Swift Heavy Ions at GANIL, an indispensable tool to understand the evolution of radiolysable materials, to nanostructure them and to ensure the nuclear power industry safety

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At GANIL, the studies on materials prone to radiolysis (*i.e.* decomposed under ionizing radiation, called hereafter radiolysable materials or RMs) encompass both ***basic research*** on Swift Heavy Ions (SHI) interactions with matter and applied research interesting the ***Ion Track Technology (ITT)*** and the ***nuclear power industry (NPI)***. ***As these fields fertilize one another, we have decided to gather three related contributions in a unique, thus long document***.

<u>How do we use the GANIL facility for RMs?</u>
Swift Heavy Ions deposit their energy along the ion path in a cylinder called the track. Compared to gamma rays or electron beams, the energy deposition is heterogeneous at the nanometric scale, the corresponding Linear Energy Transfer (LET) values being high (factor of 10^3 between ^{13}C 13 MeV/A and 1 MeV e-beam in polyethylene) and the energy deposition being associated with the collective reorganization of the material.

Basic research with SHI on radiolysable materials (RMs) began at GANIL in the late 1980s. At that time, they aimed at understanding how the high densities of electronic excitation induced by SHI influence the radiation-induced modifications in RMs, in terms of defect creation (structure, type and concentration). Since then, studying the combined effects of the irradiation environment, the temperature and the LET has allowed a better understanding not only of the defect creation mechanisms and kinetics, but also on how SHI irradiation differs from γ or β irradiation. Notably, energy transfers, important processes in organic materials irradiation are known to be effective under γ irradiation; we have demonstrated that although reduced, they remain effective under SHI as long as the LET is low enough to prevent fragmentation from prevailing. The ultimate goal of basic researches is to coin a comprehensive model enabling the prediction of the radiation-induced evolution of any RMs, based on its chemical composition, its microstructure and the irradiation characteristics (LET, environment, temperature...).
Speaking of the combined effect of LET and environment, the presence of oxygen during irradiation induces one of the major aging processes leading to organic materials loss of properties. Being able to predict their evolution over long time periods and high doses requires an excellent understanding of the oxidation chain reaction kinetics and the knowledge of the corresponding kinetic constants. The available data are based on kinetics derived from thermo-oxidation and do not take into account the specific structure of the energy deposition induced by particles and some hypotheses used are not experimentally proven. To overcome these drawbacks, we plan, in the upcoming decade at CIMAP, to develop the appropriate *in-situ* analyses set-up and the associated methodology for accessing fast and ultra-fast reactions involving oxidized radicals during the irradiation physical-chemical and chemical stages (10^{-15}-10^{-8} sec) by combining experimental and theoretical works.

A lot has already been done in basic science. Still, great challenges remain in the comprehension of the interactions between SHI and RMs, especially for materials of biological interest. One of them concerns the behavior of healthy tissues, as structural materials, during hadrontherapy. Notably, in

the polymer group at CIMAP studies of the evolution under SHI of the triple helix structure of Collagen II, the major constituent of the joint cartilage, are ongoing. The objective is to understand how the biomechanical properties of healthy cartilage are altered under carbon ion irradiation during the hadrontherapy treatment of chondrosarcoma, a radio-resistant and inoperable cancer of bone and cartilage.
In the same context, the relative efficiency of hadrons at the Bragg peak in damaging tumor cells, compared to surrounding healthy cells, could be increased by irradiating with pulsed ion beams and even more so when nanoparticles are inserted in the tumor cells. This idea is based on the FLASH protocol, stemming from basic research on water radiolysis, recently developed at Curie Institute that shows a net increase in the beam efficiency in damaging tumor cells compared to healthy cells when using macro-pulses of MeV-electrons. The NIMBE Laboratory plan to address the underlying mechanisms under SHI by applying the pulse radiolysis technique, at a time resolution going from the nanosecond to the millisecond, using the inherent time structure of the ion beams and an electrical field modulation.

The wealth of knowledge acquired through basic research on RMs under SHI at GANIL has set off several domains of ***industrial research***, which in turn feed basic research. SHI are widely used to structure polymers at the nanometric scale, thanks to latent tracks. These tracks, once etched, are used either as they are (membranes for filtration such as commercial Nucleopores membranes from Whatman™ or membranes for osmotic energy recovery) or functionalized. Nanostructured functional polymers have gained growing interest in high value-added applications such as sensors, analytical devices and/or diagnostics. Pushed by the recent EU policy on environmental norms, important industrial groups in France, such as VINCI Construction for soil leachate («Quick Soil Analysis» CEA project - norm NF-EN-12457-2-) and TOTAL for on-site water quality control in offshore oil production platforms (OSPAR regulation), have already financed the R&D on these sensors; more is still to come. Based on their expertise in functionalizing nanopores made by ITT in polymer thin films, PCnano team (DRF/IRAMIS/LSI) is notably developing a portable early warning sensor for toxic metals that monitors the water quality. The future of membrane irradiations for ITT appears very bright with a growing number of industries interested in such sensors. A recent market study by Erdin Cabinet (2018) revealed that the Business to Business market represents around 135 M€ in France, 900 M€ in EU and 3.2 billion Euros in the world. Ongoing Business to Client market study is now under evaluation revealing that customers are ready to pay for water tests at home[a]. Sensors for Lab-on-chip medical applications are also on constant growth and will remain dynamic.

The main aim of applied research for the NPI is to improve the knowledge on the evolution of RMs under irradiation with α particles from actinides. For this purpose, radiation-induced modifications such as the hydrogen emission and the chemical and microstructural altering, have to be quantified and understood at high doses (*i.e.* long time). We have demonstrated, a little less than 20 years ago, that SHI can effectively simulate the effects of α particles on materials, provided ions and energy are ingeniously chosen so to meet the LET and the radial dose repartition induced by α particles. This innovative use of SHI at GANIL allows a homogeneous irradiation of materials over thicknesses much greater than those attainable with radionuclides, under increased safety. The use of GANIL ions in the framework of nuclear waste and of spent fuel reprocessing has enabled the acquisition of

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essential data on 1) the safety of RM-rich nuclear waste packages under disposal, transport and storage conditions, and 2) the safety and the efficiency of the spent fuel reprocessing process at La Hague. Studying the behavior of cable sheaths in nuclear power plants, in the event of a serious accident, is also part of the work for which the SHI at GANIL are of great importance for the community. The basic science results on radiation-induced oxidation will bring new outcomes in the NPI for the simulation of long term behavior of polymers constituting cable sheaths or composing organic-rich nuclear waste packages. Besides, in the context of the nuclear waste package reprocessing, considering the fact that former packages used large quantities of bitumen, the need for further studies of organic materials under α irradiation - and therefore access to the GANIL beams - should at least remain stable. In addition, due to the UOX to MOX fuels transition which induces an increase in radiation levels, a comprehensive study on the nitric acid radiolysis, with or without atoms simulating fission products, is mandatory. This will surely require the development of a specific device.

The importance of the GANIL facility for RMs under SHI

Thanks to the fruitful basic and applied research studies performed at GANIL these past decades, we have acquired an important expertise both in the behavior of RMs under SHI and in the development of specific set-ups for real-time monitoring of radiation-induced alteration of the materials (liquid or solids) over an unequalled temperature range (8K- 500K). These *in-situ* set-ups are of great importance to discard the post-irradiation chemical reactions the RMs are prone to. These devices have enabled to answer not only questions related to basic science but also more specific requests of ANDRA on RM-rich nuclear waste packages and on the effect of fission-products irradiation on the efficiency of the nitric acid solution in the spent fuel reprocessing; under CEA-ORANO (ex-AREVA) bilateral or CEA-ORANO-EDF trilateral contracts. Within the framework of ITT, the device developed for single ion irradiation of membranes, used in lab-on-chip applications, enables an opening rate close to 90%; the highest among SHI irradiation facilities.

The multidisciplinary and the versatility of ion beams and lines provided by GANIL, combined with the development of unique or near to unique set-ups, make GANIL an irreplaceable and essential tool for research on RMs under SHI and α particles. Important factors for this field are the access to X-Y scanned beams on wide surfaces (6x5 cm^2), the similarity of the dosimetry procedure across the lines, the huge variety of available ions and the wide energy range enabling access to a wide map of ion/energy couples and thus a wide range of LETs and radial dose distribution. As already stated, the modulation of these two parameters is a key factor in the comprehension of RM behavior under particles irradiations and for α effects simulations. ***Factually, studies on RM use mainly three beam lines***:

1) Basic research: ***IRRSUD*** (C to Kr, up to 1 MeV/A), ***IRASME*** (C to Xe, up to 13.7 MeV/A) and ***IRABAT*** (C to Ar, up to 95 MeV/A),
2) ITT: ***IRASME*** (Xe or Kr 10 MeV/A),
3) NPI: ***IRASME*** (C to Ar, 6-13 MeV/A) and ***IRABAT*** (C to Ar, up to 95 MeV/A).

The IRRABAT line is crucial for thick samples and for *in-operando* irradiations related to the nuclear power industry as they require high gas pressures and large samples making thick windows mandatory. In the best of all worlds, the ***annual beamtime*** necessary for ***a dynamic and quality research on RMs***, is evaluated at ***1 to 2 weeks on IRRSUD, between 8 to 12 weeks on IRASME*** and ***at least 2 weeks of C and Ar beams on IRRABAT***. For an agile research on RM, those beams should be ***scheduled*** not as a unique beam session for each beam type but ***as a two-session beamtime on two trimesters***. These conditions were fulfilled until four to five years ago when the beamtime started shrinking significantly. This shortage in beamtime has shed the light on the necessity to come back to the former beamtime availability to maintain a pertinent research on RMs.

Based on the minimum (let alone the optimal) beamtime necessary for a comprehensive and dynamic research on RMs under SHI in France, related irradiations cannot be integrally transferred to another European facility without creating unnecessary competition and a huge backlog on said machine, both very counterproductive. Although the LINAC could deliver potentially applicable beams (C-Ni), ***Spiral 2 phase 1 up to 1++ should hardly be applicable for RMs under SHI*** until an appropriately equipped cave is available. ***GANIL is thus meant to remain a unique, priceless and essential installation for RMs***. Better yet, ***two main evolutions*** of this facility can ***impact positively and trigger new research for RMs*** at GANIL. The ***first*** one would be the ***construction of a low energy*** (between ARIBE and IRRSUD energies) ***line in the D1 cave (IRASME) so to combine low and medium energy*** irradiations, leading to the combination of multiple LET and radial dose distributions. This configuration would enable to take fully into account the complexity of actual irradiation in nuclear waste packages and refine long term aging simulations. This would also be of great interest for related basic science.
The ***second*** evolution concerns the ***construction of an industrial machine exclusively devoted to membrane irradiations for ITT*** (under study thanks to an EU founded mission). This machine will be of great use to maintain a dynamic and agile research around innovative high value-added devices. It will advantageously enlarge the GANIL offer, which will undoubtedly drive the attention of many industrials. However, ***for this to become viable***, set-ups enabling irradiations under inert and controlled atmospheres should be developed.