Our group is engaged in research activities in the field of nuclear reactor technology, including the materials chemistry and chemical thermodynamics of nuclear materials. Our research areas encompass the safety assessment of nuclear fuels for current, i.e., Light Water Reactors (LWRs), and next generation nuclear reactors, i.e., Sodium-cooled Fast Reactors (SFRs) and Molten Salt Reactors (MSRs). This covers the investigation of the fuel basic properties and performance, chemical compatibility with coolant and cladding, behaviour under irradiation, and corium chemistry for severe accident studies. We have a prime interest in the structural properties, chemical state, thermochemistry and transport behaviour of fission products, and are also involved in the field of waste materials. Our activities are focused on the coupling between experimental investigations (using X-ray and Neutron Diffraction, Calorimetry, X-ray Absorption Spectroscopy) and thermodynamic modelling using the CALPHAD method.

The RPNM research group has a wide range of experimental laboratories and facilities, including the radiological laboratories at the Reactor Institute Delft (www.rid.tudelft.nl/) for the experimental work with uranium and thorium. Moreover, our close collaboration with the Reactor Institute Delft (2MW experimental neutron research reactor) allows us access to the reactor beamlines and its irradiation facilities.

Fission products chemistry and scenario analysis of severe accident progression at Fukushima-Daiichi Nuclear Power Station: investigation of the Ba-Sr-Cs-Mo-O system

(Chemistry (BEP/MEP)
Anna Smith

Fission products such as (Cs, I, Te, Mo, Ba, Sr) are generated with a high fission yield during irradiation, and are subject of primary concern for the public, as they are the main cause for the radiological consequences of a severe accident (SA). The severe accident at the Fukushima-Daiichi Nuclear Power Station has highlighted stringent needs of research on radionuclides with a potential long-term radiological impact. Ba and Sr are particularly important because they are the next most important fission products with respect to public health hazards after volatile Cs, I and Te. The chemistry of molybdenum in irradiated nuclear fuel is also particularly important and complex, as it can form metallic precipitates or oxide phases depending on the burn-up, temperature and oxygen potential of the fuel. Moreover, recent post-irradiation examinations of the PHEBUS Fission Product Program have also shown a clear association of Ba and Mo forming oxide precipitates at grain boundaries.

Very little is known to this date on the Ba-Mo-O and Sr-Mo-O systems, however, and the thermodynamic descriptions using the CALPHAD method are either tentative or non-existent. The lack of thermodynamic information on such systems means that when evaluating SA scenarios, especially the release of Ba, Sr, and Mo from the fuel, the analysis remains uncertain.

In this project, we will look at the structural and thermodynamic properties of the ternary phases formed in the Ba-Mo-O and Sr-Mo-O systems. The work will involve solid state synthesis and characterization using X-ray diffraction and neutron diffraction, the study of the

compounds thermal expansion using high temperature X-ray diffraction, as well as calorimetric measurements (Differential Scanning Calorimetry, Solution Calorimetry, Thermal-relaxation calorimetry) and possibly Knudsen effusion mass spectrometric measurements. In addition, the experimental results will be coupled with thermodynamic calculations and modelling using the Factsage and Thermocalc softwares.

Safety assessment of nuclear fuel for Generation IV SFRs and LFRs: thermodynamic investigation of the (Cs-Te-Pu-U-O) fuel-fission product systems

(Chemistry MEP)
Anna Smith

Light water reactors (LWRs) are currently the reference in the nuclear industry, but do not provide a fully satisfying response to the social-political concerns. To replace these reactors at the end of their operating licenses, Generation IV reactors are currently being developed. In Europe, the research has been focused mainly on two designs: the Sodium-cooled Fast Reactor (SFR) and the Lead (and lead-bismuth)-cooled Fast Reactor (LFR). The safety of a nuclear reactor is directly linked to the performance of the fuel, which is at the heart of the energy production process. UO_2 is the most common fuel used in LWRs, whereas the $(U,Pu)O_{2-x}$ mixed oxide fuel (MOX) is currently the reference for the SFR and LFR. The nuclear fuel is subjected to extreme conditions of temperatures, gradients and radiation damage. In addition, the fission reactions lead to the formation of fission products (FPs), making the nuclear fuel an extremely complex multi-component system.

Several questions are still open on the thermodynamic and thermophysical properties of the fuel-fission product systems in Generation IV SFRs and LFRs. In particular, irradiation tests in prototype fast neutron reactors (i.e. *Phenix*, in France) have highlighted the formation of a fission product layer, never observed in LWRs, between the fuel pellet and the cladding, called **Joint-Oxide-Gaine** or **JOG**. The JOG forms due to the higher temperatures and gradients in fast neutron reactors and the migration of fission products such as Cs, Te, I, Mo from the centre of the pellets toward its colder periphery. The investigation of the JOG thermodynamic properties- which are currently mostly unknown- is fundamental for the safety assessment of the fuel for fast neutron reactors.

In this project, we will look at the structural and thermodynamic properties of the Cs-U-Pu-Te-Mo-O system by combining experimental studies and thermodynamic modelling. The experimental work will involve solid state synthesis of the ternary compounds expected in the reactor conditions and their characterization using X-ray diffraction, and neutron diffraction, as well as calorimetric measurements (Differential Scanning Calorimetry, Solution Calorimetry, Thermal-relaxation calorimetry, Thermogravimetry), and Knudsen effusion mass spectrometric measurements for vapor pressure studies. In addition, the experimental results will be coupled with thermodynamic calculations and modelling using the Factsage and Thermocalc softwares.

The work will be done partly at the Delft University of Technology (TU Delft, The Netherlands) in the Department of Radiation Science & Technology (www.nera.rst.tudelft.nl/), and partly at the Joint Research Centre in Karlsruhe (JRC-Karlsruhe, European Commission, www.ec.europa.eu/jrc/en/about/jrc-site/karlsruhe).

Physico-chemical properties of molten salt fuel for MSRs.

(Chemistry (BEP/MEP)
Anna Smith

The molten salt reactor (MSR) was selected as one of the promising designs by the International Generation IV Forum for the next generation of nuclear reactors. Running on a liquid molten salt fuel as opposed to the current generation of nuclear reactors, the Molten Salt Reactor technology provides a safe and truly innovative concept. Moreover, it can be coupled to a thorium fuel cycle, which produces much less long-lived radioactive waste and allows a more sustainable energy production, as thorium is three times more abundant on Earth than uranium. However, before the Molten Salt Reactor technology can be realised, a thorough safety assessment of all components of the reactor must be carried out. In particular, understanding the chemistry of the liquid fuel and acquiring a thorough knowledge of its physical and chemical properties such as density, viscosity, heat capacity, thermal conductivity and vapour pressure, is essential.

An extensive amount of work has been carried out in the past few years on fluoride salts proposed as fuel and coolant for the MSR, because of their advantageous neutronic and physico-chemical properties (melting temperature, vapour pressure, heat capacity, viscosity, thermal conductivity, solubility for fissile material). A wide range of compositions have been under study: examples for the fuel systems include ^{7}LiF-UF_4-ThF_4-(PuF_3) for the MSFR (Molten Salt Fast Reactor) concept; examples for the primary and secondary coolant systems include LiF–BeF_2 or LiF-NaF-KF. A comprehensive thermodynamic database has been developed for fluoride salts using the quasichemical formalism and the CALPHAD method. Chloride salts is a second option for the fuel and coolant system, and the preferred choice for a number of start-up companies around the world. However, there is to this date no such extensive thermodynamic database available for chloride salts.

To fill this gap, the proposed research will look at the physico-chemical properties of chloride molten salt fuel and will involve both experimental studies and theoretical modelling. The experimental investigations will include solid state synthesis, characterisation using techniques such as X-ray and neutron diffraction, measurement of thermodynamic properties using calorimetric techniques, as well as thermodynamic modelling assessments using the CALPHAD method with the Factsage software.

Study of the oxide fuel-cladding chemical interaction in a fast breeder reactor

(Chemistry) (BEP/MEP)

Anna Smith

The chemical interaction between $(U,Pu)O_2$ mixed oxide fuel, fission products and cladding materials is one of the major factor limiting the integrity and lifetime of a fuel pin in a fast breeder reactor. Type 316 stainless steel is currently the reference for fast reactors such as the Sodium-cooled Fast Reactor (SFR). During irradiation, the highly corrosive fission products cesium (Cs), tellurium (Te), and iodine (I) are generated in the fuel pins, which are particularly volatile. These elements are gases at the fuel temperature and migrate radially and axially to the colder temperature regions (towards the cladding) where they accumulate in the gap between fuel and cladding. The generation of Cs, Te and I is the main cause of attack of the stainless steel cladding.

Understanding the chemistry of the interaction between Cs, Te and I and the cladding depending on conditions of temperature and oxygen potential as well as the corrosion mechanisms is essential for the safety assessment of the reactor during operation and accidental conditions. The effects of Cs and I are fairly well-understood but there are little data on the role of tellurium in the chemical attack. In this research project, we will look at the structural and thermodynamic properties of the ternary phases formed in the M-Te-O (M=stainless steel components Fe,Cr,Ni,Mo,Mn) and Cs-M'-O systems (M'=Te,Cr,Mo,Ni,Mn). The work will involve solid state synthesis and characterization using X-ray and neutron diffraction, Mössbauer spectroscopy, the study of the compounds thermal expansion using high temperature X-ray diffraction, as well as calorimetric measurements (Differential Scanning Calorimetry and Thermal-relaxation calorimetry). In addition, the experimental results will be coupled with thermodynamic calculations using the Factsage and/or Thermocalc softwares.

Investigation of alkali and alkaline-earth fission products in oxide fuel: safety assessment of fast breeder reactors

(Chemistry (BEP/MEP)
Anna Smith

Alkali and alkaline-earth metals such as cesium (Cs), rubidium (Rb), potassium (K), lithium (Li), barium (Ba), strontium (Sr), calcium (Ca) and magnesium (Mg) are generated during irradiation in fast breeder reactors, which makes the chemistry of the nuclear fuel particularly complex. (U,Pu)O2 mixed oxide fuel is currently the reference for fast reactors such as the Generation IV Sodium cooled Fast reactor (SFR). With a view to improve the sustainability of the fuel cycle, the incorporation of minor actinides elements (Np,Am,Cm) to the fuel is also envisaged, corresponding to the composition (U,Np,Pu,Am,Cm)O2. Some of the fission products generated during burn-up are soluble into the fuel matrix, while others form oxide precipitates depending on conditions of temperature and oxygen potential in the reactor. Ternary alkali and alkaline earth actinide oxide phases can be formed with lower density and thermal conductivity than the mixed oxide fuel. This leads to fuel swelling and temperature increase, which affects the fuel behaviour.

Understanding the chemistry of the interaction between fuel and fission products, in particular the conditions required for the formation of the ternary phases, their thermal stability and thermodynamic properties, is essential for the safety assessment of the reactor during operation and accidental conditions. In this research project, we will look at the structural and thermodynamic properties of the ternary phases formed with uranium in the (Cs,Rb,K,Li,Ba,Sr,Ca,Mg)-U-O systems. The work will involve solid state synthesis and characterization using X-ray diffraction and neutron diffraction, the study of the compounds thermal expansion using high temperature X-ray diffraction, as well as calorimetric measurements (Differential Scanning Calorimetry and Thermal-relaxation calorimetry) and possibly Knudsen effusion mass spectrometric measurements. In addition, the experimental results will be coupled with thermodynamic calculations using the Factsage and/or Thermocalc softwares.

Thermochemistry of noble metals in fluoride salts (BEP/MEP)

Molten Salt Reactors, which are a promising type of future fission reactors, utilize a liquid molten salt mixture as nuclear fuel. Fluoride salts are one of the best option as candidate salts and their physico-chemical properties is under investigation since many years. However, little information is available on the behaviour of salt containing fission products. In particular, the thermochemistry and the phase stability of the so-called “noble metals” (e.g. Mo, Ru, Te, Pd, Tc) is not yet fully established.

The research project reported here aims to calculate the behaviour of these noble metals as it depends on the system temperature and fluorine potential. First, a literature review will be carried out to determine the possible stable phases of the selected noble metal with fluorine. The thermochemical properties of these phases will then be calculated using a combination of Density Functional Theory (DFT) and statistical mechanics calculations. The final goal is the assessment of all the binary systems, which allows the prediction of the thermodynamic equilibrium of complex systems and the speciation of the noble metals.

Info: Dr. Elisa Capelli **e-mail:** E.Capelli@tudelft.nl

Assessment of uncertainty in CALPHAD predictions for Molten Salt Reactor fuel (BEP)

Understanding and predicting nuclear fuel behaviour in innovative type of reactors, such as the Molten Salt Reactor, is a key step for their future development and deployment. The CALPHAD (CALculation of PHAse Diagrams) method is a proven and indispensable tool in this endeavour and it is currently used to generate customized thermodynamic databases. Based on the developed models, thermochemical equilibrium calculations are performed allowing the prediction of the thermodynamic properties and the evaluation of the safety margins for the potential fuel mixtures.

For reactor designer and regulatory bodies, knowledge of the uncertainty associated with the results from CALPHAD is crucial. Currently however, the reliability of these predictions is only inferred by comparing the calculated results to experimental phase equilibria data, resulting in a region of confidence which is limited to known composition and temperature regimes. Rigorous, comprehensive evaluation of uncertainties is lacking. At the same time there is substantial knowledge about uncertainty propagation and evaluation methods applicable to generic computational problems. The goal of this project is to make the first step towards the accurate and computationally affordable prediction of uncertainties in CALPHAD calculations by using and adapting advanced uncertainty quantification methods.

Info: Dr. Elisa Capelli, Dr. Zoltán Perkó **e-mail:** E.Capelli@tudelft.nl, Z.Perko@tudelft.nl

Fission product extraction in Molten Salt Reactor (BEP/MEP)

The Molten Salt Reactor is an innovative type of nuclear reactor that meets the Generation IV goals in terms of safety, reliability, proliferation resistance and economics. The very unique feature of this reactor is the liquid nature of the fuel, which is composed by a mixture of molten fluoride salts. One of the advantages of having a liquid fuel is the possibility of controlling and extracting the fission products while operating the reactor. Helium bubbling is one of the reprocessing steps and is used to separate the gaseous fission products from the fuel in order to keep good neutronic properties. Furthermore, this process has the potential to remove via flotation the insoluble particles, such as noble metals, that might otherwise deposit on the metallic surfaces. In the current project, the efficiency of particles removal via flotation will be assessed.

The test facilities available at TU Delft allows the investigation of flotation both in static conditions and in a forced flow system. Simulant fluids are used in the present setup to study the underlying mechanisms of the process and understand the dependence of the extraction efficiency with the process parameters (e.g. bubble size, particle properties, fluid properties). In addition to the experimental work, numerical simulation could also be performed to support the interpretation of the experimental results and optimize the process design.

Info: Dr. Elisa Capelli **e-mail:** E.Capelli@tudelft.nl

Innovative synthesis routes for the production of nuclear materials (Chemistry) (MEP)

Anna Smith

New synthesis routes for high-melting ceramic and metallic materials for nuclear applications will be investigated. The focus will be on the direct synthesis from primary materials (such as aqueous, liquid or gaseous precursors) at low/moderate temperatures. The work will include (i) a critical review of potential innovative manufacturing methods, including the chemical safety aspects, (ii) systematic review and selection of potential precursor materials, (iii) the design of an experimental set-up that would be suited to produce the material on a laboratory-scale while also allowing the study of the reaction mechanism and kinetics, (iv) equilibrium chemical thermodynamic calculations using the Factsage software to assist the feasibility assessment and the design of the production route.