

## Résumé de thèse Joelle Costantine

### « Chemistry of molten chloride salt for molten salt nuclear reactor »

Molten-salt nuclear reactors (MSRs) are one of six concepts selected by the Generation IV International Forum (GenIV) for developing fourth-generation nuclear reactors. Their specificity lies in using a liquid fuel consisting of molten salt. This concept meets GenIV objectives regarding safety, sustainability, and minimization of final waste. Indeed, using a liquid fuel brings intrinsic safety to the reactor since when the temperature rises, the salt expands, thus stopping the chain reaction. Moreover, these reactors can fission minor actinides that contribute most of the long-term radioactivity in nuclear waste.

The first molten-salt reactors, developed by Oak Ridge Laboratory in the USA, used a fluoride-based salt consisting of a LiF-BeF<sub>2</sub> mixture. While this salt is particularly suitable for the <sup>232</sup>Th/<sup>233</sup>U cycle, it is not suited to the French nuclear cycle based on <sup>238</sup>U/<sup>239</sup>Pu. The U/Pu cycle requires a fast neutron spectrum to overgenerate plutonium, which fluoride salt cannot provide. Chloride-based molten salts are therefore more suitable for the U/Pu cycle. The NaCl-MgCl<sub>2</sub> salt was considered for this fuel type in the 1970s based on melting temperature, neutronics, and thermal-hydraulics criteria. Another salt of interest is the binary salt NaCl-ThCl<sub>4</sub>, with a melting point of 360°C. The use of ThCl<sub>4</sub> in molten salt lowers the medium's temperature, which is a desired outcome. ThCl<sub>2</sub> has also been mentioned in the literature. Thermodynamic data show that it is an amphoteric compound that could control the solvent's redox domain at potentials preventing corrosion of structural materials. As ThCl<sub>4</sub> is not commercially available, studying the binary salt NaCl-ThCl<sub>4</sub> was impossible, and only thorium as a solute could be investigated.

This thesis has three main objectives: studying the chemistry of the NaCl-MgCl<sub>2</sub> binary, investigating thorium chemistry in molten chloride salt, and examining the separation of lanthanides (Ln)/actinides (An) in molten chloride salt. The studies were conducted using a combination of thermodynamic calculations and various experimental analytical techniques. The distinctive feature of NaCl-MgCl<sub>2</sub> salt is its oxo-acidic nature, which theoretically prevents PuO<sub>2</sub> or UO<sub>2</sub> precipitation in the reactor. However, this property makes it highly reactive toward water and oxygen, as demonstrated both computationally and experimentally. This reactivity leads to the formation of Cl<sub>2</sub> and HCl, which are powerful toxic oxidants. Chloroacidity, or chloride ion activity, is an essential property of chloride salts as it allows prediction of solute solubility in the solvent. Experimental determination of this data for the NaCl-MgCl<sub>2</sub> salt has led to the following classification: LiCl-KCl > NaCl-CaCl<sub>2</sub> > NaCl-MgCl<sub>2</sub>. The chemistry of ThCl<sub>4</sub> was studied in NaCl-CaCl<sub>2</sub>. A single stable soluble oxidation state, Th(+IV), was identified. Th(+IV) remains stable when the medium's oxoacidity is controlled. Without control, thorium precipitates as ThO<sub>2</sub>. The activity and diffusion coefficients of ThCl<sub>4</sub> were determined.

The An (U and Th)/Ln (Ce, Nd, Gd, La) separation was studied by electrolysis on solid Al electrode in NaCl-CaCl<sub>2</sub> salt after identifying stable oxidation states and redox potentials on inert and Al electrodes. While Th/Ln separation is possible, U/Ln separation is less efficient as uranium is not depolarized on the Al electrode.