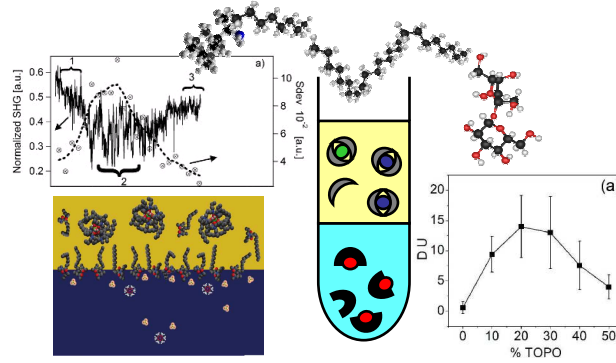




UMR 5257 CEA-CNRS-UM2-ENSCM

**INSTITUT DE CHIMIE SEPARATIVE
DE MARCOULE
ICSM**





Comprendre la séparation

Optimiser la séparation

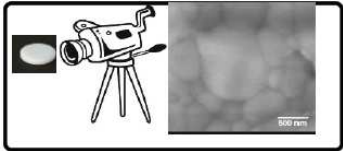


Sonoluminescence de l'uranyle

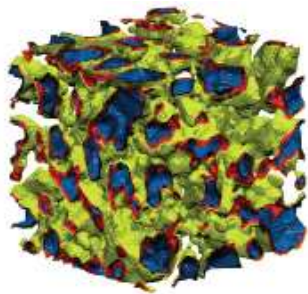
Chimie verte

Anticiper le cycle de vie des matériaux

Méthodes et théorie



Frittage "in situ" 1400°C



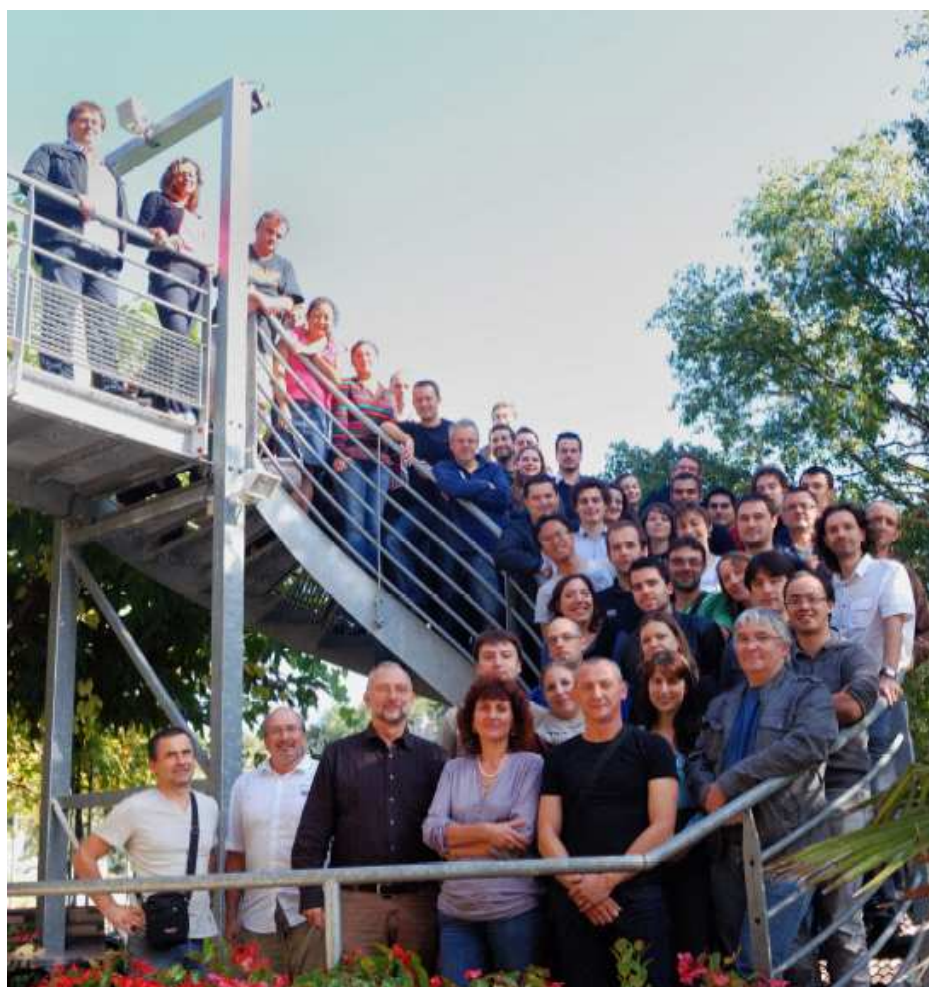
Modèle de microémulsion pauvre en eau





Institut de Chimie Séparative de Marcoule

SCIENTIFIC REPORT 2009 - 2012 Part 3



Permanent staff at ICSM as in October 2012



7 – Scattering and diffraction

L'équipe est constituée au 1^{er} décembre 2012 de :

- 1 permanent CEA responsable d'équipe (O. Diat),
- 1 enseignant chercheur ENSCM (J. Cambedouzou)
- 1 technicien CEA (B. Corso)
- 2 ingénieurs d'étude CNRS (A. Jonchère et X. Le Goff)
- 1 post-doc (J. Nicole)
- 2 doctorants (T. Nardin et E. Scoppola)



Deux équipements de diffusion de rayons X ont été mis en place dans le laboratoire transverse diffusion/diffraction à l'ICSM: un diffractomètre BRUKER (D8 Advance) multi-usage et un banc de diffusion aux petits angles assemblé par la société XENOCS. De part la pression d'utilisation sur le premier équipement un second diffractomètre de poudre co-financé par l'ICSM est en cours d'installation sur le centre de Marcoule et sera accessible 30% du temps.

Ces diffractomètres sont des équipements que l'on trouve sur catalogue ; il sont utilisé avec une source au cuivre et un ensemble de collimation échangeables permettant d'accéder à une large gamme d'analyse structurale à l'échelle atomique : l'identification de phases et la détermination de leur fraction volumique (composition chimique), la mesure de paramètres de maille, l'analyse de structure atomique en utilisant la méthode de Rietvelt, la détermination de taille de cristaux, des mesures en fonction de la température (four Anton Paar pouvant atteindre 1200°C). Les géométries d'analyse peuvent être adaptées en fonction de l'échantillon (/ son absorption et sa quantité) pour travailler en réflexion ou transmission. Il est possible d'effectuer également des mesures de réflectivité afin de déterminer des profils de densité électronique perpendiculairement à des surfaces de couches minces. Toute cette instrumentation a été calibrée et optimisée pour répondre déjà à un nombre important d'analyses dédiées à l'ICSM mais aussi aux autres laboratoires environnants.

Pour des études plus spécifiques et qui concernent des analyses structurales de systèmes colloïdaux, de fluides complexes, de couches minces absorbantes, de matériaux mésoporeux, tous ayant en commun la particularité de contenir des espèces à haut Z, un dispositif de diffusion aux petits angles non conventionnel et recouvrant petits et grands angles de diffusion ($>$ à deux ordres de grandeur en vecteur d'onde) en une seule acquisition a été spécifié par l'équipe et réalisé par une société française XENOCS, ceci pour la première fois.

Ce dispositif utilisant une source au Molybdène (17 keV), entièrement automatisé et permettant de réaliser des expériences relativement simplement est opérationnel depuis le mois d'avril 2009. La mise en place de fentes anti-diffusantes de dernière génération (avec cristaux clivés en bord de fentes) simplifie considérablement l'alignement de ce type de montage et permet d'atteindre aisément $1.8 \cdot 10^{-2} \text{ \AA}^{-1}$ en q_{\min} . En ce qui concerne l'environnement échantillon, nous avons mis en place un équipement porte capillaire thermostaté pouvant couvrir une gamme de température continue de -10 à 120°C, l'ensemble étant automatisé. Toutes les mesures en solution mais aussi en poudres sont traduites en échelle absolu et peuvent être analysées en utilisant un logiciel gratuit et suivi par PSI et HMI : SASfit.

Ces deux équipements complémentaires sont intégrés à une plateforme technique de Montpellier afin de pouvoir offrir un service à un maximum de scientifiques.

Enfin une petite plate-forme d'optique non linéaire est en cours d'élaboration avec la collaboration d'une équipe à Lyon (UCB, LASIM) et d'ingénieurs opticien du CEA-Marcoule (DRCP/LAMM). Elle permettra d'appréhender les phénomènes interfaciaux de complexation et de transfert ionique à la surface ou à l'interface de deux liquides non miscibles.

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

J. Cambedouzou, B. Corso, A. Jonchère and O. 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 (Beck, 1992) and SBA-15 (Zhao, 1998). The same symmetry can be found in carbon mesoporous materials, for example in FDU-15 structures (Meng, 2005).

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 based on the formalism proposed by Spalla *et al.* (2003). 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.

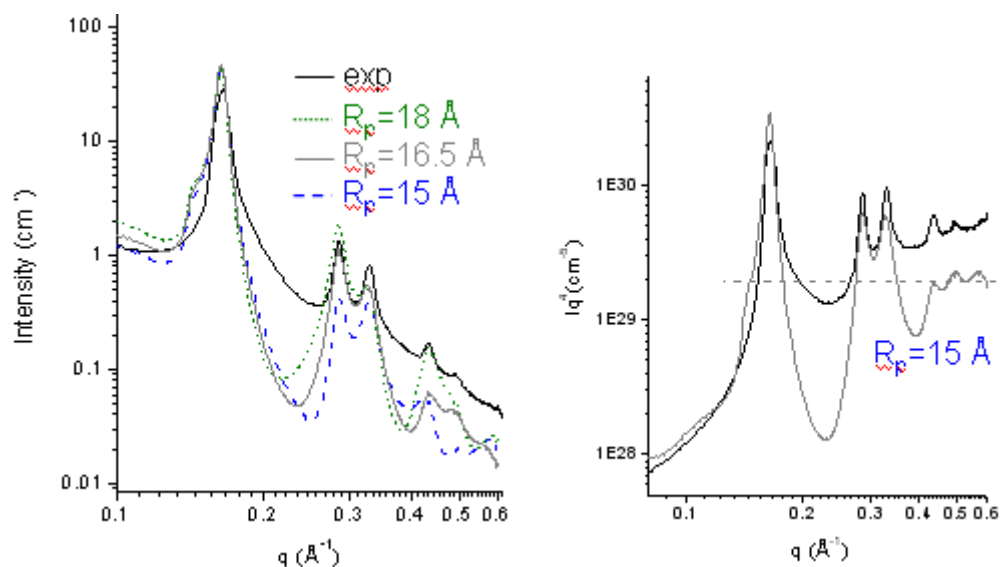


Fig: left -SAXScattering from MCM41 powder sample (black line) plotted as a function of q with other model scattering curves varying the pore radius of cylindrical pores aligned on a triangular network. Right – Porod plot in absolute units of experimental and the best adjusted model curve.

Reference

J. Cambedouzou and O. Diat, "Determining the specific surface of hexagonal mesoporous materials using small angle scattering", *J. Appl. Cryst* 45 (2012) pp662-673

Time-resolved SWAXS experiments for studying a geopolymerization

¹P. Steins, ¹A. Poulesquen, ¹F. Frizon, B. Corso and O. Diat

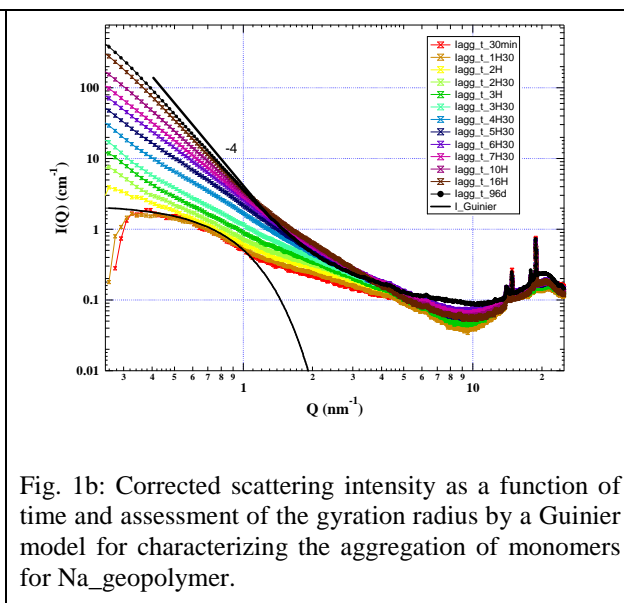
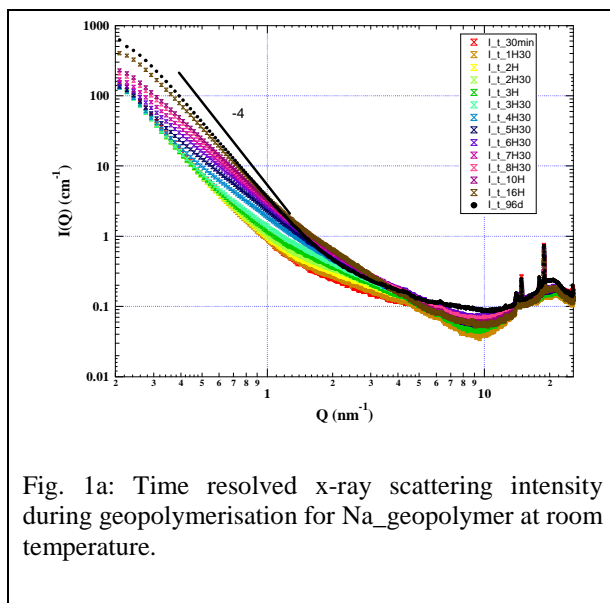
As an alternative to Portland cements for building or packaging, geopolymer made from an hydrolysis of an aluminosilicate source followed by a polycondensation of aluminate and silicate species in alkalin solution are studied for a long time for their interesting mechanical properties and being “economic” in greenhouse gases.

Various techniques such as spectroscopies, scattering, microscopies were used to understand the various chemical and physical mechanisms that come into the fabrication processes. Although SAXS is recognized as a highly suitable technique to probe a multiscale structure evolution it was not so often applied for studying in-situ geopolymerisation.

Using a laboratory “moly” source, we were able to perform time resolved SAXS/WAXS on metakaolin-derived geopolymer and to get an insight on the structural evolution from the aqueous dispersion until the solidification steps.

These polymers are inorganic synthesized by alkaline activation of an aluminosilicate source (metakaolin) in aqueous solution. Different steps during a specific dissolution/polycondensation mechanism were distinguished. A structural analysis allows to characterize these mechanisms at the nanoscale and to show that the growth of the geopolymer is due to an aggregation of oligomers with a size which is even smaller than the cation from the alkali activator (Na^+ , K^+ and Cs^+) is chaotrope. The final state of geopolymers structure prepared under various alkalin conditions were compared with respect to their porosity evaluating simultaneously gas adsorption and small angle x-ray scattering data.

Moreover complementary data from rheology and electron paramagnetic resonance confirm the analysis in time evolution deduced from SAXS data.



Reference

P. Steins, A. Poulesquen, O. Diat and F. Frizon, "Structural evolution during geopolymerization, from early age to consolidated material" Langmuir 28(22) (2012) pp 8502-10

¹ CEA, DEN, DTCD/SPDE/L2ED-Marcoule

In situ HT-XRD study of precursor thermal conversion

B. Corso, J. Martinez, N. Clavier, O. Diat, N. Dacheux

The D8 BRUKER AXS diffractometer available at ICSM was implemented with a HTK 1200 Anton Paar temperature chamber ($T_{\max.} = 1200^{\circ}\text{C}$) (Figure 1) in order to assess the structural behavior of materials during heating steps. Such device is able to operate under controlled pressure of air or inert gas (up to 1 bar above atmospheric pressure) or under vacuum (10^{-4} mBar). Also, only dry atmospheres can be used, thus avoiding the possibility to work under moist environment. Finally, alumina sample holder was used, leading to a poor reactivity with the samples studied.

Such device was particularly helpful during the study of the decomposition of crystallized precursors used in the preparation of actinides and/or lanthanides-bearing mixed oxides, as models for Gen-III or Gen-IV nuclear fuels¹. As an example, the conversion of uranium-based oxalate was investigated by the means of *in situ* HT-XRD studies. On the one hand, HT-XRD allowed the *in situ* observation of the oxalate behavior during heat treatments between 30°C and 1000°C . The subsequent diffractogram analyses led to the determination of the successive chemical steps during the conversion of oxalate to oxide, namely successive dehydrations and oxalate decomposition into CO and CO_2 .

Indeed, the results obtained under inert N_2 atmosphere first evidenced between 30°C and 90°C the characteristic orthorhombic lattice previously reported for uranium oxalate dihydrate². The structural changes observed thereafter corresponded to the dehydration of the sample toward oxalate monohydrate the anhydrous form at 250°C . Fluorite-type uranium oxide is then formed above 350°C : the evolution in the crystallinity of the samples was then evidenced during the calcination up to 1000°C through the progressive narrowing of XRD lines.

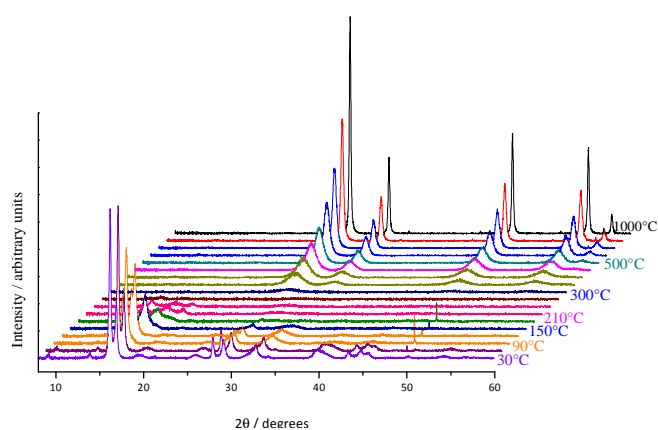
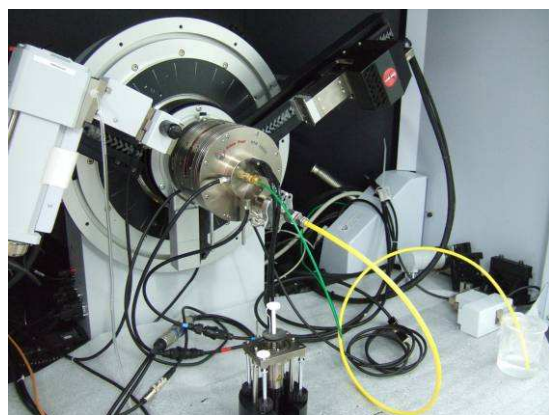


Fig.1: Picture of the HT-XRD experimental setup and variation of the XRD diagrams of uranium-based oxalate versus heating temperature.

Additional experiments were also performed in similar operating conditions by the means of TG/DT analyses and allowed to validate the results obtained by HT-XRD. The combination of such techniques then led us to propose a mechanism for the thermal decomposition of uranium-based oxalates.

Référence

- ¹ N. Hingant, N. Clavier, N. Dacheux, S. Hubert, N. Barré, R. Podor, L. Aranda. "Preparation of morphology controlled $\text{Th}_{1-x}\text{U}_x\text{O}_2$ sintered pellets from low-temperature precursors". Powder Technol. 208 (2011) 454-460.
- ² L. Duviol-Garela, N. Vigier, F. Abraham, S. Grandjean. "Adaptable coordination of U(IV) in the 2D-(4,4) uranium oxalate network: from 8 to 10 coordinations in the uranium (IV) oxalate hydrates". J. Solid State Chem. 181 (2008) 1899-1908.

What can we learn from combined SAXS and SANS measurements of the same sample?

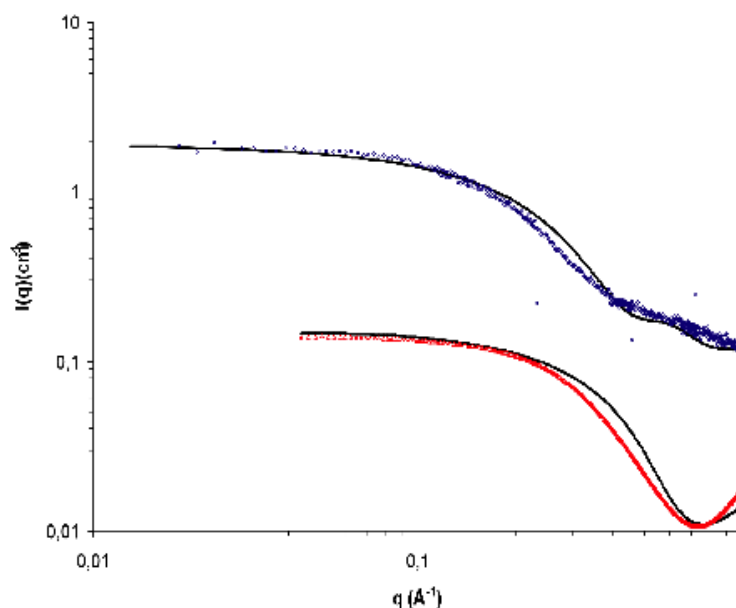
Thomas Zemb, Olivier Diat

An enormous increase in the micro-structural information is gained when one studies the same sample by SANS and SAXS on the *same* sample. Unique information of chemical systems or nanoreactors or heterogeneous solids can be obtained if intensities $I(q)$ are determined and used on absolute scale as well as over a large q -window, thus extending to the « Porod limit » asymptotic range.

Comparing SAXS and SANS peak positions (when present) shifts versus volume fraction variation allows unambiguous identification of structure factors separated from underlying form factors. Absolute scale refers to scattering cross-section while resolution relates to the q_{\max}/q_{\min} ratio. Taking into account "external" knowledge of molecular volumes in constrained fitting from explicit models gives better results on aggregation numbers as well as on interfacial thickness than considering only Patterson functions.

This general methodology applies to adsorption isotherms on surfactant films as well as equations of state quantifying colloidal interactions. Identification of the topological origin of swelling behaviour are made possible by using combined SAXS and SANS on the largest possible q -range. Best results using this general methodology up to now were obtained by considering data separated from background up to $q_{\max} = 0.6 \text{ \AA}^{-1} - 0.8 \text{ \AA}^{-1}$.

Fig.1: Scattered intensity in log-log and absolute scale in SANS (top) and SAXS (bottom) spectrum of the same reverse micelle, as obtained with a triple chain amphiphilic molecule, compared to models using simultaneous fitting with only one parameter, the area per molecule and the average aggregation number of the small w/o reverse micelles in thermodynamic equilibrium with monomers². Solvent is deuterated heptane. Co-solubilized water contained in the core is determined separately by titration.



If osmotic coefficients and partial molecular volumes, this method is the only method to obtain parameter free aggregation numbers, areas per head-group and curvature of a molecular aggregate, including those responsible for ion separation in hydro-metallurgy.

Référence

¹ Thomas Zemb and Olivier Diat – “Can we learn from combines SAXS and SANS measurements of the same sample?” *Journal of Physics IOP: Conference Series 247 (2010) 012002*

² Erlinger C et al. , 1998 Solvent Ext. Ion Exch. 16 707 and Y. Meridiano, PhD thesis 2010

8 - Microscopies

L'équipe est constituée de :

- 1 permanent CNRS responsable d'équipe (Dr. Renaud Podor),
- 2 ingénieurs d'études CNRS (Sandra Maynadié, Johann Ravaux),
- 1 ingénieur CEA (Henri-Pierre Brau)
- 1 apprenti ingénieur CNRS (J. Salacroup)



L'objectif scientifique du LM2E est de développer l'expérimentation *in situ* en utilisant la microscopie électronique à balayage environnementale, que ce soit dans des conditions d'humidité contrôlée ou en température. La majorité des actions scientifiques menées sous l'intitulé « microscopies » a été réalisée en collaboration interne à l'ICSM ou avec d'autres laboratoires. D'autres microscopies (classiques ou associées aux grands instruments) ont été mises en œuvre pour caractériser plus finement certains matériaux et apporter des informations complémentaires ou supplémentaires. A titre d'exemples, il convient de noter la microscopie électronique en transmission (classique ou cryomicroscopie), la microtomographie par rayons X (ESRF - Grenoble) ou la microscopie par rayons X mous (Bessy – Berlin).

Un premier ensemble de résultats porte sur la caractérisation de matériaux fortement hydratés, de la matière molle ou de suspensions d'objets nanométriques, matériaux difficilement observables par les techniques de microscopies classiques. Ces objets peuvent être trop petits dans au moins une de leurs dimensions (de l'ordre de quelques nanomètres à quelques centaines de nanomètres) pour être imagés par les microscopies optiques ou trop sensibles au vide pour être placés dans la chambre d'un microscope électronique conventionnel. Aussi, l'utilisation du microscope électronique à balayage environnemental – couplée à des dispositifs expérimentaux spécifiques – permet l'observation fine et sans altération de la morphologie de ces objets avec une résolution de quelques nanomètres (Figure 1). Au-delà de la « simple » observation morphologique, la stabilité dans la chambre du MEBE sous le faisceau de ces objets permet d'envisager d'observer leur comportement sous contrainte (augmentation de la température ou modification du taux d'hygrométrie) et de déterminer certaines de leurs propriétés mécaniques ou des grandeurs thermodynamiques.

Un second ensemble de résultats porte sur l'étude de la réactivité des matériaux en fonction de la température. Ces résultats sont principalement issus de collaborations externes à l'ICSM. Ces études mettent en œuvre les compétences du LM2E acquises dans la manipulation de la chambre haute température associée au MEBE. Elles ont porté sur la caractérisation du caractère auto-réparant de composites verre-intermétalliques (application joints de scellements pour les piles à combustible ; coll. UCCS – UMR 8181), l'élaboration « one-pot » de barrières de diffusion et thermiques pour des superalliages base-Ni (application aéronautiques ; coll. LaSIE FRE-CNRS 347), la cristallisation dans les liquides silicatés (applications optiques ; ICMCB - UPR 9048) ou la réactivité entre un calcinat et une fritte de verre (stockage des déchets radioactifs – Coll. CEA/DTCD). Ces résultats ont contribué à démontrer l'intérêt l'expérimentation *in situ* et de l'utilisation de la microscopie électronique à balayage à haute température (HT-MEBE) pour l'étude de problématiques très variées. Ces activités scientifiques contribuent à la reconnaissance de l'expertise acquise au LM2E dans ce domaine.

Le dernier ensemble de résultats est relatif à la problématique du frittage des céramiques. Les résultats obtenus contribuent directement à l'acquisition de savoir-faire et de connaissances dans le domaine de l'élaboration du combustible nucléaire. L'utilisation de la HT-MEBE permet l'observation directe de la consolidation des poudres par frittage, à l'échelle du grain, pour une gamme de température allant jusqu'à 1400°C. Les systèmes étudiés sont des céramiques base CeO_2 , ThO_2 et UO_2 . L'ensemble des données obtenues ont d'ores et déjà permis d'obtenir des résultats expérimentaux originaux relatifs à des données cinétiques locales telles que les vitesses de déplacements de joints de grains, la mobilité des pores, les mécanismes d'élimination de la porosité proche de la surface ou la coalescence des grains. Ces données expérimentales peuvent directement être utilisées pour améliorer les modèles du frittage des matériaux. Par ailleurs, en couplant ces données avec des résultats issus d'autres techniques, une méthodologie inédite de détermination des cartes de frittage des céramiques a été mise en place.

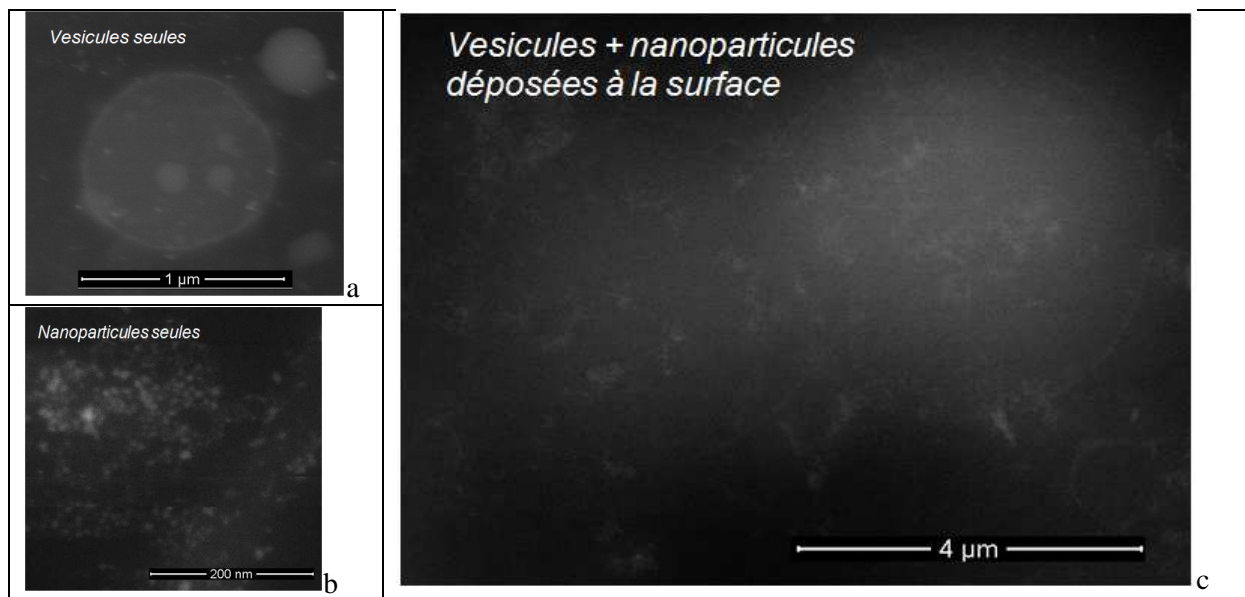


Figure 1. Characterization of the presence of nanoparticles at the vesicle surface using Wet-STEM. A) Direct observation of vesicles in water. b) Direct observation of nanoparticles alone in water and c) direct observation of vesicles with nanoparticles deposited at the surface in water. The presence of water has been checked by complete sample dehydration. (Coll. CEA Saclay / Lions – D. Carrière)

Autonomic 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)

A new process that enables glassy materials to self-repair from mechanical damage have been developed. Contrary to intrinsic self-healing, which involves overheating to enable crack healing by glass softening, this process is based on an extrinsic effect produced by vanadium boride (VB) particles dispersed within the glass matrix. Self-repair is obtained through the oxidation of VB particles, and thus without the need to increase the operating temperature. The VB healing agent is selected for its capacity to oxidize at a lower temperature than the softening point of the glass. Thermogravimetric analyses indeed show that VB oxidation is rapid and occurs below the glass transition temperature. Solid-state nuclear magnetic resonance spectroscopy indicates that VB is oxidized into V_2O_5 and B_2O_3 , which enable the local formation of glass. The autonomic self-healing effect is demonstrated by an in situ experiment visualized using an environmental scanning electron microscope. It is shown that a crack could be healed by the VB oxidation products.¹

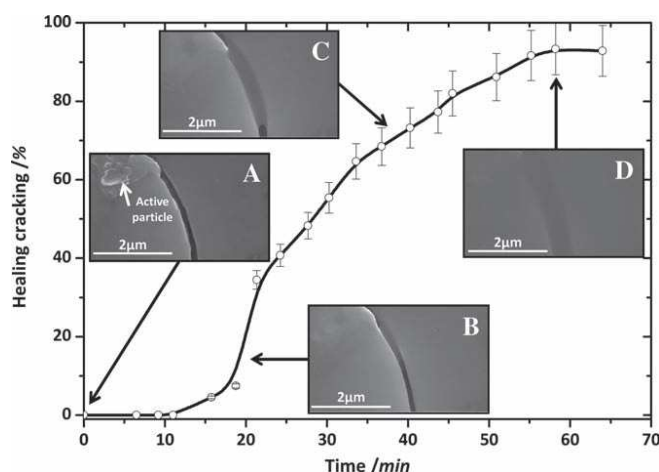


Fig.1: Healing ratio plotted as a function of heat-treatment duration and ESEM images of a glass + VB composite. A crack (0.5 μm wide, 15 μm long) was generated by Vickers indentation. An isothermal treatment at 700°C in air led to the oxidation of VB and formation of V_2O_5 and B_2O_3 , which flowed and filled the crack. ESEM images (magnification $\times 7,500$) were taken after: A) 0 min; B) 20 min; C) 40 min; and D) 60 min.....

In situ high-temperature healing of cracks in composites made of glass and vanadium boride (VB) particles was observed using an environmental scanning electron microscope equipped with a high-temperature chamber (HT-ESEM). HT-ESEM is an adequate tool for studying the self-healing property of these materials. The change in crack length as a function of redox atmospheric conditions is reported. No self-healing behaviour was observed under reducing conditions, while a complete and rapid healing of the cracks was measured under oxidizing conditions. HT-ESEM image analyses enabled the monitoring of the healing effect. The self-healing mechanism was identified as a consequence of the VB active particles oxidation and subsequent pouring of fluid oxides into the cracks. Several other active particles have also been tested². These innovative composites offer an interesting potential in the domain of solid oxide fuel cell sealants³.

New developments are under progress to extend the temperature domain to higher temperatures. Specific glassy materials are now available to be used up to 1150°C. Parallel, they have also been deposited on different substrates as multilayered thin films (from 0.5 to 5 μm).

¹ D. Coillot, F. O. Méar, R. Podor, L. Montagne, « **Autonomic Self-Repairing Glassy Materials** », Adv. Funct. Mater. 2010, 20, 4371–4374.

² D. Coillot, R. Podor, F.O. Méar, L. Montagne, “**Influence of the active particles on the self-healing efficiency in glassy matrix**”, Adv. Eng. Mater. 2011, 13(5) 426-435

³ D. Coillot, R. Podor, F.O. Méar, L. Montagne, “**Self healing process in glassy materials**”. Book chapter 269-290

Initial stage of shape-controlled oxides sintering

*Renaud Podor, Nicolas Clavier, Galy Ingrid N'Kou Bouala,
Johann Ravaux 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 Coble¹, and then suffer from a lack of experimental data. The purpose of this study was then to elaborate lanthanides model oxides with a controlled morphology then to study their behaviour through *in situ* observations by the means of HT-ESEM (fig. 1).

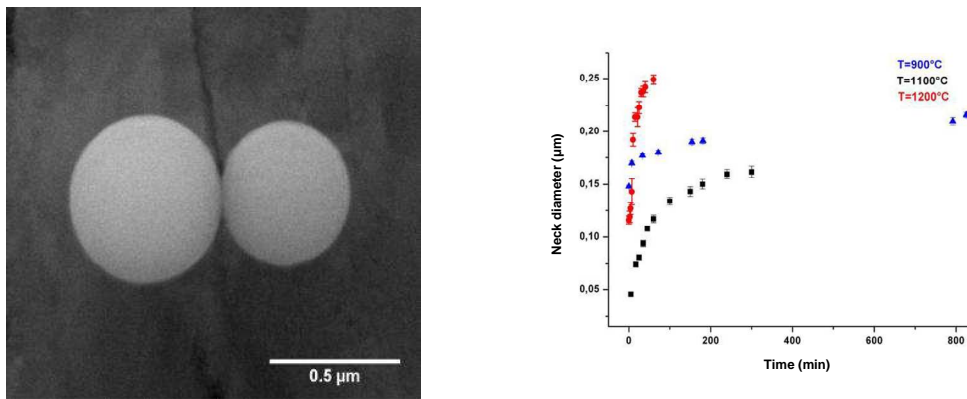


Fig.1: ESEM observation of CeO_2 microspheres and subsequent evolution of the neck diameter at different heating temperatures.

The synthesis of the spherical particles was first performed through two different methods, both involving the initial precipitation of hydroxocarbonates precursors². 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. The *in situ* observations of such patterns during heating in the HT-ESEM chamber ($T = 900\text{--}1200^\circ\text{C}$) then led for the first time to the kinetics associated to various phenomena such as neck growth or evolution of the dihedral angle. As it was stated by the theoretical models, an equilibrium state was reached with a rate strongly depending on the temperature considered. The main difference with the models reported in the literature arose from the polycrystallinity of the microspheres prepared since the two grains-approaches usually considered single crystals instead of aggregates of crystallites.

In these conditions, 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 first order kinetic law for various temperatures and led to the corresponding activation energy ($E_A \approx 160 \text{ kJ}\cdot\text{mol}^{-1}$ for CeO_2). Such value then differed significantly from that determined from a bulk material³, probably enlightening the important role played by the surface energy associated to the spherical shape.

Such data will now be implemented in numerical models in order to forecast the sintering kinetics of real compounds. Additional experiments will also be performed on materials with different shapes and chemical compositions, involving the incorporation of actinides.

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

² S. Wang, F. Gu, C. Li, H. Cao, **Shape-controlled synthesis of CeOHCO_3 and CeO_2 microstructures**, J. Cryst. Growth, 307 (2007) 386-394.

³ R. Podor, N. Clavier, J. Ravaux, L. Claparede, N. Dacheux, ***In situ* HT-ESEM observation of CeO_2 grain growth during sintering**, J. Amer. Ceram. Soc. 95 (2012) 3683-3690.

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

Torsten Sievers, 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. We herein present a study on the thermodynamics of cylindrical neodymium MOF particles containing an organic ligand. The cylindrical MOF particles are constituted by the aggregation of crystalline nanoparticles. Solvent (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 mesoparticle 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 H_{vap} , 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.

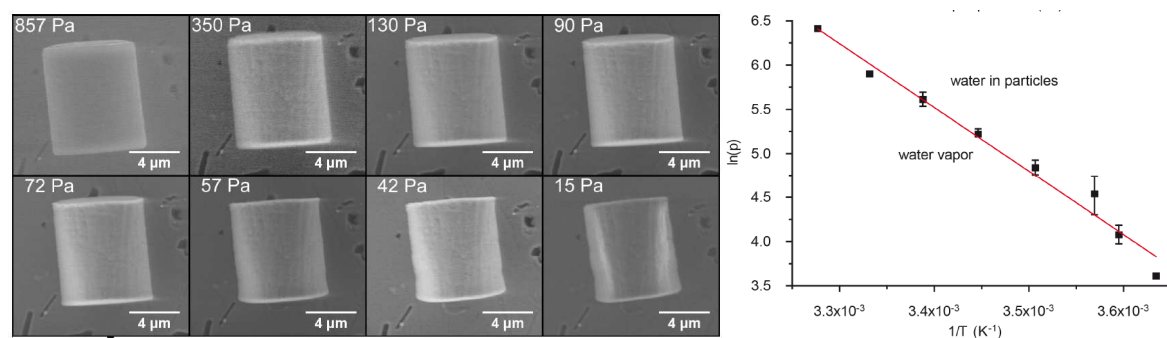


Figure 1: a) Size changes of Nd-DHBQ particles with vapor pressure. b) The logarithm of the water vapor pressure, at which the size starts to change, is plotted vs. reciprocal temperature. The measurements mark the coexistence curve between water in particles and water in vapor, which is fitted by the Clausius-Clapeyron equation.

9 - Mesoscopic Modelling and Theoretical Chemistry

L'équipe est constituée actuellement de :

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

Post-doctorant :

- Steven Van Damme (DEN, 2011-2012) : Modélisation des phases organique pour la séparation

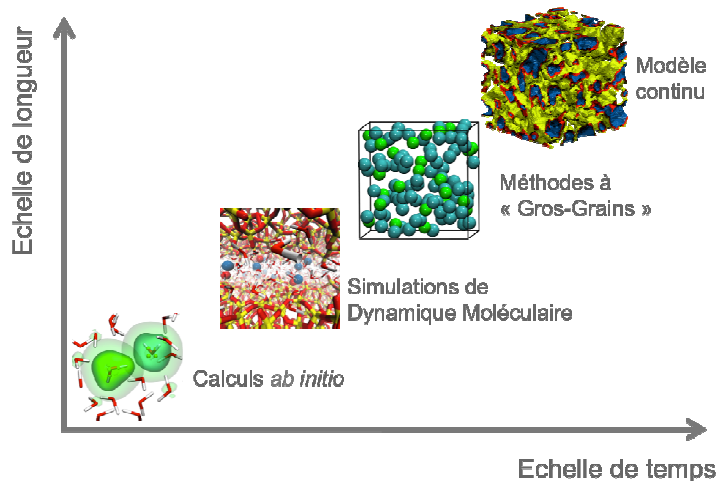
Doctorants :

- Arnaud Villard (bourse MESR, 10/2012) : Etude de la séparation par les oxydes poreux.
- Nghi Thanh Nguyen (CEA/DEN, 10/2012) : Modélisation moléculaire de l'extraction liquide-liquide.
- John Molina (MESR UPMC 2008-2011, coll. Avec laboratoire PECSA UPMC-Paris6) : Modélisation multi-échelle des ions en solution.
- Pierre-Marie Gassin (CEA, coll. LIIA et LCPA, 10/2010) : cinétique d'extraction



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).

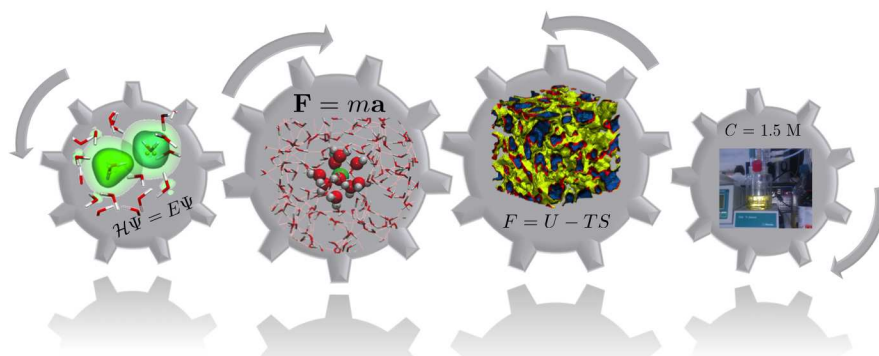
Les moyens mis en œuvre par l'équipe sont représentés sur les figures qui suivent. La description la plus fondamentale est celle de la mécanique quantique (calculs *ab initio*) capable de représenter l'acte élémentaire. Elle est en particulier étudiée pour déterminer la complexation moléculaire et elle peut aider également à améliorer les modèles classiques. Ceux-ci peuvent être étudiés par la dynamique moléculaire pour caractériser la structure des milieux, leur 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, équation intégrales, fonctionnelles de la densité (classique), couplage de modes, théorie des interfaces, etc.) qui sont implémentés pour décrire la physico-chimie des processus et faire le lien avec le génie chimique. L'originalité du laboratoire 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.



Modelling diffusion and hydration forces in confined silica

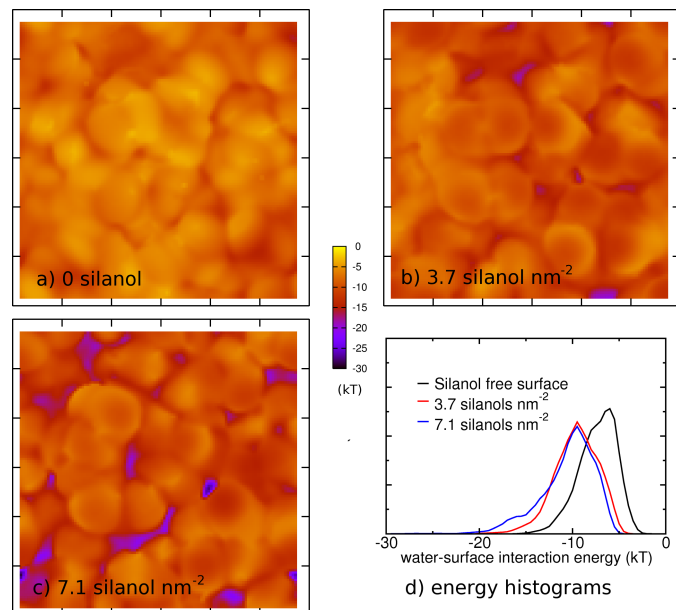
B. Siboulet, J.-F. Dufrêche P. Turq
B. Coasne (ICG & MIT)

Realistic models of amorphous silica surfaces with different silanol densities are built using Monte Carlo simulated annealing. These models are necessary for studying diffusion in confined silica and hydration forces between silica. We produce a variety of hydroxylated surfaces so as to vary hydrophilicity and quantify the variation in diffusion coefficients and repulsion. For diffusion, results exhibit a hydrophilic to hydrophobic transition as the amorphous surfaces vary from highly hydroxylated to purely siliceous. Hydration forces in confined systems are universal repulsive forces. We study both the impact of varying hydrophilicity and ionic specific effects on hydration forces.

Diffusion in silica pores: influence of hydrophilicity

Porous silicas are both of fundamental and practical interests as they exhibit a large specific surface and a porosity network that can be tuned precisely. Our realistic slit pore models of amorphous silicas allow connecting the surface chemistry of materials and their affinity for water. The thermodynamics and dynamics of water confined in the materials with various surface chemistries show a hydrophobic to hydrophilic transition as the silanol density increases (figure 1). We modeled diffusion coefficients, adsorption isotherms and Poiseuille flows. All results show a hydrophobic to hydrophilic transition. Increasing hydrophilicity reduces slip length. The flow between hydrophobic surfaces is increased by slip length. Our results showed the importance of a realistic surface model¹.

Figure 1. The interaction of a single water molecule with surface is mapped with the 3 silanol surface concentrations. As the silanol density increases, the interaction increases. On the above adsorption plots, the transition from hydrophobic to hydrophilic appears between 0 and 3.7 silanols nm^{-2} . Consistently, water surface interaction comes below -17 kT , which is the water vaporization energy, within the same silanol density range. These surface energy mapping differences are consistent with calculated diffusion coefficients variation



The dynamics of water at the vicinity of the surface² has also been examined. It is shown that irradiation strongly modifies the underlying transport properties.

1 Siboulet B., Coasne B., Dufrêche J.-F., and Turq, P., "Hydrophobic transition in porous amorphous silica", Journal of Physical Chemistry B, 115 (24), 7881-7886, 2011.

2 Siboulet B., Coasne B., Dufrêche J.-F., and Turq, P., "Water diffusion at irradiated glass surfaces", submitted to Molecular Physics.

Modelling hydration forces

In many cases, an extra non-DLVO repulsive contribution needs to be added to the description of surface force: the hydration forces. This very general phenomenon at very small distances can be as high as 10^4 bar and increases drastically upon distance reduction. Typically, reducing the intersurface distance by 0.3 nm increases the repulsion force by 10. Ions solvated between surfaces have a specific impact on hydration forces: Li^+ induces stronger forces between mica surfaces than Cs^+ .

We use atomistic models, such as Molecular Dynamics (MD) or Monte Carlo (MC) in order to investigate this phenomenon. We aim at giving a new explanation of the origin of hydration forces for such a system. Despite numerous theoretical analyses of hydration (including the case of silica surfaces), there is no, to our knowledge, attempt to quantitatively link hydration forces to structures existing between surfaces. The situation represented in Figure. 2 is quite complicated. A detailed evaluation of the effects is required because the total pressure does not indicate the origin of repulsion. Two pairs of facing hydration spheres are shown in Fig. 3. At this separation distance, second hydration spheres from each side come into contact. We can divide the system into clearly defined parts: surfaces, ions, first and second hydration spheres, and last, other water molecule. We can also divide the pressure into corresponding contributions. From that model, the pressure values, which only include ions and their hydration spheres, are calculated via a thermodynamic integration scheme, which allows a quantification of the various contributions.

Figure 2. Hydration forces occur at very low intersurface distances. We show a typical distance below which hydration repulsion occurs. This figure shows a complex situation, and the need to analyse it in terms of defined structure is clear. Oxygen atoms are in red, hydrogen in white, silica in yellow. Water surrounding ions in their first hydration shell are shown with balls, others with sticks.

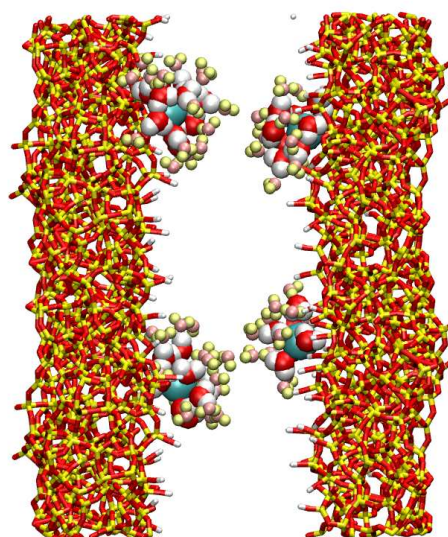
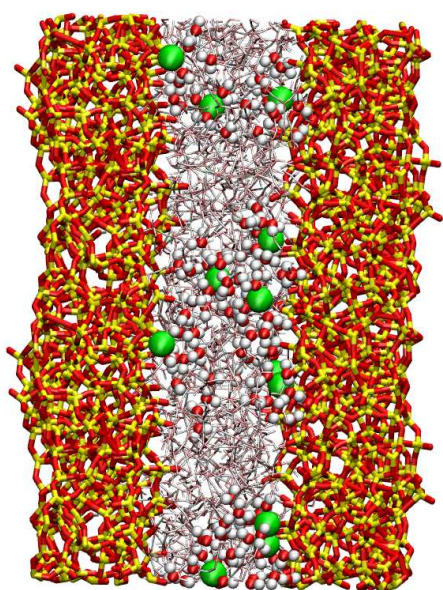


Figure 3. At very low separation distance, hydration spheres of counterions come into contact. Caesium atoms are in green. First caesium hydration spheres are in red and white. Second caesium hydration spheres are in pink and yellow. At this distance, second hydration spheres come into contact. The structuration shown in this image corresponds to a numeric division of pressure into separated contributions.

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)

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 to better understand 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. We use the hypernetted-chain integral equation to obtain solvent averaged effective potentials that accurately describe the ion-ion interactions in solution, without any explicit reference to the solvent. These effective potentials are then used in implicit-solvent Monte-Carlo simulations to study the thermodynamic and structural properties of the fluid.

This coarse-grained technique has been applied to study simple 1-1 electrolytes in solution, as well as more complicated 3-1 electrolytes such as lanthanoid chloride aqueous solutions. The agreement with the atomic and coarse-grained descriptions is found to be excellent^{1,2}. 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).

¹ Molina, J. J.; Duvail, M.; Guilbaud, Ph. and Dufrêche, J.-F.: “**Atomistic Description of Binary Lanthanoid Salt Solutions: A Coarse-Graining Approach.**” *J. Phys. Chem. B* (2011), 115(15), 4329 – 4340.

² Molina, J. J.; Dufrêche, J.-F.; Salanne, M.; Bernard, O.; Jardat, M. and Turq, P.: “**Models of electrolyte solutions from molecular descriptions: The example of NaCl**”. *Phys. Rev. E* (2009), 80, 065103 – 4.

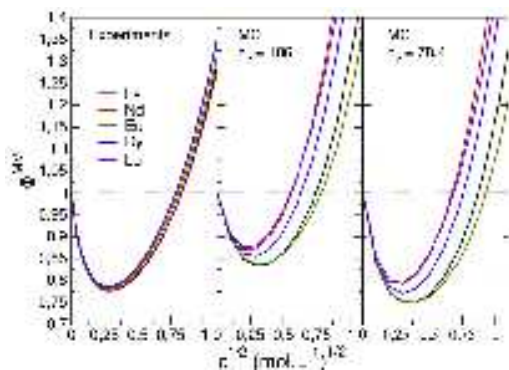


Figure 1: Osmotic coefficients in the McMillan-Mayer frame of referenced obtained from coarse-grained atomistic simulations of a series of lanthanoid chloride solutions as a function of the square root of the concentration.

The correction of the dielectric permittivity of the water model (from 106 to 78) improves the agreement.

While the use of implicit-solvent models in Monte-Carlo simulations reduced the complexity considerably, with respect to an atomistic description of both solvent and solute particles, it still requires a relatively costly numerical solution. When an explicit expression is needed for the properties of the fluid (thermodynamic, structural, or dynamic), these methods cannot be used. In these cases, one resorts to the use of some simple physical model for which the solution is known. For electrolyte solutions, this is the primitive model, which describes the system in terms of charged hard-spheres moving in a dielectric background. The MSA solution (and its improvements, *e.g.* BIMSA) of this model has been extensively used, but the parameters of the model have usually been fitted to reproduce some experimental data. We have shown that it is possible to use Liquid Perturbation theory to derive the best possible representation from just the effective ion-ion potentials. Thus, we are able to go from an explicit solvent atomistic description, to an implicit solvent description for which exact results are available. It is important to note that no fitting parameters are used: outputs at one level of our multi-scale modelling are used as inputs for the next level.

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 $\text{UO}_2(\text{NO}_3)^+$), we first focus on the uranyl chloride UO_2Cl^+ complex in aqueous solution (Fig. 2).

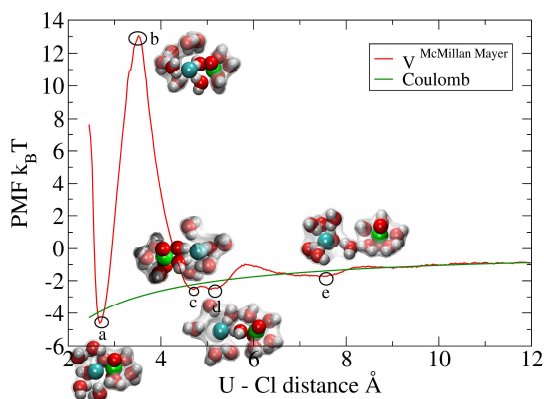


Figure 2: McMillan-Mayer potential profile of $\text{UO}_2^{2+}-\text{Cl}^-$ in water calculated using "umbrella-sampling" molecular dynamics simulations. Characteristic snapshots of hydrated UO_2Cl^+ complexes are also shown.

A multi-scale approach to ion transport in clays

M. Duvail, J.-F. Dufrêche

M. Jardat, P. Turq, B. Rotenberg, A. Obliger, M. Levesque, V. Marry, (PECSA/UPMC), E. Giffaut (ANDRA – Chatenay-Malabry)

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).

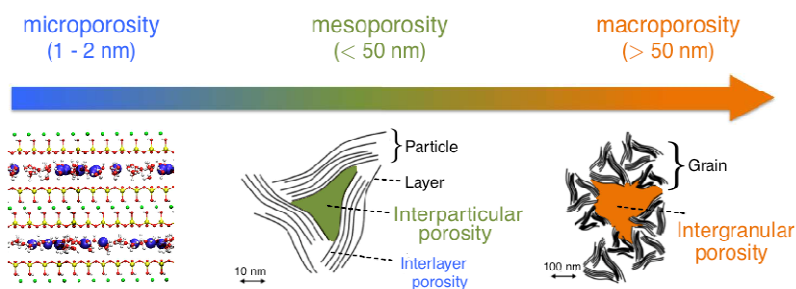


Figure 1: Schematic description of clays from the (lamellar) atomic scale to the macroscopic media with various porosities.

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 agreement¹ (Fig. 2).

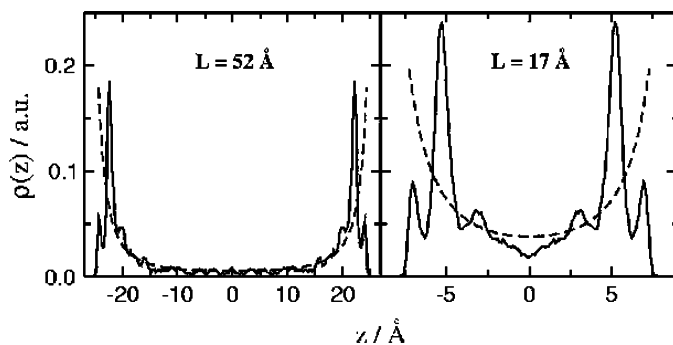


Figure 2: Cation distributions between two sheets obtained from atomistic (solid line) and mesoscopic (analytical Poisson-Boltzmann, dashed line) for two interlayer distances: 52 Å (left) and 17 Å (right), corresponding to $N = 100$ and 33 water molecules per cation, respectively.

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, Brownian Dynamics² (BD) and Lattice Boltzmann Electrokinetics³

¹ Rotenberg B.; Dufrêche J.-F.; Bagchi B.; Giffaut E.; Hansen J.-P. and Turq P.: “Modelling water and ion diffusion in clays: A multiscale approach.” *Compt. Rend. Chimie* (2007), 10(10-11), 1108 – 1116.

² Jardat, M; Hribar-Lee, B.; Dahirel, V. and Vlachy, V.: “Self-diffusion and activity coefficients of ions in charged disordered media.” *J. Chem. Phys.* (2012), 137, 114507 – 9.

³ Rotenberg, B.; Pagonabarraga, I. and Frenkel, D.: “Coarse-grained simulations of charge, current and flow in heterogeneous media.”, *Faraday Discuss.* (2010), 144, 223 – 243.

(LBE) simulations have been carried out. These two methods have been compared in order to check the validity of the Lattice Boltzmann Electrokinetics scheme, since in this latter ions and solvent are described in terms of densities of probability, whereas in Brownian Dynamics ions are explicitly described in a continuous solvent (Fig. 3).

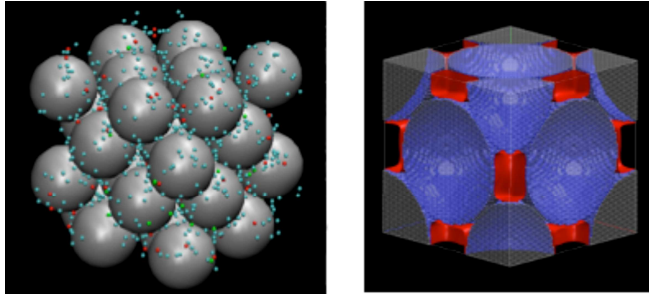


Figure 3: Typical simulation boxes: (left) Brownian Dynamics, and (right) Lattice Boltzmann Electrokinetics.

Obstacles negatively charged are represented in gray, counterions (cations) in blue, co-ions (anions) in red, and neutral tracers in green (only for Brownian dynamics).

Both methods allow the determination of the mesoscopic properties of solutes through charged porous media. These methods provide similar radial distributions functions (Fig. 4). However, when the porosity is small (compared to the size of ions) and for high ionic forces, the diffusion properties of ions and neutral tracers determined *via* the Lattice Boltzmann Electrokinetics simulations are over-estimated compared to the ones calculated from Brownian Dynamics. This may be due to the fact that the effects of excluded volume are neglected in the Lattice Boltzmann Electrokinetics scheme since ions are described in terms of density of probability, and not explicitly.

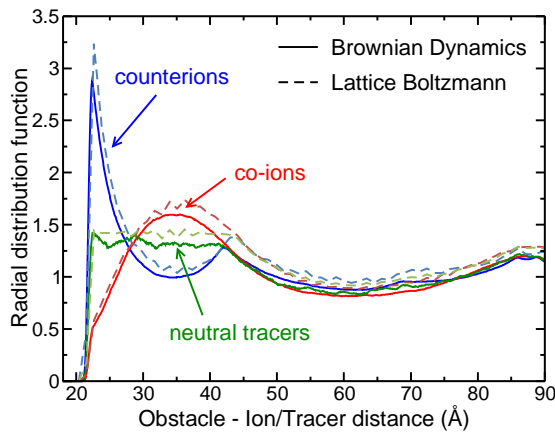


Figure 4: Obstacle – Counterions (blue), Obstacle – Co-ions (red), and Obstacle – Neutral tracers (green) radial distribution functions calculated from Brownian Dynamics simulation (solid line) and Lattice Boltzmann Electrokinetics (dashed line).

Another point that must be taken into account in the Lattice Boltzmann Electrokinetics simulations is the adsorption of counterions at the liquid – solid interface. Indeed, potentials are used in Brownian Dynamics to describe the interactions between the solid and the ions, which was not the case when simulating the transport of ions using the Lattice Boltzmann Electrokinetics method. The use of adsorption – desorption constants for ions at the solid – liquid interface⁴ (in LBE simulations) may improve the comparison between both methods (LBE and DB).

⁴ Levesque, M; Bénichou, O.; Voituriez, R. and Rotenberg, B.: “Taylor dispersion with adsorption and desorption.” *Phys. Rev. E* (2012), 86(3), 036316 – 5.

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 reverse micelles have been up to now considered as spherical aggregates, even with typical volume fractions of up to 30 percent. In the diluted regime, w/o reverse micelles, that selectively up-take some ions, have been approximated as spheres containing 4 to 10 molecules of extractants, few water molecules, and complexed ions. 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 Marčelja¹. The thermodynamics of the interface is here determined by the Helfrich free energy²

$$\mathcal{H} = \int_S dA [2\kappa(H - H_0)^2 + \kappa'K] \quad (1)$$

that depends on the mean (H), spontaneous (H_0) and Gaussian (K) curvatures, and also the bending (κ) and Gaussian (κ') elastic constants. While the spontaneous curvature (H_0) corresponds to the preferred curvature of the unconstrained surfactant film, the bending and Gaussian elastic constants 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. Therefore, this allows us to generate all possible microstructures thermalized of two immiscible liquids separated by a layer of surfactant, the surfactant having the desired rigidity thanks to the values of κ and κ' .

Thanks to this method, we have explored how the swelling of microemulsions in terms of the evolution of the peak position versus the (a)polar volume fraction allows for the identification of different families of microemulsions³. 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).

¹ Arleth L.; Marčelja S. and Zemb Th.: “Gaussian random fields with two level-cuts – Model for asymmetric microemulsions with nonzero spontaneous curvature?” J. Chem. Phys. (2001), 115(8), 3923 – 3936.

² Helfrich W.: “Elastic Properties of Lipid Bilayers – Theory and Possible Experiments.” Z. Naturforsch. C (1973), 28, 693 – 703.

³ Duvail M.; Dufrêche J.-F.; Arleth L. and Zemb Th.: “Mesoscopic modelling of frustration in microemulsions.” Phys. Chem. Chem. Phys. (2012 – Submitted).

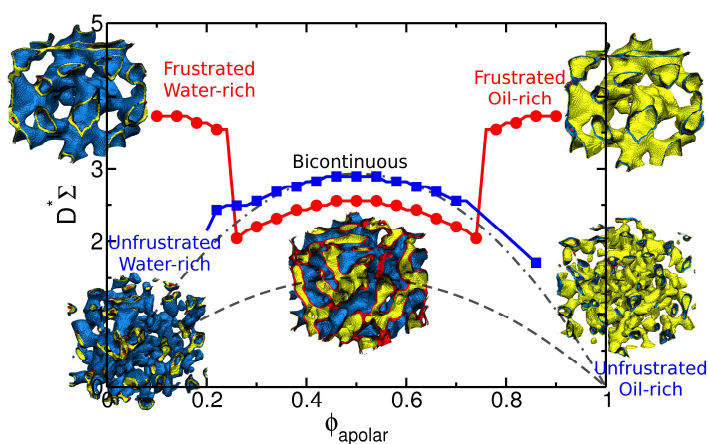


Figure 1: Scaled peak positions from flexible (blue) and rigid (red) microemulsions plotted as a function of the volume of apolar phase for a volume fraction of surfactant of 15%.

3D field projections of the direct space representation of microemulsions predicted by the Gaussian random field model are also shown. For the 3D structures water is blue, oil is yellow and the surfactant red.

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 simulations⁴ (Fig. 2).

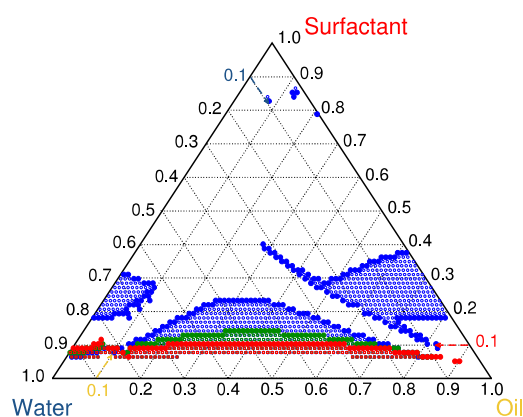


Figure 2: Ternary phase diagrams calculated for a fixed value of the bending elastic constant ($\kappa = 2 k_B T$) and different values of the Gaussian elastic constants: $\kappa' = 0$ (blue), 1 (green) and $2 k_B T$ (red).

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 now 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 terms⁵, 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.

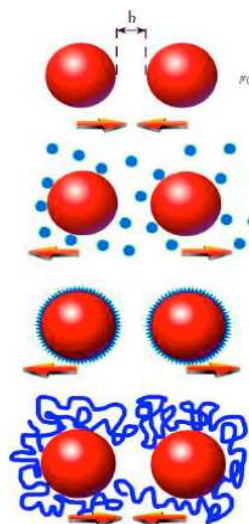
⁴ Duvail M.; Dufrêche J.-F.; Arleth L. and Zemb Th.: "Stiff and flexible water-poor microemulsions: disconnected and bicontinuous microstructures, their phase diagrams and scattering properties." Colloid and Interface Chemistry for Nanotechnology – Progress in Colloid and Interface Science Series, CRC Press (To Be Published June, 15th 2013).

⁵ Dufrêche J.-F. and Zemb Th.: "Effect of long-range interactions on ion equilibria in liquid-liquid extraction." J. Phys. Chem. Lett. (2011 – Submitted).

Long range interactions at work : universality of the hydration force

Thomas Zemb, V A Parsegian (U. Mass at Amherst) and Bruno Demé (ILL-Grenoble)

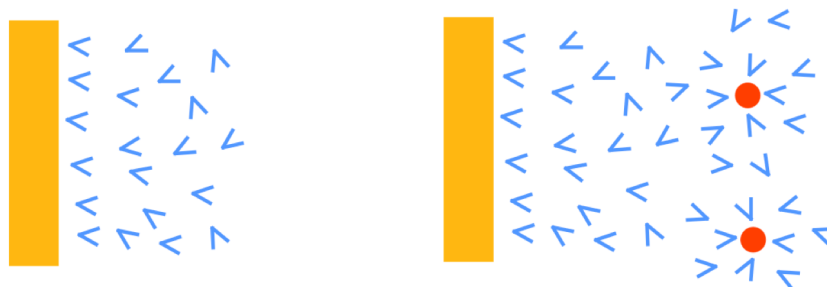
All known separation processes are driven by a combination of strong binding towards one or two first neighbours, either via metal-ligand complexation or electrostatics and long-range interaction extending beyond the first neighbour when ions and molecules are considered.



The so-called chemical Long Range Interactions “LRI” are known since over a century. Till 1950, it was thought that Dispersion forces and electrostatics, in closed from DLVO theory, would be the general frame-work for understanding all separation processes involving equilibria between complex fluids. DLVO theory relies on dispersion forces combined to electrostatics (the two top schemes on the figure left).

Since Osawa, papers in the fifties and the proposition of Marcelja and Radic in 1976 to explain stability of uncharged colloids such as lipids as evidenced by Parsegian, we know that this is not true. Nearly ten thousand of experiments reported required a significative participation of hydration forces or depletion force to explain the established phase diagram: fourteen reviews on different systems have been assembled in a special issue of Current Opinion in Colloids and interfaces¹.

The hydration force appears universally as an exponentially decaying interaction with a decay length of 0.2 nm². The contact pressure but not the decay length is linked to enthalpy of adsorption of the first water layer, as is verified in the case of neutral carbohydrates³. 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 to 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 force⁴.



¹ Thomas Zemb and V. Adrian Parsegian "Editorial overview: Hydration forces." Current Opinion in Colloid & Interface Science (2011). 16(6): 515-516.

² R H French, V. Adrian Parsegian, et al. (2010). "Long range interactions in nanoscale science." Reviews of Modern Physics 82(2): 1887-1944

³ Bruno Demé and Thomas Zemb (2011). "Hydration forces between bilayers in the presence of dissolved or surface-linked sugars." Current Opinion in Colloid & Interface Science 16(6): 584-591.

⁴ V Adrian Parsegian, and Thomas Zemb (2011). "Hydration forces: Observations, explanations, expectations, questions." Current Opinion in Colloid & Interface Science 16(6): 618-624.

Scientific program of the LEA “SONO” 2012 and 2013

Marcoule: Th. Zemb, O. Diat, P. Bauduin, C. Micheau, P.-M. Gassin, M. Jehannin
Potsdam: H. Möhwald, H. Riegler, L. Bertinetti, E. Skorb, A.-L. Heilig and V. Soulié

1- Precipitation by reactivity between coalescing sessile aqueous droplets

A new method for preparation of refractory advanced cermics involves precipitation of the metals initially present as a concentrated slurry solution in the form of a water/oil emulsion. The precipitating agent, such as oxalic acid or similar is also present as water in oil emulsion, or as polar solute in the oil main phase. The confinement is broken whenever coalescence occurs; But Arangoni and hydrodynamic flow induced by the reaction produce strong shearing. The growing particles of oxide are under dynamic suspension of droplets. This reduces largely the polydispersity and formation of micron-sized to millimeter-sized particles. It turns out that solubilizing, compacting as well as sintering is easier using ceramic precursors prepared in using this droplet-controlled synthesis allowed by this general route of mixing emulsions. Nucleation-growth and precipitation are controlled by the properties of the emulsified droplets involved.

The associated experimental work performed within the LEA in Potsdam and Marcoule will concern (from September 2012), the mechanisms that govern oxide precipitate mass, polydispersity and compacity. Then predictive modelling using mass balance and surface tensions –like in the generic “coffee-ring” problem, based on surface tensions of the droplets with air first, and in a second step the surface tension with the solvent phase, as well as cohesion energies of the solvent used, taking into account Laplace pressure effects.

First step will be description of the role of the droplet interface:

-is a supersaturation of the draining films formed when two droplets coalesce involved in the precipitation?

- is surface nucleation of oxide nanoparticle important?

- How do Marangoni effects come into play?

We will use coalescence of droplets of water or solution of fatty acids or inducing oxalic precipitation of Ce and Nd in the form of cations as model system for the experimental approach.

2- Metallic corrosion development during drying-wetting cycles by aerosols containing sodium chloride

In the presence of humid atmosphere, condensation/drying cycles are produced at the surface of metals. We consider the case of iron based metals, taken as standard widely used iron-based alloys with weak “inox” properties.

Wetting and drying cycles are ubiquitous in natural environment (near to the sea, morning dew), but also in industrial sites, when humidity/temperature cycles are present intrinsically. Atmosphere is the source of salt-spray, i.e. aerosols containing salts, sodium chloride being the most abundant in practice. Upon drying this salt spray is deposited on the surface, and the water evaporates. The residue is a particle with extremely high specific area, i.e. a strong reactivity versus redox reactions, enhanced by the presence of oxygen and the metallic surface acting as an electrode. Controlling variable is water activity, i.e. osmotic pressure, which is also dependent on the concentration of salt.

The cycles of water under- and over- saturated atmosphere produce successive formation of ionic solid precipitates in the form of micro-crystals and then re-wetting using these microcrystals as seeds for condensation of vapour along the atmosphere-crystal-metal contact line.

During these, drying and re-wetting daily, cycles, liquid nucleation sites are micro-crystals of sodium chloride, which are present in aerosols. The evolution of the shape and number density of microcrystals

deposited at the surface of metal will be determined and modelled. It is not known if an equilibrium distribution exists.

Moreover, during the phases where sodium chloride crystals dissolve in the presence of water coming from atmospheric condensation, electric currents are generated at the virtual electrode which is around the contact line between the sodium chloride crystal, the solution, the metal and the source of atmospheric oxygen.

The first objective of the experimental work will be to determine the shape and mass of crystals deposited at the end of the drying cycle, as well as the traces of oxidation leading to local dissolution on the metal left during the “wet” phase of the cycle. This involves interferometric microscopy as well as LISP-based scanning of species present, as well as modelling the transfer of chemical species involved, taking into account water activity gradients, i.e. relative humidity versus osmotic pressure. First half of the thesis will be located in Potsdam and second half in Saclay.

The model system considered first will be a droplet containing oxidizing chaotropic or cosmotropic salts under drying/rewetting cycles produced by temperature/humidity control system. Final objectives of the work proposed will be experimental characterization of the corrosion generated:

- multi-scale evolution of the micro-crystal dispersion generated at the surface
- Evaluate and model the evolution of the concentrations adsorbed at the interfaces present: solid salt/ brine/metal oxide.
- Electrochemical characterization of the interfaces involved, taking standard sodium chloride/ metal electrode as a reference

This work will be performed in Potsdam during the first 18 months, and then in Saclay (supervision: Philippe Prené and Th. Zemb).

3- Develop atomic force microscopy at an active oil-solvent interface

In liquid-liquid extraction, metal ions are transported from an aqueous phase into an oil phase by assistance of surfactant and extractant molecules. This process is currently applied on large scale in industrial application such as the treatment of waste from consumed nuclear fuel, and is considered for more general metal recycling processes associated with renewable energy production.

Although the process is thus widely used, the knowledge on the fundamentals of the transfer of metal ion from aqueous to organic phase is limited. Currently, there are efforts to promote understanding of these processes by investigating the colloidal properties of the system and identify individual interaction or contribution of molecules within this process. Within the framework of this project it is the aim to establish a complementary method to e.g. sum frequency generation that allows for determining surface properties of the buried liquid-liquid interface.

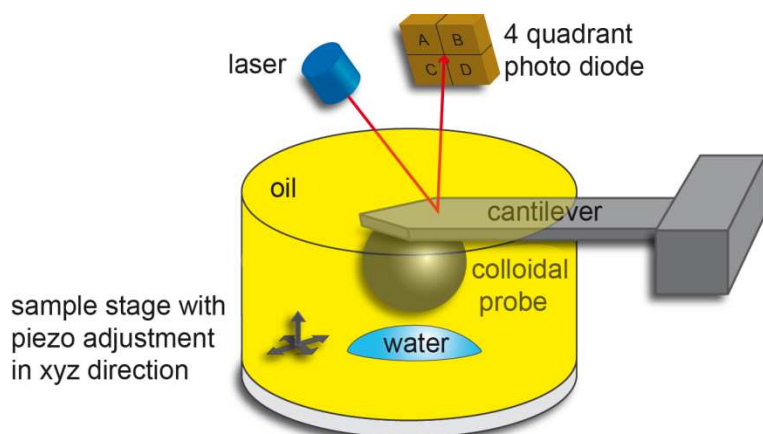


Figure 1: A schematic representation of the AFM setup for the investigation of the liquid-liquid interface is given. Atomic force microscopy (AFM) with a colloidal probe is used to probe the interface and thus the interfacial tension and the osmotic pressure in vicinity to the interface.

Our initial studies were mainly concerned with establishing an appropriate combination of equipment and materials that are suitable to fulfill the requirements implied by an investigation of the liquid-liquid interface. To investigate kinetic phenomena as well as the surface tension by AFM, it is necessary to utilize an AFM with a closed loop scanner allowing for a reduced scanner creep of less than 1 nm per minute. Due to small forces under investigation, it is also necessary to exclude electrostatic effects originating from a charge build up in the liquid cell, which is commonly made of an inert polymer such as Teflon®. With this experience and proof of feasibility of in-situ AFM experiments exploring the solvent-brine active interface we are now in a position to follow at AFM resolution the surface tension of the in situ oil-water interface.

After the feasibility experiments made by Torsten Sievers, we are now in the position to study the morphology and fluctuations of the oil-water interface at AFM resolution when recognized and unrecognized ion pairs are present. We mean here “recognized” ion as an ion which is selectively recognized by a “specific” extracting molecule. We will use first HDEHP, the most classical one also considered for decorporation after an accident dispersing toxic f-elements.

The influence of surfactants, extractants and their mixture should be studied. The data will be used to establish the required post data treatment finally used to begin with the study of metal-ion extraction kinetics by mimicking a real metal extraction experiment performed in hydrometallurgy, for example nickel/iron or cobalt/iron separation in the presence of silicates, in situ in the liquid cell of a modified AFM.

4- Identify possible chemical control of mechanoluminescence and surface defect formation during sonochemical stress

The physico-chemical behaviour of crystalline silicon under acoustic cavitation was investigated in water at low temperature (10 and 20°C). The spectroscopic investigations made in 2011-2012 in the frame of LEA (work of Matthieu Viot and coworkers) revealed that argon (bubbling continuously through the liquid phase during experiments) can be ultrasonically-excited via mechanoluminescence (i.e., the emission of light caused by a mechanical action on a solid). This phenomenon (highlighted for the first time on an extended solid surface using these conditions) results from an interaction between the acoustically generated bubbles and the Si surface. The concomitant physical and chemical transformations induced at the solid-liquid interface were investigated (SEM, AFM and XPS) to characterize the generated stress and defects in combination with roughness and wettability increases. Phase transformations of the Si lattice were finally highlighted very recently in Potsdam, via Raman spectroscopy and TEM. A first general paper about surface evolution, and chemical reactions present, as well as their signature via the specific spectrum of light emitted, has been submitted in March 2012.

These experiments evidenced the complex stress state induced by the acoustic cavitation on the Si crystal structure. It has also been shown that presence of anti-corrosion agents or “solubilizers” can enhance or quench by orders of magnitude the chemical reactions involved during Si sonication. In 2012, our aim is to screen a few of these agents quenching or enhancing /dissolution, by mass spectroscopy analyses of the species formed. We also would like to know if the amphiphilic character or the anti-radical nature of these additives is the dominant in their function. Parts of this work may lead to practical solutions, to be tested to current methods uses by a company to be started in Potsdam by the MPIKG.

Hydration force in wood as a multi-scale material: modelling of wood fibres swelling/deswelling by atmospheric humidity

Luca Bertinetti, Peter Fratzl, Thomas 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 (grey in fig. 1) embedded in a matrix of a much softer, less anisotropic, gel of hemicelluloses (orange in fig. 1), lignin and water. This matrix is hygroscopic and swells with increasing relative humidity providing a source of internal stress while the cellulose fibrils, winding with a spiral angle (the microfibril angle, MFA) around the central lumen, passively reorient following the stress applied to them. Depending on the MFA, wood fibres exhibit a wide range behaviour and mechanical properties, being able to act as stiff material to bear load, or shrink or expand in the longitudinal direction upon swelling, generating in this way either large tensile or compressive stresses or large strains.

We establish for the first time to our knowledge an equation of state of the wood matrix, using the same method than R. 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 crystals¹. 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 and in the presence of salts known for inducing specific (Hofmeister) effects.

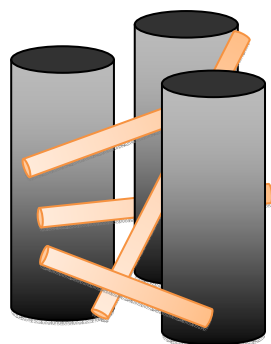
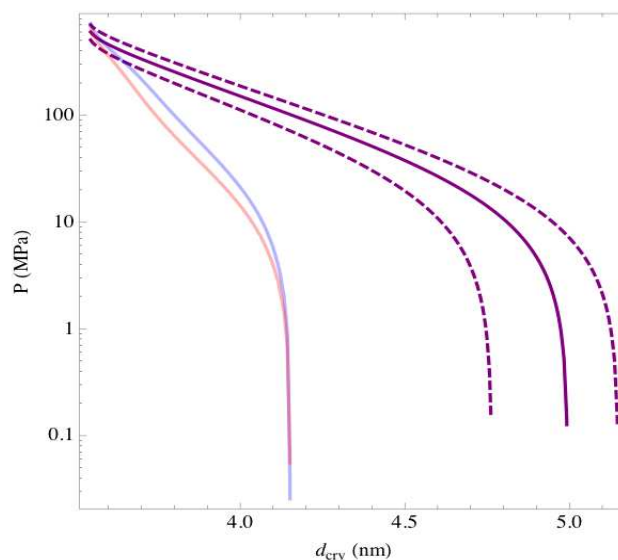


Figure : left: Structural model of cellulose fibers (gray) embedded in a matrix of hemicelluloses (orange) ; left: the osmotic pressure-distance equation of state expected at room temperature in the absence of entropic effect and lignin (right) in violet , compared to the swelling/deswelling hysteresis observed experimentally with wood with average lignin content.



¹ Luca Bertinetti, Peter Fratzl and Thomas Zemb: “Hydration force controlling the swelling of wood matrix” (in preparation).

Separation in flotation of a rare-earth based microparticles

Oliver Zech, Martin F Haase, Dmitry G Schukin, Thomas Zemb and Helmuth Möhwald

There is a still growing interest in the recovery of rare earth elements due to their manifold industrial and technological applications. Colloidal structures in a nonequilibrium state, i.e. systems that are kinetically hindered to minimize their surface energy, are nowadays implemented in manifold separation methods. In this context, foams stabilized by solid nano- or microparticles have attracted remarkable attention in recent years because of their unique foaming properties and the wide field of potential applications.

It is well-known that the combination of surfactant molecules with solid particles, which results in an adsorption at solid/liquid interfaces, can be used to either stabilize or destabilize foams. However, it is only recently that foams solely stabilized by nanoparticles have been reported. For example, Benrard Binks and coworkers have investigated aqueous foams stabilized by silica nanoparticles with different hydrophobicity depending on the degree of silanization of surface silanol groups. The case of foam stabilization with nanoparticles only, i.e. in the absence of surfactant is extremely delicate, but stable foams can be obtained in a narrow range of contact angles. A very important case in applications is the case of froth flotation when mineral particles of typically a few microns have to be separated.

We present here a simple and effective method for the enrichment of micrometer sized La_2O_3 particles via microparticle stabilized foams. By using the short chain amphiphile (1-hexyl)trimethylammonium bromide (C6TAB) foam that is generated by surface modified particles only can be generated. This technique allows a more selective and specific particle transport mechanism. The results are discussed in terms of surface charges, transport mechanisms and the effects of particle concentration, pH and amphiphile concentration have been studied and evaluated¹.

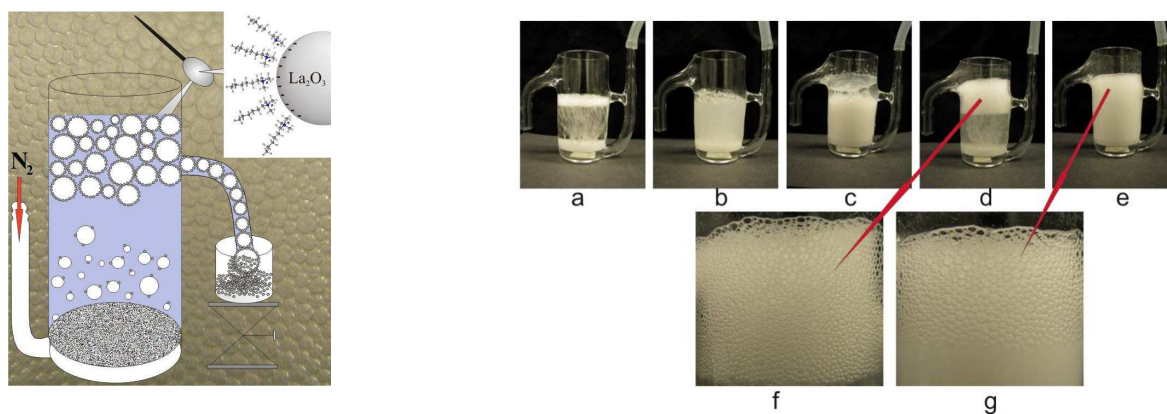


Fig. 1. Left: principle of flotation. Right : Typical foam obtained with different flux of bubbles used to optimize flotation

¹ Oliver Zech, Martin F. Haase, Dmitry G. Schukin, Thomas Zemb,* and Helmuth Moehwald « **Froth flotation via microparticle stabilized foams** » (in press,)

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**”,
- the annual practical separation chemistry summer-school .
- the “Thursday Lectures on separation chemistry”. 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 programm of the two last years is shown in Annex.

The **CSMP** masters programm was launched in 2005 together by UM2, ENSCM and INSTN. The training is followed this year by 12 students plus 14 students from ENSCM for the M1 level and 12 students plus 8 from ENSCM for the M2 level. The number of students increases from year to year, despite of a strong selection at M2 level. Teaching will progressively be done in English 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 summerschool of Marcoule in separation chemistry** started in 2005 in Montpellier and has been held every year since then. It was held in Marcoule jointly by ICSM, INSTN with the support of ACTINET program. Twenty hours of teaching chemistry at cutting edge level are complemented by practicals (3 half days) devoted to the application of the theoretical courses.

The 2012 edition of the school was extended to the four UMR of Montpellier, and based on theory and practice around long-range interactions (program can be found in Annex) with Bernard Meunier and Gérard Ferey as senior lecturers.



First summer school of the Labex “Chemisyst” – September, 14th 2012, lecturer: Pr. Gérard FEREY

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 Péresse 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 80% of the final size planned. The nine teams have started to take their recognized leading place on international level of discussion and advancement of separation chemistry, with a balance between structure and thermodynamics at Nano-scale. All nine 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 is allied to 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.

Progresses in separation chemistry and nuclear material will be made by strengthening links with national and international laboratories such as IPC-Moscow as well as Jülich-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.

Stéphane Pellet-Rostaing

Thomas Zemb



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

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Account / Revue

Complex fluids, divided solids and their interfaces: Open scientific questions addressed at the Institute of Separation Chemistry of Marcoule for a sustainable nuclear energy

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Annexe A : Les missions scientifiques de l'Institut de Chimie Séparative de Marcoule

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 II et l'Ecole Nationale Supérieure de Chimie de Montpellier II se groupent pour créer l'Institut de Chimie Séparative de Marcoule, autour des neuf équipes associées aux thématiques de recherche suivantes 1 :

Thématique 1- Chimie et chimie physique des actinides

Cette thématique comprend l'étude de propriétés chimiques et physico-chimiques des actinides présents en quantités pondérales dans des solides macroscopiques ou à l'état de matière ultra-divisée. La spécificité des orbitales 5f et 6d est dans leur participation à la formation des liaisons entre un élément actinide et son environnement n'est à ce jour correctement décrite que dans un nombre très limité de cas et en général résulte de l'étude de composés simples tels que des halogénures d'actinides.

La recherche à développer doit dépasser la liaison de complexation où l'ion hydraté est en interaction au niveau des nuages électroniques avec un « site complexant » identifié, modélisable au niveau quantique, et doit donc s'étendre aux actinides dans un solide cristallisé, dans un sel fondu ou dans un fluide complexe dans des agrégats ioniques géants et dans des états de valence non usuels. Ceci permettra d'ouvrir de nouveaux choix aussi bien pour les matrices de déchets que pour de nouveaux combustibles.

L'étude des composés dans lesquels la liaison présente un caractère covalent marqué permettra d'améliorer la compréhension du comportement physique des matériaux et des fluides complexes comprenant des actinides (y compris l'Uranium et le Thorium) et représente une étape clef pour l'établissement des relations structure-réactivité et des nouveaux procédés.

Thématique 2 - Chimie des ions aux interfaces actives

La chimie aux interfaces -ou chimie colloïdale des fluides complexes- est en pleine mutation. Une opportunité est donc ouverte par les progrès de la chimie des interfaces entre fluides, 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. Déclinées 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 que des systèmes méso et microporeux chauds qui pourront être étudiés expérimentalement dans Atalante. Comme indiqué ci-dessus, dans les domaines non nucléaires, les progrès dans cette direction cognitive sont porteurs de progrès en décontamination notamment.

Thématique 3 - Tri ionique par les systèmes moléculaires auto-assemblés

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

1 M. Leroy, M.-H. Hengé-Napoli et Th.Z. Comptes Rendus Chimie (2007), 10(10-11), 1042-1049.

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 est un système 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 « longues distance » telles que les forces de dispersion (effets de type Hofmeister alias chaotrope/cosmotrope, forces d'hydratation) sont alors abordées.

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). 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.

Thématique 4 - Sonochimie dans des fluides complexes

Lorsque des gaz sont dissous sous forme moléculaire dans un fluide, ils peuvent nucléer sous forme de nano- puis de micro-bulles sous l'influence d'ultrasons par un processus d'oscillation entretenue de bulles. En raison de la taille des bulles, de la valeur de la tension interfaciale dynamique, contrôlée par les espèces tensioactives mobiles à l'interface, les pressions peuvent être localement très importantes. Au moment de l'implosion de la bulle, des températures de plusieurs milliers de degrés -origine des phénomènes de sonoluminescence- peuvent être atteintes pendant des durées extrêmement courtes (microsecondes). Ce confinement inertiel dans des fluides peut favoriser des réactions chimiques très difficiles à obtenir autrement.

L'interface transitoire fluide-gaz comprimé joue le rôle de catalyseur. Il est important pour le cycle de combustible du futur ainsi que pour des procédés liés à la chimie du développement durable qu'une équipe pluridisciplinaire associant acousticiens-physiciens des surfaces, chimistes des amphiphiles et chimistes du solide, puisse maîtriser les réacteurs sonochimiques du point de vue des espèces dissoutes aussi bien dans le domaine nucléaire que pour la séparation/recyclage des métaux. La maîtrise de la réactivité sonochimique dans des fluides complexes (micellaires, multiphasés etc...) est un domaine nouveau, pouvant engendrer des procédés novateurs en chimie « furtive ». L'industrie nucléaire pourrait avoir besoin de cette chimie non productrice de déchets pour développer de nouvelles technologies de dissolution, de décontamination ou de traitement de déchets secondaires liés au cycle des nouveaux combustibles et matrices de conditionnement. Le domaine de la sonochimie dans les fluides complexes et aux interfaces solides hors domaine nucléaire est développée au niveau international au sein du laboratoire européen associé MPG-CNRS « Sono » répartie entre Postdam (technologie monobulle) et Marcoule (technologie multi-bulles).

Thématique 5 - Nanomatériaux pour l'énergie

Cette thématique porte principalement sur la recherche sur les nanomatériaux utilisés dans le domaine de l'énergie, matériaux d'usage intervenant dans les procédés de recyclage divers, comme le recyclage de la biomasse. Les thématiques de recherche couvrent les méthodes innovantes de synthèse de matériaux nanostructurés, de leur fonctionnalisation, leur caractérisation et l'étude de leur comportement.

Il s'agit de développer une classe de matériaux à structure hiérarchique, dans lesquels une fonctionnalité particulière forme des structures nanométriques, organisées dans un hybride micronique, pour une mise en forme dans un matériau d'usage. Par ce type de structure hiérarchique, on peut obtenir pour les propriétés physiques (fissuration) aussi bien que pour les propriétés chimiques (lixiviation), des « performances » hautement non linéaires par rapport à celles des matériaux de base. Une modélisation prédictive, qui utilise la connaissance structurale à différentes échelles, est nécessaire pour améliorer les performances de ces matériaux formulés.

Dans ce cadre général, accordera à l' ICSM une attention toute particulière à la maîtrise de l'élaboration qui pourra intégrer les avancées modernes de la chimie douce, notamment en impliquant des précurseurs à grande surface spécifique, pour obtenir des réactivités lentes et contrôlées, tout comme l'utilisation de conditions de synthèses non usuelles, comme l'eau sous-critique, les liquides ioniques inorganiques ou la présence de rayonnement. Une bonne maîtrise de la « nanochimie » autour des grains élémentaires devrait permettre de concevoir des matériaux de la chimie séparative et également des matériaux auto-cicatrisants après un stress (radiatifs ou chimiques). Ainsi l'objectif de cette recherche est de concevoir des matériaux pour lesquels leurs structures hiérarchiques et leurs fonctionnalisations induisent des réactions secondaires conduisant soit à un processus de séparation soit à une amélioration de leurs propriétés au cours du temps, notamment sous l'effet des rayonnements.

Thématique 6 - Surfaces de matériaux en renouvellement

La conception de nouveaux procédés et de nouveaux matériaux pouvant être mis en œuvre à des températures et des pressions significativement plus élevées permettra des avancées technologiques nécessaires aux réacteurs nucléaires du futur. Ces mêmes matériaux devront pouvoir résister à l'agressivité chimique, telle que celle des sels fondus (corrosion) et, bien sûr, à l'irradiation.

Les couches de surface des matériaux résultent souvent d'un renouvellement et sont très loin de l'équilibre thermodynamique. L'aspect théorique concerne la chimie de surface des solides hétérogènes et la cinétique des milieux extrêmes, afin de prévoir l'évolution de la surface d'un matériau lorsque les contraintes thermiques et radiolytiques deviennent comparables aux forces de cohésion, en tenant compte des défauts ainsi que des recristallisations possibles en surface. Une surface en évolution rapide est une surface de solide (soit surface externe pour les matrices, soit surface développée en interne dans le cas des combustibles) qui se forme à une échelle suffisamment rapide pour être peuplée d'atomes qui ont été amenés là soit par diffusion dans le fluide en contact, soit par échange de sites, échange dont la vitesse est déterminée par les courbures et les « épaisseurs » de l'interface. Dans le premier cas, la détermination de la spéciation des espèces libérées et re-fixées est nécessaire alors que, dans le deuxième cas, il faut déterminer la micro- et nano- structure de l'interface en tant que telle. L'équipe travaillant sur cette thématique devra maîtriser expérimentalement et théoriquement la caractérisation et la modélisation de ces deux approches, avec une priorité pour les matériaux comprenant de l'Uranium ou du Thorium. Le problème pratique posé est souvent d'obtenir une dissolution complète et ciblée. Les mécanismes de dissolution efficaces et non surdimensionnés ne peuvent être abordés que par des expériences suivies d'une modélisation prédictive multi-échelle combinant les trois expertises : thermodynamique hors d'équilibre, chimie interfaciale et nanomécanique.

Pour progresser au meilleur niveau mondial dans leur positionnement défini, les équipes thématiques 1 à 6 doivent pouvoir s'appuyer sur des « méthodologies » au sens large. Par exemple, dès qu'il s'agit d'interfaces de solides, il est crucial de pouvoir étudier les structures du nanomètre au micron aussi bien dans l'espace réel que dans l'espace réciproque sans perturber l'objet d'étude par la préparation de l'échantillon. De même, l'attention particulière portée non seulement à température et pression, mais aussi aux potentiels chimiques des solvants (soit la pression osmotique permet aux théoriciens la modélisation prédictive des comportements, a minima par distinction des situations d'équilibre et de blocage cinétique des fluides utilisés dans les procédés qu'il s'agit de comprendre.

Thématique 7 – Equipe transverse de microscopies électroniques et environnementale

Pour aller vers une microscopie « quantitative », il est nécessaire de maîtriser les paramètres physiques, comme la pression de vapeur d'eau dans des microscopies de tous modes. De même, les avancées récentes en microscopies à rayons X et électronique permettant de voir directement des agrégats supra-moléculaires en solution. Les matériaux auto-cicatrisants et les associations faibles de molécules ayant des propriétés de transport ionique particulières ne peuvent être compris que par observation dans l'espace direct de haute sensibilité même en cas de faible contraste. Une analyse chimique couplée à une imagerie pour des surfaces en évolution permet un suivi des mécanismes de réarrangement de surface, allant jusqu'à de réelles expériences de recuit sous faisceau. Au-delà de la collaboration étroite avec les équipes spécialisées, la pratique et l'interprétation physique et chimique des images obtenues est une discipline scientifique à part entière, conduisant des recherches propres au sein de la communauté des microscopistes et à des collaborations scientifiques directes avec des équipes externes à l'ICSM.

Thématique 8 – Equipe transverse de diffusion-diffraction

La caractérisation multi-échelle 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. Au-delà de la collaboration étroite avec les équipes spécialisées, la pratique et l'interprétation physique et chimique des spectres de diffusion-diffraction obtenues est une discipline scientifique à part entière, conduisant des recherches propres dans la communauté se reconnaissant 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 9 – Equipe transverse modélisation mésoscopique

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 au Pole Balard et de la dynamique moléculaire dans les Départements de R/D de Marcoule, ce laboratoire de chercheurs essentiellement théoriciens constitue une équipe transverse collaborant avec les autres équipes de l'ICSM. L'approche est multi-échelle : la matière est décrite par des modèles à des niveaux de descriptions variés, du plus microscopique (description atomique) jusqu'au niveau macroscopique (modèles 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.

Annexe B: Programm of Practical summer school in Separation Chemistry

B1 - *SIXTH* European Practical Summer school of separation and analytical chemistry of Marcoule - From July, 17th to July 22th 2011

Marcoule, bâtiment ICSM

Travaux Pratiques à ICSM et salle de TP AFM INSTN/SBTN/ICSM

Organismes associés et sponsors :

ICSM, INSTN, CETAMA, SBTN et cette année, DRCP et la Fédération 3105 Balard

Comité de programme :

Eric Ansoborlo, CETAMA

Pr André Ayrat, Professeur à l'ENSCM

Agnès Hagège, Chercheur CNRS

Pr Marie-Hélène Hengé, Unité d'enseignement INSTN Marcoule

Deborah Jones, Fédération Balard

Pr Christophe Poinssot, Adjoint au Chef de Département de RadioChimie et Procédés CEA/Marcoule

Pr Thomas Zemb, ICSM, Président du comité de programme 6^{ème} EPE

Comité d'organisation :

Mariette Ferrier, Unité Communication Marcoule

Eric Ansoborlo, CETAMA

André Ayrat, Professeur à l'ENSCM

Agnès Hagège, Chercheur SBTN

Marie-Hélène Hengé, Chef d'Unité d'enseignement INSTN Marcoule

Deborah Jones, Directrice de la Fédération FR3105 Balard du CNRS

Christophe Poinssot, Adjoint au Chef de Département de RadioChimie et Procédés CEA/Marcoule

Cédric Garnier, Responsable Communication Marcoule,

Christian Guérin, Professeur émérite à l'Université de Montpellier 2

Dominique Ferrebeuf, Responsable Unité Juridique Marcoule

Michael Lecomte, Assistant Scientifique Direction Marcoule

Thomas Zemb, ICSM

Practical summer school of separation and analytical chemistry

Practicals 1 : Synthesis of functional surface materials and analytical/Structural characterisation (A. Ayrat and NN.)

Practicals 2 : Advanced modelling of ion speciation: programme utilisé au DPC – enseignant DOC ou CHESS (*Ecole des Mines de Paris*)

PROGRAMM

Sunday, July 17:

Two introductory conferences:

Olivier Boutin DEN-Marcoule:

Separation by ion exchange resins : new opportunities in non conventional conditions

Christian Guizard CREE St Gobain-Cavaillon :
Processing of powders for advanced reactive ceramics

Monday, July 18

Introduction to the school: Bernard Meunier and/or Valerie Cabuil (1*15 mn)

Th. Zemb

Non covalent interactions and separation 45 mn

M. Barboiu (IEM-Montpellier)

Long range interactions as basis for systems with an emerging function, 45 mn

Scientist from DEN/DPC Marcoule (D. You or P. Reiller)

Prediction of speciation by using thermodynamic data base : status and limitations
Introduction to the practicals session 45 mn

B. Coasne (ICG-Montpellier)

Modelling ions competing for separation near interfaces and in pores : statics and dynamics
45 mn

Afternoon:

Practicals I, from 2 pm -6 pm

In parallel :

I - Nanoporous material from separation under drying (2 groups of 8) : A. Ayril and NN from ICSM or SBTN.

II - Computer simulation of speciation using CHESS and equivalent (1 group of 8) : DPC and E. Ansoborlo

6pm- 8pm : Evening lectures :

NN.

Free slot

M. Antonio (ANL- Chicago)

Aqueous and Organic experimental speciation -if available

Tuesday, July 19th morning

9 am – 10.30 am :

S. Kalmykov (IPC Moscow) (2 * 45 mn): *Redox processes in radionucleide propagation and biological implications*

I- Talks from participants participating to practicals session I -: 12 talks
Talks by participants 10 minutes each, including discussion
Subject of oral presentation by each participant:
Origin, goal of research and points of interest in the summer school (4-5 slides).

Chairman: B. Meunier and/or V. Cabuil

Afternoon :

Practicals II (from 2 pm - 5.30 pm)

In parallel :

I - Nanoporous material from separation under drying (2 groups of 8) : A. Ayril and NN from ICSM or SBTN.

II - Computer simulation of speciation using CHESS and equivalent (1 group of 8) : D. You or P. Reiller and E. Ansoborlo

II- Talks from participants participating to practicals session I -: 12 talks
Talks by participants 10 minutes each, including discussion
Subject of oral presentation by each participant:
Origin, goal of research and points of interest in the summer school 4-5 slides.

Chairman: B. Meunier and/or V. Cabuil

Wednesday, July 20, special participants day

9 am - 10.30 am :

D. Horinek (Regensburg) - 2* 45 mins

Ions separated by interfaces and adsorbed to proteins or surfactants: driving forces

10.30 am – 12 am :

M-Ch. Charbonnel (DRCP) – 45 mins

Thermodynamic aspects of complexation in organic and aqueous environment

André Ayrat (ENSCM) (1* 45 min)

Lessons from practicals : preparation of porous nanostructured material from and for separation

2 pm - 6 pm :

VISIT OF VISIATOME AND PHENIX

6.30 pm : Evening Historic lecture:

possibility :

NN. (to be confirmed)

The history of actinides and the Curie saga

Thursday, July 21

Morning:

Mihai Barboiu (Balard) (1*45 mn)

Adaptive systems: underlying mechanisms and examples

Nicolas Guiseppone (1*45 mn)

Towards self-fabricating materials

Jean Francois Dufrière (1*45 mn)

Mesoscopic modelisation of ions near highly curved interfaces : prediction of observable quantities

A. Geisst, Karlsruhe (1* 45 min)

Kinetic limitations for separation processes

Afternoon:

H. Möhwald (Potsdam) (2* 45 min)

Chemistry at Interfaces triggered by mechanical excitation

C. Sorel (DRCP-Marcoule) (1* 45 min)

Chemical engineering based on process modelling at macroscopic scale

S. Le Caer (IRAMIS-Saclay) (1* 45 min)

Radiolytic mechanisms of homogeneous solutions

6.30 pm : Evening conference:

G. Wipff, Uni Strasbourg

Equilibrium and dynamics at liquid-liquid interfaces by molecular dynamics

Friday, July 22 morning

Ludmila B Boinovitch: (2 * 45 mn)

Beyond DLVO : from superhydrophilic to superhydrophic swelling to dewetting

Hans Riegler : (2 * 45 mn) :

Hydrodynamics, nucleation and growth linked to reactions between aqueous solutions in initially separated droplets

End of school, Friday, July 22nd, 12.30 am



Ecole d'été 2011

B2 – First Practical summer school of the Labex “Chemisyst”

Présentation de l’Ecole d’été CheMISyst 2012-12-04

La première Ecole Pratique d’été CheMISyst aura lieu du mercredi 12 au samedi 16 septembre 2012 et du lundi 5 au mardi 6 novembre.

Format : 4 jours en résidentiel dans l'arrière pays et 2 jours à Montpellier.

L'objectif de cette Ecole est de proposer aux chercheurs, en particulier aux plus jeunes, des équipes du Pôle Chimie Balard et des trois laboratoires extérieurs associés dans le projet, une mise à jour et des approfondissements pratiques et théoriques sur des sujets relevant des thématiques du LabEx.

Les participants et l’ensemble des intervenants partiront à St Martin de Londres (Hérault) pour la partie théorique (du mercredi 12 au samedi 15 septembre).

Des leçons théoriques traitant des liaisons, des interactions, des phases, de la diffusion, de l’électro-transport, les illustrations via des travaux de recherches et, en fin de séjour, la restitution des travaux pratiques.

Des conférences internationales sont programmées.

La partie expérimentale (TP) se déroulera ensuite sur deux jours (lundi 5 et mardi 6 novembre) à l’Institut Européen des Membranes de Montpellier.

Sujet : mise en évidence de l’effet des charges et de la complexation sur la nanofiltration de solutions aqueuses de sels de lanthanides. Les expériences réalisées seront de trois types : les filtrations membranaires, les analyses chimiques des solutions et les simulations numériques de la séparation à l’aide d’un logiciel dédié.

Le Comité d'organisation de l'école d'été CheMISyst est composé des personnalités suivantes :

- Responsable du comité d’organisation : Thomas Zemb
- Responsable scientifique et pédagogique : André Ayrat
- Mihai Barboui, IEMM
- Hervé Cottet, UM2
- Caroline Genre, ICSM
- Corine Gerardin, ENSCM
- Jose-Marie Lopez-Cuesta, EMA
- Julian Oberdisse, UM2
- Stéphane Pellet-Rostaing, ICSM

**1^{ERE} ECOLE PRATIQUE D'ETE LABEX CHEMISYST – POLE CHIMIE BALARD
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, **André Ayrat et Thomas Zemb**
9h30 – 10h00 Présentation de l'École (**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, André Vioux, Mihai Barbiou (recherche), André Ayrat (formation), , Gilles Subra 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 FERREY**

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**.

Annexe C : Thursday lectures in Separation Chemistry

C1 – Season 2010 – 2012



Année universitaire 2011/2012



Année scolaire 2011/2012

COURS M3/D1 DE CHIMIE SEPARATIVE

à Marcoule, le jeudi à 13h15

Auditoire : tous thésards présents sur Marcoule intéressés (ED 459 ou autre). Le suivi des cours (feuille de présence) donne lieu à crédits EDs.

Tutelle : ED 459 de Chimie de Montpellier, reconnu par les autres ED pour crédits.

Les cours, destinés aux thésards de première, deuxième ou troisième année, sont ouverts aussi aux chercheurs permanents et non-permanents intéressés.

Suivi « A la carte » : La série de cours est conçue pour être compréhensible aussi indépendamment les uns des autres, à l'unité, sur un problème particulier, ouvert aux chercheurs et post-docs DRCP, DTEC et DTCD.

Jeudi 27 octobre 2011 **Session préparatoire à la théorie.**
Cours-TD (salle de cours Becquerel)

09h30-11h15 « Introduction à la Modélisation Moléculaire » (Benoit Coasne, CNRS)
11h30-12h15 « Interactions Colloïdales I » (Luc Belloni, CEA/DSM)
14h00-15h00 « Interactions Colloïdales II » (Luc Belloni, CEA/DSM)
15h15-16h15 **Séminaire invité: « Carborane chemistry for redox potentials to reactivity versus grafting » (Francesc Teixidor, Barcelone)**

Jeudi 3 novembre 2011 **Cours inaugural** (salle de cours Becquerel)

13h15-14h00 « Aspects supra-moléculaires et colloïdaux de la distribution d'ions entre phases de fluides complexes » (Thomas Zemb)
14h15-15h15 **Séminaire inaugural 2011-2012 :**
« Théorie de la séparation isotopique par complexation : au-delà de Bigeleisen ? » (Stéphane Pellet-Rostaing)

Jeudi 10 novembre 2011 **Cours n° 2** (salle de cours Becquerel)

13h15-14h00 « Principes de la diffusion de rayonnement, application aux liquides » (Olivier Diat)
14h15-15h00 « Cours à définir » (Jean-François Dufrêche)
15h15-16h15 **Séminaire : « Quelques exemples de caractérisation de solides poreux par diffusion par SAXS » (Julien Cambedouzou)**

Jeudi 17 novembre 2011 - pas de cours (célébration 100^{ème} promotion de l'ENSCM)

Jeudi 24 novembre 2011 Cours n° 3 (salle de cours à préciser)

- 13h15-14h00 « Les bases de la chimie des actinides en solution : redox, complexation et polarisabilités » (*Daniel Meyer*)
- 14h15-15h00 « Densité d'énergie : ordres de grandeur en électrochimie, en chimie séparative, en chimie douce sous-critique et en pyrochimie » (*Jean-François Dufrêche*)

Jeudi 1^{er} décembre 2011 Cours n° 4 (salle de cours Becquerel)

- 13h15-14h00 « La force d'hydratation (I) : de la pratiques aux diverses théories, cas des molécules d'intérêt biologique » (*Thomas Zemb*).
- 14h15-15h00 « Effets spécifiques des ions en solution » (*Jean-François Dufrêche*)

Jeudi 8 décembre 2011 Cours n° 5 (salle de cours Becquerel)

- 13h15-14h00 « La force d'hydratation (II) : de la stabilité sans charge électrique dans le monde minéral » (*Thomas Zemb*)
- 14h15-15h00 « Modélisation des verres » (*Jean-Marc Delaye*)

Jeudi 15 décembre 2011 Cours n° 6 (salle de cours Becquerel)

- 13h15-14h00 « Cours théorie (III) » (*Jean-François Dufrêche*)

Jeudi 5 janvier 2012 Cours n° 7 (salle de cours à préciser)

- 13h15-14h00 « De l'ion, colloïde et microparticules : propriétés communes de Debye à Onsager » (*Thomas Zemb*)
- 14h15-15h00 « Thermodynamique du « coarse graining » : probabilités de paires et d'agrégats d'ions en solution : du sol au gel ? » (*Jean-François Dufrêche*)
- 15h15-16h15 Séminaire : « Des matériaux via la liaison CN » (*Daniel Meyer*)**

Jeudi 12 janvier 2012 - pas de cours (Comité de pilotage ICSM)**Jeudi 19 janvier 2012 Cours n° 8 (salle de cours Becquerel)**

- 13h15-14h45 « Modélisation atomistique de sels fondus » (*Christian Simon*)

Judi 26 janvier 2012 **Cours n° 9** (*salle de cours Becquerel*)

- 13h15-14h45 « Quels apports de la radiochimie et de la chimie à l'échelle des indicateurs à la chimie séparative et à la chimie de l'environnement ? Dangers de la dilution. » (*Nicolas Dacheux*)
15h00-16h00 **Séminaire : « Corrosion » (Damien Féron)**

Judi 2 février 2012 **Cours n° 10** (*salle de cours Becquerel*)

- 13h15-14h00 « Cours théorie IV » (*Jean-François Dufrière*)
 14h15-15h00 « Electrophorèse capillaire et spéciation des métaux : un point particulier sur l'uranium » (*Agnès Hagège*)

Judi 9 février 2012 **Cours n° 11** (*salle de cours Becquerel*)

- 13h15-14h00 « Etat de l'art du traitement de la contamination des radionucléides » (*Eric Ansoberlo*)
14h10-15h10 **Séminaire : « Conception et modélisation des colonnes d'extraction liquide-liquide » (Jean Duhamet)**
15h20-16h20 **Séminaire : « Vieillissement dans les verres » (Stéphane Gin)**

Judi 1^{er} mars 2012 - pas de cours (Séminaire Balard à Montpellier)**Judi 8 mars 2012** **Leçon terminale 2011-2012** (*Auditorium ICSM*)

- 13h15-14h00 « Verrouiller la synergie extractive : des bolaformes aux geminis » (*Stéphane Pellet-Rostaing*)
14h10-15h10 **« Les quatre axes de la chimie verte, une synthèse des douze principes : quelques exemples » (Stéphane Sarrade)**
15h20-16h20 **« Membranes céramiques, multifonctionnalité et protection de l'environnement » (André Ayrat)**

Judi 15 mars 2012 **Cours supplémentaire (sous réserve)**

- 13h15-14h00 « Cours théorie IV » (*Jean-François Dufrière*)
 14h15-15h00 « Transport dans les milieux chargés » (*Pierre Turq*)



Année universitaire 2012/2013



COURS M3/D1 DE CHIMIE SEPARATIVE

à Marcoule, le jeudi à 13h15

Andisoir : tous thésards présents sur Marcoule intéressés (ED 459 ou autre). Le suivi des cours (feuille de présence) donne lieu à crédits EDs.

Tuile : ED 459 de Chimie de Montpellier, reconnu par les autres ED pour crédits.

Les cours, destinés aux thésards de première, deuxième ou troisième année, sont ouverts aussi aux chercheurs permanents et non-permanents intéressés.

Suivi « à la carte » : La série de cours est conçue pour être compréhensible aussi indépendamment les uns des autres, à l'avis, sur un problème particulier, ouvert aux chercheurs et post-docs DRCP, DTWC et DTCD.

Jeudi 8 novembre 2012 Leçon inaugurale (salle de cours Boquerel)

Introduction Marcoule /Dir et responsable master des cours M3/D1

13h15-14h00 « Les interactions faibles et les procédés de la chimie verte : une introduction » (Thomas Zemb)

14h15-15h00 Séminaire invité inaugural 2012-2013 :
Utilisation de l'énergie dégradée : quelques perspectives (Henri Safa)

Jeudi 15 novembre 2012 Cours n° 1 (salle de cours Boquerel)

13h15-14h00 « L'interaction d'hydratation : interface rigide et interface flexible »
(Thomas Zemb)

14h15-15h00 « Nucleation-croissance de cristaux moléculaires »
(Mathieu Roskotz, Lille) -----

Jeudi 22 novembre 2012 Cours n° 2 (salle de cours Boquerel)

13h15-14h00 « L'interaction électrostatique : au-delà du 1-1 ponctuel »
(Jean-François Dufrêche)

14h15-15h00 « Vases attractifs et vases répulsifs » (Pierre Lavie, UPMC)

Jeudi 29 novembre 2012 Cours n° 3 (salle de cours à préciser)

13h15-14h00 « Les bases de la chimie moléculaire des actinides » (Daniel Meyer)

14h15-15h00 « Durée entre chocs et mouvement brownien :
L'approche Schmoluchowski » (Jean-François Dufrêche)

Jedi 6 decembre 2012 Pas de cours : journée scientifique Balard à Montpellier

Jedi 13 decembre 2012 Cours n° 4 (salle de cours Bequerel)

13h15-14h00 « Les cristaux liquides lyotropes : du cristal à l'amorphe » (Thomas Zemb)
 14h15-15h00 Séminaire invité Chemisyst :
 « Chimie du bois » (Di Renzo ou Françoise Quignard)

Jedi 10 janvier 2013 Cours n° 5 (salle de cours Bequerel)

13h15-14h00 « Effets spécifiques des ions en solution » (Jean-François Dupêche)
 14h15-15h00 Séminaire invité à définir

Jedi 17 janvier 2013 Cours n° 6 (salle de cours Bequerel)

13h15-14h00 « De l'ion, collatde et microparticules : propriétés communes de Debye à Onsager » (Thomas Zemb)
 14h15-15h00 « Depletion : mécanismes et expression simple, d'Osawa à BMSA » (Jean-François Dupêche)

Jedi 24 janvier 2013 Cours n° 7 (salle de cours à préciser)

13h15-14h00 « Fluctuation-dissipation des molécules aux interfaces » (Jean-François Dupêche)
 14h15-15h00 « Fluctuations aux interfaces : diffusion linéaire et non linéaire de la lumière » (Olivier Diot)

Jedi 31 janvier 2013 Cours n° 8 (salle de cours Bequerel)

13h15-14h00 « Chimie à l'ée de traces (I) » (Nicolas Dacheux)
 14h15-15h00 « Extraction par précipitation : la méthode des Curie » (Nicolas Dacheux)

Jedi 7 février 2013 Cours n° 9 (salle de cours Bequerel)

13h15-14h00 « La diffusion aux petits angles : utilisation des contrastes, et des asymptotes et invariants » (Olivier Diot)
 14h15-15h00 « La diffusion aux petits angles : modélisation quand le solvant n'est plus continu : petits agrégats » (Philippe Guillebaud)

- Jeudi 14 février 2013** **Cours n° 10** (*salle de cours Becquerel*)
- 13h15-14h45 « Physi-sorption et chimi-sorption pour la séparation/décontamination »
(*Agnès Grandjean*)
- 15h00-16h00 **Séminaire invité :**
« Fluctuations électroniques et bruit de grenaille »
(*Nicolas Clément, IEMN, CNRS, Lille*)
-
- Jeudi 21 février 2013** **Cours n° 11** (*salle de cours Becquerel*)
- 13h15-14h00 « Nombre de contacts et cinétique : de Schmoluchowski à DLA/RLA »
(*Jean-François Dupêche*)
- 14h15-15h00 **Séminaire invité :** « Vieillessement dans les verres » (*Etienne Vernaz*)
-
- Jeudi 28 février 2013** **Cours n° 12** (*salle de cours Becquerel*)
- 13h15-14h00 « Effets biologiques des rayonnements ionisants : ordres de grandeur, mécanismes et extrapolations non linéaires »
(*Marta-Hélène Mengé*)
- 14h15-15h00 **Séminaire invité :** « La pertraction : avantages, inconvénients »
(*Jean Duhamel*)
-
- Jeudi 7 mars 2013** **Cours n° 13** (*salle de cours Becquerel*)
- 13h15-14h00 « Molécules et Supramolécules » (*Daniel Meyer*)
- 14h15-15h15 **Séminaire invité-cours :** « Principes de la cristallisation contrôlée d'organiques » (*François Puel*)
-
- Jeudi 14 mars 2013** - pas de cours (Séminaire Balard à Montpellier)
- Jeudi 21 mars 2013** **Cours n° 14** (*salle de cours Becquerel*)
- 13h15-14h00 « Etat de l'art du traitement de la contamination des radionucléides »
(*Eric Anoborio*)
-
- Jeudi 28 mars 2013** **Leçon terminale 2011-2012** (*Auditorium ICSM*)
- 13h15-14h00 « Les clefs chimiques de la séparation isotopique par complexation en solution » (*Stéphane Pallat-Rostang*)
- 14h15-15h15 **Séminaire invité :** « sujet à définir »
Conclusion DENDir

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 connectivities, 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 to foresee a fundamental transition from supramolecular design constitutional selection approaches,^{7,9} which might give great potential in various applications. Already now, these conceptions 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 range 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 approaches 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 analytical "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 predict 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 knowledge-based processes at colloidal scale related to recycling matter in a context 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 which 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 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 organelles in the cell.

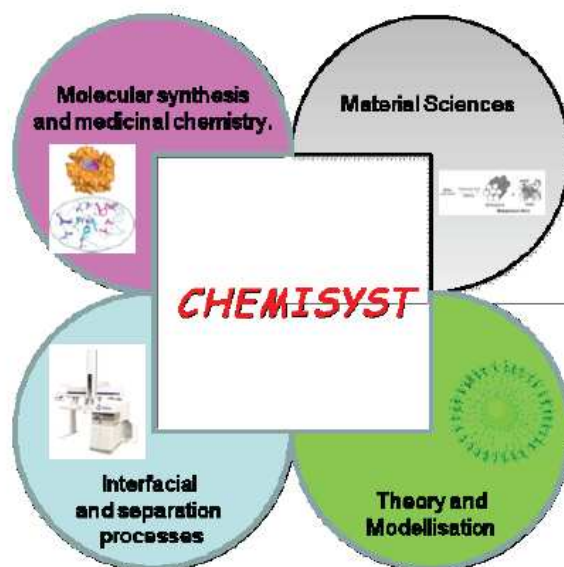
Besides the necessary identification of the molecular species involved in the functioning of living organisms which was the main stream of research in the past decades in life sciences, the design and synthesis of molecular machines inspired by the functioning of cells ensure the emergence of dynamical 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 also 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 characteriz 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, cuurrently 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 interaction, indeed modelling at the mesoscale between the scale where quantum mechanics is used and the macroscopic scale when frosted and reactive 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 specialized 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.

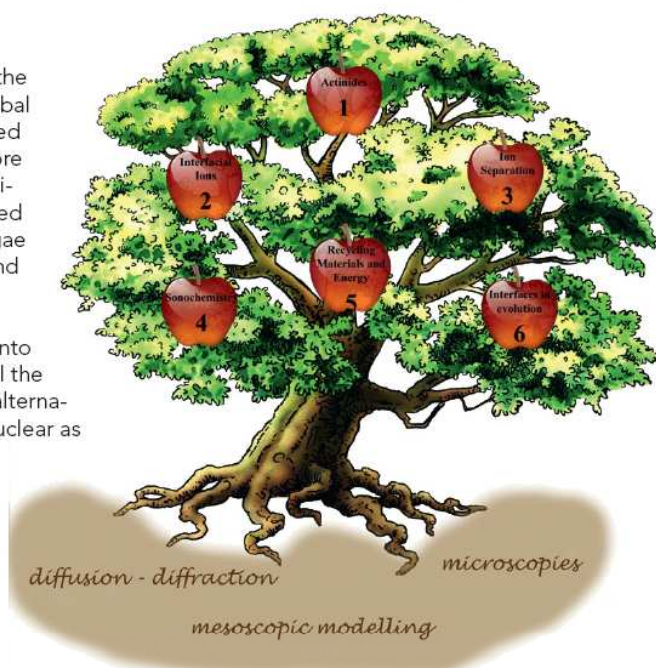
References:

- 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

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 agriculture 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 nine teams of ICSM by the four associated research Institutions: Commissariat à l'Énergie atomique et aux Énergies alternatives, Centre National de la Recherche Scientifique, University of Montpellier 2 and Ecole Nationale Supérieure de Chimie de Montpellier:

- Chemistry and physical chemistry of actinides (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 (Agnès GRANDJEAN)
- Evolution of surfaces of materials (Pr Nicolas DACHEUX)
- Electronic and environmental microscopies (Renaud PODOR)
- Diffusion-diffraction (Olivier DIAT)
- Mesoscopic modelisation and theoretical chemistry (Pr Jean-François DUFRECHE).

Séparative de Marcoule



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, synthesize, 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 has been directed by Thomas Zemb since then. The laboratories were functional in January 2010. ICSM is located 100km NE of Montpellier and 25 km North of Avignon along the Rhone. One team of ICSM is associated to Max Planck Institute for colloids and interfaces in Potsdam. A strong collaboration on actinides exists with ITU Karlsruhe. 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 forty permanent and forty non-permanent scientists, plus staff devoted to administration and infrastructure. Open national and international PhD, post-doc and tenure-track positions are available on web-site: www.icsm.fr.



Appendix A

Liste des publications ICSM 2009-2012 triées par Année, Facteur d'Impact décroissant, 1^{er} Auteur

Remarques

Le facteur d'impact indiqué est le dernier paru à savoir celui issu du Journal of Citation Report 2011 (Thomson-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

2012

1. Kunz W, Zemb T, Harrar A. Using ionic liquids to formulate microemulsions: Current state of affairs. *Current Opinion in Colloid & Interface Science* 2012;17(4):205-211. - [IF=8,010]
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Appendix B

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Parc instrumental opérationnel



ICP-AES

μ Raman spectrometry



BAG



Drop tensiometer



Acoustosizer



SEM FEI quanta 200 ESEM FEG

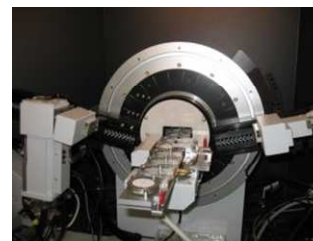


Surface adsorption
ASAP 2020

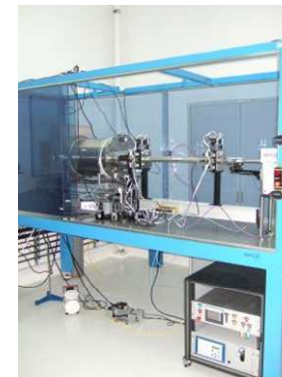
Small angle
X-ray scattering



DTA / GTA
Sestys Evolution 18



Diffraction
(Brucker D8 ADVANCE)



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'ingénieur.

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 pilotage 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 montpellierain. 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.

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The scientific council of ICSM on December 4th, 2012

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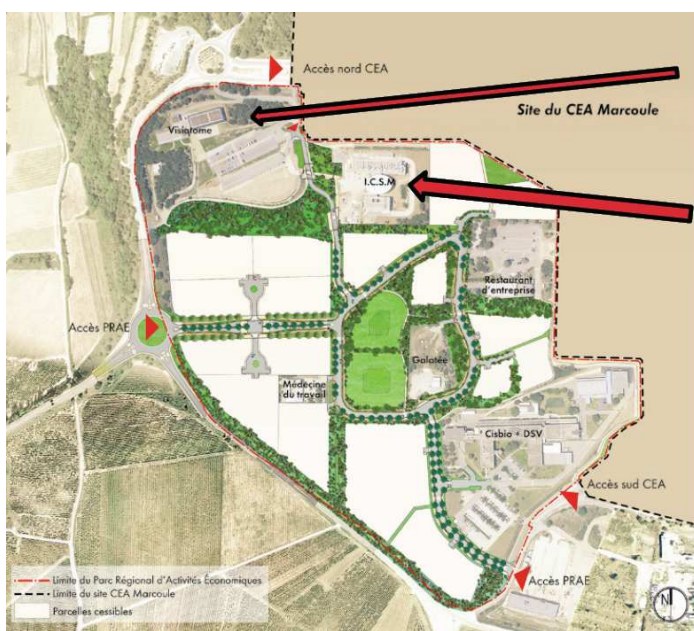
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Le bâtiment de l'ICSM dans la partie du Parc Marcel Boiteux.



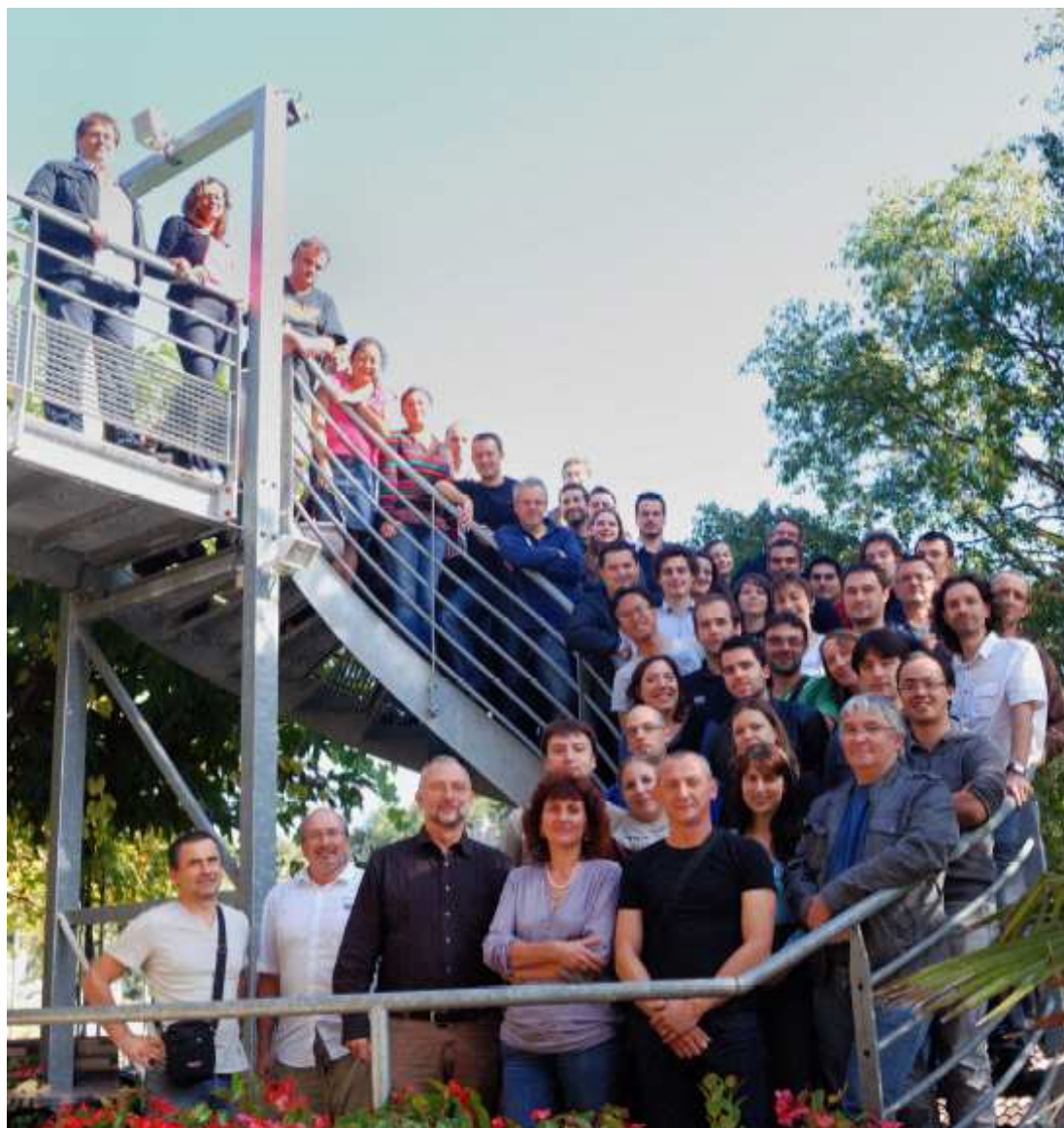
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Institut de Chimie Séparative de Marcoule



Les chercheurs, techniciens et agents administratifs de l'ICSM (photographie prise en octobre 2012)

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