Thesis topic (CDD 3 years):

VITARIS: Mechanistic study of thermal reactivity and physico-chemical interactions within radioactive waste bunkers

Application to the field of fire safety

1. Context

The conditioning of medium-level long-lived radioactive waste (MA-VL) in a bituminous matrix was implemented in France as early as the 1960s, leading to the production of several tens of thousands of barrels of bituminous mix (FEB). These wastes are notably generated from the treatment operations of nuclear fuel reprocessing effluents after its use in reactors. The process involves insolubilizing radionuclides by a successive addition of salts that have a particular chemical affinity with these radionuclides. The sludge thus formed, separated from the liquid phase by filtration, is then coated with bitumen by extrusion [1-2]. At the exit of the extruder, bituminous coatings are obtained, namely a dispersion of inorganic salts in a bitumen matrix. These wastes are now stored, pending their final storage in a deep geological layer (Cigéo project at about 500 meters depth, within an argillite layer) to isolate and confine them for the very long term. However, FEB presents a major safety issue: the organic reducing nature of bitumen and the presence of certain salts promote exothermic redox reactions [3-5]. These can be triggered by an external heat input (for example during a fire) and develop along two main paths:

• Reactions between salts themselves.

• Reactions between certain oxidizing salts (nitrates, nitrites) and the bituminous matrix.

These mechanisms can generate a release of heat and flammable gases, likely to lead to a reaction runaway and, in extreme cases, a pyrolysis followed by an ignition of the bituminous coatings. This would compromise the expected safety functions, in particular the containment of radionuclides. Understanding the reactivity of FEVs is therefore essential to assess the safety demonstration at all stages of their management (transport, storage and warehousing).

2. Scientific problematic

The reactivity of asphalt, although identified, remains insufficiently understood in its phenomenological complexity while it constitutes a major issue to anticipate their thermal behavior. Several scientific obstacles persist:

• Concomitance of reactions: reactions involving different salts and the bituminous matrix occur simultaneously, making it difficult to use thermograms and discriminate between dominant/less dominant reactive compounds.

• Synergistic and catalytic effects: some combinations of salts seem to accelerate or trigger reactivity, but the precise mechanisms remain poorly understood.

A quadripartite study program was conducted by Andra, ORANO, CEA and EDF to assess the control of risks related to the storage of FBFs, followed by a second one currently underway. This programme as a whole has combined trials at different scales and modelling, including the use of an experimental design (EXP). This statistical approach was an asset to link the composition of asphalt (proportions of salts and bitumen) to their thermal behavior and identify the most influential factors. However, its purely descriptive nature limits the mechanistic understanding of phenomena. Moreover, the current program seeks to define thermal reactivity envelope curves, but their robustness remains discussed due to the high variability of compositions and the complexity of reactions involved. Thus, the lack of detailed characterization of the physico-chemical and thermal mechanisms involved in bituminous mixes, such as the kinetics of exothermic reactions and associated decomposition processes, is today a handicap in assessing the relevance of the results of these two quadripartite programmes.

In this context, the ASNR wishes to develop a mechanistic approach, allowing to characterize elementary reactions, quantify kinetics and understand interactions between components as well as the resulting reaction mechanisms. This approach aims to quantify the critical parameters, and, ultimately, to provide a basis for assessing the safety demonstrations presented by the waste producers and ANDRA, however without entering into the risk-taking that this approach would constitute to reconstruct the entire underlying data for a full demonstration which is up to the industrialists.

3. PhD objectives

The overall objective of the PhD is to develop an understanding of the thermal behavior of asphalt based on a detailed characterization of physico-chemical mechanisms, products formed and their kinetics from inactive systems (without radioactivity) representative.

More specifically, it will be about:

i. Characterize the thermal reactions of asphalt by taking into account their chemical variability, via a level-of-complexity approach, from pure compounds to simplified systems (monosalt, bisel, etc.), up to more heterogeneous matrices:

- Identify the respective roles of different salts in thermal reactions.
- Study and quantify the interactions between bitumen/salts and salts/salts, by determining their energy contributions (enthalpies, triggering thresholds, critical conditions).

ii. Identify thermal decomposition products:

- Characterize the gases and solid residues formed.
- Associate the identified decomposition products with the corresponding reaction mechanisms.

iii. Study the chemical kinetics of reactions:

- Determine the kinetic and rate constant laws associated with major thermal transformations.
- Evaluate the influence of the composition of asphalt on the kinetics and evolution of reactions.
- Highlight the triggering reactions (fast) compared to slow processes (aging, gradual oxidation).

4. Woks ans methods

The strategy adopted is based on a multi-step and multidisciplinary approach combining experimentation, physico-chemical analysis and kinetic modeling in order to better understand the thermal reactivity of asphalt. She understands:

1. Development of model mixes: preparation of samples in the laboratory by extrusion, allowing precise control of salt composition and content (mono-, bi- and multi-salts).Analyses thermiques :
   • Thermogravimetric analysis (TGA): measurement of mass loss as a function of temperature and time, allowing the identification of critical decomposition temperatures and mass loss kinetics.
   • Differential scanning calorimetry (DSC) and microcalorimetry: quantification of heat fluxes associated with chemical reactions and phase transitions.
2. Chemical and structural characterization:
   • Environmental scanning electron microscopy (ESEM): observation of the microstructure of asphalt, salt distribution and local heterogeneity.
   • X-ray diffraction (XRD): identification of crystallographic phases and monitoring of structural transformations after heat treatment.
   • Fourier transform infrared spectroscopy (FTIR): tracking chemical changes in the organic matrix and identification of functional groups.
   • Gas chromatography coupled with mass spectrometry (GC-MS): identification and quantification of volatile organic compounds emitted during thermal decomposition.
3. Kinetic analysis and modeling of reaction mechanisms:

• Application of advanced kinetic analysis methods, including multi-step modeling, to decompose complex reactions and determine elementary reaction mechanisms.

• Experimental-modeling coupling: integration of thermo-analytical data into kinetic models to improve the understanding of reaction mechanisms and determination of kinetic parameters by inverse methods.

• Development and/or adjustment of a modeling tool within the framework of the thesis, in order to meet the specific needs for simulation and interpretation of reaction mechanisms.

5. Communications

The results of the thesis will be disseminated through several scientific publications in peer-reviewed journals. Among the publications planned: the kinetics of thermal decomposition of bitumen as well as the study of the reaction mechanisms of bitumen-salts decomposition by multi-step kinetic modeling. In parallel, these works will be the subject of oral presentations and posters during national and international congresses, allowing to share the advances, to exchange with the scientific community and to reinforce the impact of the thesis work.

6. References

[1] IAEA, Bituminization processes to condition radioactive wastes, Vienna, 1993.

[2] IAEA, Predisposal Management of Organics in Radioactive Waste, 427 (2015) 1–87.

[3] S. Mouffe, Maîtrise de la réactivité thermique lors de l'élaboration d'un conditionnement par le bitume : Thèse Université De Technologie De Compiègne (Diffusion restreinte), (2004).

[4] G. Matta, Comportement thermique d'enrobés bitumineux de déchets radioactifs, Thèse de doctorat, ICN, 2023.

[5] IRSN, DEMANDE D'AUTORISATION DE CREATION DU PROJET CIGEO « GP2 » - SURETE EN EXPLOITATION Rapport IRSN N° 2024-00623, 2024.

7. Place of the PhD

The thesis will take place on two sites. The first 18 months will take place at the ASNR site in Fontenay-aux-Roses (92), within the Laboratory for study and research on transfers and interactions in basements (LETIS). The second half of the thesis will take place at the Pprime Institute (UPR 3346 CNRS – University of Poitiers – ISAE-ENSMA), within the Heterogeneous Combustion team, Futuroscope site – Chasseneuil (86).

8. Candidate Profile

The candidate must hold a Master's degree or an engineering degree in materials chemistry, physical chemistry or nuclear sciences. A solid training in organic and inorganic chemistry, as well as good knowledge of thermal characterization techniques (notably ATG/DSC) will be particularly appreciated.

Skills in kinetic data analysis and modelling, as well as an interest in simulation methods and the processing of experimental data, will be an important asset.

The thesis project has a strong experimental and multidisciplinary component, the candidate must demonstrate a real interest in laboratory work, great scientific rigor, a spirit of initiative and a marked curiosity for applied research. An ability to interact with specialists from different fields (chemistry, materials, experimental and modeling research) will also be valued.

9. How to candidate

Candidates are invited to apply via the ASNR website, by consulting the offer available at the following link: https://asnr-career.talent-soft.com/offre-de-emploi/emploi-etude-mecanistique-de-la-reactivite-thermique-d-enrobes-bitumineux-radioactifs-env26-2-h-f_1502.aspx

For any question related to the thesis topic, the progress of the work or the hosting conditions, interested parties can contact the subject managers directly by email at the following address: georges.matta@asnr.fr ; thomas.rogaume@univ-poitiers.fr ; benjamin.batiot@univ-poitiers.fr