

## SYNTHESIS of the beamline project for radioactive matter

**Name : MARS beamline**

*Main characteristics of the beamline*

Source	Energy range	Optics (main elements)	resolution (E/ $\Delta$ E) flux spot size (H x V)	Experimental station(s)
<b>Bending magnet</b>	<b>3.5 - 36 keV focused</b>	<b>- collimating mirror - double crystal monochromator sagittally focusing - focusing mirror - single crystal monochromator elliptically bent - additional KB system for micro analysis</b>	<b><math>10^4 - 6 \cdot 10^3</math>  <math>3 \cdot 10^{12}</math> Ph/s at 10 keV  <math>100 \times 130 \mu\text{m}^2</math> (FWHM)</b>	<b>Diffraction station  Fluorescence and absorption station  Dispersive station  Sample environment : glove boxes, high pressure cells, electrochemical cells, furnace, cryostat</b>

A range of current technological, geological and environmental issues requires systematic investigation of the properties of radioactive samples by synchrotron radiation. Many of these fields are already the subject of on-going research using current synchrotron beamlines and ad hoc confinement sample holders. These studies have demonstrated the potential of synchrotron X-ray radiation to solve many physico-chemical problems, but they have also emphasized the need for a first-rate modern X-ray beamline allowing experiments carried out on highly irradiating samples or on low irradiating samples under more drastic in situ conditions (high temperature, liquid state ...).

Then, MARS beamline will be fully dedicated to advanced structural and chemical characterization of radioactive matter, coupling advanced analytical tools like XAS, XRD, fluorescence and associated micro characterization techniques, and a high level of personnel protection against radioactivity. The beamline will accept a large variety of radioactive samples ( $\alpha$ ,  $\beta$ ,  $\gamma$  and n emitters) with an activity up to 18.6 GBq per sample (500 mCi), and will fully comply with the specific regulations for preparation, handling, storage and transport of radioactive materials.

## **Abstract of Scientific Program**

### **Solution Chemistry**

Changes in speciation with temperature may well increase the solubility of actinides under natural conditions. Hydrothermal conditions can then promote the molecular association of solution species that are fully hydrated at ambient temperature and pressure. So, knowledge of the geometry of such complexes is essential to understand and predict changes with temperature of properties such as electrophoretic mobility, chemical reactivity in solution or toward surfaces, diffusivity in nanopores or in mineral and solid defects, and with respect to other solution species.

Separation of fission products and actinides from nuclear spent fuel is currently performed by selective extraction techniques, whereby an organic ligand selectively complexes U and Pu under controlled chemical conditions and the organometallic complex is then dissolved in an extractant liquid phase. Optimisation of these radionuclides (RN) separation techniques hinges on resolution of key issues such as the selectivity of organic ligands with respect to a specific RN. A better understanding of the electronic and coordination interactions between the ligand and the dissolved RN are required to increase this ligand affinity and specificity.

Natural Organic Matter (NOM: oxalate, acetate, humic and fulvic acids...) is very diverse both in nature and concentration of possible binding groups which can significantly alter the solubility and the mobility of RN complexes. Detailed characterizations of the conformation and chemical properties of NOM versus pH, redox potential, hydration state and ionic strength, and of the structure and stability of the NOM-RN complexes are needed to predict the NOM-RN affinity.

*The XAS and XANES approach with fluorescence detection for highly dilute samples is fully adapted to answer these questions*

### **Chemistry and solid state physics**

Carefully understanding the structural behaviour of nuclear fuels and ceramics, fuel claddings and nuclear core elements are fundamental to optimising the design of new generation nuclear reactors.

Indeed, the components of the structural framework of nuclear reactors are subject to intense neutron fluxes and heat-carrying water. Irradiations can dramatically alter the properties of these solids by creation of defects, and formation of important amounts of activated elements. The corrosion processes and the evolution upon irradiation of the chemical and structural properties of zirconium claddings and structural steel materials will be investigated.

Mixed oxide fuel (MOX) has been designed to recycle Pu from spent fuel and warheads. Optimal burning of Pu in MOX depends on the homogeneity of the solid solution and may be limited by the presence of structural defects, which in turn are connected to the protocol of fuel synthesis. The characterization of the physical and chemical properties of MOX as a function of synthesis route and irradiation conditions will lead to a correlation between the heterogeneity of the microstructure and the fuel's mechanical and thermochemical properties, as well as its capacity to retain fission gases. Similar studies will apply to heterogeneous fuels, such as carbide or nitride ceramics dispersed in a ceramic or a metallic matrix developed to optimise actinide burning (Am, Cm).

Due to severe thermochemical constraints and the formation of a wide variety of fission and activation elements, aged fuel constitutes an extremely complex system that should be studied

step by step. Therefore, first of all, simpler systems will be studied, like fresh probes into which a limited number of defects and/or doping elements are introduced with high precision by irradiating with ion beams (*e.g.*,  $e^-$ ,  $H^+$ ,  $He^+$ ,  $Kr^+$ ,  $Xe^+$ ,  $Cs^+$ ,  $\Gamma$ ) of well controlled energy. Such experiments should provide an accurate determination of the location of activation and fission products in the fuel lattice, or the accumulation of defects upon irradiation by ions with selected energies under controlled conditions of temperature and pressure.

During the storage time of the burned fuel, this latter may react with oxygen or radiolysis products. Understanding the oxidation reactions is required to model the behaviour of spent fuel over timescales of decades to eons. Characterisation of the chemical environment of long lived fission products and neutron poisons is also crucial to predict release rates of RN during storage.

High-level wastes generated by fuel processing are currently encased in glasses, and may in future possibly be occluded in ceramics with enhanced retention properties. The long-term tolerance of such matrices to RN decay and internal irradiation must be carefully evaluated to permit successful confinement of RNs over geological time scales. In addition, identifying the mechanisms of alteration and natural weathering of these materials is a prerequisite in the assessment of the impact of water intrusion into the radioactive waste repositories.

Characterising and understanding the ageing processes of nuclear weapons is essential to validate the lifetime of existing and future weapons, yielding to a full characterisation of the ageing processes at microscopic and molecular scales. Therefore, microscopic investigations of tritium-storing materials and of pure (or alloyed) metallic plutonium are needed. Indeed, the unique physical properties of the actinides and their alloys often arise because of the complex role of the  $5f$  electrons in bonding. Among them, pure metallic Pu presents specific behaviours with numerous allotropes, like the  $\alpha$ - and  $\delta$ -phases. Preliminary measurements suggest that the nature of the alloying element and its concentration control the Pu alloy phase stability and that the pressure affects the Pu phase diagram, leading to new crystallographic structures that have not been characterised yet. Current models will be validated from accurate experimental data collected over a wide range of pressure, density, and temperature.

*For all the issues presented above, the coupling of structural methods like powder diffraction, WAXS (wide angle anomalous scattering) and EXAFS with spectroscopic tools like XANES will be mostly efficient together with the microfocusing option for heterogeneous materials. Moreover, for high pressure, high temperature experiments requesting a beam energy above 25 keV, an access to the High Pressure Beamline in preparation is considered.*

### **Chemistry at interfaces**

Understanding and modelling of RN transfer from the waste site to subsurface environments is the key issue in designing waste disposal sites. Waste package structures as well as man-made barriers are engineered to protect each other and delay RN migration, and the geological site is selected to provide an additional natural retention barrier which is effective over geological timescales. To quantify this possible migration correctly, the mechanisms of sorption of the most mobile RN ions and their incorporation in all the barriers, and mechanisms of retention influencing migration, must be assessed by a detailed characterization. One should also note that concrete confinement barriers are expected to play a significant role in the retention of RN released either in a reactor accident, or from a nuclear waste repository.

*Near surface sensitive geometry with depth resolution will be accessible.*

**Personnes et Laboratoires prêts à participer à la mise en place de la ligne et de ses équipements**

**CEA - Direction de l'Energie Nucléaire**

Service de Chimie Physique et Analytique, CEA-Saclay  
Service de Recherches Métallurgiques Appliquées, CEA-Saclay

**CEA - Direction des Applications Militaires**

Service d'Etudes de Métallurgie Physique, CEA-Valduc

**Communautés potentiellement concernées**

**CNRS-IN2P3 / Université**

UMR 5822 - Institut de Physique Nucléaire, Groupe de Radiochimie, Lyon  
UMR 8608 - Institut de Physique Nucléaire, Groupe de Radiochimie, Orsay  
UMR 6457 - Subatech, Groupe de Radiochimie, Nantes  
UMR 8609 - Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse, Equipe physico-chimie de l'irradiation, Orsay  
UMR 7500 - Institut de Recherches Subatomiques, Lab. de Chimie Nucléaire, Strasbourg

**CNRS**

UPR 2801 – Centre d'Etudes de Chimie Métallurgique (CECM), Groupe de radiochimie, Vitry  
UPR 33 – Centre d'Etudes et de Recherches par Irradiations (CERI), Orléans

**CNRS-SC / CEA**

URA 331 – Laboratoire Claude Fréjacques, CEA-Saclay  
UMR 9956 - Laboratoire Pierre Süe, CEA-Saclay

**CNRS-SC / Université**

UMR 5084 – Lab.de Chimie Nucléaire Analytique et Bio-environnementale, CEN, Bordeaux-Gradignan

**Université**

Laboratoire de Radiochimie et Radioécologie, Nice

**CEA - Direction des Sciences de la Matière**

Service de Chimie Moléculaire, CEA-Saclay

**CEA - Direction de l'Energie Nucléaire**

Service d'Analyse et Migration des Radioéléments, CEA-Cadarache  
Service de Caractérisation et de Contrôle des Déchets, CEA-Cadarache  
Service d'Etudes Procédés, CEA-Cadarache  
Service d'Etudes et de Simulation du Comportement des combustibles, CEA-Cadarache  
Service Plutonium, Uranium et Actinides mineurs, CEA-Cadarache  
Service d'Etudes des Matériaux Irradiés, CEA-Saclay  
Service de Chimie des Procédés de Séparation, CEA-Valrhô

Service de Conditionnement des Déchets et Vitrification, CEA-Valrhô  
Service d'Etude des Systèmes de Confinement, CEA-Valrhô

**Laboratories associated to French reseach program on radioactive materials**

GDR 1115 - Practis-Paris, GDR 2023 - Nomade, GDR 788 – FORPRO

**European Laboratories**

Radiochemistry Centre (U. Manchester), Immobilization Science Lab. (U. Sheffield),  
Radiochemistry Lab. (Imperial College, London), Institute for Transuranium Elements  
(Karlsruhe), Institut für Radiochemie (Forschungszentrum Rossendorf), Institut für  
Kernchemie (Universität Mainz)

## II Recommandations du Comité Scientifique Consultatif (6-7 Fev 2003)

### ***Beamline proposal n° 14 : “Radioactive Materials”***

SAC strongly supports the project and underlines the lack of such a beamline in Europe. The choice of SOLEIL for hosting it is very relevant in view of the proximity of CEA, the major actor of the project. The handling of radioactive samples requires special additional equipment for radiation protection, which is well described in the project. Generally speaking, the line has been well described, combining advanced analytical tools like XAS, microcharacterization, dispersive EXAFS and XRD. Some important points have to be accounted for:

- The adjacent use of the neighbouring High Pressure beamline for the high energy part of the program is approved but should not result in a performance compromise for this latter beamline. In particular the dead time induced by the switch from radioactive to non radioactive materials should be optimised
- The extra cost induced by the special protection structure which is necessary, should not result in a lowering of the beamline performances. This additional cost should be clearly identified and relevant funding established from the beginning
- An effort should be made to open the beamline to a wider community. SAC asks for a stronger involvement of external users (chemistry - waste treatment – medical studies etc...). Two types of access should be envisaged: special access (without program committee) and regular access.
- As stated before, this beamline should be unique in Europe. Its opening to European users is encouraged and should be clarified.

*SAC approves the presented proposal and encourages its opening to a wider community*

### III Propositions de la Direction de SOLEIL

La réalisation de cette ligne doit être prise en compte très tôt dans le programme de construction de SOLEIL à cause des infrastructures très spécifiques à développer et des contraintes particulières à prendre en compte au niveau de la sûreté nucléaire. La gamme étendue en énergie justifie l'utilisation d'un dipôle magnétique comme source de rayonnement, permettant en particulier d'étudier les actinides. Pour satisfaire les études faisant intervenir des hautes pressions, un couplage à temps partiel est prévu avec la ligne adjacente dédiée aux matériaux sous conditions extrêmes.

Le coût d'une telle ligne dépasse largement la capacité de financement de SOLEIL, tel que défini pour 24 lignes de lumière (soit 2.44 M€ pour une ligne « dipôle » ou une ligne sur insertion hors retenue pour onduleur). La direction de SOLEIL demande donc une participation supplémentaire du CEA , acteur majeur du programme scientifique de cette ligne, pour assurer le financement complet de cette ligne avec la répartition proposée ci-dessous dans ses grandes lignes.

#### Budget estimé (à affiner en phase APD)

poste	Montant total	SOLEIL	CEA
Optique (miroirs, monochromateurs 2C et 1C, microfocalisation, fentes, moniteurs)	1335 k€	1335 k€	-
Station Expérimentale (diffractomètre, four, détecteurs, cellules HP, laser, boîtes à gant)	1619 k€	800 k€	819 k€
Infrastructures (sécurité rayonnement, ventilation, détritiation, câblage...)	1344 k€	-	1344 k€
Contrôle-commande	152 k€	152 k€	-
Vide	152 k€	152 k€	-
<b>total</b>	<b>4602 k€</b>	<b>2439 k€</b>	<b>2163 k€</b>