Thesis subject at the UCCS (Modelling and Spectroscopies Team) in collaboration with the IRSN

Theoretical study of the AgI and CsI aerosol chemical reactivity

In case of severe nuclear accident in a nuclear plant, iodine released in the atmosphere, will be one of the major sources of radioactivity. Several experimental and theoretical works have made it possible to partially understand and model the mechanisms leading to the formation of gaseous iodine in the primary cooling circuit of nuclear plant.

The experimental work of D. Obada has shown that, in air, the reaction between aerosols CsI/ AgI deposited on stainless steel-type surfaces leads to the formation of cesium chromate and volatile iodine and that the water vapour tends to limit the formation of iodine gas without preventing it. He also illustrated the influence of boron and NO_x on the formation of volatile iodine in the primary circuit.

H. Hijazi has shown by theoretical chemistry that CsI and AgI particles can lead to the formation of I_2 gas due to the reaction with the HO° radicals, formed by the radiolysis of water vapour, and that the formation of iodine is not favourable thermodynamically in the absence of oxidants. H. Hu studied the mechanisms of AgI, CdI2, RuO4 and RuO2 adsorption on iron and chromium oxides surfaces and studied reactions that can lead to the release of iodine and ruthenium gaseous compounds.

However, under the effect of temperature, CsI aerosols deposited on a gold surface (chemically inert) partially decompose into volatile iodine (nearly 20% in the associated tests). This indicates the existence of volatile iodine formation mechanisms taking place on the surface of the aerosol itself without the involvement of the support on which the aerosols are deposited. These experimental results suggest chemical reactions involving CsI(g)/AgI(g) and / or CsI(s)/AgI(s) (as aerosols before the deposition on a surface) and the gas phase, in particular NOx and borated species, but no theoretical studies have been carried out on this subject.

The objective of this thesis is therefore to complete work on modelling the behaviour of iodine in the primary circuit and to determine the effect of the Nox and borates on its formation. To do this, the possible chemical reactions leading to the formation of gaseous iodine in the primary circuit will be studied theoretically, at the DFT level, and the associated energy barriers will be computed for the most relevant reactions to estimate the iodine formation reaction rates. Secondly, the most relevant reaction will be integrated into programs used to model the dissemination of the radioactive compound in the atmosphere (ASTEC / SOPHAEROS), the theoretical results will then be compared to the experimental tests (CHIP, CHIP +, ESTER and PHEBUS). Finally, lessons can be drawn with regard to reactor applications.

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