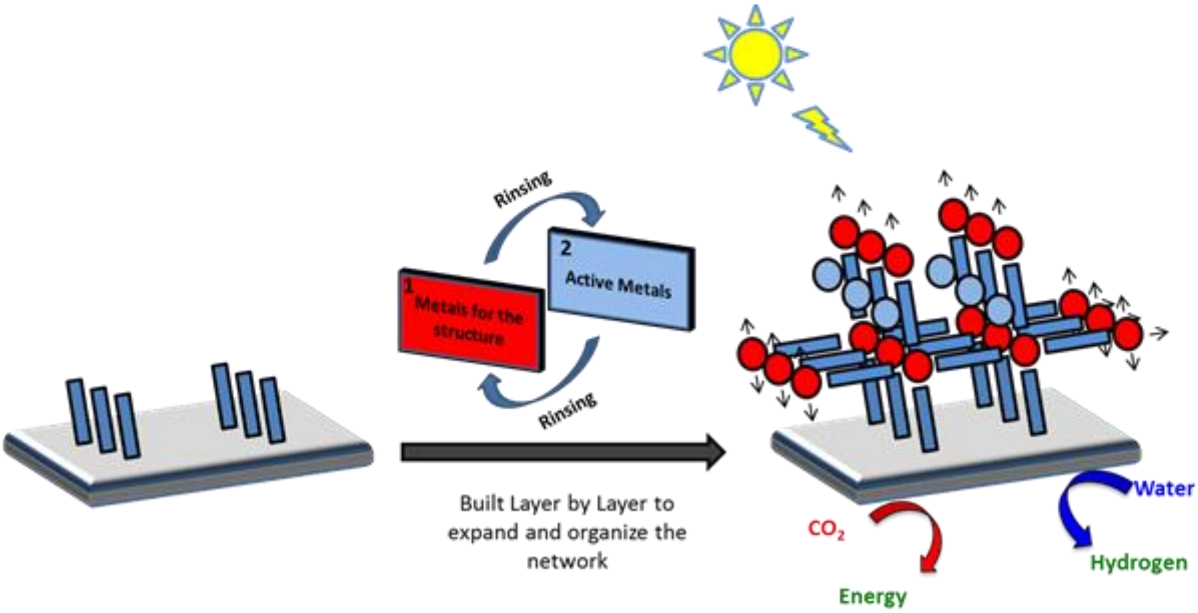

Figure 1 : Layer-By-Layer construction of efficient light harvesting device on a solid support

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[1] New activity of the LHYS

Controlled precipitation of metals in solution for solid/liquid extraction

M. Carboni, D. Meyer

Separation of critical metals is gaining high consideration due to the increase of their commercial utilization and for a strategically purpose (more than 95 % of the world production is made in China). The chemical behaviour of all lanthanide ions is almost identical, due to the fact that 4f orbitals are hidden behind the 4d and 5d orbitals, making it quite difficult to separate by conventional techniques. It is now necessary to find a new and different way to separate rare earths elements with high efficiency. For this purpose, we want to design ligands and experiments to use the specific coordination properties of Ln to co-precipitate with d-metals in an established auto-assembly fashion and create high value materials for various applications.

Metal Organic frameworks (based on a linker and a cluster of metals) have already demonstrated to be very efficient in metals extraction. The unique physical properties of these materials and the easy tunability of the linker can be used to obtain a high selective separation of the rare earth metals even in drastic conditions (acidic or basic). Our effort will be focus to develop these materials in 2 different axes. First, we are working to design an efficient linker able to create a MOF composed of a d-metals secondary building unit and containing lanthanides in the cavity by self-assembly directly from a mixture of various metals (Figure 1-1). The other strategy will be to accommodate an efficient cryptand on the linker, inside the MOF cavity, known for specific lanthanide extraction in the liquid/liquid processes and give the opportunity to test and compare it in a solid/liquid process (Figure 1-2).

Our expectation is to finally develop an efficient and original way to extract lanthanides and to obtain heterometallic materials with a high interest[1].

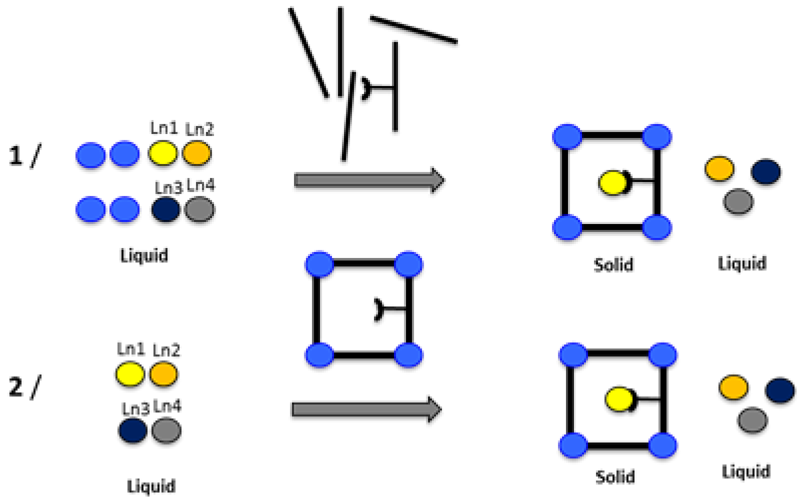

Figure 1 : Exemple for lanthanide metal recycling with high value output 1/ Selective precipitration by Self-assembly 2/ Use of a MOF to selectively bind lanthanide for solid/liquid extraction

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[1] New activity of the LHYS

Fluorinated vs hydrogenated molecules: organic phase model systems

M.C. Dul, D. Bourgeois, S. Dourdain, S. Pellet-Rostaing, 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.

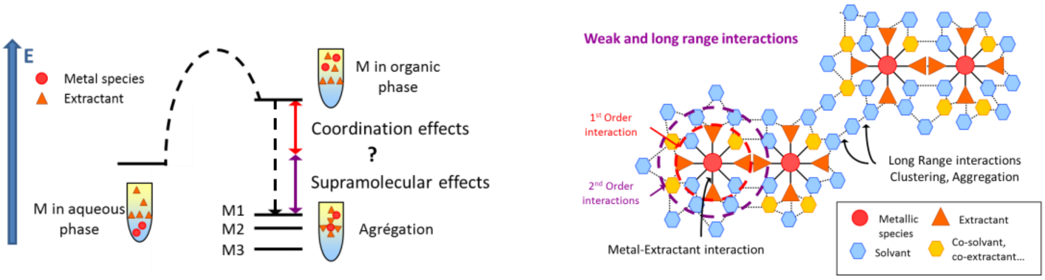
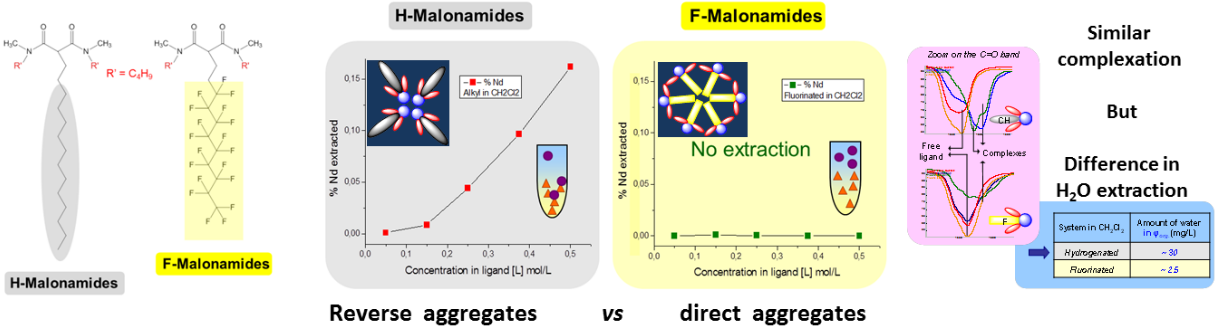


Figure 1: Thermodynamic consideration in a liquid-liquid system and the related interactions

One part of this challenge is to elucidate the role of the interactions which can take place at the molecular level (Fig. 1), especially the relations between first order interactions (such as chemical bonding or electrostatic interactions) and low energy second order interaction (H bonding, polarisation, dipole…).
In this study we focused our interest on the importance of Van der Waals forces in the solubilisation of metal species in organic media using a comparative study between fluorinated and hydrogenated amphiphilic extractants. A key point is to keep the molecular volume and the polar part of the extractant as much as possible unchanged. This is of prime importance in order to minimize the impact of any other interactions, especially the volumic entropic term and the coordination interactions of the polar part with the metal center. To reach this aim, we have first developed the synthesis and purification of several fluorinated extractants (diamide, phosphate, phosphonate…).1
The short term objective is to study the differences in organization of the organic phase when a flurorinated extractant is used in place of a hydrogenated analog and correlate these structural hints with the extraction behavior (amount of extracted metal and specificity of the behaviour).



System in CH_2Cl_2	Amount of water in $\varphi_{org.}$ (mg/L)
Hydrogenated	~ 30
Fluorinated	~ 25

Figure 2:Fluorinated vs hydroganated molecular systems

Thus we are comparing the supramolecular behaviour of diamide-dichloromethane-lanthanide phases as model system, from the extraction, solubility and structural points of view. First results show that the extraction behavior is very different: the hydrogenated system extracts the lanthanides whereas the fluorinated system does not (Fig. 2). The related structural studies (NMR, DOSY, SAXS, SANS) are still in progress to better understand this difference of behavior that probably comes from a different organization of the organic phases (reverse vs direct aggregates).

---

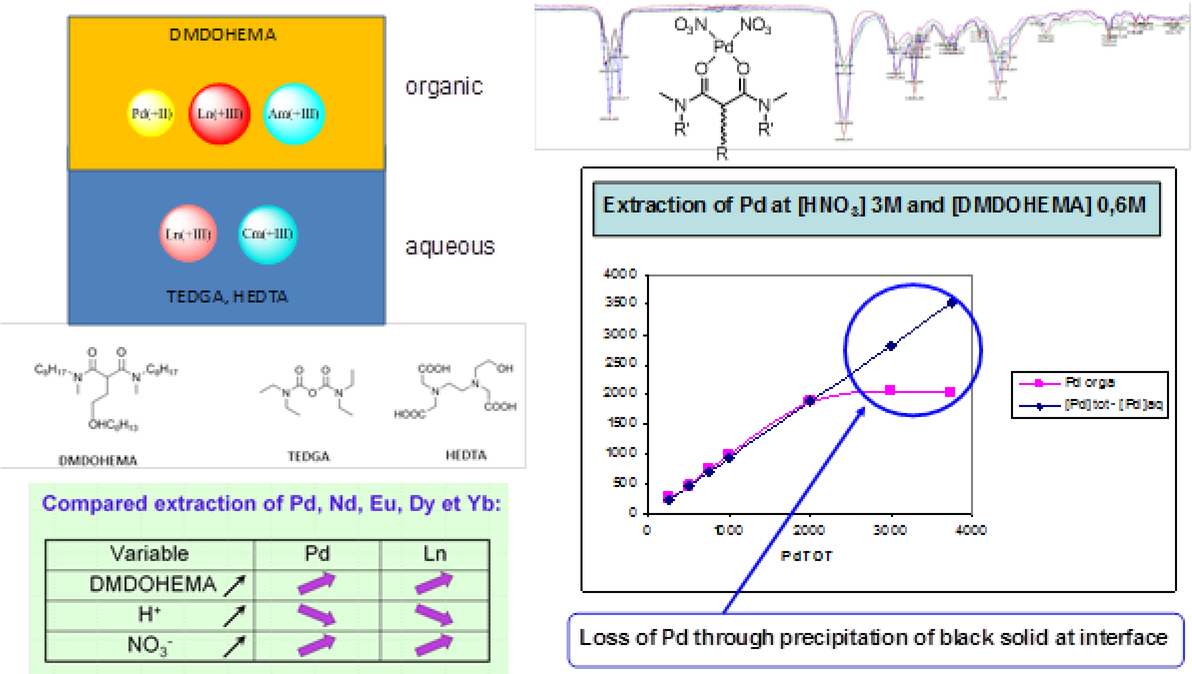
[1] "**Synthesis of fluorinated malonamides and use in L/L extraction of f-elements**", MC. Dul, D. Bourgeois, J. Maynadié, D. Meyer, *Tetrahedron Lett.*, **2013**, *54*, 6271-6274.

Liquid/Liquid Extraction of Palladium with diamides

R. Poirot, D. Bourgeois, D. Meyer

Extraction and separation of multivalent cations is a subject of particular relevance for the retreatment of nuclear wastes. In this frame, the EXAM process was designed at the CEA to enable selective recovery of americium from a PUREX raffinate. During this process, Am(+III) is separated from Cm(+III), light lanthanides (at the +III oxidation state as well) follow the Am, and heavy lanthanides stay in the aqueous layer with Cm. Palladium follows americium during the whole process, although its physico-chemical behaviour is anticipated to be completely different: Pd(+II) is a cation softer than Ln(+III), and with a higher charge density. As a metal of particular interest, palladium has already been the subject of several L/L extraction study, but mostly devoted to hydrochloride media. We thus decided to explore the behaviour of palladium in presence of diamide-type extractants of interest (DMDOHEMA, TODGA, see Fig. 1), and in nitric media.

L/L extraction of Pd with the sole DMDOHEMA malonamide was fully characterised.1 Comparison with lanthanides reveals similar trends (Fig. 1), but the quantitative influence of parameters differs between +II and +III cations (number of diamide ligands, number of co-extracted nitrate counter-ions, influence of H+ concentration).



Loss of Pd through precipitation of black solid at interface

Compared extraction of Pd, Nd, Eu, Dy et Yb:

Variable	Pd	Ln
DMDOHEMA ↗	↗	↗
H^+ ↗	↘	↘
NO_3^- ↗	↗	↗

Figure 1: General behaviour of Pd during L/L extraction with DMDOHEMA from HNO_3 solutions

Interestingly, diverse precipitation phenomena were highlighted during these studies: formation of Pd black, PdO and Pd rich phases (third phase) were evidenced. On-going studies include the complexation behaviour of Pd with diamides (XRD, IR, NMR), the supramolecular state of the organic layer (SAXS, DLS), the characterization of RedOx processes during extraction, the theoretical speciation of aqueous layer (JChess modelling with thermodynamic databases), and the experimental detection of Pd colloids at low acidities (SAXS, DLS).

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[1] "**Palladium extraction by a malonamide derivative (DMDOHEMA) from nitrate media: Extraction behavior and third phase characterization**", R. Poirot, D. Bourgeois, D. Meyer, *Solvent Extr. Ion Exch.*, **2014**, *32*, 529-542.

Uranyl interaction with bone mimics

D. Bourgeois, G. Chatelain, D. Meyer
C. Vidaud (CEA-DSV Marcoule), G. Boivin (INSERM Lyon),
M. Denecke (KIT Karlsruhe), K. Dardenne (KIT Karlsruhe), J. Rothe (KIT Karlsruhe)

Whatever its entry route into the body, the uranyl cation (UO22+) 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 UO22+ into the skeleton.[1]

Bone is a mineralized composite tissue with 5−10% water, 50−70% apatite [Ca10(PO4)6(OH)2], and 20−40% organic compounds composed mainly of collagen I protein (90%). Throughout the lifetime, bone tissue is continuously remodeled by cycles of events occurring at the same sites, alternating resorption and mineralization, mediated by osteoclasts and osteoblasts respectively. We recently set-up a method to synthetize biomimetic collagen-apatite hybrid materials, into which we can introduce uranium at various levels (Fig. 1).2 These samples are then used as bone cell culture support, and analysed and compared with biological samples using various techniques (XRD, IR, Raman, SEM, XANES, EXAFS, SLRT).

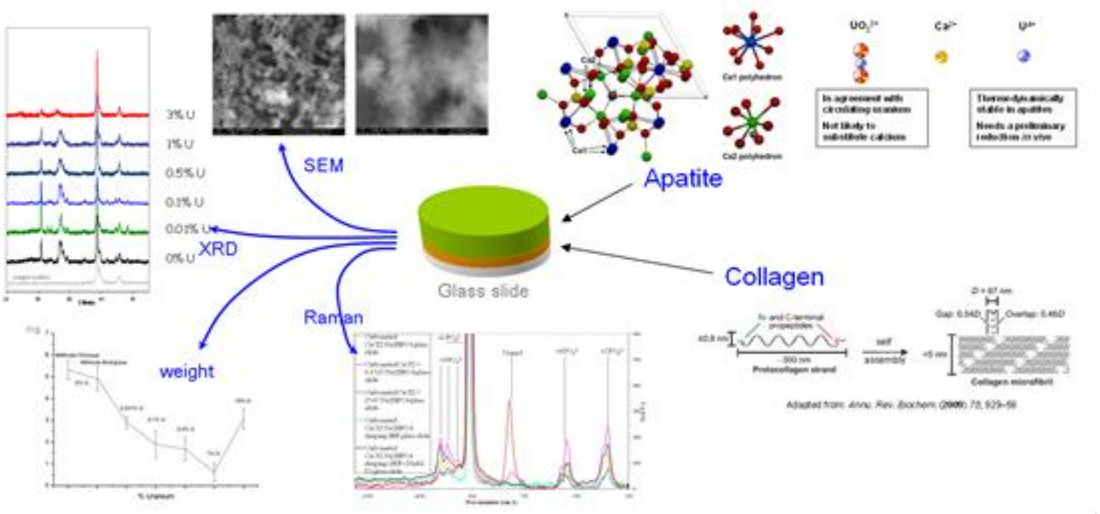

Figure 1: Biomimetic collagen-apatite hybrids prepared and some analytical results accounting for the influence of uranium on these systems

The interaction between uranium and the bone matrix is very complex. At the sole chemical level, several species can be obtained, and the presence of carbonate ions in the medium adds another complexity level. We have already established that low levels of uranium lead to a decrease in the mineralization efficiency, and also to a less crystalline material. Speciation studies at the molecular level are ongoing to establish the nature of the uranium species sorbed at the apatite surface. And further studies will be devoted to the factors governing the chemical equilibria between uranium(VI) and these biomimetic matrixes.

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[1] "**Bone as target organ for metals: The case of f-elements**", C. Vidaud, D. Bourgeois, D. Meyer, Chem. Res. Toxicol., 2012, 25, 1161-1175.

[2] "**Alternate dipping preparation of biomimetic apatite layers in the presence of carbonate ions**", G. Chatelain, D. Bourgeois, J. Ravaux, O. Averseng, C. Vidaud, D. Meyer, *Biomed. Mater.*, **2014**, *9*:015003.

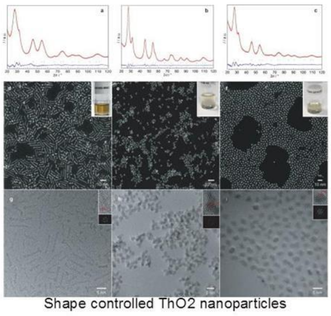
AnO2 nanocrystals (An=U, Th, Np, Pu)

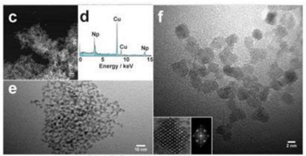
D. Hudry (JRC-ITU Karlsruhe Germany) J. Maynadié, D. Meyer

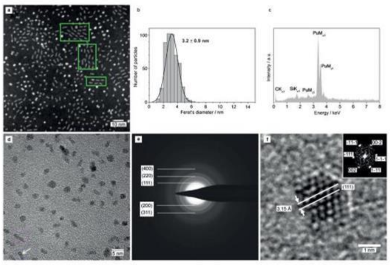
These studies are done in the frame of the fundamental behaviour of 5f species and are focused on the controlled synthesis of nanocrystals of actinide dioxides.

The approach developped consisted in the use of ternary (oleic acid, oleic amine, benzilic ether) and quarternary (oleic acid, oleic amine, benzilic ether, phosphine oxide) molecular systems with different actinides precursors (nitrate, acetate, acetylacetonate). Studies were done on Th, U, Np and Pu [1].

The main results show that it is now possible to get several kind of nanoparticles with different properties compared to the micrometric material.


Shape controlled ThO2 nanoparticles


NpO2 nanoparticles


Pu O2 nanoparticles

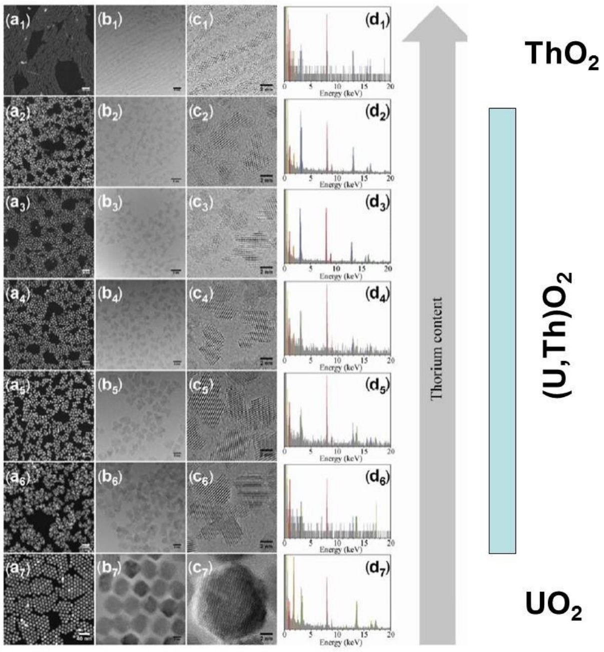


Figure 1: Actinide oxide nanoparticles from Th to Pu with different shapes and mixed Th-U oxides.

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[1] **"Non-aqueous Synthesis of Isotropic and Anisotropic Actinide Oxide Nanocrystals",** Damien Hudry, et al., Chemistry - A European Journal, 18, 2012, 8283.
"Controlled Synthesis of Thorium and Uranium Oxide Nanocrystals", Damien Hudry, et al., Chemistry - A European Journal, 19, 2013, 5297.
"Synthesis of transuranium-based nanocrystals via the thermal decomposition of actinyl nitrates", Damien Hudry, et al., RSC Advances, 2013, 3, 18271.
"Thorium/uranium mixed oxide nanocrystals: Synthesis, structural characterization and magnetic properties", Damien Hudry, et al., Nano Research 2014, 7(1): 119–131.
"Ultra-Small Plutonium Oxide Nanocrystals: An Innovative Material in Plutonium Science", Damien Hudry, et al., Chem. Eur. J. 2014, 20, 10431.

Electric car batteries recycling
(Direct collaboration with VEOLIA/SARPI)

E. Perez, D. Meyer,
J. Borrini, F. Hyvrard (VEOLIA/SARPI)
M. Fontecave (College de France)

A first step of this project was to recover as pure as possible Li from electrode material coming from Li-ion electric car batteries dissolution solutions [1]

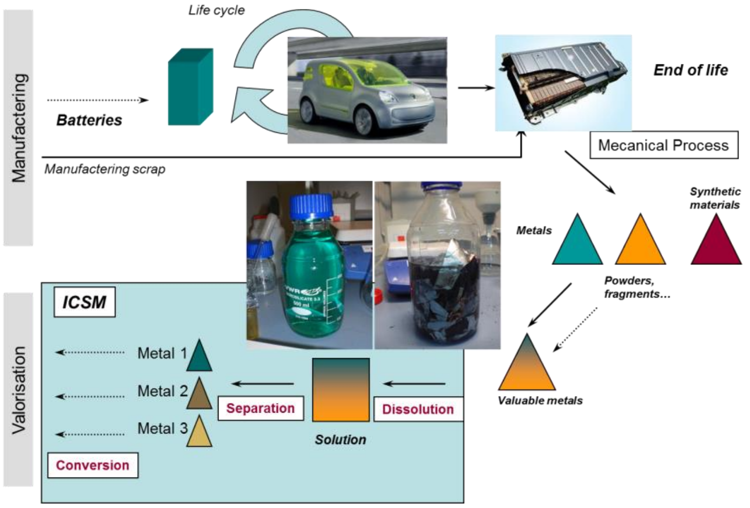

Figure 1: Li-ion car battery recycling

This project is now focusing to recover all valuable elements using a hydrometallurgic approach. Several techniques where studied and tested at the laboratory scale.

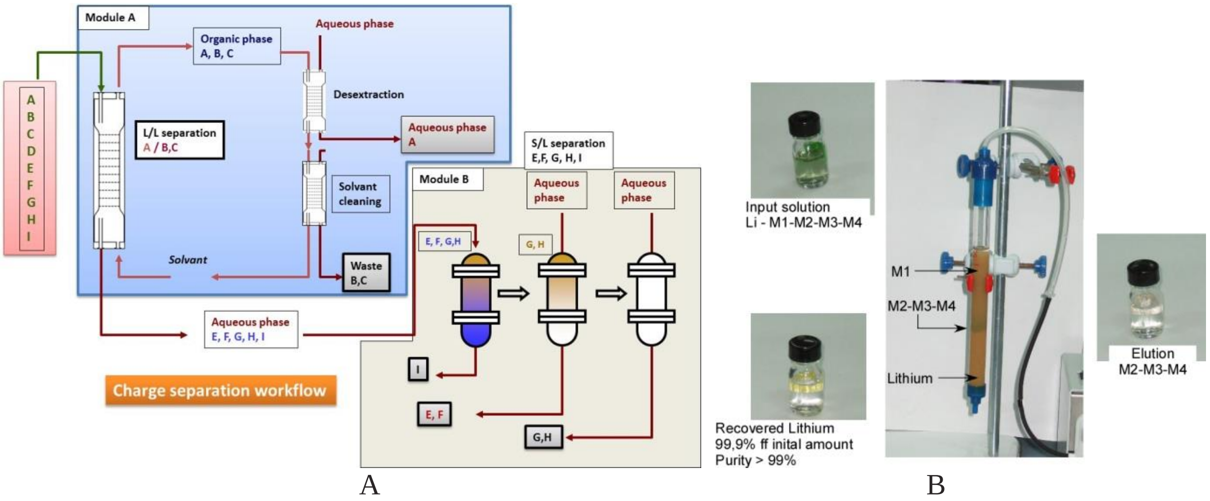

Figure 2 (A) Exemple of a separation integration based on a charge separation workflow using a 2 techniques approach. (B) Column test.

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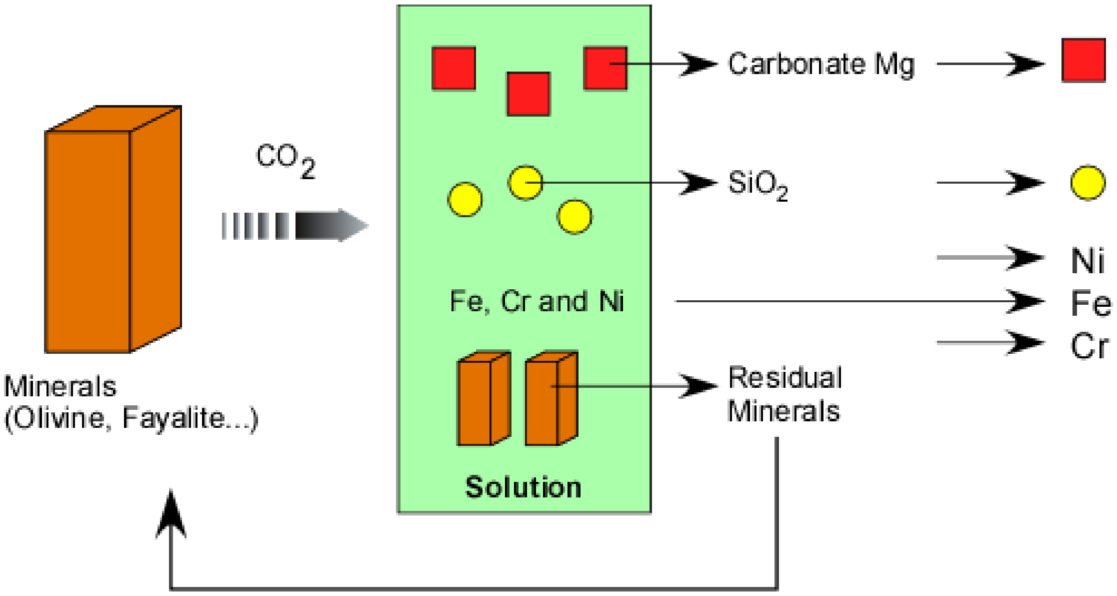
[1] « Procédé de séparation de métaux à partir de batterie contenant du lithium » VEOLIA/ SARPInd, FR2976295, Borrini J., Meyer D., Fontecave M., Penelieu F.

CO_2 Valorisation by silicate carbonatation (ADEME project VALORCO)

N. Bangoy, S. Szenknect, D. Meyer
L. Turri, F. Lapique, H. Muhr (LRGP nancy)
E. Deconinck, S. Bertucci (Arcelor-Mittal)

Partner: Arcelor Mittal, Air-liquide, IFPEN, Institut de Chimie Clermont-Ferrant, Univ. de Lyon, Institut Jean Lamour, ICSM, CNRS, LRGP (Nancy), Instituts d'Excellence sur les Energies Décarbonées

The VALORCO project is dedicated to reduce the CO_2 footprint by several approaches, one includes carbonating minerals. This task, part of the whole project, is dédicated to the valorisation of magnesium carbonate, silica, iron, nickel and chromium by carbonatation of silica minerals (olivine…) by CO_2 produced by metallurgic industry.



Aim of the study is to recover the valuable elements by hydrometallurgical approaches in order to purify the carbonate and provide all the recovarable elements in a pure form with acceptable costs regarding the economic model

2 – Ions at Interfaces

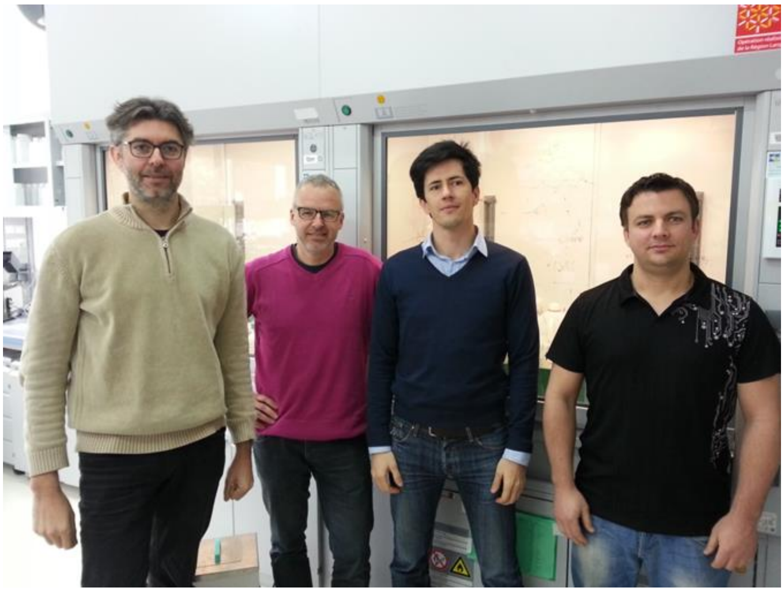
L’équipe est constituée au 1er décembre 2014 de :
1 chercheur CEA responsable d’équipe (Dr. O. Diat),
1 chercheur CEA (Dr. P. Bauduin),
1 enseignant-chercheur ENSCM (Dr. L. Girard),

Post-doctorants :

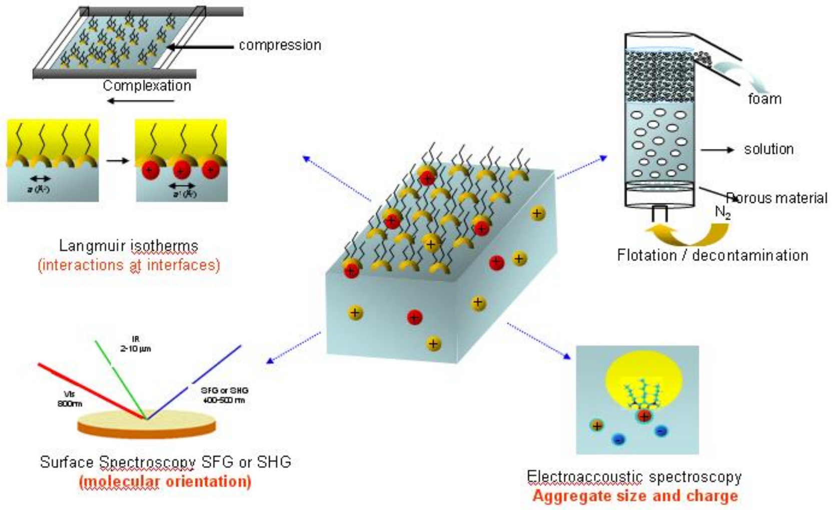
- Dmytro Dedovets (DEN, 2014-2015) : Programme RSNR « Demeterres », flottation du césium d’effluents aqueux.
- Bappaditya Naskar (DEN-ANR CATASURF, 2013-2014) : Interaction entre macroions et interfaces
- Hasnaa El Ouzzani (DEN – SACSESS, 2014-2015) : LL interface via SHG
- Rym Boubekry (Labex Chemisyst, 2013-14) : Interface liquide/liquide et ultrasons.

Thésards :

- Ernesto Scoppola (DEN/Institut Laue-langevin - Grenoble, 10/2012) : Réflectivité sur interfaces « liquide/liquide ».



Parmi tous les phénomènes physiques et chimiques liés à la fabrication du combustible nucléaire et des déchets de dissolution, à la problématique de l’extraction et la séparation des ions et de leurs stockages dans différents types de matrices, le vieillissement de ces matériaux sous différents stress chimiques ou radiatifs qui sont examinés dans les laboratoires de l’ICSM, le groupe des "ions aux interfaces actives" (3 chercheurs dont un enseignant chercheur à l’ENSCM) prend plus particulièrement en charge une recherche fondamentale concernant la distribution d’espèces telles que des ions, des molécules ou des agrégats à proximité d'interfaces fluides d’échange et les conséquences de cette répartition sur la réactivité de ces interfaces.



Ions to be separated between phases must cross fluid interfaces: knowledge of distributions in the last 3 nanometers is crucial to understand thermodynamics as well as kientics of ion séparation. The figure shows the principles of the experimental techniques used to investigate ion distribution and mobility at fluid interfaces.

Le génie chimique lié à cette activité de séparation des ions en solution et développé entre autres au CEA doit utiliser au maximum le potentiel des matières colloïdales pour assurer une sélectivité ionique et une séparation dans un processus continu après la dissolution du combustible nucléaire. Ces méthodes requièrent une connaissance approfondie de l'adsorption des ions à partir d'une solution aqueuse vers une interface liquide-solide ou liquide-liquide ou encore liquide-air. Plus que les interactions électrostatiques décrites dans une théorie DLVO, la polarisabilité, les forces de dispersion, le réseau des liaisons hydrogène, la complexation ionique, les interactions entre les ions et leurs environnements doivent être considérés; c'est pourquoi des systèmes modèles ainsi que des géométries d'analyse sont à imaginer pour permettre de mettre l'accent sur la physique et chimie de la spécificité de chaque effet.

Dans ce rapport, parmi les nombreux sujets en cours qui nous impliquent mais impliquent aussi des collaborations extérieures, nous avons sélectionné des exemples sur lesquels nous sommes porteurs ou plutôt les acteurs principaux : un premier exemple concerne donc l'étude d'interface liquide/liquide par une technique de reflectivité du rayonnement (rayons x et neutrons) afin de pouvoir appréhender l'organisation des ions et molecules extractantes autour de l'interface pendant un processus de transfert d'espèces. C'est un travail de thèse inclus dans un programme ANR blanche plus large (« ILLA ») avec d'autres équipes d'expérimentateurs (LASIM/UCB/LYON + DEN/DRCP) et de théoriciens (MSM/Univ Strasbourg + DEN/DRCP). Un second exemple choisi (thèse CEA) concerne le transfert d'une molécule tensioactive qui se partitionne à l'équilibre entre une phase aqueuse et une phase huile. C'est un sujet modèle pour essayer de comprendre la cinétique du transfert entre deux milieux non miscibles en prenant en compte une cinétique de sorbtion à l'interface. Un troisième exemple (thèse universitaire terminée) concerne l'auto-assemblage de macros ions amphiphiles (dicarbollide) de formes particulières (sans queue ni tête) et étant sélective du Cs et Sr et donc utilisés en extraction liquide/liquide pour le nucléaire pour former des espèces neutres (paires d'ions) dans des milieux de polarité moyenne. Le quatrième exemple choisi concerne un procédé de séparation alternatif à la séparation liquide/liquide : il s'agit de la flottation ionique. Ce sujet a été abordé aussi dans le cadre d'une thèse en partenariat avec le DEN/DTCD avec la compréhension de l'équilibre effet moussant et effet de complexation ou d'interaction ionique aux interfaces liquide/air. Une étude en collaboration avec un autre département de la DEN (DRCP) a été menée dans le cadre d'une thèse dont il avait la responsabilité et autour de la modélisation des phases huileuses chargées en molécules extractantes et en équilibre avec une phase aqueuse. Cette étude devrait permettre d'analyser plus finement les équilibres et ensuite les cinétiques des mécanismes thermodynamiques et thermocinétiques de l'extraction liquide/liquide. Enfin un dernier exemple concerne un travail autour des systèmes « catasurf » (ANR blanche avec une équipe de Lille, de Paris et un industriel hollandais – DSM) faisant intervenir des macro-ions de types polyoxometalates à une interface eau/huile avec en arrière plan la problématique des macros-ions polarisables en interactions aux interfaces.

Extractant molecules at interfaces – Liquid/liquid Reflectivity

E. Scoppola, *G. Fragnetto*[1], *L. Porcar*[1], *O. Diat*

Ion separation by phase transfer (liquid/liquid extraction) which are the most selective are also the slowest. Fundamental reason comes from the statistics of organized fluids. The Brownian agitation of the hydrated ions selected by amphiphilic extractant molecules explore the number of ways (or of try) across the interface of both non miscible phases in contact to which are associated activation energies. Beyond the cycle of nuclear fuel, this is also valid in various fields such as enzymology or the catalysis, the membrane permeation or the reprocessing of polluted waters.

We have seen in the previous pages how it is important to better understand the amphiphilic properties of the extractant molecules involved in the liquid/liquid extraction processes. We have previously analysed systems in which extractant molecules where associated with surfactant to build liquid crystal phases or microemulsions in order to analyse how these molecules affect the thermodynamic of these self-assembly phases. Another way to identify their behaviour at water/oil interface is to perform radiation reflectivity on buried interfaces. This was the objectives of a PhD program on the Grenoble site where neutron and x-ray reflectivity measurement can be carried out.

First experiments were successful and using different contrasts (scattering length density of nuclei or electrons), density profiles of extractant molecules perpendicular to the interface and as a function of the extractant concentration and water activity can be obtained. Then these results will be compared with MD simulation developed by the group of G. Wipff in the frame of an ANR program (ILLA).

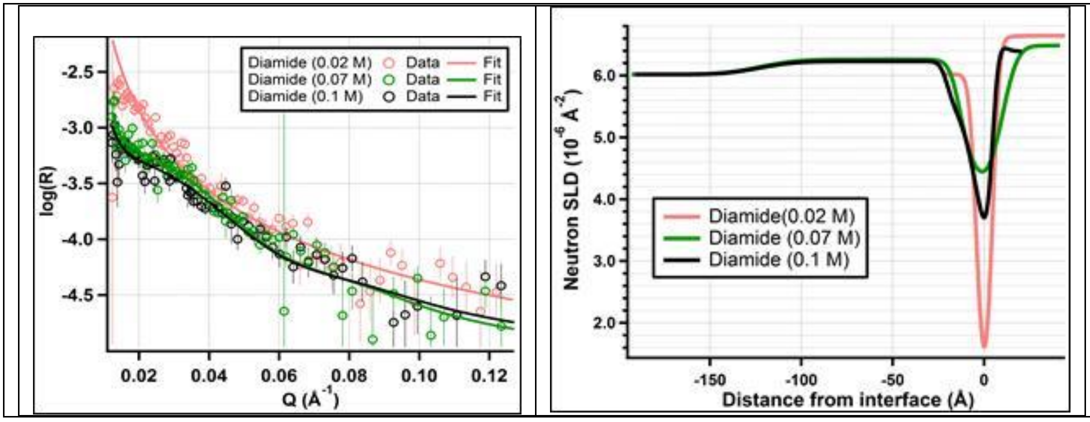


Fig.1: left: neutron reflectivity curve from LL interface at various extractant concentrations in the organic bulk phase: Right: corresponding SLD profiles across the LL interface deduced from the reflectivity data

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[1] Institut Laue Langevin (ILL)

Surfactant transfer across a liquid/liquid interface probed with dynamics interfacial tension measurements

P-M Gassin, G. Martin-Gassin, J-F Dufreche, O. Diat

The transfer of amphiphilic solutes through an interface between water and an organic solvent has been studied numerically by simulations based on a general diffusion/reaction model. This description predicts the evolution of the solute concentrations and the transfer across the liquid/liquid interface. It especially focuses on the dynamic interfacial tension (IFT) evolution that can be measured by a pendant drop tensiometer. Both the bulk diffusion and the adsorption/desorption rate on both sides of the liquid interface are assumed to contribute to the global transfer kinetic. The calculations provide an understanding on how both kinetic exchange at the interface and diffusion transport through the bulk determine the dynamic interfacial tension evolution. In particular, complex interfacial tension evolutions with a non-trivial behavior are predicted in some special cases when diffusion and kinetic exchange are of the same order of magnitude. Finally, this model[2] is used to re-interpret experimental data about triton X-100 transfer at a water-oil interface[1].

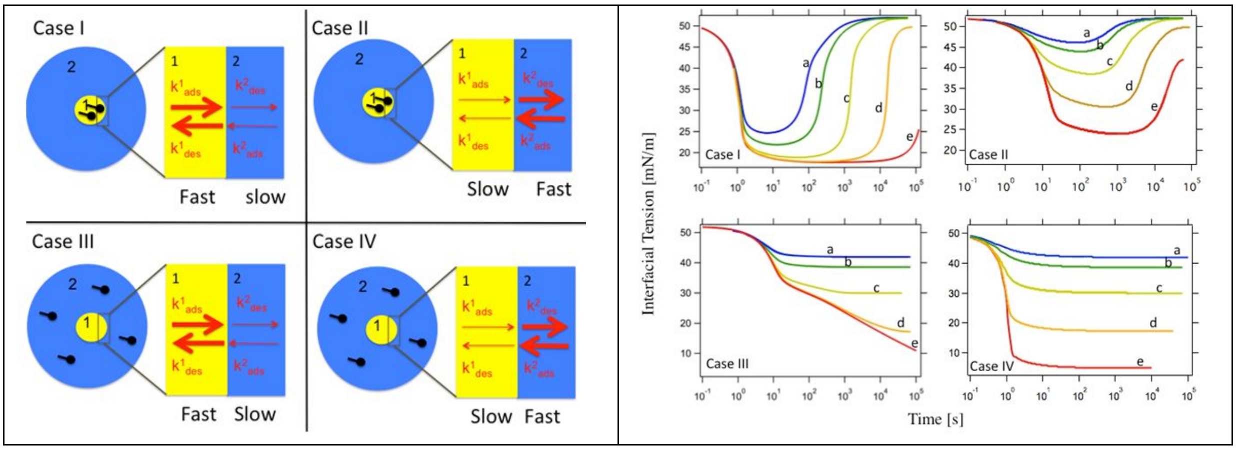

Fig.1 [1]: left - The four situations studied by the mixed model with values of k_{ads} listed in table 1. Right - Dynamic IFT calculated for the cases I, II, III, and IV. The blue curve (a) is for equilibrium partition coefficient $K_{(1,2)} = conc_1/conc_2 = 0.01$, green curve (b) for $K_{(1,2)} = 0.02$, yellow curve (c) for $K_{(1,2)} = 0.1$, orange curve (d) for $K_{(1,2)} = 1$ and red curve (e) for $K_{(1,2)} = 10$.

Table 1. *The kinetics rate used in each case for the calculation[1]*

	Case I	*Case II*	*Case III*	*Case IV*
k^1_{ads} (cm.s^{-1})	*0.1*	*0.001*	*0.1*	*0.001*
k^2_{ads} (cm.s^{-1})	*0.001*	*0.1*	*0.001*	*0.1*

References

(1) Gassin, P. M. Champory R. Martin-Gassin G. Dufrêche J-F. Diat O. **"Surfactant Transfer Across a Water/Oil Interface: a diffusion/kinetics model for the interfacial tension evolution"** Colloids and Surfaces A: Physicochemical and Engineering Aspects 213, 436(5) 1103 – 1110.

(2) Gassin, P. M.; Martin-Gassin, G.; Meyer, D.; Dufreche, J. F.; Diat, O. **"Kinetics of Triton-X100 transfer across the water/dodecane interface: analysis of the interfacial tension variation"** Journal of Physical Chemistry C 2012, 116, 13152.

A Theta-Shaped Amphiphilic Cobaltabisdicarbollide Anion

D. Brusselle, P. Bauduin, O. Diat, L. Girard, C. Viñas[1] and F. Teixidor[1], I. Ly[2]

Lyotropic lamellar phases are ubiquitous on earth, they occur naturally and are a key architecture for life to appear as they enable closed cell topologies to occur. But in addition to the latter, enabling life means that the same solvent must be on both side of the cell membrane, hence a, at least, double layered membrane structure is necessary. For this a lamellar phase must be enabled. The present contribution shows, for the first time, that the formation of lamellar phases is not exclusive to alkyl chain based surfactants with a well-defined amphiphilic structure but that it can also be obtained with metalla-carborane clusters, described previously as θ-shaped amphiphiles [1]. Similarly to phospholipids cell membranes the lamellae formed here can exist both in the liquid and in the solid states depending on temperature. The determination of the 2D molecular arrangement in the lamella proved that the formation of intermolecular dihydrogen bonds, such as -C-H□□…□□□-H-B-, is the driving force in the lamella self-assembly process. Compared to the common bilayer structure that originates from the hydrophobic effect, θ-shaped amphiphiles form lamella with a peculiar monomolecular structure reminiscent of lamellar sheets observed in inorganic layered systems. Nano-scale ordering of planar organic-inorganic hybrid sheets is here controlled with temperature and concentration through a self-assembly process.

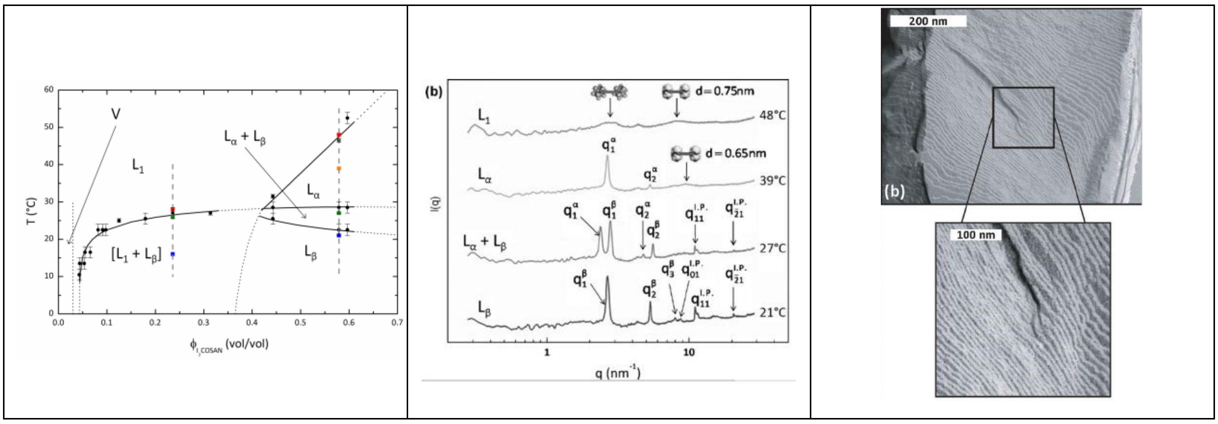

Fig: left- Binary phase diagram of H[I2COSAN] in water showing the existence of lamellar lyotropic phases, L□ and L□, isotropic micellar (L1) and vesicular (V) phase. [L1+L□] refers to a "gel" phase being a microscopic demixion of L1 and L□.. Middle – SWAXS spectra of H[I2COSAN] in water at different temperatures at 59% v/v.Right: Freeze-fracture TEM picture of the pure L□ phase showing the lamellar arrangement with an apparent inter-lamellar distance of roughly 5 nm confirmed by SWAXS.

Reference

P. Bauduin, S. Prevost, P. Farràs, F. Teixidor, O. Diat and T. Zemb, "A Theta-Shaped Amphiphilic Cobaltabisdicarbollide Anion: Transition From Monolayer Vesicles to Micelles" Angew. Chem. Int. Ed., 50(23), 2011, pp 5298

D. Brusselle, P. Bauduin, L. Girard, A. Zaulet, C. Viñas, F. Teixidor, I. Ly and O. Diat, "Lyotropic lamellar phase made of monolayered θ-shaped amphiphiles" Angew. Chem. Int. Ed. 2013, 52(46), 12114 – 12118

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[1] *ICMAB CSIC, Campus de la UAB, 08193 Bellaterra, Spain*

[2] *CRPP, Talence*

Ion flotation for decontamination

C. Micheau, P. Bauduin, O. Diat, D. Dedovets, S. Faure[1]

The process called *ion flotation* allows to concentrate ions or other charged entities from aqueous solution within a foam that can be produced at the top of the solution. Foam is created by introducing gas bubbles in the solution that contains surfactant molecules at very low concentration (≤ CMC). The supplementary properties of such amphiphilic species is to be able to complex cations. Afterwards the drainage of the foam leads to concentrate the metal ions and the surfactant. The skimming of the foam enables ultimately to extract metal ions from the native solution. Moreover ion separation can be achieved by using selective complexing surfactants. To obtain an efficient ion extraction, the surfactant needs to combine good foaming and complexing properties. *Ion flotation* covers two main application fields: recovery of valuable material and water decontamination (Our team is now involved in a national RSNR program “Demeterres” for Cs recovery from aqueous effluents). Compared to solvent extraction, used for example in the nuclear fuel recycling, *ion flotation* shows the main advantage of using gas instead of an organic solvent.

In a PhD study, the investigated surfactant is composed of an alkyl chain, ethoxy groups keeping efficient the foaming property, even after complexation, and a carboxylic acid function which acts as a complexing part when it is under its charged carboxylate form.

Ion flotation of multivalent cations was investigated as a function of pH and ionic strength. Titration, UV-vis spectroscopy, ICP, Zeta potential, small angle neutron scattering, conductimetry are complementary techniques used to determined and understand the interaction of the cations with the foam structure and more accurately with the polar head of the surfactant. This can be compared when amphiphiles are self-assembled into micelles. The extraction yield obtained by chemical analysis was discussed in terms of the surfactant and cation speciations.

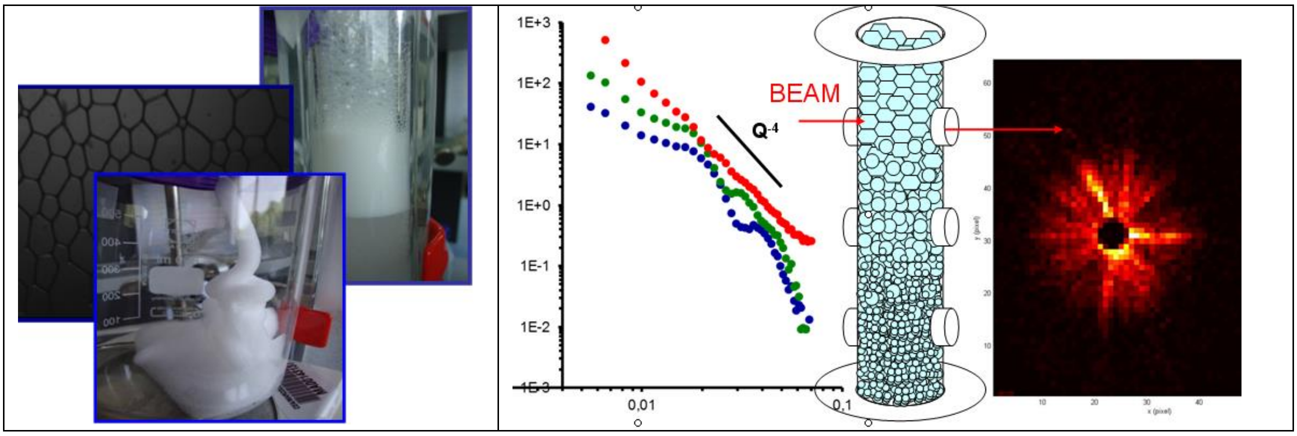

Fig : left – pictures of flotation column + zoom on the foam structure. Right: exemple of SANS curves from foam structure at different height within the column (drainage effect).

Reference

C. Micheau, S. Faure, P. Bauduin, O. Diat, Eufoam 2012
C. Micheau, P. Bauduin, O. Diat and S. Faure **"Specific salt and pH effects on foam film of a pH sensitive surfactant"**, Langmuir 2013, 29(27), 8472-8481
Micheau C. Bauduin P. Diat O. French patent submission n°13 60601

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[1] DTCD/LCFI

Elucidation of the Structure of Organic Solutions in Solvent Extraction by Combining Molecular Dynamics and X-ray Scattering

G. Ferru[1], D. Gomes Rodrigues[1], L. Berthon[1], P. Guilbaud[1], O. Diat, P. Bauduin

Knowledge of the supramolecular structure of the organic phase containing amphiphilic ligand molecules is mandatory for full comprehension of ionic separation during solvent extraction. Existing structural models are based on simple geometric aggregates, but no consensus exists on the interaction potentials. In a recent article through collaboration with DEN/DRCP/SMCS/LILA team, it was demonstrated that molecular dynamics crossed with scattering techniques offers key insight into the complex fluid involving weak interactions without any long- range ordering [1]. Two systems containing mono- or diamide extractants in heptane and contacted with an aqueous phase were selected as examples to demonstrate the advantages of coupling the two approaches for furthering fundamental studies on solvent extraction.

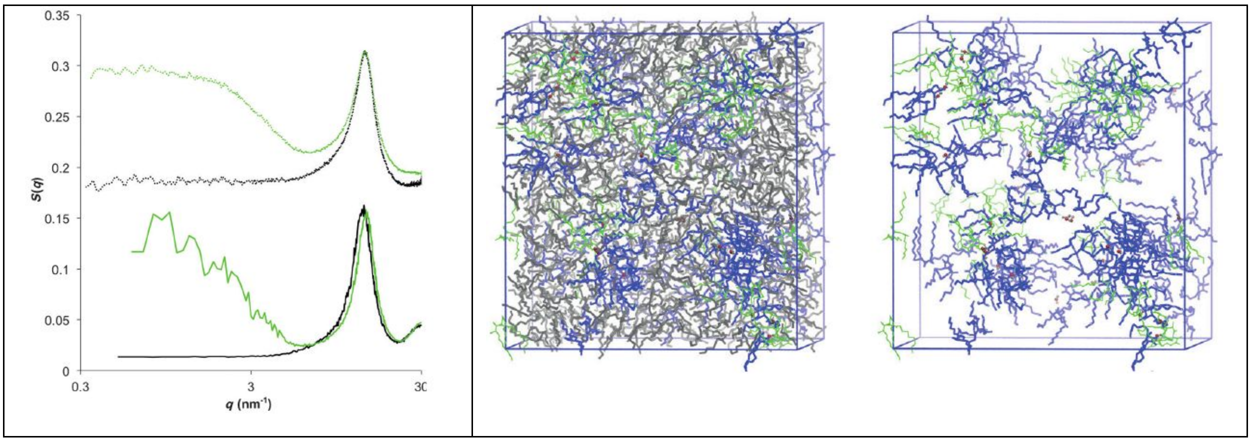

Fig.1 [extracted from 1]: Left: Comparison of the experimental (dotted lines) and theoretical (solid lines) SWAXS profiles obtained for pure n-heptane (black) and 0.6m DMDOHEMA in n-heptane (green) after contact with pure water. Right: Molecular-dynamics simulation-box snapshot of the 0.6m DMDOHEMA solutions, represented with (right) and without (left) the n-heptane solvent. Gray: n-heptane, green: DMDOHEMA monomers,blue: DMDOHEMA aggregates.

This study specifically addressed for the first time the complex structure of the organic phase in solvent extraction with a quantitative description of the molecular and supramolecular organization of the extractant in oil at a wide range of concentrations. The classical fitting treatment applied to scattering spectra, for which the form and structure factors of dense aggregates dispersed in a homogeneous fluid are considered, has two major limitations that can be overcome by using MD simulation: 1) it cannot be applied at high extractant concentrations at which P(q) and S(q) cannot be decoupled, and 2) it is not valid in the high q range above 6nmÀ1, in which intermolecular distances become important. Therefore, the procedure proposed herein appears to be especially well-adapted for weakly aggregating amphiphiles, such as hydrotropes in water or lipotropes in oils, which are typically characterized by high critical micellar concentration values and low aggregation numbers.

Reference

[1] Ferru, D. Gomes Rodrigues, L. Berthon, O. Diat, Pierre Bauduin, P. Guilbaud **“Elucidation of the Structure of Organic Solutions in Solvent Extraction by Combining Molecular Dynamics and X-ray Scattering”** Angewandte Chemie International Edition, 2014, 53, 1-6

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[1] CEA Marcoule, DEN/DRCP/SMCS/LILA

Amphiphilic Polyoxometalate : Self-Aggregation Properties

Jonathan Lai, Vincent Jallet[1], Véronique Rataj[2], Geoffroy Guillemot[1], Séverine Renaudineau[1], Anna Proust[1], Pierre Bauduin

The Development of surfactants exhibiting catalytic properties (ANR CATASURF) is a crucial issue since their localisation at liquid interfaces is likely to increase both the water-oil compatibility and the kinetics of the catalytic reaction. Polyoxometalates (POMs) are molecular oxo-clusters of the early transition metals in their highest oxidation states. They can be considered as small water soluble oxide or large polyanions (1-4nm).[M.T. Pope, 1991] They have shown numerous applications in medicine, analytical chemistry and material science thanks to their relevant properties among them catalytic properties are noteworthy. New class of POMs surfactants composed of two alkyl chains covalently bound to a tungstosilicate POM ([g-SiW10O36]8-) by varying the alkyl chain length (C8, C10 and C12) have been synthesized by the group of A. Proust. Their aggregations properties are of significant interest for understanding the basics of self-aggregation in relation to their catalytic properties. By coupling small angle X-rays scattering (SAXS), dynamic light scattering (DLS) and freeze fracture - transmission electron microscopy (FF-TEM), aggregation behavior in water is investigated.

A key issue is the stabilization of these amphiphiles in an aqueous phase. New covalent soluble POMs are under investigation.

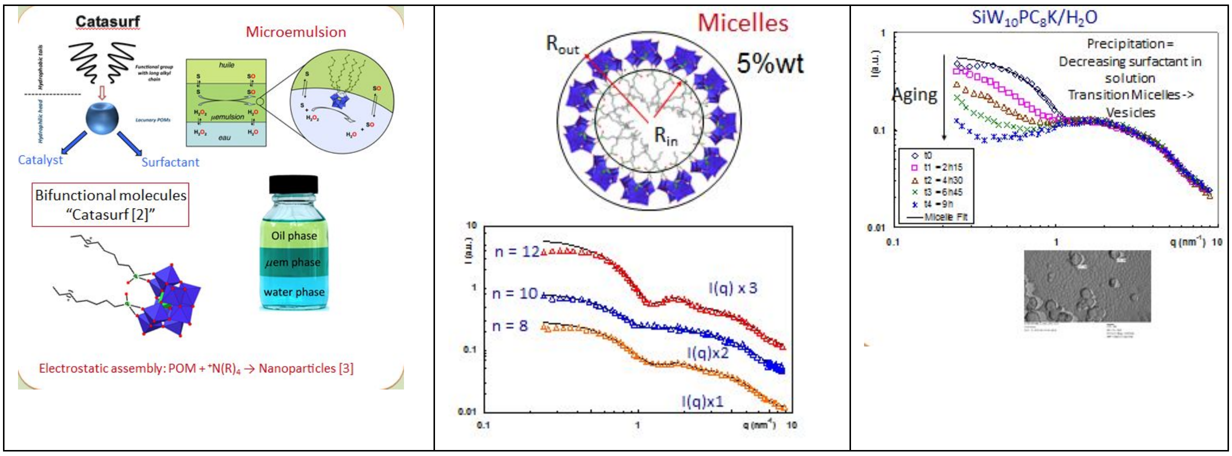

Fig : left – Synthesis of bi-functional molecules for making micro-emulsions [V. Nardello-Rataj et al 2008] that allow an enhancement of the accessible surface for catalysis as well as a compartmentalization between organic and queous phases. Middle – SAXS profiles fitted using a "micelle" model for different alkyl chain lengths. Right: Observvation by SAXS of the micelle destabilization that can be analysed in the frame of a micelle-to-vesicle transition. FF-TEM pictures (CRPP collaboration) from vesicles coalescence.

Reference

L. Leclercq, A. Mouret, P. Bauduin, and V. Nardello-Rataj **"Supramolecular Colloidosomes Based on Tri(dodecyltrimethylammonium) Phosphotungstate: A Bottom-Up Approach"** Langmuir, 2014, 30 (19), pp 5386–5393.

V. Jallet, G. Guillemot, J. Lai, P. Bauduin, V. Nardello-Rataj and A. Proust **"Covalent amphiphilic polyoxometalates for the design of biphasic microemulsion systems"** Chem Comm 2014, 50, 6610-6612

B. Hong, J. Lai, L. Leclercq, M. Collinet-Fressancourt, JM. Aubry, P. Bauduin and V. Nardello-Rataj **"Binary and ternary phase behaviors of short double-chain quaternary ammonium amphiphiles: surface tension, polarized optical microscopy and SAXS investigations"** J. Phys. Chem. B 2013, 117 (47) 14732–14742

L. de Viguerie, A. Mouret, H.-P. Brau, V. Nardello-Rataj, A. Proust and P. Bauduin "Surface pressure induced 2D-crystallization of POM-based Surfactants: preparation of nanostructured thin films"CrystEngComm 2012, 14, 8446 – 8453

Leclercq, A. Mouret, A. Proust, V. Schmitt, P. Bauduin, J.-M. Aubry, V. Nardello-Rataj **"Pickering emulsion stabilized by catalytic polyoxometalate nanoparticles: a new effective reaction medium for oxidation"** Chem. Eur. J. 2012, 18, 14352-14358

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[1] *Université Pierre et Marie Curie, Sorbonne Université, France*

[2] *Université de Lille 1, France*

Surfactant-free micelles and microemulsions: an urban legend or new possibilities for separation processes ?

T. Zemb, S. Prévost (ERSF, Grenoble), I. Grillo, Bruno Demé (ILL, Grenoble), Olivier Diat
Didier Touraud, Michael Klossek, Julien Marcus,Dominik Horinek and Werner Kunz
(Université de Ratisbonne), and S. Marcelja (Université Nationale Australienne, Canberra)

Adding slightly hydrophobic compounds to water can lead to structure-less solutions, aggregate formation or even to the formation of defined structures, such as micelles, in the case where the added compound is a surfactant. In ternary or quaternary mixtures containing at least one type of surfactant, usually the formation of microemulsions occurs in specific parts of the phase diagram. These macroscopically homogeneous, transparent liquids are composed of well-defined structures. Since the seventies, it was suspected, based on ultra-centrifuge observation and unexplained enzymatic activity that micellar w/o aggregates of defined size could exist. This was not believed by the vast majority of physical chemists, since there was absolutely no reason of a minimum in free energy for a given size. We study the formation of micelles in dynamic equilibrium, in certain point of ternary phase diagrams containing an hydrotrope, water and some water immiscible fluid[1].

While light and X-ray scattering were ambiguous, we have demonstrated the existence of well-defined interface. It is now proven without ambiguity that these surfactant-free micelles or microemulsions form in a large number of ternary systems. They form far from the critical point, but close to a liquid-liquid demixtion with ultra-low surface tension between the two separating phases. Molecular dynamics is able to show typical snapshots of surfactant-free microemulsions (figure 2). We have developed a general theory, replacing the lateral equation of state for surfactants by an equilibrium between the universal hydration force and mixing entropy.

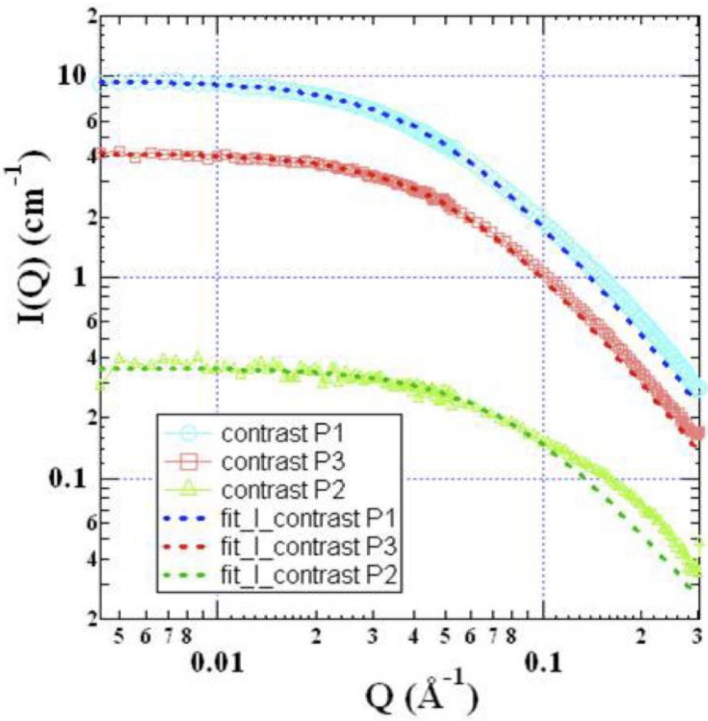

Figure 1: the three SANS spectra of a ternary solvent water-ethanol-octanol in the pre-ouzo region, taken with the there possible contrasts: two components deuterated and the third one proonated, after substraction of the incoherent background: the signal associated to interfacial thickness is clearly different form the scattering of one surfactant-free aggregate[2].

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[2] [Diat O, Klossek ML, Touraud D, Demé B, Grillo I, Kunz W, et al. **Octanol-rich and water-rich domains in dynamic equilibrium in the pre-ouzo region of ternary systems containing a hydrotrope** ; J Appl Crystallogr 2013;46:1665–9.

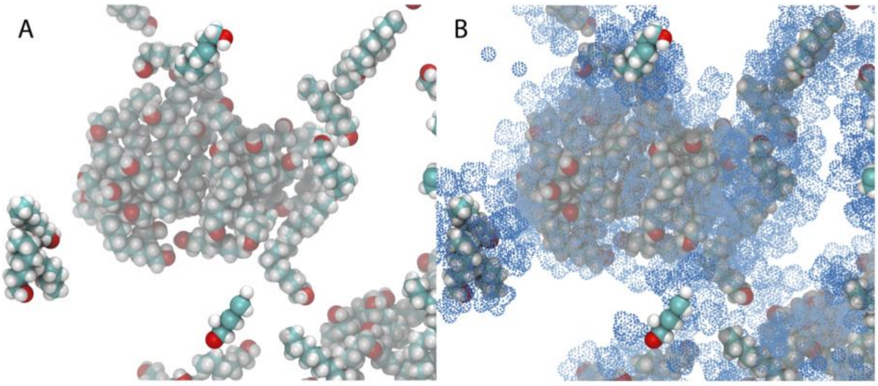

Figure 2: Snapshots given by molecular dynamics of the SFME made from octanol aggregates stabilized in water by a layer dense in ethanol, but not a surfactant monolayer. A: octanol only are drawn with van der Waals radii: a typical small micelle made of twenty molecules ; B: octanol and the ethanol molecules "bound" via long range interactions to an octanol-rich aggregate are shown : wit this representation,, the structure remembers the bicontinuous microemulsions1.

When water or some more immiscible liquid is added to a fluid containing pre-ouzo micellar aggregates, a phase separation occurs. The two phase separated have different Hansen parameters, and hence, have different solubilisation properties. Their interfacial tension is low (as shown on figure 3), but the phase remixing can be tuned. Since the two phase separating do not contain any extractant, surfactant and complexing agent, the route is open for radically... old processes for separation, purification and extraction of metal salts or non-electrolytes from biomass and agricultural residues. Moreover, weak aggregation also occurs in water-poor reverse micelles, in the form of weak aggregates. Those are structured upon the addition of trivalent salts. The knowledge of the two states of reverse micelles will be the source of radically new separation processes consuming less acids or solvents in the future2.

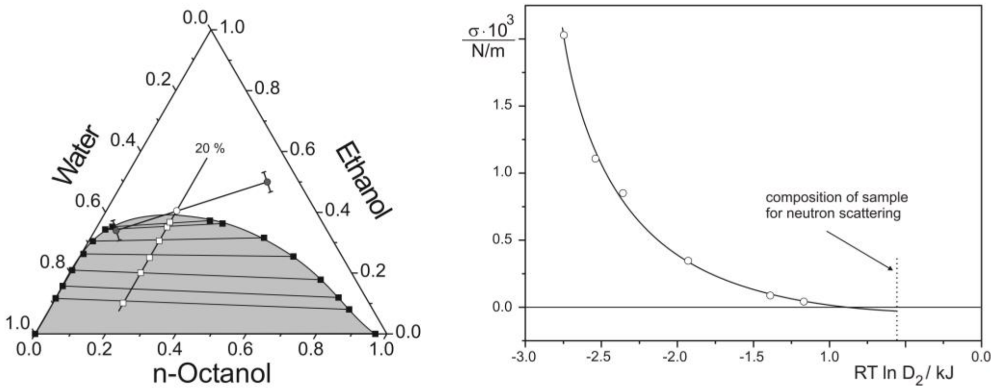

Figure 3: (left) : ternary phase diagram, the phase separation is shown in grey. The strongest pre-ouzo SFME structuration effect is obtained along the line containing 20% of octanol. The composition of the aggregates and the bulk pseudo-phase domains in the single-phase region is shown as black dots. (left): the surface tension between the two coexisting phases measured at the positions of the empty circles3

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[1] Schöttl S, Marcus J, Diat O, Touraud D, Kunz W, Zemb T and Horinek, D « **Emergence of Surfactant-Free Micelles from Ternary Solutions** ». Chemical Science (2014)

[2] Guilbaud P, Zemb T. « **Solute-induced microstructural transition from weak aggregates towards a curved film of surface-active extractants »**. Chemphyschem 2012;13:687–91.

[3] W.Kunz et al.; **« How to explain microemulsions formed by solvents mixtures without surfactants ",** submitted.

3 - Ion separation using supra-molecular self-assembled colloids

L'équipe est constituée actuellement de :
1 DR CNRS responsable d'équipe (Stéphane Pellet-Rostaing),
1 MDC UM2 (Guilhem Arrachart)
1 Ingénieur CEA/DSM (Sandrine Dourdain)
1 Technicienne CEA (Véronique Dubois)

Post-doctorants :

- Raphaël Turgis (ANR SILEXE, 2014-2016) : TSIL pour le recyclage de métaux stratégiques.
- Antoine Leydier (CEA/DEN, 2012-2014) : extraction de l'uranium en milieu phosphorique.
- Raphaël Turgis (LABEX Chemisyst, 2012-2014) : Recyclage des métaux stratégiques en IL.
- Fanny Mary (CEA/DEN, 2012-2013) : Ligands sélectifs des terres rares en milieu phosphorique, sulfurique et nitrique.
- Stéphanie Gracia (CEA/DEN, 2011-2013) : analogues du h4tpaen pour la séparation Am/Cm.
- Raphaël Turgis (CEA/DEN, 2010-2012) : extractants spécifiques de l'uranium.

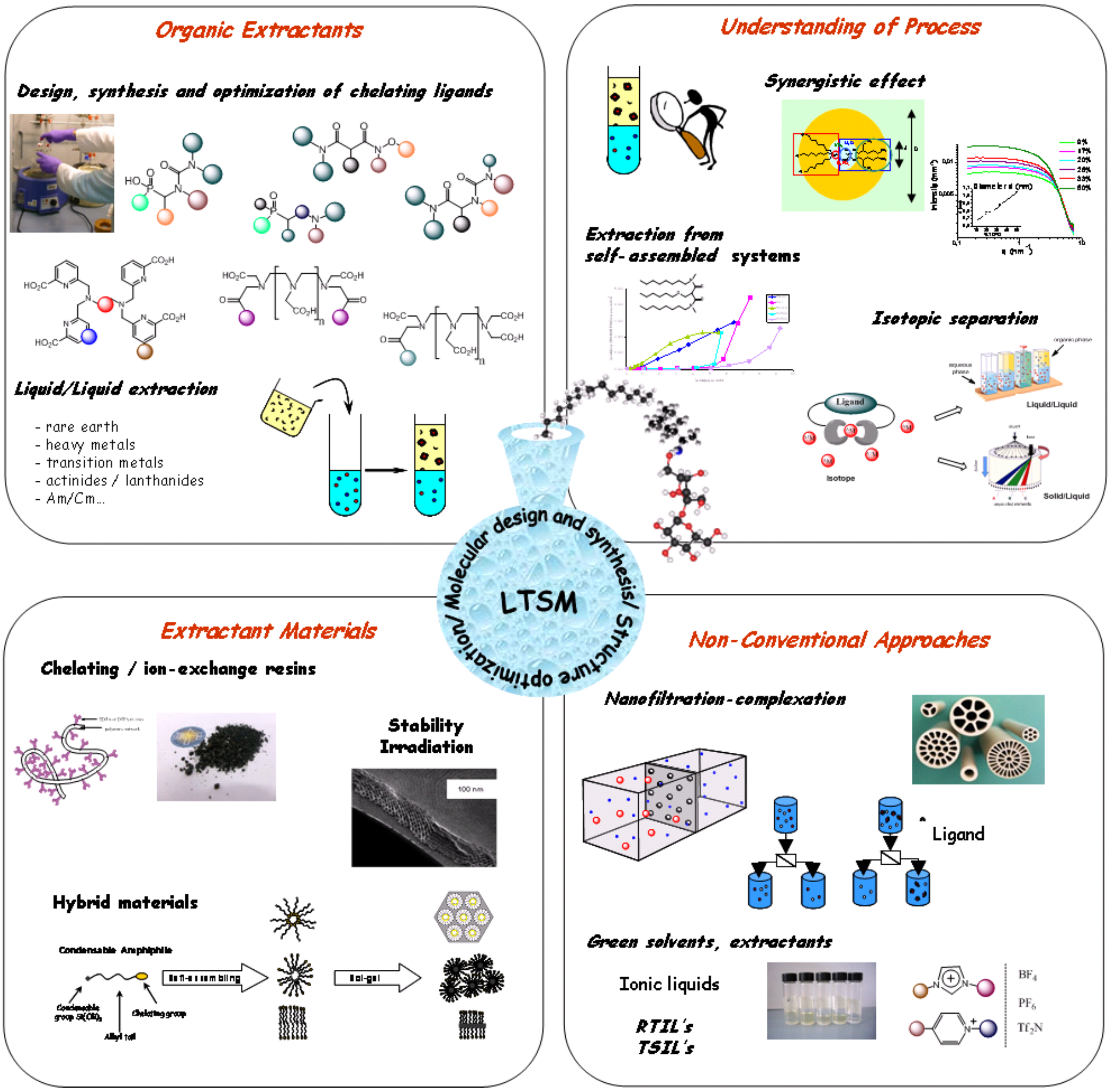
Thésards :

- Simon Chapron (CEA/DEN, 2011-2014) : analogues du TEDGA dans le procédé EXAm. (direction thèse)
- Olivia Pécheur (AREVA, 2011-2014) : mécanismes synergiques d'extraction de l'uranium.
- Marie Guillot (CIFRE FCBA, 2011-2014) : traitement de la biomasse en eau sous-critique (direction thèse).
- Romain Besnard (CEA/DSM, 2012-2015) : synthèse one-pot de matériaux extractants hybrides (direction Thèse).
- Moussa Touré (CEA/DEN, 2012-2015) : pertraction pour le recyclage de métaux stratégique (direction thèse).
- Donatien Gomez-Rodriguez (Carnot/Labex, collaboration ICSM/ICGM/IEM 2012-2015) : membranes organiques fonctionnalisées pour le recyclage des terres rares en phase aqueuse.
- Julien Rey (DEN/ERC, 2013-2016) : Synergisme et extraction sélective des terres rares (direction thèse).
- Moheddine Wehbi (Cèdre Franco-Libanais, 2013-2016) : méthodologies de synthèses de macrobicycles calixaréniques pour le recyclage et la décontamination (co-direction thèse).

Initiées depuis la création de l'institut, les différentes thématiques que développe l'équipe « Tri Ionique par des Systèmes Moléculaires Auto-assemblés » (LTSM) s'appuient au départ sur les compétences et le savoir-faire des chercheurs qui composaient l'équipe à sa création (Thomas Zemb et Christophe Déjugnat CR CNRS ayant muté au 01/2010), aidés d'une technicienne CEA (Mme Dubois, arrivée en 2009).
L'arrivée du Dr Stéphane Pellet-Rostaing (DR CNRS, mutation au 01/2009) comme nouveau responsable d'équipe, la nomination de Guilhem Arrachart au poste de Maître de Conférence UM2 et plus récemment de Sandrine Dourdain comme Ingénieur CEA/DSM affectés au LTSM ont permis à l'équipe d'initier concrètement des travaux de recherche dans le domaine de la synthèse de ligands et matériaux spécifiques pour la séparation d'ions, mis en œuvre dans des procédés d'extraction classiques (liquide/liquide,

solide/liquide) ou non conventionnels (membranes, liquides ioniques) avec une orientation dans la compréhension des mécanismes qui gouvernent la séparation.

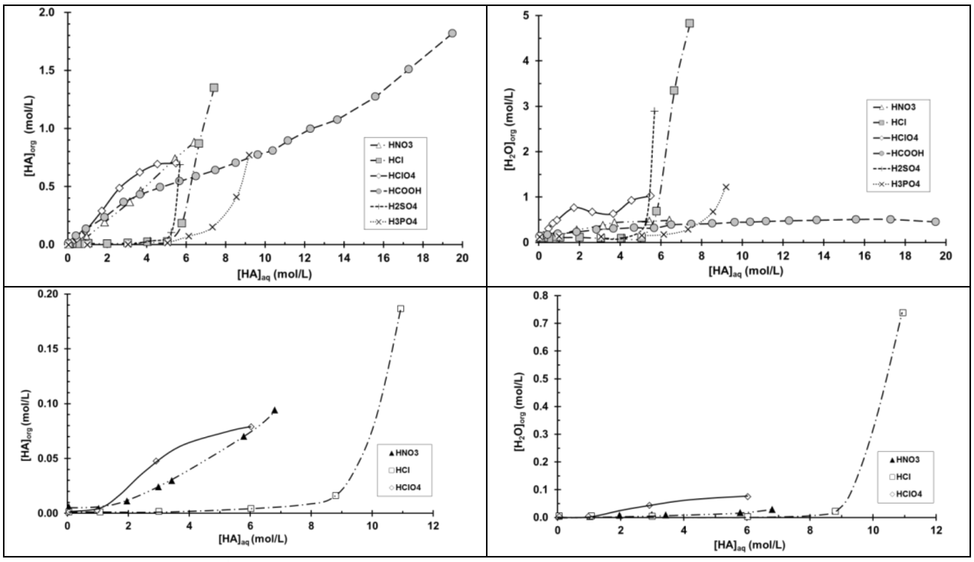
Dans les procédés associés au recyclage nucléaire ou non, lorsqu'un ion en solution est en équilibre à travers une interface avec une dispersion de complexants en conditions d'usage, la phase aqueuse, ainsi que la phase non-aqueuse sont des solutions loin de l'idéalité. Ce sont des systèmes moléculaires organisés : micelles, microémulsions, 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. Cet axe de recherche visant l'optimisation des procédés de tri ionique par l'élaboration et la synthèse d'extractant spécifiques originaux ainsi que par l'étude des mécanismes associés qui gouvernent la sélectivité, notamment par des phénomènes coopératifs supramoléculaires, est au cœur des missions du groupe LTSM. La possibilité d'exalter la complexation par auto-association des complexants sous forme de micelles, fibrilles ou cristaux liquides, doit être explorée, pouvant conduire à des procédés en rupture de tri ionique qui seront ensuite à développer en partenariat avec les équipes actuelles de Marcoule de R/D en ingénierie chimique. Au-delà du domaine purement nucléaire, ces effets sélectifs sont à étudier et à mettre 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.

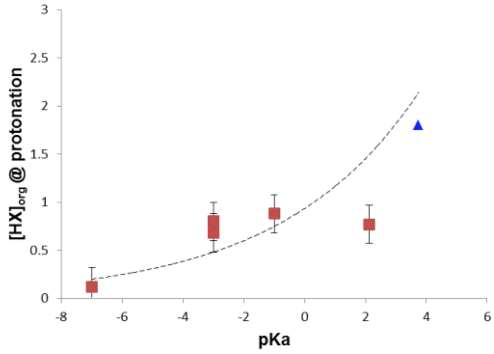


Liquid-liquid extraction of acids by a malonamide: I. Anion specific effects on the polar core microstructure of the aggregated malonamide

C. Déjugnat, L. Berthon, V. Dubois, Y. Meridiano, S. Dourdain, D. Guillaumont, S. Pellet-Rostaing, T. Zemb

In a solvent extraction process, the compositions of the phases in thermodynamic equilibrium (described as a Winsor-II regime) must be determined to obtain the extraction isotherms of ions as well as co-extracted water. By comparing the extractions of a series of acids by the malonamide DMDOHEMA (N,N'-dimethyl-N,N'-dioctyl hexylethoxy malonamide) in n-heptane, the specific anion effects regarding third phase formation and the strength of the acid-extractant interaction were investigated. It is shown that third phase formation is driven by hydration enthalpy of acid, while the polar core microstructure is controlled by the pKa of the acids. Upon acid extraction, the promotion of third phase formation follows the series $H_2SO_4 \approx H_3PO_4 \approx HClO_4 > HNO_3 > HCl > HCOOH$, which correlates to hydration enthalpy of acid in the case of monoacids. The combination of IR spectroscopy and DFT calculations revealed two different modes of acid extraction, either by hydrogen bonding (extraction of non-dissociated acid: HA) or by protonation of the extractant (extraction of dissociated acid: H+A−). The strength of the amide-acid interaction (protonation vs. hydrogen bonding) is correlated to the pKa of the acid and is responsible for the microstructure of the solution.[1]





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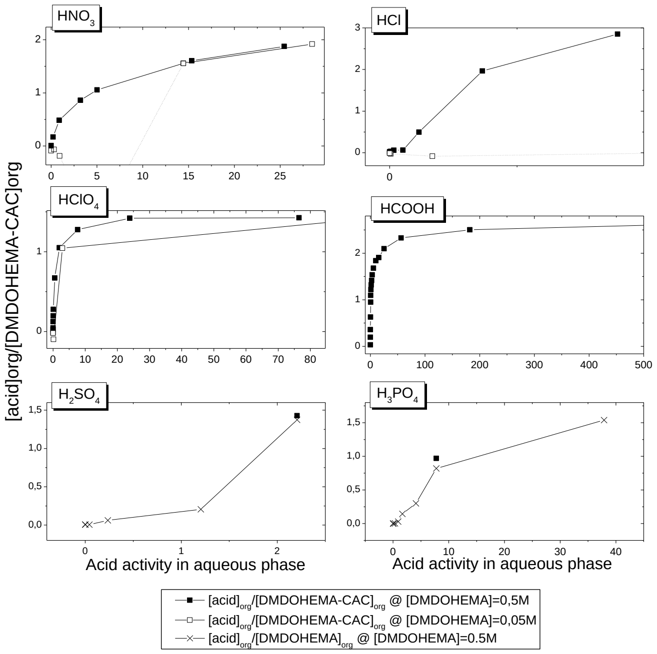
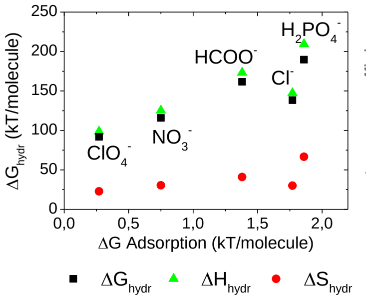
[1] C. Déjugnat, L. Berthon, V. Dubois, Y. Meridiano, S. Dourdain, D. Guillaumont, S. Pellet-Rostainq, T. Zemb, "**Liquid-liquid extraction of acids and water by a malonamide: I. Anion specific effects on the polar core microstructure of the aggregated malonamide**" Solvent Extraction and Ion Exchange, 32: 601–619, 2014.

Liquid-liquid extraction of acids by a malonamide: II- Anion specific effects in the aggregate-enhanced extraction isotherms

S. Dourdain, C. Déjugnat, L. Berthon, V. Dubois, S. Pellet-Rostainq, J.-F Dufrêche, T. Zemb

Non-electrostatic ion-specific effects are strong for anions when water is involved. We study here the thermodynamic equilibrium of a water-in-oil microemulsion stabilized by a surfaceactive extractant in aWinsor-II regime. Acid extraction isotherms for different anions located differently in the Hofmeister series have been investigated. A Langmuir like model was written for the specific case of acids treated as electrolytes, describing acid extraction as the adsorption of extracted electrolytes on the polar/apolar interface of the aggregates. Except for sulfate, isotherms can be described at first approximation as simple Langmuir-type isotherms when plotted as a function of the acid activity in the aqueous phase. The validity of the model being hence demonstrated, acid extraction free energies could be derived and compared, taking into account the effect of the anion position in the Hofmeister series. The case of phosphate, chloride, and sulfate as kosmotropes can be distinguished. They are significantly extracted, only above a threshold since the sphere-to-rod transition of the reverse aggregates has to be triggered by high chemical potential of the acid required to compensate anion dehydration.[1]





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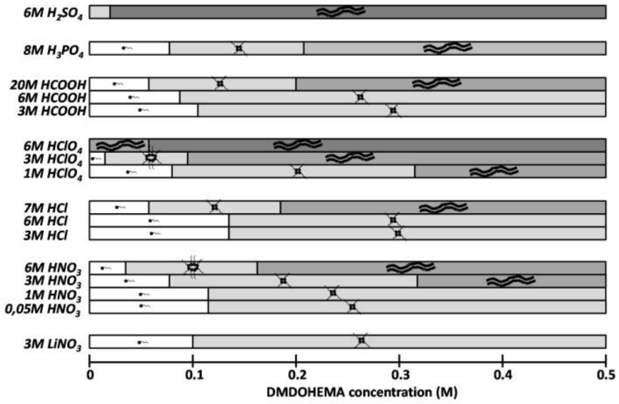
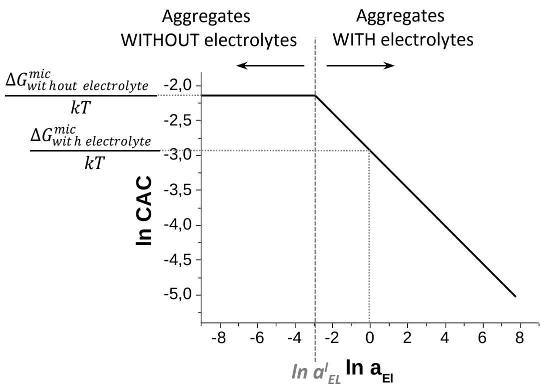
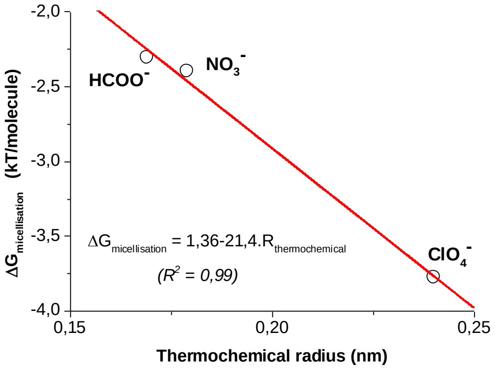
Reverse aggregate nucleation induced by acids in liquid-liquid extraction processes

C. Déjugnat, S. Dourdain, V. Dubois, L. Berthon, S. Pellet-Rostaing, J.-F Dufrêche, T. Zemb

We show in the case of N, N'-dimethyl-N, N'-dioctyl-2-(2(hexyloxy) ethyl)-malonamide (DMDOHEMA) chosen as a typical oil-soluble extractant with surface activity that the free energy of formation of reverse micelles in the solvent phase strongly depends on the presence of polar solutes. Free energies per molecule vary typically from 0 to 2 kT per molecule (5 kJ/mol), depending on the kosmotropic/chaotropic nature of the anion extracted. Variations of the reverse aggregation free energy introduced by acids and other co-extracted solutes as deduced from the critical aggregation concentrations cannot be neglected while modelling extraction. With typical aggregation numbers of 4-6, the free energy of formation of one reverse aggregate varies up to 20 kJ/mol, which is four times the typical difference in free energy of one single cation transfer between a "target" and a non-target ion in practical extraction and stripping industrial processes.[1]







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[1] Dejugnat, C., Dourdain, S., Dubois, V., Berthon, L., Pellet-Rostaing, S., Dufreche, J. F., & Zemb, T. "**Reverse aggregate nucleation induced by acids in liquid-liquid extraction processes**" (2014). Physical Chemistry Chemical Physics, 16(16), 7339-7349

Synergistic mechanisms for uranium extraction from phosphoric ores

O.Pecheur, S.Dourdain, D.Guillaumont, F.Testard, G. Arrachart, R. Turgis, J.-F Dufrêche,
S. Pellet-Rostaing, T. Zemb

Phosphate rocks, mainly mined for the production of fertilizers and phosphoric acid, are also known to contain uranium in a small proportion. An estimation leads to a concentration between 50 and 250 ppm which represents 9.10^6 tons of uranium considering the worldwide reserve of phosphate ores.

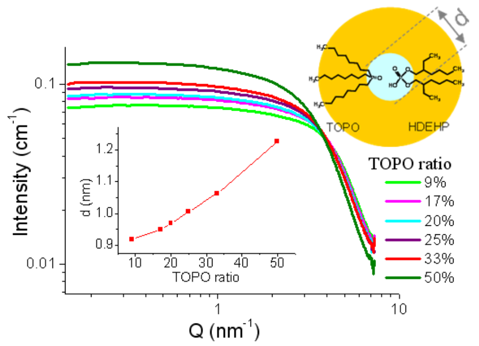
The URPHOS process has been designed in the 80's to recover uranium from phosphoric ores. It uses two organic extractants: TOPO (Tri-n-octylphosphine oxide) and HDEHP (Bis(2-ethylhexyl) hydrogen phosphate) extracting in synergism: the effect of the two molecules used simultaneously is greater that the sum of the effects of the two molecules used separately. But this process has two main disadvantages:

- the distribution coefficient of uranium is too small for only one cycle
- the selectivity of uranium versus iron is too weak

To optimize the process, new extractant systems have to be designed but the synergistic mechanisms are still not completely understood. In this work we investigate URPHOS process using new approaches in order to develop a better comprehension of synergistic systems.

Two different scales are considered:

- the supramolecular scale: the species formed by HDEHP, TOPO and the cations are considered as small aggregates with peculiar properties: CAC (Critical Aggregation Concentration), number of aggregation, …etc. These properties have been investigated with neutron (SANS) and X-ray scattering (SAXS) and related to extractant properties
- the molecular scale: the molecular structures of uranyl and iron complexes inside the aggregates are investigated through spectroscopic and theoretical studies. The theoretical part consists in modeling the complexes and the aggregates and the experimental part consists in acquiring data to probe the structures of the complexes.



SAXS data: aggregation of TOPO/HDEHP. The bottom inset shows the deduced aggregate diameter.

This approach was also applied to understand the extraction properties of a bifunctional extractant molecule which was designed from the combination of HDEHP and TOPO to improve the URPHOS process[1].

Further on, the solvent effect on synergism has been studied and brought new insight on the synergistic mechanisms on the HDEHP/TOPO system.

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[1] S. Dourdain, I. Hofmeister, O. Pecheur, J.-F. Dufrêche, R. Turgis, A. Leydier, J. Jestin, F. Testard, S. Pellet-Rostaing and T. Zemb, Langmuir 28(31), 2012, pp 11319-11328[1]

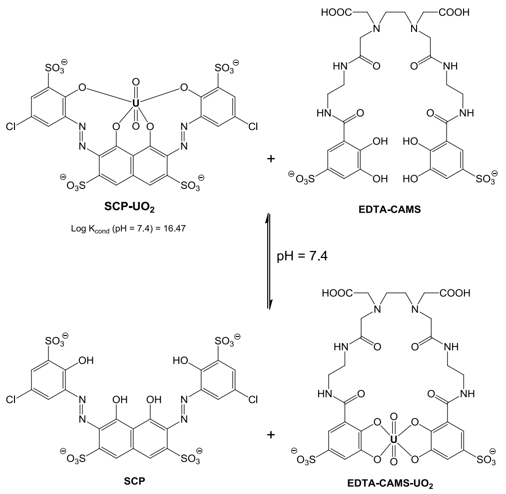
Sequestering agents for uranyl decorporation

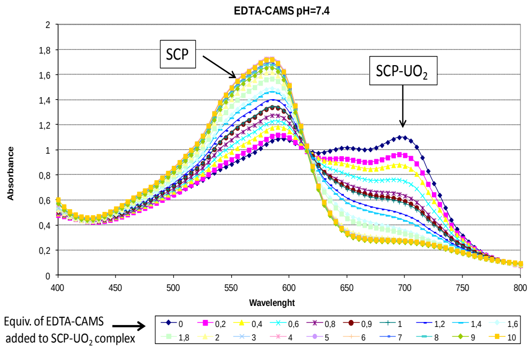
S. Pellet-Rostaing, G. Arrachart, R. Turgis
A. Leydier (CEA DRCP)
Y. Lin, A. Favre-Reguillon, M. Lemaire (Université Claude Bernard Lyon 1)
D. Lecerclé, F. Taran (CEA Saclay)

At each step of the fuel cycle: extraction, concentration, purification, enrichment or recycling, workers can be subjected to uranium contamination. Accidental internal contamination by inhalation or through skin lesions is the major risk for workers, whether acute and/or repeated. The hexavalent uranyl ion (UO_2^{2+}, U(VI)) was found to be the most stable form *in vivo* and is complexed in the blood by chelating agents such as proteins or carbonates. Inside the body, uranium creates risks both as a toxic heavy metal and as radioactive material in the case of chronic exposition. After contamination it is rapidly transferred through the blood stream to deep organs, such as kidneys and bones that assimilate it strongly. To avoid these effects, heavy metals must be eliminated from the body by administrating non toxic chelating agents.

Most efficient uranophile chelating functions are oxygen-containing ligands like multidentate sulfocatecholamides (CAMS),[1] hydroxylpyridones (HOPO),[2] carbamoylmethylphosphine oxide (CMPO),[3] calixarene derivatives [4] or bisphosphonate sequestering agents.[5]

Recently, we focused our attention on the preparation of new chelating agents based on EDTA and DTPA skeletons as potential sequestering agents for uranyl chelation. In order to increase the affinity regarding uranyl ion, we designed and synthesized a series of modified water-soluble EDTA and DTPA using various substituted amines.[6] A series of 16 ligands were synthesized and their binding abilities towards uranium were investigated using UV spectrophotometry (competitive uranium binding with sulfochlorophenol - SCP) in aqueous media under physiological pH (close to neutral) as well as under acidic and basic conditions. In regard to decorporation applications the best uranophile ligand was found to be the EDTA-CAMS, which exhibits significant association constants under the range of pH studied. Further investigation before a possible evaluation of their in vivo efficiency will be necessary.





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[3] F. Sansone, M. Galletta, E. Macerata, E. Trivellone, M. Giola, R. Ungaro, V. Böhmer, A. Casnati, M. Mariani, *Radiochim. Acta* 2008, 96, 235.

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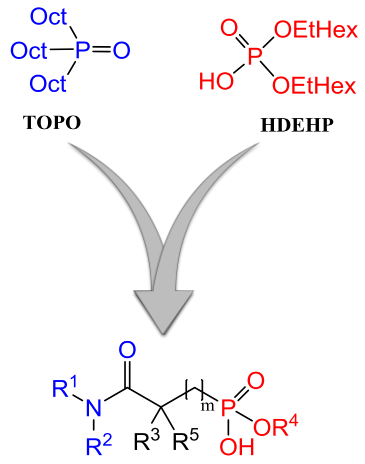
Synthesis of new molecules for the extraction of uranium from phosphates

Raphael Turgis, Guilhem Arrachart, Stéphane Pellet-Rostaing,
Antoine Leydier, Gilles Bernier, Manuel Miguirditchian (CEA DRCP)

Phosphate rocks represent a suitable alternative source for uranium production from sources other than uranium ore. Numerous teams has focused their research on the extraction of U from the phosphoric media and industrial unities has been created in the 80s with a process based on the extraction of U(VI) using a synergic system such as the URPHOS process which consists in a mix of Bis(2-ethylhexyl) phosphate (HDEHP) with trioctylphosphine oxide (TOPO). However, the extraction coefficients of U are not high enough to propose an extraction purification process in one step. Moreover, this system extracts also the iron which forms non soluble precipitates during the back extraction process. The use of a single molecule that combines the properties of the two functions of the synergistic mixture is of interest not only to simplify the process but also to potentially enhance the distribution coefficients and selectivities.

We developed a high yielding synthesis of bifunctional extractants carrying an amide group and a phosphoric acid group. Such ligands possess and mimic the two properties of the two components of the HDEHP/TOPO synergistic mixture in one entity. The phoshonic acid group acts as the cationic exchanger similar to HDEHP and the amide moiety can be considered as a donor - solvating group similar to the TOPO in the synergistic system.

These new bifunctional ligands were found to extract selectively hexavalent uranium U(VI) with high distribution coefficient (D) and selectivity towards iron Fe (III) in 5 M phosphoric acid solution. From a structure-activity approach a specific ligand called DEHCNPB has been put forward in regards to the outstanding results obtained for the selective extraction, and quantitative recovery of uranium compared to the URPHOS reference system. Investigations have been carried out in order to emphasize the properties of this ligand: acid extraction, ligand, acid and uranium concentration dependency.[1]



Molecular design and influence on extraction efficiency:

- length and ramifications of alkyl chains on amid group (R^1 and R^2)
- spacer length and degree of steric hindrance on the spacer (m, R^3 and R^5)
- length of alkyl chain of free phosphonic acid functions (R^4)

	[U] initial (mg/L)	[Fe] initial (mg/L)	D_U	$SF_{U/Fe}$
HDEHP/TOPO (4/1) 0.25 M	**250**	**2500**	**4**	**200**
DEHCNPB 0.25 M	**250**	**2500**	**120**	**>2000**

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R. Turgis A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguirditchian, S. Pellet-Rostaing "**Uranium extraction from phosphoric acid using bifunctional amido-phosphonic acid ligands" Solvent Extraction and Ion Exchange**, **2014**, 32(5), 478.

R. Turgis A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguirditchian, S. Pellet-Rostaing "**Carbamoylalkylphosphonates for dramatic enhancement of uranium extraction from phosphates ores**" Solvent Extraction and Ion Exchange, **2014**, in press.

Actinides (III) / Lanthanides (III) separation by aqueous extracting agents

S. Gracia, S. Chapron, G. Arrachart, S. Pellet-Rostaing
C. Marie, M.Miguirditchian (CEA DRCP)

The framework of the 2006 French Waste Management Act has defined several strategies to totally or partially recycle minor actinides from spent nuclear fuels. Among them the recovery of minor actinides such as americium alone is one of the options investigated. For this purpose the EXAm process has been developed by the CEA in order to recover americium alone contained in the PUREX raffinate.

In such process, the americium is firstly extracted in the organic phase together with some light lanthanides, while curium and other lanthanides remain in the aqueous phase.

In an additional stage the Am is subsequently selectively back extracted from the light lanthanides.

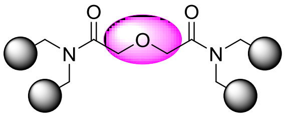
Selective back-extraction and the concept of selectively retaining ions in an aqueous phase during a solvent extraction process has been shown to hold great promise in processes for An(III)/Ln(III).

The goal of the work is to develop aqueous extracting agents or hold-back agents which can be used to improve the selectivity of extraction solvents in the both main step of the EXAm process.

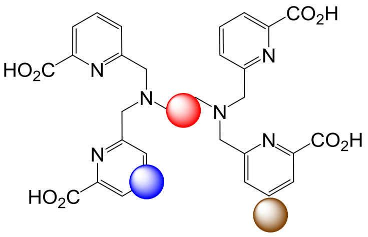
In the first step of the process (extraction/scrubbing) a complexing agent TEDGA (N,N,N',N'-tetraethyl-diglycolamide) is added in the aqueous phase to increase Am/Cm and Am/heavy Ln selectivity. Several diglycolamides analogues of TEDGA were synthesized in order to evaluate the impact of the amidic alkyl chains (length and steric hindrance) and the diglycolamide skeleton on the Am/Cm selectivity.[1]

In the final step of the process (Am stripping), the Am is selectively stripped from light lanthanides using a weakly acidic aqueous phase containing a polyaminocarboxylic acid (HEDTA or DTPA). It has been demonstrated that the use of dipicolinic or picolinic moieties attached to a suitable linker on a pre-organized chemical structure (h4tpaen) improves the An(III) and Ln(III) extraction.[2]

In order to improve the solubility and selectivity of such ligands a recent study has been initiated focused on the synthesis of new ligands and their characterization in regards to the actinides (III) / lanthanides (III) separation.[3]



Diglycolamides derivatives for the Am/Cm separation



H4tpaen derivatives for the Am/Ln separation

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[1] S. Chapron, C. Marie, G. Arrachart, M. Miguirditchian, S. Pellet-Rostaing **"Synthesis and evaluation of new diglycolamides for the Americium/Curium separation by liquid-liquid extraction"** Solvent Extraction & Ion Exchange 2014, submitted.
S. Chapron Ph-D 2011-2014.

[2] X. Heres, F. Burdet, J. Borrini, M.-T. Duchesne, M. Mazzanti, G. Bernier, S. Pellet-Rostaing, A. Favre-Reguillon, M. Lemaire, **"Process for separating americium from other metallic elements present in an acidic aqueous or organic phase and applications thereof"** PCT WO 201269573 - FR2968014.
J. Borrini, A. Favre-Reguillon, M. Lemaire, S. Gracia, G. Arrachart, G. Bernier, S. Pellet-Rostaing, **"Water soluble PDCA derivatives for selective Ln(III)/An(III) and Am(III)/Cm(III) separation"** Solvent Extraction & Ion Exchange 2014, submitted.

[3] S. Gracia, S. Chapron, G. Arrachart, C. Marie, M. Miguirditchian, S. Pellet-Rostaing **"Extraction - separation of Am (III) with water soluble H4tpaen derivatives"** Solvent Extraction & Ion Exchange 2014, submitted.

Extraction process for selectively recovery of tantalum and niobium from aqueous acidic solution by 4-methylacetophenone[1]

R. Turgis, *G. Arrachart*, *M. Toure*, *J. Duhamet* *(CEA/DTEC)*, *S. Pellet-Rostaing*

In June 2010, the European Commission at the end of a work of experts, made a list of strategic metals including tantalum and niobium. In fact, tantalum has become in recent years a highly sought metal for its high corrosion resistance. It is mainly used in the form of powders or wire for electronic capacitor (Fig. 1) production particularly for mobile electronics (cell phones, laptops, tablets, etc ...). Niobium, although less popular than tantalum, nevertheless represents an essential metal for some industries. Indeed, it used in the manufacture of alloys for the aerospace industry, nuclear industry, and petrochemicals. So to secure the supply of metals such critical, and respond to a need recycling industrial and urban waste containing them it would be desirable to have a robust process. In this framework, the liquid-liquid extraction is conventionally used, but solvents present certain disadvantages. In fact, the MIBK which is most used in the world, has a high solubility in water(1.7 to 2.2% w/w), high volatility and low flash point (14 ° C).

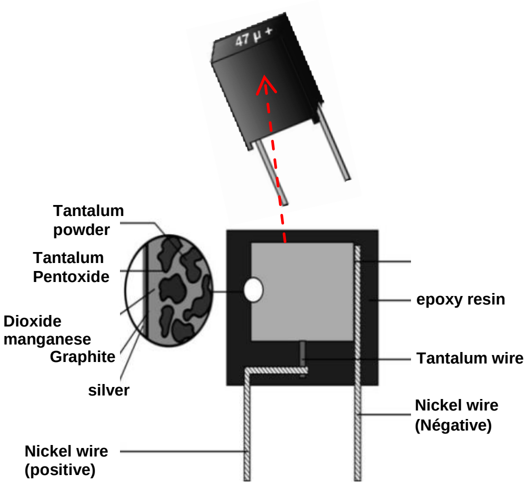

Figure 1: *Tantalum capacitor with solid electrolyte from FIRADEC.*

In security terms, the use of mixers and pumps may create electrostatic charges and sparks in plant and explosions may ensue. However, in the context of this project, the 4-methylacetophenone, which has a very low water solubility (<0.2 % w/w), a relatively high flash point (85.1 °C), moderate viscosity (1.88 mP.s) which varies little in the presence of metal cations, and, in addition, is stable in the presence of strong acids, is able to co-extract the tantalum and niobium from an acidic aqueous phase and selectively extract tantalum from model waste of a capacitor (Figures 2, 3). Finally, the process scheme (Figure 4) below, not only allows the selective extraction of tantalum and niobium but also recycling of the 4-methylacetophenone by back-extraction and washing.

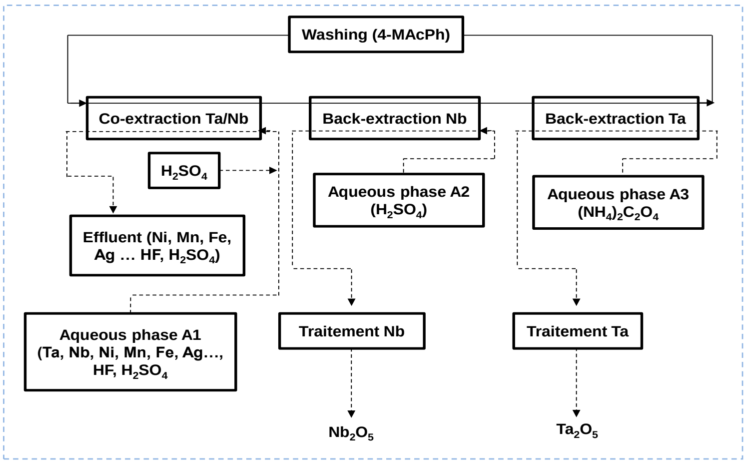

Figure 4 : process scheme

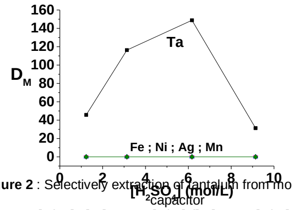

Figure 2 : Selectively extraction of tantalum from model waste of a capacitor

[Ta] = [0,19– 0,1] g/L, [Fe] = [0,19 – 0,1] g/L, [Ni] = [0,2 – 0,1] g/L, [Ag] = [0,19 – 0,1] g/L, [Mn] = [0,2 – 0,1] g/L et O/A =1.

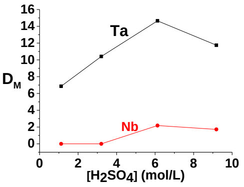

Figure 3 : Selectively extraction of tantalum and niobium from mineral model

[Ta] = [1,85 – 1, 59] g/L,
[Nb] = [2,14 – 1,63] g/L et O/A =1.

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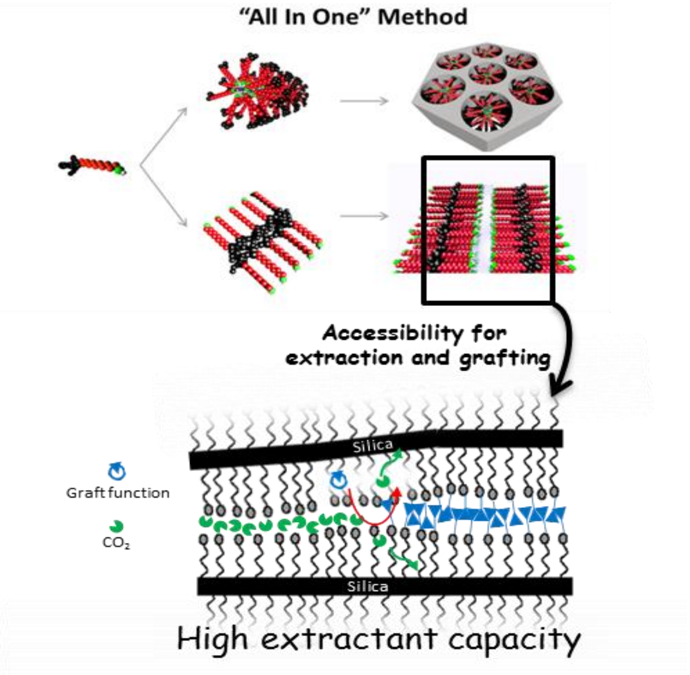
[1] « Procédé d'extraction du Tantale et/ou du Niobium d'une phase aqueuse acide et procédé de récupération du Tantale et/ou du Niobium à partir d'une phase aqueuse acide mettant en œuvre ce procédé d'extraction » S. Pellet-Rostaing, J. Duhamet, M. Tourré, R. Turgis, G. Arrachart CEA/CNRS/UM2, FR 14 55539 du **17 juin 2014**

Development of a methodology for the synthesis of hybrid silica with high extractant capacity

R. Besnard, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing

The sol-gel process is a convenient method for the preparation of hybrid organic-inorganic materials which are widely used in many applications including solid-liquid extraction.
The ability to control the structure of the materials on the nanoscale is of great interest for the design and the improvement of material properties.
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 obtained with conventional approaches.
Nanoporous silica-based materials with a densely functionalized surface have recently been prepared from condensable amphiphile molecules. Based on their amphiphilic properties, such organosilica precursors could be hydrolyzed to spontaneously give structured materials without requiring further addition of external surfactant.
The aim of this work was to develop a suitable "all-in-one" approach using condensable surfactant precursor either for preparation of hybrid materials or functionalization of the channel walls of mesoporous silica. Recently, we described the self-assembly of a simple amine (amino-undecyl-triethoxysilane) as a model, leading to hybrid organic-inorganic materials of hexagonal and lamellar structure.[1] The project aims at the study of phenomena that influence the self-associative properties of amphiphilic molecules in the controlled preparation of mesoporous materials and nanoparticles with specific chelating properties.
The characterizations of such materials highlight a very high extractant capacity without any degradation of the structure.

This study presents a very promising result for hybrids materials used for solid-liquid extraction. The method was extended on similar amphiphilic precursors with different functional groups which modify the amphiphilic behavior and the final structure.



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[1] R. Besnard, J. Cambedouzou, G. Arrachart, O. Diat, S. Pellet-Rostaing, "**Self-Assembly of Condensable "Bola-Amphiphiles" in Water/Tetraethoxysilane Mixtures for the Elaboration of Mesostructured Hybrid Materials**", *Langmuir,* **2013**, 29, 10368-10375.

“Superchelating resins” for remediation, extraction and recycling of strategic metals

G. Arrachart, *S. Pellet-Rostaing*

Extraction of specific targeted species (rare earth, heavy metals, transition metals, radionuclides) from industrial and nuclear effluents is an important issue in the recycling and / or decontamination processes**.** Selective complexation and ion exchange of a targeted metal ion are mainly based on liquid/liquid extraction, solid/liquid extraction, association of nanofiltration / complexation, and ion-exchange processes.

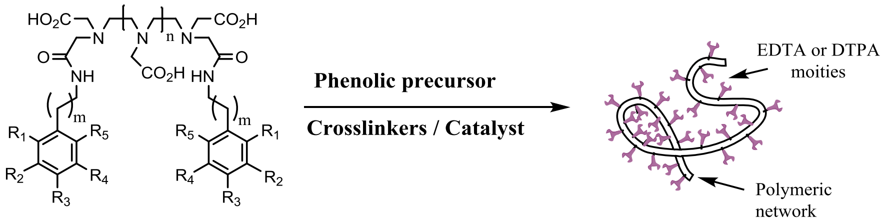
Selective complexation and ion exchange for the removal and recovery of a targeted metal ion by a given polymeric reagent is an important objective for many applications such as water treatment or extraction of strategic metals. Ion-exchange resins have a wide application in industry and in environmental remediation. Separation procedures employing such resins are frequently made more selective by the addition of complexing agents during sorption or elution. Metal-specific ligands incorporate in the structure of the resin itself is an interesting way to perform ion separation taking the advantage of the selectivity of chelating agents.

The aims of this project are the synthesis of chelating original systems and the preparation of specific ion exchange resins. The ligands are used to form polymers by condensation with a crosslinking agent (formaldehyde, acetaldehyde…) and optionally with various phenolic precursors such as phenol, catechol or resorcinol.

Ion-exchange phenolic resins based on EDTA or DTPA moieties have been synthesized and evaluated for the co-extraction of Cs^+ and Sr^{2+} radionuclides for wastewater treatment. [1] The formo-phenolic-like resins have both ion-exchange and chelating groups in their structure. These synthesized resins were able to separate the above mentioned radionuclides from other cations, indicating that these resins were indeed efficient in the remediation of Cs^+ and Sr^{2+}, even in salted aqueous solutions.

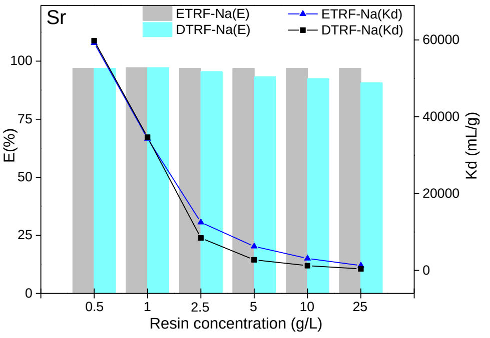
The design of formo-phenolic-like resins bearing various different functional groups are under investigation in regards to specific strategic metals.

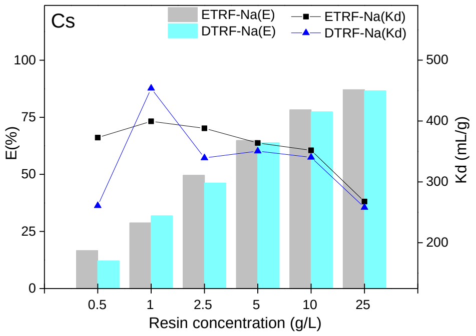
Chelating formo-phenolic-like resins



Chelating precursor
EDTA- and DTPA-modified ligands

Solid-Liquid Extraction
Remediation of Sr^{2+} and Cs^+





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[1] S. Pellet-Rostaing, G. Arrachart, A. Kenaan, S. Gracia, R. Turgis, V. Dubois, “**Ion-exchange resin with chelating properties, its method of preparation and its uses**” PCT WO 2014 086788 - FR 2998816.

Origin of the phase behaviour and limits of concentrations in water-poor reverse micelles in polyphasic equilibrium

C. Bauer, S. Dourdain, O. Diat, M. Duvail, S. Pellet-Rostaing, Th. Zemb,
Collaboration F. Testard (LIONS/IRAMIS-Saclay)

Recycling chemistry of metals and oxides relies on three steps: dissolution, separation, and material reformation. Modern colloidal approach of the transfer of ions between two complex fluids is at the basis of the liquid-liquid extraction technology. This approach allows for rationalizing in an unified model transformations such as accidently splitting from two to three phases, or uncontrolled viscosity variations, as linked to the transformation in the phase diagram due to ion transfer. Moreover, differences in free energies associated to ion transfer between phases that are the origin of the selectivity need to be considered at the meso-scale beyond parameterization of an arbitrary number of competing “complexes”. Entropy and electrostatics are taken into account in relation to solvent formulation. By analogy with electronics dealing about electrons transported in conductors and semi-conductors, this “ienaic” 1 approach deals with ions in transported between nanostructures present in colloidal fluids under the influence of chemical potential gradients between nanostructures coexisting in colloidal fluids..

To understand and therefore predict the behaviour of any liquid-liquid extracting system, the aspects must be considered simultaneously:

A. the location of the water-solvent equilibrium in a pseudo-ternary phase diagram. The knowledge of this phase diagram allows to identify the physical origin of the safety limits in composition used in engineering experiment plan to delimitate safe compositions for plant operation.

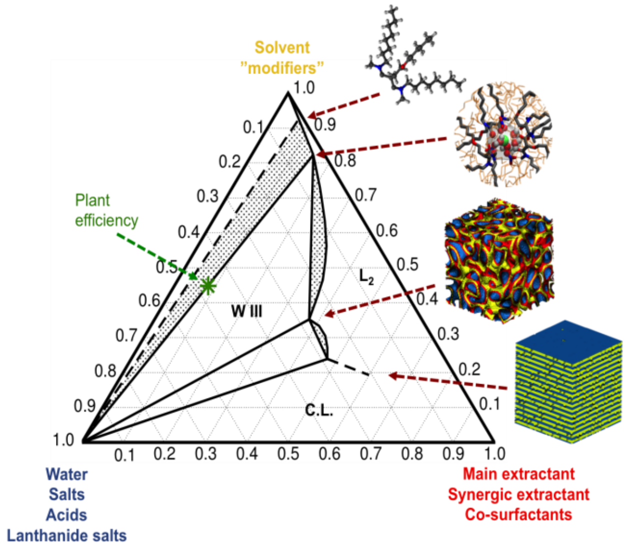

Figure 1: *The isothermal generic phase triangle: water, solvent and an oil-soluble “poor “surfactant. In the dilute region, solute monomers in oil are dominant; at higher concentration, reverse aggregates are the most frequent form of association. Increasing the concentrations, bi-continuous polar/apolar domain networks with preferential curvatures are formed. The two-phase domain used in hydrometallurgy is connected to the water corner of the phase diagram. The one on the left is only rarely used in practice, since the multi-phase samples in that domain are extremely viscous and phases do not separate easily Domains in the phase diagram close to the three-phase body and efficient for liquid-liquid formulation in industrial plant feed is indicated by the green arrow. Two phase domains are represented with light blue backgrounds*[2].

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[1] *Ienaics*: By similarity with electronics, “ieanics” is derived from the Greek root “ιεναε”, i.e. the object that is moving, ienaics is the science of controlled transfer of hydrated ions and other charged colloidal aggregatesbetween coexisting complex fluids. Ienaics is the science at the basis of separation processes used in processes designed for recycling of electrolytes, such as metal salts,. In this review, we focus on salts of rare earths.

[2] Bauer C, Bauduin P, Dufreche JF, Zemb T, Diat O. « **Liquid/liquid metal extraction: Phase diagram topology resulting from molecular interactions between extractant, ion, oil and water** ». Eur Phys J Spec Top 2012;213:225–41.

B. The double difference in chemical potential that is at the origin of selectivity as shown in figure 2.

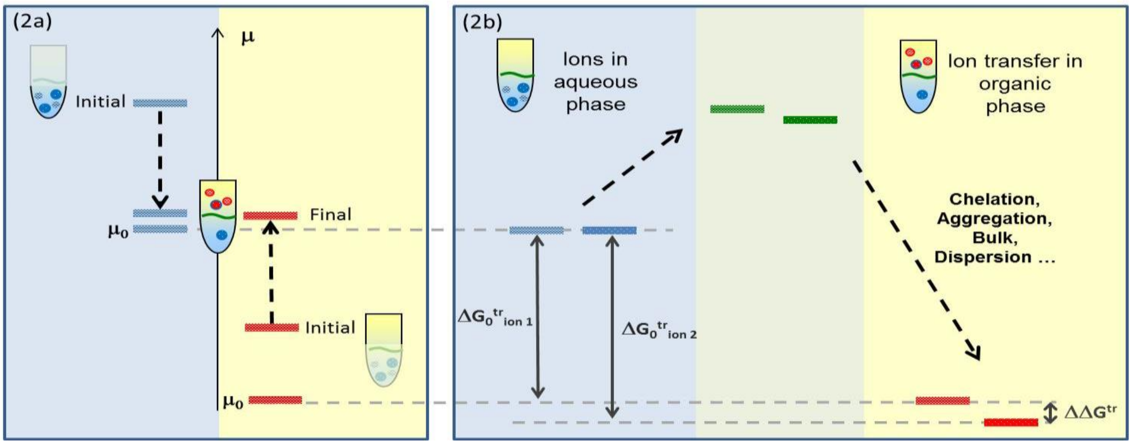

***Figure 2**: (a) Evolution of the chemical potentials of ion pairs during a water-solvent extraction. The reference chemical potential of an ion complexed in water and an ion complexed in reverse aggregates are shown. Initial state is all ions to be extracted in water: in the final state; ions have been extracted and the tranbsfer ends when the chemical potential is equal in coexisting phases. Enrichment of extracted species is understood as differences in the reference potentials in water and solvent, favouring the solvent phase (lower level on the yellow part of diagram (b) The origin of selectivity ($\Delta\Delta G^{tr}$) between ion 1 and ion 2 (considering common anion): the reference standard chemical potential levels of salt (ion pairs) compared in the water phase (blue background) and in the solvent phase (yellow background). The step in free energy per ion pair extracted from aqueous to solvent phase is $\Delta G_{transfer}$ for ion 1 and 2, respectively. The selectivity between ion 1 and 2 at thermodynamic equilibrium is the double difference between the two steps, i.e., $\Delta\Delta G^{tr}$. The kinetics of ion transfer in transient states may be influenced by an intermediary activated state (green energy level), i.e., when the species to be extracted (or not) interact via dehydration and adsorption with the monolayer at the macroscopic interface shown in green in figure 1.*

C. The free energy of formation of aggregates, as they are nucleated by extracted species, as well as the interaction between aggregates under Brownian motion in the solvent phase: understanding this behaviour allows to avoid third phase formation as well as unexpected divergences in viscosity, as shown in figure 3[1].

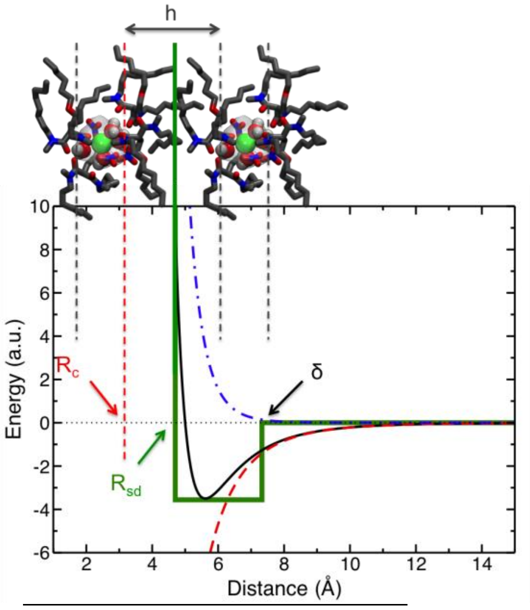

***Figure 3**: An example of net interaction potential between w/o aggregates. Pictures shown at the top of the figure are coming from molecular modelling of aggregates. A hard polar core is made of extracted molecules and surfactant head-groups. Protruding chains wet by penetrating solvent produce steric stabilisation are shown schematically in the blue dotted line. The van der Waals attraction between the polar cores is shown in red. These functions cannot yet be measured independently: however, the net potential taken as a step delta function for sticky hard sphere is measured via the structure factor and is typically of the order of 1-2 k_BT.*

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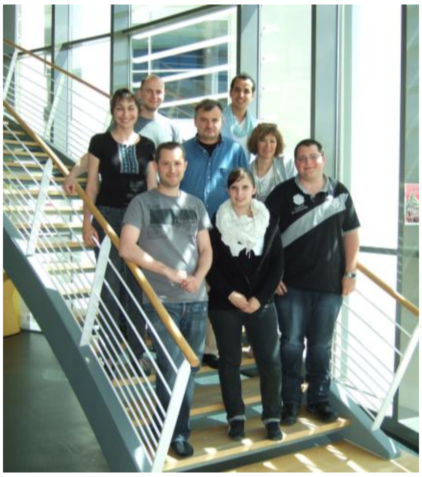
[1] Thomas Zemb , Caroline Bauer, Pierre Bauduin, Luc Belloni , Christophe Déjugnat, Olivier Diat, Véronique Dubois, Jean-François Dufrêche, Sandrine Dourdain, Magali Duvail, Chantal Larpent , Fabienne Testard and Stéphane Pellet-Rostaing: **Recycling metals by controlled transfer of ionic species between complex fluids: en route to "ienaics"** .Colloid and Polymer science (2014) in press.

4 - Sonochemistry in Complex Fluids

Sergueï Nikitenko (CNRS)
Rachel Pflieger (CEA/DEN)
Tony Chave (CNRS)
Matthieu Virot (CEA/DEN depuis avril 2012)

Julia Schneider : L'étude de SBSL et de MBSL (thésarde, MPI Potsdam / ICSM) soutenance 04/2012
Matthieu Virot : Cavitation à l'interface solide/liquide (post doc CEA/DEN 2010- 2011 et CNRS 2011-2012)
Nathalie Navarro : Dégradation sonocatalytiques de polluants organiques (thésarde, CEA/DEN/DRCP/AREVA – ICSM) soutenance 11/2012
Abdoul Aziz Ndiaye : Spectroscopie de sonoluminescence (post doc ANR NEQSON) 04/2011 – 03/2013
Camille Cau : Synthèse sonochimique de nanocatalyseurs (thésarde, codirection ICGM/CMOS – ICSM, ANR NEQSON) soutenance 11/2013
Xavier Beaudoux : Dissolution sonochimique d'oxydes des actinides et des lanthanides (thésard, codirection CEA/DEN/DRCP-ICSM) depuis 01/2012
Vincent Morosini : Colloïdes de plutonium (post doc CEA/DEN) 06/2012- 05/2014
Temim Ouerhani : Spectroscopie de sonoluminescence (thésard, UM2 – ICSM) depuis novembre 2013
Elodie Dalodière : Colloïdes des actinides (depuis Octobre 2014, codirection ICSM-CEA/DEN)
Andrés Salazar: Synthèse de nanomatériaux (depuis Octobre 2014, Erasmus Mundus – ICG/IEM/ICSM - University of Messina – University of Delft)
Florence Nouaille: Sonochimie d'uranium (depuis Fevrier 2014, BDI CNRS-AREVA, co-direction ICSM- University of Lille)



Domaines de recherches

(i) Sonoluminescence dans les fluides complexes

(ii) Cavitation à l'interface solide-liquide

(iii) Synthèse sonochimique de nanocatalyseurs et sonocatalyse

(iv) Sonochimie des actinides

Projets (partenaires)

- Sonoluminescence dans les fluides complexes (LCME, Chambéry ; Université de Melbourne, Australie ; LEA SONO avec MPI Potsdam, Allemagne, jusqu'en avril 2012 ; DPI Göttingen, Allemagne)
- ANR-2010-BLAN-0810 NEQSON "Sonochimie en conditions hors équilibre" (ICG/CMOS/UM II, CEA/DEN)
- Dissolution sonochimique des oxydes d'actinides (CEA/DEN, AREVA)
- Dégradation sonochimique des composés organiques (CEA/DEN, AREVA)
- Sonochimie d'uranium (Comurhex/AREVA, PARIS)
- Sonochimie du plutonium (CEA/DEN, NEEDS)
- Colloïdes de plutonium(IV) (CEA/DEN, TALISMAN)

Study of the nonequilibrium plasma formed during ultrasonic cavitation in water

A.A. Ndiaye, R. Pflieger, B. Siboulet, J. Molina, J.-F. Dufrêche, S.I. Nikitenko

Sonoluminescence 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° and HO° 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 sonoluminescence spectrum by means of a spectrograph coupled to a CCD camera.

The sonoluminescence (SL) spectra of OH ($A^2\Sigma^+$) excited state produced during the sonolysis of water sparged with argon were measured and analyzed at various ultrasonic frequencies (20, 204, 362, 609, and 1057 kHz) in order to determine the intrabubble conditions created by multibubble cavitation.[1] The relative populations of the OH ($A^2\Sigma^+$) v′ = 1−4 vibrational states as well as the vibronic temperatures (Tv, Te) have been calculated after deconvolution of the SL spectra. The results of this study provide evidence for nonequilibrium plasma formation during sonolysis of water in the presence of argon. At low ultrasonic frequency (20 kHz), a weakly excited plasma with Brau vibrational distribution is formed (Te ~ 0.7 eV and Tv ~ 5000 K). By contrast, at high frequency ultrasound, the plasma inside the collapsing bubbles exhibits Treanor behavior typical for strong vibrational excitation. The Te and Tv values increase with ultrasonic frequency, reaching Te ~ 1 eV and Tv ~ 9800 K at 1057 kHz. Moreover, the effect of the gas nature was studied: replacement of Ar by Xe leads to a hotter plasma whatever the ultrasonic frequency.

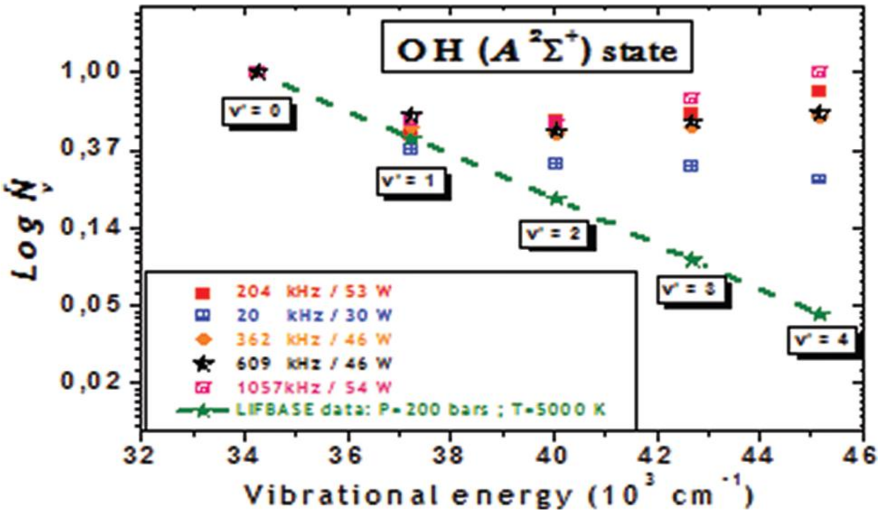


Figure 1: Relative vibrational population distribution of the OH($A^2\Sigma^+$) state as a function of vibrational energy for different ultrasonic frequencies.

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[1] Ndiaye, AA; Pflieger, R; Siboulet, B; Molina, J; Dufreche, J-F; Nikitenko, SI., "**Nonequilibrium Vibrational Excitation of OH Radicals Generated During Multibubble Cavitation in Water**" in Journal of Physical Chemistry A (2012), 116(20), 4860-4867

[2] Ndiaye, AA; Pflieger, R; Siboulet, B; Nikitenko, SI., **"The Origin of Isotope Effects in Sonoluminescence Spectra of Heavy and Light Water"**, in Angewandte Chemie, Int. Ed. (2013), 52(9), 2478-2481

Single-bubble sonoluminescence studies: line emission and similarities with multibubble sonoluminescence

J. Schneider, R. Pflieger, S. I. Nikitenko
D. Shchukin, H. Möhwald (MPIKG-Potsdam, Germany)

A single-bubble sonoluminescence (SBSL) reactor was developed as a model system for standard multibubble (MB) sonochemical reactors since the single-bubble is free of interaction with other cavitation bubbles. Mechanisms leading to MBSL and SBSL were long considered as different since MBSL spectra exhibit characteristic atomic and molecular emission lines on top of a broad continuum, whereas measured SBSL spectra were consisting of a sole continuum.[1] New perspectives to study SBSL were opened by the recent works of Young[2] and Liang[3] who determined the experimental conditions necessary to observe line emission in SBSL.

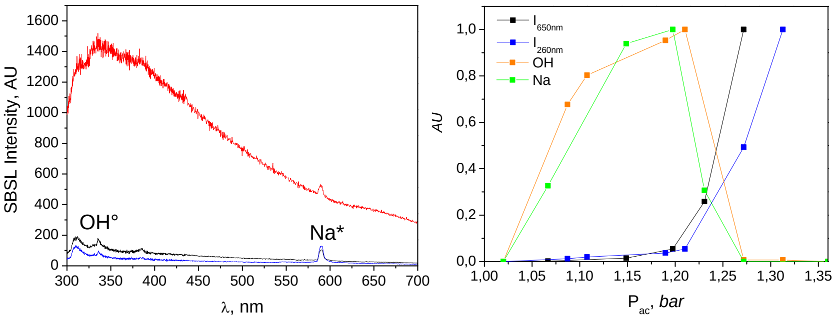

Fig.1: Left : Evolution of the SBSL spectra of 0.5M NaCl equilibrated with 70 mbar Ar with the acoustic pressure (blue: 1.13 bar, black: 1.20 bar, red: 1.25 bar). Right: Evolution with the acoustic pressure of the peak heights of $OH^{\bullet}$ and Na*, and of the continuum (represented by SBSL intensities at 650 and 260 nm); 0.5M NaCl, 70mbar argon.

This work[4] consists of spectroscopic studies of SBSL in water and aqueous sodium chloride solutions with defined concentrations of argon. The broad-band continuum ranging from 200-700 nm is characterised by fits using Planck's law of blackbody radiation. The obtained blackbody temperatures are in the range of 10^4 K and reveal to be independent from the presence of salt and from the acoustic pressure whereas the SL intensity is increasing more than 10-fold within the studied acoustic pressure range. The different trends followed by SL intensity and blackbody temperatures question the blackbody model.

In solutions with 70 mbar of argon line emissions of excited $OH^{\bullet}$ radicals and Na are observed. The shape of the excited $OH^{\bullet}$ radical emission spectrum is very similar to that in MBSL spectra indicating the strong similarity of intra-bubble conditions of SBSL and MBSL under certain experimental conditions. Increase of the acoustic pressure causes the continuum to overlap the lines until they become indistinguishable. This is explained by non-radiative deactivation of excited $OH^{\bullet}$ and Na with increasing acoustic pressure arising from quenching by hot particles issued from a plasma core.

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[1] Matula, T. J.; Roy, R. A.; Mourad, P. D. Phys. Rev. Lett. 1995, 75, 2602.

[2] Young, J. B.; Nelson, J. A.; Kang, W. Phys. Rev. Lett. 2001, 86, 2673.

[3] Liang, Y.; Chen, W. Z.; Xu, X. H.; Xu, J. F. Chin. Sci. Bull. 2007, 52, 3313.

[4] J. Schneider, R. Pflieger, S.I. Nikitenko, D. Shchukin, H. Möhwald, **"Line emission of sodium and hydroxyl radicals in single-bubble sonoluminescence spectra"**, J. Phys. Chem. A, 2011, 115, 136-140.

Excitation of chemical species in solutions by ultrasound

R. Pflieger, J. Ravaux, S.I. Nikitenko.
N. Barré, P. Moisy, J. Schneider, A. Brotchie, D. Shchukin, H. Möhwald, C. Cairos, R. Mettin
IPNO, Orsay BP1-9140 France, CEA/DEN/MAR/DRCP Marcoule BP 17171 France,
MPI-KG Potsdam Germany, DPI Göttingen Germany

Power ultrasound has shown to be effective for in situ excitation of volatile and non-volatile species in solutions in many cases. The observed effects are generally attributed to acoustic cavitation which is the nucleation, growth, and rapid implosive collapse of vapor filled micro-bubbles during the ultrasonic irradiation of a liquid medium. However the mechanism(s) of excitation and the corresponding optimal experimental conditions remain largely unclear.

Bubble collapses in liquids produce chemically active species (excited species and radicals such as OH°) as well as sonoluminescence (SL, emission of light from the core of collapsing bubbles). Some species in solution may be excited directly by in situ produced photons (SL), others by collisions with hot species from the collapsing bubbles, others by the produced radicals (e.g. OH°). We showed that under proper conditions, the uranyl ion can be excited by SL and exhibits ultrabright sonoluminescence even in relatively diluted solutions.[1] Also lanthanide ions can be excited under ultrasound, and their excitation mechanism (photons or collisions) depends both on the ion nature and on the conditions (single vs. multibubble system).[2] Quenching is shown to be more intense under ultrasound, by sonolytical products and in the overheated zone at the bubble interface.[2] Besides, we determined, in the framework of the LEA SONO (collaboration with MPI-Potsdam), the conditions in which luminol can be excited (sonochemiluminescence) by OH° radicals produced by a single cavitation bubble.[3]

Finally, the effects of argon sparging rate, ultrasonic power, and frequency on multibubble sonoluminescence spectra (in particular on Na emission) and bubble dynamics in NaCl aqueous solutions was studied in the framework of a collaboration with the DPI Göttingen, Germany.[4]

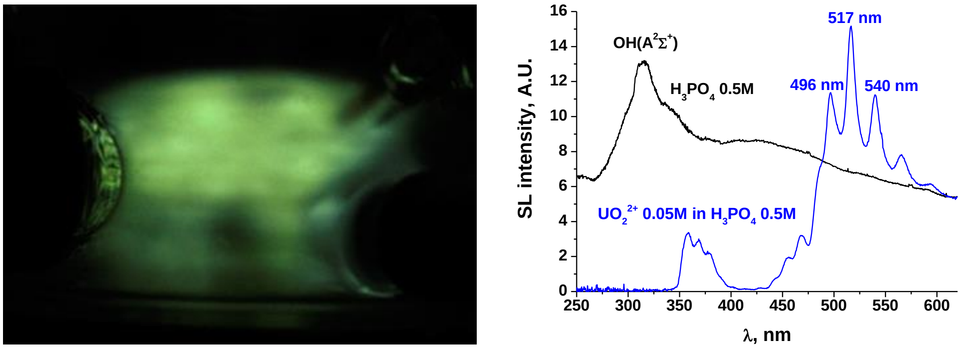

Figure 1: Photograph of 0.031M UO_2^{2+} sonoluminescence in 0.5M H_3PO_4 at 203kHz under argon flow, LP = 63W, T = 10°C, exposure time 30 sec, and sonoluminescence spectra of 0.5M H_3PO_4 and 0.05M UO_2^{2+} in 0.5M H_3PO_4 at 203kHz, LP = 61W, T = 10°C, Ar.

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[1] Pflieger, R; Cousin, V; Barré, N; Moisy, P; and Nikitenko, SI., **"Sonoluminescence of Uranyl Ions in Aqueous Solutions"** in Chemistry – a European Journal (2012), 18(2), 410-414

[2] Pflieger R, Schneider J, Siboulet B, Möhwald H, and Nikitenko SI , **"Luminescence of Trivalent Lanthanide Ions Excited By Single-Bubble and Multibubble Cavitations"**, in Journal of Physical Chemistry B (2013), 117(10), 2979-2984

[3] Brotchie A, Schneider J, Pflieger R, Shchukin D, Moehwald H, **"Sonochemiluminescence from a Single Cavitation Bubble in Water",** in Chemistry-a European Journal (2012), 18(36), 11201-11204

[4] Cairos C; Schneider J; Pflieger R; Mettin R, **"Effects of argon sparging rate, ultrasonic power, and frequency on multibubble sonoluminescence spectra and bubble dynamics in NaCl aqueous solutions"**, in Ultrasonics Sonochemistry (2014) 21(6) Special Issue, 2044-2051

Mechanisms and applications of sonochemical reduction of noble metals

T. Chave, N.M. Navarro, S.I. Nikitenko
S. Nitsche (CiNAM, Marseille), A. Ayral (IEM, Montpellier), P. Lacroix-Desmazes (ICG-Montpellier)

Noble metal nanoparticles have been widely studied especially for their unique size-dependent properties. Several metal have drawn the attention like gold, palladium or platinum which can be found in many applications such as catalytic converters or industrial processes. Platinum nanoparticles (NPs) can be prepared by Pt^{IV} or Pt^{II} reduction with a large array of synthesis routes in the presence of templates, stabilizers, or surfactants. However, surfactants or amphiphilic polymers adsorbed at the surface of NPs would modify their catalytic activity.

Initially focused on platinum, we reported the design of a synthetic route for monodispersed NPs in pure water without any templates or capping agents using ultrasonic irradiation at 20 kHz [1]. This study provided new insights on the sonochemical reduction of Pt^{IV} at low ultrasonic frequency in pure water and under Ar/CO atmosphere but also in presence of formic acid under Ar. The obtained results confirmed that even in pure water the reduction of Pt ions can be triggered by in situ formed hydrogen but the reaction remains incomplete even after several hours due to the steady formation of oxidizing species under ultrasonic irradiation namely OH radicals and H_2O_2 accumulated in solution. Addition of only 10% of CO in the gas phase leads to an effective scavenging of OH° radicals and also contributes to the direct reduction of Pt ions. Similar results can be obtained in presence of 3M HCOOH. Carbon monoxide or formic acid ability to reduce platinum ions at room temperature is enhanced due to the local heating in the liquid shell surrounding the bubble during its collapse. In these conditions the sonochemical reduction at room temperature could be observed within few hours and lead to the formation of metallic Pt particles within the range of few nanometers (Fig. 1a). Finally, Pt catalyst activity prepared under ultrasonic irradiation was accessed with oxalic acid degradation in nitric media and show similar to better activity compared to catalysts made by incipient wetness impregnation with hydrogen reduction in temperature. This synthesis route can be applied in a large array of experimental conditions with various supports such as metal oxides (TiO_2, CeO_2…) but also with thermal sensitive materials like polystyrene beads. In fact, in another study is reported the sonochemical deposition of platinum on the surface of polystyrene beads (PSBs) and the transfer of obtained Pt nanoparticles into a porous silica matrix using the PSB as a sacrificial template.[2] After ultrasonic treatments for few hours, well dispersed Pt nanoparticles within the range of 3–5 nm deposited on PSB were obtained. Samples were then mixed with TEOS, dried, and heated at 450°C to ensure the PSB removal from the silica matrix. TEM and SEM results clearly show that final silica pore size is within the same order of magnitude than initial PSB. Finally, platinum decorated silica matrix with chosen pore sizes was successfully prepared (Fig. 1b).

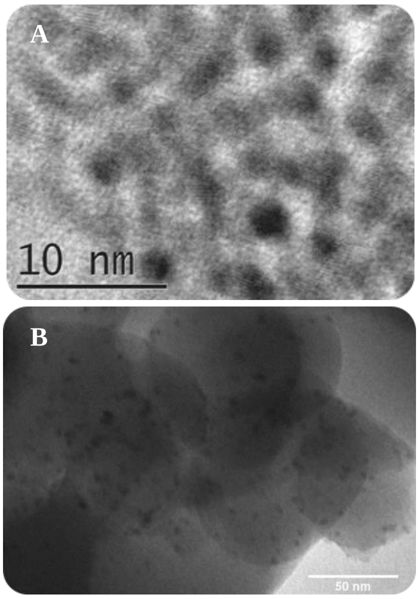

Figure 1 : TEM pictures of Pt NPs obtained in pure water under Ar/CO atmosphere and 20 kHz ultrasonic irradiation (a) and of platinum decorated silica matrix using sacrificial PSB template after Pt NP deposition under 20 kHz ultrasound and Ar/CO atmosphere (b).

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[1] T. Chave, N. M. Navarro, S. Nitsche, S. I. Nikitenko, **“Mechanism of Pt^{IV} Sonochemical Reduction in Formic Acid Media and Pure Water”** *Chemistry - A European Journal*, 2012, 18, 3879.

[2] T. Chave, A. Grunenwald, A. Ayral, P. Lacroix-Desmazes, S. I. Nikitenko, **“Sonochemical deposition of platinum nanoparticles on polymer beads and their transfer on the pore surface of a silica matrix”** *Journal of Colloid and Interface Science*, 2013, 395, 81.

Sonochemistry under hydrothermal conditions and the synthesis of (Ce,Zr)O2 mixed oxides with enhanced catalytic performance

C. Cau, T. Chave, S. I. Nikitenko
P. Pochon (CEA/DRCP Marcoule), Y. Guari and J. Larionova (ICG Montpellier)

Ultrasonic irradiation is applied in a wide range of applications going from the synthesis of nanomaterials to the degradation of organic compounds in wastewaters. On the other hand, hydrothermal conditions are commonly used in similar fields of applications. The coupling of both methods could in this way be a promising approach to design new processes and material synthesis. Actually, hydrothermal treatment under ultrasonic irradiation was already considered for the degradation of acetic acid in presence of hydrogen peroxide or for the synthesis of nanocrystalline materials. Nevertheless, a literature survey revealed a lack of data about sonochemical reactions under hydrothermal conditions. During one of our study, evidence of sonochemical activity in water at 200°C and 13 bars is reported for the time within a homemade sonohydrothermal reactor (Figure 1).[1] The formation of H2 (Figure 2) and D2 during sonolysis of H2O and D2O was actually monitored and proves the existence of transient cavitation under such conditions. Hydrogen peroxide was nevertheless not observed because of its thermal instability. These experiments finally prove that acoustic cavitation can be observed under hydrothermal conditions which is a crucial factor for successful sonochemical synthesis and destruction of organic pollutants.

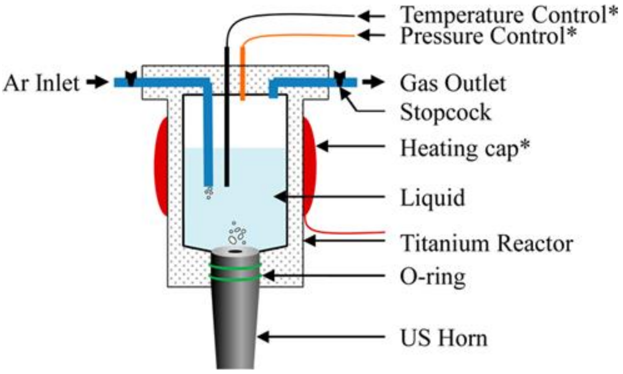

Figure 2: Description of the hydrothermal sonochemical reactor. The reactor was made from TiAl6V4 titanium alloy and equipped with a 19 cm^2 ultrasonic horn powered by a 130W electric generator with a 20 kHz transducer.

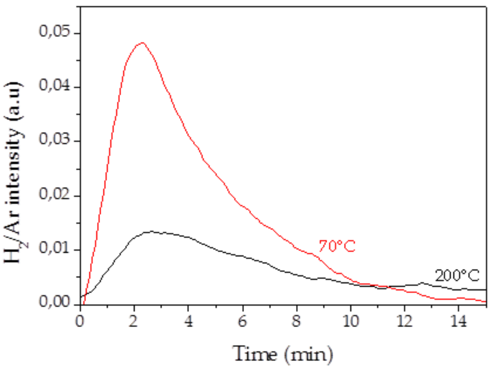

Figure 2: Mass spectrometric measurements of H_2 released after 3h of sonohydrothermal treatment of water saturated with argon at 40% of ultrasonic amplitude.

The coupling of ultrasonic irradiation with hydrothermal conditions was then applied for the synthesis of nanocrystalline $Ce_{0.5}Zr_{0.5}O_2$. [6] Comparative study was actually made between mixed oxides obtained by various synthesis procedures involving ultrasonic irradiation, silent conditions, successive ultrasonic irradiation and hydrothermal conditions, one-pot sonohydrothermal treatments or degradation of metal b-diketonate precursors.[2] Structural and morphological analyses of synthetized products indicate that the mixed oxide obtained under sonohydrothermal conditions exhibits high specific surface area above 100 $m^2.g^{-1}$ with external mesoporous surface area higher than for a material prepared by coprecipitation under ultrasonic irradiation and successive hydrothermal treatment. Catalytic wet air oxidation of formic acid was finally conducted after deposition of 1.5 wt% of platinum on the different mixed oxides. Sample prepared under sonohydrothermal conditions gives the highest catalytic performance for 0.1M HCOOH oxidation at 40°C under air and demonstrates very good stability during CWAO experiments.

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[1] C. Cau, Y. Guari, T. Chave, J. Larionova, P. Pochon, S. I. Nikitenko, **"Sonohydrothermal Synthesis of Nanostructured (Ce,Zr)O₂ Mixed Oxides with Enhanced Catalytic Performance"***Journal of Physical Chemistry C*, 2013, 117, 22827

[2] C. Cau, Y. Guari, T. Chave, J. Larionova, S. I. Nikitenko, **"Thermal and sonochemical synthesis of porous (Ce,Zr)O₂ mixed oxides from metal b-diketonate precursors and their catalytic activity in wet air oxidation process of formic acid"** *Ultrasonics Sonochemistry*, 2014, 21, 1366.

Sonocatalytic degradation of oxalic acid in the presence of oxygen

T. Chave, N. M. Navarro, S. I. Nikitenko
P. Pochon (CEA/DRCP Marcoule), N. Perkas and A. Gedanken (Bar-Ilan University, Israel)

Water remediation and treatment of industrial wastewaters containing organic compounds are today's topics. Several techniques appear promising for the treatment of such kind of aqueous effluents like advanced oxidation process or wet air oxidation for more concentrated aqueous effluents. Sonochemistry is another promising approach that can be considered for water treatment. Despite the extreme local conditions observed during acoustic cavitation phenomenon, using ultrasonic irradiation alone is efficient only at low concentration in organic pollutants. Several attempts were also made in presence of solid phase especially TiO_2 alone under low and high ultrasonic frequency or with deposition of noble metals. In any cases, organic compound concentrations were quite low and remain within the range of $\mu mol.L^{-1}$ to few $mmol.L^{-1}$.

In a recent study, oxalic acid degradation kinetics, with an initial concentration of 0.05M, were followed under various conditions, in presence or not of Pt/TiO_2 catalyst at a steady temperature of 40°C under silent conditions or ultrasonic irradiation at 20 kHz and 360 kHz.[1] Experiments were conducted within tightly closed glass reactor allowing the gas atmosphere to be controlled and oxalic acid degradation rate comparison between argon, Ar/O_2 mixture (20 vol% O_2) and pure O_2 conditions was achieved. Oxidation of oxalic acid was followed by measuring the total amount of carbon within the solution during the different treatments. Catalysts were characterized by various methods including XPS, TEM, XRD and BET surface area determination. Oxidation rate increase of oxalic acid was measured under Ar/O_2 atmosphere in presence of Pt/TiO_2 catalyst due to strong dispersion effect of both low and high ultrasonic frequency and formation of chemically active species by sonolysis as depicted on Figure 1. High frequency ultrasonic irradiation under Ar/O_2 atmosphere gives the highest kinetic increase compared to silent conditions with oxalic acid degradation rate around 0.8 $mmol.h^{-1}$ at 40°C with 2 $g.L^{-1}$ of 3 wt% Pt on P25 TiO_2 catalyst.

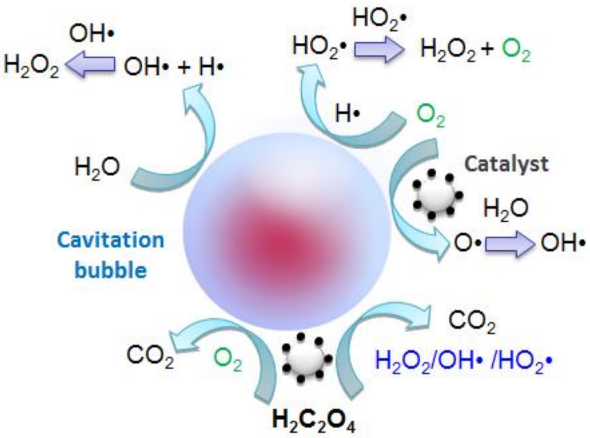

Figure 1: Description of the synergism effect observed during the degradation of oxalic acid between ultrasound, catalyst and oxygen.

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[1] T. Chave, N. M. Navarro, P. Pochon, N. Perkas, A. Gedanken, S. I. Nikitenko, **"Sonohydrothermal Synthesis of Nanostructured (Ce,Zr)O_2 Mixed Oxides with Enhanced Catalytic Performance"** *Catalysis Today*, 2014.

Catalytic dissolution of ceria under mild conditions

M. Virot, *T. Chave*, *D. Horlait*, *N. Clavier*, *N. Dacheux*, *J. Ravaux*, *S. I. Nikitenko*

The dissolution of ceria is studied through a catalytic reduction process involving platinum nanoparticles in mild conditions at near ambient temperature. The deposition of platinum nanoparticles is made by sonication (Ar, 18 W.cm^{-2}, 20 kHz), and further dissolution is studied as a function of different parameters such as stirring, sonication, dissolution media, and temperature. The dissolution is evaluated using UV-Vis spectrophotometry, ICP-AES, and SEM. The quantitative dissolution of ceria can be performed in HNO_3 - HCOOH - $[N_2H_5][NO_3]$, $[HNO_3]$ - $[N_2H_5][NO_3]$ or H_2SO_4 - HCOOH mixtures at 40°C. Nevertheless, it is shown that the combined use of ultrasound with nitric media in the presence of platinum nanoparticles can lead to passivating phenomena resulting in a decrease of the dissolution rate.

Catalytic dissolution of CeO_2/Pt material offers a simple and non-expensive route to separate cerium and platinum potentially suitable for catalysts recycling. Furthermore, the observed phenomenon can have a significant impact on the chemical durability of ceria-based catalysts involved in catalytic and sonocatalytic wet air oxidation processes of organic pollutants in solutions. Finally, the dissolution of CeO_2 is often considered as a model system for the dissolution of refractory PuO_2 which is an important process in the manufacturing of nuclear materials.

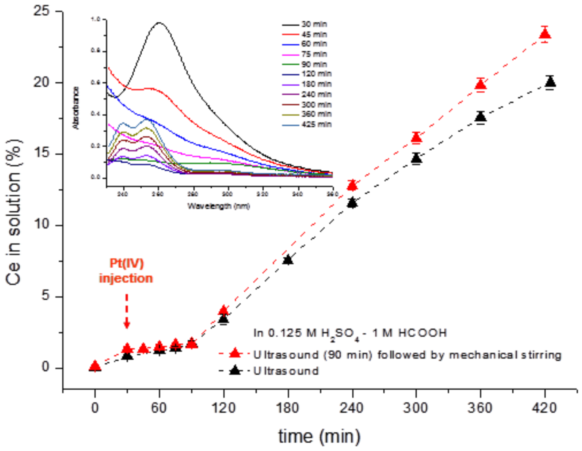

Figure 1. Kinetics of CeO_2/Pt catalytic dissolution (40°C, Ar, SBET = 54 m^{2}g^{-1}) under ultrasound or mechanical stirring (after reduction of Pt(IV) with ultrasound at 18 Wcm^{-2}) in H_2SO_4 - HCOOH mixture. Insert shows the evolution of the UV-VIS spectra for the treated solution which corresponds to Pt(IV) reduction (~260 nm) and Ce(III) accumulation in solution (~255 nm).

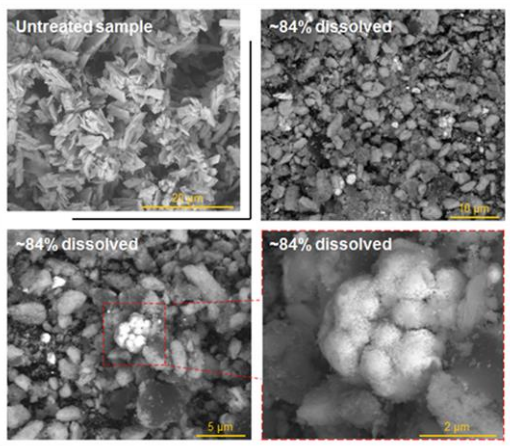

Figure 2. SEM images of CeO_2 powder after catalytic dissolution at 40°C. Platinum is observed as bright white globular aggregates, checked with X-EDS.

M. Virot, T. Chave, D. Horlait, N. Clavier, N. Dacheux, J. Ravaux, S. I. Nikitenko.; **"Catalytic dissolution of ceria under mild conditions"** In J. Mat. Chem. 2012, 22, 14734-14740.

Uranium carbide dissolution in nitric solution: sonication vs. mechanical stirring

M. Virot, S. Szenknect, T. Chave, N. Dacheux, P. Moisy (CEA/DRCP), S. I. Nikitenko

Uranium carbide (UC) is considered as an attractive candidate in view of the development of nuclear fuels for the next fourth generation reactors (GENIV) including high-temperature gas-cooled reactors. This so-called “advanced nuclear fuel” is a material of interest in comparison with the currently used oxide fuels while it provides several physical advantages related to its high thermal stability, higher density of fissile atoms, and very good thermal conductivity (~10 times higher than the oxide). Furthermore, UC possesses a high fusion temperature and can incorporate a large quantity of metallic element, plutonium, and minor actinides. The development of a simple and effective technology for UC based fuel reprocessing is therefore an important challenge which is still not yet overcome. Particularly, dissolution step is of paramount interest since it conditions the dissolved species in view of their separation, recycling, and subsequent fuel re-manufacturing.

The dissolution of uranium carbide (UC) in a nitric media is considered by means of power ultrasound (sonication) or magnetic stirring. The induction period required to initiate UC dissolution was found to be dramatically shortened when sonicating a 3 M nitric solution (Ar, 20 kHz, 18 W.cm-2, 20°C). At higher acidity, mechanical stirring offers faster dissolution kinetics compared to sonication. Ultrasound-assisted UC dissolution is found to be passivated after ~60% dissolution and remains uncompleted whatever the acidity which is confirmed by ICP-AES, LECO and SEM-EDX analyses. The various dissolution kinetics and related induction periods are linked to the in situ generation of nitrous acid in agreement with the general mechanism of UC dissolution; the nitrous acid formation is reported to be faster under ultrasound at low acidity due to the nitric acid sonolysis. The carbon balance shared between the gaseous, liquid, and solid phases is strongly influenced by the applied dissolution procedure and HNO3 concentration.

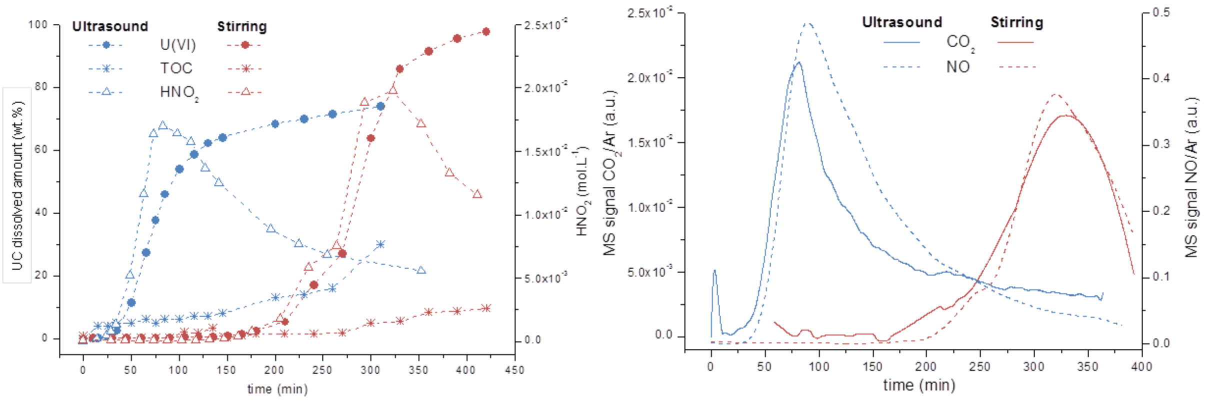

Figure 1. UC dissolution (20°C, Ar, 3 M HNO_3) as a function of the dissolution time (min) and the procedure used (sonication at 18 $W.cm^{-2}$, or mechanical stirring). The Figures are illustrating U(VI) (●), HNO_2 (Δ), and the total organic carbon (*) evolution in solution (left image). The emitted gases (right image) as a function of time (c.) are also showed.

M. Virot, S. Szenknect, T. Chave, N. Dacheux, P. Moisy, S. I. Nikitenko.; **"Uranium carbide dissolution in nitric solution: Sonication vs. silent conditions"** In J. Nucl. Mater. 441, 2013, 421-430.

Sonochemistry of actinides in homogeneous solutions

M. Virot, L. Venault (CEA DEN), P. Moisy (CEA/DRCP), S. I. Nikitenko

The adjustment of the actinide oxidation state in recycling processes of spent nuclear fuel (e.g. PUREX) is important for their recovery and separation necessarily performed with very high yields. The industrial addition of chemicals within recycling processing of nuclear fuel arouses the question of wastes and effluent management in addition to the already existing security limitations. High-power ultrasound offers the opportunity to generate in-situ redox species with controlled kinetics and therefore suggests the possible application of ultrasound in actinide chemistry. Since the first investigations devoted to the chemical influence of ultrasound irradiation towards actinides, only a few studies have been reported in the literature. Mainly, the studies are dealing with the dissolution of oxides and the valency control of actinide ions in aqueous solutions. Note that more recently, the sonochemical excitation of uranyl ions has been demonstrated during sonoluminescence studies by our group. The aim of the present work is to evaluate the influence of ultrasound towards the redox behavior of actinide ions in homogeneous systems, particularly aqueous nitric solutions. For this study, sonochemical set-up have been developed in a “hot” glove box in Atalante facility (CEA Marcoule). The set-up allow the control of several experimental parameters such as the gaseous atmosphere, the temperature, the possibility of sampling solution, the measurement of UV-VIS absorption spectra with a spectrometer connected to the glove box.

The behavior of Pu(IV) and Pu(III) was investigated in aqueous nitric solutions under ultrasound irradiation (Ar, 20 kHz). In the absence of anti-nitrous reagents, ultrasound has no effect toward Pu(IV) while Pu(III) can be rapidly oxidized to Pu(IV) due to the autocatalytic formation of HNO_2 induced by HNO_3 sonolysis. In the presence of anti-nitrous reagents (sulfamic acid or hydrazinium nitrate), Pu(IV) can be sonochemically reduced to Pu(III). The reduction follows a first order reaction law and leads to a steady state where Pu(IV) and Pu(III) coexist in solution. The reduction process is attributed to the sonochemical generation of H_2O_2 in solution. The kinetics attributed to the reduction of Pu(IV) are however higher than those related to the formation of H_2O_2 which, after several hypotheses, is explained by the sonochemical erosion of the titanium-based sonotrode. Titanium particles therefore generated can be solubilized under ultrasound and generate Ti(III) as an intermediate specie, a strong reducing agent able to react with Pu(IV).

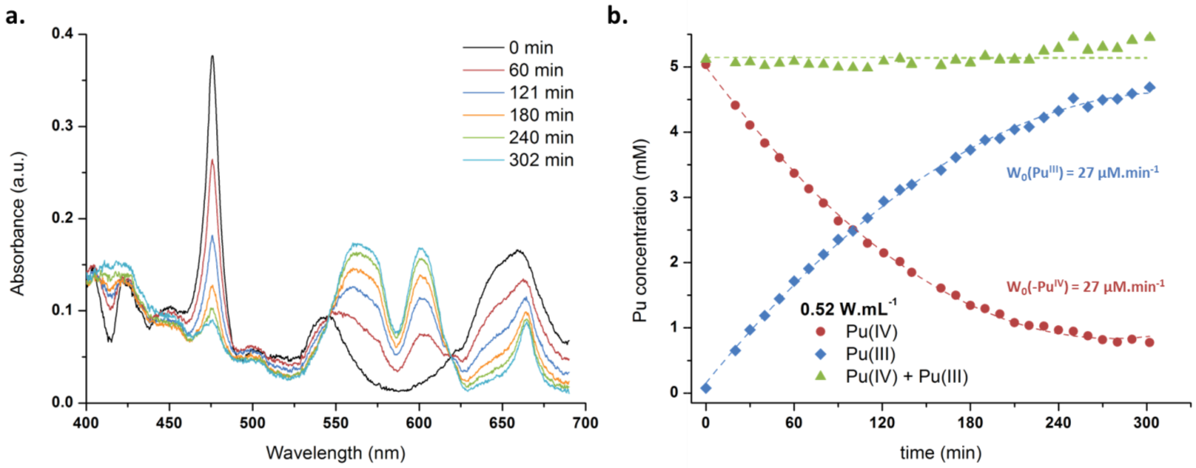

Figure 1. (a.) UV-vis absorption spectra and (b.) the corresponding plotted data observed during the sonochemical (20 kHz, Ar, 26°C) reduction of Pu(IV) in 1 M HNO_3 in the presence of 0.1 M $[N_2H_5][NO_3]$ at 0.52 $W.mL^{-1}$.

Effect of ultrasonic frequency on the mechanism of formic acid sonolysis

<u>N. Navarro</u>, <u>T. Chave</u>, <u>S.I. Nikitenko</u>
P. Pochon, I. Bisel (CEA/DRCP)

Over the last decade, considerable interest has been expressed in the application of advanced oxidation processes (AOP) to destroy hazardous organic compounds in industrial waste streams. Among different techniques (catalytic wet air oxidation, Fenton process, photocatalytic oxidation, ozonation) the sonochemical oxidation is considered as a promising way for the degradation of such kinds of pollutants. The kinetics and mechanism of formic acid sonochemical degradation has been studied at 20, 200 and 607 kHz ultrasonic frequencies under argon atmosphere at 20°C.[1] Total yield of HCOOH sonochemical degradation increases in approximately 6-8 times when the frequency increases from 20 to 200 or 607 kHz. At low ultrasonic frequency HCOOH degradation is attributed to the oxidation with $OH^{\bullet}$ radicals issued from water sonolysis and to the HCOOH decarboxylation occurring at the cavitation bubble-liquid interface. At high-frequency ultrasound sonochemical reaction is also influenced by HCOOH dehydration. The fact that degradation of formic acid takes place at the bubble interface and not inside the bubble was confirmed by the still intense sonoluminescence emission in the presence of formic acid. Besides, a spectroscopic study of sonoluminescence attested the formation of CO at high frequency.[2]

Whatever the ultrasonic frequency, sonolysis of HCOOH yields H_2 and CO_2 in the gas phase as well as the trace amounts of oxalic acid and formaldehyde in the liquid phase, whereas CO and CH_4 were only detected at high-frequency ultrasound. The most striking difference between low-frequency and high-frequency ultrasound is that the sonolysis of HCOOH at high ultrasonic frequencies initiates Fischer-Tropsh hydrogenation of carbon monoxide.

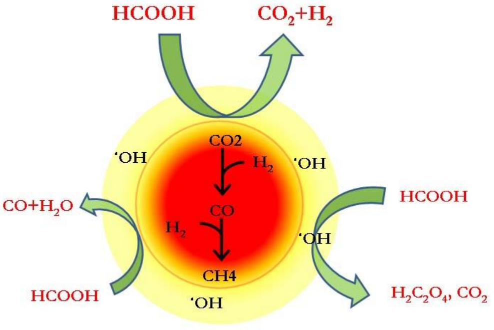

Figure 1: Mechanism of HCOOH sonochemical degradation.

Sonochemically driven Fischer-Tropsch hydrogenation of CO causes formation of methane and formaldehyde as by-products of HCOOH degradation. Finally, we found the catalytic decomposition of sonochemically formed H_2O_2 on the surface of titanium particles originated from the cavitation erosion of the ultrasonic probe at low-frequency ultrasound. This finding is important for proper interpretation of the sonochemical experiments.

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[1] Navarro N., Chave T., Pochon P., Bisel I., Nikitenko S.I. **“Effect of ultrasonic frequency on the mechanism of formic acid sonolysis”**, J. Phys. Chem. B, 2011, 115, 2024-2029

[2] Navarro NM, Pflieger R, Nikitenko SI, **“Multibubble sonoluminescence as a tool to study the mechanism of formic acid sonolysis”**, in Ultrasonics – Sonochemistry, 2014, 21(3), 1026-1029

Sonoluminescence of Tb(III) at the extended solid-liquid interface

M. Virot, R. Pflieger, J. Ravaux, and S.I. Nikitenko

For the first time, acoustic cavitation was used as a source of excitation for photoactive species contained in an extended solid phase. Spectroscopic measurements performed during the sonication of $(Ce_{0.9}Tb_{0.1})PO_4$ sintered pellets with 20 kHz power ultrasound in cooled water under argon showed the Tb(III) light emission resulting from $^5D_4$–^7F_j f–f transitions. The emission spectra were measured as a function of the focus within the cavitation zone, as a function of the distance between the pellet and the ultrasonic horn, or using sonoluminescence quenchers (air or *tert*-butanol). Bubbling of air into the sonicated water presaturated with argon results in a dramatic decrease of SL including OH* and Tb(III). Once argon is totally replaced with air, the SL is no more observable. Although SL disappears in the presence of air, acoustic cavitation at the surface is known to still occur. Hence, this experiment supports the idea that Tb(III) emission is induced by sonoluminescence. When compared with the sonication of the pellet in argon saturated water, the addition of 0.1 M *tert*-butanol decreases dramatically the SL intensity. In addition, OH* emission, as well as Tb(III) lines, almost completely vanishes. By contrast, new particular features appear and stand at 431, 469, 515, and 550–563 nm. These lines are attributed to the transitions $d^3\Pi_g$–$a^3\Pi_u$ of the excited C_2* molecules, also called Swan bands. The large and intense peak at 431 nm was assigned to a combination of $\Delta\upsilon = +2$ of the $d^3\Pi_g$–$a^3\Pi_u$ Swan transition and to the $A^2\Delta{-}X^2\Pi$ transition of CH. The formation of C_2* species in the sonochemical reactions is attributed to the pyrolysis of organic molecules or to their reactions with $OH^{\bullet}$ radicals inside the cavitation bubbles. Even if the total SL is decreased, the presence of Swan bands emission in our system univocally indicates that acoustic cavitation still occur in the presence of *tert*-butanol. Since Tb(III) lines disappear while acoustic cavitation still operates, this experiment definitely confirms the sonophotoexcitation origin of Tb(III) emission.

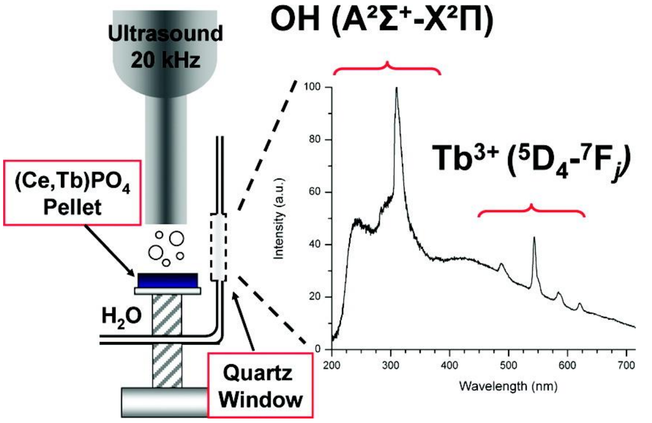

Figure 1: Schematic reprsentation of the emission of Tb(III) during 20 kHz sonication

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M. Virot, R. Pflieger, J. Ravaux, S. I. Nikitenko, **"Sonoluminescence of Tb(III) at the Extended Solid–Liquid Interface"** *J. Phys. Chem. C* 2011, 115, 10752.

Preparation of intrinsic plutonium colloids by sonolysis of PuO2 in water

Morosini V., Chave T., Virot M., Den Auwer C. (Nice University, France), Dumas T. (CEA DEN, France), Tyliszczak T., Shuh D. K. (BNL, USA), Moisy P. (CEA/DRCP) Nikitenko S. I.

Sonolysis of a PuO_2 suspension in pure water under Ar or Ar/CO bubbling leads to the formation of a green colloid solution which remains stable for months after the removal of big PuO_2 particles by centrifugation (Fig. 1). The concentration of Pu in colloidal solution is increased approximately linearly with time of ultrasonic treatment. On the other hand, the same experiment performed with ThO_2 as a model of PuO_2 does not lead to the formation of colloids. Therefore, the mechanical effects of ultrasound along cannot explain colloids formation. Consequently, chemical reactions between PuO_2 and sonochemically generated chemical species should be taken into account. In pure Ar acoustic cavitation causes the homolytic splitting of water molecules followed by the formation of H_2 and H_2O_2. In the presence of oxygen (Ar/O_2 gas mixture) the yield of H_2 is sharply decreased and the yield of H_2O_2 is raised due to the scavenging of H atoms. Interestingly, the sonolysis of PuO_2 in the presence of Ar/20%O2 gas mixture does not lead to any formation of Pu colloids. By contrast, the rate of Pu colloids formation was found to be increased in the presence of Ar/10%CO gas mixture compared to pure Ar. Carbon monoxide plays a role of $OH^•$ radicals scavenger providing a higher yield of H_2. Therefore, it can be concluded that the mechanism of Pu colloids formation consists of Pu(IV) reduction by hydrogen produced during water sonolysis. Then, Pu(III) soluble species are re-oxidized to Pu(IV) yielding colloids. Most probably, Pu(IV) reduction occurs due to the local transient heating generated by cavitation bubble collapse. Presumably, Pu(III) is oxidized in solution by $OH^•$ radicals and/or by H_2O_2.

The Vis/NIR spectrum of sonochemical colloids exhibits the similar characteristic peaks as a hydrolyzed one (Fig. 1). On the other hand, the spectrum of sonochemical colloids demonstrates strong Mie scattering which can be related to larger particles compared to hydrolyzed ones. The EXAFS spectrum of Pu sonocolloids reveals Pu-O and Pu-Pu distances quite similar to those in PuO_2 [10] indicating the resemblance of their structures. By contrast, the EXAFS spectrum of colloids obtained by Pu(IV) hydrolysis demonstrates the strong contribution of shorter Pu-O distances attributed to Pu-OH bonds. Smaller contribution of Pu-Pu bonds in the spectrum of hydrolyzed colloids may indicate a higher structural disorder of these species compared to sonochemical Pu colloids. The STXM images reveal that sonochemical Pu(IV) colloids are composed of nearly monodispersed nanoparticles with the average size less than 20 nm.

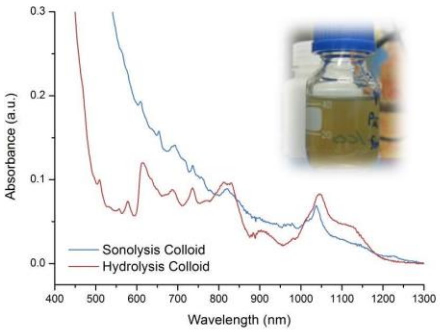


Fig. 1. The Vis/NIR spectra of Pu colloids obtained by PuO_2 sonolysis (pH~6) and Pu(IV) hydrolysis (pH~2.5), [Pu]= (7-9)•10-3 M, l= 1 cm. Inset – photograph of sonochemical Pu colloidal solution after centrifugation at 9000 rpm.

Morosini V., Chave T., Virot M., Den Auwer C., Dumas T., Tyliszczak T., Shuh D. K., Moisy P., Nikitenko S. I. "**Preparation of intrinsic plutonium colloids by sonolysis of PuO2 in water**" *Plutonium Futures – The Science 2014, September 7-12, 2014, Las Vegas, Nevada, USA.*

5 – Nanomaterials for Energy and Recycling processes

L'équipe est constituée actuellement de :
- 1 chercheur CEA/DEN responsable d'équipe (Dr. X. Deschanels (HDR)),
- 2 chercheurs CEA/DEN (Dr. D. Rebiscoul (HDR) et Dr. J. Causse)
- 1 enseignant-chercheur ENSCM (Dr. G. Toquer)
- 1 IE de l'UM2 (C. Rey)

Post-doctorants :
- Alicia Sommer (RSNR Demeterres, 2013-2014) : Développement monolithes pour décontamination Cs, Sr.
- Micheal Moloney (GDR NEEDS Déchets, 2013-2014) : Synthèse de silices mésoporeuses fonctionnalisées pour étude de comportement sous radiolyse.
- Fabien Gasc (Labex Collaboration ENSCM – IAM, 2013-2014) : Recyclage de métaux stratégiques par des copolymères complexants en voie CO_2 supercritique – Application aux métaux nobles.
- Micheal Moloney (CNRS, 2012-2013) : Fonctionnalisation TiO_2 pour extraction des terres rares.
- Alexei Tokarev (ANR Menfis, 2012-2013) : Fonctionnalisation par des ferrocyanures de membranes sélectives du Cs

Doctorants :
- Clémentine Mansas (CEA/DEN, 2014 – 2017) : Extraction sur phases solides à partir de matériaux cœur-couronne : un cœur extractant sélectif, une couronne comme précurseur de matrice de confinement.
- Yu Lou (CEA/DEN, 2013 – 2016) : Comportement des silices mésoporeuses sous irradiation ionique (co-direction thèse).
- Moustapha Coulibaly (CEA/DEN, 2012 – 2015) : Développement de céramiques nanocomposites carbure par voie sol-gel (direction thèse).
- Alvaro Saravia (CEA/DEN, 2012 – 2015) : Effets de la nature des précurseurs sur les propriétés physico-chimiques de carbures d'uranium et leur aptitude au frittage (direction thèse).
- Alban Gossard (CEA/DEN, 2011-2014) : Synthèse d'oxydes par voie sol-gel colloïdale - Application aux précurseurs de combustibles nucléaires.
- Aude Charlot (CEA/DSM-DGA, 2011-2014) : Elaboration et caractérisation de revêtements submicroniques par électrodéposition de nanoparticules de silice (direction thèse).
- Cyril Lavaud (CEA/DEN, 2010-2013) : Traitements d'effluents aqueux par complexation en milieu micellaire et précipitation par voie sol-gel (direction thèse).
- Sabah El Mourabit (CEA/DEN, 2010-2013): Matériaux hybrides inorganiques-organiques pour l'extraction d'uranium en milieu acide phosphorique (direction thèse).
- Carole Delchet (UM2, 2009-2012): Matériaux hybrides pour la séparation et le confinement d'élements mobiles – Application au césium (direction thèse).
- Aurélie Merceille (CEA/DEN, 2008-2011) : Etude d'échangeurs d'ions minéraux pour la décontamination liquide en strontium (direction thèse).
- Bernhard Smutek (2008-2011): Organic reactions of alcohols under hydrothermal conditions (co-direction these).

Personnels non permanents :
- Najat Talha (CEA/DEN, 2014 – 2015) : CDD
- Arnaud Bex (CEA/DEN, 2012 -2014) : Apprentissage technicien (BTS Lycée Sainte-Marie Bagnols-sur-Cèze)
- Olivier Bruguier (CEA/DEN, 2009-2012) : Apprentissage ingénieur (ISTP St Etienne)

Les recherches développées par cette équipe ont été construites dans le cadre décrit à la création de l'ICSM. L'axe de recherche principal du laboratoire, qui est le développement de nanomatériaux poreux architecturés à différentes échelles, a été affirmé au cours de la période 2010-2014 par de nombreuses publications (33) et brevets. En 2014, des changements notables, concernant le personnel du laboratoire, ont été enregistrés. Diane Rebiscoul (CEA/DEN) a été mutée en juin, en remplacement d'Agnès Grandjean, la responsable du laboratoire, qui a rejoint un laboratoire du département de Traitement et de Conditionnement des Déchets. Ces mouvements ont nécessité un rééquilibrage des activités, toutefois l'axe central de recherche qui concerne les nanomatériaux poreux, a été maintenu en confiant la responsabilité du laboratoire à Xavier Deschanels.

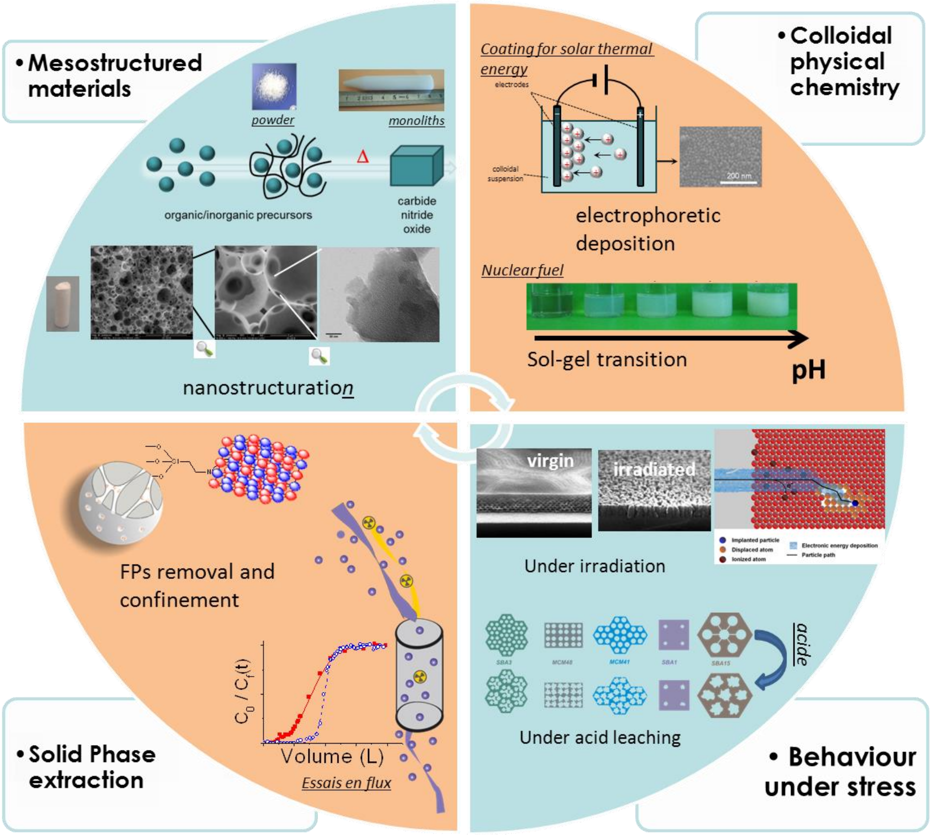
Durant la période 2010-2014, l'équipe a accompagné la soutenance de sept thèses, quatre thèses sont en préparation, et quatre post doct ont travaillé dans le laboratoire.

Le laboratoire 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, 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, 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 2010-2014 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) ;
- Physico-chimie des suspensions colloïdales : propriétés de la suspension et mécanismes mis en jeu lors de la mise en forme (électrophorèse, coating, transition sol-gel) ;
- Propriétés extractives des matériaux fonctionnalisés : du macroscopique (courbe de percée, procédé continu) au nanoscopique (à l'échelle de l'extractant « hybride - solide »).
- Etude de l'impact d'un stress physique (irradiation, compaction) ou chimique (milieu très acide ou très basique) sur la structure hiérarchique d'un matériau.



Mesoporous materials in the field of nuclear industry

J. Causse, F. Goettmann, X. Deschanels, C. Rey, G. Toquer, A. Grandjean

In a context of increasing global energy demand associated with high prices for classical fossil fuels and raising concerns about CO2 emissions, nuclear power is attracting a renewed interest. Despite the recent accident in the Fukushima power plant, numerous countries maintain very ambitious nuclear programms. The Generation IV international forum1 (an initiative launched by the US Department of Energy in 2000 to coordinate and promote efforts to design the next generation of nuclear power plants) supports works to develop new power plant designs and innovative concepts in the nuclear fuel cycle. These new concepts aim at achieving higher levels of security and resource efficiency as well as a higher resistance towards nuclear proliferation. Because of this blossoming of new ideas, mesoporous materials, which are already widely found in applications such as catalysis, sensing and optics, are expected to make their way in the field of nuclear power production. Up to now, some (hybrid) mesoporous solids have already been investigated as solid ligands to remove actinides and fission product contaminants from liquid effluents, but also as model materials to investigate radiation defects, as possible nuclear waste disposal form and as functional materials to be placed in or close to new forms of nuclear waste matrices [1].

Our own group has been working on some of the above mentioned applications for the last four years and we are convinced that there are great potentialities for mesoporous solids in many nuclear fields:

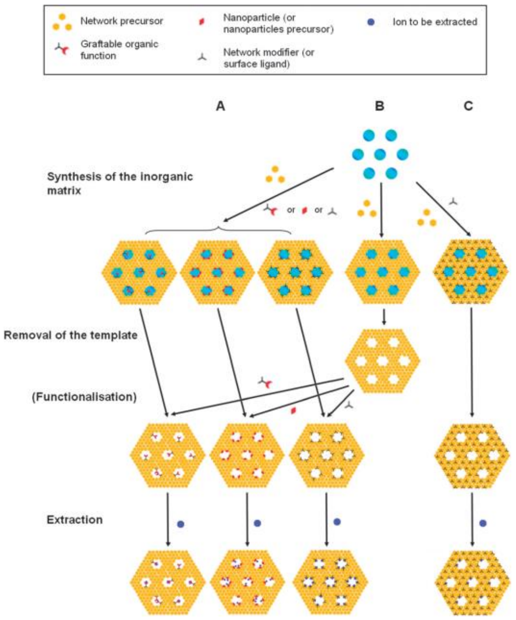
(i) In separation chemistry for actinide extraction or for the development of selective sorbents and/or getters. Desirable improvements in this field are the enhancement of the chemical stability of both the mesopores [2] and the grafted functions (especially in very aggressive acid media) and the design [3-4] of tailored macrostructures for the materials (to be able to really employ these hybrid materials in daily processes or to make them fit to existing experimental set-ups);

(ii) In waste management for the confinement of mobile or volatile radioactive species inside the porosity of such materials (using soft treatment to close the porosity). Here again, the development of suited macrostructures is required.

(iii) In the design of new fuel forms, which can accommodate gaseous fission product and sustain the important associated pressure increases;

(iv) In the study of irradiation defect using mesoporous solids as model materials. Here, the development of analytical techniques suited to characterize the materials after irradiation tests has to be undertaken (taking into account that for practical reasons the amount of tested material is often very low).

This team aimed at highlighting the great interest of the use of mesoporous solids in the field of nuclear research, but also to evidence that there still is plenty of work to be done.



Schematic view of the three main ways to access functional mesoporous materials. Way A is the so-called one step way, where both the inorganic precursors and the functional groups are put together at the beginning of the synthesis. Way B is the multi step process in which the mesoporous inorganic matrix is preformed and a post functionalisation s done after wars. The third way (C) is less common and is a variation of the one pot approach. Here network modifier are added to the synthesis of the mesoporous matrix to yield an intrinsically functional material.

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[2] S. El Mourabit, M. Guillot, G. Toquer, J. Cambedouzou, F. Goettmann and A. Grandjean, **"Stability of mesoporous silica under acidic conditions ",** RSC Advances, 2012, 2 (99), 10916-10924.

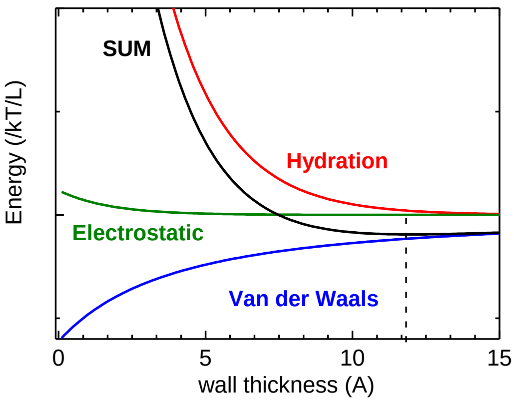
[3] A. Grandjean, G. Toquer, Th. Zemb, **"Wall thickness prediction in precipitated precursors of mesoporous materials"**, Journal of Physical Chemistry C, 115 (2011), 11525-11532.

[4] G. Toquer, C. Delchet, M. Nemec, A. Grandjean, "**Effect of leaching concentration and time on the morphology of pores in porous glasses",** Journal of non crystalline solids, 357 (2011) 1552-1557.

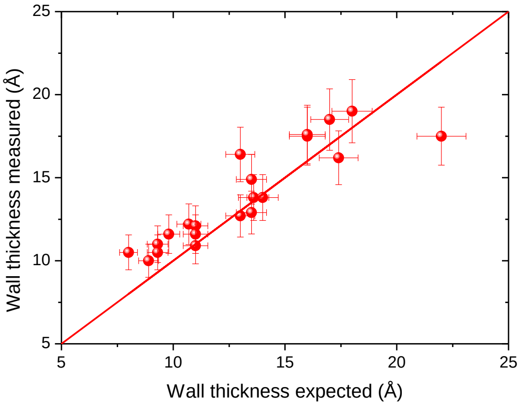
Molecular force balance allows the prediction of wall thickness of mesoporous materials

A. Grandjean, G. Toquer, Th. Zemb

Since the discovery of mesoporous materials using micelle templates two decades ago, the booming of this field has been impressive. This kind of synthesis has been developed for diverse applications as catalysis, sensing, separation and much kind of oxides (silica, titania, zirconia). This synthesis is based on the layout of semi-rigid cylinders of surfactant in a water-phase solution. These self assembled surfactant acts as template during the sol gel process which occurs in the space left between the cylinders. Next, the wet dispersion of precursor material in the surfactant solution is aged, washed and finally calcined to remove the template. The control of surfactant geometrical parameters during the inorganic polymerisation impacts directly the properties of the final mesoporous materials. For example, the diameter of templating cylinder controls the final pore size. Nevertheless, in spite of several experiment attempts to control wall thickness, any clear and unquestionable explanation is not yet available. In this way, we develop a simple analytical model which predicts variations of wall thickness through experimental conditions. This model is free parameter and is in great agreement with experimental data available from the literature for the case of hexagonal array of cylindrical pores. The model concept consists of three main uncoupled driving forces : repulsive electrostatic, repulsive hydration and attractive Van der Waals. By adding all these supramolecular interactions and searching a minimum in potential, this latter gives then the equilibrium distance value between surfactant cylinder and consequently an expected wall thickness. The confrontation of our model with experimental data is illustrated here by several examples in order to better understand the wall thickness variation with the experimental process. This simple analytical model based on molecular force balance proposed here explains qualitatively and quantitatively in some simple cases, the wall thickness of silica-based mesoporous materials obtained via the sol-gel route.



A typical example of a force balance calculation with the dominant interactions: Hydration, Van des Waals and Electrostatic. The equilibrium interaxial distance is given by the minimum value of sum of the 3 forces.



Wall thickness measurement versus wall thickness expected from force molecular balance by using several experimental data

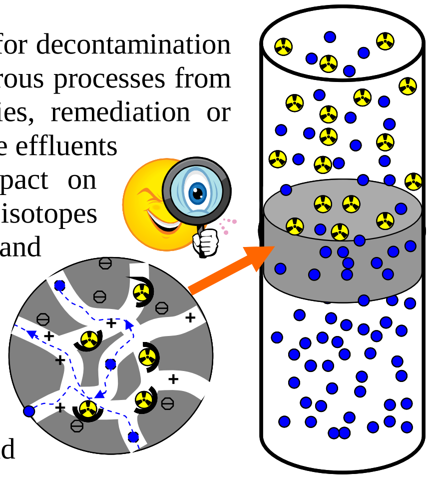
A. Grandjean, G. Toquer, Th. Zemb, **"Wall thickness prediction in precipitated precursors of mesoporous materials"**, Journal of Physical Chemistry C, 115 (2011), 11525-11532.

Elaboration and partitioning chemistry properties of functionalized mesoporous materials

J. Causse, G. Toquer, C. Rey, F. Goettmann, A. Grandjean, X. Deschanels

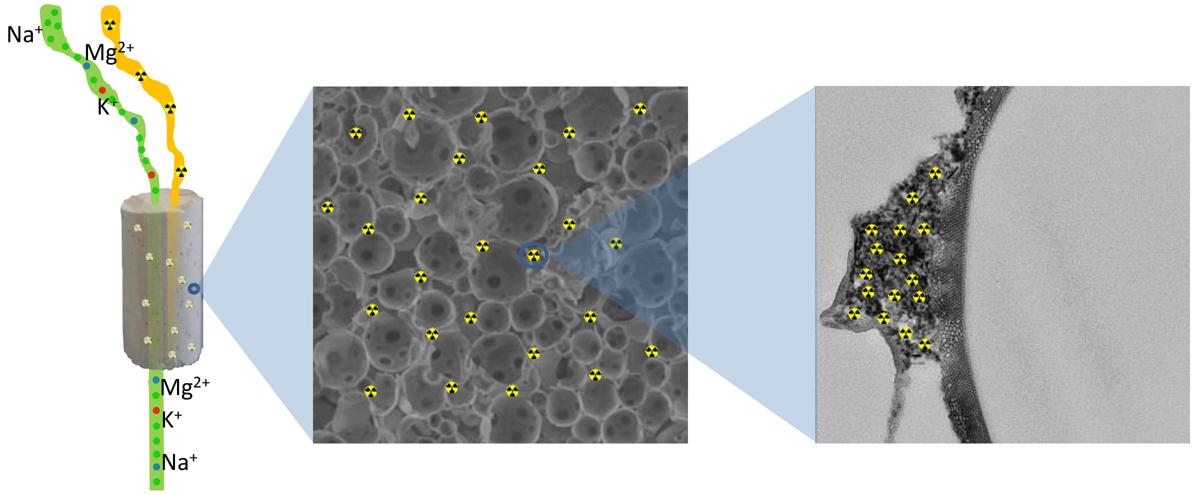
Mesoporous materials are promising materials for applications in the field of ion separation, environmental remediation, or even metallurgical purposes. Thus far, numerous hybrid mesoporous solids have been investigated as “solid ligands”, particularly for extracting heavy metal cations from waste fluxes. For example concerning the extraction of uranium (or rare earth metals) from new ores, less concentrated, feed stocks, we studied the use of mesoporous silica or carbon functionalised with specific ligand.

We have also proposed functionalised mesoporous materials for decontamination processes (ruthenium [1], or for cesium [2-3]). Indeed, numerous processes from nuclear facilities (fuel processing, power plants, laboratories, remediation or removal and others) generate important volumes of radioactive effluents which should be treated in order to minimize their impact on environment. Among those, radioactive cesium and strontium isotopes are ones of the most abundant fission products of uranium and have to be removed. Recently we have proposed a new approach to an efficient and selective extraction of Cs^+ ions from pure water, or saline water enriched with $^{137}Cs^+$ by using porous silica- or glass-based nanocomposites containing Prussian blue type nanoparticles, $Me^{2+}/[Fe(CN)_6]^{3-}$ (Me = Co, Cu or Ni) covalently linked and homogeneously distributed into the matrix pores [2].



The kinetics of cesium sorption is faster and the sorption capacities per gram of metal hexacyanoferrate are higher in the case of the nanocomposites compared to the bulk Prussian blue analogues. This fact may be attributed to the high surface area of the Prussian blue nanoparticles in the case of nanocomposites. Moreover the nanocomposite materials also present a high selectivity to Cs^+ comparable to the bulk materials even in the presence of high concentration of sodium in saline water.
In case of strontium removal, sodium nonatitanate - a layered material that contains exchangeable sodium ions between layers- and Zeolite A - an aluminosilicate structure also with exchangeable sodium ions -are known to selectively trap strontium ions [4-5]. We have compared these two materials and shown that sodium nonatitanate has good decontamination properties for solutions with low calcium content and is only slightly affected by the presence of sodium. Conversely, zeolite is not affected by the presence of calcium, but its sorption properties decrease in solutions with a high sodium content. We have also proposed the used of novel material: a macroporous zeolite A monolith for efficient removal of Sr^{2+} ions from salty aqueous solutions in continuous flow process. This monolith shows high efficiency and selectivity for the in-flow treatment of radioactive water and possesses a decontamination capacity higher in comparison to batch processes [6].

We have therefore shown the great potential of monolithic materials for applications in separation chemistry. That is the reason why we are also developing multiscale porous monoliths from emulsion templates (as shown in the sketch below) exhibiting macro- and mesoporosity. This synthesis route is very interesting. For instance, the sharp control of the shearing rate used in emulsification process allows to tune the size of macroporosity due to the fact that emulsion oil drops act as soft template. Moreover, the understanding of the mechanisms involved in the synthesis allows us to consider the incorporation of selective extractants (organic or inorganic, molecular or nanoparticles) within the porosity of these monoliths. The emulsion template used in this method allowed us to develop a one-pot procedure and therefore to avoid the use of non-green solvents that are generally used for impregnation step of pristine materials (toluene…). The one-pot procedure also allowed the insertion of more active functions due to the fact that in this case, functionalization step does not depend on the surface density of hydroxyl groups [7-9]. Therefore, the location of the active function depends on the hydrophilic-lipophilic balance of the active function. It could be either inside silica walls in the case of hydrophilic active functions in oil-in-water emulsion or covering the macropores for amphiphilic active function. This point is currently under study and is a prospect for this project.



Emulsion templated silica monoliths functionalized with Copper Hexacyanoferrates used for decontamination of liquid outflows containing ^{137}*Cs*

[1] A. Tokarev, A. Grandjean, Y. Guari, J. Larionova, R. Pflieger, C. Guérin, "**Functionalized porous glass for the removal and the confinement of ruthenium from radioactive solutions**" Journal of Nuclear Materials, 400 (2010) 25-31.

[2] C. Delchet, A. Tokarev, X. Dumail, G. Toquer, Y. Barré, Y. Guari, Ch. Guérin, J. Larionova, A. Grandjean, "**Extraction of radioactive cesium using innovative functionalized porous materials** " RSC Advances, 2 (2012), 5707-5716.

[3] A. Grandjean, J. Larionova, Y. Guari, Y. Barré, « **Matériau solide nanocomposite a base d'hexa et d'octacyanomatallates, son procédé de preparation et procédé de fixation de polluants minéraux le mettant en œuvre.**» FD11351. N° d'enregistrement FR 09/53379. Numéro de publication FR 2945756.

[4] A. Merceille, E. Weinzaepfel, Y. Barre, A. Grandjean, "**Effect of the synthesis temperature of sodium nonatitanate on batch kinetics of strontium-ion adsorption from aqueous solution**" Adsorption, (2011) 17, 967-975.

[5] Aurélie Merceille, Evelyne Weinzaepfel, Yves Barré, Agnès Grandjean, "**The sorption behaviour of synthetic sodium nonatitanate and zeolite A for removing radioactive strontium from aqueous wastes**" (2011) Separation and Purification Technology, 96 (2012), 81-88.

[6] A. Sachse, A. Merceille, Y. Barré, A. Grandjean, F. Fajula and A. Galarneau "**Macroporous LTA-monoliths for in-flow removal of radioactive strontium from aqueous effluents: Application to the case of Fukushima**" Microporous and Mesoporous Materials, 164 (2012) 251-258.

[7] J. Causse, A. Tokarev, J. Ravaux, M. Moloney, Y. Barré, A. Grandjean, "**Facile one-pot synthesis of copper hexacyanoferrate nanoparticle functionalised silica monoliths for the selective entrapment of ^{137}Cs**", J. Mater. Chem. A, 2014, 2, 9461-9464, DOI: 10.1039/C4TA01266F

[8] Turgis, R.,Arrachart, G.,Delchet, C.,Rey, C.,Barre, Y.,Pellet-Rostaing, S.,Guari, Y.,Larionova, J.,Grandjean, A., "**An Original "Click and Bind" Approach for Immobilizing Copper Hexacyanoferrate Nanoparticles on Mesoporous Silica**", Chemistry of Materials, 25, (2013), 21, 4447-4453

[9] J. Causse, A. Grandjean, A. Tokarev, Y. Barré, « **Matériaux monolithiques inorganiques alvéolaires échangeurs cationiques, leur procédé de préparation, et procédé de séparation les mettant en œuvre.** », FD14859, demande déposée le 20/12/2013, n°13 63329.

Colloidal Physical chemistry

Application to nanoparticle electrophoretic deposition and nanostructured materials as simulating nuclear fuel

A. Gossard, A. Charlot, A. Grandjean, X. Deschanels, G. Toquer

This theme deals with controlled destabilization (under external or inherent forces) of initial stable colloidal dispersion towards the formation of nanostructured material associated with specific properties. In this way, two different main studies are currently in progress: The first one is focused on stable charged ceramic nanoparticle dispersion which is electrodeposited on substrate with tunable thickness. The final aim is to obtain a nanostructured film for controlled reflectance properties as a simulating selective optical material. The second one concern the oxide mixtures (of nuclear interest) based on colloidal sol-gel transition. We focus more precisely on the kinetic condensation of colloidal oxide mixtures into gel to understand and predict their gel point. Afterwards, these systems will be transposed to nanocasting step by templating initial stable colloidal dispersion in order to obtain nanostructured hybrid materials.

Nanoparticle electrophoretic deposition

Electrophoretic deposition (EPD) has been an attractive technique to obtain uniform films of high thickness (several microns) on large surface area substrates. In particular, it has been shown that EPD is an important tool for the fabrication of wide range of materials [1]. Nanoparticle electrophoretic deposition (NEPD) method is developed here to understand the mechanisms and the kinetic rate deposition of thin film (several nanometres) based on ceramic nanoparticles (SiO2, ZrO2, SiC, TiO2…). The coating on the electrode surface is based on the migration of charged particles in a polar medium under an electric field (see figure a). This step implies necessary some physical-chemical conditions in order to reach an efficient electrophoretic mobility (better known as nanoparticle Zeta potential) and also a monodisperse system (studied by SAXS or DLS). Nanoparticles at the viscinity of the working electrode are expected to be sufficiently fixed due to attractive Van der Waals interactions. Further, nanoparticles coagulate and the rate of deposition depends mainly of the nanoparticle concentration, deposition time and electric field magnitude [2]. During NEPD, the electric field strength is the driven force promoting particle packing, affecting thereby the film density and the final thickness but the drying process at post-deposition seems also to be a crucial step for the film adhesion behaviour. The composition of the films as well as the amount of the deposited material are analysed by X-film software from MEB measurements. Selective optical properties [3] are analysed by coupling these latters with Fourier transform Vis-IR spectroscopy measurements.

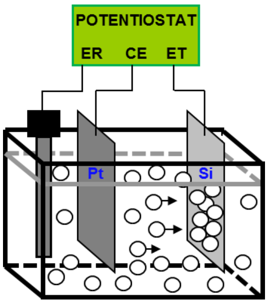


Figure a: three electrodes device for nanoelectrophoretic deposition

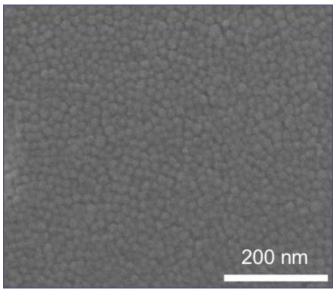


Figure b: SiO_2 nanoparticles electrodeposited on Pt substrate.

Nanostructured materials as simulating nuclear fuel

The technology process of nuclear fuel U-Pu (MOX type) or transmutation target is currently based on oxide powders converted into green pellets and then by sintering them in reductive area at high temperature (1700°C) into pellets. The major drawback is then the powder radioactive dust formation all along the process. Consequently, the transmutation target material or advanced nuclear fuel having high radioactive actinide elements such as 233U, 241Am, 242-248Cm cannot be then considered. Thereby, an innovating way is to explore a powder free synthesis of oxide mixture based on colloidal sol-gel transition in order to obtain mesoporous hybrid materials. Several composite gels have already been investigated starting from colloidal zirconia [4] and recently colloidal uranium oxide. More precisely, Zirconium hydrolysis occurs at low pH (≈3) followed by a rapid precipitation of oxy-hydroxide. A specific complexant as acetylacetone is used in order to control the chemical surface of formed colloid and shift also the optimal pH for the condensation. By adjusting the physicochemical compounds, the kinetic of condensation and thus the sol-gel transition are well controlled [5]. The gel point (main key parameter) of our systems is analyzed by rheology coupled with SAXS and Raman spectroscopy. Recently, our systems have been templated by external way (by using soft oil droplets [6] or hard polymeric spheres as seen on figure d). After removal of the template, the final step is to fill the obtained mesoporous material by colloidal sol actinide as Am, Cm to finally reach a nanostructured composite material as simulating nuclear fuel.

Figure c: sol-gel transition

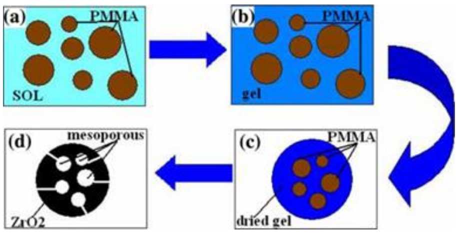


Figure d: hard sphere templating

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[2] Charlot, A.; Deschanels, X.; Toquer, G., "**Submicron coating of SiO2 nanoparticles from electrophoretic deposition**". Thin Solid Films 2014, 553, 148-152.

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Soft chemistry routes for the synthesis of carbides

A. Saravia, M. Coulibaly, D. Hérault[*]*, G. Arrachart, O. Fiquet*[**]*, S. Szenknect, X. Deschanels,*
[*]*Centrale Marseille, Aix Marseille Université, CNRS, iSm2 UMR 7313, 13397, Marseille, France*
[**]*CEA-Cadarache, DEC/SPUA/LCU, 13108 St-Paul Lez Durance*

Soft chemistry routes are used for the production of carbide powders 1-2. In a first, two approaches (colloidal and molecular routes) were compared in terms of temperature synthesis, microstructural characteristics, for the synthesis of silicon carbide. In a second step, these methods have been implemented for the synthesis of other carbides (TiC, ZrC, UC) or composite carbides (SiC-TiC).

Synthesis of silicon carbide powders

Two different routes are used for the production of silicon carbide powders. The first, called the “colloidal route”, is inspired by methods used by H-P Martin 3 and consists of the carboreduction of colloidal silica (nanometric or micrometric powders) by sugar. The second route, called the “molecular route”, uses a molecular chemistry approach, based on the immobilization of sugar derivatives in silica. Both synthesis routes use the same carbon source (carbohydrate) to achieve the carbothermal reduction of the silica depicted by the following equation:

$\mathrm{SiO2(s) + 3C(s) = SiC(s) + 2\ CO(g)}$

In both cases, □-SiC powders with a high yield of submicrometric particles were successfully synthesized in the temperature range between 1300 and 1550 °C (Fig. 1).

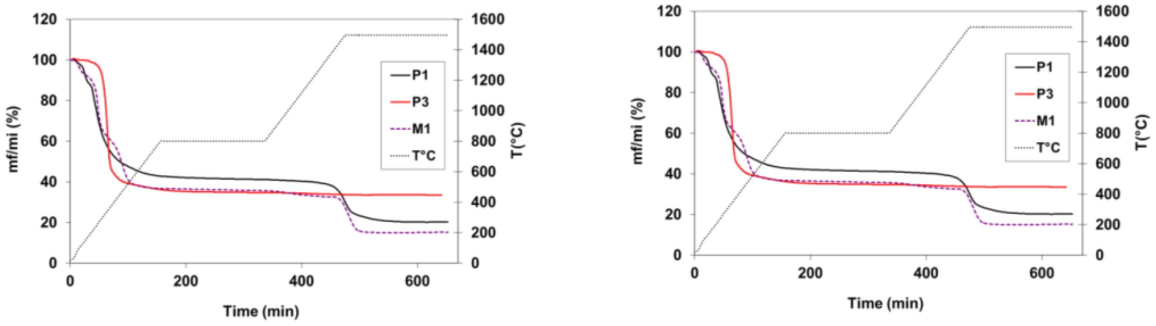

Figure.1: TGA curves (in argon) of precursors P1 (fumed silica + sucrose C/Si=3.6),P3 (fumed silica + mannitol C/Si=3.6), M1 (molecular route, C/Si=8).

Characterization of the carbides

The powders obtained by the two routes exhibited a mesoporous structure. The structure of these materials was composed of grains of carbides embedded in a matrix of carbon (Fig. 3). Their characteristics depend on the amount of residual carbon, and the mesoporosity is located within the carbon matrix surrounding the carbide grains (Fig. 4). The largest surface area, 722 m2/g, was measured for a sample synthesized via the molecular route. A mechanism related to the release of the CO gas produced during the carbothermal reduction was invoked to explain the evolution of the surface area versus the volume fraction of residual carbon.

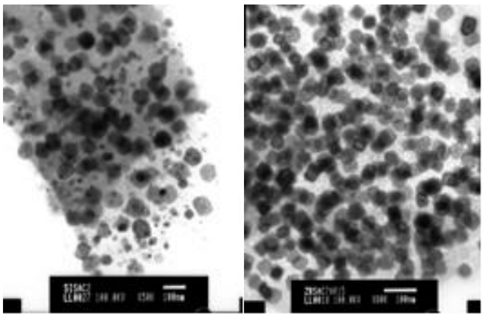

Figure. 3: TEM observations of powders pyrolyzed at 1550°C C/M=24, a)P1-type (SiC+C), b) P3-type (ZrC+C).-

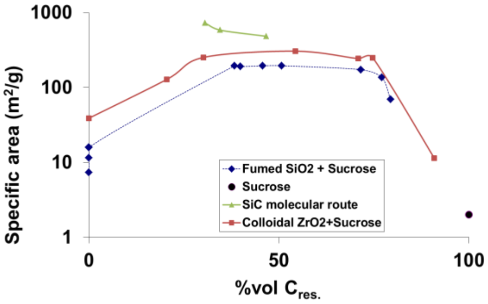

Figure 4: SBET of precursors P1, P2, P3, P4 pyrolysed at 1550°C versus volume fraction of residual carbon. Specific surface area of pyrolyzed sucrose is 2 m^2/g.

Synthesis of uranium carbide and composite carbide powders

These "soft-chemistry" routes were successfully implemented for the development of nuclear materials, i.e. fuels (UC) or structural material, and high temperature solar photothermal absorbers (SiC-TiC). The synthesis of uranium carbides was developed in collaboration with a laboratory of CEA Cadarache (DEC/SPUA/LCU). This new route[4] leads to a decrease in the temperature of the carbothermal reduction. Furthermore, a decrease in the size of the powders was observed, which can be advantageous for the subsequent sintering process.

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[2] X. Deschanels, D. Herault, G. Arrachart, C. Rey, A. Grandjean, G. Toquer, R. Podor, G. Cerveau, T. Zemb, R. Corriu "**Comparison of two soft chemistry routes for the synthesis of mesoporous carbon/b-SiC nanocomposites**" J Mater Sci (2013) 48:4097–4108.

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Irradiation of mesoporous thin silica films under ionic irradiation

Y. Lou, X. Deschanels, S. Dourdain, A. Grandjean, C. Rey, G. Toquer, D. Simeone[*]
(*)CEA, DEN, LRC CARMEN, CEA Saclay, F-91191 Gif/Yvette, France

Over the past two decades, the development of nanoscale composites and mesoporous materials provided a number of new possibilities for encapsulating nuclear wastes [1]. Mesoporous silicates are typically synthesized under mild or hydrothermal conditions using a structure-directing agent or template that can be removed subsequently, leaving a material with void spaces. These relatively soft synthetic routes are a first determining advantage of mesoporous solids as conditioning matrices for volatile species (ie, I and Cs). A second advantage is that their porosity can be closed (again under relatively soft conditions like mild thermal treatment, suited chemical stresses, in order to ensure a durable confinement. This ability of mesoporous structure to collapse under given stresses is thus of great advantage regarding the foreseen applications, but it also raises the question of the behaviour of such materials under self-irradiation.

In this study, our objective is to investigate how the damages caused by ions irradiation affect the structure of mesoporous silica. For this purpose, mesoporous silica thin films deposited on Si-substrate (e~100nm) were irradiated by swift ions (H, He, Ne, Ar, Xe, Au) having a total stopping power varying between 0,1 to 9 keV/nm. It is well known that dense silica is sensitive to the damages caused by swift ions. For an electronic stopping power higher than a threshold of about 2-4 keV/nm, such damages result in the formation of amorphous tracks and may give rise to macroscopic deformation. In similar irradiation conditions, Klaumünzer [2] has observed shrinkage of the mesoporosity of Vycor glass attributed to the formation of tracks in the glass.

Structural parameters of such films were obtained from the X-rays reflectivity measurements (XRR) [3-4]. A typical XRR curves are presented on Fig. 1a. We observe Kiessig oscillations (better visible between 0.04 and 0.1 $Å^{-1}$ on Fig. 1a) that are characteristic of thickness (T) of the film. The periodicity d of the stacking of pores produces Bragg reflections, located for example at Q=0.085, 0.160 and 0.244 $Å^{-1}$ for the pristine film (Fig. 1a). A cross section of a 2D hexagonal mesoporous film is illustrated at bottom inset of figure 1a, showing the hexagonal organisation of the cylindrical pores and the parameters T and d. It should be noted that the parameter d is not equal to lattice parameter of the 2D hexagonal structure, but to the distance between two layers of pores in the direction perpendicular to the film. After irradiation with He ions, it appears that the two first Bragg reflections remain visible, showing that the mesopores are still present and organized in the z direction. The decrease of their intensity and their broadening indicate however that the organisation of the pores is altered. Their shift to the higher Q values is due to a collapse of the periodicity d of the stacking of pores.

The thickness T is sensitive to the stopping power of the incident ion (Fig.1b). SEM observations (Fig. 2) are in agreement with this result, and clearly show that the samples irradiated with helium are much less damaged than those irradiated with argon. In the former sample, the porosity of the film is observable while the film is fully dense in the latter.

Work is underway to assess more accurately the behaviour of the mesoporous silica in other irradiation conditions (effect of the ratio between the electronic / nuclear stopping power, effect of the fluence), in order to conclude on the possibility of closing the porosity.

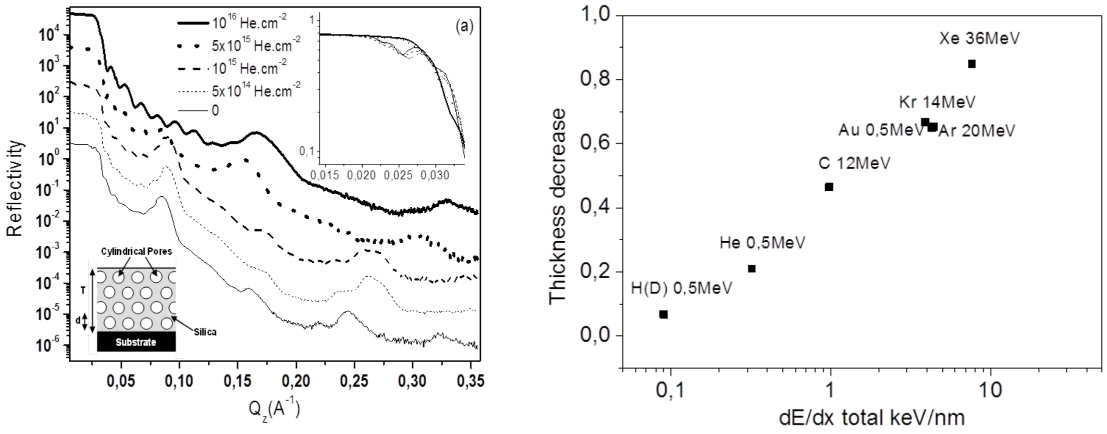
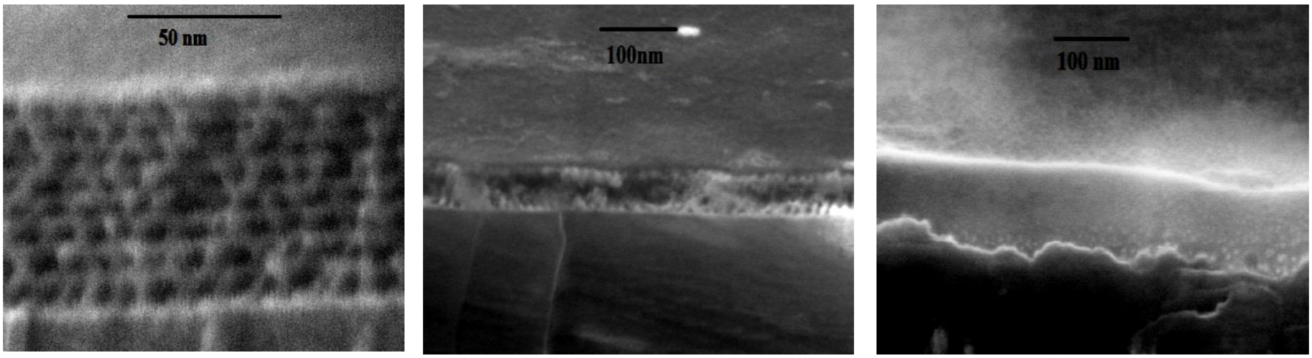


Fig. 1: (a) XRR curves of 2D hexagonal mesoporous thin film versus fluence for He - 0.5 MeV
(b) Evolution of the thickness obtained from XRR curves versus total stopping power of the incident ion for a fluence □ = 1015 ions/cm2



a) b) c)

Fig. 2: SEM observations *of mesoporous thin film a) Virgin sample; b) Sample irradiated by 0.5MeV-He,* 10^{16}*cm*$^{-2}$*, c) Sample irradiated 20MeV-Ar,* 10^{15}*cm*$^{-2}$*.*

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Specific Characterisation of nanostructured materials

C. Rey, A. Grandjean

The ICSM possess various pieces of equipment for the characterisation of new and novel materials. The managment of these equipments is undertaken by a number of groups including the Laboratory of Nanomatrials for Energy and Recycling (LNER).

The LNER research group is in charge of: a gas adsorption-desorption device (BET), a high temperature thermal analyser (TGA/DTA) which can be coupled to a gas analysers. This group also manages a Carbon-Sulfur and an Oxygen-Nitrogen-Hydrogen analyser, as well as a capillary ionic chromatography device. The managment of these devices includes the planning, maintenance and development of measurement methods for materials which are synthesised in all the team of the Institute.

The Gas Adsorption-Desorption device can be used to characterise the surface shapes and surface areas of adsorbents and the porosity of various nanomaterials. The example illustrated below (Figure 1) shows a nitrogen adosrption-desorption isotherm from a sample of Vycor Glass.

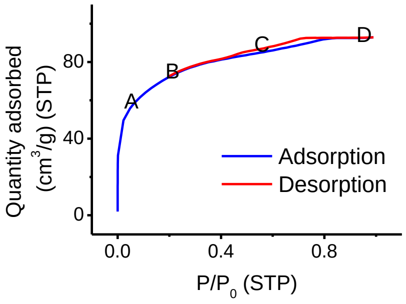


Figure 1: Nitrogen Adsorption-Desorption Isotherm of Vycor Glass (A) Microporous stage P/P0<0,05 (B) Gas pressure increased to form a monolayer and the surface area determined using the BET method, P/P0 < 0,3 (C) Gas pressure increased to form a multilayer which allows us to determine pore diameter. (D) Total adsorption on extern surface

Adsorption and desorption analyses using different gases such as water vapour or krypton (for materials with low surface area) are also performed as well as micropore. In the future we plan to develop chemisorption analyses.

High temperature thermal analyses, (TGA/DTA), provides us with the ability to measure temperatures ranging from the ambient (thermocouple S, B) to as high as 2400 °C (thermocouple W).

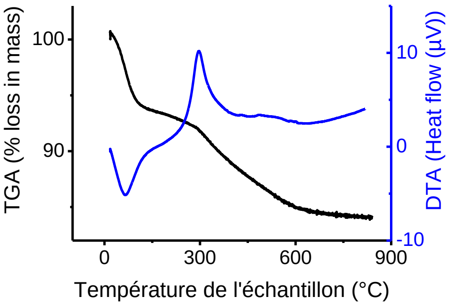


Figure 2: TGA (black line) measures the variation in the mass of a sample as the temperature is increased (i.e. 100°C and 400°C respectively). The DTA (blue line) detects transformations in the sample structure, i.e. fusion, crystallisation, etc. Recently, the LNER group has been equipped with a gas analyser which allows us to identify the emitted vapours and therefore better understand the transformation mechanisms which occurs during the thermal

Combined with a carbon and an oxygen-nitrogen-hydrogen analyser, we are also able to characterise materials functionalised with organic molecules.

Once these materials have been characterised, we then test their capacity for extraction thanks to an ionic chromatography device which can simultaneously detect the presence of cations (alkaline and earth alkaline; organic acid) and anions in solution.

The above mentioned equipment allows the LNER group to not only characterise the materials which we synthesis but also to analysis the efficiency of these materials.

6 – Evolving interfaces in materials

L'équipe est constituée de :

- 1 Professeur des Universités, responsable d'équipe (Pr. N. Dacheux)
- 2 chercheurs CNRS (Dr. N. Clavier ; Dr. A. Mesbah)
- 1 chercheur CEA (Dr. S. Szenknect)
- 1 maître de conférences (Dr. L. Claparède, depuis le 1er septembre 2014)

Doctorants :

- Julien MARTINEZ (CEA/DEN, 2011-2014) : Frittage d'oxydes mixtes à base d'uranium et de cérium ou de plutonium
- Florent TOCINO (CEA/DEN, 2012-2015) : Impact des phénomènes rédox et des paramètres microstructuraux sur la dissolution d'oxydes à base d'uranium et/ou de thorium
- Clémence GAUSSE (UM2, 2013-2016) : Synthèse, frittage et dissolution d'échantillons monazitiques
- Théo CORDARA (CEA/DEN, 2014-2017) : rôle des éléments platinoides sur la dissolution d'oxydes à base d'uranium
- Alvaro SARAVIA (CEA/DEN, 2012-2015) : Précurseurs de carbures d'uranium et aptitude au frittage
- Galy Ingrid NKOU BOUALA (CEA/DEN, 2013-2016) : Processus élémentaires lors du frittage de billes nanométiques d'actinides ou de lanthanides

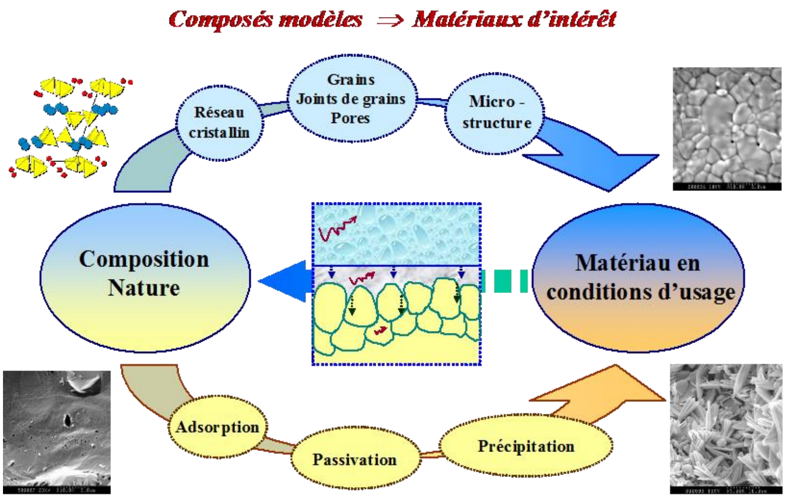
Le laboratoire d'étude des Interfaces de Matériaux en Evolution (LIME) a pour objectif de décrire et de comprendre les phénomènes siégeant aux interfaces solide/solide et solide/liquide, aussi bien au cours d'étapes de frittage (densification) que de dissolution (ou d'altération) sous contraintes de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

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 usuellement accessibles 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. 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) pour l'aval ou l'amont du cycle électronucléaire. Cette démarche consiste, en particulier, à appréhender et à comprendre les liens étroits reliant d'une part, la morphologie d'un solide et d'autre part, sa propension à se dissoudre ou à s'altérer.

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 ($Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_2$, $Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$, …) en privilégiant l'usage de précurseurs cristallisés du type oxalate, hydroxyde, … de manière à améliorer l'homogénéité, la réactivité et la « frittabilité » des oxydes préparés à haute température. Les étapes de conversion des précurseurs en matériaux oxydes ultimes sont alors examinées à travers le couplage de nombreuses techniques (thermiques, diffractions, microscopiques, spectroscopiques). Il en découle l'identification des transformations et des intermédiaires réactionnels successifs intervenant lors de la conversion. Plusieurs structures cristallines ont ainsi été précisées. A titre d'exemple, pour les solutions solides $Ce_{1-x}Nd_xO_{2-x/2}$, l'affinement des paramètres de maille des échantillons préparés après traitement thermique du précurseur oxalate à 1000°C a confirmé l'existence de deux domaines distincts (structures fluorine et bixbyite) résultant d'une organisation des lacunes en oxygène nécessaires à la compensation de charges. En outre, l'utilisation de méthodes de synthèse par voie humide, généralement favorables à l'amélioration de la répartition cationique au sein du solide, a permis d'étendre le domaine d'existence de telles solutions solides.

Sur la base de ces résultats, le frittage des oxydes mixtes $Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_2$, $Ce_{1-x}Nd_xO_{2-x/2}$ et $Th_{1-x}Ln_xO_{2-x/2}$ a été étudié de manière à identifier les paramètres d'intérêt hérités de l'histoire thermique de la poudre initiale (surface spécifique, homogénéité, influence de la présence de carbone résiduel, …). Il a ainsi été possible de mettre en évidence un lien direct entre le précurseur utilisé, sa conversion en oxyde, et la microstructure finale du compact densifié (Thèse de Julien Martinez, Bourse CTCI, ICSM-DEC-AREVA, 2011-2014). Par ailleurs, des premières 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 pour CeO_2 et ThO_2 jusqu'à 1400°C. De plus, le couplage de ces résultats avec ceux issus de l'analyse dilatométrique a permis de construire rapidement des trajectoires de frittage permettant *in fine* de contrôler la microstructure des matériaux céramiques considérés. En outre, les travaux entrepris dans le cadre de la thèse de Galy Ingrid Nkou Bouala (Bourse CFR, ICSM-DEC, 2013-2016) sur des composés modèles de morphologie sphérique contrôlée (CeO_2, ThO_2 et UO_2) ont d'ores et déjà conduit à l'acquisition de données expérimentales cinétiques et thermodynamiques inédites relatives à la première étape du frittage (élaboration des ponts) pouvant être ensuite implémentées dans les modèles numériques d'ores et déjà développés au CEA/DEC.

Concernant l'étude des interfaces solide/liquide, des expériences de dissolution ont été entreprises en conditions de faible ou de fort renouvellement. Pour les solutions solides $Th_{1-x}U_xO_2$, une étude multiparamétrique a été développée afin d'évaluer l'influence relative de chaque paramètre sur la durabilité chimique des matériaux. Il est rapidement apparu qu'en milieu nitrique, la fraction molaire en uranium (IV) constituait un paramètre d'influence majeure sur la vitesse de dissolution des solides. A ce titre, l'amélioration de la distribution cationique au sein du solide permet de limiter l'influence de la composition, probablement du fait de la disparition de zones enrichies en uranium tandis que la réduction du nombre de joints de grains induit la diminution des vitesses de dissolution normalisées d'environ un ordre de grandeur par rapport à celles déterminées pour les échantillons préparés par précipitation directe. Cela confirme les liens étroits existant entre la microstructure du matériau (à travers, entre autre, l'homogénéité et la réactivité de surface, …) et sa résistance à l'altération ou à la corrosion aqueuse. Par ailleurs, la progression de la réaction de dissolution est généralement associée à une modification significative de la surface réactive. Dans le but de corriger le biais en découlant, une méthode de suivi *in operando* de cette évolution par ESEM a été développée.



Représentation synoptique de paramètres physico-chimiques étudiés lors de l'évolution d'un matériau en cours de dissolution.

Concernant les solutions solides $Ce_{1-x}Nd_xO_{2-x/2}$ et $Th_{1-x}Nd_xO_{2-x/2}$, l'influence de plusieurs paramètres tels que la composition chimique, la température, l'acidité du milieu et la présence d'agents complexant sur la vitesse de dissolution normalisée a été examinée. Contrairement aux solutions solides $Th_{1-x}U_xO_2$, les tests de dissolution menés sur les composés $Ce_{1-x}Nd_xO_{2-x/2}$ ont montré une forte influence de la composition chimique, principalement liée à la fragilisation du réseau cristallin consécutive à la formation des lacunes en oxygène. Par ailleurs, le contrôle de la réaction de dissolution par des réactions de surface a été mis en évidence, à la fois *via* la détermination de l'énergie d'activation (voisine de 90-100 $kJ.mol^{-1}$) qu'à travers la saturation des sites actifs de surface au-delà de 2M en acide nitrique. Ces travaux initiés au cours des thèses de Laurent Claparède (2008-2011) et de Denis Horlait (2008-2011) sont actuellement poursuivis dans le cadre des thèses de Florent Tocino (Bourse CTBU, ICSM – DRCP/LED, 2012-2015) et de Théo Cordara (Bourse CTCI, ICSM – DRCP/AREVA, 2013-2016). Un aspect particulier du travail consiste à étudier le rôle des réactions rédox à l'interface solide/solution à partir de la comparaison des systèmes $An_{1-x}Ce_xO_2$, $An_{1-x}Ln_xO_{2-x/2}$ (An=Th,U) et $Th_{1-x}U_xO_2$ ainsi que le rôle des éléments platinoides.

Un second axe de recherches, en lien avec l'amont du cycle, a été initié en partenariat avec le DRCP (CEA Marcoule) dans le cadre de deux thèses (Dan T. Costin : 2009-2012 et Fanny Crétaz : 2010-2013). Les expérimentations relatives aux systèmes phosphate et vanadate d'uranium (VI) sont actuellement poursuivis en partenariat avec AREVA tandis que celles portant sur les silicates de thorium et d'uranium (IV) font l'objet d'une collaboration internationale (Prof. R.C. Ewing, Université de Standford, Prof. P. Burns, Université de Notre Dame). Les premières études ont d'abord porté sur le système thorium – uranium – silicate, à travers la préparation de solutions solides d'uranothorite $Th_{1-x}U_xSiO_4$ puis de la coffinite $USiO_4$ en conditions hydrothermales. Des méthodes de purification des échantillons, par séparation chimique des phases oxydes $Th_{1-y}U_yO_2$ et SiO_2 présentes en tant que phases secondaires pour les forts taux d'incorporation d'uranium ont été mises au point. Pour le système uranium-silicate, le mécanisme de formation de la coffinite a été élucidé tandis que le rendement chimique et les conditions de purification des échantillons ont été optimisés. Les données de solubilité préliminaires acquises sur des échantillons purifiés d'uranothorites ou de coffinite ont d'ores et déjà permis d'apporter des conclusions sur la réaction «d'uranothoritisation » en fonction des conditions d'altération et de la nature des solides. Celles relatives à la coffinité sont actuellement en cours d'acquisition.

Le second volet de l'étude a porté sur les systèmes uranium-phosphate et uranium-vanadate, plus particulièrement à travers la synthèse et la caractérisation d'autunite, de torbernite, de carnotite ou d'ankoléite. Pour l'ensemble de ces systèmes, la démarche a consisté à déterminer les vitesses de dissolution des échantillons (cinétique) et les données de solubilité afin d'accéder *in fine* aux données thermodynamiques (K_S, $\Delta_R H°$, $\Delta_R G°$, $\Delta_R S°$) nécessaires pour évaluer le comportement de ces phases minérales lors de leur mise en contact avec une solution. Par ailleurs, pour l'ensemble des systèmes examinés, une comparaison directe entre échantillons modèles et réels a été entreprise à travers le développement de cette méthodologie parallèlement sur des minéraux uranifères et sur des échantillons synthétiques.

Plus récemment, un troisième axe de recherches a été initié sur l'étude de la phase monazite en tant que matrice de confinement spécifique de certains radionucléides. Ces travaux, réalisés en collaboration avec le groupe du Professeur D. Bosbach (IEK 6 – FZ Jülich) dans le cadre de la thèse de Clémence Gausse (Bourse MENRT, 2013-2016), ont d'abord consisté à préparer des échantillons pulvérulents, notamment à travers des précurseurs obtenus par voie humide (tels que la rhabdophane). Il s'agira, dans un second temps, d'examiner l'aptitude au frittage des différents précurseurs et d'acquérir les premières données de solubilité sur des échantillons frittés.

From the precursor to the dense pellet: how to control the microstructure of nuclear ceramics ?

Nicolas CLAVIER, Julien MARTINEZ, Adel MESBAH, Nicolas DACHEUX
Fabienne AUDUBERT (DEN/DEC – CEA Cadarache)
Laurent BRISSONEAU, Marie GABARD (DEN/DTN CEA Cadarache)
Bénédicte ARAB-CHAPELET, Thibaud DELAHAYE (DEN/DRCP – CEA Marcoule)

The microstructure of ceramic materials, including grain size, density, pores distribution and cationic homogeneity, is known to drive several of their properties in use. The control of the microstructure is thus of primary importance, particularly in the framework of the nuclear fuel cycle where ceramic materials are currently playing a major role as fuel, and could be also used as waste matrices or as oxygen probes in the near future [1]. Nevertheless, despite the numerous works dedicated to the impact of the operating conditions used for the densification process (temperature, holding time, atmosphere, …), far less studies were devoted to the influence of the starting powder. A transverse approach, including both synthesis and densification processes, was thus set up to study such impact and propose original routes for the fabrication of nuclear ceramics, with a particular emphasis on oxide materials.

At first, the development of wet chemistry routes for the preparation of ceramics from low-temperature precursors was used to tune and monitor the properties of the initial powders. A variety of materials were then considered as precursors, such as nitrates, hydroxides [2], or metal-organic complexes [3] and led to contrasted characteristics in terms of morphology, reactivity and homogeneity. The extensive characterization of the precursor samples was also pursued *in situ* during their conversion into the compounds of interest, using classical TGA-DTA or more recent HT-XRD, HT-MEBE. From these results, it appeared that preliminary heat treatment generally preserve the morphology of the powders but could drastically modify chemical features such as cationic distribution or residual carbon content.

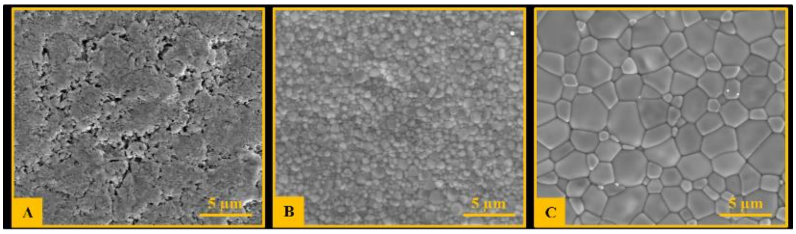


Fig.1: SEM micrographs of sintered $U_{0.9}Ce_{0.1}O_2$ pellets prepared from highly reactive precursors after sintering at 1350°C (A), 1450°C (B) and 1550°C (C) [2].

Last step of the studies was devoted to the sintering through the joint use of usual techniques (dilatometry, pycnometry) with that developed at ICSM such as *in situ* HT-ESEM. In the case of oxide materials, this methodology led to develop highly reactive powders that allow to decrease the sintering temperature of AnO_2 oxides by at least 200°C (Fig. 1). It also allowed us to optimize the microstructure of $(Th,Y)O_2$ ceramics to be used as solid electrolytes in oxygen sensors. Finally, ongoing studies are also developed in the field of nuclear waste management in order to improve the densification of several ceramic wasteforms, such as monazite.

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Dynamic aspects of ceramic sintering

Nicolas CLAVIER, Renaud PODOR, Johann RAVAUX, Nicolas DACHEUX

The solid state sintering involves two major phenomena occurring simultaneously: pore shrinkage and grain growth. The microstructure evolution of a solid during sintering is related to the kinetics of change in the grain size and pore distributions. The modifications of these distributions are directly linked to atom and pore mobilities (and more generally to mass transfer) that generates grain boundary as well as intergranular and intragranular pores displacements. Even if numerous models were developed to predict these processes on the basis of diffusion equations and energy minimization, there is a lack of experimental data in this domain. A specific methodology was then developed, using the opportunities offered by Environmental Scanning Electron Microscopy (ESEM) implemented with a high temperature device. It was then possible to directly observe the sintering mechanisms of ceramics at the sub-micrometer scale [1].

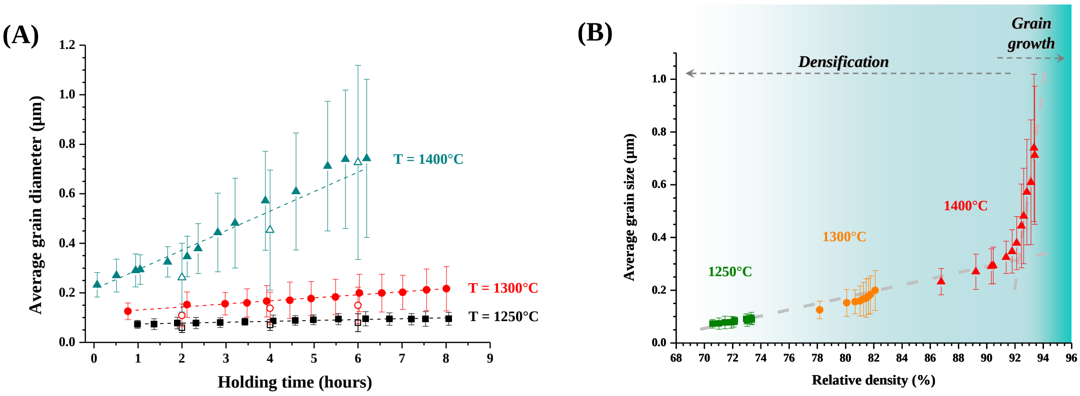

Fig.1: (A) Evolution of the average grain size during heat treatment at various temperatures from ex situ (open symbols) or in situ (full symbols) conditions. (B) Sintering trajectory of ThO_2 obtained from the HT-ESEM/dilatometry combined approach.

The sintering of various MO_2 oxides (M = Th, Ce) was then studied directly in the ESEM chamber from 1000 to 1400°C [2]. The morphological modifications of a single grain population were observed for 6 to 8 hours and good quality images were recorded. Kinetic parameters were then extracted from the obtained image series. The local grain growth determined from the single population studied *in situ* was compared to the general grain growth obtained by the classical *ex situ* technique in order to validate the use of HT-ESEM for sintering study. From the image series, kinetic parameters such as grain boundary velocities were also determined.

In the case of ThO_2 sintering, the data determined from *in situ* HT-ESEM images (Figure 1A) was correlated to *ex situ* dilatometric measurements, and the sintering map for ThO_2 was obtained [3] (Figure 1B), which still remains a premiere for an actinide-based material.

As these first results pave the way to a faster and more easy control of the microstructure of ceramic materials, the methodology set up on MO_2 oxides is now applied to several other materials of interest for the nuclear fuel cycle, including ceramic waste forms (*e.g.* monazite and associated cheralite).

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Influence of redox reactions, cationic homogeneity and microstructural parameters on the fluorite-type (An,Ln)O2 mixed oxide dissolution

Nicolas DACHEUX, Nicolas CLAVIER, Stéphanie SZENKNECT, Adel MESBAH,
Florent TOCINO, Laurent CLAPAREDE, Théo CORDARA

Actinide mixed dioxides are currently used in PWR nuclear reactors and considered as reference fuels for several Gen III and Gen IV concepts. Moreover, they could act as matrices for the recycling of minor actinides, either directly in the reactor core or in fertile blankets. In these conditions, the consequences of the incorporation of trivalent elements, such as americium or curium (and lanthanides as surrogate elements), in the fluorite-type structure of MO_2 should be carefully assessed when dealing with key-steps of the nuclear fuel cycle, such as reprocessing.

On the one hand, the dissolution of UO_2 matrix in acid media is driven by the oxidation of U(IV) in U(VI) at the solid-liquid interface. Thus, the dissolution rate strongly depends on the protons and oxidants activities in the solution. On the other hand, the normalized dissolution rate of $Ce_{1-x}Ln_xO_{2-x/2}$ or $Th_{1-x}Ln_xO_{2-x/2}$ is found to be strongly accelerated by the trivalent lanthanide incorporation rate, due to the presence of oxygen vacancies decreasing the sample cohesion [1,2,3,4]. The effects of trivalent elements in U-based mixed dioxides dissolution remain widely unknown. Especially, the relative contribution of redox reactions occurring at the solid/solution interface compared to oxygen vacancies must be evaluated. In order to underline the influence of those parameters, various dissolution experiments were carried out on different compositions (i.e. $U_{0.75}Ce_{0.25}O_2$, $U_{0.75}Th_{0.25}O_2$, $Th_{0.75}Nd_{0.25}O_{1.875}$ and $U_{0.75}Ln_{0.25}O_{1.875}$ with Ln = Nd, Gd). These tests were performed on sintered pellets in nitric acid solutions (from 10^{-2} M to 4 M) at different temperatures (22°C to 90°C) under dynamic conditions. Therefore, a multiparametric study of the dissolution kinetics was then achieved in order to determine the partial order regarding to the H_3O^+ activity and the activation energy of the dissolution reaction. The obtained results gave evidence of the strong dependency of the dissolution rate with the nitric acid concentration (Figure 1).

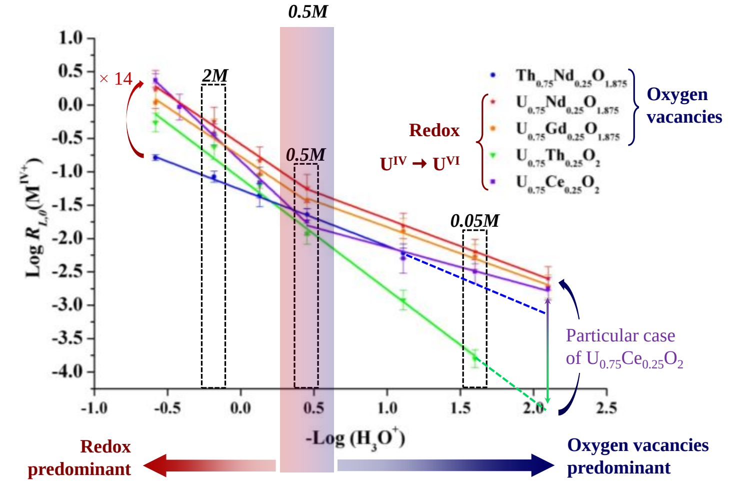

Fig. 1: Variation of Log $R_{L,0}$(i) versus the opposite log (H_3O^+) for various mixed oxide.

For concentrations higher than 2 M, the dissolution process was almost controlled by the oxidation of U(IV) to U(VI). On the contrary the effect of oxygen vacancies became predominant for acid concentrations lower than 0.5 M. Under these conditions, the systems containing trivalent elements

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exhibited the lowest chemical durability. The partial order of the reaction regarding to the H_3O^+ activity reached n = 2.1 for $U_{0.75}Th_{0.25}O_2$ and was found to be almost constant over the entire acidity range. For $U_{0.75}Ln_{0.25}O_{1.875}$ solid solutions, a variation of this partial order was observed along the nitric acid concentration range, that underlined the predominance of different controlling reactions in the dissolution mechanism: surface-controlling reaction involving H_3O^+ at low pH (*i.e.* n < 1) for $C_{HNO_3} \leq 0.5$ M, and uranium oxidation (*i.e.* n > 1) for $C_{HNO_3} \geq 1$ M [1].

Another significant effect of composition was found to arise from the cationic homogeneity of the solid solutions considered. Such effect was particularly observed for $Th_{1-x}U_xO_2$ samples, whose dissolution is often promoted by redox reactions involving U(IV) [2]. In these conditions, the kinetics of alteration was generally slowing down when improving the distribution of cations at the microscopic scale, namely by using wet chemistry routes of preparation. Indeed an increase by a factor 300 of the normalized dissolution rate (U) was observed in the case of dissolving the heterogeneous sample. Moreover, while the dissolution of $Th_{0.5}U_{0.5}O_2$ was perfectly congruent (r = R_L (U) / R_L (Th) = 0.93), the ratio of congruence deviates from unity in the case of heterogeneous sample (r = 2.3). This difference in behavior was assigned to the preferential dissolution of enriched uranium zones, which present a lower chemical durability. This behavior was confirmed by ESEM observations performed *in operando* during the dissolution process allowed imaging the preferential alteration of uranium enriched zones (Figure 2). These latter parameters must be taken into account when studying the evolution of the solid/solution interface. Also, it allowed pointing out the effect of surface heterogeneities on the dissolution kinetics as well as the strong evolution of the reactive surface during the dissolution of the ceramics. This information appears of main importance when working with normalized dissolution rate and led to consider limit cases for using such variables.

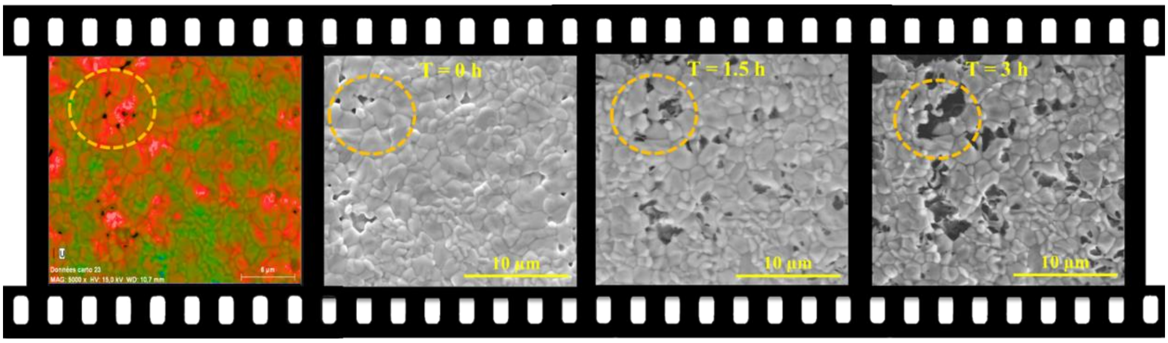

Fig. 2: In operando ESEM observations performed during the dissolution of $Th_{0.5}U_{0.5}O_2$ (2M HNO_3, T = 90°C).

Microstructural parameters were generally found to be significant only for samples of high chemical durability, *i.e.* ThO_2, CeO_2, and derived solid solutions. In these conditions, the crystallization state of the samples could influence the kinetics as much as the acidity of the leachate while density or grain size remain second order parameters. Nevertheless, these latter parameters have been considered when studying the evolution of the solid/solution interface. Indeed, ESEM observations performed *in operando* during the dissolution process allowed imaging the preferential alteration zones for several solids which can be located either within the grain boundaries, triple junctions or through intragranular corrosion pits (Figure 2) [3]. Also, it allowed pointing out the effect of surface heterogeneities on the dissolution kinetics as well as the strong evolution of the reactive surface during the dissolution of the ceramics. This information appears of main importance when working with normalized dissolution rate and led to consider limit cases for using such variables.

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Thermodynamic properties of uranothorites and coffinite from solubility measurements

Stéphanie SZENKNECT, Adel MESBAH, Nicolas CLAVIER, Dan COSTIN, Nicolas DACHEUX
Christophe POINSSOT (DEN/DRCP – CEA Marcoule)
Rodney C. EWING (CISAC, Stanford University)

Secondary phases which could be formed during radwaste leaching represent important sinks for U and other radionuclides, and thus control the subsequent mobility and the ultimate distribution of the radiotoxic elements in the surrounding environment. Sites under investigations for underground repository are for the greatest part located in undisturbed clayrocks exhibiting reducing and silica-rich environment. Such geochemical conditions favor the formation of U(IV) secondary phases after the dissolution of UO_2 matrix. Under these conditions, $USiO_4$ coffinite is suspected to precipitate depending on the relative stability of coffinite and uraninite. However, thermodynamic properties of coffinite, especially solubility constant, remain largely unkown. Very few reliable thermodynamic data related to coffinite formation or solubility are available in the literature. None were determined based on solubility experiments.

Since attempts reported in literature for the last fifty years, failed to synthesize large amounts of single phase coffinite in order to perform solubility studies, an indirect method based on solubility measurements of $Th_{1-x}U_xSiO_4$ uranothorite solid solutions was envisaged. The preparation of $Th_{1-x}U_xSiO_4$ samples was successfully undertaken under hydrothermal conditions (T=250°C) by Costin *et al.*[1-2]. The formation of a complete solid solution between x = 0 (thorite) and x = 1 (coffinite) was evidenced from XRD, Raman spectroscopy[3] and EDS analyses. In parallel, a systematic study was conducted to determine the effect of experimental parameters such as pH, heating time, U/Si mole ratio and temperature in order to establish the optimal synthesis conditions for the preparation of a sufficient amount of well crystallized coffinite. This optimized protocol was used to obtain pure coffinite samples that were fully characterized before and after solubility experiments. Finally, a set of experiments on the dissolution of intermediate members of the uranothorite solid solution ($0 \leq x \leq 0.5$) and coffinite was carried out under the same conditions. Once the equilibrium was reached, the solubility constant of each compound was determined and a relation was established between uranothorite solid solutions and coffinite solubility constants (*Figure 1).* Finally, the results enable to conclude on the relative stability of the coffinite and uraninite[4].

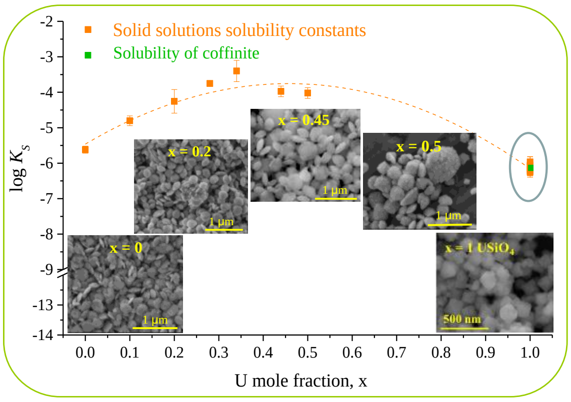

Fig.1: Variation of the solubility constant along the uranothorite series determined by under-saturation experiments at 298 K under anoxic conditions.

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Dissolution of uranyl phosphates and vanadates: from synthetic analogues to natural samples

Stéphanie SZENKNECT, Fanny CRETAZ, Nicolas CLAVIER, Nicolas DACHEUX
Christophe POINSSOT (DEN/DRCP – CEA Marcoule)
Michael DESCOSTES (AREVA, Business Group Mines, DR&D-projet Envir@Mines)

Uranyl minerals form as secondary phases within uranium deposits represent potential new uranium resources[1] but also affect the distribution of uranium and others radionuclides and their subsequent mobility in the vicinity of nuclear waste repository settings or at sites of groundwater contamination. Due to their extremely low solubility, uranyl phophates and vanadates are ubiquitous within uranium ore deposits and strongly affect uranium fate and transport in soils and aquifers under oxidizing conditions[2]. Considering uranyl phosphates and vanadates as potential phases of interest for ore exploitation, it is essential to evaluate their thermodynamic properties, and to acquire reliable kinetic data in the perspective of sustainable ore treatment process development.

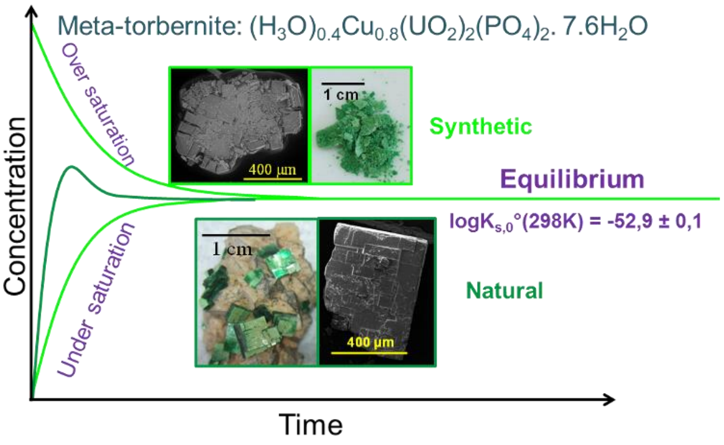

Fig.1 Methodology used for the determination of meta-torbernite solubility constant.

Reliable measurements of the Gibbs free energy of formation of a mineral phase can be derived from solubility studies only if the mineral of interest is pure and stable under the experimental conditions. The preparation of synthetic samples is thus usually required. The congruence of the dissolution as well as thorough characterization of the raw and leached solids indicates the stability of the studied phase. Establishment of mineral-water equilibrium is demonstrated by approaching the equilibrium state from undersaturated (dissolution) and oversaturated (precipitation) conditions. This methodology was used to determine thermodynamic data associated to relevant phases in the $\{P_2O_5\text{-}V_2O_5\text{-}UO_2\}$ system. Pure and single phase autunite, $Ca(UO_2)_2(PO_4)_2.2\text{-}6H_2O$, torbernite, $Cu(UO_2)_2(PO_4)_2.8\text{-}12H_2O$, carnotite $K_2(UO_2)_2(VO_4)_2.3H_2O$ and its phosphate analogous ankoleite $K_2(UO_2)_2(PO_4)_2.6H_2O$ were synthesized then exhaustively characterized and finally submitted to dissolution experiments. The determination of solubility constants, $K_S°$ (Figure 1) was performed in various media and at several temperatures then associated thermodynamic data ($\Delta_R G°$, $\Delta_R H°$ and $\Delta_R S°$) were evaluated[3]. Finally, the comparison of these values (especially $K_S°$) with that obtained from natural minerals allowed us to evaluate the behaviour of natural samples during dissolution.

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Synthesis, Sintering and Leaching of Monazite-type Wasteforms

Adel MESBAH, Clémence GAUSSE, Stéphanie SZENKNECT, Nicolas CLAVIER, Nicolas DACHEUX
Stefan NEUMEIER, Yulia ARINICHEVA, Dirk BOSBACH (FZ Julich)

Monazite ($LnPO_4$) is a widely-spread mineral naturally containing large amounts of thorium and of uranium. Therefore, logically, it has been considered for long as a suitable matrix to host specific radionuclides coming from the back-end of the nuclear fuel cycle in the scenario of an underground repository. Indeed, among several other properties of interest, monazite structure is able to accommodate a large variety of elements through cationic and/or anionic substitutions and has been reported to be very resistant to radiation damages [1]. However, if the incorporation of actinides has been stated in both natural and synthetic samples, the methods used to prepare these latter were frequently based on dry chemistry routes that can decrease both the sinterability and the chemical durability of the final material.

In this context, the preparation of monazite-type compounds was reconsidered with the use of wet chemistry methods, particularly involving the initial precipitation of hydrated precursors such as $LnPO_4$. 0.667 H_2O rhabdophane. Once the conditions of preparation optimized, the crystal chemistry of this phase was investigated, and a new monoclinic structure (Fig. 1) was proposed in correction of the well-known hexagonal $P6_222$ [2]. The incorporation of tetravalent uranium and thorium in this structure is also under study.

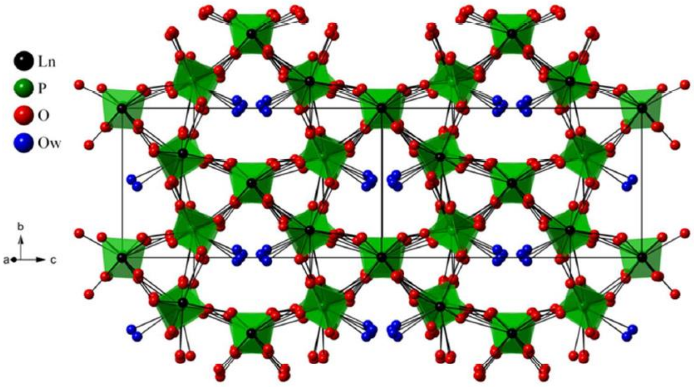

Fig.1: General view of the structure of $SmPO_4$. 0.667 H_2O along the [101] direction.

After the thermal conversion of the hydrates into monazite, the optimal conditions for the densification of the various samples prepared are currently examined. In this framework, various sintering methods are under progress (natural sintering, hot pressing, SPS), while the new possibilities offered by HT-ESEM will be used to build sintering maps.

Finally, the chemical durability of the monazite-type samples is evaluated, mainly through leaching tests performed in acidic conditions. The data obtained from these experiments will thus allow to assess the long-term performances of the matrix. Also, the neoformed phases precipitated in the back-end of the initial leaching will be characterized extensively and the associated thermodynamic data will be evaluated. Particularly, the comparison of the solubility products of rhabdophane and monazite will shed the light on the conditions of stabilization of both phases, which will be of interest both in terms of long-term behaviour and for geochemistry matters.

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[1] N. Dacheux, N. Clavier, R. Podor "**Why monazite appears as a promising long-term radwaste matrix ? Benefits from high structural flexibility and chemical durability**", *Am. Miner.* 2013, 98, 833.

[2] A. Mesbah, N. Clavier, E. Elkaim, C. Gausse, I. Ben Kacem, S. Szenknect, N. Dacheux "**The monoclinic form of the rhabdophane compounds : $REEPO_4$ 0.667 H_2O**" *Cryst. Growth Des.* 2014, 14, 5090.

7 – Microscopies in Environmental Method

L’équipe est constituée de :
1 ingénieur de recherches CNRS responsable d’équipe (Dr. Renaud Podor),
1 maître de conférences de l’ENSCM (Dr. Julien Cambedouzou)
3 ingénieurs d’études CNRS (Sandra Maynadié, Johann Ravaux, Xavier Le Goff),
1 ingénieur CEA (Henri-Pierre Brau),
1 technicien CEA (Bruno Corso)

Contrat d’apprentissage:
- Johan Salacroup (apprentissage Master) Développement d’une cellule d’observation in situ de matériaux céramiques en cours de dissolution par microscopie électronique à balayage environnementale, 2012-2014, CNRS

Doctorants :
- Sandra Castanié (thèse) « Matériaux vitreux autocicatrisants pour applications haute température », 2010-2013, DGA (Coll UCCS – Lille)
- Thibaud Nardin (thèse) “ Elaboration de carbure de silicium poreux et mésoporeux par voie moléculaire”, 2012-2015, CEA/DSM - bourse CFR
- Benoit Gouze (thèse) “ Structuration de fluoroalcanes amphiphiles en milieu non-aqueux - vers un SiC à mésoporosité contrôlée”, 2012-2015, ANR FANTASIC
- Galy Ingrid Nkou Bouala (thèse) Etude du frittage d'oxydes de lanthanides et d'actinides de géometrie contrôlée : de l'observation microscopique à la modélisation, 2013-2016, CEA/DEN – bourse CFR
- Hélène Arena (thèse) « Effets compétitifs et cumulatifs des éléments chimiques sur la vitesse résiduelle d’altération de verres nucléaires », 2012-2016, CEA/DEN, CTCI Areva (Coll. CEA/DTCD - Marcoule)

Post-doctorant :
- Jimmy Nicolle (Post Doctorat) « Nanotubes de carbone fonctionnalisés pour l’extraction du césium », 2012-2014 (CEA/DEN)

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.

- Les avancées récentes en microscopies à rayons X et électroniques permettent d'accéder l'observation directe des agrégats supra-moléculaires en solution avec une résolution inégalée à ce jour, sans nécessité de mettre en œuvre des techniques de préparation d'échantillons lourdes et génératrices d'artéfacts.

- L'apport de ces nouveaux modes d'imageries à la compréhension fine de certaines propriétés des matériaux (auto-cicatrisation, frittage, dissolution, réactivité chimique…) est essentiel. L'expérimentation in situ, 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.
Le couplage de l'observation des matériaux à l'échelle microscopique avec une caractérisation statistique permet de décrire précisément les matériaux divisés, leurs surfaces, leur interaction avec les fluides, leurs mélanges et les associations faibles de molécules ayant des propriétés de transport ionique particulières.

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 d'avoir déterminé, sur la base d'images MEB enregistrées dans des conditions parfaitement maitrisées, l'énergie d'association de l'eau dans un composé auto-assemblé de type MOF. 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 la cicatrisation de matériaux autoréparants (application joints de scellements pour les piles à combustible ; coll. UCCS – UMR 8181), le moussage des verres (application recyclage ; coll. UMR XXX), ou encore l'élaboration de barrières thermiques (application aéronautiques ; coll. LaSIE FRE-CNRS 347) ont également été étudiées avec succès dans le cadre de collaboration avec des laboratoires d'autres universités.

Un second ensemble de résultats porte sur l'utilisation de la diffusion des rayons X aux petits angles (SAXS) pour l'étude de la matière sous forme de fluide complexe ou de matériau granulaire. Tout d'abord, des études de SAXS sur des liquides complexes et des gels à base d'alcanes semi-fluorées et de silanes ont permis d'étudier la structure de ces mélanges et de comprendre les propriétés d'auto-association de ces molécules. Ces études sont mises à profit dans le cadre d'un projet innovant visant à élaborer du carbure de silicium par des voies moléculaires (ANR FANTA-SiC).

Le dernier ensemble de résultats est relatif aux travaux couplés menés dans le cadre du L2ME en 2014. Deux premières études ont d'ores et déjà permis de concrétiser la fusion des équipes des LDD et

LM2E au travers de publications. De nouveaux outils ont été développés afin d’accéder à une caractérisation quantitative des paramètres structuraux, et en particulier de la surface spécifique de poudres de silices mésoporeuses par SAXS[1]. Ces outils ont pu être mis à profit dans le cadre d’une étude de SAXS *in situ* couplée avec de la RMN du ^{29}Si solide sur la dissolution des silices mésoporeuses[2]. Dans un autre contexte, le mécanisme de formation de mésosphères d’oxydes d’uranium a pu être établi en corrélant des données de diffusion aux petits angles et des images de microscopie en mode environnemental[3].

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[1] J. Cambedouzou and O. Diat, **Quantitative small-angle scattering on mesoporous silica powders: from morphological features to specific surface estimation**, J. Appl. Cryst 45 (2012) 662-673.

[2] B. Gouze, J. Cambedouzou, S. Parres-Maynadie and D. Rebiscoul, **How hexagonal mesoporous silica evolves in water on short and long term: Role of pore size and silica wall porosity**, Micr. Mes. Mat. 183 (2014) 168-176.

[3] G.I. Nkou Bouala, N. Clavier, R. Podor, J. Cambedouzou, A. Mesbah, H.P. Brau, J. Lechelle and N. Dacheux, **Preparation and characterisation of uranium oxides with spherical shape and hierarchical structure**, CrystEngComm 16 (2014) 6944-6954.

Self-Repairing Glassy Materials

Renaud Podor
Sandra Castanié, Daniel Coillot, François O. Méar, Lionel Montagne (Unité de Catalyse et Chimie du Solide - UMR-CNRS 8181 -Université Lille Nord de France),
H. Suhonen (ESRF, Experiments Division, 38043 Grenoble, France)

The development of solid oxide fuel cells and high-temperature hydrolysers has led to the need for high temperature sealants, for which glass and glass-ceramics are among the most efficient solution. However, they suffer of cracking when subjected to thermal cycles. Self-healing is a promising solution to overcome this problem, for which two mechanisms exist: intrinsic and extrinsic. The intrinsic self-healing is based on the overheating of glass beyond its softening temperature, but it requires therefore external intervention. Conversely, the extrinsic self-healing is obtained by adding particles to the glass matrix, which will form a new glass upon contact with atmosphere in a crack, and thus it requires no external intervention.

The crack healing in composites made of glass matrix and boron particles has been observed with both High Temperature Environmental Scanning Electron Microscopy (HT-ESEM) and X-ray Micro-Tomography. HT-ESEM is a very efficient instrument for the in situ observation of the healing process. This technique allowed to characterize directly at T=600-800°C and under adequate gaseous conditions the formation of the liquid oxides as well as the crack filling as a function of time[1]. However, HT-ESEM imaging only enables to observe the healing of a crack that emerges at the surface of the sample. Since the particle oxidation occurs with the gas coming from outside the crack, it is highly interesting to observe how the healing occurs inside the crack, i.e. in the depth of the material. This can be achieved using a tomographic method. As the crack width observed in our samples is generally equal to 200nm, i.e. below the resolution of conventional X-ray micro-tomography, and the sample volume to be analyzed is too large (typically 50 to 200µm in depth) to use electron tomography (limited to sample sizes below few hundred of nanometers in one direction), a new technique was used to observe the 3D healing process with the adequate resolution: hard X-ray phase micro-tomography, which has been developed at the European synchrotron radiation facility (ESRF) micro-imaging end station ID22NI.

A HT-ESEM image series was recorded on a crack at high temperature. The healing property is obtained by the spreading of molten boron oxide, formed by the oxidation at 700°C of boron particles and the partial filling of the cracks was observed. The same sample is used to perform hard X-ray phase micro-tomography at the same location where the HT-ESEM images have been recorded. Image correlation showed that crack healing is obtained at the surface even in the bulk of the sample, where oxygen diffusion may be limited, by the same healing mechanism. The recorded images indicate that boron particle oxidation is not complete after a healing cycle, meaning that several cycles can be conducted with the same composite. X-ray fluorescence imaging gave evidence that molten boron oxide reacted with the glass matrix to form Ba and Ca borates, which also contributed to heal the cracks.

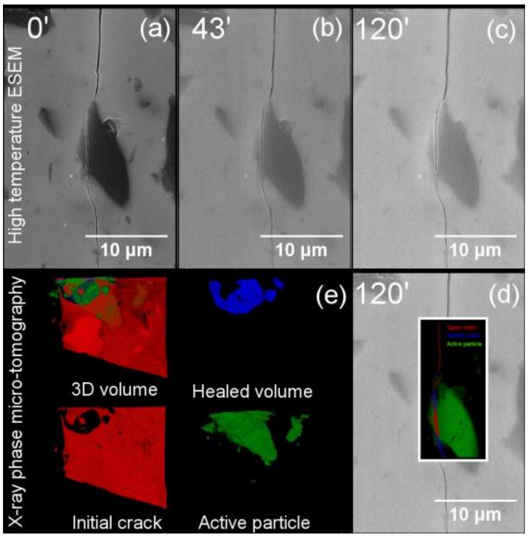

Fig.1: HT-ESEM micrographs of a crack observed at the sample surface during heat treatment at 700°C under 750Pa O_2 at different durations (a, d and c). After the heat treatment, hard X-ray phase micro-tomography is performed on the same location. Image reconstitutions of the sample surface (d) and of the sample volume (e) show the crack healing going throughout the material.

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[1] D. Coillot, F. O. Méar, R. Podor, L. Montagne "Influence of the Active Particles on the Self-Healing Efficiency in Glassy Matrix, **Adv. Eng. Mat.** 2011, 13(5), 426-435.

Initial stage of spherical shape oxides sintering

Galy Ingrid Nkou Bouala, Renaud Podor, Nicolas Clavier, Jacques Lechelle and Nicolas Dacheux

The initial state of solid state sintering is usually defined by the formation of necks between the grains of a green pellet. This process poorly contributes to the density achievement but constitutes a key-step ensuring the mechanical properties of the compact. However, the models describing the associated diffusion phenomena are generally based on simplified geometries, such as in the approaches built from spherical grains approximation by Kuczynski or Coble[1], and then suffer from a lack of experimental data. The purpose of this study is to elaborate lanthanide and actinide model oxides with a controlled morphology then to study their behaviour through *in situ* observations by the means of HT-ESEM (fig. 1).

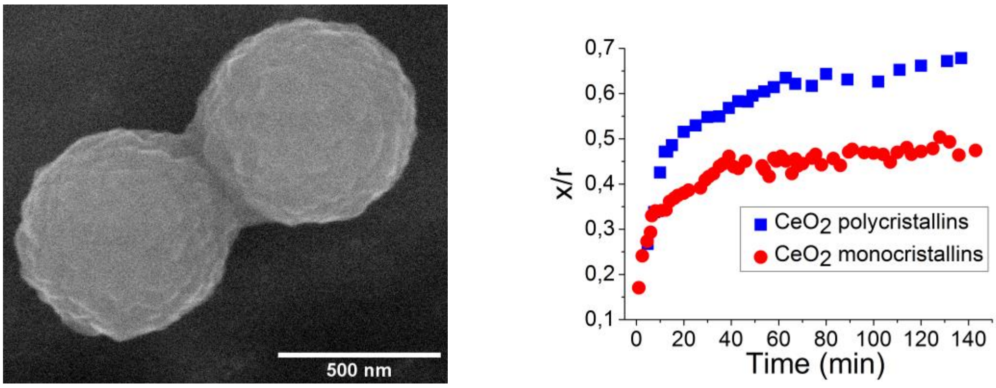

Fig.1: ESEM observation of CeO_2 microspheres and subsequent evolution of rate of sintering (x/r) at T=1100°C.

The synthesis of the spherical shape particles was first performed for CeO_2, ThO_2 and UO_2[2]. The resulting samples were dispersed in ethyl acetate to be deposited on a platinum foil then fired at 500°C to ensure the formation of the corresponding oxides. Such procedure resulted in the formation of aggregates of 2, 3 or 4 spheres along with the existence of isolated grains. These systems where observed *in situ* in the HT-ESEM chamber (T = 900-1200°C).

The observation of isolated spheres also allowed us to monitor the grain growth in a finite space. The evolution of the crystallites number was then modeled by a two step kinetic law for various temperatures. This led us to evidence two mechanisms for the growth of crystallites. For short heating times, oriented attachment was correlated with a low value of activation energy (120 ± 30 $kJ.mol^{-1}$), while more energetic diffusion processes (390 ± 75 $kJ.mol^{-1}$) were found to occur for long-term heating durations. Also, a precise control of the CeO_2 aggregate inner structure (*i.e.* number of crystallites and density of the particle) was achieved and described as a nanostructure map.

Two grains systems with polycrystalline (fig. 1a) or monocrystalline grains where also studied for the first time. The kinetics associated to various phenomena such as neck growth, evolution of the dihedral angle or rate of sintering (fig. 1b) indicate that sintering is controlled by grain boundary diffusion in both cases. Nevertheless, the sintering of polycrystalline grains is enhanced due to the fact that inter- and intragranular effects must be considered in this case while only intergranular sintering can occur between monocrystalline grains.

Such data will now be implemented in numerical models in order to forecast the sintering kinetics of real compounds.

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[1] R.L. Coble, **Initial sintering of alumina and hematite**, J. Am. Ceram. Soc. 41 (1958) 55-62.

[2] G.I. Nkou Bouala, N. Clavier, **R. Podor, J. Cambedouzou**, A. Mesbah, **H.P. Brau**, J. Lechelle and N. Dacheux. **Preparation and characterisation of uranium oxides with spherical shapes and hierarchical structures**, CrystEngComm 16 (2014) 6944-6954

Determination of thermodynamic properties of Metal Organic Framework mesoparticles using in situ ESEM

Torsten Sievers (LEA”SONO”DFC-CNRS), Renaud Podor, Henri-Pierre Brau, Johann Ravaux, Thomas Demars, Caroline Genre and Daniel Meyer

Metal-organic frameworks (MOFs) are under active investigation due to their potential application in several domains. Many efforts are put into controlling their properties. Were herein present a study on the thermodynamics of cylindrical neodymium MOF particles containing an organic ligand[1]. The cylindrical MOF particles are constituted by the aggregation of crystalline nanoparticles. Solvant (ie water) is entrapped in the inter-particle space in the liquid form. The study bases mainly on an elaborated environmental electron scanning microscopy (ESEM) investigation to derive the phase diagram of solvent inside and outside the particles and thus its association energy in the particles.

The experiments are performed in an ESEM, controlling both water pressure in the chamber and sample temperature using a Peltier stage. We assume that water vapor in the microscope chamber is in equilibrium with presumably liquid water in the Nd- DHBQ meso-particles. Starting at high water vapor pressure (1000-2000Pa), pressure was gradually decreased at different drop rates. At a certain pressure, we observed isotropic particle shrinkage (Figure 1a), which we interpret as follows: initially, water vapor pressure around the particles is larger than vapor pressure between gaseous water and liquid water in the particles. With decreasing pressure, we reach and exceed this vapor pressure. As a result, the particles lose water and shrink. It is, therefore, possible to determine the transient pressure, at which the water vapor pressure in the particles becomes larger than in the ESEM chamber by monitoring the size change. This reasoning was confirmed by combining particle shrinkage under controlled water pressure with XRD analyses.

The comprehensive study was designed as follows. For each measurement series, we investigated washed particles from one single synthesis at temperatures between 2 and 32°C in water vapor. We have investigated how the transient pressure, the pressure at which the particle size starts to change, correlates with temperature and how this correlation can be used to obtain insights into the meso-particle thermodynamics. When the transient pressure is plotted versus temperature, we obtain a phase diagram where the transient pressure marks the coexistence curve. At a pressure larger than the transient pressure, water remains in the particles. Below the transient pressure, it is released from the particles and evaporated into the gas phase. Coexistence curves are described by the Clausius-Clapeyron-relation (Figure 1b), from which we can derive the vaporization enthalpy Hvap, equal to 60 ± 6 kJ/mol. Notably this vaporization enthalpy is the energy needed to separate water and particles and to evaporate the water. With the vaporization enthalpy of water of 44 ± 0.5 kJ/mol, we can calculate the association energy of water in the mesoparticles, which amounts to 16 ± 6.5 kJ/mol.

The described solvent vapor pressure dependent ESEM investigation is novel and unique and expands the current capability of ESEM imaging. With this setup, ESEM is suitable to perform thermodynamic studies of materials and to obtain association and vaporization energies.

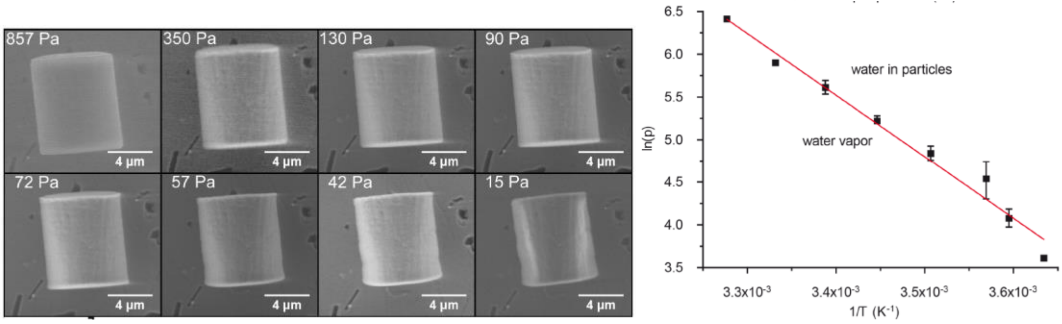

Figure 3: a) Size changes of Nd-DHBQ particles with vapor pressure. b) The logarithm of the water vapor pressure, at which the size starts to change, is plotted vs. reciprocal temperature..

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[1] T. K. Sievers, C. Genre, F. Bonnefond, T. Demars, J. Ravaux, D. Meyer and R. Podor, **Vapour Pressure Dependence and Thermodynamics of Cylindrical Metal-Organic Framework Mesoparticles: an ESEM study**, Phys. Chem. Chem. Phys. 15 (2013) 16160-16166.

How hexagonal mesoporous silica evolves in water on short and long term: role of pore size and silica wall porosity

Benoit Gouze, Julien Cambedouzou, Sandra Parrès-Maynadié and Diane Rébiscoul

In this study[1], we have determined the evolution of the morphology and the structure of mesoporous silica MCM41 and SBA15 in saturation condition during short and long term alteration by water at 60°C. These materials were characterized using *in-situ/ex-situ* Small Angle X-ray Scattering (SAXS), and *ex-situ* by nitrogen adsorption-desorption and ^{29}Si Nuclear Magnetic Resonance (NMR).

The results have shown that MCM41 lost its hexagonal order of pores (figure a and b). This phenomenon has been attributed to a change of the pore shape probably due to the dissolution of silica wall and to the recondensation of hydrolysed silica on the pore surface leading also to a partial pore clogging at high alteration progress.

In the case of SBA15, as soon as the porous silica is in contact with water, an altered silica layer is formed at the pore surface (figure c) and dissolved at a rate of 120 nm.year^{-1} leading to a pore size increase. When an equilibrium between dissolution and recondensation of the silica is reached, the silica dissolution rate strongly decreases (7 nm.year^{-1}) and the altered layer growth follows a diffusive process with a diffusion coefficient of $D = 1.4\ 10^{-24}$ m^{2}s^{-1} (figure d).The differences of evolution between the two silica are explained by their different pore diameter and the presence of microporosity in the case of SBA15.

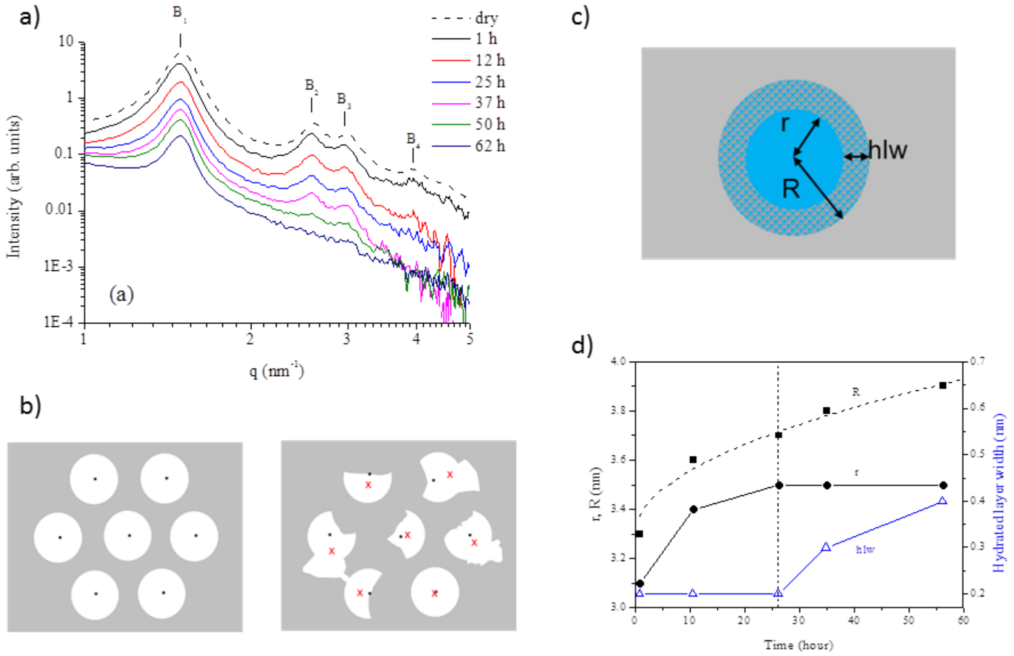

Figure: a) SAXS patterns of MCM-41 in hot water for different durations, b) schematic representation of the structural evolution of MCM-41, c) schematic representation of a SBA-15 pore with its alteration layer, d) evolution of structural parameters of SBA-15 during alteration.

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[1] B. Gouze, J. Cambedouzou, S. Parres-Maynadie and D. Rebiscoul, **How hexagonal mesoporous silica evolves in water on short and long term: Role of pore size and silica wall porosity**, Micr. Mes. Mat. 183 (2014) 168-176.

Elaboration of Structured Silicon Carbide by Soft Templating Approach

Thibault Nardin, Benoit Gouze, Julien Cambedouzou, Damien Bourgeois, Michel Wong Chi Man (AM2N, ICGM), Xavier Deschanels, Daniel Meyer and Olivier Diat

Silicon carbide (SiC) exhibit unique properties (high temperature stability, oxidation resistance, mechanical resistance or thermal conductivity) making them attractive for a number of applications. SiC materials of controlled porosity would be desirable for nuclear fuel cladding or catalyst supports.

We propose here a new and innovative method for porous SiC elaboration by “soft templating” approach (STA) [1]. Indeed, STA can efficiently be used for the introduction of well-defined porosity in hard ceramics such as SiC[2]. The porosity and the structure of the final material are defined by the self-assembly of a soluble directing agent (SDA) into a solvent, the former acting as a supramolecular template and the latter having the function of SiC precursor.

The SDAs studied are semifluorinated alkanes and partially fluorinated tetraalkylsilane with respective empirical formula $C_nF_{2n+1}C_mH_{2m+1}$ and $C_nF_{2n+1}C_2H_4Si(C_mH_{2m+1})_3$. The solvent and SiC precursor used is the 1,3,5-trisilacyclohexane which after molecular condensation and calcination leads to the desired ceramic.

The porous SiC elaboration has been studied from the supramolecular organization step of the SDA in the TSCH to the final porous SiC. The obtained SiC present structuration, porosity and a specific surface around $30 m^2.g^{-1}$. This study confirms the feasibility of this approach and comforts the STA as a promising method to obtain porous and mesoporous SiC.

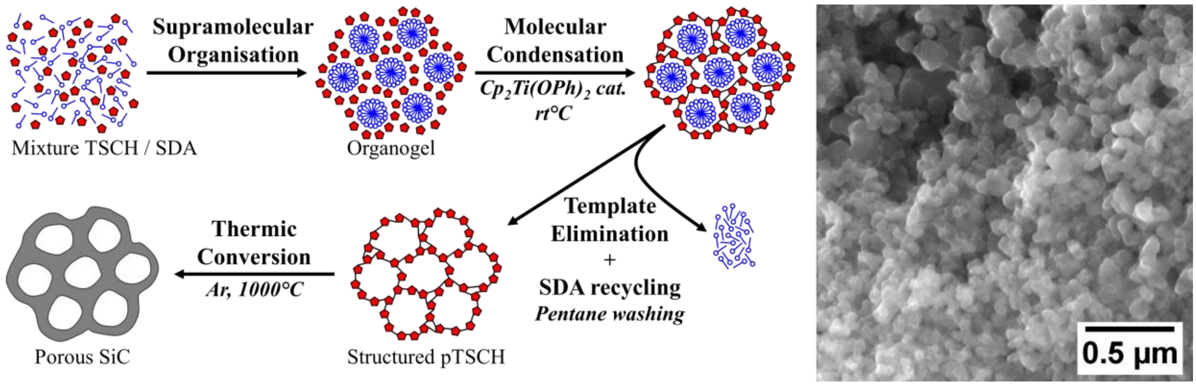

Fig : left – STA General Principle. Right – Scanning Electron Microscopy Image of a structured SiC obtained by STA using $C_{12}F_{25}C_2H_4Si(C_2H_5)_3$.

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[1] Y. Wan, Y. Shia and D. Zhao, *Chem. Commun.* 9 (2007) 897–926.

[2] L. Borchardt, C. Hoffmann, M. Oschatz, L. Mammitzsch, U. Petasch, M. Herrmann and S. Kaskel, *Chem. Soc. Rev.* 41 (2012) 5053–5067.

Quantitative small angle scattering on mesoporous silica powders: from morphological features to specific surface estimation

Julien Cambedouzou, Bruno Corso, Alban Jonchère and Olivier Diat

Development of porous Silica or carbon material with high specific surface area is of a particular interest in the field of materials science given their potential interest in a wide range of applications including catalysis, water treatment or drug delivery. Among these mesoporous structures, those consisting of one-dimensional pores aligned along a compact hexagonal packing are of prime importance and can be referred to as “hexagonal mesoporous materials” (HMPM). The most famous silica structures of this kind are MCM-41 and SBA-15. The same symmetry can be found in carbon mesoporous materials, for example in FDU-15 structures.

The precise characterization of HMPM is necessary for most of the applications envisioned for these materials (pore size, pore density, specific surface and sometimes the thickness of the functionalization layer). Small angle X-ray scattering (SAXS) techniques offer the opportunity to determine the mean structural parameters of HMPM. Although different approaches can be found in the literature in order to numerically reproduce the experimental data obtained on HMPM or hexagonal liquid crystals, when the sample is a powder, fitting the experimental data in absolute scale with numerical models becomes necessary. We propose a comprehensive study devoted to the quantitative interpretation of small-angle scattering patterns of HMPM in terms of structure and specific surface estimation[1] based on the formalism proposed by Spalla *et al.* in 2003[2]. In the case of two real samples, namely a SBA-15 and a MCM-41 powder, the specific surface area of the mesopores was estimated and discussed in the light of gas adsorption measurements.

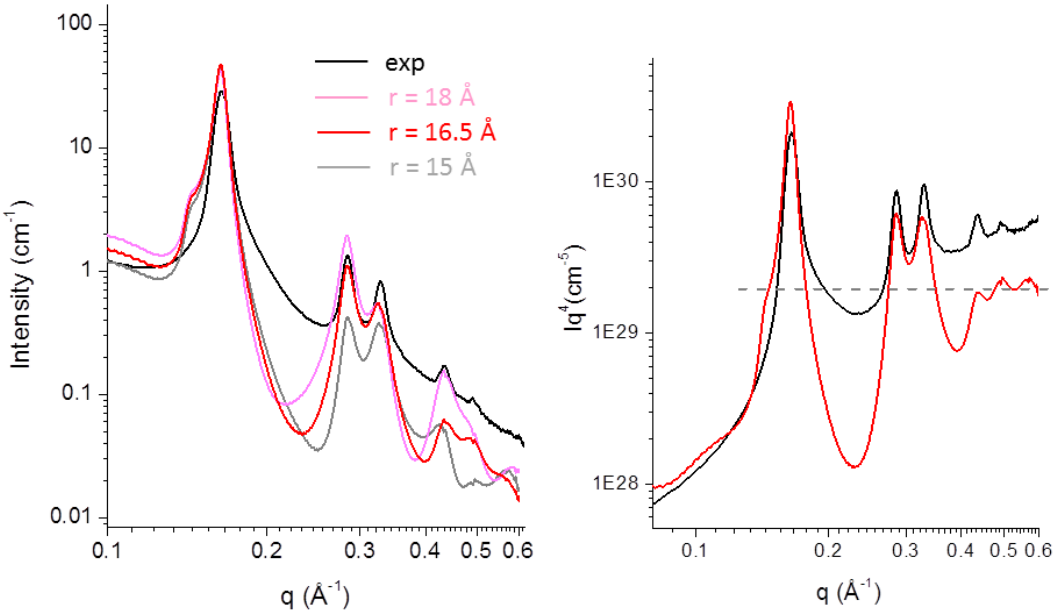


Fig: left -SAXScattering from MCM41 powder sample (black line) plotted as a function of q with other model scattering curves varying the pore radius of cylindrical pores aligned on a triangular network. Right – Porod plot in absolute units of experimental and the best adjusted model curve.

[1] J. Cambedouzou and O. Diat, **Quantitative small-angle scattering on mesoporous silica powders: from morphological features to specific surface estimation**, J. Appl. Cryst. 45 (2012) 662-673.

[2] O. Spalla, S. Lyonnard and F. Testard, **Analysis of the small-angle intensity scattered by a porous and granular medium**, J. Appl. Cryst. 36 (2003) 338-347.

8 - Mesoscopic Modelling and Theoretical Chemistry

L'équipe est constituée actuellement de :

- 1 Professeur Université Montpellier 2, responsable d'équipe (Jean-François Dufrêche),
- 1 Chercheur-Ingénieur CEA/DSM (Magali Duvail)
- 1 Chercheur-Ingénieur CEA/DEN (Bertrand Siboulet)

Post-doctorants :

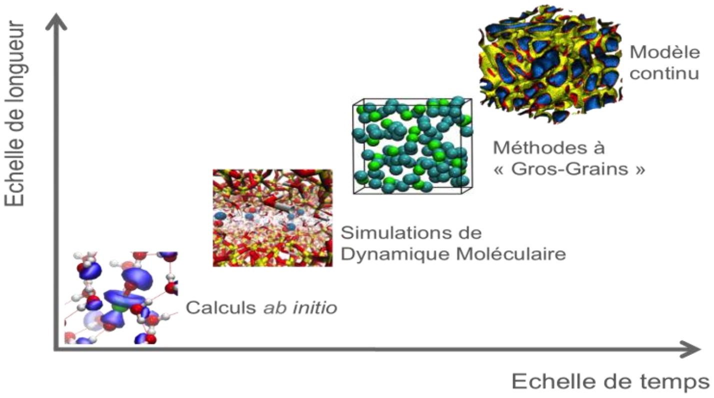
- Yushu Chen (DEN, depuis 2013) : Modélisation des phases organique pour la séparation
- Anwesa Karmakar (DSM, ERC REE-Cycle, depuis 2014) : Extraction des terres rares

Doctorants :

- Arnaud Villard (MESR UM2, depuis 10/2012) : Etude de la séparation par les nonatitanates poreux.
- Thanh-Nghi Nguyen (CEA/DEN, depuis 10/2012) : Modélisation moléculaire de l'extraction liquide-liquide.
- Sarah Hocine (MESR UM2, depuis 10/2014) : Modélisation moléculaire des oxydes pour la séparation
- Pauline Moyaert (CEA/DEN, depuis 11/2013) : Thèse en collaboration, localisée au DRCP/SMCS/LMPR, encadrée par Ch. Sorel (DRCP/SMCS/LMPR) sur le lien avec le génie chimique.

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).

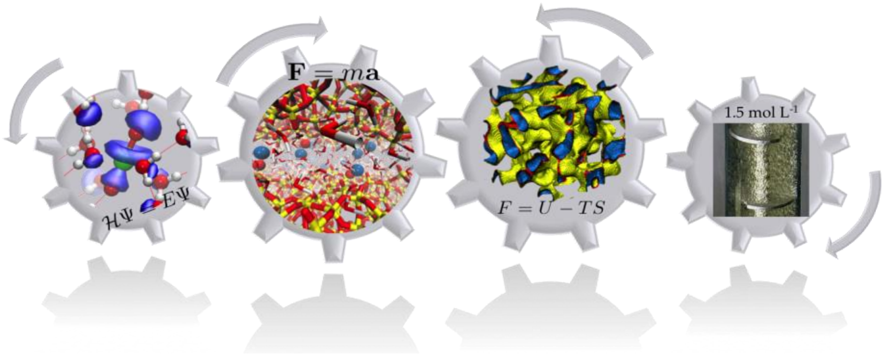
Les moyens mis en œuvre par l'équipe sont représentés sur les figures qui suivent. La description la plus fondamentale est celle de la mécanique quantique (calculs *ab initio*) capable de représenter l'acte élémentaire. Elle est en particulier étudiée pour déterminer la complexation moléculaire et elle 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.

Liquid silica interfaces: fundamentals of solid liquid extraction and retention

B. Siboulet, S. Hocine, M. Duvail, J.-F. Dufrêche
B. Coasne (ICG & MIT)

Mesoporous oxide materials are a tool for decontamination and separation. Understanding ion specificity, mobility, adsorption in confined media, is a fundamental step towards modelling extraction and retention of radionuclides. We study diffusion in confined silica, ion adsorption, and mesoscopic interaction potentials. Realistic models of amorphous silica surfaces with different silanol densities were built using Monte Carlo simulated annealing. We first study the impact of varying hydrophilicity on water adsorption, and on normal or parallel water self-diffusion. As a next step, we include ions in our models, so as to analyse ion mobility, ion exchange, and ion adsorption on various silica surfaces.

Self-irradiation impacts diffusion in confined silica

Porous silicas are both of fundamental and practical interest as they exhibit a large specific surface and a porosity network that can be tuned precisely. Our realistic slit pore models of amorphous silica allow connecting the surface chemistry of materials and their affinity for water: hydrophilicity increases as we add more silanols on surfaces[1]. Estimating normal diffusion coefficient, i.e., in the direction normal to surface, requires an analysis of molecular dynamics data (Fig. 1) based on Smoluchowski equation, since standard mean square displacement analysis do not allow the inclusion of the surface potential[2].

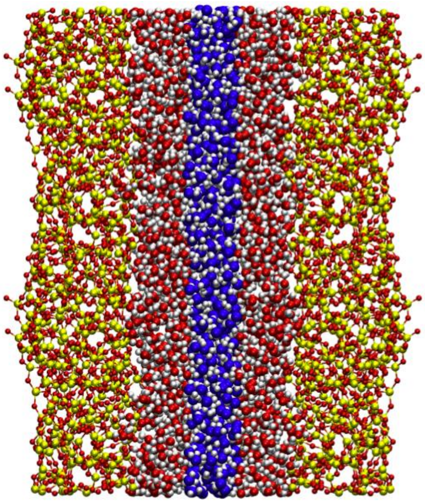


Figure 1: Modelling normal diffusion rests on the statistical analysis of mean first passage time. Molecules presented in blue are initially located in the pore centre. Statistical analysis of their diffusion by Smoluchowski equation produces diffusion coefficients in the centre layer.

The thermodynamics and dynamics of water confined in the materials with various surface chemistries show a hydrophobic to hydrophilic transition, e.g., in the diffusion coefficients (Fig. 2). Irradiation by radionuclides confined in glass tends to induce this hydrophilic to hydrophobic transition.

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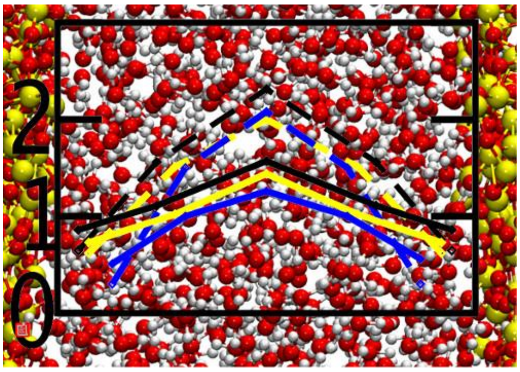
[1] B. Siboulet, B. Coasne, J.-F. Dufrêche, and P. Turq. **“Hydrophobic transition in porous amorphous silica.”** J. Phys. Chem. B 115, 7881 – 7886 (2011).

[2] B. Siboulet, B. Coasne, J. J. Molina, J.-F. Dufrêche, and P. Turq. **“Water self-diffusion at the surface of silica glasses: effect of hydrophobic to hydrophilic transition.”** Mol. Phys. 111, 3410 – 3417 (2013).

Figure 2: Diffusion coefficients (10^{-9} m^2 s^{-1}) as a function of position in the water slot. (Width of the water slot: 2 nm.) Analysing molecular dynamics in the frame of Smoluchowski equations shows that normal diffusion coefficients (full lines) are affected in the vicinity of surface, as well as parallel diffusion coefficients (dashed lines). Moreover, surface hydrophilicity globally reduces diffusion (increasing silanol density from black to yellow and blue lines).



Modelling mesoporous solids for separation and retention of ions

Electrodynamics is the field of all phenomena resulting from charges at liquid-solid or liquid-soft matter interfaces, such as electrophoresis, electro-osmosis, sedimentation potential or streaming potential. As so, electrodynamics is the basis of ion separation or retention in mesoporous solids. Modelling electrodynamics should be the based on description at the atomic level, such as provided by molecular dynamics. This is still challenging and most publications use mesoscopic or macroscopic models with fitted parameters. We studied the interaction between a surface and an ion at the molecular level (Fig. 3). This is a first step towards modelling electrodynamics on complex systems, in which many charges exist on the surface, and many ions in solution.

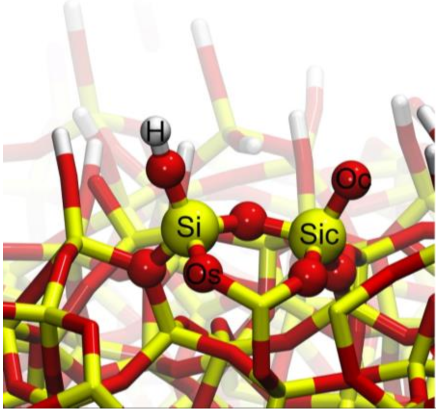


Figure 3: The silica surface bears a single charge, on the Oc oxygen atom. The silica is amorphous, and the silanol density is monitored between realistic limits, namely between 1 and 57 silanols per nm^2.

We model potentials of mean force (PMFs) within the frame of umbrella sampling[1] (Fig.4). This method is a statistical analysis of molecular dynamics. Ion-surface distance is monitored by adding a harmonic potential. This gives a series of local profiles of the interaction potential, which are fitted together so as to produce a global PMF. The derivative of this potential is the average force experienced by the ion. Our main results are the following. We find a universal surface-ion repulsion which dominates electrostatic attraction, regardless of the ion type. Hydrophilicity has an impact on adsorption for the more hydrated ion. Indeed, it appears that, in the case of lithium, increasing hydrophilicity increases bond strength. The result is opposite in the case of Caesium.

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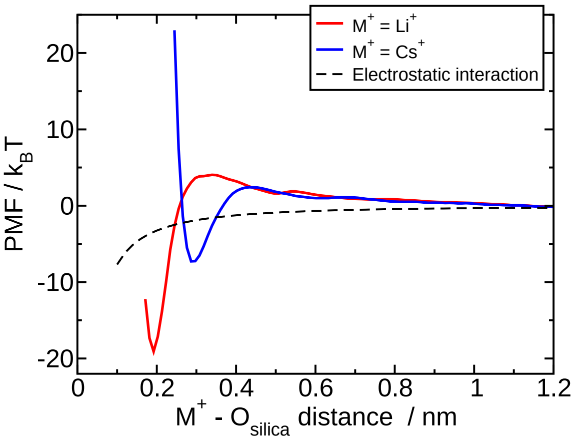
[1] B. Siboulet, M. Duvail, S. Hocine, B. Coasne, J.-F. Dufrêche, and P. Turq. **“Potential of mean force between an ion and a silica surface.”** To be published (2014).

Figure 4: Bond strength is very ion specific. It is stronger for lithium, although this ion is the more strongly hydrated, which necessarily reduces bond strength. A universal and fundamental result is the hydrophilic interactions, which is evidenced by the steady decrease of PMF from the first peak up to a few nm. From this molecular free energy calculation curves, it is possible to extract the thermodynamics constant of adsorption K$_d$.



Bonding is very strong in most cases. Our results show that most published results concerning ion adsorption cannot be equilibrated for the molecular dynamics runs are far too short. As a consequence, these systems should be modelled at the mesoscopic level. This is why we also study ion surface systems at the Density Functional Theory (DFT) level.

Multi-scale modelling of electrolyte solutions

J.-F. Dufrêche, M. Duvail, T. N. Nguyen,
J. J. Molina (PECSA/UPMC and ICSM), P. Turq, M. Salanne (PECSA/UPMC), Ph. Guilbaud (DEN/DRCP-Marcoule), B. Bagchi (IISc – Bangalore, India), K. Bohinc (Univ. Ljubljana, Slovenia)

Recycling methods for strategic metals often rely on equilibria between phases. In these processes such as the liquid-liquid extraction, the metal is selectively transferred from an aqueous phase to an organised organic phase. The separation between elements relies on the affinity differences for both solutions. Modelling such process is complex since different scales of description and various effects have to be taken into account: electrostatic force, solvation effects, importance of the complexation, extractant molecules aggregation, *etc*.

The study of electrolytes in solution has relied heavily on computer simulations, which have allowed us for better understanding the microscopic and macroscopic properties of these systems, complementing the available experimental techniques. In order to obtain a complete description of electrolyte solutions, the different length and time scales that need to be considered require distinct levels of description: from *ab initio* quantum calculations to classical Molecular Dynamics simulations, and finally to simple implicit solvent descriptions. We attempt to develop a unified (consistent) multi-scale description of electrolyte solutions:

(1) Classical polarizable force fields suitable for ions in aqueous solution.

(2) Integral equation theories were used to derive solvent averaged potentials from the structural information obtained from classical Molecular Dynamics simulations. These solvent averaged potentials were then used in implicit solvent Monte-Carlo simulations to determine the ion activities.

(3) Liquid perturbation theory was used to determine the best implicit solvent description in terms of charged hard-sphere type models, for which approximate (but accurate) analytical solutions for the thermodynamic and structural properties are known.

Classical Molecular Dynamics simulations provide a convenient way of studying the microscopic properties of ions in solution. However, obtaining macroscopic thermodynamic properties, such as activities and osmotic coefficients is notoriously difficult. To reduce the complexity of the system, coarse-grained, i.e., implicit solvent models, are derived from the microscopic structure of the fluid.

This coarse-grained technique has been applied to study simple dissociated atomic electrolytes in solution, as well as more complicated 2-1[1] and 3-1[2] electrolytes. The agreement with the atomic and coarse-grained descriptions is found to be excellent. However, considerable discrepancies are found when comparing to experimental data, due to the fact that the underlying atomic force fields are generally parameterised to reproduce ion-water properties, and the ion-ion correlations are not necessarily properly described. Thus, the use of coarse-grained models provides an efficient method for fine-tuning atomic force fields to experimental data (Fig. 1).

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[1] T.-N. Nguyen, M. Duvail, A. Villard, J. J. Molina, Ph. Guilbaud, and J.-F. Dufrêche. **"Multi-scale modelling of Uranyl chloride solutions."** J. Chem. Phys., submitted (2014).

[2] J. J. Molina, M. Duvail, Ph. Guilbaud, and J.-F. Dufrêche. "**Atomistic Description of Binary Lanthanoid Salt Solutions: A Coarse-Graining Approach**." J. Phys. Chem. B 115, 4329 – 4340 (2011).

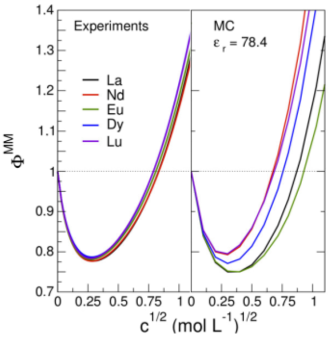


Figure 1: Osmotic coefficients in the McMillan-Mayer frame of referenced for the series of lanthanoid chloride solutions obtained experimentally (left) and from coarse-grained atomistic simulations (right) as a function of the square root of the concentration.

This approach is also used to describe the thermodynamics properties of molecular ions (uranyl UO_2^{2+}, nitrate NO_3^-, …) in aqueous solution. The description of the thermodynamics properties of such ions is more complex than the monoatomic ones (e.g., lanthanoid cations and chloride anions) because of their molecular character. Indeed, describing a monoatomic ion as a charged hard-sphere is relatively easy to understand. But what about a non-spherical molecular ion like NO_3^- and UO_2^{2+}? In order to reduce the complexity of the system, i.e., an aqueous solution containing complexes formed by several molecular ions (like $UO_2(NO_3)^+$), we focused on the uranyl chloride UO_2Cl^+ complex in aqueous solution (Fig. 2).

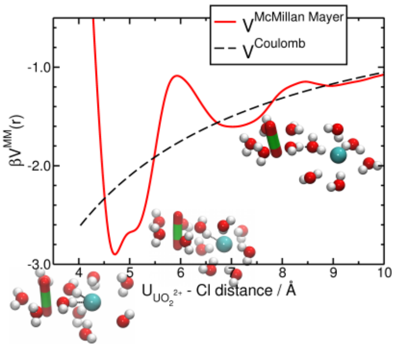
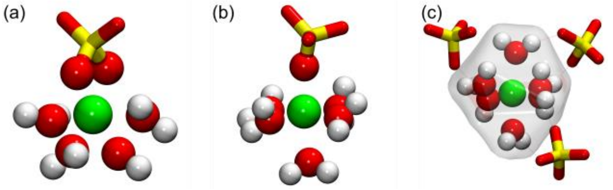


Figure 2: McMillan-Mayer potential profile of $UO_2^{2+}-Cl^-$ in water calculated using "umbrella-sampling" molecular dynamics simulations. Characteristic snapshots of hydrated UO_2Cl^+ complexes are also shown. Uranium is coloured in green, chlorine in cyan, oxygens in red, and hydrogens in white.

Recently, we also applied such multiscale approach to others molecular electrolytes, such as $ZnSO_4$ and $MgSO_4$ salts, for which the association is predominant[1]. Indeed, we proposed a theory based on the Smoluchowski equation and on the mean spherical approximation. The values of the association constant calculated for $ZnSO_4$ and $MgSO_4$ aqueous solutions are consistent with further methods of measurements. Comparison between molecular dynamics and Brownian dynamics simulations in the case of $MgSO_4$ enlightens that the pair is a global association phenomenon since it corresponds to several association phenomena: contact ion pair and solvent separated ion pair (Fig. 3).

Figure 3: Snapshots issued from molecular dynamics simulations presenting the different coordination modes of the SO_2^- (red and yellow) anion in the Mg^{2+} (green) hydration shells: contact ion pair (CIP) in the (a) bidentate and (b) monodentate coordination mode, and solvent-separated ion pair (SSIP).



Thanks to the elimination of fast variables method, we show that the theory can be generalised to any association in solution. Further developments have been performed in this domain (especially about uranyl ions at interfaces and about the viscosity of electrolyte solutions).

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[1] J.-F. Dufrêche, M. Duvail, B. Siboulet, M. Jardat, and O. Bernard. **"Modelling of mutual diffusion for associated electrolytes solution: $ZnSO_4$ and $MgSO_4$ aqueous solutions."** Mol. Phys. 112, 1405 – 1417 (2014).

A multi-scale approach to ion transport in clays

M. Duvail, J.-F. Dufrêche
M. Jardat, P. Turq, B. Rotenberg, A. Obliger, V. Marry, (PHENIX/UPMC), M. Levesque (ENS – INC), E. Giffaut (ANDRA – Chatenay-Malabry), G. Allaire, R. Brizzi (Ecole polytechnique), A. Mikelić (Univ. Lyon 1)

A multi-scale approach has been developed for the diffusion of ions in clays. This media is microscopically a charged lamellar system for which water molecules and ions are confined between charged sheets. Nevertheless, at the macroscopic scale, this structure does not hold anymore and the system is made of different porosities. Because clays are multi-scale porous media, modelling the transport of solutes through such systems requires a good description of the solutes transport properties at the different scales, *i.e.* from the microscopic to the macroscopic (Fig. 1).

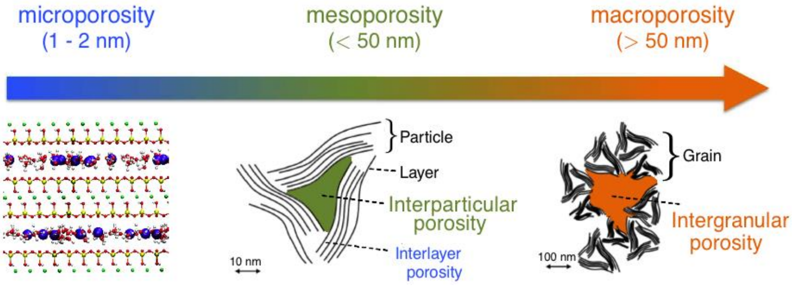

Figure 1: Schematic description of clays from the (lamellar) atomic scale to the macroscopic media with various porosities.

At the atomic level description, Monte-Carlo and molecular dynamics simulations have been performed. These results (for hydrated clays) have been compared to the continuous description based on hydrodynamics and non-equilibrium thermodynamics. Even for small intersheets distances, the ion distributions calculated from atomic and mesoscopic models provide results in good agreement (Fig. 2).

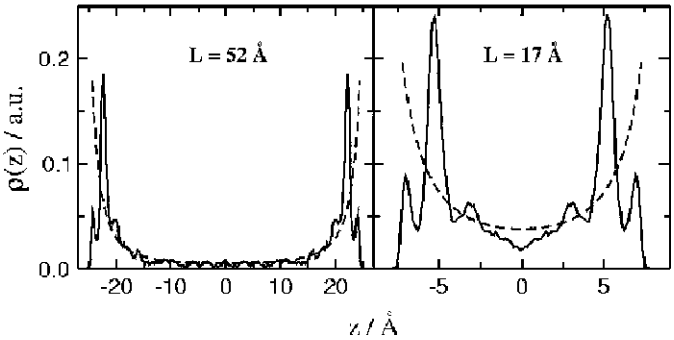

Figure 2: Cation distributions between two sheets obtained from atomistic (solid line) and mesoscopic (analytical Poisson-Boltzmann, dashed line) for two interlayer distances: 52 Å (left) and 17 Å (right), corresponding to N = 100 and 33 water molecules per cation, respectively.

An alternative study has been performed for dehydrated clays. The adsorption constants K_d have been calculated and the results have been compared to broadband dielectric spectroscopy. It should be noted that the method is quite general and independent on the nuclear waste storage issue.

To access the macroscopic diffusion properties of electrolytes through clays, it is crucial to describe correctly the transfer and diffusion properties of these solutes through the mesoporosity of clays, typically 5 – 50 nm. To this end, Lattice Boltzmann Electrokinetics (LBE) simulations have been carried out. This allows for calculating all the transfer coefficients that couple the solvent and ionic fluxes through a charged pore under gradients of pressure, electrostatic potential, and concentration[1].

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[1] A. Obliger, M. Duvail, M. Jardat, D. Coelho, S. Békri, and B. Rotenberg. **“Numerical homogenization of electrokinetic equations in porous media using lattice-Boltzmann simulations.”** Phys. Rev. E 88**,** 013019 – 11 (2013).

Furthermore, in order to be consistent with the experiments, the present method has been extended to take into account the adsorption and desorption phenomena in the calculation of mesoscopic dynamical properties of ions in porous media[1].

The present method can be applied to:

- simulate transport in complex porous media,
- investigate the full dynamics.

The results obtained at this scale of modelling can be used as an input for describing the transport at larger scales, e.g., in the framework of pore network models. Such models, in which the void space of the porous medium is represented by an idealized geometry of pore bodies joined by pore throats, can be adapted to a given experimental structure to compute the transport properties (Fig. 3).

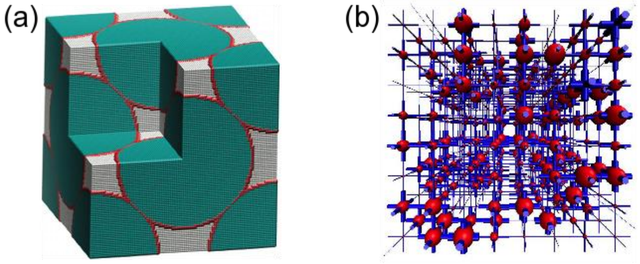

Figure 3: (a) Perspective view of a unit cell of a face-centered cubic packing of sphere used for LBE simulations. Solid nodes are coloured in blue, interfacial fluid nodes, are coloured in red, and non-interfacial fluid nodes are in white. (b) 3D representation of a pore network model where the pores are coloured in red and the channels in blue.

We also studied homogenization[2,3,4] (or upscaling). In that case, the macroscopic laws are obtained thanks to a mathematical explicit derivation. It can be shown that the general macroscopic law are actually linear in terms of response. A general analytic expression of all the transport coefficients can be obtained. It requires only the knowledge of the stationary solutions.

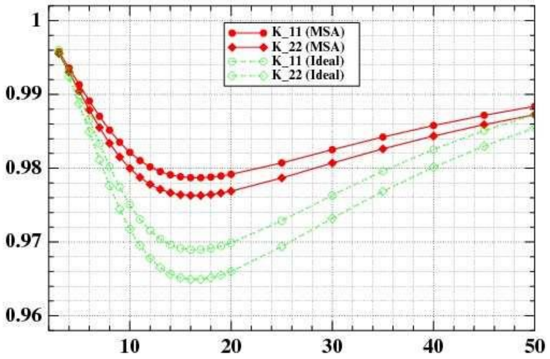

Figure 4: Relative hydrodynamic permeability (Darcy's law coefficients) of a model of porous clays calculated from homogenization. The red curve corresponds to the real model for which the departures from ideality are taken into account thanks to the MSA approximation. The green curve is the very popular ideal model (very often called Poisson-Nernst-Planck PNP). The difference represents the role of the electrostatic charge and the one of the ionic sizes.

Realistic non-ideal effects are taken into account by an approach based on the mean spherical approximation (MSA), which takes into account finite size ions and screening effects. This formalism is able to describe transport and equilibrium properties of electrolyte solutions up to molar concentrations. Our results show that the realistic model confirms qualitatively the conclusions obtained using the ideal model but there are quantitative differences arising that can be important at high charge or high concentrations. The effects strongly depend on the physical phenomena, but they cannot be neglected if a quantitative representation of porous media is required.

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[1] M. Levesque, M. Duvail, I. Pagonabarraga, D. Frenkel, and B. Rotenberg. **"Accounting for adsorption and desorption in lattice Boltzmann simulations."** Phys. Rev. E 88, 013308 – 6 (2013).

[2] G. Allaire, R. Brizzi, J.-F. Dufrêche, A. Mikelić, and A. Piatnitski. **"Role of non-ideality for the ion transport in porous media: derivation of the macroscopic equations using upscaling."** Phys. D- Nonlinear Phenomena 282, 39 – 60 (2014).

[3] G. Allaire, R. Brizzi, J.-F. Dufrêche, A. Mikelić, and A. Piatnitski. **"Ion transport in porous media: derivation of the macroscopic equations using upscaling and properties of the effective coefficients."** Computat. Geosci. 17, 479 – 495 (2013).

[4] G. Allaire, J.-F. Dufrêche, A. Mikelić, and A. Piatnitski. **"Asymptotic analysis of the Poisson–Boltzmann equation describing electrokinetics in porous media."** Nonlinearity 26, 881 – 910 (2013).

Mesoscopic modelling of microemulsions

M. Duvail, Th. Zemb, J.-F. Dufrêche
L. Arleth (University of Copenhagen, Denmark), S. Marčelja (Australian National University – Canberra, Australia)

Recycling of metals, either rare earths for recycling magnets in windmills, lanthanides from electronics or actinides from nuclear wastes, into valuable material relies on ion specific separation, basis of the hydrometallurgy. All efficient methods known for separating ions are based on equilibria between complex fluids (concentrated acidic or basic and reverse micelles) in the Winsor II regime, *i.e.* water in oil (w/o) microemulsions. These w/o reverse micelles, that selectively up-take some ions, have been up to now considered as spherical aggregates, even with typical volume fractions of up to 30 percent. However, it is known that in industrially relevant cases of liquid – liquid extraction (recycling of nuclear fuel, lanthanide refinement, nickel refining), extractant aggregates cannot be described as simple metal-ion complexes spherical on average, since the high conductivity observed in the oil phase proves a bicontinuity degree of the system.

Realistic examples of nonionic w/o microemulsions have been simulated using the two level-cuts of a Gaussian random field based on wavelets originally proposed by Arleth and Marčelja. The thermodynamics of the interface is determined by the Helfrich free energy that depends on the mean, spontaneous (corresponding to the curvature preferred of the unconstraint surfactant film) and Gaussian curvatures, and also the bending and Gaussian elastic constants, which refer to the rigidity of the surfactant film in terms of energies. In our model, the free energy is minimized as a function of the bending and Gaussian elastic constants and the spontaneous curvature of the surfactant film.

This method allows us for generating all possible microstructures thermalized of two immiscible liquids separated by a layer of surfactant. We have explored how the swelling of microemulsions allows for the identification of different families of microemulsions[1]. Our simulations point out a change in the microemulsion morphology as function of the surfactant film rigidity and the composition of oil, water and surfactant (Fig.1).

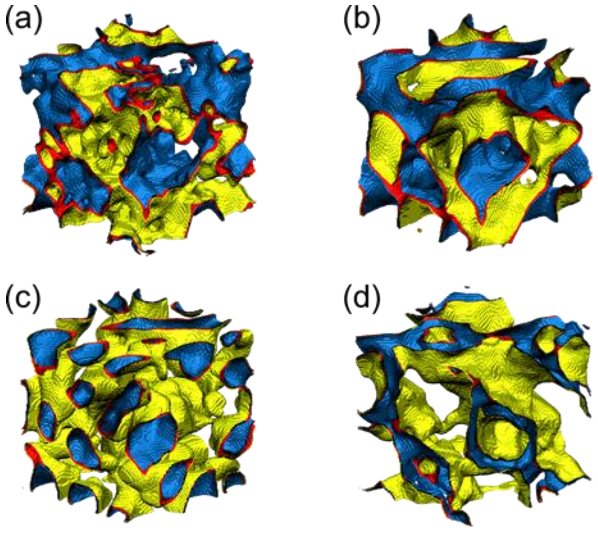

Figure 1: 3D field projections of the direct space representation of microemulsions with different compositions and parameters, as predicted by the Gaussian random field model. The side lengths of figures are 20 π nm ≈ 63 nm. For the illustrations, water is blue, oil is yellow and the surfactant is red. Only separation surfaces between the domains are represented.
(Top) Bicontinuous (a) flexible and (b) rigid microemulsions. (Bottom) Oil-rich microemulsions: (c) water droplets in oil, and (d) oil in water droplets in oil.

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[1] M. Duvail, J.-F. Dufrêche, L. Arleth, and Th. Zemb. "**Mesoscopic modelling of frustration in microemulsions.**" Phys. Chem. Chem. Phys. 15, 7133 – 7141 (2013).

Locally lamellar structures are found for rigid microemulsions, whereas for more flexible ones, the connected-droplet and/or bicontinuous structures are preferred. Furthermore, we have shown that the microemulsion swelling versus the volume fraction gives a specific signature of the microemulsion microstructure. This allows for discriminating between different types of microemulsions: flexible, frustrated and unfrustrated (close to biliquid foams), and connected structures as molten hexagonal and cubic phases. Frustrated and unfrustrated microemulsions appear near instabilities related to transition towards lyotropic liquid crystals. Microstructures can be distinguished *via* qualitative features on the scattering. Ternary phase diagrams are also calculated from the simulations[1] (Fig. 2).

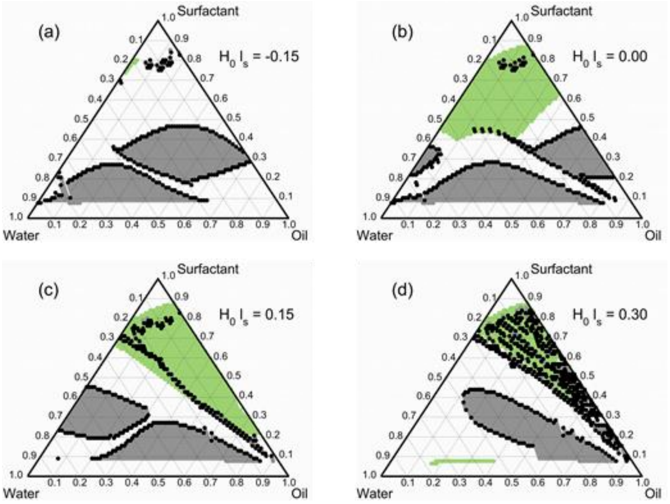

Figure 2: Ternary phase diagrams calculated for different values of spontaneous curvatures (H_0 l_s): (a) −0.15, (b) 0.00, (c) 0.15, and (d) 0.30. Points represent the spinodal (black and gray) and lamellar (green) instabilities.

However, it is well known that efficient surfactants used for such processes are mainly ionic. Therefore, it is crucial to develop a more realistic model taking into account (i) the ionic character of the surfactant, and (ii) the presence of cations in solutions. Up to know no predictive model of the free energy of transfer of ions between phases exists. Taking into account, in a same model, both the metal complexation and the colloidal terms[2,3], will provide predictive modelling of ion separation. This includes lanthanides as well as caesium and actinides. Thus, the next step of this study will be the accounting of the presence of cations in the free energy term derived from the Helfrich formalism.

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[1] M. Duvail, L. Arleth, Th. Zemb and J.-F. Dufrêche. **“Predicting for thermodynamic instabilities in water/oil/surfactant microemulsions: A mesoscopic modelling approach.”** J. Chem.Phys. 140, 164711 – 11 (2014).

[2] Th. Zemb, M. Duvail and J.-F. Dufrêche. **“Reverse Aggregates as Adaptive Self-Assembled Systems for Selective Liquid - Liquid Cation Extraction.”** Isr. J. Chem. 53, 108 – 112 (2013).

[3] J.-F. Dufrêche and Th. Zemb. **“Effect of long-range interactions on ion equilibria in liquid-liquid extraction.”** Chem. Phys. Lett. Accepted (2014)

Organic phases modelling for the liquid-liquid extraction: a molecular approach

M. Duvail, S. Van Damme, Y. Chen, J.-F. Dufrêche
Ph. Guilbaud (DEN/DRCP-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 organised organic phase. Modelling such processes remains quite difficult since many phenomena occur: complexation, solvation, electrostatic interactions, polarisation forces, *etc.* Furthermore, these interactions occur at different length sizes. Indeed, recently, experiments and simulations pointed out the presence of supramolecular aggregates, similar to reverse micelles, and having characteristic sizes of several nanometers.

This suggests that the extraction process may be complex since it relies on the selective formation of such compounds. In each aggregate, a polar core is surrounded by a more or less stretched interface composed of extractant molecules. Therefore, modelling such processes makes necessary the calculation of the aggregates free energies. An important term to consider is the free energy of the carbon chains that impose the spontaneous and stretched curvature of the surfactant film. However, a lack remains concerning its role, as well as its intensity.

The description of the aqueous phase is being relatively well established, but for the organic phase nothing exists from a predictive point of view. The main goal of this study is the understanding of the various effects (solvation, electrostatic and van der Waals forces, entropy), which drive the transfer from one aqueous phase to an organic organized phase. A method based on density functional theory (classical DFT) will allow for the calculation of the ion distribution in the various reverse micelles. Then, the thermodynamical properties of the system will be calculated. The experimental support will be first the extraction of lanthanide nitrate salt $Ln(NO_3)_3$ thanks to the DMDOHEMA molecule for which experimental data have been measured (Fig. 1).

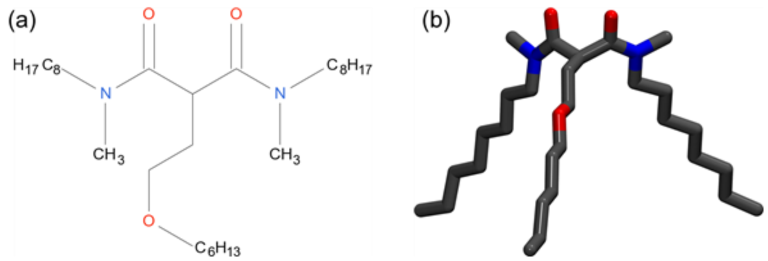

Figure 1: (a) 2D and (b) 3D representations of the DMDOHEMA molecule.

We propose to determine the carbon chains free energy in small molecular aggregates with small ions in organic phase by means of molecular dynamics simulations. This project aims at proposing a model aggregate for which the size of the polar core will change.

In order to determine changes in the free energy as a function of the size of the polar core, a method based on thermodynamics integration has been used, namely by umbrella-sampling molecular dynamics simulations[1] (represented in Fig. 2). We have shown that the global free energy of the system is consistent with soft matter theory. Thus, the aggregates (or complexes) around metal ions in the organic phases for liquid-liquid extraction are not very different from inverse micelles. This result is important because it proves that the macroscopic theory elaborated for the description of such

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[1] M. Duvail, S. Van Damme, Ph. Guilbaud, Y. Chen, Th. Zemb, and J.-F. Dufrêche. **"The role of chain configurations for liquid-liquid extraction."** To be published (2014).

systems can be actually applied for separation chemistry.

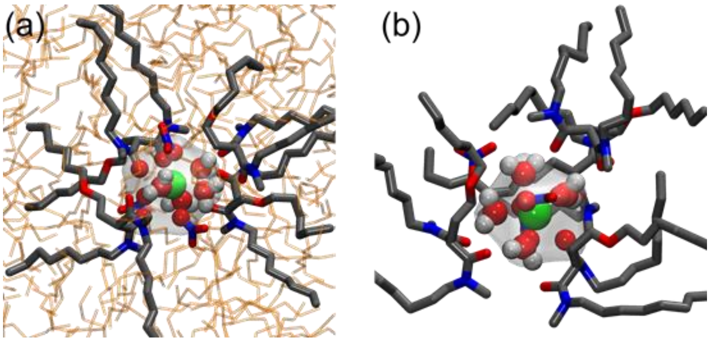

Figure 2: Snapshots issued from molecular dynamics simulations showing the aggregate $La(NO_3)_3(H_2O)_4(L)_4$ *in heptane described (a) explicitly and (b) implicitly.*
For the illustrations, La^{3+} *is in green, oxygen atoms are red, hydrogen atoms are light gray, nitrogen atoms are blue, and carbon atoms are black. In the case of explicit solvent (a), heptane molecules are coloured in orange.*

Simulations in implicit (described at the molecular level) and explicit (described by its dielectric constant) solvents has pointed out that it is crucial to take into account explicitly the solvent in order access the physical parameters, and especially those for the solvation effects, needed for the mesoscopic theories based on phenomenological packing parameters or based on the concepts of Gaussian curvatures, *e.g.*, the Helfrich free energy model.

An other part of this project is focused on the stability of the reverse micelles composed on one lanthanide cation La^{3+}, three nitrate anions NO_3^-, and four extractant molecules DMDOHEMA in organic phase as a function of the number of water molecules in the polar core of the aggregate, *i.e.*, in the La^{3+} first coordination shell[1]. Indeed, although experiments methods provide an average number of four water molecules in the polar core, other stoichiometries could be as stable as this one. Therefore, we investigated the changes in free energy these aggregates when introducing successively one water molecule in the polar core

$$[\mathrm{La(NO_3)(H_2O)}_{x-1}\mathrm{L_4}]_{(\mathrm{org})} + \mathrm{H_2O}_{(\mathrm{org})} \rightleftharpoons [\mathrm{La(NO_3)(H_2O)}_x\mathrm{L_4}]_{(\mathrm{org})} \qquad \text{with } x = 1 \text{ to } 5$$

where L is the DMDOHEMA ligand.

Again, umbrella-sampling molecular dynamics simulations have been used. From the preliminary results obtained it seems that the aggregate composed on three water molecules in the polar core presents the highest stability in heptane. However, the difference in the free energy calculated with four water molecules is quite small, typically less than 1 k_BT (0.5 k_BT). Thus, this small difference can explain the average number of four water molecules in the polar core *via* experimental methods. This approach is able to calculate the association constants used in chemical engineering.

Such theoretical modelling methods already exist in literature since 20 years for detergents and lipids. These results are the base of the detergent formulation and the membrane transport. However, it has never been used for extractant molecules. We plan to apply the soft matter theoretical framework for liquid-liquid extraction in the future, in agreement with these molecular simulations.

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[1] Y. Chen, M. Duvail, Ph. Guilbaud, and J.-F. Dufrêche. **"Organic phases modelling for the liquid-liquid extraction: a molecular approach."** To be published (2014).

Weak adsorption of salts and oil-water solubility balance of peptides: Is the concept of molecular intrinsic hydrophilicity self-consistent?

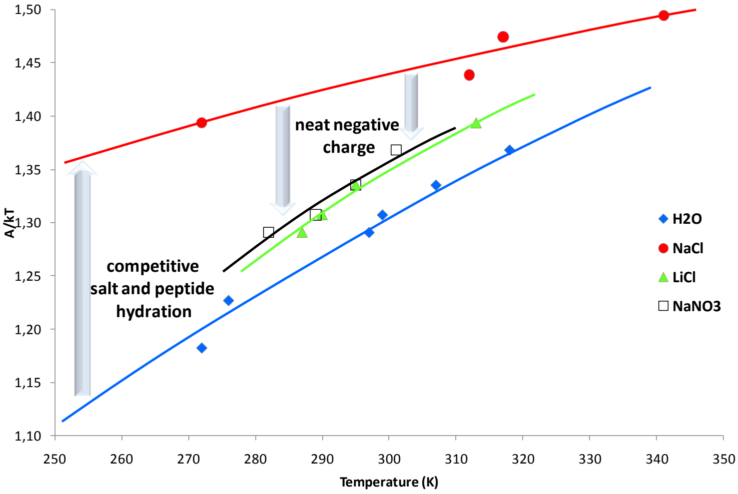
Th. Zemb, J.-F. Dufrêche
C. Déjugnat (ICSM – IMRCP Université Toulouse 3)

We show that an amphiphilic hexapeptide has been used as a model to study how specific ion effects can tune the hydrophilic/hydrophobic balance and induce phase diagram modifications. N-merisation of the peptide has been studied in water and octanol as well as its water/octanol partition: role of H-bonds and ions adsorbed are evidenced. In the presence of electrolytes, competitive interactions are involved: "battle for hydration water" makes the peptide more hydrophobic due to salt addition in the water phase, whereas charging *via* chaotropic ion adsorption can increase the hydrophilicity. These interactions also strongly affect phase separation upon heating (cloud point). These effects can be rationalized considering the salt-decorated peptide as a van der Waals fluid. Weak salt adsorption is the motor of oil-water buoyancy, in the thermodynamic approach of "hydrophilicity", as proposed by Charles Tanford as a concept based on observed free energy of transfer and hence relative solubility in the form of monomers.

Increasing further the salt concentration induces a phase separation by coacervation. This coacervation can be modelled as due to dispersion force, partially quenched by adsorption of ionic species. The energy associated to the adsorption of chaotropic ions is measured and compared to the buoyancy effect. The result questions the concept of intrinsic hydrophilicity, which should be dependent of the nature of the salt dissolved in the water, i.e., the nature of the "buffer".

In summary, the weak interaction responsible of the salt adsorption leads to charges of the order of one par peptide and energy associated is of the same order than water-solvent transfer of this type of amphiphilic peptide considered as a bio-inspired "extractant"[1].

Figure 1: The apparent Hamaker A/k_BT constant driving towards coacervation of the hexapeptide decreases with temperature due to weak adsorption of salt. Sodium chloride is salting-in, while specific ion adsorption-desorption induces partial quenching of the attraction due to electrostatic repulsion after adsorption of chaaotropic ions. This is the proof that "Hydrophilicity" of this hexapetide is NOT a molecular property, but depends on the salt of buffer present.



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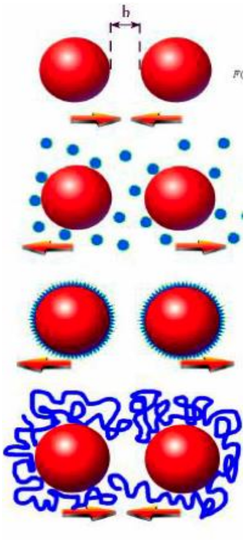
[1] C. Déjugnat, J.-F. Dufrêche, and Th. Zemb. **"Ion-specific weak adsorption of salts and water/octanol transfer free energy of a model amphiphilic hexapeptide."** Phys. Chem. Chem. Phys. 13(15), 6883 – 6893 (2011).

Long Range Interactions at work: universality of the hydration force

Th. Zemb, E. Leontidis (University of Nicosia), V. A. Parsegian (U. Mass at Amherst) and B. Demé (ILL-Grenoble)

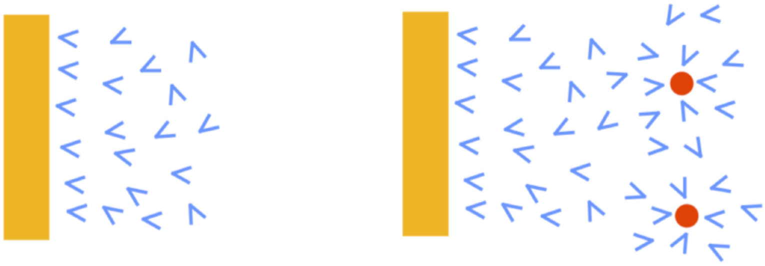


All known separation processes are driven by a combination of strong binding towards one or two first neighbours, either via metal-ligand complexation or electrostatics and long-range interaction extending beyond the first neighbour when ions and molecules are considered.

The importance of so-called chemical Long Range Interactions “LRI”, i.e., non covalent interactions extending beyond the first neighbour is known since WWII, when DLVO was developed independently in Utrecht and Moscow, and shown to be crucial for understanding oil lubrication at low temperature as well as luminosity and contrast in early radar screens. Till 1960, it was thought that dispersion forces and electrostatics would be the general framework for understanding all separation processes involving equilibria between coexisting complex fluids. The DLVO theory combines dispersion forces to electrostatics, the two top schemes on the figure left).

Since Asakura and Oosawa, the generality of depletion mechanism, an attraction introduced by non-adsorbing solutes and the proposition of Marčelja and Radic in 1976 to explain stability of uncharged colloids by the hydration (alias solvation) force. This force is a combination between solvent adsorption enthalpy and progressive loss of orientation near any interface (bottom scheme). Nearly ten thousand of papers report nowadays required a significant participation of hydration forces combined with the depletion force to explain the established phase diagram[1]: fourteen reviews on different systems have been assembled in a special issue of Current Opinion in Colloids and interfaces[2].

The hydration force (third scheme from the top) appears universally as an exponentially decaying interaction with a decay length of 0.2 nm[3]. The contact pressure but not the decay length is linked to enthalpy of adsorption of the first water layer, as observed in the case of neutral carbohydrates[4]. The theory is not yet predictive in general since ions present in the solvent are also hydrated by centro-symmetric water “layer”. There is a competition of interfaces and ion hydration, giving rise to so-called secondary hydration force. The latter is difficult to combine with the primary hydration force dominant when no solute are present in the water as shown in the right part of the figure below, i.e., when decay of order parameter when moving away from the surface is the key process in the repulsive LRI hydration force[5].



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[2] Th. Zemb and V. A. Parsegian. **“Editorial overview: Hydration forces.”** Curr. Opin. Colloid Interface Sci. 16(6), 515 – 516 (2011).

[3] R. H. French, V. A. Parsegian, R. Podgornik, R. F. Rajter, A. Jagota, J. Luo, D. Asthagiri, M. K. Chaudhury, Y.-M. Chiang, S. Granick, S. Kalinin, M. Kardar, R. Kjellander, D. C. Langreth, J. Lewis, S. Lustig, D. Wesolowski, J. S. Wettlaufer, W.-Y. Ching, M. Finnis, F. Houlihan, O. A. von Lilienfeld, C. J. van Oss, and Th. Zemb. **“Long Range Interactions in nanoscale science.”** Rev. Mod. Phys. 82(2), 1887 – 1944 (2010).

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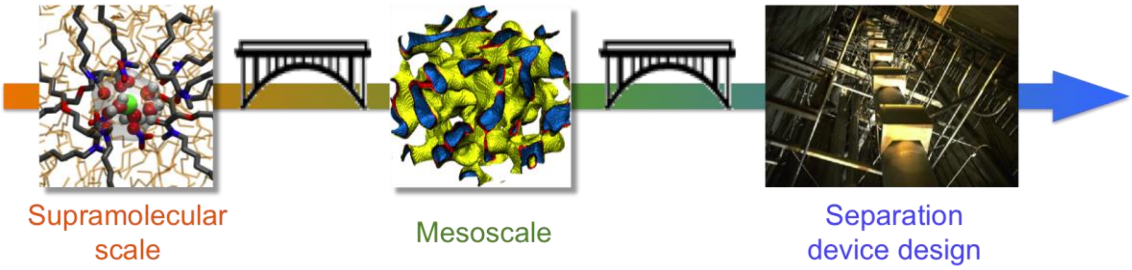
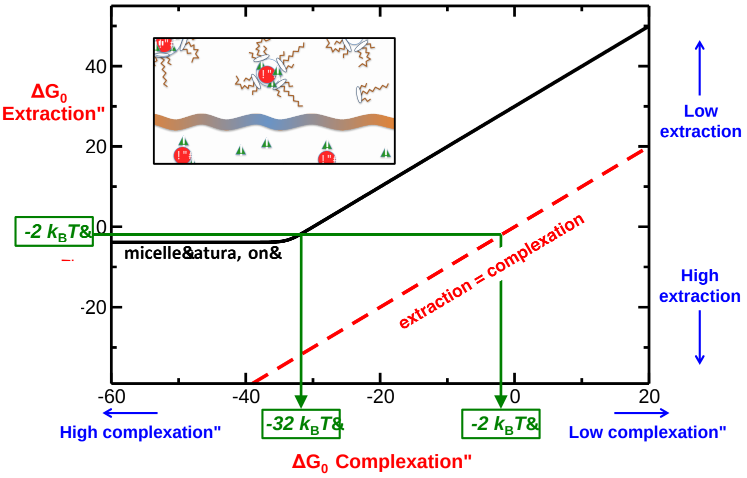
Linking supra-molecular scale to mesoscale for multiphasic systems containing several ions: en route for predictive extraction modelling

M. Duvail, Th. Zemb and J.-F. Dufrêche

Efficient, economically viable and ecologically acceptable recycling requires a multi-scale approach. This is valid as well for the nuclear cycle of the fourth generation –which may not be an extrapolation of the existing technologies– but also for alternative energies: recycling materials and fluids used for alternative energies. An illustrative example is the required for the recycling of magnets contained in offshore eolian generators.



Efficient plant design rests on mass transfer equilibrium and kinetic modelling. Input parameters for process design are apparent free energy of transfer of species to and from a concentrated aqueous solution and a complex fluid, usually a highly concentrated oil-soluble extractant, i.e., a surfactant with complexing properties. Output design of supramolecular and colloidal chemistry are differences of energies of complexation in bulk aggregates as well as free energies linked to the microstructure transformations, that may be unstable[1]. The Graal of the recycling chemistry is predictive modelling of the selectivities versus temperature, composition, pH, i.e., link safely extraction in the process and complexation in the test-tube containing one phase, no interface *etc*.[2] The first example published linking free energy of extraction (Y-scale) and complexation free energy (X-scale), applied to diamide extraction of trivalent species[3], is shown in the figure here.



Colloid Interface Sci. 16(6), 618 – 624 (2011).

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[2] Th. Zemb, M. Duvail, J.-F. Dufrêche. **"Reverse Aggregates as Adaptive Self-Assembled Systems for Selective Liquid-Liquid Cation Extraction"**. Isr. J. Chem. 53, 108 – 12 (2013).

[3] J.-F. Dufrêche and Th. Zemb. **"Effect of long-range interactions on ion equilibria in liquid-liquid extraction."** Chem. Phys. Lett. Accepted (2014)

Project: **R**are **E**arth **E**xtraction and **R**ecycling with low harmful emissions (2013-2018)

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

Aim of the project (feb. 2012): It is a matter of strategic independence for Europe to urgently find processes taking better account of environmental and economic issues, when mining and recycling rare earth elements (REE). Currently THERE IS NO SUCH INDUSTRIAL PROCESS AVAILABLE 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 is on one hand to develop the fundamental understanding involved in the process' complex fluids (both experimental and theoretical) and on second hand to use it to develop a new, cost effective and environmentally friendly REE recycling process. We will achieve this: (i) by enabling, for the first time ever, the fast measurement of free energy of mass transfer between complex fluids; hence it will now be possible to explore and understand an extensive number of process formulations and phase diagrams (just one such study usually takes years but will then be performed in a matter of days); (ii) develop predictive models of ion separation including the effect of long-range interactions between metal cations and micelles; (iii) by using the experimental results and prediction tools developed, we will design an advanced & environmental-ly friendly process formulations and pilot plant; (iv) by enhancing the extraction kinetics and selectivity, by implementing a new, innovative and selective triggering cation exchange process step (ca. the exchange kinetics of a cation will be enhanced). This will represent a major breakthrough in the field of transfer methods between complex fluids.

An expected direct consequence of REE-CYCLE will be that acid waste volumes and other harmful process wastes will be reduced by one to two orders of magnitude. This will bring RRE recycling and mining environmental impact to levels acceptable for the world as well as greatly reduce process running costs. Hence, industrial processing plant will be able to re-open in Europe.
Furthermore, this new understanding of mechanisms involved in selective ion transfer should be applicable to respond to other unresolved problems such as heavy metals, hormones, or drug contamination in drinkable water as well as open new recycling possibilities and 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 project started in July 2103 for a period of sixty months and is organized in five work-packages, four of them started gradually:

Work-package 1:

A new fast real-time and on-line analytic tool to determine phase diagrams and ion equilibria

In charge : J.-Ch. Gabriel

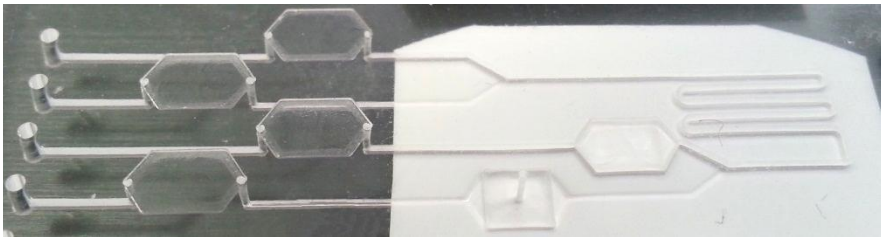


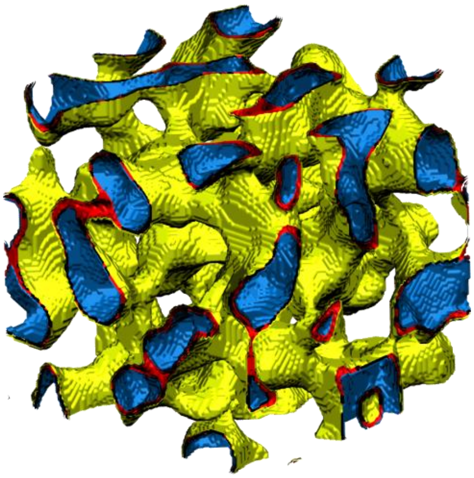
Figure 1: the first PMMA based microfluidic card with cation exchange through a membrane, and designed for real time experiment and on-line analysis of ion content and solvent activity: channel diamtre 0.4 mm, first successful testing November 2014 (Photography and realisation :Johannes Thiesen)

Work-package 2:

Progressing towards predictive modelling of cation equilibrium in emulsified microemulsions

In charge : J-F. Dufrêche

Figure 2 : a concentrated solution of extractants represented at meso-scale. Hydrophobic parts(solvent, chains of extractants, modifiers are shown in yellow), ions, water, acids are shown in yellow; polar heads of extractants
Are shown in red. The snapshot in thermodynamic equilibrium shown on the left has a scale of 10 nm.
The aim of WKP 2is to evaluate selectivities, i.e. free energy differences when different ions are introduced in the microstructure, going beyond models based on complexation only, but taking into account entropy, long range inetractions and free energy associated to solvent reorganisation



Work-package 3:

Operating new pertraction devices enhanced by ultra-sound frequency interfacial excitation

In charge : Jean Duhamet (DEN/DTCD-Marcoule)

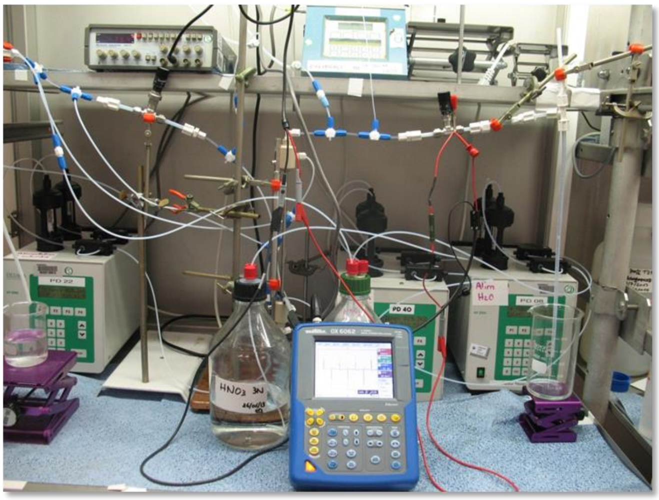


Figure 3: the first pertraction device assembled for testing new extractant formulations under excitation at Ultra-sound specific frequencuies, as suggested by M. Eigen (Nobel Prize 1967)

Work-package 4:

Imagine, synthetize and implement new formulation based on synergy AND bi-functional molecules in engineered solvents.
In charge : Stéphane Pellet-Rostaing

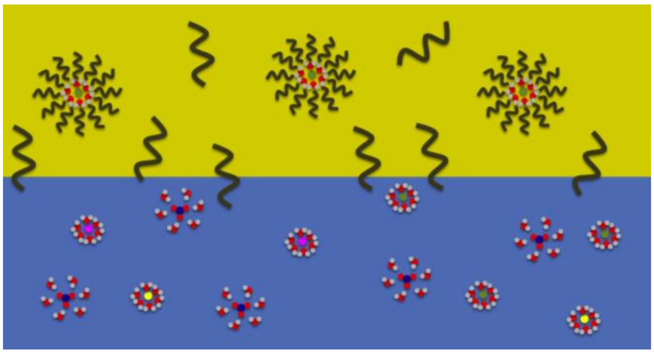


Figure 4: The ionic equilibria between a concentrated solution of mixed electrolytes and a "solvent" phase made from concentrated extractant molecules organized around polar cores. The extractant monolayer at the macroscopic oil-solvent interface is not represented.

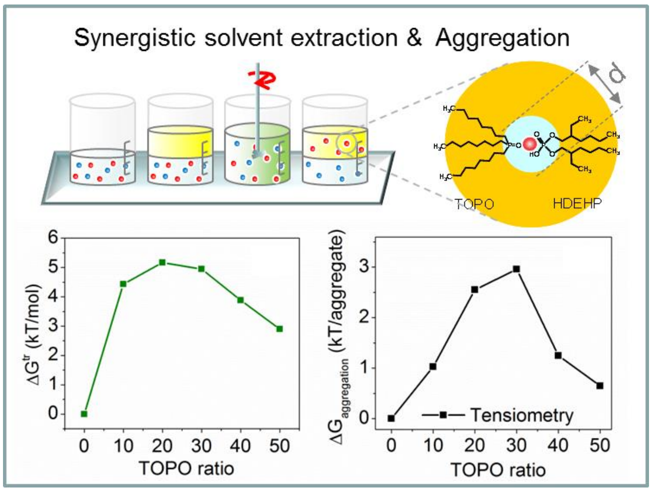


Figure 5: the free energy required to form complexes, weak aggregates or bicontinuous structures in the solvent phase is compared to the energy of extraction. The latter can be evaluated from Small angle X-ray scattering, osmometry and surface tension experiments. The driving force, is the enthalpy of complextion at supramolecular scale, is counter-balanced by entropy, image charge, surfactant film bending and tearing.

The figure 5 shows free energy of transfer (left) and free energy of aggregate formation (right) versus TOPO mole ratio in a (yet) unexplained synergy process heavily used in hydrometallurgy.

Work-package 5 (to be started 2016)

Assemble a device for real-time control of efficiency and stability combining real-time analysis of solvent and ion activities, to be implemented in pilot plants.

Figure 6: This lake outside the town of Xinguang in Baotou, Inner Mongolia of China, contains acid sludge from rare earth processing (after: New York Times). The insert shows a man situated near the corrosive discharge flows (Photo: ZUMA Press)

LIA CNRS-MPG “RECYCLING” 2014-2017

Team leaders
in Potsdam: Helmuth Möhwald, Hans Riegler, Luca Bertinetti
in Marcoule: Thomas Zemb, Jean-François Dufrêche, Sophie Charton
in Saclay: Damien Féron, Philippe Prené

PhD:
- Marie JEHANNIN (co-tutelle MPI/CEA/DEN, 2012-2015): Oxalic precipitation emulsion: study of the role of coalescence on mixing and nucleation
- Virginie SOULIE (CEA/DEN, 2012-2015): Mouillage-séchage de surfaces et corrosion associée
- Aurélio BARBETTA (LABEX, 2013-2016): Thermodynamics of water absorption in model structured molecular systems including analogues of hemicelluloses, crystalline cellulose and lignin

Technician:
Anne HEILIG

This 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 wet nanomaterials. Special attention is given 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. As a consequence, the central scientific objectives of the LEA “RECYCLING” for the four years period 2014-2016 will be focused on the following topics:

1. **Droplet coalescence under reactive conditions**: we aim to develop quantitative caracterization 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, undersaturated 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 characterisation 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. This shall serve an optimized molecular, supra-molecular or colloidal exchange across the water-oil interface.

More generally, our aim is to **make use of the ion specific ultra-sound adsorption** to excite oil/water interfaces and trigger transfer of species.. This shall serve an enhanced molecular, supra-molecular or colloidal exchange across the water-oil interface. We have shown in the previous cooperation that ultrasound can be used to enhance the phase transfer between oil and water phase and thus also to dissolve ions[1]. This work shall be extended in cooperation between the LEA and Univ. Montpellier.

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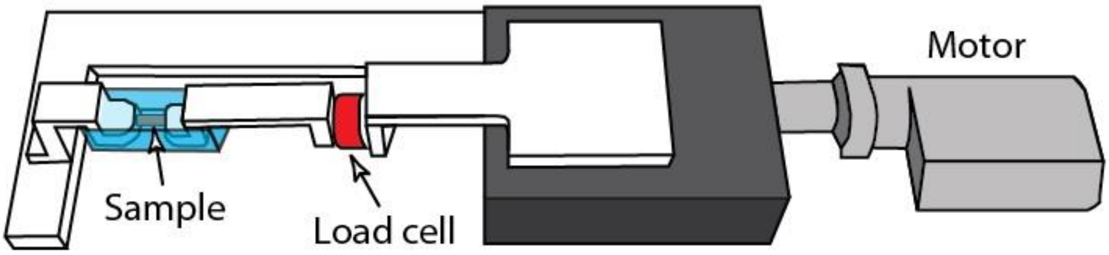
[1] Key initial reference originating from first LEA CNRS_MPG« SONO” 2008-2010 : G. Toquer, T. Zemb, D.G. Shchukin, H. Möhwald:

There we will make use of the ion specific absorption of ultrasound that leads to streaming. In first experiments we use an already existing set-up to study the smearing of interfaces by ultrasound by ellipsometry. Later we intend also to study the interfaces by X-Ray reflectivity and second harmonic generation. The key issues here will be to study how much phase transfer can be enhanced. In a microfluidic system ultrasonic absorption may also lead to a deflection of a liquid beam which may be used for separation after a threshold concentration has been exceeded.

5. **Study the specific ion effects on interaction between cellulose-based fibers** and hydrosoluble polymers mediated by surrounding ions. This includes direct measurement of osmotic pressure due to concentration gradients of metal ion with respect to the surrounding liquid. This study covers in an unified approach free energy of chemical, colloidal and mechanical energy, with a wide domain of application as knowledge-based treatments of wood against (or in favor) of swelling/deswelling under osmotic stress.



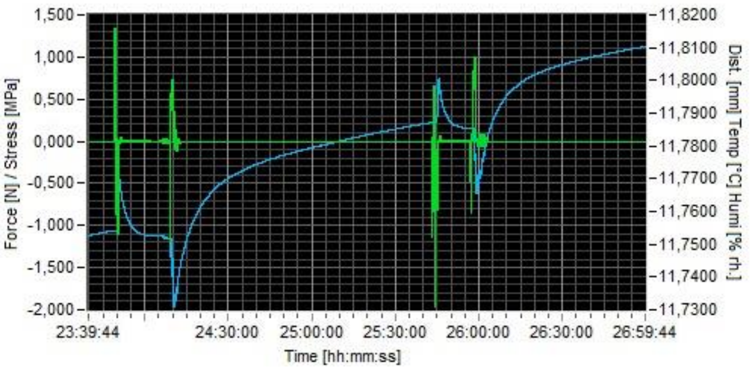


Figure: the device constructed to measure wood slabs (150 micrometer thickness) or collagen fibre stress-stress under impregnation via salt solutions of known osmotic pressure: the stage is set at iso-stress and the strain is measured during impregnation, typical response curve of stress (green) and strain (blue) versus time is shown.

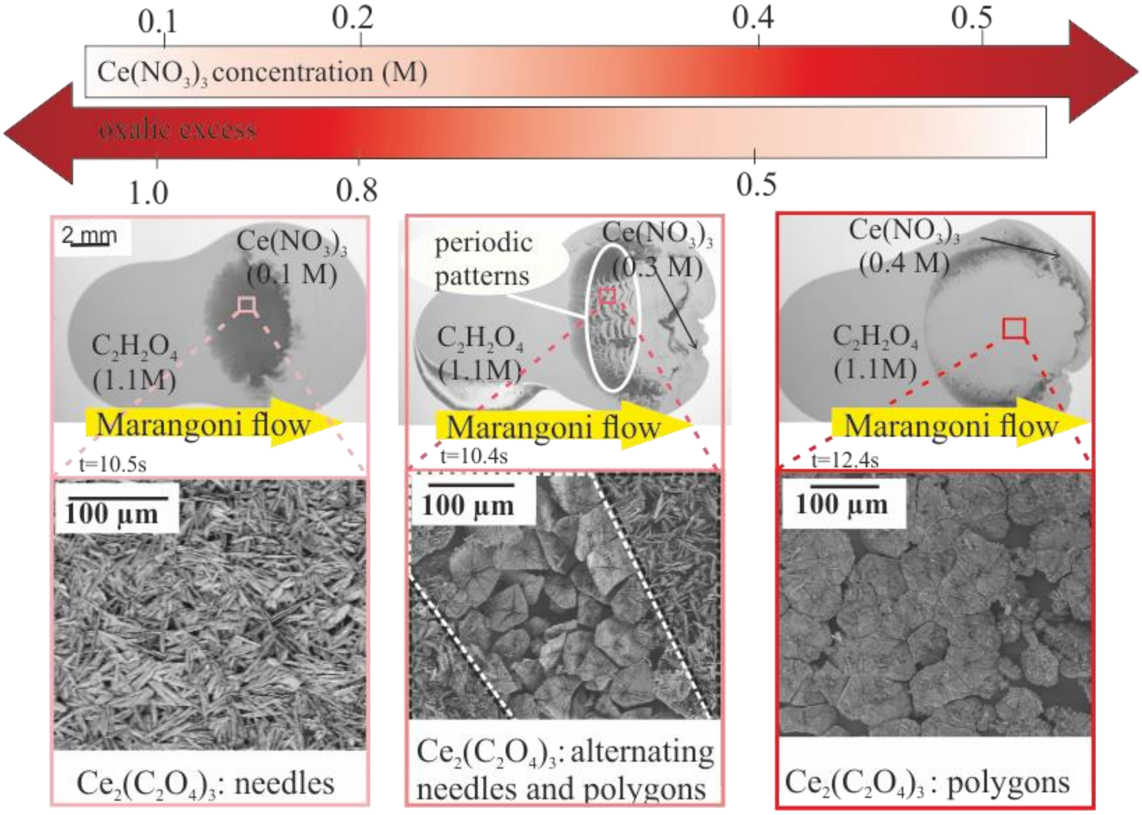
"Ionic Physisorption of Bubbles induced by pulsed Ultrasound" PCCP 12 (2010) 14553)

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. The study was therefore focused on the characterization of these stripes: what are they made of? When do they appear? What are the responsible phenomena?

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.



<u>Figure 4</u> : Top: Coalescence of sessile drops for different initial concentration of cerium nitrate at a constant surface tension difference (Δγ=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).

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 (without drying), the height (i.e. 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) during the first seconds of coalescence, are due to nanoparticles having different light diffraction properties and not to grown crystals. However, after coalescence is achieved, these nanoparticles will grow and/or aggregate in the quiescent daughter droplet, and during the drying process, to give preferably either polygons or needles.

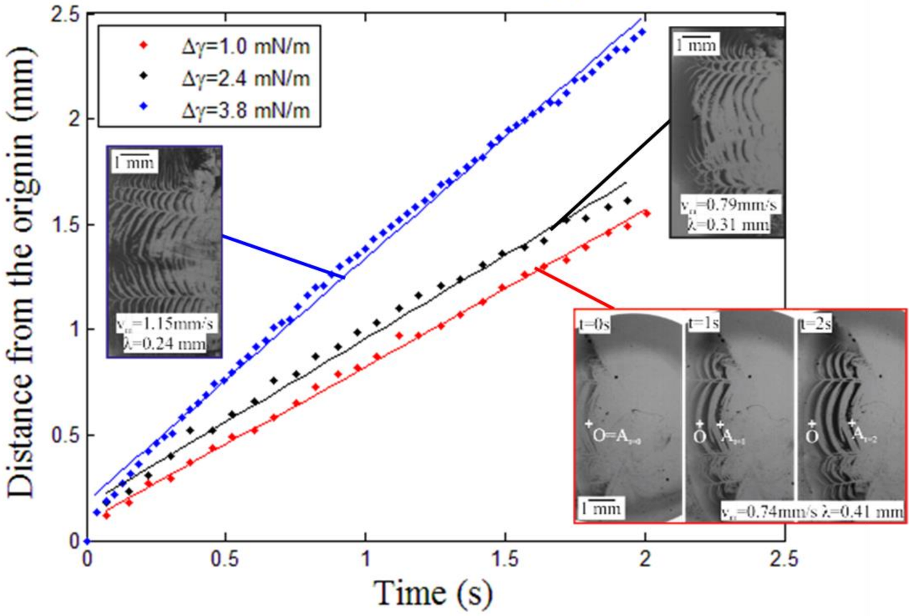


Figure 5 : Distance from the origin evolution in time during fringes formation at different surface tension gradient Δγ. The oxalic excess (0,6M) and the average contact angle (θ_a=9+0.5°) are identical for all experiments. The Marangoni flow speed, v_M, increases with the surface tension gradient whereas 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 will enable the development a theoretical model for the coalescence of reactive droplets.

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

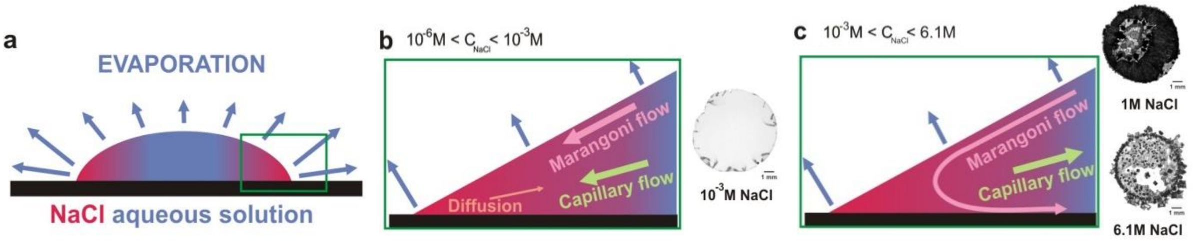


Figure 6: (a) Evaporation behavior of a sessile droplet from aqueous sodium chloride solutions. Locally varying evaporation rate and resulting concentration gradient: below (b) or above (c) 10^{-3}M NaCl. Typical microscopy images of the final deposit patterns from droplets of 10^{-3}, 1 and 6.1M NaCl on silica wafers at T = 25°C and RH = 0%.

Thermodynamics of water adsorption in model structured molecular systems including analogues of hemicellulose, crystalline cellulose and lignin

A. Barbetta (MPIKG/ICSM), L. Bertinetti, H.Moehwald, T. Zemb

"Wood material" is a complex, highly anisotropic and hierarchically organized nanocomposite. At the nanometric scale, it is characterised by stiff crystalline cellulose nanofibres, parallel to each other, and embedded in a matrix of a much softer, less anisotropic gel of hemicellulose, lignin and water. When samples are immersed in solution, the solvent uptake is controlled by molecular forces like entropy, Hydrogen-bonding of polysaccharides to cellulose nanocrystals, and hydration force. The matrix is hygroscopic, and swells with increasing relative humidity providing a source of internal stress, while the cellulose fibrils, winding with a spiral angle around the central lumen (so called "microfibrillar angle", MFA), passively reorient following the stress applied to them. Depending on the MFA, wood fibres can exhibit a wide range of behaviours and mechanical properties.

The study of water absorption of untreated softwoods as a function of relative humidity changes led to the elaboration of a first equation of state including terms of different nature (entropic, chemical, colloidal, mechanical), that can be further integrated with electrostatic terms derived from the presence of electrolytes in water. This is one of the goals of this project, which combines the expertise of the MPI of Potsdam in wood mechanisms with the experience in colloidal systems of the ICSM .

First part of this work has been focused on producing experimental data to test the effects of solutes introduced by equilibration with a solution used as osmotic reservoir.The setup allows to measure the volume changes the sample undergoes through the axial strain of the tissue. Samples have been immersed cyclically in water and then in salt solution, and their strain has been plotted as a function of the number cycles.Results can be interpreted both from a dynamic and a thermodynamic point of view.

In general, the kinetics of water and electrolytes diffusion depends on the charge of the ions. Passing from water to salt solutions, we observed a fast decrease in the sample length, followed by a progressive swelling. Two processes are occurring at different times: at the beginning an osmotically driven process determines the flowing out of the water from inside the tissue to the external salt reservoir, where the relative humidity is lower (relative humidity is related to osmotic pressure by a logarithmic dependence). Then, electrostatic swelling occurs, due to the absorption of ions within the tissues. The kinetics of this process is basically determined by the hydrodynamic size of the ions. While passing from salted solution to water, we can exactly observe the reverse process: water flows inside the tissue, and slowly ions come out (water molecules are always moving faster).

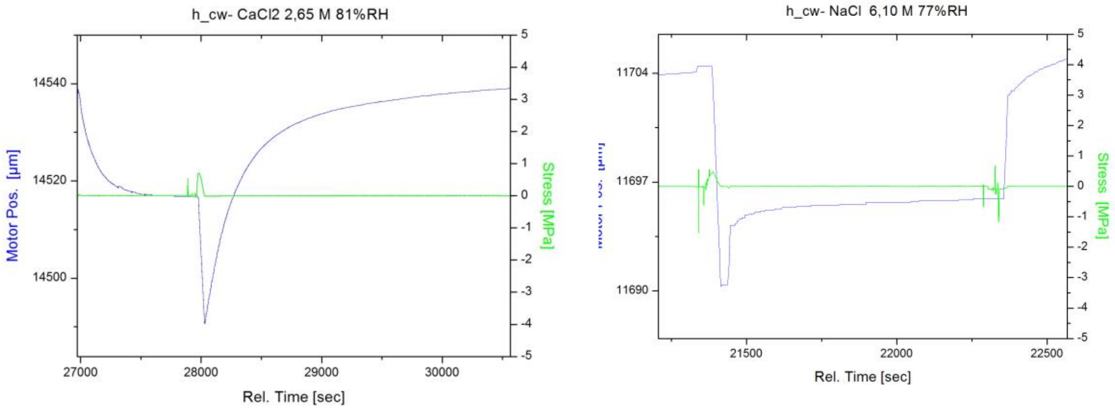
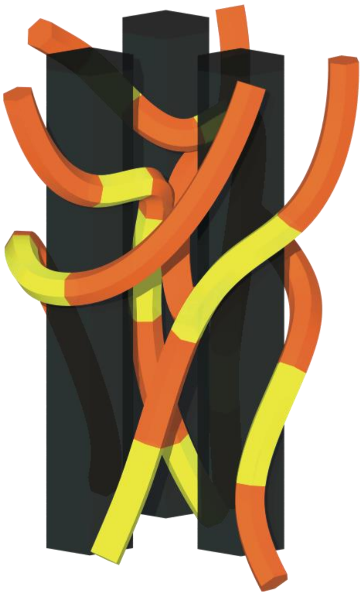


Fig.1 : (left): length versus time at constant strain when impregnating from a concentrated Calcium Chloride solution right: same experiment impregnating from a concentrated Sodium Chloride solution

As a general trend, all salts determine a positive strain of the sample, i.e. promote the water uptake by wood tissues. For a semi-quantitative analysis, it can be useful to keep in mind the Hofmeister classification(Fig.3), in which salts are defined according to their capacity to interact with water weaker than water itself (structure-breakers, or "chaotropes") or to have the opposite effect (structure-makers, or "kosmotropes").

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 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/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:

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

We establish for the first time to our knowledge an equation of state of the wood matrix, using a similar approach than Rudi Podgornik and co-workers for the equation of state of condensed DNA. At the molecular level, the hydration force of the crystalline cellulose separated by the gel and the hydration force of the hemicelluloses are combined with van der Waals and structural mechanisms. We reproduce the experimental equation of state at several temperatures, with and without additives with only one single free parameter: the binding energy of hemicelluloses, seen as chemical snapping on crystals[1]. From the energy balance, the osmotic pressure is computed and the expected sorption isotherm is calculated. 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.

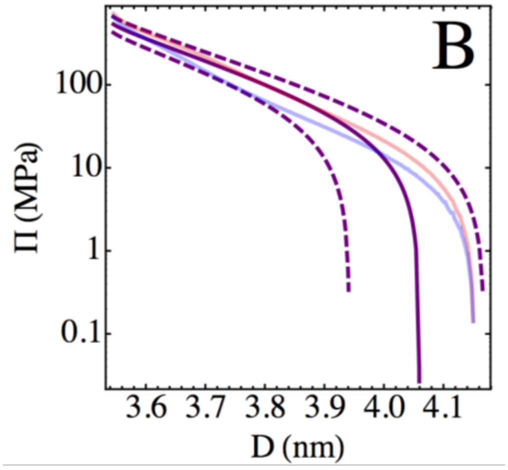


Figure 1: EOS of wood cell wall in the form of osmotic pressure versus spacing between cellulose crystals. Single parameter theory at room temperature of soft wood (violet, with uncertainty range in dashed line), compared to the swelling/de-swelling hysteresis observed experimentally with a representative sample. Wood preservation treatments and dissolution depend on chemical modification influencing the EOS.

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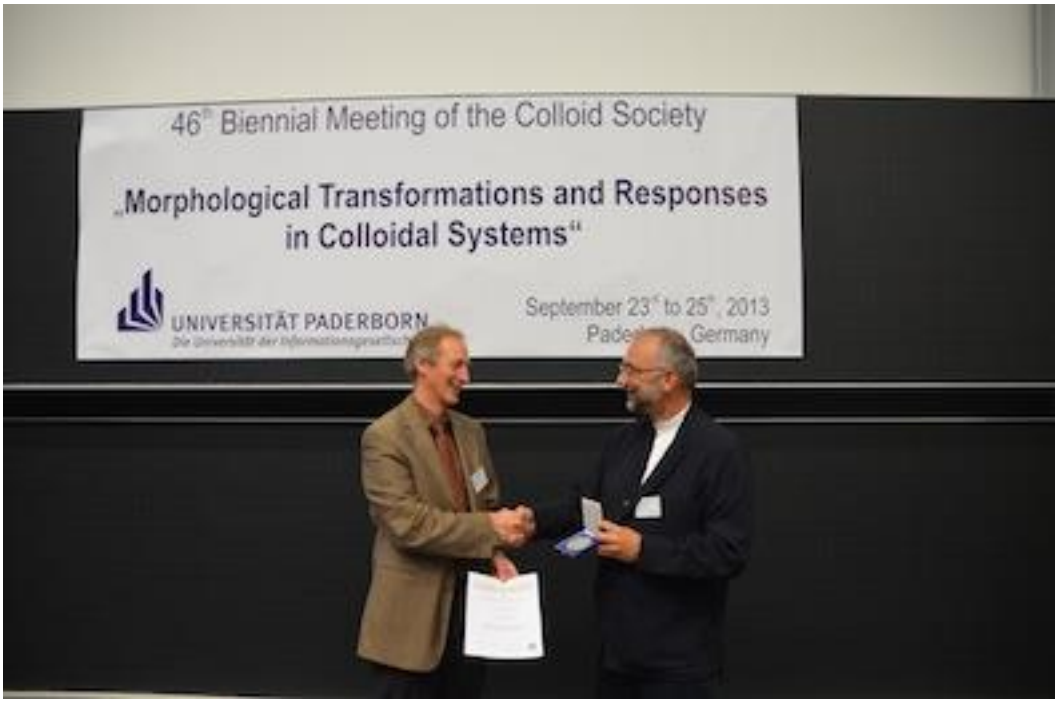
[1] L. Bertinetti, P. Fratzl, and Th. Zemb. **"Swelling and absoption of water in wood cell wall: towards and equation of state."** (submitted).



URKUNDE

Die Kolloidgesellschaft verleiht durch ihren Vorstand
anlässlich der 46. Hauptversammlung in Paderborn

Herrn Prof. Dr. Thomas Zemb

den

Thomas-Graham-Preis

in Würdigung seiner grenzüberschreitenden Arbeiten
zur Strukturaufklärung von komplexen Fluiden
sowie kationisch/anionischen Systemen.

Paderborn, den 23.09.2013

Kolloid-Gesellschaft e.V.

Prof Dr Thomas Zemb received the Thomas Graham medal from the Deutsche Kolloid Gesellescheft at the UNiversity of Paderborn in September 2013 and gave a lecture on: Recycling metals by controlled transfer of ionic species between complex fluids: en route to “ienaics" (open access in Colloid and Polymer Science 2014)

ANR ICSM 2010 - 2014

CATASURF

(Novembre 2010 – Novembre 2014): Catalytic surfactants for the design of "green" oxidizing polyphasic microdispersed reaction media. Application to microfluidic.

Partenaires :
Université Lille 1 Science et Technologie (coordinateur)
ICSM (UMR 5257)
UPMC
DSM (industriel)

Today, "Green Chemistry" is a central issue in both academia and industry with regard to chemical synthesis in the 21st century. Without this approach, industrial chemistry is not sustainable. Among the diversity of transformations required for the manufacture of pharmaceuticals, fine chemicals, agrochemicals, synthetic fibres, plastics... oxidation holds a prominent place as a core technology for converting petroleum-based materials to useful chemicals of a higher oxidation state. However, oxidation is among the most problematic processes. Traditional oxidation methods based on metal or organic stoichiometric oxidants are unacceptable for practical synthesis because of their high cost, their high waste or their toxic reagents and dangerous processing. Hence, there is a need for the invention of clean and safe oxidation procedures. Catalytic oxidation methods are attractive from an economic, environmental and safety viewpoint. Among the various oxidants used in catalytic oxidation reactions, molecular dioxygen, O_2, and hydrogen peroxide, H_2O_2, are still receiving much attention because of their relevance to sustainable chemistry and we can foresee that H_2O_2 and O_2 (or air) oxidation will be complementary useful clean oxidants in practical chemical synthesis. If surely more advisable, gaseous O_2 is also more complicated to handle, especially at the industrial scale. On the other hand, H_2O_2, as an adduct of H_2 and O_2, is a very attractive oxidant for liquid-phase reactions. Within this context, the basic research CATASURF project aims at developing new "green" catalytic processes for fine-chemicals manufacture with a low environmental impact involving H_2O_2 as the oxidant. The project mainly comprises two approaches driven both by the development of an environmentally friendly and safe process, and by the respect of the molecular and energy economy principles:

1) Elaboration of efficient oxidizing microdispersed reaction media such as three-phase microemulsion systems based on catalytic surfactants and environmentally friendly solvents, ensuring an easy recovery of both products and catalyst.
2) Transfer of the systems based on catalytic surfactants studied in 1) from the batch reactor technology to the microreactor technology.

The problem solving requires a multi-disciplinary approach requiring highly complementary research groups (CNRS, CEA, University) specialized in synthetic organic oxidation chemistry, polyoxometalates, surfactants, (micro)emulsions, colloidal chemistry and microfluidic. The industrial collaboration with a chemicals producer, DSM (The Netherlands), ensures optimum process conditions and proper translation of academic findings into a possible industrial application. DSM is recognized as a global technology leader with respect to application of microreactor technology for the manufacture of chemicals. On its Linz (Austria) production site, microreactor facilities are applied for the production of chemical intermediates that are impossible to prepare otherwise on a commercial of several hundreds of tons per year. The anticipated findings of this project are expected to enable further strengthening and broadening of DSM's leadership position in this field.

NEQSON
(Octobre 2010 – Septembre 2013) : Sonochimie en conditions hors équilibre

Partenaires :
ICSM-UMR 5257 (Coordinateur)
Institut Charles Gerhardt, Chimie Moléculaire et Organisation du Solide (CMOS), UMR 5253
CEA Marcoule, Département de Radiochimie et Procédé (CEA/DEN/DRCP)

Le projet NEQSON vise à étudier la sonoluminescence et la sonocatalyse. La spectroscopie d'émission UV/Vis/PIR est utilisée pour étudier les espèces excitées créées dans les bulles de cavitation lors de l'application d'ultrasons à différentes fréquences. Les espèces excitées générées dans les bulles de cavitation pourraient jouer un rôle central dans les réactions sonocatalytiques. Ces processus sont étudiés dans le but d'améliorer le procédé de traitement des eaux usées. L'approche innovante de ce projet est d'utiliser le plasma hors équilibre généré par les bulles de cavitation non seulement comme un outil pour étudier les mécanismes des réactions qui ont lieu à l'intérieur des bulles, mais également comme initiateur de réactions sonocatalytiques en solution. Les bulles de cavitation peuvent être considérées comme des sources micrométriques générées in situ de lumière et de forte chaleur transitoire. Ainsi, l'utilisation de la sonochimie simplifiera la gestion des déchets industriels. Plusieurs nanocatalyseurs fonctionnalisés sont développés dans le cadre du projet NEQSON en particulier en utilisant des ultrasons et des conditions hydrothermales de façon simultanée. L'efficacité des systèmes sonocatalytiques a été testée sur des solutions modèles d'eaux usées, et en particulier des déchets radioactifs.

MEMPHIS
(Février 2011 – Février 2015) : Membranes Fonctionnalisées Innovantes pour la Séparation de Radioéléments

Partenaires :
ICSM-UMR 5257 (Coordinateur)
UM2/ICGM-UMR 5253
CEA/DEN/DTCD
CTI (industriel)
ONECTRA (industriel)

The treatment of effluent and wastewater has become a major environmental concern of our society. Whatever the application area, regulations on wastewater discharges are becoming more severe and require efficient reprocessing technologies. This must take into account the recycling or conditioning of some products and water reuse after decontamination. Perhaps more than any other industrial activity, a strong requirement for the nuclear industry is to reach radioactive releases as low as possible with the best technology available at an economically acceptable cost. Thus many industrial and nuclear scientists are now mobilized to improve the efficiency of decontamination processes of radioactive effluents. In France, the activity of these effluents after decontamination is far below current standards, and is still decreasing since few years. However, to reach the ambitious objective of an activity of the waste close to zero, it is necessary to develop innovative treatment processes. The needs of the nuclear industry waste water treatment concern (i) fixed installations such as reactors and power stations, liquid waste treatment (STEL) of plants or research centres (ii) more specific applications to specific waste, and often abroad. In general, treatment of effluent requires particle filtration and extraction of a series of radionuclides such as cesium, cobalt, nickel, etc., by ion exchange resins, or by a selective co-precipitation. The current processes of extraction, simple and robust present some drawbacks to solve: for example, in the case of ion exchange resins, their capacity is limited, and the water retains some activity mainly due to 60Co. On the other hand the radioactive nature of extracted elements may cause a deterioration of the resin in storage conditions. In the case of coprecipitation process, the amount of waste generated is high and the recovery of particles after precipitation remains a limiting step. The objective of this project is to provide a method of complexation-filtration membrane for decontamination of radioactive waste, competitive with current processes. The use of membrane process is actuallyinteresting in order to decrease effluent volume and to improve the waste confinement. The originality of this project is that in addition to filtering of particles this process also allow thanks to the membrane's functionalization extracting soluble components. The development of functionalized membrane technology implies a field of interdisciplinary research involving chemists for the synthesis of new materials, physical chemists for the characterization of these materials and description of their transport properties, but also specialist's chemical engineering to optimize the implementation process on an industrial scale. The known-how and experience of the different teams and partners can achieve this goal: for the "academic" point of view a chemist's team will be responsible for the synthesis of materials and their functionalization, the second research team of the consortium will follow their characterization; regarding the industrial side, an industrial specialist of filtration membranes and an industrial active in the field of decontamination of radioactive waste are both partners of this project. Recent developments made by our teams at the laboratory scale in using of solid supports functionalized with specific Cs ion-exchange groups, allow us to look at this project from their implementation on an industrial scale, with industrial teams project partners. The generalization of this concept to other radioisotopes is a scientific and technological challenge to be met if the project is accepted.

FANTA-SIC

(Novembre 2012 – Décembre 2015): Utilisation de semi-fluoroalcanes amphiphiles pour le soft-templating en milieu non acqueux, vers la synthèse de SiC à porosité contrôlée

ICSM-UMR 5257: jeune chercheur

This project is dedicated to fundamental research on structural organisation mechanisms in totally anoxic and aprotic media. Through the establishment of the ternary phase diagram involving silicon-alkanes, perfluoroalkanes (PFA) and semi-fluorinated alkanes (SFA), we intend to propose a new soft-templating approach to synthesize Silicon Carbide (SiC). This approach would allow us to control the porosity of the SiC at the mesoscopic scale, and opens a perspective for elaborating monoliths.

To date, it is indeed very difficult to achieve monoliths of pure SiC (without oxide) combining exceptional mechanical and thermodynamical properties with a high specific surface area, a property of major interest for catalysis supports. Thanks to the recent progresses i) in the synthesis of organosilane molecules of controlled Si:C (1:1) stoichiometry, ii) in the control of their polymerization and iii) in the physical chemistry of fluorinated amphiphilic molecules, it becomes possible to envision an original synthesis route towards SiC, using amphiphilic molecules of SFA in presence of PFA molecules. The molecular organisation of SiC molecules can be controlled at the mesoscopic scale by tuning the proportion of fluorinated species and the temperature. In such mesophases, precursor molecules are pre-organized around a soft template made of SFA and PFA molecules. The in situ polymerization of the SiC precursor molecules allows their organization to be conserved once the fluorinated template is washed out. A subsequent thermal treatment under controlled atmosphere therefore results in a SiC ceramic of controlled mesoporosity.

This project associates **fundamental studies** (understanding the organisation of fluorinated amphiphilic molecules at the molecular scale in totally anhydrous and anoxic media) and a strong applied stake: the production of SiC with moulded shape and controlled porosity. The **bottom-up approach** presented in this project starts from the synthesis of organosilicon precursor molecules and amphiphilic molecules and stretches to the production of the SiC ceramic. A special emphasis will be put on the determination of ternary phase diagrams of {organo-silicon molecules / PFA / SFA} systems using X-ray scattering techniques

In evolution with regards to the activities of the Institut de Chimie Séparative de Marcoule, this **transversal project** gathers specialists of organometallic chemistry, of complex fluid physical-chemistry and of material science. In this sense, it perfectly fits the federative objectives pursued in the partner institute.

CELADYCT

(Décembre 2010 – Novembre 2014): Catalytic surfactants for the design of "green" oxidizing polyphasic microdispersed reaction media. Application to microfluidic.

Partenaires :
PECSA (EPSCI, UPMC, UMR 8284, coordinateur)
ICSM-UMR 5257
Department of environmental fluid mechanics, TU Delft (Pays bas)
Cordouan Technologies (industriel)

A key aspect of colloidal particles is that most of them bear an electrical charge that controls their interactions with the surrounding medium. Properly characterizing this charge is then of prime importance for understanding numerous phenomena such as for instance, heavy metal and natural organic matter adsorption in environmental systems, recycling by extraction processes or coagulation/flocculation phenomena. The electrical charge influences not only the organisation of the colloidal system but also the dynamics of the particles, which can both be exploited to determine the colloids charge. Dynamical methods are usually faster, and less expensive, but more difficult to analyse from a theoretical point of view.

In this project, we aim at coupling two underused dynamical methodologies that are very sensitive to the charge, namely electroacoustics and dynamic conductivity, using a synergetic experimental and theoretical approach.

Electroacoustics consists in applying an ultrasonic wave to an electrolyte solution and measuring the induced electric field, originating from the local separation of charges. Dynamic conductivity is the measure of the electrical conductivity in electric fields ; oscillating at various frequencies. These two methods are deeply related to each other, as they both imply the motion of charged species under the constraint of an external field. As only few people utilize these methods, there is still a considerable amount of work to do to build adapted and reliable devices. Indeed, the commercially available instruments are not fully adapted to the scientific challenges associated to the study of real and complex colloidal systems. To perform precise measurements, there is no alternative but constructing optimized homemade devices. There is also a need for performing standard measurements that can be used as references to calibrate those devices and validate the theories, and that can be shared with the scientific community. These tasks constitute the first part of our project. The presence of an industrial company within our partners will enable the development of commercial devices from the prototypes we'll build.

A successful characterization of colloidal suspensions does not only depend on a wellcontrolled experimental setup, but also depends on the reliability of the theoretical tools used to interpret the experimental results. For most real systems, the majority of available theories fail, in part because they neglect or treat approximately important interactions. The second part of our project concerns the improvement of the existing theories. In order to test the new versions of the theories, we will use the most advanced multiscale numerical methods, from Molecular Dynamics to Lattice Boltzmann mesoscopic simulations. The results of those simulations should provide the range of validity of the theories, and also help to find the ingredients that should be added to the theories. Once the theories are validated, the analytical formula for the experimental signals will be derived, which will enable the interpretation of the experiments in term of meaningful parameters that characterise the charge of the colloids. The new methodology will then be used to study charged colloidal systems of environmental and industrial interest. Firstly, we will investigate the charge properties of clays, which are of paramount importance as they control the behaviour of the system. In particular, we'll investigate the influence of the positions of the charges within the clay on the effective charge. Secondly, we'll apply our new experimental and theoretical tools to study liquidliquid systems that are used to extract ions with charged nanodroplets. The objective is to understand the link between the charge properties of the nanodroplets and their extraction capacities.

ILLA
(Mars 2012 - Mars 2016) : Interfaces Liquide-Liquide Actives

Partenaires :
ICSM-UMR 5257 (Coordinateur)
CEA/DEN/DRCP-LILA)
Institut Lumière Matière UMR 5579, Villeurbanne
Modélisation et Simulations Moléculaires UMR 7177, Strasbourg

Le projet ILLA rassemble trois équipes étudiant par des approches complémentaires des interfaces liquide/liquide mises en jeu lors de la séparation d'ions métalliques par extraction liquid-liquide (transfert sélectif de l'eau vers "l'huile", effectué par des molécules extractantes hydrophobes). Ce processus est à la base de la séparation d'ions métalliques "précieux", parfois polluants, d'intérêts industriels, sociétaux et écologiques majeurs. En combinant des expériences spécifiques de surface et la simulation moléculaire, on étudie les caractéristiques des interfaces LL (taille, polarité, intermiscibilité, dynamique) ainsi que la concentration et l'orientation d'espèces "adsorbées" (extractants, complexes, …), en suivant quatre tâches bien définies. En se focalisant sur le cas des ions lanthanides Ln3+ extraits par des diamides hydrophobes ou des ligands azotés, nous nous proposons ainsi de décrire au niveau moléculaire les différentes étapes-clé de l'extraction à l'interface ainsi que la nature et la solvatation des espèces extraites dans "l'huile".
ILLA est un projet fondamental mettant en œuvre, pour la première fois, optique non linéaire couplée à des mesures de tension de surface, synthèse de molécules extractantes chromophores comme sonde de l'interface, et simulations de dynamique moléculaire. Au-delà des interfaces planes ou courbes "au repos" (par ex. avec des sels de lanthanide seuls, ou les extractants seuls), on étudiera les interfaces "en activité", c.à.d. leur évolution temporelle lors de complexation et de transfert d'ions, permettant de suivre la cinétique des processus élémentaires à l'interface. Les études expérimentales et les simulations sont loin d'être routinières, mais faisables. Les résultats permettront de mieux comprendre ce qui se passe à l'interface, et ainsi d'améliorer la cinétique et la performance de systèmes existants, voire d'en développer de nouveaux. Les développements méthodologiques (e.g. prédiction et interprétation du signal SHG, dispositifs expérimentaux) devront aussi permettre d'étudier d'autres interfaces, comme en catalyse biphasique.

VECT'OLEO
(Septembre 2014 - Septembre 2017) :

Partenaires :
ICSM-UMR 5257 (coordinateur)
OLEOS, Lunel(industriel)

L'extraction par un corps gras naturel, une huile, un beurre ou une cire végétale, de principes actifs contenus dans des végétaux est à la base du concept technologique développé et breveté par OLEOS qui propose ainsi une nouvelle génération d'actifs cosmétiques éco-conçus: les Oléoactifs®. La présentation huileuse d'un extrait végétal permet d'offrir une forme originale à la fois stabilisée et vectorisée de différentes molécules mêmes fragiles et oxydables, par exemple des flavonoïdes ou autres antioxydants phénoliques, qui s'organisent dans la phase huileuse continue au cours de l’extraction et sont ainsi protégées en formulation. Le principe repose sur la théorie du « paradoxe polaire des antioxydants »: Il y a un intérêt à ajouter dans une huile végétale des antioxydants polaires pouvant s’organiser et agir en synergie avec les antioxydants apolaires. Ce concept valorise aussi la synergie biologique in vivo en particulier dans la peau, entre les propriétés des acides gras et des micronutriments de l’huile et celles des différents bioactifs extraits. Mais cette technologie reste à ce jour limitée par deux verrous majeurs: 1/ la concentration en composés polaires lipo-extractibles par une huile est limitée, 2/ l’organisation moléculaire et colloïdale des différents composés extraits par une huile n’est pas connue et de ce fait les résultats de l’oléo-extraction restent empiriques et difficilement pilotables au niveau industriel. Or, l’oléo-extraction ou l’obtention d’huiles végétales structurées est aujourd’hui un enjeu industriel prometteur pour obtenir des éco-ingrédients verts, sans chimie ni synthèse, plus bio-disponibles et plus facilement formulables que des extraits hydro-alcooliques classiques.

L’ICSM est un laboratoire expert de l’étude des organisations supramoléculaires et des processus dynamiques de molécules amphiphiles et d'ions aux interfaces dans le cadre de l’extraction liquide/liquide. Ce laboratoire a une connaissance scientifique et mécanistique poussée et assez unique des huiles structurées et de la complexation d’ions et d’autres molécules polaires en vue de leur séparation en système huile. Il dispose d’un équipement performant pour conduire des études physico-chimiques, thermodynamiques, microscopiques et structurales sur ces milieux. L’expertise de l’ICSM est donc tout à fait complémentaire de celle d’OLEOS sur les lipides et l’oléo-extraction. Le LABCOM VECT’OLEO permettra de mettre au point des systèmes ternaires [huile végétale + complexant naturel + composé bioactif] offrant des performances accrues en terme de concentration et de stabilité par une meilleure maitrise de l’organisation mésoscopic en système continue huile. Ce LABCOM permettra d’établir de façon durable un échange de connaissances, de créativité et d’outils analytiques permettant de piloter la création d’Oléoactifs® innovants et plus performants qui seront mis sur les marchés alimentaires et cosmétiques par OLEOS.

Au-delà des pistes d’innovation produits et procédés que VECT’OLEO apportera directement à OLEOS pour son développement concurrentiel, ce laboratoire commun contribuera à la compréhension nécessaire à l’optimisation des voies et procédés d’extraction par des solvants huileux apolaires, à la modélisation des transferts transcutanés d’espèces polaires et apolaires via des huiles structurées, à l’étude de l’impact des processus d’oxydation sur les phénomènes de stabilité de la vectorisation huileuse au sein d’une structure cellulaire (fortement dépendant de la structuration et de la dynamique des espèces chimiques aux échelles moléculaires et supramoléculaires).

Le LABCOM VECT’OLEO propose une recherche et un développement axés « 100% naturel » couplés à une gestion des ressources renouvelables (huiles végétales, plantes) et limitées en terme de demande énergétique (utilisation des ressources végétales locales) pour les axes santé et bien-être, avec des applications en dermo-cosmétique et en nutrition.

GTM

(Novembre 2013 - Octobre 2016) : Gestion thermique des moteurs

Partenaires :
CEA DRT (Coordinateur)
IRCE Lyon – UMR 5256
ICSM-UMR5257
CTI (industriel)
Renault (industriel
ICGM – UMR 5253
LC2P2 – UMR 5265

In the actual context, European emission standards become particularly severe for motor vehicle air pollution problems (EURO 5 & 6). But emission standards become more and more strict. The evolution from Euro 5 to Euro 6 (2014) aims to reduce NOx by 56% (65% efficiency), while Euro 7 will target an efficiency of 80%. The actual limitation in efficiency of car exhaust treatment comes from the thermal activation at low temperature. The GTM (Thermal Management thanks to materials) project aims to maximize the time slot catalytic activity of the post-treatment systems used in automotive vehicles. Today, an increase in pollutant emission at low temperature is observed, due to new combustion processes developed to reduce fuel consumption (lean-burn technologies) and therefore also CO2 emissions. We observe a temperature reduction in modern exhaust line, and this phenomenon has direct consequences on post-treatment systems, unable to operate knowing that they are not in their optimal temperature range. With GTM materials, the temperature ignition will be lowered from 10 to 40%. Direct pollutants include carbon monoxide (CO), hydrocarbons (HC=propene...) and nitrous oxides (NOx or NO+ N2O +NO2), whereas ozone belongs to the family of indirect pollutants produced in-situ by contact between ambient oxygen, NOx and HC. The most toxic pollutant at the moment is NOx. To reduce the production of NOx, a first approach consists of maximizing the combustion efficiency. Motor management allowed making significant gains in CO2, while reducing the exhaust gas temperatures. GTM project proposes a passive solution to develop a thermal buffer reservoir (based on SiC) coupled with precious metals coating directly on honeycombs ceramics. The GTM consortium is composed of complementary teams. It includes Renault, specialized in defining and qualifying exhaust systems, CTI, wash-coater and supplier of ceramic honeycombs and four research institutions, which are complementary in the value chain : CEA (nanomaterials and process), C2P2 (catalysis synthesis), l'ICSM / ISCM (barrier coatings and thermal reservoir) and l'IRCELYON (efficiency characterisation versus CO, HC and NOx abatement). Experimental and theoretical approaches (thermal simulations) will be implemented so as to be complementary during the whole project. Pre-dimensioning of SiC quantities and the head loss induced will be analysed in relation to the obtained thermal gain. Successive generations should allow improving the striking and the efficiency at high temperatures (hot-start materials), the head loss and the aging properties. The purpose is to reduce the NOx contents by 80% using the deNOX technologya t a temperature as low as 200°C.

SILEXE

(Juin 2014 – Décembre 2017): Strategic metal recycling in Ionic Liquids by EXtraction and Electrodeposition process

Partenaires :
ICSM-UMR 5257 (Coordinateur)
LCME (EA 1651, Chambery)
IJL (UMR 7198, 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, BF_4^-, NTf_2^-, …) 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…).

Teaching activities linked to ICSM

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

ICSM develops teaching activities in three directions:

- the master "Chimie Séparative, Matériaux et Procédés: application au cycle du combustible nucléaire", created in 2005 by INSTN/VALRHO by Pr Marie-Hélène Hengé and Pr André Ayral and Porfessor Loel Moreau. Two years of teaching (M1/M2) associating separation chemistry, material chemistry and process chemical engineering, The practical includes five months of teaching. The teaching program as is in 2014 is shown. For the practical part, ICSM is strongly bound to the European masters program COSOM/EMASCO in operation between Univesity of Regensburg And the Réseau Gay-Lussac, with a centre point at ENSC-Lille, coordinated by Pr Jean-Marie Aubry : ten masters educated initially in Germany, performed a »Diplomarbeit » with practicals at ICSM.

- the Annual practical separation chemistry summer-school: Full five day sessions, including 2 days of practicals and an session devoted to understanding experimental results on the light of the concepts developed in the lecture part. This summer school, initially created in 2007 by INSTN for the whole research Marcoule, has been speciliazed for ICSM from 209. Since 2012, the teachers ad students are coming from the Six UMR associated in Chemisyst project (detailed programs are found in the Annex).

- the "Thursday Lectures on separation chemistry", as M3/D1 program aimed for masters and phD students (credits given by ED459° One lesson more on the experimental side and one more theoretical side are delivered in the ICSM building every Thursday (during months of winter-time).The detailed program of the two last years is shown in Annex.

From 2005, The CSMP masters program was launched UM2 and INSTN, some teaching modules are common with 3rd year option of ENSCM, and ENSCM students follow part of the nuclear modules. The training is followed every year by 10-15 students plus a similar number students from ENSCM for tat the M1/M2 level. The number of students increases from year to year, despite of a strong selection at M2 level (typically 15 from University achieve M2 every year). Teaching will progressively be diffused in English (written and oral) in the next years. 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.

The practical summer-school of Marcoule in separation chemistry started in 2005 in Montpellier and has been held every year since then. Twenty hours of teaching chemistry at cutting edge level are complemented by practicals (3 half days) devoted to the application of the theoretical courses take place every year in the summer: Alès in 2013 and in Saint Martin-de-Londres in 2014. Since 2012, the summer school is open to all six Research Units participating in the Excellence laboratory "Chemisyst".

Master CSMP 1ère année

Eléments de base en génie des procédés
Cycle du combustible : de la mine au retraitement
Etude des mécanismes réactionnels
RMN solide + IR, Raman
RMN liquide
Préparation et propriétés des colloïdes
Détermination de la structure des solides
Présentation et synthèse des matériaux inorganiques
Travaux pratiques
Anglais
Communication et insertion professionnelle
Chimie des solutions appliquée aux actinides
Eléments de base en radioactivité
Chimiométrie
Interactions rayonnement-matière. Radioprotection
Chimie des hautes températures
Matériaux de confinement
Chimie de coordination des éléments f
Radiochimie / Chimie à l'échelle des indicateurs
Travail Encadré de Recherche – Stage bibliographique
Projet Professionnel Personnalisé

Master CSMP 2ième année

Interactions faibles et chimie séparative
Stratégie Analytique pour les actinides
Procédés de traitement et de conditionnement des déchets
Procédés de séparation par membranes
Amont du cycle : chimie extractive et séparative
Dissolution et irradiation de matrices céramiques
Modélisation pour la séparation et le confinement
Droit Nucléaire : Sûreté
Combustibles : synthèse et refabrication
Extraction liquide-liquide : thermodynamique, cinétique, procédés
Comportement à long terme : matrices vitreuses
Chimie moléculaire et supramoléculaire de métaux f et d
Communication, vie de l'entreprise
Anglais

La grande majorité des cours est effectuée par les Professeurs INSTN de Marcoule (Pr Marie-Hélène Hengé (responsable INSTN du master), Pr Philippe Moisy, Pr Etienne Vernaz et Pr. Philippe Moisy ainsi que les huit Enseignants-chercheurs UM2 et ENSCM affectés pour la partie recherche à l'ICSM.

Le master est completé chaque année par un stage en laboratoire ou en entreprise, et validé par un rapport de stage écrit.

Outlook...

Initial period of the growing of our institute since inauguration in June 2009 has been based on the objectives as recommended initially by the “Jean-Roucel report” (1992), further by three reports of the French academy of Science.

After the grand opening in June 2009 by Valérie Pécresse and Georges Frêche of the building and access offices in 2010 of the nine laboratories, all of the topics have produced major innovations: from the proof of plasma under bubble implosion in sonochemistry and first direct imaging of sintering of metal oxides containing uranium to first measurement of the synergistic effect in liquid-liquid extraction and predictive theory through modelisation at meso-scale. Asymmetric w/o microemulsions have been modelled for the first time,

ICSM has now grown to 90% of the final size planned. The eight teams have started to take their recognized leading place on international level of discussion and advancement of speration chemistry, with a balance between structure and thermodynamics at Nano-scale. All none teams share with a constant bias towards atomic and alternative renewable methods of production of energy, with as low as possible environmental imprint.

Two new major steps have been made: ICSM is at the core of the excellence laboratory project 2012-2020 Chemisyst (Abstract in Annex), involving chemists and physical chemists from Montpellier, but also Alès and Maroule. In a common project centred on knowledge –based on the usage of chemical Long-Range Interactions (LRI), Chemisyst focuses on multi-scale functional materials, new molecular systems based on self-assembled biomolecules for health and agronomy as well as on new separation processes for metal recycling. In the latter domain, the urgent need for more environmental-friendly recycling of strategic metals is the basis of the Rare Earth recycling with low harmful emission “REE-CYCLE” project 2013-2018, supported by the European Research Council in a project where four teams of ICSM are gathered as a strong team in process control via nano-devices from Grenoble led by Jean-Christophe Gabriel and in the Max Planck in Potsdam with the help of Helmuth Möhwald.

Progress in separation chemistry and nuclear material will be made by strengthening links with national and international laboratories such as IPC-Moscow as well as Jühlich-Karlsruhe-Dresden-Rossendorf German galaxy for the nuclear side and the team around Werner Kunz in Regensburg, the world leader in the renaissance of engineered complex assembled solvents for green chemistry.

T Zemb

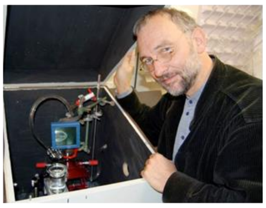
Stéphane Pellet-Rostaing ***Thomas Zemb***

De gauche à droite: Thomas ZEMB, S. Pellet-Rostaing, D. Alpe-Conchy,

ANNEXES

Annexe A: LABEX Chemisyst Activity

THEMATIC ACTIVITY REPORT
LabEx CheMISyst
2012 - 2013 – 2014-
LabEx CheMISyst - Scientific Council
October 16th 2014



Porteurr/coordinateur:
Thomas Zemb

Research activity

Le LabEx CheMISyst est « avant tout un ensemble de chercheurs d'une même discipline et d'un même site se lançant ensemble dans une direction de recherche nouvelle ». Cette direction de recherche est celle des systèmes moléculaires et interfaciaux contrôlés par des interactions non-covalentes au-delà du premier voisin. Ces « Long Range Interactions » (LRI), qui sont les interactions à portée nanométrique, contrôlent le comportement des systèmes chimiques colloïdaux étudiés et il y a un fort besoin de développement théorique à l'échelle mésocopique pour comprendre les comportements des systèmes chimiques observés.

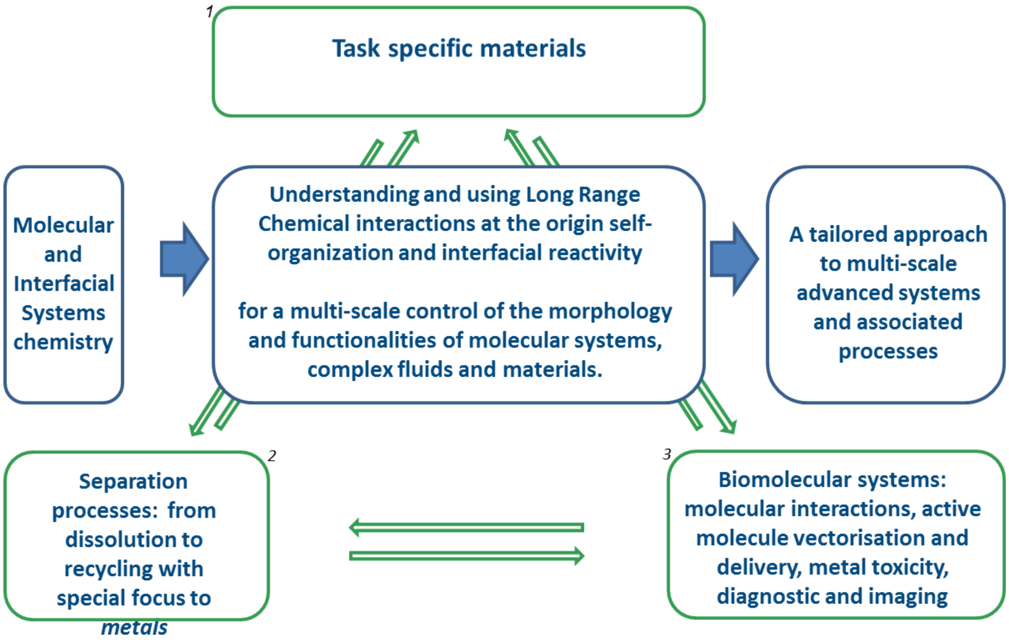
Les figures ci-contre décrivent les axes scientifiques initiaux ainsi que leur évolution en cours : la synthèse et le contrôle des structures obtenues, la mesure directe ou indirecte des LRI, ainsi que caractérisation et modélisation du comportement se côtoient harmonieusement. Les trois domaines d'excellence reconnus de Montpellier, matériaux, biomolécules et chimie séparative côtoient ainsi des actions émergentes dès 2013, associant les domaines de la chimie structurale, analytique et physico-chimie des interactions faibles et des structures mésoscopiques. A partir de l'Ecole d'été annuelle, des ateliers d'une journée et réunions scientifiques diverses co-organisées par le LABEX Le Labex s'est ainsi auto-organisé en quatre « clusters ».

La chimie et la physico-chimie des systèmes moléculaires et interfaciaux sont déclinées dans les domaines traditionnels d'expertise des physico-chimistes et chimistes de Montpellier : depuis son démarrage en 2012, la trentaine de projets de recherche s'est auto-organisée en quatre clusters de recherche à but cognitifs et un cluster de recherche orientée vers la valorisation, avec des activités couplées à l'Institut Carnot chimie Balard.

Le porteur du projet de Labex, nommé par la ministre de la recherche, V. Pécresse fin 2011, est le Pr. Thomas Zemb.

Les pages suivantes décrivent les projets Chemisyst dans lesquels au moins un chercheur ICSM et co-responsable.

LabEx project Balard 2020 :
imagine, assemble, use and model the behaviour of the multifunctional molecular and interfacial systems of the future



Task specific materials

Molecular and Interfacial Systems chemistry

Understanding and using Long Range Chemical interactions at the origin self-organization and interfacial reactivity

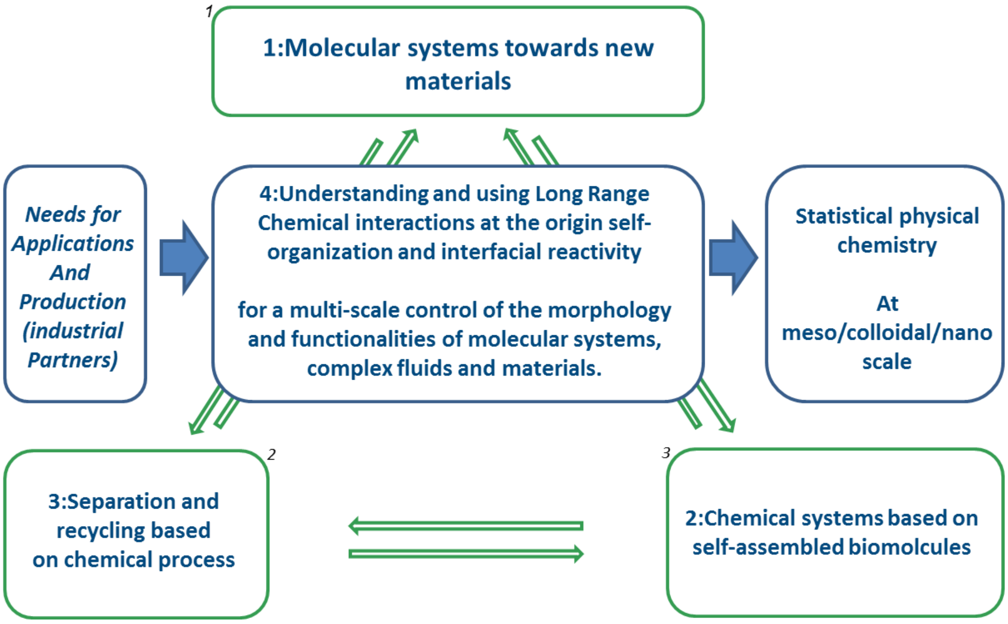
for a multi-scale control of the morphology and functionalities of molecular systems, complex fluids and materials.

A tailored approach to multi-scale advanced systems and associated processes

Separation processes: from dissolution to recycling with special focus to *metals*

Biomolecular systems: molecular interactions, active molecule vectorisation and delivery, metal toxicity, diagnostic and imaging

R/D needs driving to scientific questions and theory 2015 - 2018



1:Molecular systems towards new materials

Needs for Applications And Production (industrial Partners)

4:Understanding and using Long Range Chemical interactions at the origin self-organization and interfacial reactivity

for a multi-scale control of the morphology and functionalities of molecular systems, complex fluids and materials.

Statistical physical chemistry

At meso/colloidal/nano scale

3:Separation and recycling based on chemical process

2:Chemical systems based on self-assembled biomolcules

INnovative nanomaterials for CAesium and Thallium decontamination from human body (INCA)

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	LARIONOVA	Joulia	joulia.larionova@univ-montp2.fr	ICGM	CMOS
CO-RESPOSNABLE	GRANDJEAN	Agnès	Agnes.grandjean@cea.fr	ICSM	LNER
CO-RESPONSABLE 2 :	QUIGNARD	Françoise	francoise.quignard@enscm.fr	ICGM	MACS
POST-DOCTORANT :	BORDIANU	Irina	irina.bordianu@icmpp.ro		

Date de démarrage du projet :	Janvier 2013
Date de fin du projet :	Juillet 2014

Abstract :

The purpose of this project is to propose the development of innovative nanomaterials for decontamination of Cs and Tl in the human body more efficient in terms of kinetics and storage capacity than the process currently used which consists in oral ingestion of Prussian Blue (PB) capsules (Radiogardase@).

Can we design biocompatible nanocomposites based on polysaccharide matrix and containing Prussian Blue type nanoparticles for efficient cesium and thallium ions extraction which may be used for *in vivo* decontamination ?

Scientific driving question, in the context of system chemistry :

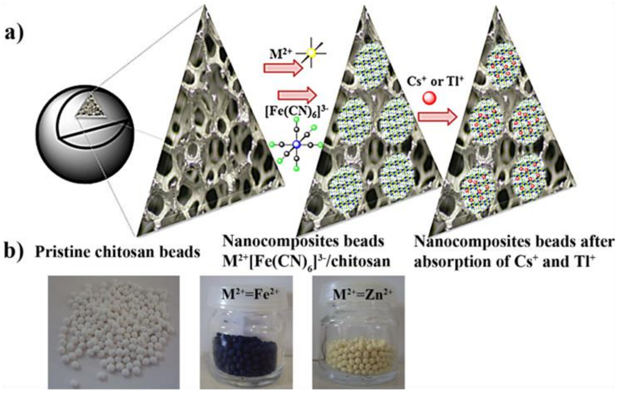


Figure 1. a) Schematic representation of the step-by step synthesis of PBA-type $M^{2+}/[Fe(CN)_6]^{3-}$ nanoparticles (M = Fe^{2+} or Zn^{2+}) into the chitosan beads;
b) Photograph of the pristine chitosan beads and $M^{2+}/[Fe(CN)_6]^{3-}$/chitosan nanocomposites obtained by the direct growth of the nanoparticles inside the porous chitosan beads

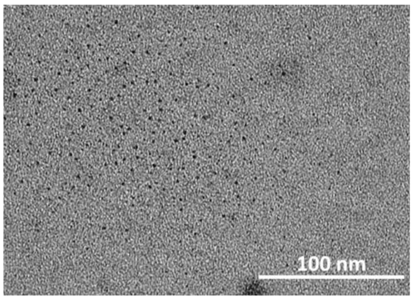


Figure 2. TEM images of the $Fe^{2+}/[Fe(CN)_6]^{3-}$/chitosan nanoparticles included into the chitosan matrix.

CLUSTER :

Systèmes moléculaires et interfaciaux pour les nouveaux matériaux

Organisateur des ateliers du cluster 2012 et 2013 :
Stéphane Pellet-Rostaing

Synthesis of zeolite monoliths with hierarchical porosity for process intensification in nuclear wastewater treatment in continuous flow

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	GALARNEAU	ANNE	anne.galarneau@enscm.fr	ICGM	MACS
CO-RESPONSABLE 1 :	GRANDJEAN	AGNES	agnes.grandjean@cea.fr	CEA	DTCD/SPDE
(POST)DOCTORANT :	SAÏD	BILEL	bilel.said@enscm.fr	ICGM	MACS

Date de démarrage du projet :	Octobre 2012
Date de fin du projet :	Octobre 2015

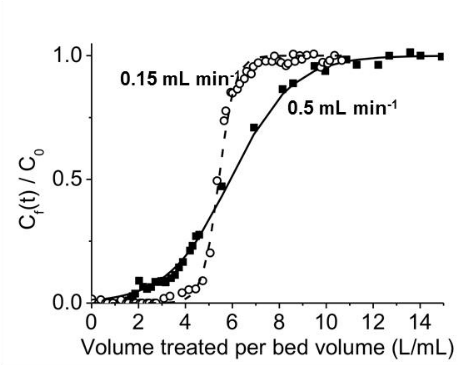
Abstract :

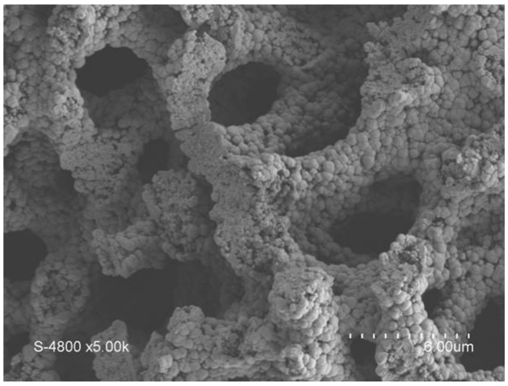
The aim of the project is to understand and control ions transport phenomena in inorganic systems with different hierarchical porosities (micro-, meso- and macroporosity) to develop the best microreactors to capture efficiently radioactive ions as Sr and Cs in continuous flow in complex seawater as Fukushima case. For safety reasons, zeolite monoliths with hierarchical porosity will be developed as an alternative to ion-exchange resins to avoid organic degradation under irradiation and to propose direct storage materials without any powder to handle. First, silica monoliths with meso- and macroporosity will be synthesized by sol-gel process combined with phase separation (spinodal decomposition) between an inorganic/polymer phase and water. Then the silica skeleton of the monolith will be transformed into high ion-exchange capacity zeolites (LTA, FAU-X) by different pseudomorphic transformations. The cladding of the monoliths by several technics will be attempted.

The project is a solution to answer to the driving question of Chemisyst concerning **"Environment urgency and eco-technolgies"**. The project aims towards the development of self-organized and nanostructured materials by design and soft-templating to enhance ion transfer pathways to improve and address safe trapping of pollutants as radioactive ions in non conventional media as complex sea water. **The control of the shape of the materials as monoliths directly provides a new separation technology in nuclear industry in continuous flow processes, avoids manipulation of toxic substances and allows a direct storage.**

A first macro-/microporous LTA monolith exhibiting micronic cristals in the skeleton has been synthesized and promising results for the capture of Sr in seawater were obtained[1]. Four times more volume of contaminated water can be treated with 1 g of material in the monolith technology in comparison to batch. In the Labex project, we have improved and developed this new technology for faster separation by enhancing the accessibility of the ions to the ion-exchange sites of the zeolite by synthesizing nanocristals in the skeleton of the monolith (SEM pictures) leading to mesopores formation. New zeolites monoliths with larger micropores as FAU-X have been also synthesized and are promising to develop radioactive Cs removal monolith technology.

(1) A. Sachse, A. Merceille, Y. Barré, A. Grandjean, F. Fajula, A. Galarneau, Micropor. Mesopor. Mater., 2012, 164, 251





Critical Metals Extraction in Ionic Liquids (EMILIE)

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	PELLET-ROSTAING	Stéphane	stephane.pellet-rostaing@cea.fr	ICSM	LTSM
CO-RESPONSABLE 1 :	VIRIEUX	David	david.virieux@enscm.fr	ICGM	AM2N
POST-DOCTORANT :	TURGIS	Raphael	raphael.turgis@cea.fr	ICSM	LTSM

Date de démarrage du projet :	Juin 2012
Date de fin du projet :	Décembre 2013

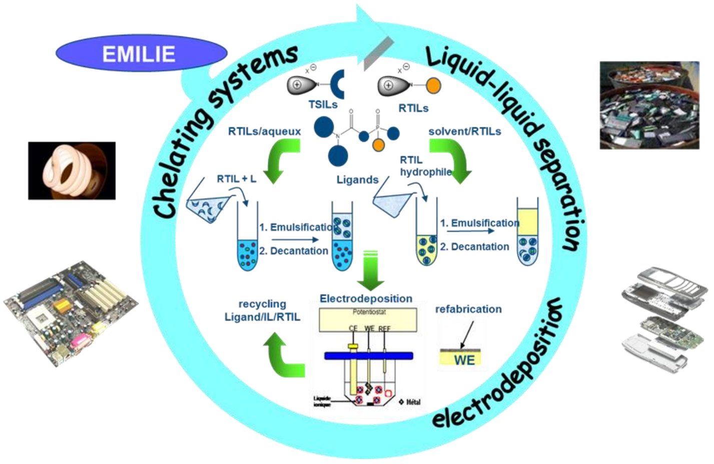
Abstract :

The purpose of this project is to study the feasibility of the implementation of a system for recovering critical metals, such as rare earth, by liquid / liquid extraction in ionic liquid medium. More particularly, the proposed organic phase will consist in a hydrophobic ionic liquid (RTIL) containing either an organic extractant or a monocationic or dicationic task specific ionic liquid (TSIL). Different extracting systems such as phosphonates, carbamoylphosphines oxides, hydroxamic acids ... Are considered. The aqueous phase is an acid medium (H_2SO_4, H_3PO_4, HCl) containing the metal simulating a leachate solution of ore (for extraction) or electronic devices (for recycling). Based on the chemistry of hydrophobic phosphorus ligands, it will assess not only the effectiveness of extractants systems (distribution coefficients, selectivity) but also to study the parameters that influence the extraction (nature of the ionic liquid, viscosity, concentration, temperature ...) and its mechanism (thermodynamic and kinetic aspects).

Can we replace organic solvents by ionic liquids for a sustainable rare earth recovery by liquid – liquid extraction ?
Which kind of mechanisms govern the extraction in such medium ?

In this project, various ligands and ionic liquids were engaged in liquid-liquid separation in order to highlight the potential of ionic liquids as alternative solvent or as chelating system (TSIL)

The behaviour of ionic liquid and mechanisms involved in the separation have been investigated. One major aspect was to recycle the ionic liquid medium and electrodeposition appeared as a promising technic.



Recycling of strategic metals by complexing copolymers in supercritical carbon dioxide: applications to noble metals

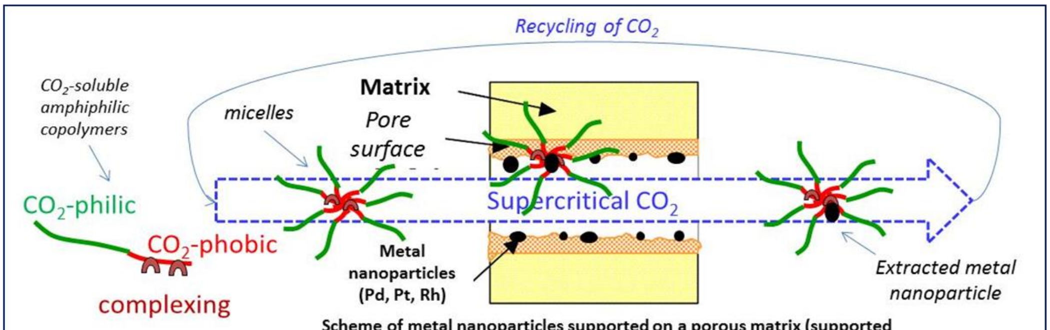
	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	LACROIX-DESMAZES	Patrick	Patrick.lacroix-desmazes@enscm.fr	ICGM	IAM
CO-RESPONSABLE 1 :	CAUSSE	Jérémy	jeremy.causse@cea.fr	ICSM	LNER
CO-RESPONSABLE 2 :	OBERDISSE	Julian	Julian.Oberdisse@univ-montp2.fr	L2C	MM
POST-DOCTORANT :	GASC	Fabien	Fabien.gasc@enscm.fr	ICGM	IAM

Date de démarrage du projet :	Mars 2013
Date de fin du projet :	Août 2014

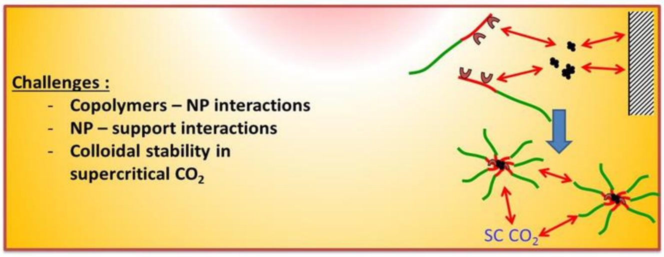
Abstract :

The projects aims at extracting nanoparticles of noble metals (Pt, Pd, Rh) from porous ceramic matrix (catalytic supports) by complexing copolymers in supercritical carbon dioxide in mild conditions in view of recycling the metals without alteration of the ceramic supports. The targeted eco-friendly technology should allow to limit the generation of secondary effluents. The proposed strategy relies on the use of amphiphilic CO_2-philic/CO_2-phobic complexing copolymers and the investigation of their self-assembly as well as their ability to complex the targeted metals in supercritical carbon dioxide. This multidisciplinary study should allow to obtain new knowledge in the field of weak interactions in a non conventional medium. The expected results will be profitable to contribute to the recycling of strategic metals.

Are the CO_2-soluble copolymers able to interact with the metal nanoparticles?
Are the copolymers able to extract the metal nanoparticles from the porous matrix (supported catalysts) under mild supercritical CO_2 conditions?



Scheme of metal nanoparticles supported on a porous matrix (supported catalyst): extraction of metal nanoparticles by amphiphilic complexing copolymers under supercritical carbon dioxide conditions


Challenges :

- Copolymers – NP interactions
- NP – support interactions
- Colloidal stability in supercritical CO_2

Scheme 2: the different interactions taking place in the studied system

Comparative screening of extraction-recovery of microalgae biomass

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	ARRACHART	Guilhem	guilhem.arrachart@cea.fr	ICSM	LTSM
CO-RESPONSABLE :	LE MOIGNE	Nicolas	nicolas.le-moigne@mines-ales.fr	EMA	C2MA
STAGIAIRES :	ROUSSEY	Sophie	Stage IUT – avril/juin 2013	ICSM	
	SYLVAIN	Olivier	Stage ENSCM – mars / septembre 2013	EMA	
	DEVILLE	Caroline	Stage IUT – avril / juin 2014	ICSM	
	DALLE	Klervi	Stage Master 2 – mars / septembre 2014	EMA	

Date de démarrage du projet :	Mars 2013
Date de fin du projet :	Mars 2016

Abstract :

Microalgae are recognised as an important renewable source of lipids, proteins and polymers which make them promising sources of food, energy, chemicals and materials.

Each of the currently available methods of extraction depends on a specific pattern phase diagram and a particular combination of cohesive energy and affinity of the extractant phase.

A clear challenge must be that the extraction process can tolerate the presence of water associated with the biomass. The purpose of this project is to make a screening of extraction process obtained by presently known methods of extraction and identify the key parameters (water content, solvent strength, pretreatment, cell-disruption) that should governed the extraction efficiency of lipids or polymers of microalgae biomass.

Scientific driving question, in the context of system chemistry :

Can we get new insight in extraction methods that does not require complex and degrading pretreatment of the algal biomass ? Can we add value of the algal biomass as a new source of materials ?

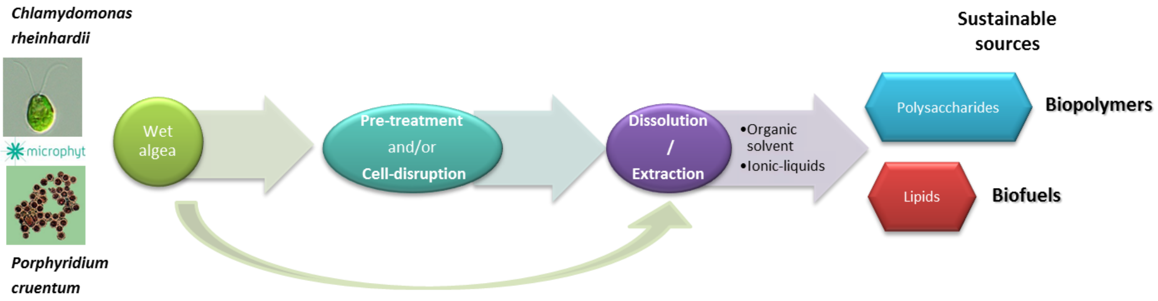
The aim of this study was to develop a method of lipids and / or polymers (mainly polysaccharides but also glycoproteins…) extraction from harvested algal biomass that does not require complex and degrading pretreatment.

The effects of solvent types, pretreatment (lyophilization, centrifugation) and cell-disruption (sonication, autoclaving process) on microalgae biomass extraction have been examined.

Compared to traditional chemical methods involving solvent addition usually organic and toxic chemicals such as hexane, ionic-liquids are tunable solvents that represent an interesting alternative for solvent extraction process (in terms of sustainable development and efficiency).

The rheological behaviour of the resulting polymer solutions show that high molecular weight molecules can be extracted, which is promising for a further implementation in material forming (film, spinning, foams).

Extraction process from dry or wet microalgae biomass



Transfer of ions and colloids through liquid-liquid interface assisted by ultra-sound

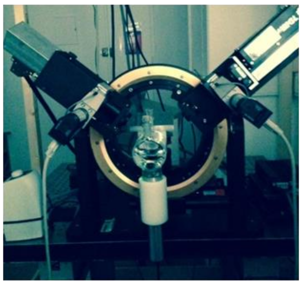
	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	DIAT	Olivier	olivier.diat@cea.fr	ICSM	Ions aux Interfaces Actives
CO-RESPONSABLE 1 :	STOCCO	Antonio	antonio.stocco@univ-montp2.fr	L2C	Matière molle
CO-RESPONSABLE 2 :	IN	Martin	martin.in@univ-montp2.fr	L2C	Matière molle
CO-RESPONSABLE 3 :	MOEHWALD	Helmuth	helmuth.moehwald@mpikg.mpg.de	MPIKG	Interfaces
POST-DOCTORANTE :	BOUBEKRI	Rym	rym.boubekri@univ-montp2.fr	L2C/ICSM	Matière molle/Ions aux Interfaces Actives

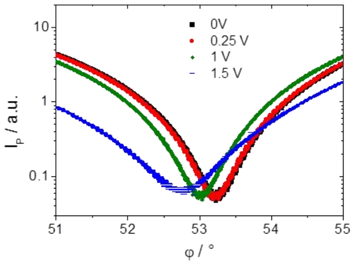
Date de démarrage du projet :	Octobre 2013
Date de fin du projet :	Mars 2015

Abstract :

This project gathers three complementary teams to study transfer process at liquid/liquid interfaces. Ion and colloid extraction from water to an non-aqueous phase under the effect of ultrasounds (US) is the main target of the Project. Here, we focus on sound wave frequencies in the MHz region, where absorption of ultrasonic energy is associated to dehydration/hydration mechanism of ionic species. Thus, we aim at investigating the chemical and physical effects on the transfer kinetics. By **coupling specific surface experiments** we have first investigated the effects of US on the fluid surface roughness and deformation. Then we have studied the adsorption of ions submitted to **high frequency ultrasounds at the water interface**. A major aim is to obtain insights into **interfacial events** involved in the transfer of ions and colloids (nanoparticles) from an aqueous to an non aqueous media upon ultrasonic waves.

Can we induce the ions transfer via their dehydration?
Can ellipsometry and surface tension measurements be used to probe the adsorption of ions at the interface?





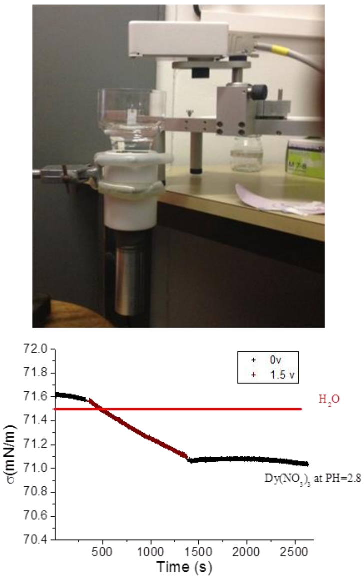
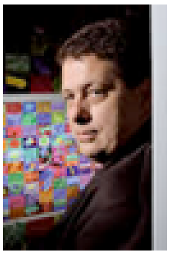


Fig. 2: Surface tension set up with an US cell (top). Surface tension evolution in time of water and dysprosium nitrate aqueous solution (down). A clear change is observed for the salt solution under 1.5 V of 10 MHz US (wine curve).

CLUSTER :

Systèmes chimiques
et interactions à longue distance

Organisateur des ateliers du cluster 2012 et 2013 :
Mihai Barboui



ION-EX : Ion exchange reactions with ionosilicas

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	PRELOT	Bénédicte	Benedicte.prelot@um2.fr	ICGM	AIME
CO-RESPONSABLE 1 :	HESEMANN	Peter	Peter.hesemann@univ-montp2.fr	ICGM	CMOS
CO-RESPONSABLE 2 :	PELLET-ROSTAING	Stéphane	Stephane.pellet-rostaing@cea.fr	ICSM	
DOCTORANT :	THACH	Ut-Dong	Ut-dong.thach@etud.univ-montp2.fr	ICGM	CMOS-AIME

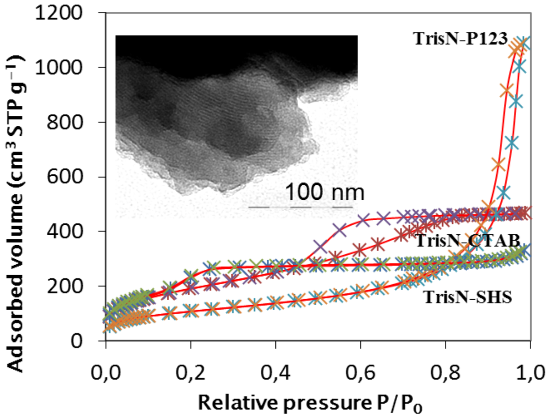
Date de démarrage du projet :	Octobre 2013
Date de fin du projet :	Septembre 2016

Abstract :

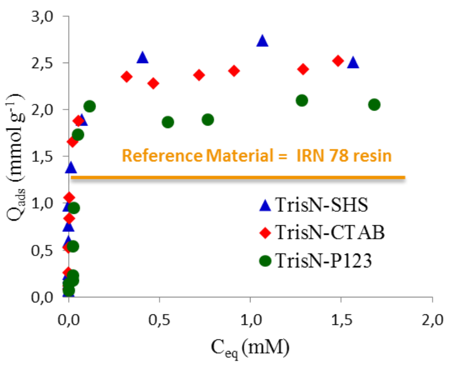
The aim of this project is to develop new and specific anions exchangers based on ionosilicas. A series of materials displaying high surface area and well-ordered pore architecture will be synthesized by template directed hydrolysis polycondensation reactions starting from various ionic precursors. This will give access to original solids, with tuneable interfacial properties, such as hydrophilic/hydrophobic contributions. Sorption capacities and related thermodynamic data will be compiled in order to evidence anionic sorption/exchange mechanisms. The ultimate objective is to develop a separation / regeneration process, based on shaped materials with potential Hoffmeister selectivity and high radiolytic stability.

Scientific driving question, in the context of system chemistry :

Elaboration of ionosilica with high exchange capacity, tuneable structure and defined physicochemical properties.
Determination of hydrophilicity/hydrophobicity, acido-basicity of the ionosilicas using molecular probes.
Thermodynamics of the anions exchange/sorption process.
Separation & regeneration cycles of anion exchangers.



N_2 adsorption isotherm and TEM images



CrO_4^{2-} adsorption capacity

Pickering emulsions stabilized by coordination polymers nanoparticles

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	CAUSSE	Jérémy	jeremy.causse@cea.fr	ICSM	LNER
CO-RESPONSABLE 1 :	GUARI	Yannick	yannick.guari@univ-montp2.fr	ICGM	CMOS
CO-RESPONSABLE 2 :	LARIONOVA	Joulia	joulia.larionova@univ-mont2.r	ICGM	CMOS
CO-RESPONSABLE 3 :	LONG	Jérôme	jerome.long@univ-montp2.fr	ICGM	CMOS
Stagiaire de niveau M2	En cours de recrutement				

Date de démarrage du projet :	Février 2015
Date de fin du projet :	Août 2016

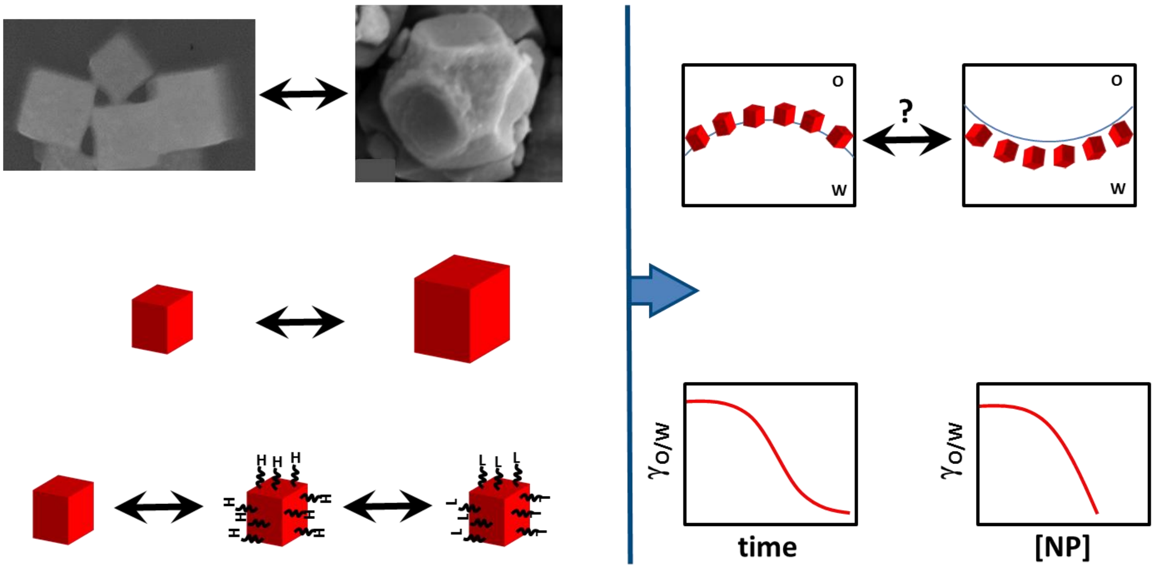
Abstract :

The goal of this project is to study the stabilization of oil/water interface with coordination polymers nanoparticles (NPs). The main idea is to prepare emulsions stabilized with solid particles, also known as Pickering emulsions, and to use it as monolithic materials precursor. In this case, the nanoparticles function is both to stabilize emulsion and to functionalize the final material.

The chosen coordination polymers come from metal haxacyanoferrate family compounds also known as Prussian Blue Analogs (PBA). The first part of this project concerns the synthesis of such NPs with various sizes, shape and hydrophilic lipophilic balance (HLB). Then, the studies will be focused on the assessment of the interfacial activity of theses NPs and more paticularly the influence of each parameter.

Scientific driving question, in the context of system chemistry :

How do NPs changes (size, shape, HLB) influence stabilization of a typical oil/water interface?



Canaux à eau synthétiques polarisés en systèmes lipidiques : vers une diode à eau- diEAUde

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
RESPONSABLE :	BARBOIU	Mihail	mihail-dumitru.barboiu@univ-montp2.fr	IEM	NSA
CO-RESPONSABLE 1 :	BONNETE	Francoise	francoise.bonnete@univ-avignon.fr	IBMM	
CO-RESPONSABLE 2 :	ZEMB	Thomas	thomas.zemb@icsm.fr	ICSM	
DOCTORANT :	KOCSIS	Isvan			

Date de démarrage du projet :	Octobre 2014
Date de fin du projet :	Octobre 2017

Abstract :

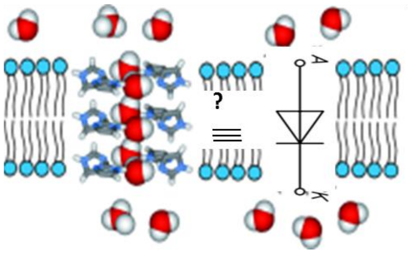
La pression osmotique peut être assimilée à une différence de potentiel *chimique*. Alors que des transistors et des diodes servent l’électronique, peut-on imaginer des systèmes analogues afin de contrôler technologiquement, cette force à la fois immuable et omniprésente dans le vivant ? La conception 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.

Scientific driving question, in the context of system chemistry :

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.



Werner Kunz : Professeur invité UM2 (2014-2014) pour la formulation avancée de solvants en chimie séparative et l'utilisation d'effets spécifiques d'ions dans de nouvelles technologies de séparation

Lors du séjour du Pr Dr Werner Kunz à ICSM, nous envisageons d' approfondir ensemble l' étude du phénomène très curieux de formation de microémulsions se formant sans tensioactif. Ce comportement avait été signalé dès 1926 pour des réactions enzymatiques concernant des enzymes membranaires qui «fonctionnent» en l' absence de toute membrane, vésicule ou autre « coacervat » comprenant une phase huileuse telle que connues à l' époque.
Ce phénomène a été étudié plus en détail dans les années 1970 au vu de résultats très surprenants obtenus lors de la séparation sous ultra-centrifugation d' un fluide « monophasique » en plusieurs phases séparées par un ménisque facilement observable. Ces « microémulsions sans tensioactif » sont tombées dans l' oubli et ont été longtemps considérées comme des légendes urbaines, car leur existence est contraire à la théorie actuelle de stabilité des colloïdes. Cependant, des preuves directe de leur l' existence, de leur localisation dans le diagramme de phases et de leur signature sans ambiguïté a été publiée en 2012 et 2013 en collaboration Regensburg-Marcoule, en utilisant les techniques de tonométrie, diffusion statique et dynamique de la lumière, diffraction de rayons X et aussi diffusion de neutrons par variation de contraste.
Le but du séjour sabbatique de Werner Kunz d' octobre 2014 à mars 2015 est d' étudier plus avant non seulement ce phénomène, mais encore son utilisation dans l' extraction sans tensioactif, sa généralisation possible dans d' autres systèmes auto-assemblés que eau-hydrotrope-alcane dans lesquels il a été découvert. Les systèmes liquide ionique polaire-alcool-eau ainsi que triglycérides-octanol-eau apparaissent très prometteurs d' applications, notamment pour le recyclage. Les retombées espérées de ce séjour sabbatique seront amplifiées grâce à a présence sur Marcoule de cinq stagiaires du Master européen COSOM franco-allemand sélectif de très haute renommée en formulation et physico-chimie COSOM-EMASCO crée par Werner Kunz en partenariat avec l'Ecole de Nationale supérieure de Lille (depuis 1997).L' enregistrement de huit cours de 45 minutes sont programmés par INSTN, en associant INSTN et UM2 pendant les séjour de Werner Kunz. En parallèle, en dans la partie « chaire d' excellence du LABEX, des cours vidéo illustrés d' expériences seront enregistrés, pour utilisation dans les MOOC INSTN/UM2.

Werner Kunz de nationalité Allemande, né en 1963, PhD sur la pression de vapeur de méthanol et d 'acétonitrile comprenant des électrolytes en 1988, habilitation 1992, puis Professeur chef de Département à l 'UT-Compiègne de 1993 à 1997, puis Professeur Chef de Département à l 'Université de Regensburg en Chemical Engineering, Membre actif étranger du conseil scientifique de TRIMATEC, 600 Citations dans web of science en Chemical Engineering,
Prix européen ECIS-Rhodia en colloïdes et Nanosciences, décerné en septembre 2012 à l'Université de Malmoe.

Goals for valorisation of Reserach within Chemisyst : 2015 - 2018

1- Separation, decontamination and recycling chemical systems

- Recycling and extraction of strategic metals from ores and urban mines
- Separation and concentration from biomass,
  with special attention on algae and biomass used currently only for heat

2- Dedicated biomolecular systems

- Vectorisation : new delivery systems , based on colloidal self-assembly
- Tissue engineering and biomaterial improvement (notably via colloidal chemistry)

3- Materials and systems chemistry

- Innovative multi-functional membranes and processes for water purification and decontamination
- Electro-mobility: New materials for energy storage and fuel cells, including new preparation routes (sonochemistry, mecanochemistry, precipitaion in organized media…)
- Recycling of polymers and eco-design of hybrid materials

Annexe B: Programm of practical summer school in Separation Chemistry

1^{IERE} ECOLE PRATIQUE D'ETE LABEX CHEMISYST – POLE CHIMIE BALARD
10-15 septembre 2012, Montpellier/Saint-Martin de Londres

Mercredi 12 septembre 2012 – Résidentiel (St Martin de Londres)

Arrivée des participants et des intervenants sur le site par leurs propres véhicules.

Matin

8h30 – 9h30 Accueil des participants
9h30 – 10h00 Présentation de l'Ecole (**Thomas ZEMB**)-Présentation des participants (tour de table).
10h00 – 11h45 Théo-1a/Liaisons non-covalente fondamentales à longue distance /**Thomas ZEMB**
Théo-1b/Liaisons non-covalente fondamentales à longue distance /**Thomas ZEMB**
12h00 – 12h45 Exp-1/ Adsorption à l'interface solide - liquide sur des systèmes nanostructurés /**Bénédicte PRELOT**

Déjeuner
Après-midi

14h30 – 16h15 Théo-2a/ Modélisation à gros grains /**Jean-François DUFRECHE**
Théo-2b/ Electrostatique dans tous ses états /**Jean-François DUFRECHE**
16h30 – 17h15 Exp-2 /Interactions non covalentes et spectrométrie de masse/ **Christine ENJALBAL**
17h30 – 19h00 Prés-1/Présentation du projet de recherche/ participants (7min / participant)

Dîner - Soirée

21h00-22h30 **Discussion autour des actions cheMISyst 2013 – Thomas ZEMB (recherche) , André Ayral (formation) et J M Devoisselle (VALO)**

Jeudi 13 septembre 2012 - Résidentiel

Matin

9h00 – 10h45 Théo-3a/Simulation moléculaire de l'adsorption et dynamique des solvants et des ions dans des nanopores /**Benoît COASNE**
Théo-3b/Simulation moléculaire de l'adsorption et dynamique des solvants et des ions dans des nanopores /**Benoît COASNE**
11h00 – 12h45 Exp-3a/Assemblages stimulables résultant de différentes interactions faibles : applications en synthèse de nanomatériaux fonctionnels/**Corine GERARDIN**
Exp-3b/ Dynamique de structuration de l'eau en milieu confiné /**Mihai BARBOIU**

Déjeuner
Après-midi

14h30 – 18h00 *Activités sportives (volley-ball, water-polo, randonnée pédestre,…) ou pure détente*
18h30 – 19h30 Prés-2/Présentation du projet de recherche/ participants (7min / participant)

Dîner - Soirée
21h00-22h30 **Conf-2/Conférence générale/ Gérard FEREY**

Vendredi 14 septembre 2012 - Résidentiel

Matin
9h00 – 10h45 Théo-4a/Formation de structures supramoléculaires par interactions faibles et leur caractérisation par diffusion de rayonnement /**Julian OBERDISSE**
Théo-4b/La force des interactions faibles: structure et renforcement dans les nanocomposites / **Julian OBERDISSE**
11h00 – 12h45 Exp-4a/ Importance de la morphologie et la structure des matériaux comme « Drug Delivery Systems » /**Jean-Marie DEVOISSELLE**
Exp-4b / Morphologie et propriétés de nanocomposites ternaires
matrice polymère/ **Jose-Marie LOPEZ CUESTA**

Déjeuner
Après-midi
14h30 – 16h15 Théo-5a/ Etude des interactions faibles entre (macro)molécules par électrophorèse capillaire : Aspects théoriques / **Hervé COTTET**
Théo-5b/ Etude des interactions faibles entre (macro)molécules par électrophorèse capillaire : Applications / **Hervé COTTET**
16h30 – 18h15 Exp-5a/Liaison organométallique : des polymères vivants aux matériaux
tridimensionnels structurés /**Caroline GENRE**
Exp-5b/Comment évaluer des milliers de molécules actives sur une cible biologique ?/ **Gilles SUBRA**
18h30 – 19h30 Prés-3/Présentation du projet de recherche/ participants (7min / participant)

Dîner de gala - Soirée libre

Samedi 15 septembre 2012 - Résidentiel

Matin
9h00-9h45 Polymer Derived Ceramics: from art to functional materials / **Philippe MIELE**
9h45 – 10h15 Chimie et nouveaux systèmes de reconnaissance biomoléculaire pour l'imagerie et la
thérapie personnalisée/ **Pascal DUMY**
10h45 – 11h45 **Conf-3/Conférence générale /Bernard MEUNIER**
12h00 – 12h30 Discussion sur le format, la date et le contenu de l'Ecole d'Eté CheMISyst 2013

Déjeuner et clôture de l'Ecole
Départs des participants et intervenants

Lundi 5 novembre 2012 – IEM – Montpellier

Après-midi

13h 30 - 14h30	Présentation des Travaux Pratiques (**André AYRAL, Stéphane PELLET-ROSTAING, André DERATANI, John PALMERI**).
14h30 – 18h00	TP1/Travaux Pratiques sur la nanofiltration de solutions aqueuses de mélanges de sels de lanthanides en présence de complexants (Groupe A : filtrations ; Groupe B : dosages ; Groupe C : simulations avec le logiciel NANOFLUX®).

Mardi 6 novembre 2012 – IEM – Montpellier

Matin

8h30 – 12h00	TP2/Travaux Pratiques sur la nanofiltration de solutions aqueuses de mélanges de sels de lanthanides en présence de complexants (Groupe A : simulations avec le logiciel NANOFLUX® ; Groupe B : filtrations ; Groupe C : dosages).

Buffet

Après-midi

13h30 – 17h00	TP3/Travaux Pratiques sur la nanofiltration de solutions aqueuses de mélanges de sels de lanthanides en présence de complexants (Groupe A : dosages ; Groupe B : simulations avec le logiciel NANOFLUX® ; Groupe C : filtrations).
17h00 – 18h00	Bilan sur les travaux pratiques : discussion des résultats avec **André AYRAL, Stéphane PELLET-ROSTAING, André DERATANI, John PALMERI et Thomas ZEMB.**

2ème ECOLE PRATIQUE D'ETE
LABEX CHEMISYST – POLE CHIMIE BALARD
1er - 6 juillet 2013 - Ecole des Mines d'Alès

Programme au 23/06/ 2013

Lundi 1er juillet 2013

Matin

10h00 - 10h30 Accueil des participants aux travaux pratiques
10h30 - 11h00 L'Ecole pratique CheMISyst de A à Z : **André AYRAL & Thomas ZEMB**
11h00 - 12h00 Présentation des Travaux Pratiques / **Nathalie AZEMA & Eric GUIBAL**

Buffet

Après-midi

14h00 - 17h30 TP1/Travaux Pratiques (Groupe A : Caractérisation des charges minérales ; Groupe B : Elaboration et mise en forme des composites ; Groupe C : Caractérisation thermique et mécanique des composites).
17h30 -19h30 Présentation orale courte (5 min) par chaque participant.

Dîner - Soirée libre

Mardi 2 juillet 2013

Matin

8h30 - 12h00 TP2/Travaux Pratiques (Groupe A : Elaboration et mise en forme des composites; Groupe B : Caractérisation thermique et mécanique des composites ; Groupe C : Caractérisation des charges minérales).

Buffet

Après-midi

14h00 - 18h00 TP3/Travaux Pratiques (Groupe A : Caractérisation thermique et mécanique des composites ; Groupe B : Caractérisation des charges minérales ; Groupe C : Elaboration et mise en forme des composites).

Dîner - Soirée libre

Mercredi 3 juillet 2013

Matin

8h00 - 8h30 Accueil des participants et des intervenants n'ayant pas suivi les travaux pratiques
8h30 - 9h00 Cours autour des systèmes moléculaires et interfaciaux / **Thomas ZEMB**

Introduction à la chimie des systèmes

9h00 - 9h45 Vision du chimiste sur quelques systèmes de transport d'eau / **Mihai BARBOIU**
10h00 - 10h45 Vision du physico-chimiste sur un système : les émulsions de Pickering / **André VIOUX**

Méthodes 1

11h00 - 12h45 Diffusion et diffraction pour et par les systèmes / **Julien CAMBEDOUZOU**

Déjeuner

Après-midi

Méthodes 2

14h30 - 15h15 Isothermes d'adsorption et calorimétrie différentielle / **Jerzy ZAJAC**
15h30 - 16h15 Pression osmotique /**Martin IN**
16h30 - 17h15 Mesure des coefficients de diffusion par analyse de la dispersion de Taylor/ **Hervé COTTET**
17h30 - 18h15 Notions de base sur la diffusion de la lumière et application à l'étude des interactions entre diffuseurs / **Luca CIPELLETTI**

18h30 - 19h30 **Conf-1 / Conférence générale / Marc FONTECAVE**

Dîner

21h00 - 22h30 Présentation orale courte (5 min) par chaque participant (hors TP)

Jeudi 4 juillet 2013

Matin

Théorie

9h00 - 10h45	Interactions faibles contrôlant le transfert d'espèces ioniques entre phases / **Jean-François DUFRECHE**
11h00 - 12h45	Modélisation et théorie de l'adsorption et du transport dans des solides poreux / **Benoît COASNE**

Déjeuner

Après-midi

14h30 - 18h00	*Activités sportives ou pure détente*
18h30 - 19h30	**Conf-2 / Conférence générale / Didier ROUX**

Dîner - Soirée libre

Vendredi 5 juillet 2013

Matin

Exemples de chimie des systèmes moléculaires ou interfaciaux en action 1

9h00 - 9h45	Nanocomposites : structuration de renforts durs par des macromolécules molles / **Julian OBERDISSE**
10h00 - 10h45	En quoi l'interface fibre/renfort constitue le maillon faible des matériaux composites à matrice polymère / **Anne BERGERET**
11h00 - 11h55	Nanocomposites à matrice polymère : mise en forme, composition, structure et propriétés / **Anne-Sophie CARO-BRETELLE & José-Marie LOPEZ CUESTA**
12h00 - 12h45	Synthèse de particules de latex par polymérisation en émulsion/ **Patrick LACROIX-DESMAZES**

Déjeuner

Après-midi

Exemples de chimie des systèmes moléculaires ou interfaciaux en action 2

14h30 - 15h15	Interactions faibles dans les milieux mésoporeux /**Thomas ZEMB**
15h30 - 16h15	Liquides ioniques : généralités chimiques, propriétés physico-chimiques et exemples de mise en forme/ **Peter HESEMANN**
16h30 - 17h15	Des agrégats de tensioactifs comme systèmes chimiques sélectifs / **Sandrine DOURDAIN**

Dîner de gala - Soirée libre

Samedi 6 juillet 2013

Matin

9h00 -10h00	Bilan sur les travaux pratiques : discussion des résultats **/ Thomas ZEMB, André AYRAL, Nathalie AZEMA & Eric GUIBAL**
10h00 - 10h45	Biomatériaux hybrides peptides-silice : une approche bottom-up / **Gilles SUBRA & Ahmad MEHDI**
11h00 - 12h00	**Conf-3 / Conférence générale de clôture/ Yves BRECHET**
12h00 - 12h30	Discussion sur le format, la date et le contenu de l'Ecole d'Eté CheMISyst 2014

Déjeuner en commun

14h30 clôture de l'Ecole

Départs des participants et intervenants

LABEX CheMiSyst summer school (17-19 September 2014, Hameau de l'Etoile, St. Martin de Londres)

Chemical functionality and weak interactions : Syntheses, Assemblies, Materials

Wednesday, 17/09		
8h30 - 9h00		Introduction : T. Zemb
9h00 – 10h00	Syntheses and activation	IL1: **F. Testard**, CEA Synthesis of nanoparticles: improving understanding of size and shape control with kinetic studies
10h00 - 10h45		O1 : **D. Virieux** Organophosphorus compounds: synthesis, complexing abilities and applications.
10h45-11h15		***Pause***
11h15-12h00		O2: **E. Colacino** Ring Closing Metathesis in micellar systems
12h00 – 12h30		O3: **G. Calléja, Sudfluor** SUDFLUOR: Expertise in Fluorine chemistry for direct fluorination applications and inorganic fluorides synthesis
12h30 – 14h00		***Lunch***
14h00 – 15h00	Surfaces and Interfaces	IL2 **R. von Klitzing**, TU Berlin Stimuli-responsive polymer coatings of different architectures
15h00 – 15h45		O4 **O. Fontaine** Scanning electrochemical microscopy: one more tool for electrochemist, or a cutting-edge tool for material chemist?
15h45 – 16h15		***Pause***
16h15 – 17h00		O5 **A. Stocco** Experimental techniques for studying interfaces
17h00 – 18h00		O6 **Students flash presentations**
18h00 – 19h00		
19h00 - 19h30		***free***
19h30		***Dinner***

Thursday, 18/09		
8h30 - 8h45		
8h45 – 9h45	Biopolymers and membranes	IL3 **M. Gradzielski**, TU Berlin Complexes of Biopolymers and Surfactants: Phase Behaviour and Relations Between Mesoscopic Structure and Rheological Properties
9h45 - 10h30		O7 **B. Nottelet** Functionnalized degradable polymers for advanced biomedical applications: from solution to surface
10h30-11h00		***Pause***
11h00-11h45		O8 **D. Quemener** Dynamic 2D/3D membranes from self-assembly of block-copolymer micelles
11h45 – 12h30		O9 **C. Pochat-Bohatier** Towards the development of environmentally friendly methods to prepare sustainable membranes
12h30 - 13h00		O10 **G. Subra, Synbio 3** SynBio3: Methodological developments for the synthesis and analysis of biomolecules
13h00 – 18h30		***Lunch*** ***Free after-noon***
18h30 - 19h30		IL4 **P. Couvreur,** Institut Galien Paris-Sud Nanomedicine and nanotheranostic to overcome resistances to the treatment of severe diseases
19h30		***Dinner***

Friday, 19/09		
8h30 - 8h45		
8h45 – 9h45	Polymers	IL5 **A. Greiner**, U Bayreuth Electrospinning: a challenge for fundamental science and advanced applications
9h45 - 10h30		O11 **S. Cavalière** Electrospun materials for fuel cell applications
10h30-11h00		***Pause***
11h00-11h45		O12 **A. Banc** Structure and rheology of model nanocomposites
11h45 – 12h15		O13 **O. Dautel, Athéor** Marking on glass for the development of industrial traceability solutions.
12h30 – 14h00		***Lunch***
14h00 – 14h45	Mesophases	O14 **A. Vioux** Ionic Liquids, structured and structuring phases. Part1: Syntheses of nanostructured materials
14h45 – 15h30		O15 **V. Peyre** Ionic Liquids, structured and structuring phases. Part 2: Colloidal dispersions in ionic liquids
15h30 – 16h00		***Pause***
16h00 – 16h45		O16 **B. Coasne** Adsorption and Freezing in Porous Media: The View from the Nanoscale
16h45 – 17h30		O17 **JF Dufrêche** Dynamical processes in electrolyte solutions: a toolbox for the characterisation of weak interactions in physical-chemistry
17h30 – 18h00		***End of the summer school***

Ecole d’été LABEX CheMiSyst– 17 au 19 septembre 2014 à St Martin de Londres

Annexe C: Thursday lectures in Separation Chemitry 2013 -2014

COURS Master 3/Doctoral "M3-D1" - ED459 (2013-2014)
PHYSICAL RECYCLING CHEMISTRY

Scientific basis for the transfer between phases:

Jeudis:	**13h30-14h15**	**14h30-15h15**
7 novembre	Chemical potential (J.F. Dufrêche)	Chemical isotopic separation (S. Pellet-Rostaing)
14 novembre	Speciation in solution: Initiation to complexation chemistry (J.F. Dufrêche)	Osmotic pressure (Th. Zemb)
21 novembre	*Conférence n°1* *Le verre : de l'Antiquité à nos jours. 1/2 (E. Vernaz)*	*Conférence n°2* *Le verre : de l'Antiquité à nos jours 2/2 (E. Vernaz)*
(28novembre)	*Pas de cours (AERES ICSM)*	
5 décembre	Entropy and temperature (J.F. Dufrêche)	Liquid-vapour separation (Th. Zemb)
12 décembre	Liquid-vapour equilibria in fluids containing micelles (Th. Zemb)	*Conférence n° 3 Solvent-free cloud point extraction without solvent ? 1/2 (Th. Zemb)*
19 décembre	Energetics of fluid interfaces (J.F Dufrêche)	*Conférence n° 4* *De l'extraction sans extractant : une légende urbaine ou une opportunité pour les énergies renovelables du futur (Th. Zemb)*
9 janvier	Aggregation and micellisation (Th. Zemb)	Binary phase diagrams and ion separation processes (Th. Zemb)
16 janvier	*Conférence n° 5* *Ionic liquids: structured AND structuring ? (André Vioux, Montpellier)*	*Conférence n° 6* *Self-assembled biomimetic channels in layered materials (M. Barboiu, Montpellier)*
23 janvier	The chemical potential of the oxygen pO_2 (J.F Dufrêche)	Trenary phase diagrams and separation processes (Th. Zemb)
30 janvier	The chemical potential of the electron (J.F Dufrêche)	Equation of state (J.F Dufrêche)
6 février	Small angle scattering: form and structure factors (Guillaume Toquer)	Radiochemistry at the trace level: dangers coming from the dilution (Nicolas Dacheux)
13 février	*Conférence n° 7* *Actinides and some physical aspects and issues (Daniel Meyer)*	*Conférence n° 8* *Extraction of radionucleides from living body: some strategies for decorporation (Eric Ansoborlo)*
20 février	Dynamic of bulk complex fluids and fluids interfaces: optical determination (O. Diat)	Small angle scattering used for determining of the specific surface in solids and complex fluids (Julien Cambedouzou)
	Dynamical methods and kinetics	
27 février	Molecular modelling: equilibrium and dynamical methods (J.F Dufrêche)	Supramolecualr chemistry and weak interactions: the nearest neighbour and beyond (Daniel Meyer)

6 mars	*Pas de cours:* *vacances semestrielles UM2*	
13 mars	*Exploitation of tie-lines in phase diagramms for separating solubilized species (Thomas Zemb)*	*Conférence n° 10* *Extraction assisted by micro-wave heating (Farid Chemat, Uni Avignon(°)[1])*
20 mars	Characterisation of aggregates by dynamic and static light scattering (Luc Girard)	Diffusion and hydrodynamics of ions near interfaces (Pierre Turq, UPMC)
27 mars	**Leçon terminale session 2013- 2014 :** **Open problems in ienaics (Pr Jean-François Dufrêche)** **Eco-design of materials (Pr Yves Brechet)**	

COURS Master 3/Doctoral - ED459 2014-2015
PHYSICAL CHEMISTRY: FROM SPECIATION TO RECYCLING

Weak interactions beyond the nearest neighbour(°)[2]

Jeudis:	13h15-13h55	14h00-14h40
6 novembre	Colloidal forces: van der Waals and dispersion forces (Th. Zemb)	Separation by physi-sorption and precipitation cycles (A. Grandjean ou N. Dacheux)
13 novembre	Electrostatic forces and DLVO stability at primitive level (J.F Dufrêche)	Ion specific effects: usage in flotation and tanning (W. Kunz)
20 novembre	*Conference n° 1* Deep eutectics: a curiosity in the laboratory or an opportunity for new separation methods? (W. Kunz)	*Conference n° 2* *Biological effects of radiation: cell and organism, from the toxicology to regulation (MH Hengé)*
27novembre	(Cours W. Kunz)	*Conference n° 3* *Ultra-sound and microwave assisted extraction : practical examples (F. Chemat)*
4 décembre	Colloidal forces : solvation and depletion forces (J.F Dufrêche)	Primary and secondary hydration forces (Th. Zemb)
11 décembre	Molecules with selective complexation (D. Meyer or S. Pellet-Rostaing)	Emulsification and phase separation (Th. Zemb)
19 décembre	*Conference n ° 3* Titre à announcer Werner Kunz	*Conference n° 4 (Noel)* *Some magic aspects of depletion forces (Thomas Zemb)*
8 janvier	Solvent cohesion, evaporation (J F Dufrêche)	Advanced methods: centrifugation and pertraction (Th. Zemb)
15 janvier	*Conference n° 5*	*Conference n° 6*
22 janvier	Adsorption isotherm on fluid interfaces (J.F Dufrêche)	Ion distribution between fluid phases and the pseudo-phase approach (Th. Zemb)

Dynamical methods and kinetics

29 janvier	Molecular modelling : equilibrium and dynamical methods (J.F Dufrêche)	Hydration of ions: chaotropy and cosmotropy (E. Leontidis Uni Chypre)

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[1] Conférence reporté en avril 2014, date à annoncer asap.

[2] Projet AVANT DISCUSSION/ HARMONISATION AVEC INSTN, U LORRAINE, AINSI QUE RETRANSMISSION MOOC possible TU Berlin

5 février	Conference n° 7	Conference n°8
12 février	Diffusion phenomena (J.F Dufrêche)	Characterisation of aggregates by light (Luc Girard)
19 février	Transport: viscosity and frequency dependant shear moduli (J F Dufrêche)	Transport of heat : conductivity and Fourier equation (J F Dufrêche)
26 février	Smoluchovski kinetics of aggregation: DLA and RLA (J F Dufrêche)	Separation by co-precipitation (N. Dacheux)
5 mars	*Pas de cours : vacances semestrielles UM2*	
12 mars	Conference n°9	Conference n° 10
19 mars	Brownian motion : self and collective diffusion (J.F Dufrêche)	Characterisation of aggregates by light (Luc Girard)
26 mars	Electrokinetic transport and hydrodynamics (J.F Dufrêche)	Gas and liquid chromatography (Guillaume Toquer)
5 avril	**Leçon terminale de la session 2014/2015 :** **The key of control of viscosity in the solvent phase for extraction :** **-Colloidal scale (Th. Zemb, Marcoule)** **-Chemical engineering scale (NN. , Nancy)**	

Recycling chemistry of metals and oxides relies on three steps: dissolution, separation, and material reformation.

About the lectures

Dissolution, separation and material reformation are the initial, central and final step of the processes used in recycling chemistry.
All the steps involve physical chemistry and chemistry in its sub-fields analytical, supramolecular, organo-metallic and colloidal chemistry, with peculiar attention given to the ultimate separation, i.e. chemical isotopic separation technologies.
The cocktail of basic science needing to perform research on separation chemistry at Masters (3rd year) and doctoral studies level will be given in the Thursday lectures in separation chemistry, with a systematic approach from practice to theory: each lecture starts from a practical example, the underlining theory being developed in the second part of the lecture.
9 lectures of 90’ are scheduled (half nuclear and half non-nuclear) for the 2015 session.

Annexe D: Goals of the project Chemisyst (2012 – 2019)

Scientific interest in complex systems is continuously growing because of their tremendous and spectacular developments at the boundaries of sciences; examples include cognitive models of thinking,[1] human genome,[2] ecosystems,[3] metabolism,[4] systems chemistry,[5] nanochemistry,[6] material science,[7,8] etc. Powerful advances in many scientific disciplines: biology, mathematics, engineering, physics, economics, computing science and recently also in chemistry and material science have emerged from research into complex networks. Within this context, multivalent interactions, representing multiple copies of a specific recognition element and exhibiting a large range of reversible connectivies, can generate adaptive networks of increased dimensional behaviours. This gives the opportunity to extend and to engineer multivalent interactions in order to control the organization of complex matter across extended scale. It generates systems which may possess novel remarkable properties not present at molecular level. This also opens wide perspectives allowing one forsee a fundamental transition from supramolecular design constitutional selection approaches,[7-9] which might give great potential in various applications. Already now, these conception of chemistry is approached via neologisms such as “Chemical collectivism”[8], “Chemical Darwinism”[9] or “Integrative Self-assembly”[7]. These are all related to chemical systems reversibly exchanging molecules or atoms and continuously organizing at the nano- or macroscopic levels, governed by on-covalent long raneg interactions. "Nanoscale" properties arise from the assembly of molecular or biomolecular species into clusters or aggregates.

Chemistry of Molecular and Interfacial Systems - Chemisyst- is a focused excellence project combining state-of-the-art of scientific and technological appraoches operating at the interface of chemistry, with biology and medicine on one side and physics on the other side in an un-precedented cross-disciplinary effort.

The potential impact that Chemisyst provides includes the following:

a. Complex systems can give rise to emergent properties and functions that result from the interactions between components and that go beyond the properties of any single component. Applications are new catalysts, electrochemical devices, colloidal lego, mini-emulsions, pores as parallel micro-reactors, separation and recycling of metals including nuclear waste and uranium/thorium ores.

b. The anylytical "Chemisyst" aims to collect information in the form of supramolecular and colloidal speciation about interacting components. Multi-scale statistical modelling should in principle be able to predcict properties of interest. Applications are in self-healing materials, advanced drug transport and targeted delivery or decorporation of toxic species as well as “chimie douce” processes using degraded thermal energy (a precious "waste" inherent to nuclear energy production) and “green chemistry”.

c. On the other hand, the interactive features of such complex networks generate new opportunities to modify and engineer further such systems, specially for crucial knoledge-based processes at colloidal scale related to recycling matter in a contact of limited resources..

d. Finally, the self-assembly may be used to embody the flow of structural information from molecular level to nano- and mesoscale dimensions. The possibility of spatial/temporal self-formation/confinement of adaptive systems chemistry approach should facilitate investigations of collective functions applied to final systems.

In this approach, chemistry plays a central role as the science whcih modifies and transform matter of all kind. An in-depth analysis of the cutting edge scientific work highlights the crucial role of long-range interactions in any of the chemical systems imagined, synthesized and used on a knowledge-based approach. Since the 60's, the archetype of electrostatics versus dispersion forces theory (alias DLVO) has been complemented by the identification of hydrophobic, depletion and hydration interactions. These interactions must be assessed to to understand their role in chemical systems as was already done with gravitation theory to understand planetary systems. In the same manner, non-covalent interactions between biomolecules forming functional active "systems" are the driving forces of biochemical processes at the colloidal level of organnelles in the cell.

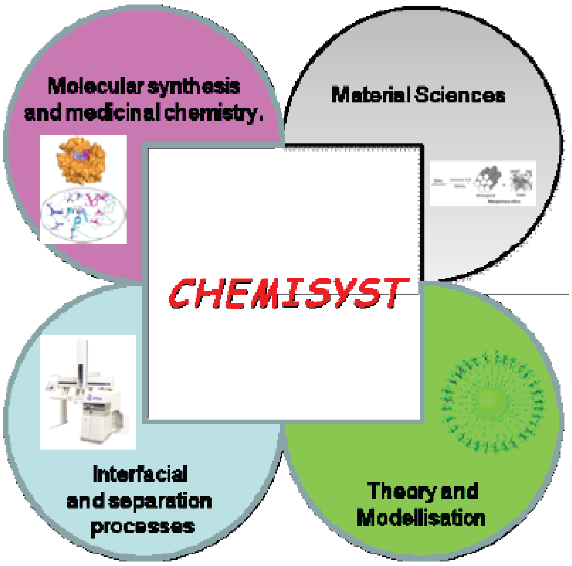
Besides the necessary identification of the molecular species involved in the functioning of living organisms which was the main stream of research in the past decades in life sciences, the design and synthesis of molecular machines inspired by the functioning of cells ensure the emergence of dynamical systems capable of self-organization that makes this area a real science of programmable matter. The challenge at the international level is to master the triple point of statistical thermodynamics (i.e. physicochemistry of soft matter), the chemistry of long-range interactions (i.e. supramolecular chemistry) and the kinetic aspects linked to the stability of fluids (i.e. fluctuations in thermal equilibrium).

An international state of the art of the profound mutation of chemistry, simultaneous to the development of synthetic, analytic and theoretical chemistry from supramolecular to colloidal and meso-scale due to thirty authors (including the coordinator of Chemisyst) from all twelve countries have been recently edited by R French and V A Parsegian (see list at end). Weak surface forces and long-range forces are the key to millimetric scale for instance in capillarity. Dispersion forces, alias van der Waals forces, are identified a the dominant factor at colloidal scale while the so-called "nano"-scale relies on complexation, electrostatics and steric forces, seen as an extension of short-range hindrances in flexible systems, i.e. depletion. The well-developed supra-molecular scale at the lower end of distances involved relies on "recognition" with the first neighbour, from hydrogen-bonding to pi-pi stacking and similar.

The unifying purpose of the CheMISyst project is to combine long range and short range specific interactions over different scales and implement them into multi-scale design. It is the ambition of the project to consider this domain beyond the supramolecular point of view. It means that there is a need to understand how fluctuation at non-zero temperature and dynamics as well as response to chemical potentials control the evolution of chemical systems. It alos means that there is a need to build up supramolecular statistical thermodynamics has to be built-up. Evaluations of free energies of supra-molecular assemblies are currently in emergence: equation of state of DNA complexed with membranes is less than ten years old! One challenge is to determine and model thermodynamics as driving force for multi-scale materials when functionality survives the synthesis and knowledge-based catalysts begin to have predictable turn-over rates, because interactions and entropy effects are separated.

In this field, the state of the art at a conceptual point of view is summarized in a prospective overview launched by an alliance NIH-Dupont and DOE in the USA. Major leaders in Europe were Utrecht and Eindhoven in the seventies, then Lund with the associated "chemical centre" from the nineties and now the emerging galaxy around Potsdam in Germany. From the experimental approach to caracteriz chemical systems, the European scale is based on large national (SOLEIL and LLB) and European facilities (ILL and ESRF), as well as the European Soft matter infrastructure, cuurently based around Juhlich-Koln-Aachen and Lausanne. Key groups in synthesis and characterisation are in Potsdam, Lund, Utrecht, Bristol. In France, UPMC Paris group is focused on materials, Saclay, ESPCI and Curie are focused on biomolecules, Strasbourg is the leading group in supramolecular chemistry, while Toulouse group focuses on electrostatics between opposite charges and supra-molecular chemistry, and Lille on formulation.

With respect to international and national concurrence, Montpellier benefits from the unique synergy of an outstanding set of expertises in theory and modelling, together with recognized expertises in three key applicative domains, which are task-specific materials, separation, decontamination and recycling processes and dedicated biomolecular systems. As detailed in 4.1, the Pole Balard from which the Chemisyst project emerges lies on four allied Institutes, which support a set of knowledge, experimental expertise and know-how extending from molecular synthesis and medicinal chemistry to materials science including colloidal processes and chemistry applied to the nuclear fuel cycle.



While classical chemistry tries to enter the complexity of matter by reducing it to an interplay of entities investigable independently of each other, conceptions appear in contemporary chemistry that are concerned with what is termed “systems”, defined as sets of interacting entities forming an integrated whole, which is not understandable by investigation of its respective parts in isolation. In other words, modern challenge would be less synthesizing new entities, than disclosing innovative combinations of existing entities. Modelling long-range interction, indeed modelling at the mesocale between the scale where quantum mechanics is sed and the macroscopic scale when froplest and rective grains are visible is at the centre of the CheMISyst project.

Crucial tool common to the three fields of "Chemisyst" for this with strong support of the LABEX is the local development in Montpellier of a local node of CECAM, part "CECAM Grand-Sud Ouest" including activity such as maintaining a toolkit of software as well as training users and organising specilaized workshops will be followed by one scientist in charge in each of the associated institutes.

Thus, the field of applications of Chemisyst project is very large aiming to tackle very important and challenging urgencies in environment, energy and health. Only scientific pluridisciplinarity will allow the birth of major scientific breakthroughs at the hearth of societal demands. Beyond the yearly practical Summer school of systems chemistry Balard, now at its sixth year, periodical lectures given by long-term invited "chairs" and systematic scientific exchanges will be promoted. Developing a common approach and language within the 450chemists involved in studies coupling realisation of materials, processes or delivery of drugs will be the objective. This visibility will attract not only industrial activity, but also attract students and scientists, as is already the case (see Annex). Thus, interdisciplinary and inter-cultural training of young scientists in a network of highly skilled research groups will represent a landmark of worldwide internationally recognized expertise.

Annexe E: ERC Project REE_CYCLE, description

Rare Earth Element reCYCling with Low harmful Emissions
REE-CYCLE

Principal Investigator: **Professor Thomas ZEMB**
Host Institution for the project: **Institute for Separation Chemistry of Marcoule, UMR 5257 UGPDSM**
Proposal full title: **Rare Earth Element reCYCling with Low harmful Emissions**
Proposal duration in months: **60 months from May 2013**

Proposal summary

It is a matter of strategic independence for Europe to urgently find processes taking better account of environmental and economic issues, when mining and recycling rare earth elements (REE). Currently THERE IS NO SUCH INDUSTRIAL PROCESS AVAILABLE 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 is on one hand to develop the fundamental understanding involved in the process' complex fluids (both experimental and theoretical) and on second hand to use it to develop a new, cost effective and environmentally friendly REE recycling process. We will achieve this: (i) by enabling, for the first time ever, the fast measurement of free energy of mass transfer between complex fluids; hence it will now be possible to explore and understand an extensive number of process formulations and phase diagrams (just one such study usually takes years but will then be performed in a matter of days); (ii) develop predictive models of ion separation including the effect of long-range interactions between metal cations and micelles; (iii) by using the experimental results and prediction tools developed, we will design an advanced & environmentally friendly process formulations and pilot plant; (iv) by enhancing the extraction kinetics and selectivity, by implementing a new, innovative and selective triggering cation exchange process step (ca. the exchange kinetics of a cation will be enhanced). This will represent a major breakthrough in the field of transfer methods between complex fluids.

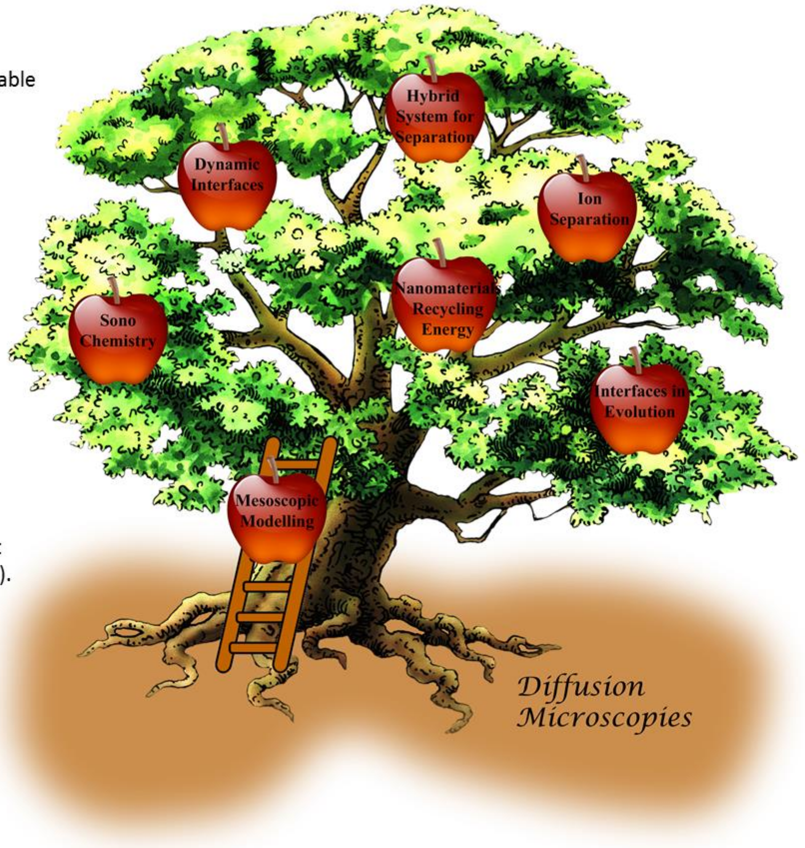
An expected direct consequence of REE-CYCLE will be that acid waste volumes and other harmful process wastes will be reduced by one to two orders of magnitude. This will bring RRE recycling and mining environmental impact to levels acceptable for the world as well as greatly reduce process running costs. Hence, industrial processing plant will be able to re-open in Europe.

Furthermore, this new understanding of mechanisms involved in selective ion transfer should be applicable to respond to other unresolved problems such as heavy metals, hormones, or drug contamination in drinkable water as well as open new recycling possibilities and 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.

References:

1- **"The colloidal domain"** by H. Wennerstroem and D. F. Evans as well as "Physical chemistry of interfaces", by Adamson and Gast,
2- **"Ion properties"** by Yishak. Markus 1997
3- **"Solvent extraction: principles and practice"**, by J. Rydberg, M. Cox, Cl. Musikas and G. R. Choppin
4- **"Specific ion Effects"**, edited by W. Kunz, World scientific publisher Singapore, 2009
5- F. Testard & **Th. Zemb**: **"Liquid-liquid extraction: An adsorption isotherm at a divided interface"**; Comptes Rendus Acad. Sc. Chimie (2007), 10, 1034-1041.

Institut de Chimie Séparative de Marcoule



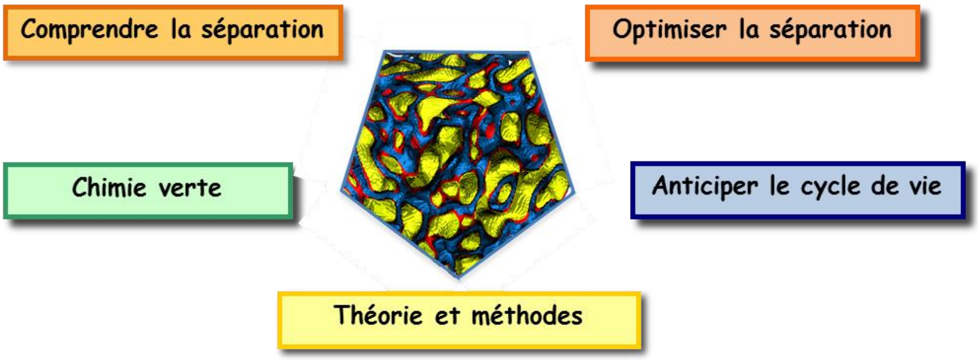
The scientific mission of ICSM originates from the unavoidable rarefaction of fossil fuels, their global impact on climate. The energy production based on gaseous, liquid or solid fossils more and more unacceptable. Moreover, improved safety requirements and the predicted lack of water required for efficient and wide-spread griculture and algae production induces a strong and urgent demand for radically new solutions linked to renewable energy production. All "atoms" materials used in energy production must be recycled taking into account the 12 principles of green chemistry till the availability of fusion energy efficient fission or alternative storable photovoltaic and wind energy. Nuclear as well as the three latter types of energy heavily rely on colloidal systems involving trivalent ions, actinides and lanthanides (French bill of July 13 2005). The future cycle of these metals cannot rely on extrapolation of existing technology: new solutions rely on nanoscience, alias colloidal science as well as the fertilizing triangle of structure determination-statistical thermodynamics and chemical engineering. One major goal is to make use the depleted Uranium and other "waste" in energy production as well as degraded "useless" thermal energy not only for heating of buildings, but also allowing alternate ways to produce molecules nowadays originating from fossil resources.

In a world limited in resources, with a fundamental duty to be able to keep some non-artificial ecosystems in a significant part of the continents, the need of new and alternate ways of producing renewable energies is immense. Closed cycles of materials and fluids used in energy production, as well as efficient usage of all atoms mined is crucial. Closing efficient cycle does not rest only on progresses on synthetic chemistry of molecules or materials, but on separation with its two linked side-processes: dissolution and reformulation. 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 crucially needed recycling industry. Allowing economical knowledge-based recycling of rare earths is the main target of application issued from nanoscience (alias colloidal) approach developed in the eight teams of ICSM by the four associated research Institutions: Commissariat à l'Energie atomique et aux Energies alternatives, Centre National de la Recherche Scientifique, University of Montpellier 2 and Ecole Nationale Supérieure de Chimie de Montpellier:

- *Hybrid materials for separation (Daniel MEYER)*
- *Ions at active interfaces (Olivier DIAT)*
- *Ionic separation by self-assembled molecular systems (Stéphane PELLET-ROSTAING)*
- *Sonochemistry in complex fluids (Sergueï NIKITENKO)*
- *Nanomaterials for energy and recycling processes (Xavier DESCHANELS)*
- *Evolution of surfaces of materials (Pr. Nicolas DACHEUX)*
- *Microscopies in environmental method (Renaud PODOR)*
- *Mesoscopic modelisation and theoretical chemistry (Pr. Jean-François DUFRECHE).*


Nanosciences

Chemistry for Energy



Understanding separation between phases: The aim is here to characterize structure and use a statistical thermodynamical approach towards functional organized molecular systems. The main target is controllable selectivities and kinetics of separation of ions, molecules and colloids. Processes under mechanistic study include liquid-solid precipitation, liquid-liquid spontaneous as well as triggered separation via phase transfer.

Optimizing the separation:

Once an efficient separation has a predictable behavior, the systems chemistry as well as chemical engineering at supramolecular, colloidal and macroscopic scale must be optimized in order to design an efficient system with economic feasibility. Here, it is needed to imagine, synthetize, formulate and implement recycling strategies, from the laboratory to pre-pilot scale, with a peculiar attention to actinides and lanthanides.

Green chemistry:

Chemistry for energy, including chemistry of separation processes, must consider and implement the twelve principles of green chemistry as well as those of “green engineering”. Mainstream concerns chemical treatment of all types of “wastes” including the degraded thermal energy present in all devices producing electricity to recover “value”. Special attention is devoted to chemical usage degraded thermal energy and to sonochemistry, the science of mastering chemical reactions induced by ultra-sound.

Anticipating life-cycle:

Observation at meso-scale of surface degradation and electro-chemical corrosion evidences that life-time extension depends not only on composition, but also from the synthesis path in phase diagram for the materials used. The knowledge of surface degradation mechanisms under stress mechanical, electrochemical and radiative stress is needed to implement better strategies in the synthesis methods and purity standards not only in materials used in recycling plants, but also to nuclear fuels and storage materials.

Methods in modeling and observations at meso-scale:

Nearly all efficient methods of ionic separation depend on self-assembled chemical “systems” of typical nanometer size. Those need to be observed without perturbation, i.e. in environmental electron microscopy, or by scattering of X-rays, light and neutrons. Beyond the level of selectable images, small angle X-ray and neutron scattering give average and thermodynamic absolute values of interfacial area and curvatures. Theoretical modeling at meso-scale of separation processes, using all types of coarse graining via statistical mechanics, should allow the long awaited coupling between supramolecular scale and macroscopic scale used in chemical engineering of separation methods, associated to liquid-liquid to liquid-solid and liquid-gas strategies

The **Institute for Separation Chemistry of Marcoule** has been created as a virtual laboratory without walls in 2007 and is directed by Stéphane Pellet-Rostaing since 2013. The laboratories were functional in January 2010. ICSM is located 100km NE of Montpellier and 25 km North of Avignon along the Rhone. ICSM is one of the partners of the Excellence laboratory “Chemisyst” 2012-2020, devoted to the Long Range chemical interactions (LRI) at work in “systems chemistry”. ICSM facilities are planned for hosting in 2019 fifty permanent and fifty non-permanent scientists, plus staff devoted to administration and infrastructure. Open national and international phD, post-doc and tenured-track positions are available on web-site: **www.icsm.fr**.

Appendix A

List of Publications ICSM (2011-2014)

triées par Année, Thématique de Recherche, Facteur d'Impact décroissant, 1^er^ Auteur

En rouge : domaine d'application nucléaire
En bleu : domaine d'application non nucléaire
En noir : recherche duale nucléaire et NON nucléaire

Remarques
Le facteur d'impact indiqué est le dernier paru à savoir celui issu du Journal of Citation Report 2011 (Thomsom-Reuters), même pour les années 2009, 2010. Si la revue n'est pas référencée dans le JCR, alors aucun IF n'est indiqué.

IF = Impact Factor JCR 2011

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Understand Separation

1. Ferru G, Rodrigues DG, Berthon L, Diat O, Bauduin P, Guilbaud P. **Elucidation of the Structure of Organic Solutions in Solvent Extraction by Combining Molecular Dynamics and X-ray Scattering**. *Angewandte Chemie-International* Edition 2014;53(21):5346-5350. - [IF=11.336]

2. Fameau AL, Zemb T. **Self-assembly of fatty acids in the presence of amines and cationic components**. *Advances in Colloid and Interface Science* 2014;207:43-64. - [IF=8.636]

3. Schottl S, Marcus J, Diat O, et al. **Emergence of surfactant-free micelles from ternary solutions**. *Chemical Science* 2014;5(8):2949-2954. - [IF=8.601]

4. Villa-Gomez DK, van Hullebusch ED, Maestro R, et al. **Morphology, Mineralogy, and Solid-Liquid Phase Separation Characteristics of Cu and Zn Precipitates Produced with Biogenic Sulfide**. *Environmental Science & Technology* 2014;48(1):664-673. -[IF=5.481]

5. Gassin PM, Martin-Gassin G, Benichou E, Brevet PF. **Tracking Molecular Aggregates at a Liquid Interface by Nonlinear Correlation Spectroscopy**. *Journal of Physical Chemistry C* 2014;118(2):1135-1141. - [IF=4.835]

6. Bealle G, Lartigue L, Wilhelm C, et al. **Surface decoration of catanionic vesicles with superparamagnetic iron oxide nanoparticles: a model system for triggered release under moderate temperature conditions**. *Physical Chemistry Chemical Physics* 2014;16(9):4077-4081. - [IF=4.198]

7. Dejugnat C, Dourdain S, Dubois V, et al. **Reverse aggregate nucleation induced by acids in liquid-liquid extraction processes**. *Physical Chemistry Chemical Physics* 2014;16(16):7339-7349. - [IF=4.198]

8. Li Y, Fabiano-Tixier A.S, Ruiz K, Rossignol Castera A, Bauduin P, Diat O, Chemat F. **Comprehension of direct extraction of hydrophilic antioxidants using vegetable oils by polar paradox theory and small angle X-ray scattering analysis**. *Food Chemistry* 173 (2015)873-880 – [IF=3.867]

9. Duvail M, Arleth L, Zemb T, Dufreche JF. **Predicting for thermodynamic instabilities in water/oil/surfactant microemulsions: A mesoscopic modelling approach**. *Journal of Chemical Physics* 2014;140(16-Apr) : p.164711-11. - [IF=3.122]

10. Nguyen T.N, Duvail M, Villard A, Molina J.J, Guibaud Ph and Dufrêche J.F. **Multi-scale modelling of uranyl chloride solutions.** *Journal of Chemical Physics* – Accepted [IF= 3.122]

11. Schottl S, Touraud D, Kunz W, Zemb Th, Horinek D. **Consistent definitions of the interface in surfactant-free micellar aggregates**. *Colloïds and Surfaces A* - [IF= 2.354]

12. Dufrêche J.F, Zemb Th. **Effect of long-range interactions on ion equilibria in liquid-liquid extraction**. *Chemical Physics Letters* – Accepted [IF= 1.991]

13. Dejugnat C, Berthon L, Dubois V, et al. **LIQUID-LIQUID EXTRACTION OF ACIDS AND WATER BY A MALONAMIDE: I-ANION SPECIFIC EFFECTS ON THE POLAR CORE MICROSTRUCTURE OF THE AGGREGATED MALONAMIDE**. *Solvent Extraction and Ion Exchange* 2014;32(6):601-619. - [IF=1.660]

14. Pfleiger R, Chave T, Virot M, Nikitenko SI. **Activating molecules, ions and solid particles with acoustic cavitation**. *Journal of visualized experiments : JoVE* 86, DOI:10.3791/51237,2014 - [IF= 1.19]

15. Benichou E, Gassin PM, Gassin-Martin G, et al. **Second harmonic generation at liquid interface: molecular organization, supramolecular assemblies and chirality**. *Organic Photonic Materials and Devices Xvi* 2014;8983

16. Fischer V, Markus J, Touraud D, Diat O, Zemb Th, Kunz W. **Towards Surfactantless and waterless microemulsions**. Submitted

17. Klossek M, Touraud D, Marcelja S, Diat O, Zemb Th and Kunz W. **How to explain microemulsions formed by solvents mixtures without surfactants**. Submitted

18. Dejugnat, C., Berthon, L., Dubois, V., Dourdain, S., Dufrêche, J.-F., Pellet-Rostaing, S., Zemb, T. **Liquid-liquid extraction of acids and water by a malonamide: Part II- Anion specific effects in the aggregate-enhanced extraction isotherms.** Solv. Extr. Ion Exch. 2014, 32, 620-636.

Optimize Separation

1. Burglova K, Noureddine A, Hadacova J, Toquer G, Cattoen X, et Man M.W.C. **A general Method for Preparing Bridged Organosilanes with Pendant Functional Groups and Functional Mesoporous Organosilicas**. *Chemistry-a European Journal* 20(33), 10371-10382 – [IF=5.696]

2. Massasso G, Long J, Haines J, et al. **Iodine Capture by Hofmann-Type Clathrate Ni-II(pz) Ni-II(CN)(4).** *Inorganic Chemistry* 2014;53(9):4269-4271. - [IF=4.794]
3. Leclercq L, Mouret A, Bauduin P, Nardello-Rataj V. **Supramolecular Colloidosomes Based on Tri(dodecyltrimethylammonium) Phosphotungstate: A Bottom-Up Approach.** *Langmuir* 2014;30(19):5386-5393. - [IF=4.384]

4. Vinas C, Tarres M, Gonzalez-Cardoso P, Farras P, Bauduin P, Teixidor F. **Surfactant behaviour of metallacarboranes. A study based on the electrolysis of water.** *Dalton Transactions* 2014;43(13):5062-5068. - [IF=4.097]

5. Virot M, Venault L, Moisy P, Nikitenko SI. **Sonochemical Redox reactions of Pu (III) and Pu (IV) in aqueous nitric solutions**. *Dalton Trans* DOI:10.1039/c4dt02330g – [IF=4.097]

6. Mouri A, Diat O, El Ghzaoui A, et al. **Phase behavior of reverse microemulsions based on Peceol (R)**. *Journal of Colloid and Interface Science* 2014;416:139-146. - [IF=3.552]

7. Guillot M, El Mourabit S, Ravaux J, Tokarev A, Goettmann F, Grandjean A. **Pseudomorphical synthesis of glasses with hierarchical macro- and mesoporosity.** *Microporous and Mesoporous Materials* 2014;197:83-91. - [IF=3.209]

8. Moloney MP, Causse J, Loubat C, Grandjean A. Sodium **" Activation" of Silano-Phosphonate Modified Mesoporous TiO2 Leading to Improved Rare-Earth Element Extraction.** *European Journal of Inorganic Chemistry* 2014;2014(13):2268-2277. - [IF=2.965]

9. Beaudoux X, Virot M, Chave T, Leturcq G, Clavier N, Dacheux N, Nikitenko S.I. **Catalytic dissolution of Ceria-Lanthanide mixed oxides provides environmentally friendly partitioning of Lanthanides and Platinum**. *Hydrometallurgy* – [IF = 2.224]

10. Kaper H, Nicolle J, Cambedouzou J, Grandjean A. **Multi-method analysis of functionalized single-walled carbon nanotubes for cesium liquid-solid extraction**. *Materials Chemistry and Physics* 2014;147(1-2):147-154. - [IF=2.129]

11. Poirot R, Bourgeois D, and Meyer D. **Palladium extraction by a malonamide derivative (DMDOHEMA) from Nitrate media**: Extration. *Solvent Extraction and Ion Exchange* 32(5), p.529-542. - [IF=1.660]

12. Turgis R, Leydier A, Arrachart G, et al. **URANIUM EXTRACTION FROM PHOSPHORIC ACID USING BIFUNCTIONAL AMIDO-PHOSPHONIC ACID LIGANDS**. *Solvent Extraction and Ion Exchange* 2014;32(5):478-491. - [IF=1.660]

13. Rodrigues F, Ferru G, Berthon L, et al. **New insights into the extraction of uranium(VI) by an N,N-dialkylamide.** *Molecular Physics* 2014;112(9-10):1362-1374 - [IF=1.642]

14. Alvarez L, Fall F, Belhboub A, Le Parc R, Almadori Y, Arenal R, Aznar R, Dieudonne-George Ph, Hermet P, Rahmani A, Jousselme B, Campidelli S, Cambedouzou J. **1D molecular crystal of phtellocyanine confined into single-walled carbon nanotubes.** *Journal of the American Ceramic Society* – Submitted

15. Causse J, Tokarev A, Ravaux J, Moloney M, Barre Y, Grandjean A. **Facile one-pot synthesis of copper hexacyanoferrate nanoparticle functionalised silica monoliths for the selective entrapment of Cs-137**. *Journal of Materials Chemistry A* 2014;2(25):9461-9464

17. Lepoitevin M, Coulon P.E, Bechelany M, Cambedouzou J, Janot J.M, Balme S. **Influence of nanopore surface charge and magnesium ion on polyAdenosine translocation**. *Nanotechnology* – Submitted

18. Nardin T, Gouze B, Cambedouzou J, Bauduin P, Wong Chi Man M, Deschanels X, Bourgeois, Meyer D, Diat O. **Elaboration of porous silicon carbide by solft templating molecular precursors with semi-fluorinated alkanes**. *Journal of Materials Chemistry A* - Submitted

19. Nardin T, Gouze B, Cambedouzou J, Meyer D, Diat O. **Elaborating porous silicon carbide from molecular soft template by (1H,1H,2H,2H- prefluorotetradecyl triisopropylsilane**. *Ceramic Transactions* - Submitted

19. Nicolle J, Le Goff X.F, Grandjean A, Cambedouzou J. **Observing and predicting the preferential functionalization of metallic or semiconducting single-walled carbon nanotubes**. *Europhysics Letters* 107, 67003 (2014) – Submitted

20**.** R. Turgis, A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguirditchian, S. Pellet-Rostaing **Carbamoylalkylphosphonates for dramatic enhancement of uranium extraction from phosphates ores** Solvent Extraction and Ion Exchange 2014, 32(7), 685-702.

Green Chemistry

1. Cairos C, Schneider J, Pflieger R, Mettin R. **Effects of argon sparging rate, ultrasonic power, and frequency on multibubble sonoluminescence spectra and bubble dynamics in NaCl aqueous solutions.** *Ultrasonics Sonochemistry* 2014;21(6):2044-2051. - [IF=3.816]

2. Cau C, Guari Y, Chave T, Larionova J, Nikitenko SI. **Thermal and sonochemical synthesis of porous (Ce,Zr)O-2 mixed oxides from metal beta-diketonate precursors and their catalytic activity in wet air oxidation process of formic acid.** *Ultrasonics Sonochemistry* 2014;21(4):1366-1373. - [IF=3.816]

3. Pflieger R, Chave T, Vite G, Jouve L, Nikitenko SI. **Effect of operational conditions on sonoluminescence and kinetics of H2O2 formation during the sonolysis of water in the presence of Ar/O2 Gas Mixture**. *Ultrasonics Sonochemistry* – [IF= 3.816]

4. Chave T, Navarro N.M, Pochon P, Perkas N, Gedanken A, Nikitenko SI. **Sonocatalytic degradation of oxalic acid in the presence of oxygen and Pt/TiO2**. *Catalysis Today* doi:10.1016/j.cattod 2014.07.040 – [IF=3.309]

5. Deschanels X, Seydoux-Guillaume AM, Magnin V, et al. **Swelling induced by alpha decay in monazite and zirconolite ceramics: A XRD and TEM comparative study**. *Journal of Nuclear Materials* 2014;448(1-3):184-194. - [IF=2.016]

6. Peuget S, Fares T, Maugeri EA, et al. Effect of B-10(n, alpha)**Li-7 irradiation on the structure of a sodium borosilicate glass**. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms* 2014;327:22-28. - [IF=1.186]

7. Bourgeois D, Boivin G. On Uranium and bone. *Biofutur* 2014(353):32-35. - [IF=0.026]

Anticipate life-cycle

1. Hudry D, Griveau JC, Apostolidis C, et al. **Thorium/uranium mixed oxide nanocrystals: Synthesis, structural characterization and magnetic properties**. *Nano Research* 2014;7(1):119-131. - [IF=6.963]

2. Li DY, Zeng YJ, Batuk D, et al. **Relaxor Ferroelectricity and Magnetoelectric Coupling in ZnO-Co Nanocomposite Thin Films: Beyond Multiferroic Composites**. *Acs Applied Materials & Interfaces* 2014;6(7):4737-4742. - [IF=5.900]

3. Hudry D, Apostolidis C, Walter O, et al. **Ultra-Small Plutonium Oxide Nanocrystals: An Innovative Material in Plutonium Science**. *Chemistry-a European Journal* 2014;20(33):10431-10438. - [IF=5.696]

4. Mesbah A, Szenknect S, Clavier N, Poinssot C, Ewing R, Dacheux N. Coffinite, **USiO4 is abundant in nature : so why is it so difficult to synthesize ?** *Environmental Science and Technology* – [IF= 5.1481]

5. Mesbah A, Rabu P, Sibille R, et al. **From Hydrated Ni-3(OH)(2)(C8H4O4)(2)(H2O)(4) to Anhydrous Ni-2(OH)(2)(C8H4O4): Impact of Structural Transformations on Magnetic Properties.** *Inorganic Chemistry* 2014;53(2):872-881. - [IF=4.794]

6. Prakash J, Tarasenko M.S, Mesbah A, Lebègue S, Malliakas C.D, Ibers J.A. **Syntheses, crystal structures, transport properties and theoretical studies of five members of the Man2Q5 family : SrU2S5, PbU2S5 and BaU2Te5**. *Inorganic Chemistry* – [IF=4.794]

7. Mesbah A, Clavier N, Elkaim E, Gausse c, Ben Kacem I, Szenknect S, Dacheux N. **The monoclinic form of the rhabdophane compounds : REEP04 0.667 H2O**. *Cryst. Growth and Design* 14, 5090-5098, 2014 – [IF=4.56]

8. Villard A, Siboulet B, Toquer G, Merceille A, Grandjean A, Dufrêche J.F. Stronium selectivity in sodium nonatitanate Na4Ti9020 x H2O. *Journal of Hazardous Materials* – Accepted [IF= 4.331]

9. Szenknect S, Mesbah A, Cordara T, Clavier N, Den Auwer C, Lozano-Rodriguez J, Poinssot C, Ewing R, Dacheux N. **First experimental determination of the solubility constant of coffinite**. *Geochim. Cosmochim. Acta* – (IF=4.25]

10. Falaise C, Assen A, Mihalcea I, Volkringer C, Mesbah A, Dacheux N, Toiseau T. **Coordination polymers of uranium (IV) terephthalate**. *Dalton Transactions* - [IF=4.097]

11. Steins P, Poulesquen A, Frizon F, et al. **Effect of aging and alkali activator on the porous structure of a geopolymer**. *Journal of Applied Crystallography* 2014;47:316-324. - [IF=3.950]

12. Bouala GIN, Clavier N, Podor R, et al. **Preparation and characterisation of uranium oxides with spherical shapes and hierarchical structures**. *Crystengcomm* 2014;16(30):6944-6954. - [IF=3.858]

13. Gouze B, Cambedouzou J, Parres-Maynadie S, Rebiscoul D. **How hexagonal mesoporous silica evolves in water on short and long term: Role of pore size and silica wall porosity**. *Microporous and Mesoporous Materials* 2014;183:168-176. - [IF=3.209]

14. Chatelain G, Bourgeois D, Ravaux J, Averseng O, Vidaud C, Meyer D. **Alternate dipping preparation of biomimetic apatite layers in the presence of carbonate ions**. *Biomedical Materials* 2014;9(1). - [IF=2.922]

15. Ban V, Sibillea R, Mesbah A, Gaudisson T, Mazet T, François M. **Spin-glass state in Ni5(OH)6(CnH2n-4O4)2 metal-organic frameworks (n=6, 8, 10,12)**. *Solid State Chemistry* 37 (2014) 154-163 - [IF=2.200]

16. Mesbah A, Skojko W, Lebègue S, Malliakas C.D, Frazer N.L, Ibers J.A. **The U5+compound Ba9Ag10U4S24 : synthesis, structure and electronic properties**. *Journal of Solid State Chemistry* – [IF=2.200]

17. Wallez G, Raison PE, Smith AL, Clavier N, Dacheux N. **High-temperature behavior of dicesium molybdate Cs2MoO4: Implications for fast neutron reactors**. *Journal of Solid State Chemistry* 2014;215:225-230. - [IF=2.200]

18. Clavier N, Szenknect S, Costin DT, Mesbah A, Poinssot C, Dacheux N. **From thorite to coffinite: A spectroscopic study of Th1-xUxSiO4 solid solutions**. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy* 2014;118:302-307. - [IF=2.129]

19. Claparede L, Tocino F, Szenknect S, Mesbah An Clavier N, Moisy P, Dacheux N. **Dissolution of Th1-xUxO2 : effects of chemical composition and microstructure**. *Journal of Nuclear Materials* - [IF=2.016]

20. Gaillard J, Venault L, Calvet R, et al. **Effect of hydration and thermal treatment on ceria surface using non-intrusive techniques.** *Journal of Nuclear Materials* 2014;444(1-3):359-367. - [IF=2.016]

21. Martinez J, Clavier N, Mesbah A, Audubert F, Le Goff X, Vigier N, Dacheux N. **An original precipitation route toward the preparation and the sintering of highly reactive uranium cerium dioxide powders** *Journal of Nuclear Materials* - [IF=2.016]

22. Monteiro A, Schuller S, Toplis MJ, et al. **Chemical and mineralogical modifications of simplified radioactive waste calcine during heat treatment**. *Journal of Nuclear Materials* 2014;448(1-3):8-19. - [IF=2.016]

23. Nabhan D, Kapusta B, Billaud P, Colas K, Hamon D, Dacheux N. **Effects of pH, surface finish and thermal treatment on the corrosion of AlFeNi aluminium alloy. Characterization of oxide layers**. *Journal of Nuclear Materials* - [IF=2.016]

24. Lucas IT, Durand-Vidal S, Bernard O, et al. **Influence of the volume fraction on the electrokinetic properties of maghemite nanoparticles in suspension**. *Molecular Physics* 2014;112(9-10):1463-1471. - [IF=1.642]

25. Baron F, Robin V, Beaufort D, Szenknect S, Dacheux N, Petit S. **Use of near infrared spectroscopy for the identification of coffinite and uranothorite**. *Journal of near Infrared Spectroscopy* 2014;22(2):149-152. - [IF=1.480]

26. Tocino F, Szenknect S, Mesbah A, Clavier N, Dacheux N. **Dissolution of uranium mixed oxides: The role of oxygen vacancies vs the redox reactions**. *Progress in Nuclear Energy* 2014;72:101-106. - [IF=0.879]

27. Horlait D, Claparede L, Tocino F, et al. **Environmental SEM monitoring of Ce(1-x)Ln(x)O(2-x/2) mixed-oxide microstructural evolution during dissolution**. *Journal of Materials Chemistry A* 2014;2(15):5193-5203

28. Huguet-Garcia J, Jankowiak A, Miro S, Gosset D, Podor R, Meslin R, Serruys Y, Costantini J.M. **In situ E-SEM and TEM observations of the thermal annealing effects on ion-amorphized 6H-SiC and nanophased SiC fiber**. *Physica Status Solidi B* – Accepted

29. Lou Y, Toquer G, Dourdain S, Rey C, Grygiel C, Simeone D, Deschanels X. **Mesoporous silica SBA-15 and MCM-41 under ionic irradiation**. *Nuclear Instruments and Methods in Physics Research Section B : Beam interactions with Materials and Atoms* – Submitted

30. Pedraza F, Podor R. **Influence of annealing conditions on the formation of hollow Al203 microspheres**. *Materials Chemistry and Physics* – Submitted

Methods and theory

1. Archibald SJ, Atkin SL, Bras W, et al. **How does iron interact with sporopollenin exine capsules? An X-ray absorption study including microfocus XANES and XRF imaging**. *Journal of Materials Chemistry B* 2014;2(8):945-959 – [IF= 6.626]

2. Noureddine A, Trens P, Toquer G, Cattoën X, Wong Chi Man M. **Tailoring the Hydrophilic/Lipophilic Balance of Clickable Mesoporous Organosilicas by the Copper-Catalyzed Azide-Alkyne Cycloaddition Click-Functionalization**. *Langmuir* 30(41), 12297-12305 – [IF=4.384]
3. Vitorge E, Szenknect S, Martins JMF, et al. **Comparison of three labeled silica nanoparticles used as tracers in transport experiments in porous media. Part I: Syntheses and characterizations**. *Environmental Pollution* 2014;184:605-612. - [IF=3.902]

4. Vitorge E, Szenknect S, Martins JMF, Barthes V, Gaudet JP. **Comparison of three labeled silica nanoparticles used as tracers in transport experiments in porous media. Part II: Transport experiments and modeling**. *Environmental Pollution* 2014;184:613-619. - [IF=3.902]

5. Navarro NM, Pflieger R, Nikitenko SI. **Multibubble sonoluminescence as a tool to study the mechanism of formic acid sonolysis**. *Ultrasonics Sonochemistry* 2014;21(3):1026-1029. - [IF=3.816]

6. Laurencin D, Vantelon D, Briois V, et al. **Investigation of the local environment of iodate in hydroxyapatite by combination of X-ray absorption spectroscopy and DFT modeling.** *Rsc Advances* 2014;4(28):14700-14707. - [IF=3.708]

7. Pfleiger R, Ndiaye A.A, Chave T, Nikitenko SI. **Influence of ultrasonic frequency on swan band sonoluminescence and sonochemical activity in aqueous tert-butanol solutions**. *Journal of Physical Chemistry B* – [IF=3.377]

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Appendix B

List of Patents

Parc instrumental opérationnel

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- R. Poirot, D. Bourgeois, D. Meyer, "Procédé de séparation du palladium des autres éléments métalliques présents dans une phase aqueuse nitrique et ses utilisations" FR 14/56878, dépôt 17/07/2014

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Appendix C

Résumé du projet de LABEX proposé par le Pole de Chimie Balard du Languedoc-Roussillon

CHIMIE DES SYSTEMES - CHEMISYST- DU PÔLE DE CHIMIE BALARD DU LANGUEDOC-ROUSSILLON

Chimie des systèmes -CHEMISYST- du pôle de chimie Balard du Languedoc-Roussillon

Le projet CheMISyst du Pôle Balard bénéficie d’une puissante dynamique initiée depuis plusieurs années :

- Tout d'abord, la volonté des chimistes de Montpellier et de sa région de travailler au sein d’une structure fédérative commune, le pôle de chimie Balard, dont la mission est d’harmoniser l’offre de formation et la valorisation entre les établissements partenaires, ainsi que la politique de recherche des Instituts dans le cadre de la fédération de recherche CNRS FR 3105 Balard. Cet ensemble rassemble plus de 400 chercheurs et enseignants-chercheurs permanents sur les sites de Montpellier, Marcoule et Alès, travaillant au sein de vingt-six équipes identifiées, dont les projets ont été notés "A+" pour onze d’entre elles et "A" pour douze autres par l’AERES (évaluation 2010).
- Ensuite, la décision récente, dans le cadre du plan campus, de créer sur Montpellier pour la chimie un lieu unique de recherche (trois Instituts), d’enseignement (nouvelle implantation de l’ENSCM) et de transfert et valorisation (un centre de recherche et innovation pour les « jeunes pousses » et un hôtel d’entreprises). En association avec le site de Marcoule et l'Ecole des Mines d'Alès, l'objectif est de créer un centre universitaire de taille critique à l'échelle européenne, sur le modèle de Lund ou Potsdam.

Trois domaines d'expertise sont actuellement bien identifiés sur le Pôle Balard. Deux domaines historiques sont d’une part celui des matériaux fonctionnels (matériaux pour la catalyse, matériaux membranaires, matériaux pour l’énergie, polymères, matériaux hybrides organiques-inorganiques, matériaux pour la santé) et celui de la synthèse et de l'assemblage des biomolécules (incluant des approches innovantes sur la conception de nouveaux médicaments, la vectorisation, le ciblage ou la toxicologie prédictive). Le troisième domaine provient des compétences uniques en Europe du CEA dans les procédés de séparation (ICSM), sur lesquelles reposent non seulement les procédés d'un nucléaire de plus en plus renouvelable, mais aussi le recyclage stratégique des terres rares et autres métaux. L’objectif du présent projet est de renforcer la synergie des équipes des différents Instituts autour d’une ambition scientifique commune s’inscrivant dans la durée et de créer un corpus d’expertises et de compétences identifiable à l’échelle internationale, tant sur le plan académique que de l’innovation industrielle.

Résumé du projet de recherche

Alors que classiquement la chimie essaie de décrire la matière dans sa complexité comme un assemblage d’unités constitutives susceptibles d’être étudiées séparément, la science moderne voit apparaître le concept de “système”, défini comme l’organisation d’espèces en interaction les unes avec les autres, formant un ensemble « intégré » dont les propriétés ne sauraient être interprétées à partir de celles de chaque constituant. Dans le futur, l’enjeu de la chimie serait moins de synthétiser des espèces nouvelles que de découvrir des combinaisons inédites d’espèces connues : nanocomposites, agrégats, clusters, colloïdes etc., porteurs de propriétés innovantes insoupçonnées. Cette approche est la clé de la chimie interfaciale qui vise à étudier des phénomènes complexes comme les interactions des ions et molécules adsorbés dans/sur des structures solides hôtes, et de relier les effets sur leur conformation, dynamique et réactivité avec les caractéristiques géométriques et électroniques de ces structures. Cette approche est également la clé vers la construction bottom-up de systèmes « intelligents » capables de répondre à des stimuli externes et / ou de manière sélective reconnaître, encapsuler, transporter ou transformer chimiquement des ions et des molécules dans les liquides, solides ou de gels. La chimie des "systèmes moléculaires et interfaciaux" est un thème transverse aux quatre Instituts de Balard, fondé sur la connaissance et la modélisation des interactions à longue distance, qui s'appuiera sur l'action CECAM à développer sur Montpellier. Cette approche "chimie des systèmes" offre à leurs projets de recherche respectifs un horizon de dépassement à moyen et long termes, avec une résonance dans la chimie du recyclage de la matière utilisée économiquement.

Projet de formation associée

L'offre de formation actuelle, qui couvre les différents domaines de la chimie et de ses interfaces avec les sciences de la vie, la physique et le génie des procédés, est déjà bien en phase avec les axes stratégiques du projet CheMISyst. Cette offre couvre également tous les niveaux en formation initiale et continue, du DUT au Doctorat, en passant par l'ingéniorat.
CheMISyst a vocation à promouvoir la création de formations innovantes et leur attractivité nationale et internationale, favorisant ainsi l'intégration des élèves diplômés sur le marché du travail.

La clé de voûte est la création de quatre chaires à vocation internationale. Ces chaires seront associées avec les trois axes stratégiques (matériaux à tâches spécifiques, séparation, décontamination et recyclage, et systèmes biomoléculaires spécifiques) et le thème transversal du projet, à savoir les interactions à longue portée. En collaboration avec les détenteurs des chaires, CheMISyst aura en charge l'organisation annuelle d'une école d'été internationale sur la chimie des systèmes, sur la base minimale de sept jours et trente-cinq participants et conçue comme une extension des thèmes de l'*European Practical Summer School of Separation Chemistry*, annuelle depuis 2007.
Cette évolution continue dans le contenu de l'offre de formation s'accompagnera par une amplification de son internationalisation, déjà bien réelle avec, en fer de lance, le master européen Erasmus Mundus EM3E coordonné par l'UM2, le master EMASCO-COSOM de la fédération Gay-Lussac piloté depuis Regensburg et le Master Chimie séparative, matériaux et procédés. Ce master, sélectif et généraliste qui couvre l'ensemble chimie séparative et énergie nucléaire est en cours d'internationalisation. De nouveaux projets de partenariats internationaux sont actuellement en construction, notamment avec la Chine (ENSCM).
Un autre axe important concerne l'amplification de la formation technologique via la constitution d'une plate-forme technologique mutualisant les moyens déjà existants sur les différents sites (UM2, ENSCM, CEA et EMA) et créant des outils complémentaires comme la plate-forme technologique dédiée aux masters (UM2).

Projet de valorisation et de diffusion des résultats

Une originalité du projet est l'intégration/immersion d'entreprises sur les sites de recherche :

- Centre d'Innovation et de Transfert de Technologies Balard (campus Balard, Montpellier) : le CIT (2000 m²) sera dédié à l'hébergement des « jeunes pousses » (starts up) générées par les innovations développées dans les Instituts.
- Incubateur Galera (Montpellier) : cet incubateur de 140 m² de laboratoires et bureaux permet d'héberger ponctuellement des équipes-projets issues de PME.
- Hôtel d'entreprise Balard (CRDI, campus Balard, Montpellier) d'une superficie de 4000 m².
- Incubateur technologique InnoV'up à l'Ecole des Mines d'Alès (point 5.4).
- Réserve foncière du Parc Marcel Boiteux à Marcoule : un critère de succès à quatre ans du LABEX CheMISyst serait le démarrage effectif de démonstrateurs de recyclage de métaux, polymères bio-sourcés et résidus de fabrication sur ce site.

Le projet de valorisation s'appuiera également sur la SATT en cours de création. Les quatre partenaires industriels, membres fondateurs de la Fondation Balard (TOTAL, AREVA, SANOFI et UIC) participent à la vie du LABEX dans son fonctionnement, comme dans l'organisation de colloques de type "Solvay" destinés aux grands groupes et (séparément) aux PME. Dès les premiers mois de fonctionnement du laboratoire d'excellence, des partenariats à long terme seront proposés aux grands groupes, comme Rhodia pour le recyclage des métaux stratégiques, ainsi que des contrats d'externalisation de la R/D au sein des équipes du LABEX et ayant accès aux infrastructures dans le cas des PME pour la mise au point de nouvelles membranes. L'interface avec les PME sont les pôles de compétitivité TRIMATEC et EUROBIOMED.

Gouvernance du LABEX CheMISyst

- Les Universités de Montpellier 1 et 2, le CNRS, le CEA et l'Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM) ont uni leurs compétences dans le Pôle chimie Balard, créé le 19 décembre 2007 par convention constitutive entre l'Etat, la Région et les membres fondateurs (http://www.enscm.fr/polechimie-balard/polechimie-balard.htm). Ce pôle dispose d'une structure opérationnelle de pilotage qui englobe quatre Instituts de Recherche regroupés au sein d'une Fédération de Recherche CNRS 3105. Il s'appuie également sur deux Chaires, une Chaire UNESCO (« Sciences des Membranes Appliquées à l'Environnement ») d'une part, une Chaire Européenne de chimie nouvelle pour un développement durable ChemSUD ; il est partie prenante de trois pôles de compétitivité (DERBI, EUROBIOMED et TRIMATEC) et contribue au développement d'un Institut Carnot (« Chimie, Environnement, Développement Durable»).
- Le Labex Chemisyst est un projet de site qui s'inscrit, d'une part, dans les trois missions fondamentales du Pôle Chimie Balard -Recherche, Formation et Valorisation- et d'autre part, dans les trois axes stratégiques de développement du Pôle : Energie, matériaux et vecteurs – Valorisation des ressources naturelles et procédés de la chimie durable - Biologie et Santé - enfin, dans les politiques des Etablissements et Organismes, membres fondateurs du Pôle.
- Le Labex représente une opération transversale pluriannuelle de Balard (2011-2020). De façon naturelle, le Labex Chemisyst sera géré sous un « mode projet » par la gouvernance du Pôle au travers de :
    - sa direction scientifique, sous forme d'un Directoire (Directeurs d'unités mixtes constituant Balard, Fédération de recherche CNRS, Ecole doctorale et recherches et Directeurs des structures contractuelles non pérennes associées) qui assurera le suivi du projet,
    - son Collège scientifique, formé de scientifiques extérieurs, principalement étrangers, choisis pour leur expertise scientifique reconnue internationalement. Ce conseil sera en charge d'éclairer la Direction et son Comité de Pilotage Stratégique sur la pertinence des grandes orientations scientifiques adoptées dans le cadre de la politique incitative du LabEx.
    - son Comité de Pilotage Stratégique, composé des représentants des membres fondateurs UM1 et UM2, l'ENSCM, CNRS et CEA, de l'Etat et de la Région. Ce comité de piloatge stratégique accompagnera la direction pour la définition d'une politique incitative du site se traduisant par la mise en place de programmes portant sur les crédits du LabEx mais aussi sur les crédits attribués par la Fondation de Coopération Scientifique de site associé au projet IDEX déposé par les Universités du site de Montpellier. La Fondation universitaire Balard est en charge notamment des partenariats industriels.

Intégration du projet de laboratoire d'excellence dans la stratégie nationale et de l'établissement.

Le projet de LABEX Chemisyst se place au point triple des alliances nationales ANCRE, dans la chimie pour l'énergie nucléaire comme pour l'électro-mobilité, AVISAN dans la partie toxicologie et pharmacologie, ainsi qu'ALLENVI pour les divers projets qui ont pour point commun l'économie d'atomes dans la synthèse et l'intensification des procédés de la chimie du développement durable. Dans ce dernier aspect, un chercheur du Pôle Balard (S. Pellet-Rostaing) co-pilote le GDR de "Synthèse et Procédés du développement durable" du CNRS (2010-2013). Le lien avec la société hors des cercles académiques se fera *via* un partenariat durable avec les musées, dont celui centré sur chimie, énergie et société au *Visiatome*, semblable au musée de la chimie de Ludwigshafen, et actuellement unique en France, ainsi que l'Institut Carnot Balard, la chaire ChemSud et des partenariats à monter avec le Pôle SHS de Montpellier sur les musées.

La synergie avec les autres pôles identifiés de l'Université de Montpellier Sud de France se fera à travers une Fondation de Coopération Scientifique chargée de la gouvernance de l'IdEx montpelliérain. Le LABEX CheMISyst se veut acteur des IRT (énergie, eau, micro-algues etc..) et aura vocation à servir d'expert et de partenaire dans les programmes associés.

Les membres du Conseil Scientifique de l'ICSM

De haut en bas et de gauche à droite

Jacques REISSE (Université libre de Bruxelles) – Jean DAILLANT (Synchrotron SOLEIL)
Mélissa DENECKE (University of Manchester) -Bruno CHAUDRET (CNRS Toulouse)
Joël MOREAU (CNRS) – Claude POUCHAN (Université de Pau) – Gérald SENENTZ (AREVA)
Véronique SCHMITT (CNRS Bordeaux) – Loïck MARTIN-DEIDIER (CEA) – Maurice LEROY (CNE2)
Gilberte CHAMBAUD (Université Marne la vallée) – Claire-Marie PRADIER (CNRS) – Valérie CABUIL (ENSCP)
Philippe MIELE (ENSCM)

Summary

Le bâtiment de l'ICSM dans la partie du Parc Marcel Boiteux.

Institut de Chimie Séparative de Marcoule

Les chercheurs, techniciens et agents administratifs de l'ICSM (photographie prise en octobre 2014)

ICSM – Centre de Marcoule
BP 17171 – 30207 BAGNOLS-SUR-CEZE CEDEX
Tél: +33 (0)4 66 79 66 28 – Fax : +33 (0)4 66 79 76 11
www.icsm.fr