The Radiochemistry Group

Prepared for the members of the:

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Introduction

The Radiochemistry Group has been founded more than 25 years ago. As per February 2024, the workforce is 42 persons with 12 Research scientists and professors, 4 postdocs, 15 PhD students, 7 engineers and technicians and 4 interns. The Radiochemistry group is one of the largest groups in its category in France. It is also the largest research group in SUBATECH. The diversity of interdisciplinary projects, which is related to major societal issues (the back-end of the nuclear power cycle, health and the environment) and to the economic players in the nuclear sector (ANDRA, EDF, ORANO, etc.) allows the group to operate mainly with own resources and a large number of staff in fixed-term contracts (post-docs and PhDs).

The laboratory area covers about 550 m^2, including 150 m^2 of supervised area. The restricted zone (ZRR) is about 200 m^2. 9 facility rooms are used for laboratory experiments and sample preparation. 6 rooms are more dedicated to instrumental techniques detailed below:

- Nuclear Metrology : Alpha Spectrometers, Liquid Scintillation Counters, Gamma Spectrometers
- Mass Spectrometry with ICP source : TQ-ICP-MS, HR-ICP-MS-(Laser Ablation)
- TOC analyser
- Chromatography : IC, LC-MS with UV, conductivity and gamma detectors
- Solid/liquid characterization: XRD, Molecular Spectroscopy and Optical Microscopy
- Sample preparation: Microwave digestion system, glove boxes, polishing device, diamond wire and disc saws, hydraulic manual press, centrifuges, drying ovens, freeze driers…..

The total investment for instrumental techniques and combined laboratory equipment is more than 2M€.

The technical staff is composed of 6.5 permanent engineers and technicians from CNRS (4.5) and IMT-A (2 on own resources).
For the operation of the radiochemistry laboratory (20-30%), a pair responsible/deputy is in charge of instrumental techniques/small equipment or lab rooms with day-to-day duties including technique operation, maintenance and formation to users. The participation of technical staff to research projects (70-80%) allows their expertise to be shared with Ph.D and internship students. Contact persons work at the SPRI (Infrastructure and Risk Management Service) interface (Radioprotection, Gas, Safety).
The technical coordination undertaken by two engineers ensures the management of the laboratory area and supports the head of Radiochemistry group (excluding human resources management). It is in charge of the communication of the technical pool and the evaluation of the laboratory running cost.
Over the five past years, the annual average cost for the laboratory operation was about 116 k€ with a contribution of academic institutions (ca. 25%) and scientific projects (ca. 75%). The main fixed expense items are instrument maintenance, consumables and gas consumption. Equipment purchase or repairing cost are more year depending. Radioactive waste evacuation costs are unforeseeable but tend to increase.
Previous "CPER" (State-Region contract plan) allowed the group to renew the analytical instrumental facility for about 450 k€. Current CPER has financed the purchase of the TQ-ICP-MS (210 k€).

From 2025, the technical pool is about to operate as an IN2P3 technical facility. The scopes and activities will be unchanged with mainly research participation for all scientific projects of the radiochemistry group in order to support the operating cost of the technical facility. The main goal is to gain in visibility towards IN2P3 for casual financial support and towards local or national partners.

The next step will be to identify the facility as a Research Platform for its declaration in calls for proposals (Regional, National and International) in order to supply the running cost and overcome the coming loss of CPER funds for the renewal of equipment.

The group's activities revolve around 5 scientific themes and are based on various skills (radiochemistry, molecular modeling, geochemistry, radiolysis, materials, radioecology etc.).

The 1th theme called '**Materials for Nuclear Applications**' is mainly dedicated to the study of the integrity of nuclear materials under the conditions of use.

The2nd theme called '**Radioelements & Environment**' focuses on the behavior of radionuclides (RN) in the environment including natural and artificial ones.

The 3rd theme called '**Radioelements & Health**' focuses on the study of radiochemistry of nuclides with applications including diagnosis and therapy.

The 4th theme called '**Radiation Chemistry**' concerns the study of fundamentals and applied research mainly with regards the nuclear energy sector.

The 5rd theme called '**Modeling**' concerns the modeling of the reactions at solid/fluid interfaces.

Furthermore, the industrial chair '**Storage and disposal of radioactive waste**', financed by ANDRA-EDF-ORANO, offers a huge opportunity to advance many subjects related to radioactive waste disposal.

The group developed many collaborations and partnerships at different levels: local, regional, national, European and international levels. This includes academic institutions, research entities, industrial partners, etc. The diversity of partnerships allows us to address fundamental and applied subjects covering the nuclear fuel cycle with its components including radioactive waste disposal, environmental impact and radiolysis, as well as the domain of applications for health in particular the study of chemistry of new radiopharmaceuticals produced in ARRONAX cyclotron. The partnerships include the major actors in the nuclear sector such as EDF, ANDRA and ORANO but also world class universities including the University of Tokyo and Stanford University.

In the following, each research theme will detailed in terms of subjects description and results, scientific production and highlights.

Research activity report for the "Materials for Nuclear Applications" theme (2019-2024)

1 Introduction

The research conducted on the Materials for Nuclear theme between 2019 and 2024 aims to deepen our understanding of materials and radioactive waste in the context of nuclear storage. We have investigated various aspects, including the behavior of radioactive waste, radionuclide diffusion in engineered barriers, and interactions at glass/steel/clay/cement interfaces.

2 Description of the research topic and the staff involved

The theme "Materials for Nuclear" brings together a diverse group of researchers, teacher-researchers, engineers, technicians, graduate students and postdoctoral fellows, and trainees. Each member brings his or her own knowledge and expertise covering a wide range of fields such as solution chemistry, analytical chemistry, solid-state chemistry, radiochemistry and geochemical modeling. The non-permanent members make a significant contribution, accounting for more than half of the research staff. Their participation is essential for the success and smooth running of our research projects.

3 Research Objectives

The main goals of our team were

1. To improve our understanding of the behavior of radioactive waste in disposal conditions, in particular by studying the behavior of ILW and HLW wastes and by exploring new approaches to improve the long-term containment of key radionuclides.
2. Analysis of radionuclide diffusion and transport processes through engineered barriers, taking into account the complex interactions between materials and environmental conditions.
3. Investigate reactions at the interfaces of matrices for conditioning and materials such as glass, steel, clay, and cement to better understand the mechanisms of radionuclide diffusion, transport, and retention.

Our work focuses on three main research areas:

3.1 Radioactive waste as a source term

Our research focuses on the behavior of ILW and HLW wastes, in particular the compacted fuel cladding and nuclear glass, in repository conditions.

- *Nuclear glass wastes doped with iodine under relative humidity*

The team is continuing the study of the behavior of nuclear glass types SON68 or ISG under disposal conditions, with a particular focus on the incorporation of volatiles such as iodine. Currently, radioactive iodine is mainly released into seawater from the La Hague fuel reprocessing plant. In collaboration with the University of Nantes and CEA and the contribution of two PhD thesis, a new approach to incorporating iodine has been developed using high pressure (0.5-2 GPa) and high temperature (~1300°C). The study involves the characterization (spectroscopy, microscopy) of the effect of initial iodine speciation (I-, I2, IO3-) on the dissolution rate within the matrix, as well as the effect of alkalis and alkaline earths on the incorporation rate. The chemical durability of these glasses is then evaluated, taking into account the effect of matrix composition, unsaturated (vapor phase) and saturated (aqueous phase) conditions, to estimate initial and residual dissolution rates.

Results show that iodine is favorably incorporated into a boron- and sodium-rich glass, where 1 iodine is surrounded by 4 Na or 2 Ca. The glass was able to retain the iodine in the matrix during the unsaturated period, while boron was released in the volatile BO_3 form. Studies have demonstrated that the retention of iodine in ISG-type polymerized glass is not significantly affected by hydration rates, whereas NH-type depolymerized glass (Na-rich, Si-poor) exhibits a significant release of B in the presence of iodine due to the charge compensation effect. Currently, aqueous phase tests are underway with a PhD thesis, with a particular focus on evaluating the initial rate.

- *Solubility of tetravalent oxides*

ILW-type nuclear waste is a category of waste that is meant to be disposed of in deep geological repositories in a cementitious environment. The waste is diverse in nature, and in the past we have worked on compacted hulls behavior and carbon-14 release, as well as its speciation in aqueous phase. Continuing with the same theme, we are interested in the solubility of the uranium and plutonium that would be implanted in the hulls and that could form a critical mass in the repository if released. Therefore, we studied and characterized the formation of a co-precipitate of uranium-plutonium oxide in a hyper-reducing and alkaline environment. The feasibility of the co-precipitation method has been established, requiring the use of a very low oxygen environment (<0.5 ppm) to stabilize the reduced U and Pu species. Co-precipitates were prepared by comparing a basic (pH 13 NaOH) and a cementitious (CEM-V type) medium. Solubility results indicate values < 10^{-10} mol/L. Characterization by LIBD and XANES is currently underway.

Besides, the hulls that have been compacted are mainly composed of zirconium, where Zr oxide is expected to be the solubility controlling phase. We conducted a study on the solubility of ZrO_2 in collaboration with KIT (shared PhD thesis) and Kyoto University to evaluate the solubility for a pH range between 10 and 12, two types of aging media ($Ca(OH)_2/CaCl_2$, NaOH/NaCl), the duration of aging, and two temperatures (22° and 80°C). The influence of aging medium on the oxide structure was demonstrated. In $Ca(OH)_2/CaCl_2$ medium, calcium could replace zirconium to form a cubic/quadratic type phase, while NaOH/NaCl medium stabilizes the monoclinic structure. Amorphous forms dominate for aging at 22°C and for short periods (<4 months), while more crystallized forms dominate at 80°C and for periods greater than 10 months. The solubilities are linked to this parameter, and they are higher for the amorphous forms and lower than the detection limit for the most crystallized forms.

These studies will continue with a contribution to the DITUSC work package (strategic study) in EURAD2, in particular on issues related to solubility and solid phases (amorphous to crystallized, particle size, characterization methods, etc.), determination of solubility constants.

3.2 Migration of the radionuclides in the cement engineered barrier

Cementitious materials are commonly used worldwide for the solidification of low- and intermediate level radioactive waste (L/ILW) prior to storage in surface or deep geological repositories. For an accurate prediction of the long term fate of this radioactive waste, a comprehensive understanding of the behavior of the radionuclides present in the waste is essential.

Thus, our scientific interest is to investigate the migration (sorption and transport) of radionuclides in cementitious materials in complex environments (effect of salt or organics plume, effect of water degradation, fractured materials,…). The applied experimental methodology is based on Through- or In-diffusion experiments combined with wet chemistry experiments (batch) on binary (RN/HCP) or ternary (RN/Organics/HCP) systems in order to acquire pertinent data for the determination of retention and transport parameters. Alongside, solutions and solids are characterized (chemical composition, mineralogy, elemental profiles) in order to obtain as complete a description as possible of the systems.

Data are interpreted by applying simple models (Kd, Langmuir isotherm, Fick laws) in order to get a global understanding of these complex systems. In certain cases, a more complex modelling could be considered.

3.3 Glass/steel/clay/cement interfaces

Our research aims to understand the reactions at the interfaces between different materials used as conditioning matrices and in storage infrastructures by varying various parameters (pH, Eh, RH%, irradiation, radiolysis). We work from simple model specimens to large scale specimens. We carefully characterize these interfaces to better understand their behavior under realistic storage conditions.

Geological disposal is a serious option for high-level nuclear waste management. A concept of multi-barrier made of steel/clay/cement is designed to slow down the access of groundwater to the waste package and therefore retarding the migration of radionuclides to the environment. We investigated the interaction between carbon and low-pH bentonitic cemet grout at high temperature (80°C). It was found that the steel in contact with the cement grout suffered from localized corrosion, triggered by the presence of sulfides.

3.4 Emerging activities: Pretreatment and recycling of radioactive waste

- *Radioactive waste pretreatment*

This activity addresses the issues of metallic wastes generated (stainless steel, inconel) during the maintenance and dismantling of nuclear facilities. The considerable quantities of this waste require effective management in order to meet the acceptance criteria set by the waste management authorities and to minimize the exposure of workers to ionizing radiation. Our research focuses on developing appropriate chemical treatments for these wastes (COREMIX process, based on the use of $KMnO_4$ and $H_2C_2O_4$ reagents) and reducing the amount of contaminated resins generated during processing mainly by precipitation approach. We also took into account the evaluation of life cycle costs and analyses, in particular regarding the energy consumption and equivalent CO_2(g) production in the optimization of the process at each step. In addition, we are investigating methods for treating radioactive metals to reduce secondary waste volumes and ionizing radiation exposure.

The perspective of this work will consist in the conditioning of the sludge generated during the treatment of the secondary effluents and it will be performed with a PhD thesis and in the workpackage STREAM in EURAD2 including the chemical-physical evaluation of the matrix as well as under irradiation.

- *Recycling of radioactive materials*

As the volume of radioactive waste increases, recycling of materials with radioactivity below clearance levels becomes an option to reduce the amount of waste in storage. We are involved in the development of advanced analytical protocols for the measurement of difficult-to-measure radionuclides (DTM). The targeted radionuclide is zirconium-93 due to its significant contribution to the total waste inventory over long timescales. These are typically evaluated using a scaling factor, based on easy-to-measure radionuclides. In addition, given future quantities, some of this metallic waste could be recycled if the level of radioactivity is below the threshold release. Then, these developments will enable us to provide a reliable and robust method for measuring DTM.

This work will continue through a PhD thesis dedicated on the measurement of Mo-93 and Nb-94 in a stainless steel matrix. It will also continue with the contribution in the workpackage ICARUS in EURAD2 with the development of a radiochemical procedure for the measure of DTM, and the standardisation of the procedure.

4 Methods and approaches

Within projects, we employ a rigorous and diversified methodological approach to achieve our research goals. We follow a detailed analytical approach, combining a variety of experimental techniques to obtain accurate and meaningful results. These data can be coupled with atomistic simulations (DFT, collaboration) and geochemical modeling (PhreeqC).

We use advanced experimental techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), micro-Raman and X-ray tomography to characterize the structure of materials. We also collaborate with specialized external laboratories for complementary analyses, including thermal analysis (ATG), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and secondary ionization mass spectrometry (SIMS).

Our chemical and radiological analyses are performed in our laboratory using techniques such as inductively coupled plasma mass spectrometry (ICP-MS), high performance ion chromatography (HP-LC), liquid chromatography coupled with mass spectrometry (LC-MS), alpha and gamma spectrometry, and liquid scintillation. We also use gas chromatography-mass spectrometry (GC-MS) to analyze volatile compounds in the gas phase.

5 Highlights

For the period 2019-2024, our research team has made significant progress in the field of radioactive waste management, which has allow us to continue activities as part of the European EURAD2 project.

- EURAD :
  - CONCORD: Steel corrosion under controlled relative humidity (RH) and gamma irradiation showed that low RH (63%) had led to high corrosion rates, which was attributed to higher yields of oxidizing radicals production.
- PREDIS :
  - As part of the activities related to the measurement of DTMs, IMT Atlantique, in collaboration with VTT, organized a webinar on this subject with the participation of more than 135 people.

- This project led to the participation of IMT Atlantique in an intercomparison exercise coordinated by VTT. This exercise will put into practice the developments achieved during the project.

6 Responsibilities

Member of this theme has responsibilities in research, teaching and the organization of scientific events.

- Research :
  - CNRS scientific representative for Eurad2 (T. Suzuki)
  - WP leader and sub-task leader in PREDIS (A. Abdelouas, T. Suzuki)
  - Task leader in EURAD/Concord (A. Abdelouas)
- Teaching :
  - Coordination of SARENA-2 (Erasmus Master in Nuclear Engineering). The only master's degree of its kind in Europe (A. Abdelouas)
- Organization of national and international conferences and summer schools:
  - 2019
    - 38th edition of the Joliot Curie International School « Nuclear energy and the interfaces with the environment » (T. Suzuki, G. Montavon)
  - 2022
    - GDR SciNEE thematic workshop "Remediation, remediation and recycling in the context of dismantling nuclear facilities: involvement of academic research" (T. Suzuki, G. Montavon)
    - PREDIS technical workshop - WP4 - Innovations in metal treatment and conditioning (A. Abdelouas, T. Suzuki)
  - 2023
    - 18th International Conference MIGRATION Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (B. Grambow, G. Montavon, T. Suzuki)
  - 2024
    - PREDIS International Thematic Webinar - WP4 - Difficult To Measure (DTM) Radionuclides: progress and new challenges (T. Suzuki)
    - Member of the steering committee for the international workshop of "Mechanisms and Modelling of Waste/Cement Interactions”

7 Research leadership

We actively participate in various steering committees at national and European levels.

- Steering board of NEEDS (C. Landesman)
- Steering board of EuradScience (T. Suzuki)
- Steering board of GdR Scinée/Fuel cycle (T. Suzuki)

8 Communications

8.1 Publications

2024

Blenkinsop, J., Rivonkar, A., Robin, M., Carey, T., Dunnett, B., Suzuki-Muresan, T., ... & Street, J. (2024). Methods for the destruction of oxalic acid decontamination effluents. Frontiers in Nuclear Engineering, 3, 1347322.

J. Marliot, S. Hedan, M. Siitari-Kauppi, J. Sammaljärvi, C. Landesman, P. Henocq, P. Sardini, Comparing fracture openings in mortar using different imaging techniques, Studia Geotechnica et Mechanica, 2024, 1-14

T. Suzuki-Muresan, A. Rivonkar, V. Bossé, M. Mokili, A. Abdelouas, G. Montavon, É. Dalmais, G. Ravier, A. Genter, Chemical and mechanical decontamination of scales from geothermal shell and tube heat exchangers in operation before anti-scaling treatment, Geothermics (2024) doi.org/10.1016/j.geothermics.2024.102960

Laffolley, H., Journeau, C. & Grambow, B. Simulant molten core–concrete interaction experiments in view of understanding Fukushima Daiichi Nuclear Power Station Cs-bearing particles generation mechanism. *Sci Rep* **14**, 6611 (2024). https://doi-org.in2p3.bib.cnrs.fr/10.1038/s41598-024-56972-9

Kazuya Tanaka, Keiko Yamaji, Hayato Masuya, Jumpei Tomita, Mayumi Ozawa, Shinya Yamasaki, Kohei Tokunaga, Kenjin Fukuyama, Yoshiyuki Ohara, Ibrahim Maamoun, Akiko Yamaguchi, Yoshio Takahashi, Naofumi Kozai, Bernd Grambow, Microbially formed Mn(IV) oxide as a novel adsorbent for removalof Radium, Chemosphere 355 (2024) 141837. https://doi-org.in2p3.bib.cnrs.fr/10.1016/j.chemosphere.2024.141837

Kanako Miyazaki, Masato Takehara, Kenta Minomo, Kenji Horie, Mami Takehara, Shinya Yamasaki, Takumi Saito, Toshihiko Ohnuki, Masahide Takano, Hiroyuki Shiotsu, Hajime Iwata, Gianni F. Vettese, Mirkka P. Sarparanta, Gareth T.W. Law, Bernd Grambow, Rodney C. Ewing, Satoshi Utsunomiya, "Invisible" radioactive cesium atoms revealed: Pollucite inclusion in cesium-rich microparticles (CsMPs) from the Fukushima Daiichi Nuclear Power Plant, Journal of Hazardous Materials, Volume 470, 2024, 134104, https://doi.org/10.1016/j.jhazmat.2024.134104.
(https://www.sciencedirect.com/science/article/pii/S0304389424006836

2023

Rivonkar, A. (2023). Optimization of chemical decontamination methods for radioactive metals. PhD Thesis 2023IMTA0375, IMT Atlantique Nantes Campus, France.

Moschetti, I., Sarrasin, L., Blain, G., Mossini, E., Mariani, M., & Abdelouas, A. (2023, October). Effect of Curing Time and Water to Binder Ratio on Magnesium Potassium Phosphate Cement Exposed to Gamma Irradiation. In International Conference on Radioactive Waste Management and Environmental Remediation (Vol. 87530, p. V001T05A001). American Society of Mechanical Engineers.

H. Zhang, T. Suzuki-Muresan, S. Gin, G. Blain, T. Sauvage, O. Wendling, J. Vandenborre, A. Abdelouas, Effects of vapor hydration and radiation on the leaching behavior of nuclear glass, J. Nucl. Mater. 578 (2023) 154368. doi:10.1016/j.jnucmat.2023.154368.

J. Goethals, …., A. Abdelouas et al. Interaction between carbon steel and low-pH bentonitic cement grout in anoxic, high temperature (80◦C) and spatially heterogeneous conditions. Corrosion Science 211, 110852 (2023).

Grekov, D.I., Robinet, J.-C., Grambow, B , Adsorption of methane and carbon dioxide by water-saturated clay minerals and clay rocks, 2023, Applied Clay Science 232,106806

Kolditz, O., Jacques, D., Claret, F., (...), B. Grambow, Theodon, L., Wendling, J. , Digitalisation for nuclear waste management: predisposal and disposal, Open Access, 2023 Environmental Earth Sciences 82(1),42

K. Fueda, T.Komiya, K. Minomo, K. Horie, M. Takehara, S. Yamasaki, H. Shiotsu, T. Ohnuki, B. Grambow, G. Law, R. Ewing, S. Utsunomiya, Occurrence of radioactive cesium-rich micro-particles (CsMPs) in a school building located 2.8 km south-west of the Fukushima Daiichi Nuclear Power Plant, Chemosphere 328 (2023) 138566, https://doi.org/10.1016/j.chemosphere.2023.138566

H. Laffolley, C. Journeau, S. Thilliez, B. Grambow, Thermodynamics of aerosols during a molten core-concrete interaction at Fukushima Daiichi Unit 2 estimated conditions, ERMSAR 2022 Conference: Severe Accident Research Eleven Years after the Fukushima Accident, Editors: Herranz, Paci, Gabrielli Annals of Nuclear Energy, 2023, 186, pp. 109770, https://doi-org.in2p3.bib.cnrs.fr/10.1016/j.anucene.2023.109770,

Gaona X, Grambow B, Kobayashi T, Cho H-R and Saslow SA (2023) Editorial: Solubility phenomena in the context of nuclear waste disposal. *Front. Nucl. Eng.* 2:1332806. doi: 10.3389/fnuen.2023.1332806

B. Grambow, R. Müller, D. Schild and X. Gaona, Solids, colloids, and the hydrolysis of tetravalent uranium in chloride media, Frontiers in Nuclear Engineering, https://doi.org/10.3389/fnuen.2023.1308064

2022 Katona, R., Rivonkar, A., Locskai, R., Bátor, G., Abdelouas, A., Somlai, J., & Kovács, T. (2022). Tafel-analysis of the AP-CITROX decontamination technology of Inconel alloy 690. Applied Radiation and Isotopes, 181, 110073.

Rivonkar, A., Katona, R., Robin, M., Suzuki-Muresan, T., Abdelouas, A., Mokili, M., ... & Kovács, T. (2022). Optimisation of the chemical oxidation reduction process (CORD) on surrogate stainless steel in regards to its efficiency and secondary wastes. Frontiers in Nuclear Engineering, 1, 1080954.

H. Zhang, J.-P. Guin, T. Suzuki-Muresan, M. Paris, S. Gin, A. Abdelouas, Impact of initial states on the vapor hydration of iodine-bearing borosilicate glass, J. Non. Cryst. Solids. 587 (2022) 121584. doi:10.1016/j.jnoncrysol.2022.121584.

N. Narayansamy …., A. Abdelouas et al. Borosilicate glass alteration in vapor phase and aqueous medium. npj materials degradation 6, 86 (2022).

E. Holt,.....A. Abdelouas et al. Predisposal conditioning, treatment, and performance assessment of radioactive waste streams. EPJ Nuclear Sciences and Technologies 80, 40 (2022). https://doi.org/10.1051/epjn/2022036.

Kazuki Fueda, Ryu Takami, Kenta Minomo, Kazuya Morooka, Kenji Horie, Mami Takehara, Shinya Yamasaki, Takumi Saito, Hiroyuki Shiotsu, Toshihiko Ohnuki, Gareth T.W. Law, Bernd Grambow, Rodney C. Ewing, Satoshi Utsunomiya, Volatilization of B_4C control rods in Fukushima Daiichi nuclear reactors during meltdown: B–Li isotopic signatures in cesium-rich microparticles. Journal of Hazardous Materials 428 (2022) 128214, https://doi.org/10.1016/j.jhazmat.2022.128214

Hugo Laffolley, Christophe Journeau, Jules Delacroix, Bernd Grambow,Christophe Suteau, Synthesis of Fukushima Daiichi Cs-bearing microparticles through molten core-concrete interaction in nitrogen atmosphere, Nuclear Materials and Energy 33 (2022) 101253, https://doi.org/10.1016/j.nme.2022.101253 ⟨hal-03830089⟩

Grambow B (2022), Mini review of research requirements for radioactive waste management including disposal. Front. Nucl. Eng. 1:1052428. doi: 10.3389/fnuen.2022.1052428

2021

V. Jolivet, Y. Morizet, J. Hamon, M. Paris, T. Suzuki-Muresan, The influence of iodide on glass transition temperature of high-pressure nuclear waste glasses, J. Am. Ceram. Soc. 104 (2021) 1360–1369. doi.org/10.1111/jace.17571.

Rivonkar, A., Suzuki, T. M., Abdelouas, A., Mokili, M., & Katona, R. (2021). Study of Existing Chemical Decontamination Methods of Radioactive Metals with a View on their Optimization (No. IAEA-CN--294).

Y. Morizet, J. Hamon, C. La, V. Jolivet, T. Suzuki-Muresan, M. Paris, Immobilization of 129I in nuclear waste glass matrixes synthesized under high-pressure conditions: an experimental study, J. Mater. Chem. A. 9 (2021) 23902–23915. doi:10.1039/D1TA05011G.

Y. Morizet, V. Jolivet, N. Trcera, T. Suzuki-Muresan, J. Hamon, Iodine local environment in high pressure borosilicate glasses: An X-ray photoelectron spectroscopy and X-ray absorption spectroscopy investigation, J. Nucl. Mater. 553 (2021) 153050. doi.org/10.1016/j.jnucmat.2021.153050.

W. Zouari, T. Suzuki-Muresan, T. Kobayashi, S. Utsunomiya, A. Abdelouas, B. Grambow, Solubility of monoclinic and yttrium stabilized cubic ZrO2: Solution and surface thermodynamics guiding ultra-trace analytics in aqueous phase, J. Nucl. Mater. 545 (2021) 152631. doi:10.1016/j.jnucmat.2020.152631.

H. Zhang, T. Suzuki-Muresan, Y. Morizet, S. Gin, A. Abdelouas, Investigation on boron and iodine behavior during nuclear glass vapor hydration, Npj Mater. Degrad. 5 (2021) 10. doi:10.1038/s41529-021-00157-6.

N. Narayanasamy, Jollivet, P., Sessegolo, L., Angeli, F., Abdelouas, A. Influence of temperature and relative humidity on vapor hydration of an AVM nuclear waste glass. Journal of Nuclear Materials 543, 152571 (2021).

Bouakkaz, B., Abdelouas, A., El Mendili, Y., David, K., Grambow, B. Alteration of 29Si-doped SON68 borosilicate nuclear waste glass in the presence of near field materials. Applied Geochemistry 111 (2019) 104436.

Narayanasamy N., Jollivet, P., Godon, N., Angeli, F., Gin, S., Cabié, M., Cambedouzou, J., Le Guillou, C., Abdelouas, A. Influence of composition of nuclear waste glasses on vapor phase hydration. Journal of Nuclear Materials 525, 53-71 (2019).

T. Kimura, S. Fukutani, M. Ikegami, F. Sakamoto, N. Kozai, B. Grambow, M. Yoneda, Effect of bacterial siderophore on cesium dissolution from biotite, Chemosphere 276 (2021) 130121

K. Morooka, E. Kurihara, M. Takehara, R. Takami, K. Fueda, K. Horie, M. Takehara, S. Yamasaki, T. Ohnuki, B. Grambow, G.T.W. Law, J.W.L. Ang, W.R. Bower, J. Parker, R.C. Ewing, S. Utsunomiya, New highly radioactive particles derived from Fukushima Daiichi Reactor Unit 1: Properties and environmental impacts, Science of the Total Environment 773 (2021) 145639

Hazard Information Profiles: Supplement to UNDRR-ISC Hazard Definition & Classification Review – Technical Report Geneva, Switzerland, United Nations Office for Disaster Risk Reduction; Paris, France, International Science Council. United Nations 2021, (B. Grambow as reviewer)

Grambow, B., 2021. Spent nuclear fuel long term behavior and performance. In: Greenspan, E. (Ed.), Encyclopedia of Nuclear Energy, vol. 2. Elsevier, pp. 577–587. https://dx.doi.org/10.1016/B978-0-12-819725-7.00155-0, ISBN: 9780128197257

F. Guido-Garcia, F. Sakamoto, K. David, N. Kozai, B. Grambow, Radiocesium in Shiitake mushroom: Accumulation in living fruit bodies and leaching from dead fruit bodies, Chemosphere 279 (2021) 130511

Denys I. Grekov, Andrey G. Kalinichev, Tomo Suzuki-Muresan, Pascaline Pré, and Bernd Grambow, Direct Experimental Evidence of the Effects of Clay Particles' Basal-to-Lateral Surface Ratio on Methane and Carbon Dioxide Adsorption, Journal of Physical Chemistry C, 2021, https://doi.org/10.1021/acs.jpcc.1c00039

Bernd Grambow, Ayako Nitta, Atsuhiro Shibata, Yoshikazu Koma, Satoshi Utsunomiya, Ryu Takami, Kazuki Fueda, Toshihiko Ohnuki, Christophe Jegou, Hugo Laffolley, Christophe Journeau, Ten years after the NPP accident at Fukushima : review on fuel debris behavior in contact with water, Journal of Nuclear Science and Technology, DOI:10.1080/00223131.2021.1966347

2020 V. Jolivet, Y. Morizet, M. Paris, T. Suzuki-Muresan, High pressure experimental study on iodine solution mechanisms in nuclear waste glasses, J. Nucl. Mater. 533 (2020) 152112. doi:10.1016/j.jnucmat.2020.152112.

I. Grenthe, X. Gaona, A.Y. Plyasunov, L. Rao, W.H. Runde, B. Grambow, R.J.M. Konigs, A. Smith, E.Moore, Second Update of the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium, ed. M. E. Ragoussi, J.S. Martinez and D. Costa, 1503 pages, OECD;Nuclear Energy Agency, Data Bank, France 2020, https://doi.org/10.1787/20743300

Denys Grekov, Pascaline Pré, Bernd Grambow, On the use of manometry method for measurement of gas adsorption equilibria and characterization of clay texture with Derivative Isotherm Summation, Applied Clay Science, Volume 184, January 2020, 105372, https://doi.org/10.1016/j.clay.2019.105372

Ryohei Ikehara , Kazuya Morooka, Mizuki Suetak, Tatsuki Komiya , Eitaro Kurihara , Masato Takehara, Ryu Takami, Chiaki Kino , Kenji Horie , Mami Takehara, Shinya Yamasaki, Toshihiko Ohnuki, Gareth T.W. Law, William Bower, Bernd Grambow, Rodney C. Ewing, Satoshi Utsunomiy,Abundance and distribution of radioactive cesium-rich microparticles released from the Fukushima Daiichi Nuclear Power Plant into the environment, Chemosphere 241 (2020) 125019, https://doi.org/10.1016/j.chemosphere.2019.125019

Denys I. Grekov, Tomo Suzuki-Muresan, Andrey G., Kalinichev, Pascaline Pre, Bernd Grambow, Thermodynamic data of adsorption reveal the entry of CH4 and CO2 in a smectite clay interlayer, Phys.Chem.Chem.Phys., 2020, 22, 16727, https://doi.org/10.1039/d0cp02135k

E. Kurihara, M. Takehara, M. Suetake, R. Ikehara, T. Komiya, K. Morooka, R. Takami, S.Yamasaki, T. Ohnuki, K. Horied, M. Takehara, G.T.W.Law, W.Bower, J. Frederick, W. Mosselmans, P. Warnicke, B. Grambow, R.C.Ewing, S.Utsunomiya, Particulate plutonium released from the Fukushima Daiichi meltdowns, Science of the total environment, 743, 2020, 140539, https://doi.org/10.1016/j.scitotenv.2020.140539

B. Grambow, M. Lopez-García, J. Olmeda, M. Grivé, N.C.M. Marty, S. Grangeon, F. Claret, S. Lange, G. Deissmann, M. Klinkenberg, D. Bosbach, C. Bucur, I. Florea, R. Dobrin, M. Isaacs, D. Read, J. Kittnerova, B. Drtinova, D. Vopalka, N. Cevirim-Papaioannou, N. Ait-Mouheb, X. Gaona, M. Altmaier, L. Nedyalkova, B. Lothenbach, J. Tits, C. Landesman, S. Rasamimanana, S. Ribet, Retention and diffusion of radioactive and toxic species on cementitious systems: Main outcome of the CEBAMA project, Applied Geochemistry 112 (2020) https://doi.org/10.1016/j.apgeochem.2019.104480

Lara Duro, Marcus Altmaier, Erika Holt, Urs Mäder, Francis Claret, Bernd Grambow, Andres Idiart, Alba Valls, Vanessa Montoya, Contribution of the results of the CEBAMA project to decrease uncertainties in the Safety Case and Performance

Assessment of radioactive waste repositories, Applied Geochemistry 112 (2020) 104479, https://doi.org/10.1016/j.apgeochem.2019.104479

2019 V. Jolivet, L. Jossé, M. Rivoal, M. Paris, Y. Morizet, L. Carole, T. Suzuki-Muresan, Quantification of boron in aluminoborosilicate glasses using Raman and 11 B NMR, J. Non. Cryst. Solids. 511 (2019). doi:10.1016/j.jnoncrysol.2018.12.038.

D. Grekov, P. Pre, B. Grambow, On the use of manometry method for measurement of gas adsorption equilibria and characterization of clay texture with Derivative Isotherm Summation, Applied Clay Science, /doi.org/10.1016/j.clay.2019.105372

Kazuya Tanaka, Naofumi Kozai, Shinya Yamasaki, Toshihiko Ohnukia,Daniel I. Kaplan, Bernd Grambow, Adsorption mechanism of ReO4 on Ni–Zn layered hydroxide salt and its application to removal of ReO4 as a surrogate of TcO4, Applied Clay Science 182 (2019) https://doi.org/10.1016/j.clay.2019.105282

Suetake, M.; Nakano, Y.; Furuki,G; Ikehara, R; Komiya, T; Kurihara, E; Morooka, K; Yamasaki, S ; Ohnuki, T; Horie, K; Takehara, M; Law, GTW; Bower, W; Grambow, B; Ewing, RC; Utsunomiya, S. Dissolution of radioactive, cesium-rich microparticles released from the Fukushima Daiichi Nuclear Power Plant in simulated lung fluid, pure-water, and seawater, CHEMOSPHERE 233, 633-644, 2019

Taisuke SHIMOGOUCHI, Hirochika NAGANAWA, Tetsushi NAGANO, Bernd GRAMBOW, Yuichiro NAGAME, Size Distribution of Droplets in Two Liquid-phase Mixture Compared between Liquid Spraying and Mechanical Stirring Analytical Sciences, Analytical sciences : the international journal of the Japan Society for Analytical Chemistry 35, 955-960 DOI: 10.2116/analsci. 18P508, 2019.

Research activity report for the "Radionuclides & Environment" theme (2019-2024)

Context

This theme, explored since the creation of the Radiochemistry group in 1995, focuses on studying the behavior of radionuclides (RNs) in the environment. For the period 2019-2023, it involves a team averaging 8.4 Full-Time Equivalent (FTE) personnel per year, distributed as follows: 1.4 FTE for researchers/lecturers, 2.2 FTE for engineers & technicians, 1.4 FTE for postdoctoral researchers, and 3.5 FTE for doctoral students.

It now revolves around two main issues: the management of radioactive waste and the effects of low doses of natural (U, Ra…) or anthropogenic (tritium,…) origin on ecosystems. The table below briefly summarizes the tools that enable us to undertake long-term research projects.

Table 1. Structuring tools facilitating long-term research

Level	**Structuring Tool**	**Collaboration**	**Site**	**Responsabilities (Subatech)**
Regional	Observatoire des Sciences de l'Univers Nantes Atlantique (OSUNA)	LPG-Nantes, CEA-DAM	Loire estuary	Members of the Scientific and Administrative Committees
	Labcom TESMARAC	Triskem, CEISAM	_	Direction
National	Framework contract with ANDRA	BRGM-Orléans	COx formation	_
	Zone Atelier Territoires Uranifères (ZATU)	IRSN (LT2S), LMGE, IPHC, BRGM (Orléans), INC	Springs and contaminated wetland	Co-direction Members of the Steering Committee
European	« European Radioecology Alliance » RADONORM	HZDR, KIT-INE	ZATU sites	Representation of CNRS/IN2P3
	EURAD/FUTURE	_	COx formation	_

Regardless of the project, our involvement is directed towards radiochemistry at the trace and ultra-trace levels, with a focus on speciation issues following a multi-scale approach (from molecular to macroscopic scale, from model system to natural system, and from laboratory to field) within an interdisciplinary context (Del Néro et Montavon, 2021; Bretesché et al., 2020).

We are particularly interested in the adsorption and complexation mechanisms, as well as the labile nature of the species formed (meaning the possibility of reverting to a free form in short timescales) and their availability. Analytical developments accompany this work, particularly centered around our LA-HR-ICP-MS apparatus (e.g. Loni et al., 2019 and 2021).

Activities are structured around sites of interest such as the Loire estuary, the Bure site (CIGEO project), and the workshop sites of the "Zone Atelier Territoire Uranifère" (ZATU). Additionally, our expertise contribution extends to various contexts, particularly with a link to radioactive waste management in the United Arab Emirates (2022-2023) in order to provide site-specific Kd on selected soils/sediments and Tf values (for plants).

It is also worth noting the recent establishment of the LabCom TESMARAC with the company TRISKEM which allows us to explore a new research domain, the analysis of Difficult-To-Measure RNs (DTM), and to consider the development of selective retention supports for RN, with a particular interest in Ra.

The results presented below are largely the outcome of work by 6 doctoral students (the list is provided in the list of publications) and 3 postdoctoral researchers. Perspectives are presented in a second section. Both sections are accompanied by the team's publications (provided in the appendix, average of 5 articles per year).

Results

Radioactive waste

If we expect some peripheral work, for which our involvement remains limited (Gregov et al., 2019; Zhang et al., 2022), our contribution focuses on studying the retention properties of geological barriers selected to contain radioactive waste, with a focus on the Callovo-Oxfordian (COx) formation (CIGEO project) and adsorption processes. We have particularly worked on translating adsorption data from the laboratory to the field: (i) we have demonstrated the negligible compaction effect on the adsorption properties of COx argillites for Eu, Ni, and U(VI) (Loni et al., 2021; Montavon et al., 2020; Montavon et al., 2023); (ii) a methodology has been developed to determine "site-specific" Kd values with naturally occurring elements that, in addition to knowledge of the concentrations of these same elements in the rock's pore water, provide relevant information to bridge the laboratory/field gap (Montavon et al., 2020; Montavon et al., 2022). Significant work has also been done to estimate/quantify the effects of temperature on the adsorption properties of clays and COx (Maia et al., 2021; Ribet et al., 2023); work in intact environments highlights retention phenomena other than adsorption, which are governed by other phases (pyrite, calcite) than the clay fraction (Montavon et al., 2023).

Organically bound tritium (OBT)

The most concerning form of tritium in the environment is organically bound and non-exchangeable, capable of persisting in organisms over extended periods, causing its remanence in the environment. The IAEA (International Atomic Energy Agency) labels this as NE-OBT, covering tritium bound to carbon atoms and "buried" tritium, i.e. bound to heteroatoms (and therefore supposedly exchangeable) but inaccessible during isotopic exchanges due to molecular configuration. However, ongoing debate surrounds the structural nature of tritium labelled NE-OBT, complicating analytical result interpretation. As a result, our project focuses on OBT and the labile nature of interactions at trace levels. An isotopic exchange method was proposed, using a vapor phase tritium sample labelling line (Nivesse et al., 2021a). Matrices of interest were studied to better understand and quantify the origin of "buried" tritium. It was demonstrated for the first time that the quantity of buried tritium was linked to the complex three-dimensional arrangement of certain components such as proteins, cellulose, or natural organic matter (Nivesse et al., 2020 and 2021b). This result was confirmed with cellulose: the higher the degree of crystallinity, the more efficient the three-dimensional molecular arrangement, and the greater the quantity of buried tritium (Nivesse et al., 2021c).

Questions related to Naturally-Occurring Radionuclides (NORs)

Member of European and International Long Term Ecological Research Infra-structures, the French national network of Zones Ateliers (RZA) labelled by CNRS develops a specific scientific approach based on observations and experiments on workshops sites, to conduct multidisciplinary research in the long term. Labelled in January 2015, the Zone Atelier Territoires Uranifères (ZATU) focuses on the environments characterized by chronic radiation of natural or enhanced natural origin. A contaminated wetland downstream of a mine tailings repository located in a small watershed and the presence of natural radioactive mineral sources nearby provide an ideal setting to conduct long-term radioecological research in NORs contaminated sites. Renewed for 2020-2024, the ZATU involves 22 laboratories from various research organizations (CNRS, CEA, IRSN, BRGM) and French universities.

Our focus has been particularly on the origin and nature of contamination in the wetland area (Rophin site). Based on an interdisciplinary approach (Historical documents, isotopy, radiochemistry, geochemistry, dendrology), we have revealed that the contamination, located a few centimeters below the soil surface, stems from the discharge of settling basins during mining activities in the 1960s (Martin et al., 2020; Loni et al., 2019). Uranium exists in the form of exploited minerals (UO_2, uranium (VI) phosphates), but there is also a significant fraction transported in a soluble form (Grangeon et al., 2023; Grangeon et al., 2032; Geng et al., 2024). By combining various methods (determination of site-specific Kd values, bottom-up predictive modeling, X-ray absorption experiments, microscopy), we confirmed the above conclusions and we have demonstrated that only a small fraction (~5%) is labile, consisting of U(VI) adsorbed onto the 2:1 clay minerals fraction. The presence of both labile and inert fractions was further corroborated by DET (Diffusive Equilibrium in Thin films) /DGT (Diffusive Gradient in Thin films) probes data implemented over time (Martin et al., 2021; Montavon et al., in preparation). Similar work has been conducted in the surface humus fraction of the soil, where significant U contamination was also observed (with unknown origins). U is associated with soil organic matter, and only a very small fraction (~1%) was shown to be labile (Nivesse et al., in preparation).

Perspectives

With the transition of the CIGEO project to an industrial phase, the research prospects within the partnership with ANDRA are uncertain. An action focusing on selenium (naturally present) in COx is underway (2023-2025) and focuses on the effect of oxidative perturbation on the mechanism controlling the distribution of selenium at the water/rock interface. This work, based on the methods established within the team, is accompanied by the development of a speciation protocol of Se (-II, IV, and VI) in solution at the ultra-trace level.

The research prospects specifically focus on the third five-year ZATU research program (2025-2029) and involve the majority of the current team (~60%). The contribution of Subatech is briefly outlined below.

One of the objectives is to continue completing the operational "characterization & transfer" database, which integrates the characteristics of the studied environments as well as operational parameters describing the behavior of RNs and TMEs (Trace Metal Elements) (such as Kd, available/inert fractions...). These data are used to assess the effects but also to develop a reactive transport model under construction on the scale of the wetland area of the Rophin site. Regarding Subatech, the aim is to now characterize the colloids present at workshop sites (in collaboration with KIT-INE) and to continue enriching the database with site-specific Kd values, extending them to sediment sources and other RNs (Ra, Po). The idea is also to deepen the use of DET/DGT coupling to obtain quantitative parameters (in-situ Kd, kinetic parameters). This work will initially be carried out with U, in connection with what has already been accomplished, and then continued with Ra using specific Ra DGT probes (containing Ra resin, Analig) that have already been prepared and successfully tested in the laboratory (Xu, 2022).

The objective is also to return to the laboratory to complete the database called "speciation" which addresses the interactions of RNs at the microscopic/molecular scale with the identification of the nature of species and associated formation constants. We are particularly interested in the humus layer of the contaminated wetland area; it is known that U and Ra is bound to organic matter (OM), but we were unable to predict this interaction using a bottom-up approach (blind predictions made within the framework of the European project RADONORM). It is therefore necessary to complete the "speciation" database with generic parameters to describe this interaction. Moreover, a significant fraction of U (~99%) but also of Ra (~85%) is not labile. One hypothesis is the presence of buried sites, not accessible over short contact times, which has already been observed in similar systems with tritium (Nivesse et al., 2020). Finally, in this humus layer, IPHC results show that U in the pore water is essentially in colloidal form, and these U-colloids end up outside the wetland zone in the stream that runs through it; this highlights the importance of organic colloids on U transfer. The idea is therefore to address these three questions from well-characterized shared study objects, extracted from this humus layer (a soluble organic matter fraction (SOM) and an insoluble organic matter (IOM) fraction. For the soluble fraction, it will be a matter of characterizing the elementary blocks that constitute it (work of the IPHC) and for the IOM, all the interaction sites will be qualified and quantified by NMR. The challenge for Subatech is to approach the Ra/SOM system via a bottom-up approach, from elementary blocks to SOM, by coupling experiments and calculations. By calculation, we mean molecular dynamics to reconstruct the SOM and molecular modeling to assess the reactivity of elementary blocks (EBs) using a tool developed and validated for Ra (Mohaman, 2023). For this final task, there are plans to incorporate artificial intelligence tools to assist in completing the work. This theoretical work will be accompanied by experimental work to characterize the complexation and dissociation of complexes formed with EBs and SOM. For the IOM, the labile/inert fractions will be monitored over time in parallel with the evaluation of the availability of adsorption sites (adsorption isotherm, use of tritium as a probe). For the case of U, a speciation assessment will be carried out (collaboration with HZDR).

Since Ra is a radioelement of interest for the future program at Subatech, we would also like to have access to speciation tools for it, knowing that measurement tools are already operational (Verlinde, 2019; Boudias, 2022), particularly in the field (Boudias, 2024). One challenge will be to develop a method for conducting X-ray absorption spectroscopy (XAS) analyses in collaboration with the MARS beamline and INC. We have decided to test the feasibility of such an approach, along with the development of a cell adapted for Ra manipulation, using a system that we are familiar with; it is an efficient and selective chelating agent for Ra (compared to Ba), developed within the LabCom, which will be tested in the laboratory to assess its suitability for in-situ pre-concentration (DGT, resin), compared to the selective resin for Ra available on the market, Analig. This Ra/Ba selectivity is currently being evaluated by DFT calculation, and the results will be compared to XAS results.

Concerning the "effect" aspect, as mentioned earlier, we contribute through the "transfer" database to research projects addressing this issue. They are based on two complementary approaches; the first relies on field observation, while the second is associated with controlled laboratory experiments under irradiation in addition to giant 4-DNA simulations (Kolovi et al., 2024, Baker et al., 2023a and

2023b, Mallet et al., 2024). In both cases, microorganisms are the target organisms. The idea is to propose complementary work that allows for the assessment of effects from systems reconstituted in the laboratory, with the controlled addition of RNs of interest as "sources" of irradiation (U, Ra, Po, Rn). Diatoms, on which we have already worked in the context of a thesis to evaluate the distribution/speciation of U(VI) (He et al., 2024a, 2024b), are the targeted species.

Finally, other opportunities are available to us, linked to environmental issues on which CNRS wishes the academic community to take a stance. This concerns the issue of waste dumped in the North-east Atlantic Ocean in the 1940-80s at around 3000-4000 m in depth, and the management of contaminated land in French Polynesia related to nuclear bombs testing. At the time the document is drafted, the projects are not yet finalized. Subatech, regarding dumped waste, is focusing on the development of "rapid" methods for measuring actinides (Am, Pu) in relevant compartments, in connection with developments carried out within the framework of the LabCom TESMARAC (non published data) and on the analysis of OBT-NE; this project is expected to start in 2025-2026 for a duration of four years. As for contaminated land, the objective is to propose decontamination methods through phytoextraction, in collaboration with a historical partner of OSUNA (LPG), and to link it with the availability of metallic contaminants (radionuclides are not considered in this first phase of the project); the project is scheduled for the period 2024-2027. To conclude, Subatech is included in work package 8 of EDF's radioecology program (2023-2029), which focuses on R&D. The connection is established through the SMART service, which conducts analyses as part of this nuclear power plant monitoring program. The discussions are scheduled for 2025.

However, these various opportunities available to us must still be linked to our supervision/analytical capacity and the economic model of the radiochemistry group.

Publications

PhD Thesis

Yahaya Hassan Loni **Ablation laser couplée à l'ICP-MS-HR : outil pour l'étude du comportement d'éléments d'intérêt dans l'environnement**, thèse de l'IMT-Atlantique, 2019

Anne-Laure Nivesse, **Spéciation du tritium organiquement lié dans les matrices environnementales**, thèse de doctorat de Nantes Université, 2020

Fengqi Xu, **Nouveaux développements pour la détermination du radium dans des solutions synthétiques et des eaux naturelles**, thèse de doctorat de l'IMT Atlantique, 2022

Yihua Hé, **Interaction des radioéléments (Ra, U) avec les diatomées**, thèse de l'IMT Atlantique, 2023

Ting-Ting Geng, **Origin and migration processes of radionuclides downstream of a former uranium mining site : isotopic fingerprinting, 238-series disequilibrium, and geostatistical tools**; Thèse de Nantes Université, 2023

Hamissou Mohaman **Elaboration d'une méthodologie théorique pour l'étude de la complexation du radium(II) en solution** ; thèse de Nantes Université, 2024

Articles

M. Verlinde, J. Gorny, G. Montavon, S. Khalfallah, B. Boulet, C. Augeray, D. Lariviere, C. Dalencourt, A. Gourgiotis **A new rapid protocol for 226Ra separation and pre-concentration in natural samples using molecular recognition technology, for ICP-MS analysis** Journal of Environmental Radioactivity **202**; 1-7 (2019)

A. Martin, C. Landesman, A. Lepinay, C. Roux, J. Champion, P. Chardon, G. Montavon **Flow period influence on uranium and trace elements release in water from the waste rock pile of the former La Commanderie uranium mine (France).** Journal of Environmental Radioactivity, **208-209**, pp.106010. (2019)

D. Gregov, G. Montavon, J.C. Robinet, B. Grambow **Smectite fraction assessment in complex natural clay rocks from interlayer water content determined by thermogravimetric and thermoporometry analysis** Journal of CollOid and Interface Science **555**, pp.157-165 (2019)

Y. Hassan Loni, K. David, S. Larrue, S. Ribet, P. Chardon, B. Grambow, C. Corona, G. Montavon **Uranium quantification of oak tree rings (*Quercus petraea*) from a former uranium-mining site by High Resolution Inductively Coupled Plasma Mass Spectrometry in laser ablation and solution modes** Spectrochimica Acta Part B: Atomic Spectroscopy. 161, pp.105709 (2019)

A.-L. Nivesse, A. Thibault de Chanvalon, N. Baglan, G., Montavon, G. Granger, O. Péron. **An overlooked pool of hydrogen stored in humic matter revealed by isotopic exchange: implication for radioactive 3H contamination** Environmental Chemistry Letters, **18**, 475-481 (2020)

A. Younes, C. Alliot, J. S. Ali, A.-C. Bonraisin, M. Mokili, S. Happel, A. Bombard, F. Haddad, G. Montavon. **Production of polonium from bismuthand purification using TBP resin and Sr resin;** Journal of Radioanalytical and Nuclear Chemistry, **324**, 823-828 (2020)

A. Martin, Y. Hassan-Loni, A. Fichtner O. Peron, K. David, P. Chardon, S. Larrue, A. Gourgiotis, S. Sachs, T. Arnold, B. Grambow, T. Stumpf, G. Montavon **An integrated approach combining soil profile, records and tree ring analysis to identify the origin of environmental contamination in a former uranium mine (Rophin, France)** Science of the Total Environment, **747**, 141295 (2020)

G. Montavon, C. Lerouge, K. David, S. Ribet, Y. Hassan Loni, M. Leferrec, C. Bailly, B. Grambow **Ni sorption on Callovo-Oxfordian clay rock (France) ; transferability from model system to *in-situ* conditions**, Environmental Science & Technology, **54**, 12226–12234 (2020)

S. Bretesché, G. Montavon, A. Martin, **Pour une approche interdisciplinaire du risque environnemental. Le cas de l'uranium** Natures Sciences Sociétés, (2020)

A-L. Nivesse, N. Baglan, G. Montavon, G. Granger, O. Péron. **Non-intrusive and reliable speciation of organically bound tritium in environmental matrices.** Talanta, **224**, 121803 (2021a).

F. M. S. Maia, S. Ribet, C. Bailly, M. Grivé, B. Madé, G. Montavon **Evaluation of thermodynamic data for Ca-U(VI)-CO_3 aqueous species under conditions characteristic of geological clay formation** Applied Geochemistry, **124**, 104844 (2021).

A-L. Nivesse, N. Baglan, G. Montavon, G. Granger, O. Péron. **Cellulose, proteins, starch and simple carbohydrates molecules control the hydrogen exchange capacity of bio-indicators and foodstuffs.** Chemosphere, **269** 128676 (2021b).

A. Martin, G. Montavon, C. Landesman **A combined DGT - DET approach for an** *in situ* **investigation of uranium resupply from large soil profiles in a wetland impacted by former mining activities.** Chemosphere, **279**, 130526 (2021)

A-L. Nivesse, N. Baglan, G. Montavon, O. Peron. **New insights into the accessibility of native cellulose to environmental contaminants toward tritium behavior prediction** Journal of Hazardous Materials **420**, 126619 (2021c).

Y. Hassan Loni, K. David, S. Ribet, P. Lach, C. Lerouge, B. Madé, C. Bailly, B. Grambow, G. Montavon **Investigation of europium retention on Callovo-Oxfordian clay rock (France) by laser ablation**

inductively coupled plasma mass spectrometry (LA-ICP-MS) and percolation experiments in microcells. Applied Clay Science, **214**, 106280 (2021)

M. Del Néro , G. Montavon **Les radionucléides dans l'environnement: enjeux sociétaux et défis scientifiques** Actualité Chimique, N°460-461 (2021)

M. Boudias, A. Gourgiotis, G. Montavon, C. Cazala, V. Pichon, N. Delaunay, **^{226}Ra and ^{137}Cs determination by inductively coupled plasma mass spectrometry: state of the art and perspectives including sample pretreatment and separation steps.** Journal of Environmental Radioactivity, **244-245**, 106812 (2022)

Z. Zhang, P.Y. Gao, G. Montavon, Z.Y. Chen, D.Q. Wang, Z.Y. Tan, Q. Jin,W.S. Wu,J. Wang, Z.J. Guo, **Strengthened erosion resistance of compacted bentonite by layered double hydroxide: A new electrostatic interaction-based approach** Chemosphere, **292**, 133402 (2022)

G. Montavon, S. Ribet, Y. Hassan Loni, F. Maia, C. Bailly, K. David, C. Lerouge, B. Madé, J.C. Robinet and B. Grambow **Uranium retention in a Callovo-Oxfordian clay rock formation: from laboratory-based models to *in natura* conditions**, Chemosphere, **299**, 134307 (2022)

L.A. Baker, D.G. Biron, A. Beauger, S. Kolovi, J. Colombet, E. Allain, O. Voldoire, V. Breton, P. Chardon, T. Sime-Ngando, K. David, G. Montavon, H. Michel and A. S. Pradeep Ram **Virus-to-prokaryote ratio in spring waters along a gradient of natural radioactivity** Hydrobiologia, **850**, 1109–1121 (2023a)

S. Grangeon, C. Roux, C. Lerouge, P. Chardon, R. Beuzeval, G. Montavon, F. Claret, T. Grangeon **Geochemical and mineralogical characterization of streams and wetlands downstream a former uranium mine (Rophin, France)**, Applied Geochemistry, **150**, 105586 (2023)

S. Ribet, F. Maia, C. Bailly, B. Madé, B. Grambow, G. Montavon **Temperature effect of U(VI) retention in the Callovo-Oxfordian clay rock formation** Applied Clay Science, **238** 106925 (2023)

L.A. Baker, A. Beauger, S. Kolovi, O. Voldoire, E. Allain, V. Breton, P. Chardon, D. Miallier, C. Bailly, G. Montavon, A. Bouchez, F. Rimet, C. Chardon, V. Vasselon, L. Ector, C. E. Wetzel, D. G. Biron **Diatom DNA metabarcoding to assess the effect of natural radioactivity in mineral springs on ASV of benthic diatom communities** Science of the Total Environment, **973**, 162270 (2023b)

G. Montavon, S. Ribet,C. Bailly, Y. Hassan Loni B. Madé,B. Grambow, **U(VI) retention in compact Callovo-Oxfordian clay stone at temperature (20-80 °C); What is the applicability of adsorption models?** Applied Clay Science, **244** 107093 (2023)

Mohaman, Hamissou; Happel, Steffen; Montavon, Gilles; Galland, Nicolas **Tailoring an efficient computational methodology for studying ligand interactions with heavy radiometals in solution: the case of radium** New Journal of Chemistry, **47** 12914-12925 (2023)

Kolovi, S; Fois, GR; Lanouar, S; Chardon, P; Miallier, D; Baker, LA; Bailly, C; Beauger, A; Biron, DG; David, K; Montavon, G; Pilleyre, T; Schoefs, B; Breton, V; Maigne, L **Assessing the chronic effect of the bioavailable fractions of radionuclides and heavy metals on stream microbial communities: A case study at the Rophin mining site** Plos One, 18 (2024)

Mallet, C; Rossi, F; Hassan-Loni, Y; Holub, G; Thi-Hong-Hanh, L; Diez, O; Michel, H; Sergeant, C; Kolovi, S; Chardon, P; Montavon, G **Assessing the chronic effect of the bioavailable fractions of radionuclides and heavy metals on stream microbial communities: A case study at the Rophin mining site** Science of the Total Environment, **919** 170692 (2024)

Tingting Geng, Arnaud Mangeret, Olivier Peron, David Suhard, Josselin Gorny, Louise Darricau, Mathieu Le Coz, Nicolas Ait-ouabbas, Karine David, Christophe Debayle, Pascale Blanchart, Gilles Montavon,

Alkiviadis Gourgiotis. **Combining isotopic tracers and U-238 radioactive disequilibrium to identify the origin of radioactive materials and their transport processes downstream of a former U mine site** Journal of Hazardous Materials, in revision

Yihua He, Vladyslav Sushko, René Hübner, Harald Foerstendorf, Robin Steudtner, Johannes Raff, Clarisse Mallet, Anne-Hélène Le Jeune, Aude Beauger, Vincent Breton, Olivier Peron, Susanne Sachs, thorsten Stumpf, Gilles Montavon **Interaction of uranium(VI) with diatoms: a multi-scale study**, Environmental Science and Pollution Research, in review (2024a)

Yihua He, Sean Ting-Shyang Weib, Sindy Klugeb, Katrin Flemming, Vladyslav Sushkob, René Hübnerc, Robin Steudtnerb, Johannes Raff, Clarisse Mallet, Aude Beauger, Vincent Breton, Olivier Péron, Thorsten Stumpf, Susanne Sachs, Gilles Montavon **Investigating the Interaction of Uranium(VI) with Diatoms and Their Bacterial Community: A Microscopic and Spectroscopic Study** Ecotoxicology and Environmental Safety, in review (2024b)

Marine Boudias, Anne-Laure Nivesse, Josselin Gorny, Alexandre Quémet, Nathalie Delaunay, Gilles Montavon, Catherine Landesman, Alkiviadis Gourgiotis **Microvolume analysis of ^{226}Ra by inductively coupled plasma mass spectrometry: environmental applications to high-resolution profile of wetland soil pore waters** Microchemical Journal, in revision (2024).

Research activity report for the "Radionuclides & Health" theme (2019-2024)

a. Introduction

Radiopharmaceuticals transport a radioactive isotope to the action site, such as cancerous tissue or for neurologic diseases, either to image the tissue or to deposit a dose of ionizing radiation to kill the diseased cells. To this aim, radiopharmaceuticals are compounds that deliver an isotope in the action site for imaging, therapeutic and recently for theranostic purposes. The "theranostic" approach is simply described as the concept of Therapy guided by Diagnostics. An ultimate personalized medicine theranostic system for cancer could first diagnose the type of cancer class, image the heterogeneity of the tumor, apply a tailored treatment based on the diagnostic and imaging results and finally monitor the treatment efficacy. One axis is to develop innovative theranostics radionuclides from the production up to preclinical evaluation. A key player in theranostics is nanotechnology. Utilizing particles at the nanoscale level provides numerous advantages in diagnostics and treatment. The second axis of the research deals with nanodrug and especially with the development of analytical tools to specifically monitor the integrity of the radiolabelled scaffolds. Finally, metastasis is one of the major reasons for recurrence and consequent mortality in cancer and thus there is an unmet need to specifically target and cure residual disease. The short ranges of Auger electrons of less than a cell diameter makes it theoretically possible to effectively irradiate targeted cells, while largely sparing surrounding healthy tissues. Recent developments of the team have been made on Auger electron emitters and understanding the speciation of the chemical elements is of utmost importance.

b. Research subjets

i. Scandium theranostic nuclides

Among true theranostic pairs considered Scandium radionuclides are developed from the production, the separative / speciation techniques used to understand/ quantify the chelation and with applications in breast cancer, osteosarcoma and more recently for Alzheimer disease. ^{44}Sc-radiopharmaceuticals are gaining more interest but still lack availability. The proof of principle of a ^{44}Ti/^{44}Sc generator, which can produce ^{44}Sc daily, has been established but with some limitations and drawbacks. Despite recent advances, separation of ^{44}Ti from massive quantities of scandium target material is still cumbersome. In this work, the improved radiochemical separation of ^{44}Ti from residual scandium target material was carried out. The expertise acquired on previous work on ^{44m}Sc/^{44}Sc allowed to be invited for 6 months in 2018 to the Brookhaven National Lab (USA) to develop a ^{44}Ti/^{44}Sc generator and to obtain a Fulbright prize (2019, S. Huclier). A patent has been filed with SATT Ouest Valorisation for the work on the ^{44}Ti/^{44}Sc generator. Progress are still ongoing in order to recycle the ^{44}Ti ($t_{1/2}$ = 60 y), to have additional steps suitable with peptides/ antibodies and to process with automation (microfluidic device). This work has been published in journals of high impact factor and high impact in the field. We have also developed scandium probes with polysaccharides, antibodies or peptides in order to engage the community by providing pre-clinical data.

ii. Auger emitters

The most challenging task for establishing a ^{103}Ru/^{103m}Rh generator for Auger therapy, is to reach an effective separation between the two radionuclides because of the highly unpredictable, very complicated and poorly understood chemistry. The use of ^{103}Ru as parent material to establish such generator for nuclear medicine purpose, has been avoided in the past years because the chemical behavior of Ru is infamous due to its many valence states, the presence of colloidal species, etc …. In this frame, we aim to strongly adsorb Ruthenium on the chromatographic column while eluting its decay daughter from transient equilibrium, i.e., Rhodium. HCl medium is chosen to avoid the presence of nitrates during the radiopharmaceutical's development (nitrates at high concentrations are not suitable / injectable such as in living organisms). In HCl, this work was able to evidence the formation of Ru colloids, no polynuclear specie of ruthenium-chloride was observed, and the starting material of Ru, time and temperature have a strong influence on its speciation. This work has evidenced that it is fully possible to control the speciation of Ruthenium, especially Ru(IV), within a mononuclear species; that is a huge step forward compared to literature. This work has been started recently but has been already published and lead to already quite many presentations in international conferences of the field.

iii. Astatine

The Astate project is carried out within the framework of the labex IRON and has been supported by two ANR projects. The work conducted at the Nantes site for almost 20 years in fundamental chemistry, coupling molecular modeling and experimental radiochemistry (Subatech/CEISAM), as well as the development of innovative radiolabeling protocols (CRCINA), has been reviewed in "Account of Chemical Research" (Guerard et al., 2021). During the period 2019-2023, we notably finalized the Pourbaix diagram of astatine in the water stability domain (Liu et al., 2022). After the identification of halogen bonding with astatine compounds (Guo et al., 2018), we continued to explore the nature of this bond (Sarr et al., 2020, 2021a and b, Liu et al., 2020, 2021), and this bond could be the cause of the instability problem of astatine-labeled molecules in vivo (Yssartier et al., 2024). This result opens up new radiolabeling opportunities.

iv. Nanomedicine

In the past decade, we have done some work on nanohydrogel for MRI, multimodal gadolinium-based nanoparticle contrast agents, on holmium-based microparticles envisaged to be used in radiotherapy. We have been in partnership with the Laboratoire National d'Essais (LNE), a reference in metrology, to participate in a European project MetrIno (Metrology of Innovative Nanotherapeutics). The aim is to develop and validate methods for characterizing nanomedicines, especially by the means of Field and Flow-based Fractionation techniques. This project focuses also on clinical formulations, including synthetic lipid-based nanoparticles (liposomes and LNP-RNA) and metal oxides (hafnium and iron oxides) used in MRI imaging.

We aim to develop tracers based on theranostic NP nanoparticles for the early diagnosis, prognosis and monitoring of the evolution of prostate cancer (PCa). To this end, ^{177}Lu ($T_{1/2}$ = 6.7 j) is the ideal RN for theranostics, with an β^- emission of 498.3 keV for treatment and multiple photon γ of 208 keV (11%) and 113 keV (6.4%), which are used for diagnostic assessment and dosimetry. The development of various positron emission tomography (PET) imaging probes using ^{44g}Sc ($T_{1/2}$ = 3.97 h, E_{β}+ = 632 keV (94.27%)) and ^{64}Cu ($T_{1/2}$ = 12.7 h; E_{β}+ = 657 keV (19%)) which are ideal RNs for PET will improve the diagnosis of PCa as a diagnostic companion probe.

<u>Highlight:</u>

The research activities carried out around the theme 'RN and Health Applications' have developed within the framework of a wide network of national and international collaborations and partnerships. At the national level, the work is part of La Ligue's projects. At the international level, the group actively participates in the European I²PAD project for scandium applications in neurology, in the PHC project with Greece, in the international consortium led by ISite involving (Triumf, Canada; University of Wisconsin, University of Alabama ... in the USA).

Within the framework of this theme, a network of partners has been set up and includes renowned institutions such as the IRSET in Rennes, the Inserm iBrain in Tours and the CEA (Paris and Grenoble), the PSI (Switzerland), the Polatom (Poland), the University of Prague (Rep. Czech), Horia Hulubei National Institute for Physics and Nuclear Engineering (Romania), etc.

The work carried out by the CRCINA (radiolabeling chemistry), CEISAM (molecular modeling), and Subatech (experimental radiochemistry) consortium has served as the basis for the "ERC Consolidator Grant" project SAt Radio (Stable 211 At labeled radiopharmaceuticals for targeted α therapy), led by F. Guerard (CRCINA, 2023-2028). Subatech is involved in two actions: one related to exploring the complexation chemistry of astatine (+I, +3), a subject on which the Subatech/CEISAM consortium has been working for many years (e.g. Bassal et al., 2020), and the other associated with exploring a species with an oxidation state of (+V), AtO_3^-, proposed in the 1960s, which would exist in highly oxidizing environments (in the domain of water instability).

Publications

- Scandium

J. Muñoz-Garcia, M. Mazza, C. Alliot, C. Sinquin, S. Colliec-Jouault, D. Heyman and S. Huclier-Markai. Antiproliferative properties of scandium exopolysaccharide complexes on several cancer cell lines. *Mar. Drugs* **2021**, *19*(3), 17.doi.org/10.3390/md19030174

- Astatine

F. Guérard, C. Mainguenau, L. Liu, R. Eychenne, J.F. Gestin, G. Montavon, and N. Galland Advances in the Chemistry of Astatine and Implications for the Development of Radiopharmaceuticals Acc. Chem. Res. **2021**, 54, 16, 3264.

- Auger emitters

M.Thery, C.Alliot, S. Huclier-Markai. Recent progress in Ruthenium chemistry for establishing a 103Ru/103mRh generator for Auger therapy. Accepted for publication in J. Radioanal. Nucl. Chem, **2024. In press**

- Nanomedecine

S. Huclier-Markai, C. Alliot and S. Battu. Nanoparticles in radiopharmaceuticals sciences – A review of the characterization techniques and futures challenges. *J. Mat. NanoSci.* ***2020***, 7(2), 36-61. URN:NBN:sciencein.jmns.2020v7.134

Innovation

Patent No 20306383.9 – 1212 : A method for the generation of Scandium-44 (déposé 2021 – publié 2023).

Responsabilities

- Teaching

    - Responsible of Master 2 Physics –Ionising Radiations and Medical Applications (RIA) that prepares to the national contest DQPRM (medical physicist)
- Elected President of Groupe Francophone de Fractionnement Flux Force G4F (S. Huclier)
- Elected Membre of Steering Board Association Francophone des Sciences Séparatives AFSEP (S. Huclier)
- Organization of the conference '24th International Symposium of Radiopharmaceutical Sciences' à Nantes (program chair S. Huclier)
- Organization of the conference de '23rd International Symposium of Field and Flow-based separation techniques' (co-chair S. Huclier)
- Elected Membre of Comité National des Universités section 31 (S. Huclier)
- Member of the editorial board -Frontiers in Chemistry, Analytical Chemistry (IF = 5.221); Frontiers in Medicine, Nuclear Medicine (IF = 5.058) (S. Huclier)

Research

- Scientific Day of Université de Nantes, 3 June 2022, 50 attendees. – Role: chairman «Health in FFF»
- Scientific Day of Nantes Université, 5 Juin 2023, 60 attendees. – Role: co-chairman «Les macromolécules et nanoparticules en environnement-alimentation-santé : de la préparation d'échantillons à leur analyse» In collaboration with club de chromatographie de l'ouest.
- PI of **Partenariat Hubert Curien** France-Grèce (2023-2025)
- PI of **international consortium** on Scandium radiopharmaceuticals (project Isite NeXT -2019-2024)
- National Coordinator of a **GdR** CNRS axis Agents d'Imagerie Moléculaire (AIM), axis 3 « nuclear probes » (2018-2021), now called thematic network renewed (2023-2027)
- Scientific Board (TRANSFORMED Cluster)

Editions + Invitations Lectures

Invited Speaker

S. Huclier " The challenge of "nanotheranostic" in nuclear medicine", First Indo-French symposium on Molecules and Nanosciences for Health, 7 -9 novembre **2022**, Bordeaux, France.

S. Huclier " Speciation of Ru through AF4-MALS and LDI-TOF", 22nd International Symposium on Field- and Flow-based Separations, 11-14 Septembre **2022**, Riverside, USA.

Invited Lecture

S. Huclier " Nanomedicine for Nuclear Imaging and drug delivery: what needs of characterization for what challenges?", 22 Novembre **2019**, Colorado Schools of Mines, Golden-Colorado, USA.

Guest Scientist

2024: Medical Cyclotron David Geffen School of Medicine – University of California Los Angeles (USA)

2020 New York State University at Stony Brook (USA)

2018 Brookhaven National Laboratory (BNL) on Medical Isotope Research and Production (MIRP) program – Upton, NY (USA)

Communications

- Press on iSRS2022

Awards

- Fulbright Award (2019-2020) (S. Huclier)

Expertise internationale et nationale

- Expert Member of ISO /TC 229 (depuis 2014)
- Evaluator for Natural Sciences and Engineering Research Council of Canada – Government of Canada (2023)
- Expert for Hull University (UK) (2023)
- Evaluator for Swiss National Science Fundation (SNSF) (2023)
- Scientific Expert for École polytechnique fédérale de Zurich (ETHZ) (2022)
- Evaluator for ANR (2015,-16,-17,-23)
- Scientific Expert for Comité Consultatif Régional de la Recherche et du Développement Technologique (CCRRDT) de Nouvelle Aquitaine (2018 et 2024).

PUBLICATIONS (2019-2024)

S. Huclier- Markai, E. Ntsiba, E. Thomas., C Alliot, C.S. Cutler, F. Lux, and O. Tillement. Multimodal AguiX® Nanoparticles : Size Characterization by HF5 and optimization of the radiolabeling with various SPECT/PET/theranostic tracers. *International Journal of Nano Medical Research, **2019**,* 6 (1), 027. DOI: 10.23937/2378-3664.1410027

J. Barbet and S. Huclier-Markai. Equilibrium, affinity, dissociation constants, IC5O: facts and fantasies *Pharm. Stat.* **2019**, 18(5):513-525. DOI: 10.1002/pst.1943

S. Huclier-Markai, C. Alliot and S. Battu. Nanoparticles in radiopharmaceuticals sciences – A review of the characterization techniques and futures challenges. *J. Mat. NanoSci. **2020***, 7(2), 36-61. URN:NBN:sciencein.jmns.2020v7.134

Serigne Sarr, Jérôme Graton, Gilles Montavon, Julien Pilmé, and Nicolas Galland. On the Interplay Between Charge-Shift Bonding and Halogen Bonding, Chem. Phys. Chem., **2020**, 21, 240-250.

L. Liu, N. Guo, J. Champion, J. Graton, G. Montavon, N. Galland, R. Maurice. Towards a Stronger Halogen Bond Involving Astatine: Unexpected Adduct with Bu3PO Stabilized by Hydrogen Bonding CHEMISTRY-A EUROPEAN JOURNAL, **2020**, 26, 3713-3717.

Fadel Bassal, Julie Champion, Sylvain Pardoue, Mahamadou Seydou, Andrea Sabatié-Gogova, David Deniaud, Jean-Yves Le Questel, Gilles Montavon*, and Nicolas Galland Questioning the Affinity of Electrophilic Astatine for Sulfur-containing Compounds: Unexpected Bindings Revealed Inorganic Chemistry**, 2020**, 59, 13923-13932 .

S. Huclier-Markai, Mattia Mazza, C. Alliot, and P.E. Reiller. Luminescence spectroscopic investigations of Europium (III) complexation with exopolysaccharides from a marine bacterium. Dalton Trans., **2021,** 50, 17215-17227. DOI: 10.1039/D1DT03288G

R. Mikolajczak, S. Huclier-Markai, C. Alliot, F. Haddad, D. Szikra, V. Forgacs, P. Garnuszek. Production of Scandium radionuclides for theranostic applications. Towards standardization of quality requirements. *Eur. J. Nucl. Med. Mol. Imag. Radiopharmacy and Chemistry*, **2021**, 6 (19). DOI : 10.1186/s41181-021-00131-2

J. Muñoz-Garcia, M. Mazza, C. Alliot, C. Sinquin, S. Colliec-Jouault, D. Heyman and S. Huclier-Markai. Antiproliferative properties of scandium exopolysaccharide complexes on several cancer cell lines. *Mar. Drugs* **2021**, *19*(3), 17. doi.org/10.3390/md19030174

M.Mazza, C. Alliot, C. Sinquin, P.E. Reiller and S. Huclier-Markai. Marine exopolysaccharide complexed with Scandium aimed as theranostic agents. *Molecules*, **2021**, 26 (4), 1143. DOI: 10.3390/molecules26041143

Serigne Sarr, Julien Pilmé, Gilles Montavon, Jean-Yves Le Questel and Nicolas Galland Astatine Facing Janus: Halogen Bonding vs. Charge-Shift Bonding. Molecules **2021**, 26 (15):4568. doi: 10.3390/molecules26154568.**.**

Serigne Sarr, Jerome Graton, Seyfeddine Rahali, Gilles Montavon and Nicolas Galland Delocalized relativistic effects, from the viewpoint of halogen bonding Phys. Chem. Chem. Phys., **2021**, 23, 4064.

François Guérard, Clémence Maingueneau, Lu Liu, Romain Eychenne, Jean-François Gestin, Gilles Montavon, and Nicolas Galland Advances in the Chemistry of Astatine and Implications for the Development of Radiopharmaceuticals Acc. Chem. Res. **2021**, 54, 16, 3264.

Lu Liu, Seyfeddine Rahali, Rémi Maurice, Cecilia Gomez Pech, Gilles Montavon, Jean-Yves Le Questel, Jérome Graton, Julie Champion, Nicolas Galland An expanded halogen bonding scale using astatine Chemical Science, **2021**, 12, 10855.

A. Younes, J.S. Ali, A. Duda, C. Alliot, S. Huclier, J. Wang, F. Kabalan, M.T. Nur, M. Cao, D. Nemirovsky, R. Deng, C.M. Drain, S. Alexandratos. The Uptake and Removal of Uranium by and from Human Teeth. *Chem. Res. Toxicol*., **2021**, 34, 3, 880–891. DOI: 10.1021/acs.chemrestox.0c00503

Lu Liu, Rémi Maurice, Nicolas Galland, Philippe Moisy, Julie Champion Gilles Montavon Pourbaix Diagram of Astatine Revisited : Experimental Investigations, Inorganic Chemistry, **61**, 13462 (2022)

G. Lespes, S. Huclier, S. Battu, A. Rolland-Sabaté. Field flow Fractionation (FFF): practical and experimental aspects. In Particle Separation Techniques: Fundamentals, Instrumentation, and Selected Applications. Handbooks in Separation Science. ISBN: 9780323854863. C. Contado, **2022**, Elsevier Science.

J. Ali, T. Tane, D. Hossain, J. Wang, S. Groveman, J. Samson, F. Kabalan, S. Huclier-Markai, A. Kawamura, S. Alexandratos, A. Younes. Selectivity and Affinity of Heavy Metals and Radiometals for Organic Biomass: Implications for Water Remediation Sep. Sci. Technol. **2023**, 58,9, 1703-1717. DOI: 10.1080/01496395.2023.2208282

S. Huclier, F. Haddad. Patent No 20306383.9 – 1212 : A method for the generation of Scandium-44 (2023)

Yssartier, T; Liu, L; Pardoue, S; Le Questel, JY; Géurard, F; Montavon, G; Galland, N In vivo stability of 211At-radiopharmaceuticals: on the impact of halogen bond formation RSC MEDICINAL CHEMISTRY, **2024**, 15 1 223-233.

M.Thery, C.Alliot, S. Huclier-Markai. Recent progress in Ruthenium chemistry for establishing a 103Ru/103mRh generator for Auger therapy. Accepted for publication in J. Radioanal. Nucl. Chem, **2024**.

S. Huclier-Markai, D.G. Medvedev, C.S. Cutler. Improved titanium-44 purification process for establishing a high apparent molar activity Titanium-44/Scandium-44 generator. Submitted to *Appl. Rad. Isot.* **2024**.

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Research activity report for the "Radiation Chemistry" theme (2019-2024)

a. Introduction

Radiation Chemistry is defined by all the chemical reactions which occur under irradiation (named radiolytic effects). All projects described here aim to enhance the understanding of these reactions and the radiolytic yields determination of species (production and/or consumption/degradation). Indeed, our 15 years experience in radiolysis as a fundamental research support applications in line with Subatech research main lines : nuclear for energy and nuclear for health. The Radiation Chemistry, as a transdisciplinary science, can be divided in 5 applications that are interdependent (see **Figure 1**): (1) Radiolysis for Nuclear Fuel Cycle (Pu, Np and SuperPlasticizer), (2) Radiolysis for New Energies (H_2), (3) Radiolysis for Earth Science and Life Origins (Organic Acids), (4) Alpha-Radiolysis in new RIT Radionuclide Production Processes, (5) Radiolysis in Emerging FLASH Radiotherapy. Main irradiation tools used in these projects is the ARRONAX Cyclotron facility which provides Proton, Helium ion beams and where is installed gamma source. With this large energy particle scale (from 0.66 to 68 MeV) all chemical systems can be studied for many different applications: mainly Energy (Nuclear Fuel Cycle) and Health (Radiotherapy) consistently with SUBATECH topics.

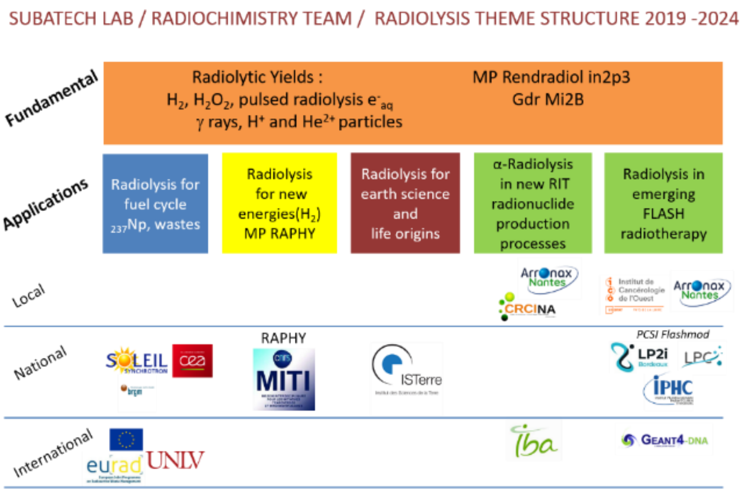

Figure 1. Radiation Chemistry Scientific Projects.

b. Scientific projects

(1) Radiolysis for Nuclear Fuel Cycle

(1.1) Np Chemistry in alkaline media (HAVL) [1]

The international collaboration (UNLV, IPNO, SOLEIL, CEA and SUBATECH) set down around the Tc speciation [2-5] under irradiation has been fruitfully developed for the new Actinide speciation study: Neptunium. A PhD started in October 2018 which deals with the Np radiolytic behavior in alkaline media in the nuclear waste case. The key topics of Np speciation in solution at pH 9, and Np^{V}oxides solubility must be addressed under alpha irradiation emitted by the nuclear wastes. The presence of radionuclides in the package leads to the radiolysis phenomenon, inducing the production of radicals and molecular species. Water and these newly formed species can interact with actinides and thus change their chemical behavior (speciation, hydrolysis, complexation …). In this context, the goal of this research is to study fundamentally the impact of radiation (α and γ) on Np chemistry, especially in an alkali medium. Np speciation under gamma and alpha radiation has been explored using acquired NIR spectroscopy datas and EXAFS studies. This PhD has been successfully defended, bringing some new features to the only few articles in the literature.

(1.2) Pu Chemistry in Nitric media (HAVL) [6]

In PUREX chemical process, high concentrations of nitric acid are exposed to high radioactivity levels due to α-emitters, especially Pu and Np. It is the key topic studied by the long-time collaboration (10 years) between SUBATECH and CEA (DEN/DRCP). Based on these extensive studies performed onto the nitric acid radiolytic behaviour in the PUREX retreatment process [7-10] ; our partners at CEA initiated a study on Pu chemistry in these specific chemical conditions. A PhD in collaboration with SUBATECH, started in October 2018, has been dedicated to this subject. The radiolytic yields of molecular hydrogen, hydrogen peroxide, nitrous acid and nitrous oxide from alpha radiolysis of nitric acid solutions containing plutonium have been experimentally investigated. The results have shown that the yields of radiolytic products depends on the nitric acid concentration as well as the oxidation state of plutonium. While radiolytic yields from plutonium(IV) nitric acid solutions have been previously investigated, this study provide radiolytic yields from alpha radiolysis of plutonium(III) and plutonium(VI) nitric acid solutions for molecular hydrogen, nitrous acid and nitrous oxide. These information provide insight into the role played by plutonium redox behaviour on the formation of radiolytic products.

(1.3) SuperPlasticizers in alkaline media (MAVL) [11]

In continuation of the studies on carboxylate ions radiolytic behaviour [12] described, SUBATECH through its radiochemistry group got involved into the European CORI project (Cement-Organic-Radionuclides-Interaction) lead by KIT within the EURAD (European Joint Programme on Radioactive Waste Management). The first task, leaded by SUBATECH and ANDRA, is called “Organics Degradation”. Its focus is on the characterization of soluble organic species generated by radiolytic and hydrolytic degradation of selected organics (PVC, cellulose, resins, superplasticizers). Studies could also include the analysis of degradation/stability of small organic molecules such as carboxylic acids and determination of degradation rates. Then, SUBATECH applied its knowledge about the carboxylate ions chemistry under irradiation to the alkaline media in the CORI scientific scope in particular to a superplasticizer such as PolyCarboxylateEther. The results show the high dihydrogen gas production during the few days gamma irradiation of PCE and the second one is the identification of the degradation products of PCE (formate, acetate, oxalate) and G-yield associated to these measurements [11].

(2) Radiolysis for New Energies (H_2) (RAPHY/MITI) [13]

The Team has a long time experience about the H_2 produced by water radiolysis [6, 12, 14-17]. Then, we can apply these works to propose an original use of nuclear wastes. They may not be considered as unusable materials in the sense that they deliver a free source of energy under the form of ionizing radiations that can be used to produce hydrogen (H_2) through water radiolysis. The current paradigm that defines these nuclear wastes as troublesome by-products which no one uses nowadays must be shifted into a new opportunity for pure H_2 production with no CO_2 emission. Here, we proposed a low-tech method to boost H_2 production by water radiolysis thanks to the catalytic effect of a suspension of TiO_2 nano-particles. We also demonstrated the relevance of this concept by scaling up our laboratory results[1]. From our calculations, this radiocatalytic process can supply until 60% of the actual global demand in hydrogen (42.9 $MtH_2.y^{-1}$) and open the door, with the green and white hydrogen productions, to the "Hydrogen century".

(3) Radiolysis for Earth Science and Life Origins (Organic Acids) [18]

As for the Tc example described in previous study showing the role of carbonate radiolysis onto Tc chemistry, we developed studies on the role of radiolytic by-products of carbonate on the media chemistry. That is the reason why, we have developed one project which deals with the carbonate medium irradiation and its radiolytic species (produced/degraded). Samples of calcite−water biphasic media, considered as one component of concrete carbonation (used in waste repositories), have been irradiated. Finally, ionic chromatography experiments with irradiated solutions allowed us to quantify the organic anions (formate $HCOO^-$, acetate CH_3COO^-, and oxalate $C_2O_4^{2-}$) formed by calcite and/or carbonate ion radiolysis and study the variation of calcium carbonate solubility under irradiation [12]. In collaboration with ISTERRE (INSU), we have shown that these low molecular weight carboxylate anions have played an important role in supporting deep subsurface microbial ecosystems. Their origin whether biological or abiotic is currently highly debated, but surprisingly, radiolytic production has rarely been considered, as it is the case for H_2. Here, we have addressed this question through dedicated irradiation experiments. Carbonate degradation occurs through three consecutive steps (Carbonate $\overset{I}{\rightarrow}$ Formate $\overset{II}{\rightarrow}$ Acetate $\overset{III}{\rightarrow}$ Oxalate) involving formate radical ($CO_2^{-\bullet}$), dihydrogen (H_2), and carbon dioxide (CO_2) generation. Dissolved carbonate radiolysis provides a consistent pathway for both enhancing two-fold the radiolytic H_2 production compared to pure water and generating carboxylic species, chiefly oxalate, readily available for microbes. Radiation-induced carbonate degradation may produce substantial amount (millimolar concentration) of carboxylate anions in ancient groundwaters from deep crystalline bedrocks. Subsurface lithoautotrophic microbial ecosystems may not only be supported by radiolytic H_2 but also by carboxylate species from carbonate radiolysis. Carbonate radiolysis can be also an endogenous source of carboxylate species on Mars and other planetary bodies [18].

(4) Alpha-Radiolysis in new RIT Radionuclide Production Processes [19]

Since years is developed in the Nantes area a collaborative and translational research networks about α-RIT (CPER Arronax+, IDEX Transformed, …). Targeted immunotherapy is a kind of radiotherapy allowing bringing the radionuclide close to the cancer cells. The 211-At alpha emitters, suitable for little and scattered tumours care, are produced by the Arronax cyclotron facility and then coupled to vectors/antibodies and finally used for radiolabelling and clinical trials by our CRCINA partner. With CRCINA (Nantes University/INSERM) we have dealed with the impact of chloroform radiolysis on astatine chemistry. Yet, the production of ^{211}At based radiopharmaceuticals is often complicated by radiolysis due to its own decay onto its production/storage media, leading to solvent degradation and then impacting astatine chemical state and radiolabeling efficiency. A better understanding of the radiolysis phenomenon is thus necessary. Two experiments have been performed: (1) pH measurement during the At extraction in chloroform medium, (2) pH determination calculated from the HCl chemical yield which is obtained during the radiolysis of chloroform medium by γ-ray. In both cases, the pH values are determined at 2.0 ± 0.5. Then, it is possible to predict the acidic conditions during the ^{211}At production by HCl radiolytic yield determination. This work demonstrated that the radiolysis induced by At during its production in $CHCl_3$ medium should be taken into account as it has a significant effect on acid-basic conditions. The work helps understanding the mechanisms of production of a major impurity generated from ^{211}At radiolysis in chloroform which alters its

[1] Déclaration d'Invention, DV4478

radiochemistry, allowing for the identification of solutions to counteract these unwanted effects These corrective actions are now daily used during the chemical extraction process of ^{211}At.

(5) Radiolysis in Emerging FLASH Radiotherapy (GdR Mi2B) [20-24]

FLASH is a promising external radiotherapy modality that spares healthy tissues while tumor efficiency is kept by mean of Ultra High Dose Rate(UHDR) beams. Last ten years, many studies have been carried out [25, 26]. However, the global mechanism from physics to biology is still to be discovered, in major the chemistry mechanism step. Indeed, even if several relevant hypotheses have been proposed, such as oxygen depletion and reactive oxygen species (ROS) contribution, a chemical mechanism linking beam physical parameters to biological consequences is still to be build. From the existing medical physic and biological collaboration leaded by G.Delpon's team in ICO-Nantes, we joined the granted FLASHMOD plan cancer project in 2021. Up to know, we bring our skill in pure water radiation chemistry to elucidate the specific mechanism of UHDR chemistry. The beam pulsing system developed by Arronax and initially dedicated to time resolved pulsed radiolysis experiment, became a powerful tool to finely tune the dose rate and the beam time structure. First joined experiments using Arronax pulsed beams leaded to the discover of the decrease in the G-value of H_2O_2 production under UHDR toward conventional dose rate(CONV) [21]. Further work is in progress. The fundamental PhD work in progress dealing with pulsed radiolysis and microsecond radiolytic yields determination of hydrated electron and radicals [27] already provide inputs to the Monte Carlo G4-DNA modelling consortium trough the LPC Clermont collaboration (L.Maigne) and LP2iB Bordeaux (H.Tran and S.Incerti). This translational approach from physics to chemistry and biology (V.Potiron, US2B, CNRS UMR 6286, Nantes University) makes Nantes an identified place for FLASH research, with submitted(European ANR with DKFZ Germany, Joao Seco joined with PRISMA team) or coming call and collaboration opportunities (European PIANO forte call-IRSN with PRSIMA team also, and IPHC Strasbourg Collab.)

c. Perspectives

Since Professor Massoud Fattahi retirement (2020), we managed to hold a high scientific production level with an only 2 permanent staff (Johan Vandenborre and Guillaume Blain), expecting a manpower reinforcement through a MCF recruitment to this rare but requested expertise inside and outside IN2P3. Despite of that, we unfortunately acknowledge that it won't be so. By consequences, J.Vandenborre move outside Subatech laboratory is expected within the coming year, with no expected future for the 1st, 2nd and 3rd axes. Since G.Delpon and and S.Chiavassa recently joined the PRISMA team of Subatech to develop FLASH RT research, a shift of G.Blain to this team in line with Subatech main line "nuclear for health" would be consistent, bringing through the 4th and 5th presented axes, a complementary applied radiation chemistry approach and support to existing topics of PRISMA : FLASH RT and Rami:Innovative RN for medicine. The more than 10 years of scientific and technic enhancement about the radiolytic key issues will be promoted in the future scientific project inside SUBATECH (FLASH one) and outside (Hydrogen one).

Scientific production (2020 – 2024)

- 11 publications [6, 13, 18-24, 28, 29] in high quality peer-reviewed journals + 2 Oral Invitation [30, 31] + 3 Vulgarization Conferences[2,3,4] + 2 Vulgarization articles[5, 6] +1 HDR [32] + 1 PhD Defense [1]
- 20 Oral and poster presentations at major international conferences (GeoKarlsruhe, FRPT)

[1]. Craff, E., *Interactions des espèces issues de la radiolyse du milieu eau/NaOH pH ≈ 9 avec le Np (+V) : Spéciation et Hydrolyse*, in *Ph.D.* **2023**, Université de Nantes: Nantes.

[2]. Ghalei, M., *Etude de la spéciation du Tc et de ses homologues Mn et Re sous irradiations γ et He2+ en milieu carbonate hautement concentré*, in *Ph.D.* **2015**, Université de Nantes: Nantes.

[3]. Ghalei, M., J. Ma, U. Schmidhammer, J. Vandenborre, M. Fattahi, and M. Mostafavi, *Picosecond Pulse Radiolysis of Highly Concentrated Carbonate Solutions*, The Journal of Physical Chemistry B, 120 (**2016**) 2434-2439.

[4]. Ghalei, M., J. Vandenborre, G. Blain, F. Haddad, M. Mostafavi, and M. Fattahi, *Oxidation and/or reduction of manganese species by γ-ray and He2+ particle irradiation in highly concentrated carbonate media*, Radiation Physics and Chemistry, 119 (**2016**) 142-150.

[5]. Ghalei, M., J. Vandenborre, F. Poineau, G. Blain, P.-L. Solari, J. Rôques, F. Haddad, and M. Fattahi, *Speciation of technetium in carbonate media under helium ions and γ radiation*, in *Radiochimica Acta*. **2019**. p. 105.

[6]. Perrin, B., L. Venault, E. Broussard, J. Vandenborre, G. Blain, M. Fattahi, and S. Nikitenko, *Influence of plutonium oxidation state on the formation of molecular hydrogen, nitrous acid and nitrous oxide from alpha radiolysis of nitric acid solution*, Radiochimica Acta, (**2022**).

[7]. Garaix, G., et al., *Alpha radiolysis of nitric acid and sodium nitrate with $^{4}He^{2+}$ beam of 13.5 MeV energy*, Radiation Physics and Chemistry, 106 (**2015**) 394-403.

[8]. Costagliola, A., et al., *Radiation chemical behavior of aqueous butanal oxime solutions irradiated with helium ion beams*, Radiation Physics and Chemistry, 119 (**2016**) 186-193.

[9]. Venault, L., G. Garaix, J. Vandenborre, and P. Moisy, *Radiolyse α des solutions aqueuses d'acide nitrique et de plutonium*, L'Actualité Chimique, 408-409 (**2016**) 106-108.

[10]. Costagliola, A., L. Venault, A. Deroche, J. Vermeulen, F. Duval, G. Blain, J. Vandenborre, M. Fattahi-Vanani, and N. Vigier, *Influence of Nitric Acid on the Helium Ion Radiolysis of Aqueous Butanal Oxime Solutions*, The Journal of Physical Chemistry A, 121 (**2017**) 5069-5078.

[11]. Altmaier, M., "Annual Report 2022-23/Institute for Nuclear Waste Disposal". ed. Accepted, 2024: KIT Scientific Publishing.

[12]. Costagliola, A., J. Vandenborre, G. Blain, V. Baty, F. Haddad, and M. Fattahi, *Radiolytic Dissolution of Calcite under Gamma and Helium Ion Irradiation*, The Journal of Physical Chemistry C, 121 (**2017**) 24548-24556.

[13]. Vandenborre, J., S. Guillonneau, G. Blain, F. Haddad, and L. Truche, *From nuclear waste to hydrogen production: From past consequences to future prospect*, International Journal of Hydrogen Energy, 64 (**2024**) 65-68.

[14]. Essehli, R., F. Crumière, G. Blain, J. Vandenborre, F. Pottier, B. Grambow, M. Fattahi, and M. Mostafavi, *H_2 production by γ and He ions water radiolysis, effect of presence TiO_2 nanoparticles*, International Journal of Hydrogen Energy, 36 (**2011**) 14342-14348.

[15]. Crumière, F., J. Vandenborre, R. Essehli, G. Blain, J. Barbet, and M. Fattahi, *LET Effects on the Hydrogen Production induced by the Radiolysis of pure Water*, Radiation Physics and Chemistry, 82 (**2013**) 74-79.

[16]. Crumière, F., J. Vandenborre, G. Blain, F. Haddad, and M. Fattahi, *Evolution of heavy ions (He2+, H+) radiolytic yield of molecular hydrogen vs. "Track-Segment" LET values*, Radiochimica Acta, 105 (**2017**) 487.

[17]. Crumière, F., *Etudes de l'effet des rayonnements ionisants sur l'eau : Rendements radiolytiques de l'hydrogène moléculaire*, in *Ph.D.* **2012**, Université de Nantes: Nantes.

[18]. Vandenborre, J., L. Truche, A. Costagliola, E. Craff, G. Blain, V. Baty, F. Haddad, and M. Fattahi, *Carboxylate anion generation in aqueous solution from carbonate radiolysis, a potential route for abiotic organic acid synthesis on Earth and beyond*, Earth And Planetary Science Letters, 564 (**2021**) 10 pp.

[19]. Ghalei, M., P.M. Khoshouei, J. Vandenborre, F. Guérard, G. Blain, M. Zarei, F. Haddad, and M. Fattahi, *How radiolysis impacts astatine speciation?*, Radiation Physics and Chemistry, (**2022**) 110224.

[20]. Blain, G., et al., *O049 - FLASH Mechanisms Track (Oral Presentations) UHDR PROTON BEAM VS. CONVENTIONAL: HYDROGEN PEROXIDE AS FLASH EFFECT SENSOR*, Physica Medica, 94 (**2022**) S31.

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[2] https://www.lanouvellerepublique.fr/indre/commune/valencay/valencay-osons-la-transition-avec-la-communaute-de-communes-ecueille-valencay , « Hydrogène : Futur ou Passé ?», Johan Vandenborre, Septembre 2023, Valençay.

[3] **Journée d'actualisation des connaissances scientifiques des enseignants du second degré -vendredi 16 juin 2023-Angers - Rectorat de Nantes** « La radiolyse : un beau potentiel », Guillaume BLAIN

[4] **Atelier scientifique à destination de Lycéen - Lycée Guist'hau – Nantes**. « La radioactivité pour la santé. »

[5] https://www.quantamagazine.org/radioactivity-may-fuel-life-deep-underground-and-inside-other-worlds-20210524/ (Quanta Magazine, US).

[6] https://lejournal.cnrs.fr/articles/la-radioactivite-naturelle-moteur-dune-vie-souterraine-insoupconnee (CNRS Journal)

[21]. Blain, G., et al., *Proton Irradiations at Ultra-High Dose Rate vs. Conventional Dose Rate: Strong Impact on Hydrogen Peroxide Yield*, Radiation Research, 198 (**2022**) 318-324.

[22]. Poirier, F., et al., *The Arronax platform for proton flash irradiation*, Physica Medica, 94 (**2022**) S105.

[23]. Saade, G., et al., *Ultra-high dose rate proton irradiation elicits reduced toxicity in zebrafish embryos*, Advances in Radiation Oncology, (**2022**) 101124.

[24]. Ghannam, Y., et al., *First evidence of in vivo effect of FLASH radiotherapy with helium ions in zebrafish embryos*, Radiotherapy and Oncology, 187 (**2023**) 109820.

[25]. Favaudon, V., et al., *Ultrahigh dose-rate FLASH irradiation increases the differential response between normal and tumor tissue in mice*, Science translational medicine, 6 (**2014**) 245ra93-245ra93.

[26]. Vozenin, M.C., J.H. Hendry, and C.L. Limoli, *Biological Benefits of Ultra-high Dose Rate FLASH Radiotherapy: Sleeping Beauty Awoken*, Clinical Oncology, 31 (**2019**) 407-415.

[27]. Sarra, T., *DETECTION ET QUANTIFICATION DES RADICAUX LIBRES RADIO-INDUITS PAR DES FAISCEAUX PULSES DE PARTICULES H+ ET He2+* in *Ph.D.* **2022-2025**, Nantes University: Nantes.

[28]. Zhang, H., T. Suzuki-Muresan, S. Gin, G. Blain, T. Sauvage, O. Wendling, J. Vandenborre, and A. Abdelouas, *Effects of vapor hydration and radiation on the leaching behavior of nuclear glass*, Journal of Nuclear Materials, 578 (**2023**) 154368.

[29]. Elidrissi-Moubtassim, S., et al., *Exploring radiation hardness of PEPITES, a new transparent charged particle beam profiler*, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 466 (**2020**) 8-11.

[30]. Vandenborre, J. and L. Truche, *Water radiolysis leads to a fun geochemistry*, in *2022 Goldschmidt Conference*. **2022**: Hawai, United States.

[31]. Blain, G., et al., *What can be known about the origins of FLASH effect from non-biological radiochemical data and measurements? - French Flashmod collaboration contribution*, in *UHDR Flash radiation Chemistry Symposium*. **2023**: University of Wisconsin-Madison - USA.

[32]. Vandenborre, J., *La Radiolyse : Quelle Utilité?*, in *HDR*. **2019**, Nantes Université: Nantes.

Research activity report for the "Modelling" theme (2019-2024)

a. Introduction

The application of classical and quantum atomistic computational modeling techniques to materials' simulations is primarily conducted in the framework of the industrial chair "Storage and Disposal of Radioactive Waste" funded at IMT Atlantique by ANDRA, ORANO, and EDF. The chair was last renewed in 2019 and is now expected to close at the end of 2024. This research is focused on the development of better quantitative atomistic understanding of hydrated clay-related and cement-related materials, their aqueous and non-aqueous interfaces, and on the adsorption and transport of various species (radionuclides, organic molecules, gases) in confined in nanopores of these materials. In 2019-2024 the following issues were identified as the most important and systematically addressed in our simulations:

1. Continuation of the ClayFF force field development and parametrization for classical molecular dynamics (MD) simulations.
2. Continuation of the more realistic model development for clayey and cementitious materials taking into account their natural compositional and structural disorder, such as interstratified illite/smectite (I/S) clay phases or C-S-H phases of cement with variable Ca/Si ratio to reflect the degree of cement degradation;
3. Quantitative investigation of the site-specific adsorption and transport of radionuclides at the surfaces of disordered clay-related and cement related materials.
4. Quantitative investigation of the effects of molecular gases (H_2, CO_2, CH_4,..) on the adsorption and transport of radionuclides in the above systems.
5. Quantitative investigation of the effects of organic matter (complexation) on the adsorption and transport of radionuclides in the above systems.
6. Quantification of the role of nanoparticle edges in the adsorption and transport in clay and cement systems.
7. Effects of temperature and other thermodynamic conditions on the above processes.
8. Molecular ordering of the effects of pH, acid-base equilibria, and proton transfer and other aspects of explicit chemical reactivity in the above systems.

The issues (1-3) have been principally addressed before 2019, but continued to be further developed in 2019-2024. In 2019-2024, our research was primarily focused on the issues (4-7), while the problems of reactivity (8) are only now coming to the forefront of our research.

It is necessary to mention that many or the issues listed above are equally important not only to the problems of radioactive waste disposal, but also to other problems of geochemistry, materials science, and environmental chemistry, such as geological carbon sequestration, mineral weathering, soil science, environmentally friendly exploration and exploitation of unconventional hydrocarbon resources (shale oil, shale gas…). Therefore, some of our research was additionally funded from the respective EU consortia or other forms of international collaboration. The results of all these projects for 2019-2024 are briefly presented below.

b. Improvements of the ClayFF force field and other methodological developments

The newly developed (2017-2019) parameterizations of the ClayFF force field for classical molecular modeling of the edges of clay particles and other similar materials is completely published [1]. These new Metal-O-H angle bending parameters for clay particle edges allow improving atomistic modeling of many other silicate materials, such as quartz, amorphous silica, glass, cement C-S-H, etc. and are already widely used in the numerous simulations. These new developments were summarized in the review paper [2], which was also featured on the cover of *The Journal of Physical Chemistry C*. The most common and useful approaches of applying the ClayFF parametrization in classical molecular simulations of clays and other nanoporous materials is also summarized in a textbook chapter [3]. All experimental and modeling approaches to the molecular-level understanding of metal ion retention in clays we also recently summarized in a high-visibility review paper [4] resulting from a large international collaboration. More recently, in collaboration with colleagues at the Canadian Nuclear Waste Management Organization and the Queen's University we have developed new parameters for Cu2+ ions in the clayey environment [5].

c. Organics and radionuclides in clay and cement materials

The detailed study of the molecular mechanisms of interactions in the three-component model system: Cement-Radionuclide-Organic additive has been completed in 2020 [6]. This work is now continued by the PhD project of Jakub Licko (2022-2025) with the focus on the effects of small organic molecules on the adsorption and transport of radionuclides (UO_2^{2+}, NpO_2^{2+}) in smectite clay with the objective to develop fundamental molecular scale understanding of the physical and chemical mechanisms controlling these interactions. In addition to the interactions with basal surfaces of clay, the interactions with clay nanoparticle edges will also be thoroughly quantitatively studied in the project.

d. Molecular gases (H_2, CO_2, CH_4,..) and their adsorption in clay nanopores

The properties of CO2 and CH4 in dry and hydrated clays in the context of nuclear waste storage and other environmental applications were extensively studied by our team in collaborations with colleagues in the US and UK during 2019-2024 [7-10]. A detailed quantitative characterization of the hydrophobic/hydrophilic nature of the clay surfaces is closely related to these studies and was conducted in collaboration with colleagues in Poland [11]. Over the last 3 years, the research focus has shifted to the investigation of H2 adsorption and transport in clays under saturated conditions [12,13]. This was the topic of the PhD thesis of Pinar Citli that was successfully defended in February 2024.

e. Quantitative modeling of the effects of clay particle edges

The adsorption and transport of metal ions and gas molecules at the edges of clay nanoparticles has been another focus of our intensive simulations [8, 10, 13] as well as collaboration with several groups of experimentalists [9, 14, 15]. In this context, *ab-initio* MD simulations of the carbonation reaction mechanisms at various crystal surfaces of portlandite nanoparticles [16] can be considered as our initial attempt to handle the issues of chemical reactivity.

f. Molecular mechanisms of nuclear waste glass corrosion and durability

Another important approach to incorporate the issues of chemical reactivity in our computational modeling research was used in in the *an-initio* and classical (ReaxFF) simulations of the atomistic-scale mechanisms of the corrosion and durability of nuclear waste glass [17]. This work was performed collaboration with colleagues at CEA Marcoule and was the topic of the PhD thesis of Kamalesh

Damodaran successfully defended in December 2022. Currently, the work of this collaboration is continued and extended by the PhD thesis of Sumit Tiwari "New insights into Monte Carlo simulation of borosilicate glass aqueous alteration: Influence of glass and solution compositions" (2022-2025). A.G.Kalinichev serves as a co-director de these for both of this projects. This is also a successful attempt to bring to the Radiochemistry groups at Subatech the significant expertise on the molecular simulations of glasses developed in CEA Marcoule for many years.

i. SAMMA - International laboratory for supercomputer atomistic modelling and multi-scale analysis

In 2017-2022 A.Kalinichev has served as an invited chief research fellow in this International Laboratory at the National Research University Higher School of Economics (Moscow, Russia). This collaboration was primarily focused on the atomistic simulations of cement related systems and has been extremely productive, resulting so far in 8 joint publications [18-25], one PhD thesis E.Tararushkin, successfully defended in November 2023) and one MS thesis (A.Glushak, 2024). It has also allowed us to approach, for the first time, the new issues of the molecular modeling of fluid flows in clay nanopores [22, 23]. The formal collaboration with this Russian institution is terminated in February 2022 with the start of the war in Ukraine, but informal contacts and collaborations with individual colleagues still continue and several high quality publications resulting from this collaboration are still in various stages of preparation.

j. Molecular modeling of nano-materials for geochemical and environmental applications (Nano-Geo-Materials)

This is the project with the Centre Informatique National de l'Enseignement Supérieur (CINES) that supports most of our team's computational needs at the level of 2-5 million CPU hours per year, equivalent to ~100-200 k€ annually). With the arrival of Dr. Sébastien Le Crom as our new team member, he is taking the leadership in this project.

k. Perspectives

In the perspective that the industrial chair "Radioactive Waste Storage and disposal" would not be further renewed beyond 2024, our focus in atomistic simulations is gradually shifting to other related projects.

1. The work on the interactions of H2 gas in different saturated and unsaturated clay and cement systems will continue for the problems of geological nuclear waste disposal. This work is thematically strongly linked with the new EURAD-GAS project and collaboration with colleagues at University of Grenoble Alpes. However, this work will be also extended to include other important technological applications, such as underground H2 gas storage.

2. Collaboration with US colleagues (Sandia National Labs, Michigan State University) on the development of the ClayFF force field will continue by potentially including the effects of chemical reactivity at the clay and cement particle edges. With the arrival of Sébastien Le Crom – an expert in the polarizable force field development and application (PIM) – we may venture into adding the effects of polarizability to the current version of ClayFF.

3. A new MD-simulation project to quantify the effects of soil organic matter on the mobility of Ra2+ ions in the environment is currently being developed in collaboration with Gilles Montavon at Subatech.

4. A new collaborative project "High fidelity multiscale modelling of solute transport in nanoporous media under fluctuating thermodynamic and saturation conditions" is also currently being developed in collaboration with colleagues from the Geological Survey of Finland and the University of Helsinki.

5. The collaboration with CEA Marcoule on the atomistic simulation of nuclear waste glass corrosion and durability will continue at least through the end of 2025.

6. A new PhD project "Atomistic Computer Simulations of CO_2 Mineralization on Magnesium Oxide Surfaces for Sustainable Carbon Sequestration" is beginning in the fall of 2024 in collaboration with Dr. Sébastien Le Crom and Prof. Jean-François Boily (Umeå University, Sweden) in the framework of the SEED program at IMT Atlantique.

Highlights of the scientific activities of the team "Molecular Modeling in 2019-2024

- 25 publications in high quality peer-reviewed journals (see the full list below)
- 3 of these publications were particularly highlighted by the editors by featuring them on the cover of the respective journals [1, 2, 16]
- 2 review articles of 2021 [2] and 2022 [4] are particularly impactful and highly cited in the research community
- 11 invited lectures and talks at major international conferences (Goldshmidt, American Chemical Society, Clay Minerals Society, International Clay Conference, Migration Conference)
- 43 other oral and poster presentations at major international conferences
- 7 articles in various stages of preparation for submission
- In 2019-2020 A.Kalinichev was elected and served as the President of the Clay Minerals Society
- A.Kalinichev is also currently:
    - the Editor-in-Chief of the section "*Clays and Engineered Mineral Materials*" òf the journal *Minerals*
    - Associate Editor of the journal *Clays and Clay Minerals*
    - Associate Editor of the journal *Frontiers in Nuclear Engineering*
    - Associate Editor of the journal *Discover - Minerals*

Publications

[1] M.Pouvreau, J.A.Greathouse, R.T.Cygan, A.G.Kalinichev (2019) Structure of hydrated kaolinite edge surfaces: DFT results and further development of the ClayFF classical force field with metal-O-H angle bending terms. J. Phys. Chem. C, **123**, 11628-11638.

[2] R.T.Cygan, J.A.Greathouse, A.G.Kalinichev (2021) Advances in Clayff molecular simulation of layered and nanoporous materials and their aqueous interfaces. J.Phys.Chem.C, **125**, 17573-17589.

[3] A.G.Kalinichev (2021) Atomistic modeling of clays and related nanoporous materials with ClayFF force field. In: C.I.Sainz-Díaz (ed.) Computational Modeling in Clay Mineralogy - AIPEA Educational Series, v.**3**, p.17-52, Digilabs Pub., Bari, Italy.

[4] X.Liu, C.Tournassat, S.Grangeon, A.G.Kalinichev, Y.Takahashi, M. Marques Fernandes (2022) Molecular-level understanding of metal ion retention in clay-rich materials. Nature Reviews Earth & Environment, **3**, 461-476

[5] Y.Pedram, Y.Zhang, S.Briggs, C.S.Kim, A.G.Kalinichev, L.K.Beland (2024) Investigating the effect of Na+, Ca2+, and Cu2+ sorption in montmorillonite using density functional theory and molecular dynamics simulations. *Computational Materials Science*, in review.

[6] I.Androniuk, A.G.Kalinichev (2020) Molecular dynamics simulation of the interaction of uranium (VI) with the C-S-H phase of cement in the presence of gluconate. Appl. Geochem., **113**, 104496.

[7] D.I.Grekov, T.Suzuki-Muresan, A.G.Kalinichev, P.Pré, B.Grambow (2020) Thermodynamic data of adsorption reveal the entry of CH4 and CO2 in a smectite clay interlayer. Phys.Chem.-Chem.Phys., **22**, 16727-16733.

[8] N.Loganathan, G.M.Bowers, B.F.Ngouana-Wakou, A.G.Kalinichev, R.J.Kirkpatrick, A.O.Yazaydin (2019) Understanding methane/carbon dioxide partitioning in clay nano- and meso-pores with constant reservoir composition molecular dynamics modeling, Phys.Chem.-Chem.Phys., **21**, 6917-6924.

[9] D.I.Grekov, A.G.Kalinichev, T.Suzuki-Muresan, P.Pré, B.Grambow (2021) Direct experimental evidence of the effects of clay particles' basal-to-lateral surface ratio on CH_4/CO_2 adsorption. J.Phys.Chem.C, **125**, 11499-11507.

[10] N.Loganathan, A.O.Yazaydin, G.M.Bowers, B.F.Ngouana-Wakou, A.G.Kalinichev, R.J.Kirkpatrick (2020) Role of cations in the methane/carbon dioxide partitioning in nano- and mesopores of illite using constant reservoir composition molecular dynamics simulation. J. Phys. Chem. C., **124**, 2490-2500.

[11] M.Szczerba, A.G.Kalinichev, M.Kowalik (2020) Intrinsic hydrophobicity of smectite basal surfaces quantitatively probed by molecular dynamics simulations. Applied Clay Science, **188**, 105497.

[12] P.Citli, A.G.Kalinichev (2024) Grand Canonical Monte Carlo simulations of hydrogen adsorption in the interlayers of hydrated montmorillonite. *Applied Clay Science*, (submitted).

[13] S.M.Mutisya, A.G.Kalinichev (2024) Selective adsorption of hydrogen gas on a water-saturated montmorillonite clay. *J. Phys. Chem. C*, in preparation.

[14] S.V.Kraevsky, C.Tournassat, M.Vayer, F.Warmont, S.Grangeon, B.F.Ngouana-Wakou, A.G.Kalinichev (2020) Identification of montmorillonite particle edge orientations by atomic-force microscopy. Applied Clay Science, **186**, 105442.

[15] A.N.Ay, B.Zumreoglu-Karan, A.G.Kalinichev, V.Rives, R.Trujillano, A.Temel (2020) Layered double hydroxide - borate composites supported on magnetic nanoparticles: preparation, characterization and molecular dynamics simulations. Journal of Porous Materials, **27**, 735-743.

[16] S.M.Mutisya, A.G.Kalinichev (2021) Carbonation reaction mechanisms of portlandite predicted from enhanced ab initio molecular dynamics simulations. Minerals, **11**, 509.

[17] K.Damodaran, J.-M.Delaye, A.G.Kalinichev, S.Gin (2022) Deciphering the non-linear impact of Al on chemical durability of silicate glass. Acta Materialia, **225**, 117478.

[18] E.V.Tararushkin, V.V.Pisarev, A.G.Kalinichev (2022) Atomistic simulations of ettringite and its aqueous interfaces: Structure and properties revisited with the modified ClayFF force field. Cement and Concrete Research, **156**, 106759.

[19] E.V.Tararushkin, V.V.Pisarev, A.G.Kalinichev (2023) Interaction of nitrite ions with hydrated portlandite surfaces: Atomistic computer simulation study. Materials, **16**, 5026.

[20] E.V.Tararushkin, V.V.Pisarev, A.G.Kalinichev (2023) Equation of state, compressibility, and vibrational properties of brucite over wide pressure and temperature ranges: Atomistic computer simulations with the modified ClayFF classical force field. Minerals, **13**, 408.

[21] E.V.Tararushkin, G.S.Smirnov, A.G.Kalinichev (2023) Structure and properties of water in a new model of the 10-Å phase: Classical and *ab initio* atomistic computational modeling. Minerals, **13**, 1018.

[22] V.V.Pisarev, A.G.Kalinichev (2022) Couette flow of pentane in clay nanopores: Molecular dynamics simulation. Journal of Molecular Liquids, **366**, 120290.

[23] M.A.Logunov, A.G. Kalinichev, V.V.Pisarev (2022) Structure of hydrocarbon fluid and couette flows in slit pores with pyrophyllite walls. Polymer Science A, **64**, 908-917.

[24] A.D.Krot, I.E.Vlasova, E.V.Tararushkin, A.G.Kalinichev (2024) Atomistic computer simulations of uranyl adsorption on hydrated illite and smectite surfaces. Minerals, 14, 109.

[25] A.A.Glushak, E.V.Tararushkin, G.S.Smirnov, A.G.Kalinichev (2024) Molecular dynamics simulation of hydrocalumite as adsorbent for anionic radionuclides. *Appl. Geochem.*, under review.