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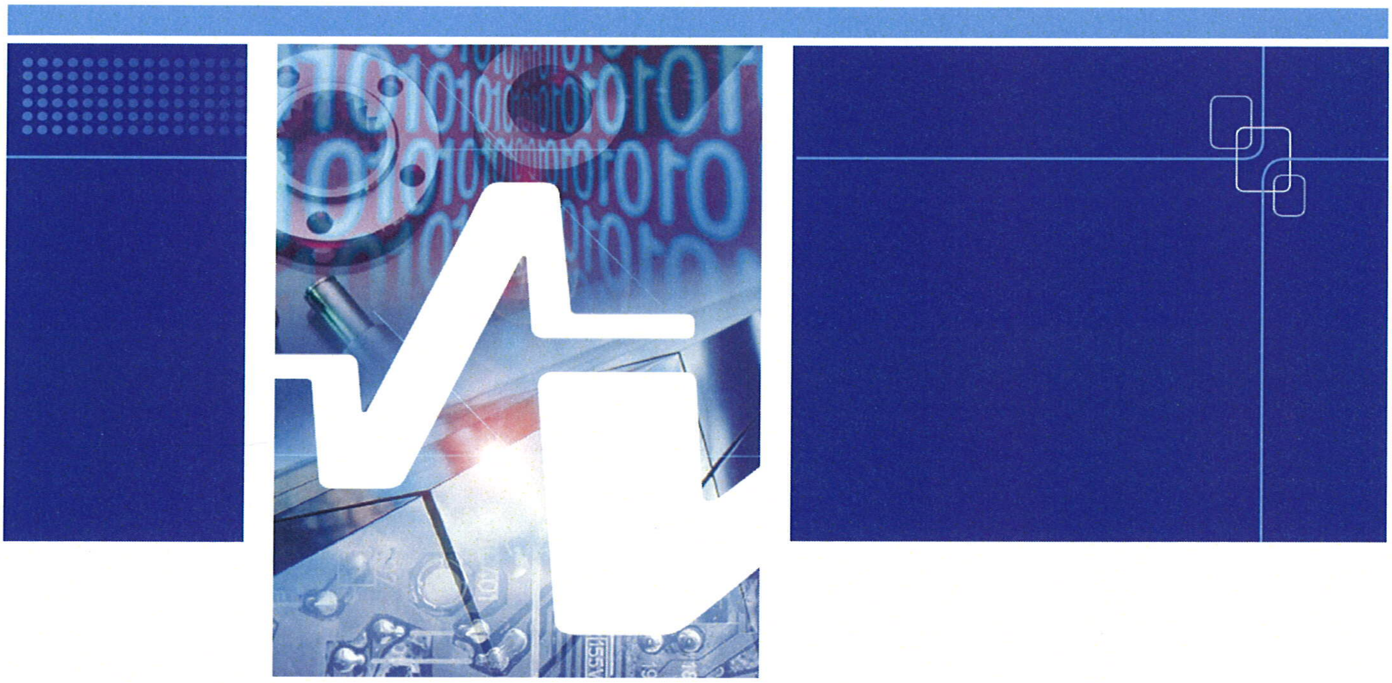

Effects of molybdenum and silver on iodine transport in primary circuit on severe nuclear accidents

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Report's title

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Summary

This experimental study was a continuation of the study conducted at VTT to investigate the effects of reactions on primary circuit surfaces to transport of gaseous and aerosol phase iodine during the hypothetical severe nuclear accident. Cesium iodide was used as a precursor in every experiment. In the experiments it was observed that the hydrogen in the atmosphere decreased the fraction of released gaseous iodine. As the temperature was lowered, less iodine was released, but the fraction of gaseous iodine from the overall released iodine was increased. As molybdenum trioxide was introduced to the precursor, the fraction of gaseous iodine from the overall released iodine was increased significantly. Also, Mo decreased the transport of Cs and caused significant depositions to the reaction furnace. Silver CsI precursor in 650 °C decreased the release of iodine as well as the fraction of gaseous iodine. In 400 °C, Ag + CsI as well as Ag + MoO_3 + CsI precursor significantly increased the release of gaseous iodine, where almost no aerosol particles were released. With B_2O_3 + CsI precursor it was observed that in the dry atmosphere, the released iodine was mostly in gaseous form. Boron was released most likely as boric acid.

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Contents

1 Introduction

During a hypothetical severe accident, fission products transport through reactor primary circuit before ending up to the containment atmosphere. Reactions of deposited fission products on primary circuit surfaces can modify the amount, composition and timing of fission product release to the containment. Starting from the year 2009, studies to investigate the effects of reactions on primary circuit surfaces to transport of iodine have been conducted at VTT. At the beginning of the program, the effects of different surface materials, as well as different precursors, on iodine transport were investigated [1]. After the first scoping studies, some improvements were made to the automated sampling system of the experimental facility. Also, two preliminary experiments were made to test the functionality of the updated experimental facility and to begin studying the formation of gaseous iodine at lower temperatures [2]

In addition to molybdenum and boron used in the previous experiments, this study features also silver as a precursor material. Silver could be present at severe accident conditions since it is one of the widely used control rod material. Previous studies have also indicated that silver could play a major role in transport of iodine during severe nuclear accidents [3]. Also, previous experiments showed that when CsI reacted with molybdenum species, gaseous iodine would be released at lower temperatures than 650 °C. For this reason, some tests in the new experiment set were conducted at lower temperatures, such as 400 °C or 550 °C.

2 Experimental work

The experimental work was conducted using updated EXSI primary circuit facility [2]. The modifications done to the facility have significantly improved the monitoring and data logging capabilities of the experimental set-up. With the updated EXSI primary circuit facility, comparison of the measurement data acquired from the different measurement devices can be done more accurately.

The crucible containing the precursors was heated in the reaction furnace. The furnace tube used in the oxidized stainless steel (AISI 304) and the reaction crucible material used in all experiments was alumina (Al_2O_3). The gaseous reaction products formed in the crucible were trapped in bubbling bottles, and aerosol particles were collected in PTFE filters. In every experiment, two consecutive bubbling bottles were used in each of the sampling lines. The elemental composition of the bubbling bottle and filter samples were analyzed with Thermo Fisher Scientific HR-ICP-MS Element2 Inductively Coupled Plasma Mass Spectrometer.

The properties of aerosol reaction products, such as particle size distribution were also monitored with online measurement devices, such as Decati Electrical Low Pressure Impactor (ELPI) and TSI Scanning Mobility Particle Sizer (SMPS) with series 3080 platform, series 3081 Differential Mobility Analyzer (DMA) and series 3775 Condensation Particle Counter (CPC). As a difference to previous experiment [1, 2], depositions to experimental facility were reduced by further improving the primary diluter design. After each experiment, the facility was washed and a sample from the wall depositions was collected for the ICP-MS analysis.

2.1 Experiment matrix and procedure

The list of experiments conducted in this study is shown in Table I. Cesium iodide (CsI) was used as the source of iodine in all experiments. Reaction furnace temperatures were varied between 400 and 650 °C in order to determine the effect of temperature in the release of gaseous and aerosol phase iodine.

Each experiment contained three different atmosphere conditions, with different fractions of steam, argon and hydrogen, shown in Table II. Each experiment proceeded from condition A to C, such that the amount of total carrier gas flow rate through the reaction crucible was kept approximately constant, at value 3.5 l/min (NTP).

TABLE I

Experiment matrix

Number	Precursor	Termerature [°C]
1	CsI	650
2	CsI	550
3	CsI + MoO_3	650
4	CsI + Ag	650
5	CsI + Ag	400
6	CsI + Ag + MoO_3	400
7	CsI + B_2O_3	650

TABLE II

Gas flow rates and volume percentages during conditions in experiments 1-6

		Condition		
		A	B	C
Argon	Flow rate [l/min] (NTP)	3.3	3.2	2.9
	Gas vol-%	94	91	82
Steam	Mass flow rate [g/min]	0.13	0.13	0.13
	Gas vol-%	6	6	6
Hydrogen	Flow rate [l/min](NTP)	0	0.1	0.4
	Gas vol-%	0	3	12

Experiment 1 was a repetition from previous studies [1, 2]. The experiment was done in order to make sure that the experimental facility was working properly. Next experiment, also with CsI precursor, was conducted in order to gain knowledge if gaseous iodine would be released in lower temperatures than 650 °C. The initial conditions were like in the first experiment, except for the lower reaction furnace temperature. After the first experiment, it was observed that in order to reduce the deposition of reaction products at the primary diluter to acceptable levels, the design of the diluter would still need to be updated. The primary diluter was already heavily improved during the previous experiments [2], and now it was further reshaped by shortening the sample flow tube inside the diluter, thus causing the sample to mix with the hot dilution gas closer to the reaction furnace. Also, a graphite block was introduced to the hot dilution gas channel to improve the mixing of the sample and the dilution gas.

Experiment 3, with molybdenum oxide and CsI as precursors, was conducted so that the effects of metallic Mo powder and MoO_3 to the iodine release could be compared. Unfortunately the H_2O feed to the carrier gas was initiated too late, which at least partly corrupted result from experiment 3. The mass fraction of MoO_3 and CsI at the beginning of the experiment was 3 to 1, respectively.

Experiments 4 and 5 featured precursor containing silver and CsI, with mass fraction 3 to 1, respectively. In experiment 5, the reaction furnace temperature was dropped to 400 °C in order to observe its effect on the iodine transport. In experiment 6, MoO_3 was included in the CsI and silver precursor. The mass fraction of Ag, MoO_3 and CsI was at the beginning of the experiment 2:2:1, respectively.

Finally, experiment 7 was conducted with boron trioxide and CsI as a precursor. In this experiment, no steam was used in the carrier gas. Gas flow rates of Ar and H were the same as in the previous experiments, shown in Table II

3 Results

This section presents the mass concentrations of gaseous and aerosol reaction products obtained from the bubbling bottle and filter samples. Also, some results from the online aerosol devises are shown. All presented mass concentration values are calculated to correspond to the gas phase concentration values present in the reaction furnace.

3.1 Experiments with CsI and MoO_3

Mass concentrations measured from the bubbling bottle and filter samples in experiment 1 are shown in Fig. 1. 57% of the released iodine was in gaseous form in condition A, 38% in condition B and 1% in condition C. The aerosol filters from samplings A and B contain more cesium than iodine, suggesting that a fraction of the iodine found from the bubbling bottles has originated from the filters. In condition A, the fraction of gaseous iodine due to reaction at 150 °C on the aerosol filter was 21%. In condition B the corresponding value was 14%. Molar fraction of cesium and iodine in condition C indicates that iodine was mostly released as CsI particles.

In experiment 2, in which the reaction furnace temperature was decreased to 550 °C, only a small aerosol particle release was observed. Most of the released iodine was in gaseous form in conditions A and C, as can be seen from Fig. 2. No gaseous iodine was observed in condition B. This was most likely caused by an error in the measurement or in the ICP-MS analysis. Also, online measurement devises ELPI and SMPS measured very small particle concentrations throughout the experiment.

Due to the lack of water vapor feed at the beginning of the experiment 3, almost no aerosol release was observed in condition A of experiment 3, as can be seen from Fig. 3. In conditions A and B cesium and iodine are again found from aerosol filters. Fraction of gaseous iodine from overall released iodine is 99% in condition A, 48% in condition B and 7% in condition C. Small fraction of molybdenum was also found from the aerosol filters in condition A and C. In condition B the molybdenum concentration in the filter was higher. Also, ICP-MS analysis of the cleanup sample showed that the deposition of I, Cs and Mo to the furnace tube was over ten times higher in experiment 3 than in the other experiments.

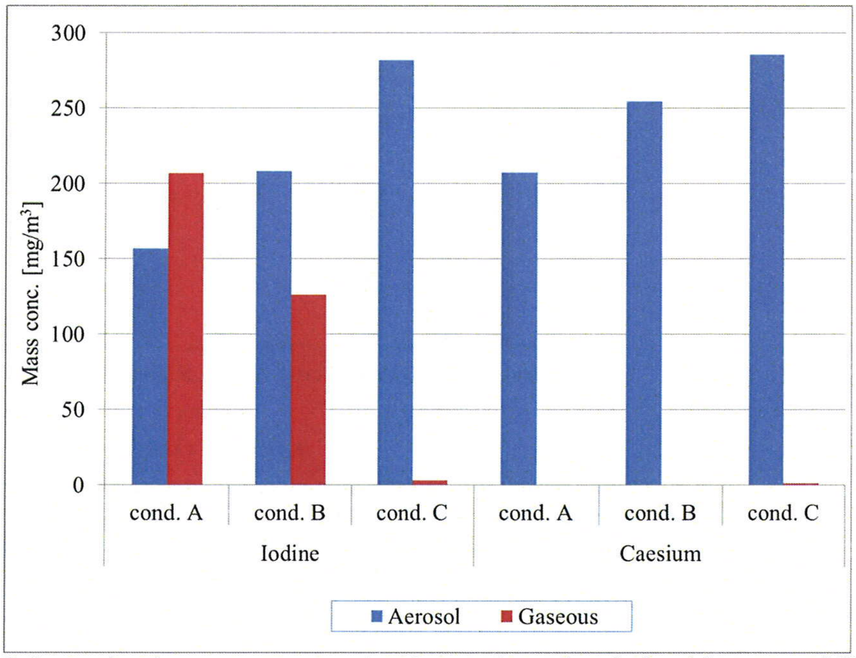

Fig. 1. Iodine and cesium mass concentrations in experiment 1, calculated from aerosol filter and bubbling bottle ICP-MS data. Condition A has Ar H_2O atmosphere where conditions B and C contain also H_2. The result is in quite good agreement with previous measurements [1, 2].

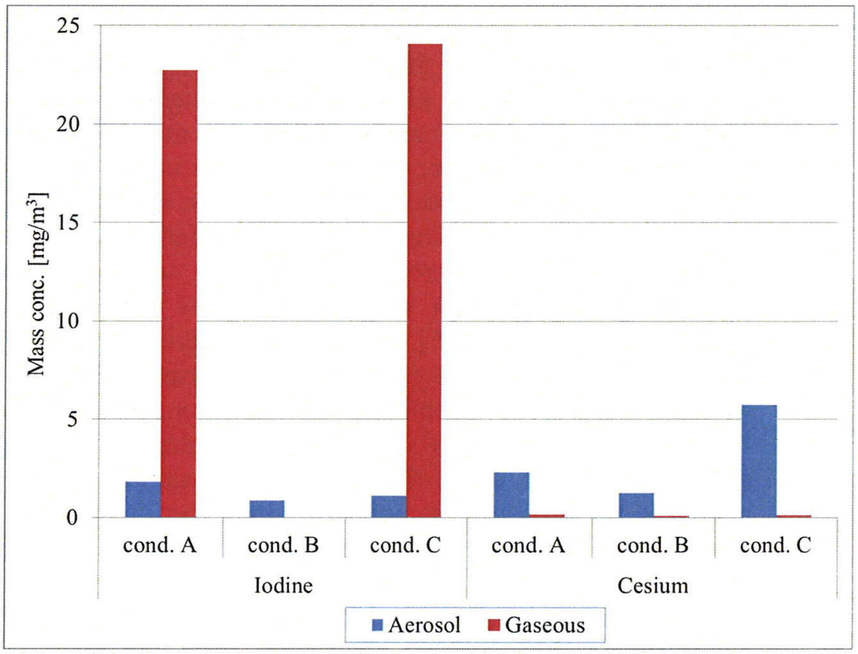

Fig. 2. Iodine and cesium mass concentrations in experiment 2, calculated from aerosol filter and bubbling bottle ICP-MS data. Condition A has Ar H_2O atmosphere where conditions B and C contain also H_2. Iodine is released mostly in gaseous form. Overall release of iodine is significantly lower than in experiment 1.

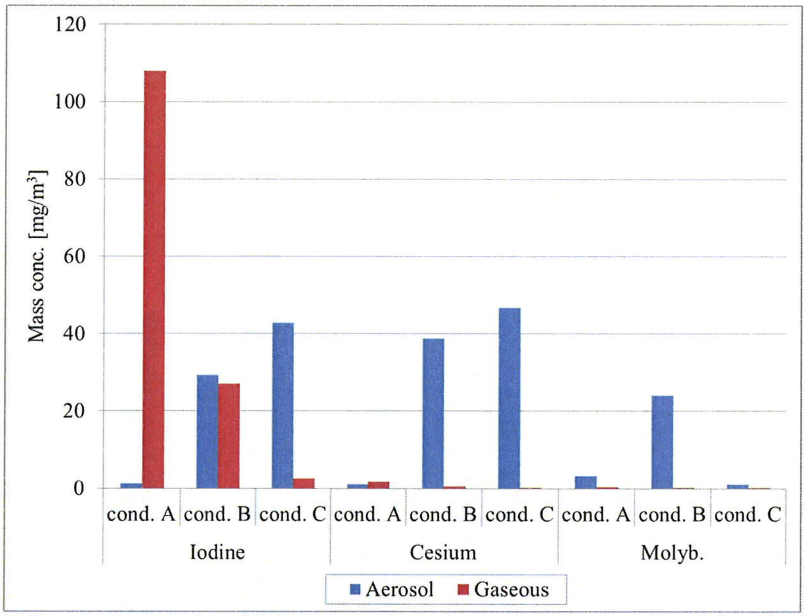

Fig. 3. Iodine, cesium and molybdenum mass concentrations in experiment 3, calculated from aerosol filter and bubbling bottle ICP-MS data. Condition A has Ar H_2O *atmosphere where conditions B and C contain also* H_2*. Due to the lack of water vapor feed at the beginning of the experiment, the results differ from the previous measurements [1].*

3.2 Experiments with silver

Mass concentrations results from the ICP-MS analysis of the bubbling bottle and aerosol filter data from the experiment 4 are shown in Fig. 4. Most of the released aerosol particles were cesium and iodine, most likely CsI. Also very small amount of silver was found from the filters in sampling A. The amount of iodine on the filter in condition A was also significantly higher than in other two conditions. This indicates that some fraction of the iodine may have transported to the filter in other forms of aerosol than CsI, or as gaseous iodine that has been trapped on the filter. The fractions of gaseous iodine from the overall released iodine are 26% in condition A, 9% in condition B and none in condition C.

The results from the previous experiment sets have shown that a complete removal of molybdenum residuals from the experimental facility after each experiment is very hard [1]. It is also been seen that the deposited Mo could have a significant effect on the gaseous iodine transport [2]. That is why after the first Mo experiment 3, all bubbling bottle and filter samples were tested also for Mo. In experiment 4, no Mo was found from the reaction product samples (Fig. 4).However, as shown in the figures, small amount of Mo was observed when analyzing the deposition samples after the experiment. From Fig. 5, it can also be seen that the most significant deposition can be found from the primary diluter and the furnace tube.

As the furnace temperature was lowered in experiment 5, the resulting mass concentration data differed drastically from the mass concentration data of experiment 4. Now almost all released iodine was in gaseous form, as can be seen from Fig. 6. In condition A, basically all of the released iodine was in gaseous form, in conditions B and C, approximately 99% in each. Also, the overall amount of released gaseous iodine was significantly higher than in the previous experiments.

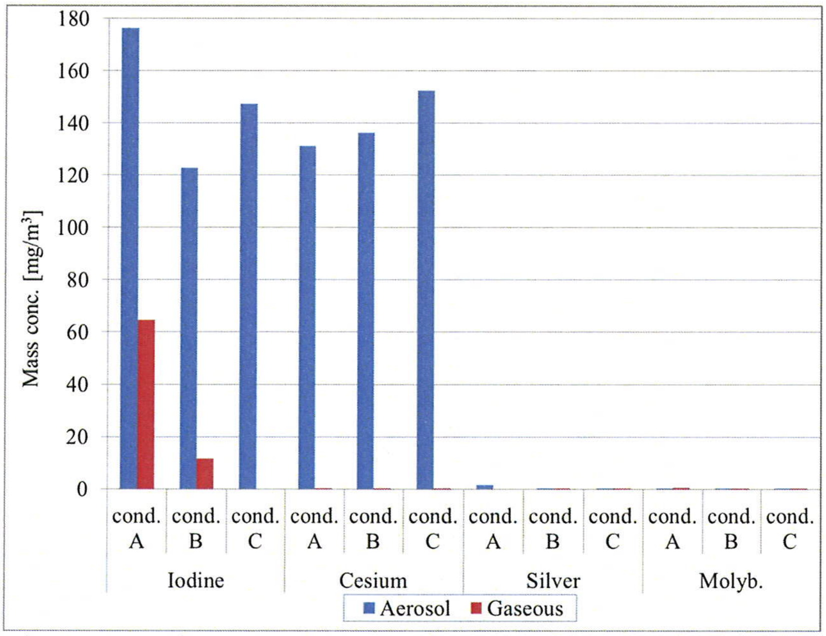

Fig. 4. Iodine, cesium, silver and molybdenum mass concentrations in experiment 4, calculated from aerosol filter and bubbling bottle ICP-MS data. Condition A has Ar H_2O atmosphere where conditions B and C contain also H_2. Iodine is released mainly in aerosol form.

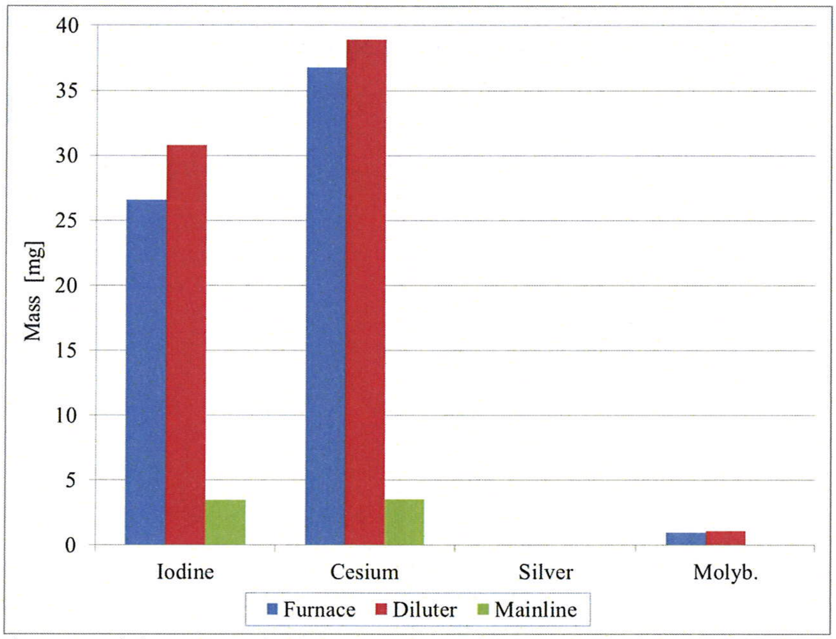

Fig. 5. The mass of depositions during experiment 4. The most significant depositions are found from the furnace tube and primary diluter. Also small fraction of molybdenum was found.

A small amount of silver was also found from the aerosol filter in condition B. Also, equally small amount of iodine was found from the filter in the same condition. These compounds have likely transported to the filter as AgI.

Very similar behavior was observed also in experiment 6, as can be seen from Fig. 7. Again, a relatively large amount of gaseous iodine was released. In condition A, gaseous iodine consisted 88% of the overall iodine release. In conditions B and C fraction of gaseous iodine was over 99%. Even though molybdenum oxide was now present at the precursor, no Mo was found in the ICP-MS analysis to the bottle samples, neither in aerosol or gaseous form.

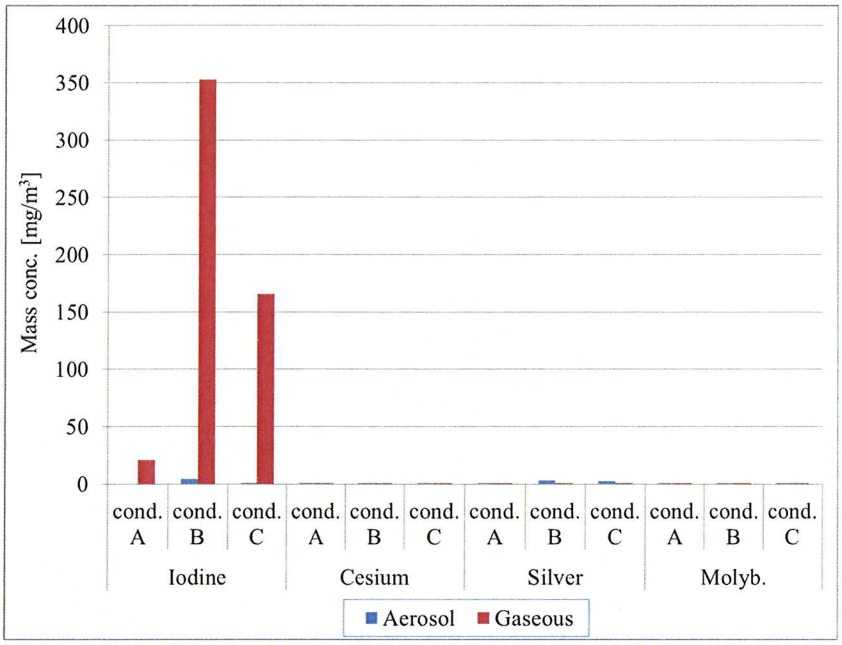

Fig. 6. Iodine, cesium, silver and molybdenum mass concentrations in experiment 5, calculated from aerosol filter and bubbling bottle ICP-MS data. Condition A has Ar H_2O *atmosphere where conditions B and C contain also* H_2*. Significant amount of iodine is released in gaseous form.*

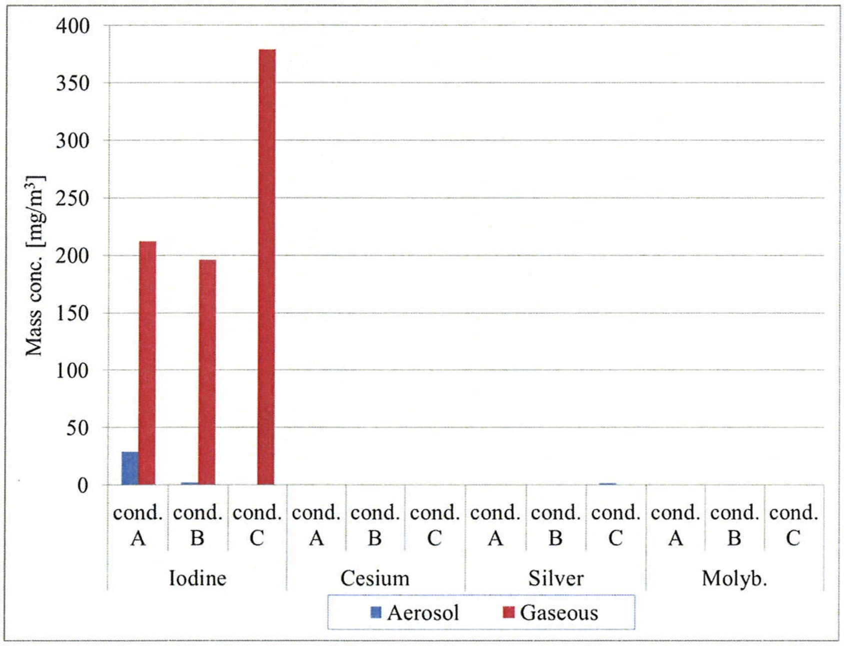

Fig. 7. Iodine, cesium, silver and molybdenum mass concentrations in experiment 6, calculated from aerosol filter and bubbling bottle ICP-MS data. Condition A has Ar H_2O *atmosphere where conditions B and C contain also* H_2*. Significant amount of iodine is released in gaseous form.*

3.3 Experiment with boron

The last experiment of this series was done with CsI and boron trioxide as precursor in dry atmosphere. Mass concentrations, obtained from the bubbling bottles and aerosol filters are shown in Fig. 8. A small fraction of the iodine was released as aerosol, most likely as CsI particles. Mostly the released iodine was in gaseous form. The fraction of iodine in gaseous form from the overall iodine released was 68% in condition A, 96% in condition B and 92% in condition.

Besides from Cs and I, a substantial amount of boron was found, mainly from the bubbling bottles. Boron had most likely transported to the sampling system as boric acid. No residuals of silver or molybdenum from the previous experiments were found from the bubbling bottles or aerosol filters. However, small amount of Mo was discovered from the diluter as the cleanup solution vas analyzed after the experiment.

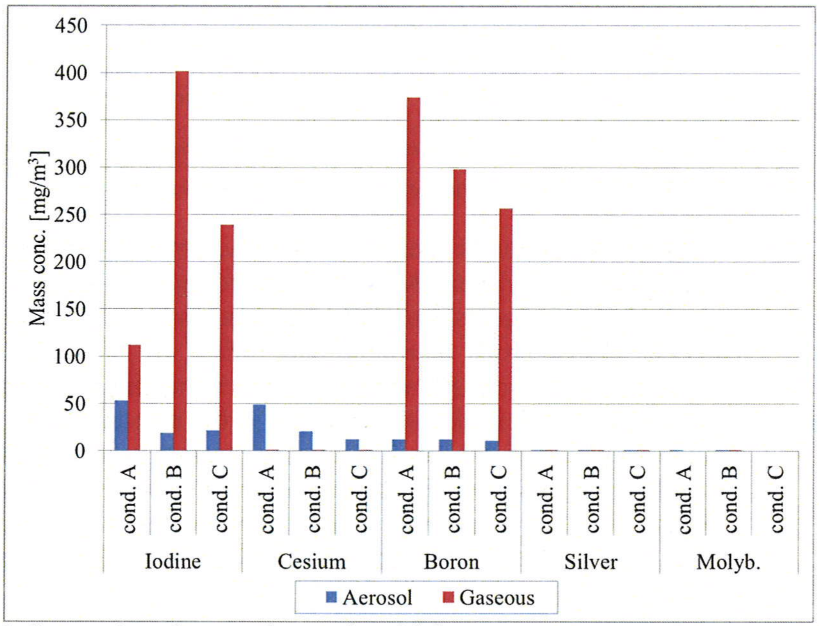

Fig. 8. Iodine, cesium, boron, silver and molybdenum mass concentrations in experiment 7, calculated from aerosol filter and bubbling bottle ICP-MS data. Condition A has Ar atmosphere where conditions B and C contain also H_2. A large amount of iodine released in gaseous form, boron most likely as boric acid.

3.4 Particle number size distributions

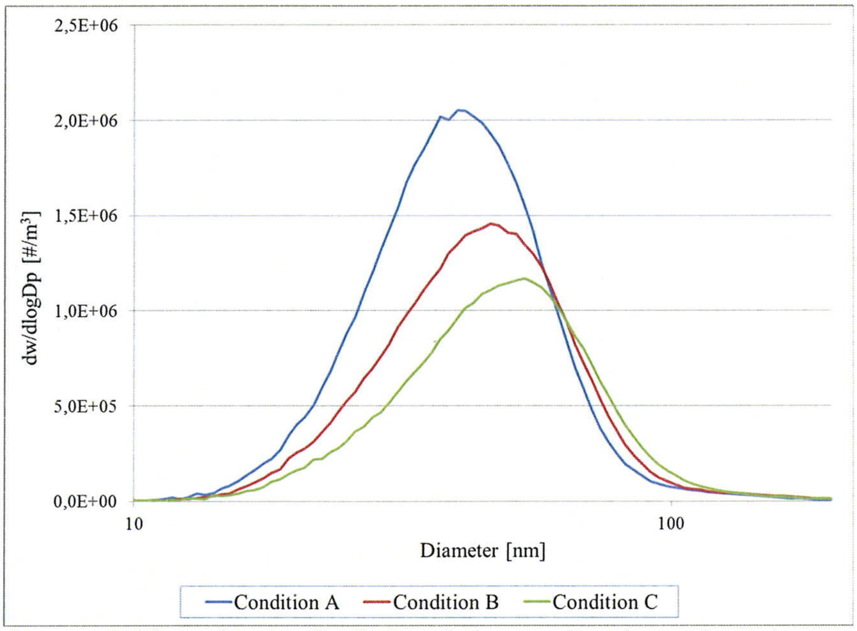

Fig. 9. Average particle number size distributions during samplings in experiment 4.

The particle number size distribution was monitored with ELPI and SMPS during each experiment. Most of the experiments produced very low number concentration of aerosol particles. The exceptions were experiments 1 and 4. The average distributions, measured with SMPS, are shown in Fig. 9. It shows that the particle number concentration drops when moving from condition A to C. Also, the average particle size is increasing as the amount of H_2 in the carrier gas is increasing. This behavior is due to the reaction product particles agglomerating into larger particles as hydrogen concentration in the atmosphere increases and thus causing the number concentration to decrease. The average particle diameters in conditions A, B and C are approximately 40 nm, 46 nm and 50 nm, respectively.

4 Discussion and Conclusions

Experiment 1 with only CsI as precursor in 650 °C was done in order to test functionality of the experimental facility, which was slightly modified since the previous experimental work [2]. As in the previous tests [1, 2], gaseous iodine mass concentration decreases and CsI mass concentration increases as the amount of H_2 in atmosphere increases. However, the amount and fraction of gaseous iodine is higher in argon steam flow than before. The gaseous iodine fraction also decreases faster when hydrogen concentration is increased. This might be mostly due to the changed reaction furnace tube material from alumina to oxidized stainless steel. Cesium may react with the new tube material thus causing the observed changes in the concentrations.

When the temperature of the furnace was dropped to 550 °C, the release of iodine containing aerosol particles decreased significantly (Fig. 2). This was quite expected result, since the temperature was dropped lower than the melting temperature of CsI, 621 °C. At 550 °C, a small amount of gaseous iodine was still released. This amount was however much lower than the amount of gaseous iodine released in the previous experiments at 400 °C with CsI and MoO_3 precursor [2]. This observation supports the claim that CsI and molybdenum oxide can react even at a relatively low temperature forming cesium molybdate and thus causing a substantial release of gaseous iodine.

Experiment 3 was conducted in order to investigate what effect, if any, would replacing the metallic Mo in the precursor with MoO_3 have for the gaseous iodine release. The lack of water vapor caused almost no CsI aerosol to be released at the beginning of the experiment (Fig. 3). Also, even after the H_2O feed had been activated the overall mass concentration of aerosol particles, mostly CsI, remained at very low level throughout the rest of the experiment. The mass concentration of gaseous iodine, even when taking in to account the peak in condition A, remained at significantly lower levels than those observed in the experiment with Mo powder precursor [1]. The extremely large deposition of I, Cs and Mo at the reaction furnace also calls the reliability of the results from the experiment 3 in to question. The deposition to the furnace tube was most likely formed during the dry beginning of the experiment, and it could be responsible for the difference in the results obtained from this and the previous experiments.

First Ag + CsI precursor experiment, done at 650 °C temperature showed similar behavior as was observed in experiment 1. The amount of released gaseous iodine decreased as the H_2 concentration in the carrier gas increased. Small amount of silver was found in aerosol form, probably transported to the filter as AgI. After the first sampling, more iodine than cesium was found from the aerosol filter (Fig. 4), which is rare compared to the other results. It is likely that this excess iodine had transported to the sampling system in gaseous form, and was for some reason retained in the filter.

As the experiment 4 was repeated at 400 °C temperature, the results changed dramatically. Gaseous iodine release was much higher compared to previous hot experiment. Also, almost no iodine containing aerosol particles were released. The same behavior was observed, as MoO_3 was added to the precursor (Fig 7). The release of large amounts of gaseous iodine was an unexpected result. When the results are compared to the ones with CsI precursor in low temperature, it seems that when Ag is included in the precursor, significant amounts of iodine is released in gaseous form. Similar results were already obtained in previous experiments with CsI + MoO_3 precursor [2].

The last experiment showed that the absence of water vapor in the atmosphere changed the results between experiment 7 and the previous CsI + B_2O_3 precursor experiment [1]. As a difference to the previous experiment, a small fraction of Cs and I were released in aerosol form, although major part of the iodine release was again in gaseous form. In both experiments, boron was found in both bubbling bottles and aerosol filters, where it had transported most likely as boric acid. The amount of released boron and gaseous iodine was higher in experiment 7 than in the previous boron experiment. Also, no glassy surface, observed in the previous experiment, was formed in the reaction crucible during experiment 7. This would indicate that steam in the atmosphere was a crucial point in the formation of the cesium borate glass surface in the previous boron experiment. The release of CsI particles in experiment 7, although small, also indicates that the formation of the glassy surface was responsible for not allowing Cs to be released from the crucible as CsI particles.

Deposition samples, obtained during the cleanup of the facility showed that the largest depositions to the primary diluter were found after experiments 1 and 4. This would indicate that the major part of the deposition is caused by released aerosol particles. The deposition sample obtained from experiment 4 (Fig. 5)

shows that the deposition contains more cesium than iodine. If the aerosol release has been mostly CsI particles, as is most likely, it would mean that after the deposition, part of the CsI has reacted on the surfaces of the facility releasing iodine in gaseous form.
The new primary circuit experiments showed that, when CsI was used as a precursor with Ag, B_2O_3 or MoO_3, significant amount of the released iodine was in gaseous form. This indicates that the reactions at primary circuit surfaces contribute to gaseous iodine transport in severe nuclear accidents. Especially, it was observed that in relatively low temperature, the released iodine is mostly in gaseous form, if some of the materials mentioned above were present. The primary circuit experiments at VTT are going to be continued in the year 2012. The new precursor materials of interest are indium and cadmium, which besides silver are widely used control rod materials in nuclear power plants. By modifying the experimental procedure we also wish to obtain more information about the role of depositions in the experimental facility on gaseous iodine transport.

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