



Chemistry of Iodine and Aerosol Composition in the Primary Circuit of a Nuclear Power Plant

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ABSTRACT

In case of a severe accident on a nuclear reactor, radioactive iodine may be released into the environment, impacting significantly the radiological consequences. Determination of the amount released, and of the physical state of iodine (gaseous form or solid aerosol form), is thus a major issue. The release of iodine from the damaged reactor core and its transport in the different parts of the reactor up to the reactor containment, have been extensively studied, particularly in the Phébus-FP large scale experiments. Phébus-FP results notably showed that a significant fraction of iodine under gaseous form can reach the containment. The models used in severe accident codes did not (and still does not) fully account for this iodine speciation. A likely explanation is that iodine keeps a gaseous form up to the containment due to some processes that limit the formation of caesium iodide in the reactor coolant system (RCS) (caesium iodide was assumed to be the dominant form of iodine in the RCS). Caesium iodide formation would be limited due to chemical kinetic limitations and due to the presence of other elements (molybdenum or boron) responsible for “trapping” the caesium. An experimental research program has been developed with the aim to study the chemical behaviour of iodine during its transport in the RCS, with presence of steam, caesium and molybdenum or boron. The paper presents results obtained with molybdenum oxide. Experiments are compared to calculations performed with the IRSN severe accident code ASTEC where a chemical kinetic model has been implemented. The second part of this paper presents first results obtained with boric acid instead of molybdenum oxide.

1 INTRODUCTION

The amount of radioiodine in gaseous form in the containment of a Nuclear Power Plant following a severe accident is one of the major issues of the nuclear safety analysis. The chemistry and the transport of iodine in the different parts of the reactor during the core degradation have been extensively studied in the Phébus-FP tests performed under Loss of Coolant Accident (LOCA) representative conditions. One of the unexpected results is the

significant fraction of iodine that was observed under gaseous form in the containment at the beginning of the post-degradation phase [1]. The models used in computer codes such as the integral code ASTEC [2] do not fully account for the measured values during this period of the transient, when gaseous iodine comes directly from the Reactor Coolant System (RCS). Persistence of gaseous iodine in the RCS at low temperature^a could be due to some processes that would limit the formation of caesium iodide (CsI) that is assumed to be the predominant form of iodine in the primary circuit^b. Gaseous iodine could be enhanced due to kinetic limitations in the gas phase or due to the presence of other elements reacting with caesium that could reduce the relative ratio cesium to iodine and so the possibility for iodine to produce stable condensed compounds with caesium. In order to provide additional results for code validation, an international research program named CHIP (Chemistry of Iodine in the Primary circuit) is currently in progress at IRSN. This program includes experimental tests carried out in different facilities. A simple test facility has been developed to study cold-leg break situations with simple chemical systems composed of steam, caesium, iodine and another element selected for its potential role on iodine or caesium chemistry in the RCS. Molybdenum was first considered because of its ability to form caesium molybdate Cs_2MoO_4 that is more stable than CsI at high temperature [3]. Furthermore, thermodynamic calculations of Phébus-FP tests confirm the presence of Cs_2MoO_4 in the RCS. Then, the study of the influence of boron has been considered. Once again, results of Phébus-FPT3 test [4], carried out with boron carbide, have shown the possible effects of boron on fission product speciation.

This paper presents the results on iodine behaviour obtained with molybdenum and with boron. Analysis of gaseous products is coupled with the study of aerosol molecular composition. Experiments are compared to calculations performed with the SOPHAEROS^c module devoted to the simulation of fission product transport in the RCS, as part of the severe accident code ASTEC [2].

2 MATERIAL AND METHODS

2.1 Test facility

The experimental line (Figure 1) consists of a 1 m long alumina (Al_2O_3) tube settled inside a high temperature furnace. Caesium, iodine and molybdenum chemical compounds are vaporized in the alumina tube from alumina crucibles and transported in a carrier gas, a mixture of steam and argon. Boron is produced by vaporization of a boric acid aqueous solution and is directly injected in the high temperature zone via a small-diameter alumina tube. The carrier gas is heated from 150°C at the inlet flange of the furnace up to a high temperature plateau about $1500\text{-}1600^\circ\text{C}$ corresponding to temperature levels encountered upstream the RCS during the degradation phase. Downstream, temperature of the fluid decreases rapidly, in a few seconds, from 1560°C to 150°C . Aerosols generated and transported in the tube are collected on quartz fibre filters and gaseous phases are trapped in liquid bubblers. Two kinds of liquid traps are used: bubblers filled with an alkaline solution in order to trap total gaseous iodine; biphasic solution composed of aqueous phase and an organic phase namely toluene in order to selectively separate hydrogen iodide HI from molecular iodine I_2 . Molecular iodine I_2 is expected to be trapped in the organic phase while hydrogen iodide would stay in the aqueous acidic ($\text{pH} = 3$) phase. Quartz plates are placed in

^a During the Phébus-FP tests, fluid temperature at the exit of the RCS is about 150°C . This temperature level corresponds to the thermal conditions encountered at a cold break leg during a LOCA.

^b CsI and its dimer are considered as non volatile iodine species because they are under condensed form at 150°C .

^c SOPHAEROS is a module of the ASTEC code developed by IRSN and GRS for severe accident of nuclear power plant.

the cooling zone in order to have information on the vapours condensed on the wall and on the particles deposited along the line.

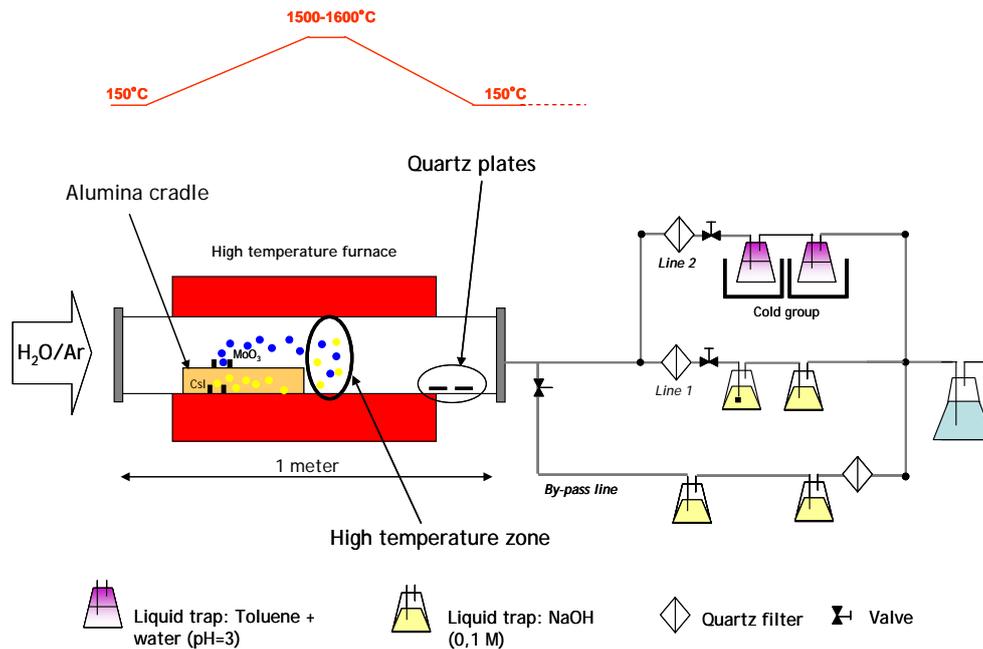


Figure 1: Schematic view of the experimental line for the {Cs, I, Mo, O, H} study

The carrier gas is composed by a fraction of steam of 80 % vol. and 20 % vol. of argon^d. The absolute pressure in the alumina tube was fixed at 1 bar. Some experiments have been carried out with the simultaneous injection of CsI and MoO₃ in the line with different Mo/Cs ratios or with the simultaneous injection of CsI and H₃BO₃ in the line with different B/Cs ratios. Mo/Cs and B/Cs ratios are in the range expected during a PWR severe accident^e.

2.2 Chemical analysis

After each test, the facility is dismantled and each part is leached to be able to establish a reliable element distribution from the high temperature zone down to the outlet gas scrubber. This also allows calculating the Mo/Cs, B/Cs and Cs/I ratios in the high temperature zone. The gaseous phase trapped in the alkaline solution has been quantified by Inductively Coupled Plasma Mass Spectroscopy^f (ICP-MS). Analysis of the organic phase solution of biphasic bubblers are made by UV-visible spectroscopy^g. The condensed species collected on the filter are analysed by analytical electron microscopy (Environmental Scanning Electron Microscope coupled with Energy Dispersive analysis of X-ray - ESEM-EDX) and by automated Raman microspectrometry. The Raman spectroscopy gives a molecular fingerprint of solid or liquid compounds and is then a powerful technique to identify the chemical species within particles. After analysis of the filters by Raman spectrometry and ESEM-EDX, they are lixiviated with alkaline solution for elemental characterization by ICP-MS.

^d The total flowrate was set to 1 NI/min corresponding to a flow residence time of about 7 s from the high temperature zone to the first point at 150°C.

^e $0.35 < \text{Mo/Cs} < 3$ and $1 < \text{B/Cs} < 40$.

^f For iodine, the detection limit was evaluated at about 4.10^{-9} mol/l and the quantification limit is about 13.10^{-9} mol/l. These limits were even lower for caesium and molybdenum. For boron, there were respectively calculated at 6.10^{-8} mol/l and 1.10^{-7} mol/l.

^g The detection limit of molecular iodine in toluene was evaluated at about $7.21.10^{-6}$ mol/l for the 498 nm peak.

2.3 Theoretical calculations

Experimental results are compared to the results given by the SOPHAEROS code [2]. Two groups of elements and compounds, initially present in gaseous phase are modelled: gaseous species that are non-condensable and volatile species that can be present in the gaseous state and in the condensable phase according to the temperature. The chemical speciation of the different gaseous species is calculated assuming thermodynamic equilibrium. Once condensed, the compounds no longer participate to the chemistry. Aerosol phenomena include homogeneous nucleation and the standard agglomeration and deposition mechanisms. Chemistry-related data are stored in a database that contains 736 vapours and 684 condensed phases. Among them, 38 concern the {Cs, I, Mo, O, H} system and 53 are involved in the {Cs, I, B, O, H} system.

In order to study possible kinetic limitations, a kinetic model devoted to iodine chemistry in the RCS is under development. A first version of this model limited to the {I, O, H} system was already implemented in the SOPHAEROS code [5]. It is based on a set of 41 homogeneous gas-phase reactions. The rate constants are defined from an Arrhenius law and some of them were deduced from theoretical chemistry calculations. The standard SOPHAEROS simulations only consider thermodynamic equilibrium and some calculations are performed adding this kinetic model for {I, O, H}.

3 RESULTS

3.1 CsI and MoO₃ simultaneous vaporization under steam

Five tests have been performed on the {Cs, I, Mo, O, H} system and one test with only CsI vaporization. This last test gives the amount of gaseous iodine that can be expected at 150°C in the absence of molybdenum. Mo/Cs ratios have been varied from 0.03 to 4.90. Simultaneous vaporization of CsI and MoO₃ under steam leads to the formation of gaseous and condensed species. When Mo/Cs ratio is higher than 0.03, on the first plate placed in the cooling zone, spots are observed that look like dried liquid whereas on the second one, needle-type particles are observed with an average size decreasing according to the axial position in the tube (Figure 2). As regards to filters, collected particles are homogeneous in morphology (thin needles 100-500 nm long).

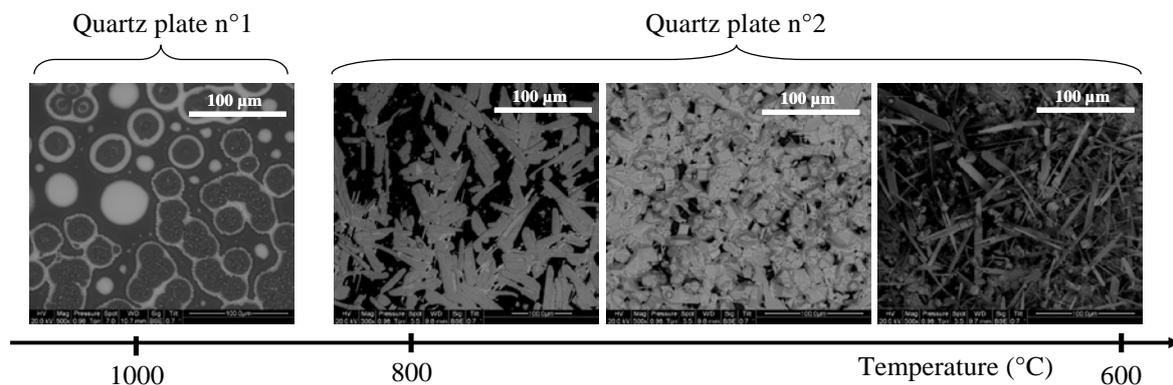


Figure 2: ESEM images of deposits and particles along the quartz plates for the Mo/Cs = 4.90 test.

On the contrary, for the CsI vaporization alone or with a Mo/Cs ratio lower or equal to 0.03, most of the particles are spherical both on the quartz plates (Figure 3) and on filters (0.1 – 0.5 μm).

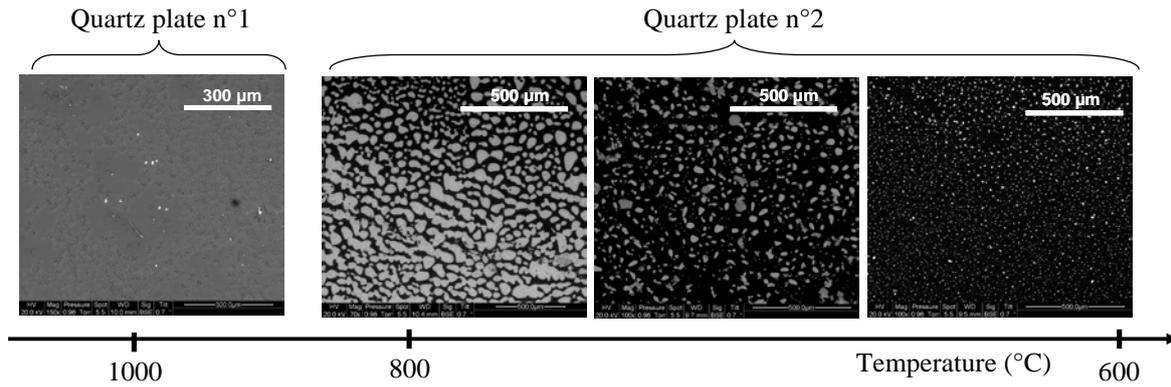


Figure 3: ESEM images of deposits and particles along the quartz plates for the Mo/Cs = 0.03 test.

Results of Raman analysis performed on quartz plates and on filters are given in Table 1. Different caesium molybdates have been identified on the basis of the spectra given by Hoekstra [6]. The higher the Mo/Cs ratio is in the high temperature zone, the richer in molybdenum the caesium molybdates are. Raman spectra of species collected on filters (150°C) are similar to those obtained in the analysis of deposits on the last plate (800°C > T > 650°C) showing that stable compounds of molybdenum and caesium are obtained for temperature below 600°C.

Table 1: Raman identified species and ICP-MS results from CsI and MoO₃ vaporization

		pure CsI	Mo/Cs < 1		Mo/Cs > 1			
		Mo/Cs	0.03	0.17	0.73	2.06	4.9	
		Cs/I	1.01	1	0.99	1	0.96	
Quartz plates	Raman identified species	–	Cs ₂ MoO ₄	Cs ₂ Mo ₂ O ₇ Cs ₂ Mo ₃ O ₁₀	Cs ₂ Mo ₂ O ₇ Cs ₂ Mo ₃ O ₁₀ Cs ₂ Mo ₄ O ₁₃	Cs ₂ Mo ₃ O ₁₀ Cs ₂ Mo ₄ O ₁₃ Cs ₂ Mo ₅ O ₁₆ Cs ₂ Mo ₇ O ₂₂	Cs ₂ Mo ₃ O ₁₀ Cs ₂ Mo ₄ O ₁₃ Cs ₂ Mo ₅ O ₁₆ Cs ₂ Mo ₇ O ₂₂	
	Filters (150°C)	Mo/Cs	–	0.05	0.15	0.52-1.00	1.39-1.94	3.11-4.61
		Cs/I	0.9	0.95	1.07	1.43-2.47	2.24-3.87	31.01-33.24
	Raman identified species	–	–	Cs ₂ Mo ₂ O ₇ Cs ₂ Mo ₃ O ₁₀ MoO ₃ ·3H ₂ O	Cs ₂ Mo ₃ O ₁₀ Cs ₂ Mo ₄ O ₁₃	Cs ₂ Mo ₅ O ₁₆ Cs ₂ Mo ₇ O ₂₂	Cs ₂ Mo ₇ O ₂₂ MoO ₃	

According to gaseous species trapped in solutions, the main observations are:

- Molybdenum and caesium are not detected in the solutions, showing that they are only under an aerosol form;
- The gaseous iodine fraction^h increases when the Mo/Cs ratio in the high temperature zone increases (Figure 4);
- From the biphasic scrubbers it is evidenced that gaseous iodine is mainly composed of molecular iodine (always > 50 %) whatever the Mo/Cs ratio.

Experimental results have been compared to calculations performed with SOPHAEROS code. Cs₂MoO₄ is the only caesium polymolybdate included in the database, so the different identified caesium polymolybdates are not represented in the code. However, Mo/Cs ratios on aerosols are close to those experimentally determined on filters by ICP-MS.

^h Gaseous iodine fraction was calculated from gaseous iodine measured in the sampling line and the total amount of iodine trapped on the sampling line.

Evolution of gaseous iodine fraction as a function of the Mo/Cs ratio is relatively close to experimental data (Figure 4). Concerning iodine speciation, only 12 % of gaseous iodine is calculated as molecular iodine. This is in contradiction with experimental data which give more than 50 %.

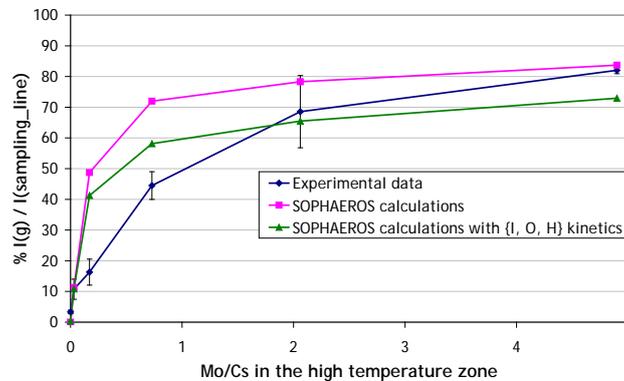


Figure 4: Evolution of the experimental gaseous iodine fraction as a function of Mo/Cs ratio in the high temperature zone compared to those calculated by SOPHAEROS code with and without the {I, O, H} kinetics

As mentioned in the introduction of this paper, an explanation to the presence of gaseous iodine at low temperature is based on kinetic limitation of chemical reactions. Calculations performed including {I, O, H} kinetic data show that the time to reach thermodynamic equilibrium in vapour-phase for temperature below 700°C is higher than the residence time of the fluid in the line.

Simulation performed with the kinetic model gives results in good agreement with data concerning gaseous iodine fraction which are also close to ones calculated with the standard version (Figure 4). Nevertheless, at 150°C, the fraction of molecular iodine, calculated with the kinetic model, reaches 90 % of the gaseous iodine. Results with {I, O, H} kinetic are in better agreement with the experimental results than the standard version. On the other hand, introduction of the {I, O, H} kinetics has no effect on the chemistry and transport of molybdenum and caesium compounds.

Molybdenum has an influence on gaseous iodine fraction. Results show that molybdenum reacts with caesium as indicated by the presence of different caesium polymolybdates. Consequently, the formation of condensed caesium iodide is limited and the quantity of gaseous iodine is enhanced. Results are in good agreement with those obtained on the CHIP line [7]. Comparison with SOPHAEROS code shows that aerosol transport is well-represented even if all the caesium molybdates are not introduced in the database. The molecular iodine formation is better-simulated using the {I, O, H} kinetics.

3.2 CsI and H₃BO₃ simultaneous vaporization under steam

A few tests have been performed with the {Cs, I, B, O, H} system. Tests with B/Cs ratios of 15 and 90 have been compared to a test performed with only CsI vaporization. Simultaneous vaporization of CsI and H₃BO₃ under steam leads to the formation of gaseous and condensed species. On the plates, submicronic spherical particles are observed. Metaboric acid HBO₂ is identified by Raman microspectrometry on the first plate (850°C – 1000°C) for both tests. On the second plate (600°C - 800°C), characteristic peaks are assignable to the presence of C₂O.B₂O₃ glasses. Very small amounts are present on the filters so it was not possible to identify compounds. Gaseous iodine fraction increases between the CsI test and tests with injection of boron (Figure 5). Molecular iodine represents more than 50 % of

gaseous iodine. It has to be noticed that boron is mainly present under gaseous form. Less than 5 % of boron in the sampling line is identified on filters.

Experimental results are compared to results obtained from SOPHAEROS code. The calculated gaseous iodine represents less than 5 % of the injected iodine. Calculations carried out by introducing the {I, O, H} kinetics show the same results. The fraction of gaseous iodine is much less than that observed experimentally (Figure 5).

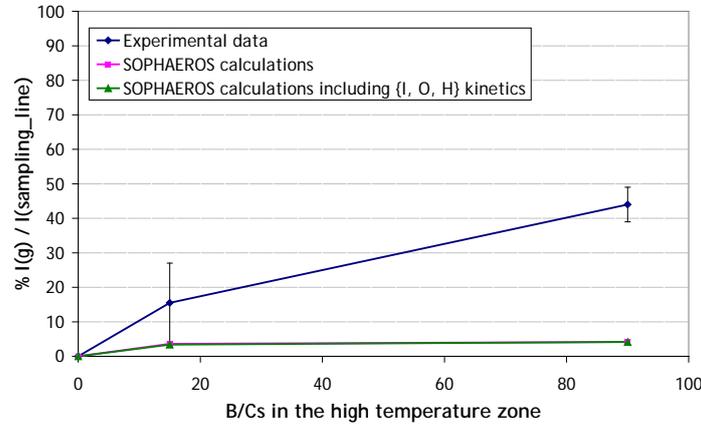


Figure 5: Evolution of the experimental gaseous iodine fraction as a function of B/Cs ratio in the high temperature zone compared to those calculated by SOPHAEROS code with and without the {I, O, H} kinetics

The speciation of gaseous iodine is calculated with SOPHAEROS as hydrogen iodide HI mainly. Even when the {I, O, H} kinetic model is introduced, the molecular iodine proportion is, at most, 20 % of the total gaseous iodine. Experimental B/Cs ratios measured on the filters are higher than calculated ones (Table 2). It might be due to gaseous boron interaction with aerosols collected on the filter or a presence of caesium borate with a higher B/Cs ratio than CsBO_2 ($\text{Cs}_2\text{B}_8\text{O}_{13}$ for example) [8]. Cs/I ratios on aerosols are also much different between experimental data and calculations. These values confirm that CsI is not the experimental predominant caesium compound at 150°C.

Table 2: Aerosols ratios determined by ICP-MS and calculations from CsI and H_3BO_3 vaporization

		B/Cs in the high temperature zone	15	90
Aerosols	B/Cs	Experimental data	4.02	4.92
		SOPHAEROS calculations	0.47	2.18
		SOPHAEROS calculations including {I, O, H} kinetics	0.47	2.18
	Cs/I	Experimental data	1.2	18.98
		SOPHAEROS calculations	1.05	1.05
		SOPHAEROS calculations including {I, O, H} kinetics	1.05	1.05

Boron has an influence on gaseous iodine fraction. As it has been suggested for study of the {Cs, I, Mo, O, H} system, boron reacts with caesium forming caesium borates. The formation of condensed caesium iodide is, then, limited and gaseous iodine is favoured. Comparing with SOPHAEROS code, it appears that gaseous iodine fraction is not well-represented. This may be due to caesium borate condensation which is not enough taken into account, for example due to the absence of caesium borate dimer in the database. Nevertheless, the boron influence on the {I, O, H} system is less pronounced than the molybdenum influence.

4 CONCLUSIONS

The influence of molybdenum and boron on the amount of iodine under gaseous form exiting the primary circuit of a PWR has been evidenced in a test facility that reproduces the conditions encountered during a severe accident. Results show that both molybdenum and boron react with caesium. These elements act as caesium “traps” and then, prevent the caesium iodide formation. As regards to experimental results, boron influence seems less important than molybdenum influence for the same X/Cs ratio ($X = \text{Mo}$ or B). The ASTEC/SOPHAEROS code correctly predicts the gaseous iodine fraction for the {Cs, I, Mo, O, H} system but has to be reviewed for the {Cs, I, B, O, H} system. New tests are needed to extend the experimental matrix for the {Cs, I, B, O, H} system and compare with the code. The use of {I, O, H} kinetics allows to better predict the speciation of gaseous iodine in the {Cs, I, Mo, O, H} system but more work is needed for better representing the {Cs, I, B, O, H} system.

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