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Chemical reactions of fission product deposits and iodine transport in primary circuit conditions

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HIGHLIGHTS

- With CsI precursor, 20% of released iodine was in gaseous form in steam flow at 650 °C.
- In similar conditions with Mo, gaseous iodine fraction was increased to 38–79%.
- Boron trapped most of the caesium and iodine was almost completely released as gas.

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ABSTRACT

The objective of this work was to examine the chemical reactions taking place on primary circuit surfaces and their effect on fission product transport in a severe nuclear reactor accident. Especially transport of gaseous and aerosol phase iodine was studied. Caesium iodide (CsI) was used as precursor material for iodine species. Also, effects of molybdenum and boron on transport of iodine were investigated.

The experimental work showed that when CsI alone was used as a precursor, as much as 20% of the released iodine was in gaseous form and the rest as aerosol particles. Aerosol particles were most likely CsI. When the amount of hydrogen in the carrier gas was increased, the fraction of gaseous iodine decreased. When Boron was added to the precursor, a glassy caesium borate surface was formed on the crucible. Boron trapped most of the caesium and also a fraction of iodine, causing almost all released iodine to be in gaseous form. When Mo was introduced in the precursor, most of the iodine was again released in gaseous form. Oxidised Mo reacted with caesium releasing iodine from CsI. The effect of Mo on iodine transport depended much on H_2 concentration and was observed to be substantially greater on stainless steel surface. When stainless steel crucible was used, Mo was found in small amounts from aerosol particles, indicating that it was probably released as caesium molybdate or as molybdenum oxide.

1. Introduction

Iodine is considered to be important in the nuclear safety analysis due to formation of several very volatile gaseous iodine compounds during a severe accident conditions. Specific activity of iodine is high and it is accumulated in thyroid gland. After released from the fuel, fission products are transported through the primary circuit before ending up to the containment atmosphere. Chemical reactions of deposited fission products on primary circuit surfaces can modify the amount, composition and timing of fission product release to the containment (Bowsher and Dickinson, 1986; Bowsher, 1987; Wright, 1994).

Phebus FP programme was initiated in 1988 and it investigated severe light water reactor accidents. It consisted of five in-pile experiments which were conducted between the years 1993–2004 (Clement and Zeyen, 2013). In the first Phebus experiment (FPT0) it was seen that when the temperature in the primary circuit was dropped to 423 K, at least 2% of iodine was still in gaseous form indicating that a fraction of the released iodine transported through the primary circuit as some chemical species that did not condense at 423 K (Clement et al., 2003). Similarly in FTP1 test, a significant concentration of gaseous iodine was observed in the containment after the first oxidation phase but only a negligible amount of gaseous iodine was measured in the cold leg, leaving open the question whether the gaseous iodine originated from the circuit (Girault et al., 2006). The initial conditions of FPT3 experiment differed the most from other experiments conducted with bundle geometry, since the material of the control rods used was boron carbide B_4C. The overall behaviour of iodine also

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differed significantly from previous Phebus tests (Haste et al, 2010). In FTP3, only a very small fraction of iodine was transported as aerosol particles in the circuit. Approximately 85% of the iodine released in the containment was in gaseous form.

Besides Phebus FP, other experimental programmes have also been initiated related to fission product release in severe accident conditions. The CHIP programme investigates the release of iodine from the gas phase reactions taking place in the primary circuit conditions (Gregoire and Mutelle, 2012; Gouello et al., 2013). VERCORS programme (Pontillon et al., 2010) investigated the release of fission products and transuranic elements from a fuel rod and on-going VERDON tests (Gallais-During et al., 2012) will further investigate the fission product release and transport under light water reactor severe accident conditions.

The purpose of this work is to study the reactions of caesium iodide on the surface of primary circuit and the possible effect of these reactions on iodine speciation. If other materials are absent, it has been observed that iodine will mainly be released to the primary circuit as CsI (Bowsher, 1987). If materials like silver and cadmium from the AIC control rods are present, other metallic compounds like AgI or CdI_2 could be formed (Wright, 1994; Cantrel et al., 2013). However, since these are the first tests conducted with this experimental setup, CsI was selected as a precursor to provide the base case for future experiments.

The fraction of the gaseous and particulate iodine is measured as well as the size distribution of the particles formed in the gas phase. In some experiments, boron or molybdenum is added to CsI containing crucible and their effect on surface reactions is observed. In the work of Bowsher and Dickinson, it was seen that volatile hydrogen iodide was formed in vapour phase reaction of CsI and boric acid and in reaction between boric acid vapour and condensed CsI (Bowsher and Dickinson, 1986). Many studies have shown that significant fraction of molybdenum is released from the fuel under severe accident conditions (Pontillon and Ducros, 2010; Clement and Zeyen, 2013) and transported to the primary circuit (Haste et al., 2013).

In addition, the effect of H_2 concentration on iodine transport is investigated. The results presented in this paper represent the first stage of the experimental programme, during which the relative importance of various potentially important factors affecting iodine transport were scoped.

2. Experimental

2.1. Experimental facility and setting

A schematic picture of the experimental facility is shown in Fig. 1. An evaporation crucible with the length of approximately 200 mm containing the precursor material(s) is placed inside the reaction furnace, which is heated to 650 °C. The reaction furnace temperature was chosen so that it would be just above the melting point of CsI and also close to the hot leg temperature (700 °C) used in the Phebus FP experiments (Clement and Zeyen, 2013). The length of the furnace tube is 440 mm and diameter 22 mm. A gas flow containing argon, water vapour and hydrogen, is fed into the heated furnace. The precursor materials react with each other, with gas and with the surface of the crucible. Reaction products are transported with the gas flow into a primary diluter where the sample mixture is diluted and cooled down to 125 °C.

From the primary diluter, sample flow enters the sampling furnace along the mainline with the approximate length of 500 mm. The temperature of the sampling furnace was kept above 100 °C in order to avoid condensation of steam to the sampling system. The sampling furnace contains three analytical sampling lines each including a plane filter and two or three bubbling bottles downstream from the filter. Each bottle contains 200 ml of 0.2 M NaOH and 0.02 M $Na_2S_2O_3$ water solution. Filters are polytetrafluoroethylene (PTFE) membrane discs, with 5 μm pore size. The Filter efficiency for particles with diameter between 0.035 μm and 1 μm is 84 to >99.99% (Baron and Willeke, 2001). The aerosol particle sample is collected on plane filters and gaseous sample is trapped in bubbling bottles. After the experiment, used filter is placed in a bottle containing 50 ml of the same liquid used in the bubbling bottles. The elemental composition of the samples are analysed with Thermo Fisher Scientific HR-ICP-MS Element2 Inductively Coupled Plasma Mass Spectrometer.

Table 1
Experimental matrix for studying primary circuit chemistry of iodine.

Experiment number:	Precursor:	Crucible material:
1	CsI (10 g)	Alumina
2	CsI (10 g)	Stainless steel
3	CsI (2 g) + B_2O_3 (6 g)	Stainless steel
4	CsI (2.5 g) + Mo (7.5 g)	Alumina
5	CsI (2.5 g) + Mo (7.5 g)	Stainless steel
6	CsI (10 g)	Alumina

After each experiment, the facility is washed with the same solution used in the bubbling bottles. The solution is then collected for ICP-MS analysis in order to determine the amount of depositions onto the facility walls. 200 ml of the solution is used for washing the alumina tube inside the reaction furnace in experiments 2, 4, 5 and 6. 400 ml of solution is used for the primary diluter and another 400 ml for the main line inside the sampling furnace after every experiment.

A sample flow is also monitored with online measurement devices. In the aerosol line, the flow is diluted using an ejector diluter and a porous tube diluter. Aerosol number size distributions are measured with TSI Scanning Mobility Particle Sizer (SMPS), with series 3080 platform containing series 3081 Differential Mobility Analyzer (DMA) and series 3775 Condensation Particle Counter (CPC) as well as with Electric Low Pressure Impactor (ELPI). Aerosol particles are also collected with an aspiration sampler (Lyyränen et al., 2009) on a copper/carbon grid for LEO (Zeiss) DSM 982 Gemini Scanning Electron Microscope (SEM) and Noran Pioneer Pulstar Si(Li) X-ray detector Energy dispersive X-ray Spectroscopy (EDS) analysis.

2.2. Experimental matrix and procedure

At the beginning of each experiment, the source material is spread at the surface of an evaporation crucible. Crucible materials used in the experiments are alumina (Al_2O_3) and oxidised stainless steel (AISI 304, which is a commonly used material in reactor primary circuits). Table 1 shows conducted experiments as well as used precursor and crucible materials. When boron or molybdenum precursors were used, their mass ratio to CsI was chosen to be 3 to 1 in order to make sure that the mixture placed on the reaction crucible surface would uniformly have excess of boron or molybdenum to caesium and iodine, so that the effect of the additive would clearly be observed. Each experiment was carried out with three different carrier gas mixtures, presented in Table 2. Even though gas composition was changed, the total gas flow rate was kept at a constant value, 3.7 l/min (NTP). Argon was introduced to the mix in order to increase to flow rate through the furnace but to keep the steam mass flow rate low enough to avoid its condensation in other parts of the facility.

Particle number size distributions were measured with ELPI and SMPS in every experiment. Also, bottle samples were collected during all experiments. Grid samples for SEM-EDS analysis were collected in experiments 2, 3 and 5. After experiments 2, 3 and 5, crosscut samples of the used stainless steel evaporation crucibles