Abstract

In 2010, the French government created an agency for the coordination of research on energy (ANCRE - www.allianceenergie.fr). Nuclear energy lies of course within the scope of this agency. During its first year of activity, the agency fostered a reflection on the scientific and technical challenges tied to the development of nuclear energy. This work resulted in the production of several roadmaps, one for each major domain of nuclear R&D. A special effort was put on chemistry for nuclear energy, because this domain has been identified as a key for sustainable, clean and competitive nuclear systems. The elaboration of this roadmap was the occasion to gather the national community of nuclear chemists for a general reflection on the stakes in chemistry for nuclear energy, the main scientific problems, the tools available to solve them, and to agree on the R&D actions that should be taken in priority.

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Keywords: Nuclear chemistry, national programme, roadmap

1. Introduction

In 2010, the French government created an agency for the coordination of research on energy (ANCRE - www.allianceenergie.fr). Nuclear energy lies of course within the scope of this agency. During its first year of activity, the agency fostered a reflection on the scientific and technical challenges tied to the development of nuclear energy. This work resulted in the production of several roadmaps, one for each major domain of nuclear
R&D. A special effort was put on chemistry for nuclear energy, because this domain has been identified as a key for sustainable, clean and competitive nuclear systems. The elaboration of this roadmap was the occasion to gather the national community of nuclear chemists for a general reflection on the stakes in chemistry for nuclear energy, the main scientific problems, the tools available to solve them, and to agree on the R&D actions that should be taken in priority. An executive summary of this roadmap will be presented here.

2. Domains of application of chemistry for nuclear energy, and the associated scientific disciplines

Chemistry is everywhere in nuclear industry. It is present in each step of the fuel cycle, as well as in the reactors operation, safety and radiation protection. Up to 18 domains of application were identified. The scientific themes that are called for in these domains are the listed in Table 1.

As chemistry calls more and more for modeling and simulation, this transverse thematic should be added to the list.

3. The stakes

In this section, the stakes (in bold italics) entailed by the applications of chemistry for nuclear energy are reviewed and transcribed into scientific problems (in italics).

3.1. Front-end of the fuel cycle

- Uranium mining and extraction (the main stakes are to master the ore dissolution, and the extraction of uranium from this ore, especially from low-grade ore and unconventional resources such as phosphates rocks).
- Conversion (renew and optimize the fluorination-defluorination facilities).
- Enrichment (watch on chemical enrichment processes).
- Fuel fabrication (control the ceramic microstructure to ensure a good behavior of the fuel in-reactor).

The scientific problems associated with those stakes are the following:

- Chemistry of f elements, complexation: the scientific challenge is to understand the selectivity of complexation, and the influence of solvent and diluent).
- Dynamics at liquid-liquid interfaces (understand the structure of the interface and the transfers through the interface).
- Heterogeneous kinetics applied to conversion (determine the rates for fluo/defluorination reactions; model flame reactors and rotating furnaces).
- Partitioning with membranes (develop selective membranes).
- Powder metallurgy (model sintering, understand the role of sintering additives, master pyrophoricity, especially for carbide fuel).
- Thermodynamics (determine the stability of actinide compounds).

3.2. Reactor operation and safety

- Coolant chemistry and in-vessel contamination transfer (minimize the contamination of the primary circuit and the deposition of the corrosion products of the secondary circuit).
- Corrosion (avoid the obstruction of the vapor generators, extend the reactor lifetime).
Table 1: Domains of application of chemistry for nuclear energy, and the associated scientific disciplines

<table>
<thead>
<tr>
<th>Domain</th>
<th>Coordination chemistry of F-elements</th>
<th>Radiolysis</th>
<th>Dynamics at gas-solid and liquid-solid interfaces (dissolution-precipitation, germination-growth, heterogeneous kinetics)</th>
<th>Dynamics at liquid-liquid interfaces</th>
<th>Speciation</th>
<th>Analytical chemistry</th>
<th>Pyrometallurgy</th>
<th>Powder metallurgy</th>
<th>Thermodynamics and thermokinetics</th>
<th>Chemistry-transport</th>
<th>Isotopic chemistry</th>
<th>Corrosion</th>
<th>(Bio)geochemistry of radionuclides</th>
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The scientific problems associated with those stakes are the following:

- **Understand and control chemical conditions in water at high temperature.** This implies in particular to be able to measure pH and eH in-vessel; The aggressive conditions require the use of dedicated instruments.
- **Master phenomena of disso-precipitation of oxides and hydroxides.**
- **Understand the mechanisms of the corrosion of steels and of Zr alloys under stress and radiolytic conditions.** Model these corrosion phenomena, and find guides for the development of corrosion-resistant materials. This entails a good knowledge of
  - Thermodynamics
  - Chemistry-transport of ions through boundary and passive layers
  - Understand the role of crystalline defects and impurities in corrosion.

3.3. Back-end of the fuel cycle

The main stake of the back-end of the fuel cycle is to **provide the community with the technological elements enabling a closed fuel cycle policy. This includes**

- **Dissolution of spent fuel** *(know how to dissolve, master nitric corrosion)*
- **Partitioning** (enhanced, grouped) *(retrieve efficiently the actinides, either jointly or separately, with minimum proliferation risks, and minimum effluent production)*.

The scientific problems associated with those stakes are the following:

- **Coordination chemistry of f-elements, complexation and selectivity** (master speciation, understand the selectivity of the complexation, and the influence of solvent and diluent).
- **Disso-precipitation** *(apply coupled chemistry-hydrodynamics modelling to the spent fuel dissolution and to oxalic precipitation) ; the same models could also apply to co-conversion, and the formation of mixed oxides solid solutions.*
- **Nitric corrosion.**
- **Dynamics at interfaces liquid-liquid interfaces** (understand the structure of the interface and the transfer phenomena through the interfaces).
- **Radiolysis** (understand free radical chemistry, with fast dynamics).
- **Pyrochemistry** (master liquid-liquid extraction and electrochemical processes in molten salts).
- **Thermodynamics, thermokinetics** (foresee the stability of species and the reaction rates from first principles).

3.4. Waste management

- **Conditioning** *(elaborate glass, concrete, bitumen, and special conditioning for volatile RN confinement).*
- **Storage and disposal** *(master the long-term behaviour of confinement matrixes, foresee RN migration).*
- **Cleanup and dismantling** *(decontaminate infrastructures and natural media).*

The scientific problems associated with those stakes are the following:

- **Master disso-precipitation phenomena in vitrification processes** *(dissolution of the calcinate; precipitation of crystallized phases in the glass melt) ; master disso-precipitation phenomena involved in the concrete
hardening; the mastering of disso-precipitation phenomena is also mandatory for the modeling of the long-term behaviour of confinement matrixes).

- RN speciation (determine the chemical forms of RN in the waste and in the geosphere).
- Steel corrosion (in storage conditions, and in an underground repository, i.e. in oxidizing and reducing conditions). This entails the mastery of
- Thermodynamics of metal-oxygen-hydrogen compounds
- Chemistry-transport couplings through boundary and passive layers.
- Sorption (physicochemistry of ion adsorption onto mineral surfaces).
- Chemistry-transport coupling in porous media (model the migration of chemical species in waste matrixes and in the geosphere).

3.5. Radiobiology, Toxicology

- Impact assessment (master the radiological impact of nuclear facilities).
- Detoxification (develop decorporating molecules).

The scientific problems associated with those stakes are the following:

- Radioecology, radionuclide migration in the biosphere (understand transfers between compartments of the biosphere).
- Analytical chemistry (detect traces of radionuclides in the environment and in the living beings).
- Speciation (determine speciation of RN in the biosphere and in the living beings).
- Determine the chemical mechanisms of radiotoxicity at the various levels of organisation of the living (molecules, cells, tissues, organisms, populations).
- Radiolysis (understand the interaction between free radicals and biomolecules).
- Improve the determination of the RN “ingestion” dose factors.

Some transverse and important problems which appear in the list above include separative chemistry, complexation, dynamics at the liquid-liquid interfaces, disso-precipitation, radiolysis, thermodynamics and corrosion.

4. The challenges

Starting from the scientific problems listed in the previous section (in black italics), we point out below the main obstacles challenging the progress of chemistry for nuclear energy.

- The coordination chemistry of 4f and 5f elements is difficult because of the necessity to take into account correlations and relativistic effects in the calculation of the electronic wavefunctions. Another difficulty is tied to the huge number of possible combinations between the ions to be complexed, the complexing molecule and the surrounding solvent. In particular, the influence of the surroundings of the complexing molecule is very important. Perhaps the biggest challenge for the models is to take into account the influence of the solvent and the diluent on the complexation.
• The main obstacle to the development of pyrometallurgy applied to actinide extraction comes from the rather low selectivity and low extraction yield. Corrosion by molten salts is also an important showstopper.

• The experimental study of radiolysis is made difficult because rapid reactions involving free radicals are hard to characterize. The modeling of radiolysis is difficult because of its multi-timescale character.

• Thermodynamic data and reaction constants at interfaces are indispensable prerequisites for the understanding and modeling of solid-liquid reactions, in particular disso-precipitation phenomena.

• Analytical chemistry offers a host of new methods. Here the main challenge is probably the improvement of the determination of speciation, both in bulk liquids and at the liquid-liquid and liquid-solid interfaces. These methods will be developed along two progress avenues: miniaturization and sensitivity, using for example microfluidics and optical techniques.

• For the dynamics at liquid-liquid interfaces, the challenge will be to understand the structure of the interface, to master the role of tensioactive compounds, and, for that purpose, to develop coupled models of kinetics, transport and electrostatics.

• The mastery of the chemistry in the primary circuit of water reactors is difficult due to the lack of measurement methods for pH and redox potential in the temperature and pressure domain of the primary circuits.

• The huge variety of chemical species and reactions involved in chemistry for nuclear energy forbid the experimental determination of all the thermodynamic and thermokinetic data that would be needed to model these systems. An important challenge is therefore to develop rapid modeling tools enabling to determine theoretically the phase diagrams and the thermodynamic and kinetic reaction constants of the involved species.

• Progress in the elaboration and in the in-pile behavior of nuclear fuel is hampered by two main obstacles: the mechanism of the action of additives on sintering is poorly understood. Fabrication processes by soft chemistry should be investigated. Moreover, the feedback of irradiation tests is very slow.

• The modeling of coupled chemistry-transport phenomena is another transverse and very important challenge for chemistry for nuclear energy, especially in cases which call for non-linear formalism, eg out-of-equilibrium situations with fast kinetics, or strong concentration gradients. The modeling of disso-precipitation phenomena and front propagation is especially difficult, and a multi-scale approach will be necessary to treat problems like pore and fracture clogging in concrete or clays.

• The assessment of the environmental impact of radioactive contaminations requests the knowledge of the speciation and mobility of radionuclides in the many compartments of a multi scale bio geochemical system which is often poorly characterized.

• Corrosion involves and couples the most complex chemical phenomena, eg heterogeneous kinetics, disso-precipitation, diffusive transport (under electrical potential gradients) through boundary and passive layers. Local chemical conditions can be very different from global ones, and even small amounts of impurities and defects can play a significant role. Corrosion under radiolysis is poorly known. It is thus a true challenge to describe and model corrosion within a general conceptual frame.

• Modeling in chemistry can take place at various scales, from the microscopic scale (atoms, ions) to the macroscopic scale (process and chemical engineering). One of the greatest challenges of simulation in chemistry will be to connect these scales through a continuous and consistent chain of models and codes, fed with inter compatible and well reviewed databases (fig. 1). Presently, the community of nuclear chemists has many models, codes and databases dedicated to the treatment of very specific problems. A great progress would be achieved if the community could dispose of a platform of general codes and databases, duly validated and structured to be interfaced, thus enabling the platform to treat a wide class of problems. The task
is immense. The construction of such a platform of simulation for chemistry for nuclear energy could be seen as a catalyst to federate the community of nuclear chemists.

5. The objectives and landmarks

Starting from the **scientific challenges** listed in the previous section, we give below the agenda of the main objectives identified in the roadmap (fig. 2). These objectives will be transcribed into proposals of collaborative actions, in the frame of the French National Research Agency (ANR). The mentioned dates indicate the time scale over which the objectives might be hopefully reached.

5.1. Coordination chemistry of f elements

- Calculation by Molecular Dynamics of the U, Pu complexation by TBP in dodecane, and comparison with the kinetic measurements (2013).
- Calculation by Molecular Dynamics of complexation of other heavy elements by other extractant molecules in other diluents (2013-2020).
- Calculation of a complexation enthalpy, taking into account conformational and electrostatic effects (2015).
- For the long-term future: explore new extraction schemes, eg extraction on solid substrates in low concentration solutions (2015).

5.2. High temperature chemistry (pyrochemistry)

- Multiphysics modeling of complexation in molten salts (2020).
- Explore new schemes of actinide partitioning, eg precipitation by polymerization in molten salts (2015).
5.3. Radiolysis

- Determination of the lifetimes of the main free radicals created by water radiolysis, and of the reaction constants of these radicals (2015).
- Calculation and experimental determination of the G(H2) coefficients of hydrogen production, as a function of the nature of the radiation, and of the dose rate (in homogeneous systems, 2013, at interfaces 2016).
- Development of criteria to foresee the degree of radiation resistance of an extractant system (complexing molecule + diluent + phase modifier) (2017).

5.4. Dissolution-precipitation

- Build a disso-precipitation thermodynamic database for the main compounds of interest in chemistry for nuclear energy (actinides and their oxides in nitric media; zirconium and its oxides in aqueous media; platinoids and actinides in glass melts; iron oxides and hydroxides in aqueous media; silicon, calcium and their oxides and hydroxides in aqueous media) (2015).
- Determination of reaction constants at the liquid-solution interface by molecular dynamics (2018).
- Construction of a generic code for the simulation of disso-precipitation, including nucleation-growth phenomena, describing the coupling between chemistry and hydrodynamics, and using the above reaction constants database (2020).
- Application of these generic tools: 1) to the determination of the main neoformed phases in glass-iron-clay interaction, with their formation kinetics in aqueous environments (2018); 2) to the modeling of the formation of Mo-Zr precipitates in spent fuel reprocessing facilities; 3) to the modeling of platinoïd precipitation in glass melts (2015).

5.5. Analytical chemistry ; speciation

- Develop reliable measurement techniques for the oxygen and fission products content in liquid sodium (2013); improve the precision of the measurement of iodine and chlorine in nuclear glasses (2013); measure on line pH and actinide concentration in the fuel cycle processes; improve the sensitivity of the detection of trace elements (especially actinides in the environment and in the living organisms (2015).
- Create a network of analytical chemistry to coordinate the activity of the main French research units (ISAB, Lyon, Pau). The development of chemical analysis techniques presents an interest which goes beyond nuclear applications, and can give rise to collaborative projects around microfluidics and lab-on-chip techniques.

5.6. High temperature chemistry in the primary circuit of light water reactors

- Develop specific electrodes for pH and eH measurements in primary water (2015).
- Validate the codes describing the chemistry of the primary circuit both in normal situation and in the case of a broken rod, by means of tracer experiments to follow the pathway of contaminants (2013).
- Consolidate the thermodynamic data relative to the structure and cladding materials (Nickel-base alloys, stainless steel, zirconium alloys) : Ni, Cr, Co, Mn, Mo, Ag, fission products and minor actinides.
- Obtain the feedback of the utilities about the localization of the contamination in the industrial reactors. Create a common database.
5.7. Thermodynamics and thermokinetics

- Improve the *ab initio* determination of the interatomic effective potentials usable in molecular dynamics simulations. (∴2020→).
- Determine phase diagrams from first principles (2020).
- Determine activation energies and reaction rates from quantum chemistry and molecular dynamics (2015).
- Develop predictive models for the simulation of the fission products migration and deposition during severe accidents.
- Complete the existing databases (Fuelbase, Mephista), and open these bases to international community. Create a collaborative structure on theoretical chemistry, and promote thermodynamics (at large) as an important axis of this network.

5.8. Fuel: fabrication and behavior under irradiation

- Determine diffusion constants (*ab initio* and experimentally) for defects and impurities in the bulk ceramics and at grain boundaries (2015).
- Develop a validated model of fuel behavior under irradiation (2013).
- Establish reasonable limits for burnup in transmutation targets (2020).
- Study the carbide fuel option (2025).
- Explore the sol-gel route for the elaboration of mixed actinide compounds (2020).

5.9. Coupled chemistry transport and radionuclide migration

- Write a model for the propagation of a neo-formed phase precipitation front in a porous medium, and apply it to the description of the near-field of a geological waste disposal facility (2013).
- Coupled Chemistry-transport models for di-phasic fluids in porous media, applied to the problems of desaturation and hydrogen production by steel corrosion in a geological waste disposal facility (2015).
- Develop a multiscale modeling of radionuclide migration in the environment, from the molecular scale to the macroscopic scale, taking into account in a coupled way geochemistry, radiochemistry and transport to predict the evolution of a radioactive contamination (2017).

5.10. Corrosion and long-term behavior of nuclear materials

- Develop a generic multiscale model of corrosion (2025).
- Develop and validate a Diffusion-Poisson simulation code for corrosion (2020).
- Develop isotopic techniques for the monitoring of the ion exchange between solid and solution.
- Determine the nature of the neoformed phases in the glass-clay interaction, evaluate their precipitation kinetics and use this as input in the glass alteration models. (2015).
- Develop anticorrosion surface treatments, e.g. by laser (2015).
Corrosion in the nuclear domain is not very specific. It might be useful to participate in research networks dedicated to non-nuclear corrosion.

5.11. Modeling and simulation in chemistry

- Build an open modeling-simulation platform for chemistry for nuclear energy (2020). For that purpose,
- build a multi-disciplinary network gathering experimentalists, theoretical chemists, modelers and mathematicians.
- Agree on the modules that should be included in the platform and distribute the work among the members of the network to construct the missing ones.
- This work is not very specifically “nuclear”, and the academic community at large can contribute.

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<th>1 – Spent fuel processing</th>
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<td>• Calculation with Molec.Dynamics of complexation and extraction selectivity</td>
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<td>• Simulation platform for the reprocessing</td>
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<td>Isofunctionality with existing code PAREX</td>
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Fig. 2: A few important landmarks of the ANCRE « Chemistry for Nuclear Energy » roadmap.

6. Conclusion and acknowledgements

The ANCRE roadmap “Chemistry for nuclear energy” gives an overview on a very vast domain: the authors hope that it will contribute to an improved structuring and prioritization of the research effort in this domain. It is a highly collective work.

Acknowledgements