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Experimental study on iodine chemistry (EXSI) - Containment experiments with elemental iodine

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Abstract

The behaviour of iodine during a severe accident has been studied in several experimental programs, ranging from the large-scale PHEBUS FP tests and intermediate-scale ThAI tests to numerous separate effect studies. Oxidation of iodine in gas phase has been one of the greatest remaining uncertainties in iodine behaviour during a severe accident.

In this study the possible formation of iodine oxide aerosol due to radiolytic oxidation of gaseous iodine is experimentally tested and the reaction products are analysed. The experimental facility applied in this study is based on the sampling system built at VTT for ISTP program project CHIP conducted IRSN. The experimental facility and the measuring technology are sophisticated and unique in the area of nuclear research as well as in the field of aerosol science.

The results from the experiments show an extensive particle formation when ozone and gaseous iodine react with each other. The formed particles were collected on filters, while gaseous iodine was trapped into bubbler. The particles were iodine oxides and the size of particles was approximately 100 nm. The transport of gaseous iodine through the facility decreased when both gaseous iodine and ozone were fed together into facility.

Experimental study on radiolytic oxidation of iodine was conducted in cooperation between VTT and Chalmers University of Technology as a part of the NKS-R programs.

Key words

Iodine, nuclear safety, severe accident, containment, ozone

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Preface

The gas phase chemistry of iodine has been studied at VTT and Chalmers during year 2008. The performed experiments have expanded the knowledge about the behaviour of gaseous iodine during a severe accident.

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1 Introduction

Amongst the released fission products iodine causes great concern in safety analysis, because its high radiotoxicity in short term and its potential to form several stable very volatile gaseous compounds in the containment building [1]. The behaviour of iodine during a severe accident has been studied in several experimental programs, ranging from the large-scale PHEBUS FP tests and intermediate-scale ThAI tests to smaller studies. Although the understanding of iodine behaviour has been improved, there still remain a number of points that should be better addressed. The existing knowledge needs to be extended to the interactions of volatile iodine with air radiolysis products in the containment atmosphere, especially to the nature and fate of oxidation products [2]. In this study the possible formation of iodine oxide aerosol due to radiolytic oxidation of gaseous iodine is experimentally tested and the reaction products are analysed. The report presents the preliminary results.

There have been a few experimental studies of the effect of radiation on gaseous inorganic iodine chemistry in the context of nuclear reactor safety [3]. The early work by Vikis [4, 5] focussed on studying the reaction of I_2 with O_3 , as the resulting conversion of gaseous iodine to solid iodine oxide aerosol has the potential to allow radioactive iodine to be removed from the containment atmosphere by filtration. The reaction product was I_4O_9 at temperatures up to 100°C , but this decomposed to I_2O_5 and I_2 at higher temperatures. A literature review on iodine behaviour, considering nuclear power plant accidents, has been recently published [3].

It is also possible that in reaction between iodine and ozone the product is I_2O_4 [6, 7, 8, 9]. When I_2O_4 is heated up to $135\text{-}190^\circ\text{C}$ it decomposes to I_2O_5 and iodine [10, 11]. On the other hand, I_2O_4 reacts slowly to form HIO_3 (iodic acid) in water though is not decomposed by moist air [12]. The reaction is fast in hot water. HIO_3 can also easily be formed after exposure of I_2O_5 (diiodopentoxide) to water or humid air [13].

2 Experimental facility

The experimental facility for iodine oxidation experiments is presented in figure 1. The design of the facility is based on the sampling system manufactured previously at VTT [14]. The experimental facility includes 8 thermocouples (K-type, the diameter of the tip is 1.5 mm) and 4 mass flow controllers. The pressure inside the facility is measured at 6 different locations. The data of these devices is stored with a computer program. The program is used also to adjust the flow rate of the mass flow controllers.

Gaseous iodine was produced in a separate flask (presented in figure 2) at the inlet of the facility. The production was done in fume hood. The procedure was to add drops of H_2SO_4 (99.7 %) from dropping funnel into iodine solution. The solution was a mixture of I_2 (12.69 g/l) in KI solution (20 g/l). The amount of iodine solution was usually 20 ml in the flask. Depending on the amount of iodine solution the production was started with 2 to 10 ml of acid. Due to reaction of acid with the solution, iodine released from the solution as gaseous I_2 . Then to maintain the production, acid was added every third minute an amount of 2 ml. There was also a magnetic stirrer below the flask and one bar magnet inside the flask. The circulation rate was 60 rpm. The surface of the flask and the gaseous iodine transport line, made of glass, were heated up to 50°C to avoid vapour condensation. Carrier gas, fed through a glass needle just above the surface of the precursor solution, transported iodine into the facility.

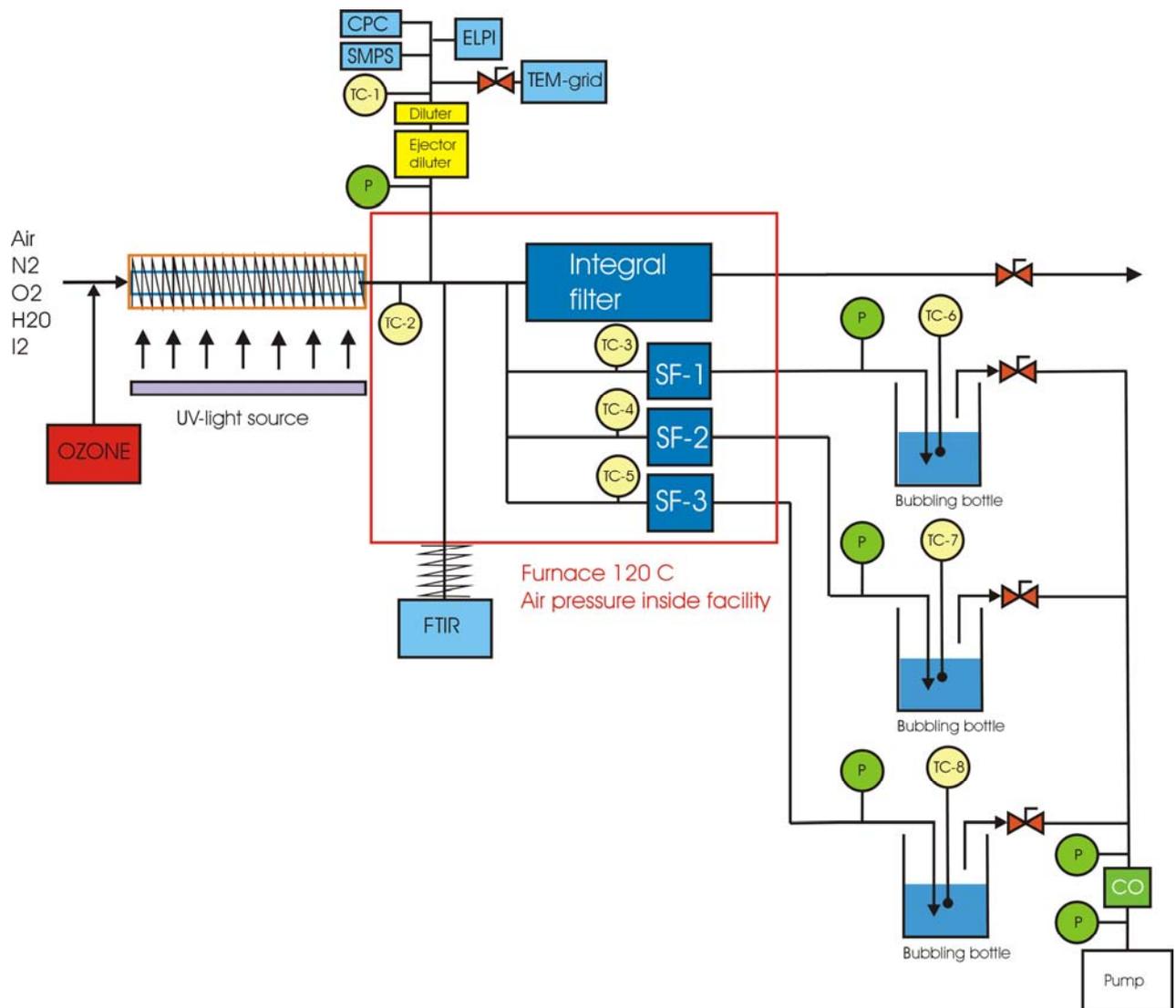


Figure 1: The schema of the experimental facility used in iodine transport experiments.

The gas flow through the facility was controlled with mass flow controllers (Brooks 5851S) and the total flow rate through the facility was customarily 6 l/min (NTP conditions 0°C, 101325 Pa). Higher flow rate was used also in some experiments. Ozone generator was applied to produce extra ozone from air or oxygen gas. The power of the generator could be adjusted. Ozone was mixed with other gasses used in experiment before feeding the mixture into the facility.

The facility consisted of a reaction furnace and a sampling furnace. Both furnaces were heated to 120°C. Pressure inside the facility was kept close to atmospheric. The material of the reaction furnace tube was fused silica. Four ultraviolet lights with short wave length radiation (c-type) were located inside the furnace around the tube. The radiation spectrum had two peaks, which were at 185 nm and 254 nm wavelengths. The UV-light ionises gas flow. When flow contains oxygen, it is expected to react with radiation to form ozone. Therefore, there were two different methods to produce ozone in the facility. Ionised gas flow was expected also to react with iodine. The reaction products were then transported into the sampling furnace.



Figure 2: The production flask of gaseous iodine.

The tube of the sampling furnace was made of stainless steel 316 L with Sulfinert coating. Sulfinert coating reduces the retention of iodine to the lines and that kind of coating is widely used in many gas chromatography applications. Inside the sampling furnace the main line was divided into filtration section, online aerosol measurement section and gas analyser.

Filtration section consisted of one integral filter and three analytical sampling lines. The integral filter was used to filter aerosols from by-pass flow before it was directed to fume hood. The analytical lines included a plane filter and two bubbling bottles in a row. Iodine aerosol was collected on plane filters and gaseous iodine species were trapped in bubbling bottles with 0.05M NaOH water solution. After experiment the aerosols in the filters were also dissolved with 0.05M NaOH water solution. All samples were then analysed with ICP-MS. Each analytical line was used separately enabling sampling from three different conditions during one heating of the facility. The flow rate through the analytical line was 2 l/min (NTP) and it was controlled with critical orifice placed downstream the bubbling bottles. The sampling time was 20 minutes per sample.

In the online aerosol measurement section the flow was diluted using ejector diluter and porous tube diluter. Dilution was needed in order to decrease the concentration of the particles low enough for the instrumentation as well to decrease the temperature of the flow below 40°C. Aerosols number size distributions were measured with a Scanning Mobility Particle Sizer (SMPS) and Electric Low Pressure Impactor (ELPI). A CPC was used to monitor particle concentration changes. The devices were measuring on-line and the corresponding time resolutions were 3 minutes for SMPS and 1 second for ELPI and for CPC. All devices are widely used in the field of aerosol science. Aerosol particles were collected also with a suction sampler on a copper/carbon grid. The grid was analysed with Scanning Electron Microscope (SEM) and in some cases with Transmission Electron Microscope (TEM). With SEM/TEM it was possible to analyse the morphology of particles. In order to achieve information about the elemental composition of particles, an energy dispersive X-ray (EDX) analysis was applied.

Gas phase composition and concentration changes were monitored on-line with Fourier Transform Infrared Spectroscopy (FTIR). Before the flow entered FTIR it was filtered. Using this technique it was possible to see the effect of different conditions on gaseous iodine

reaction products. However, FTIR is unfortunately not capable to measure bi-atomic gases such as I_2 .

3 Experiments

The oxidation of iodine was studied in conditions similar to the containment of a nuclear power plant during a severe accident. The experimental matrix is presented in table 1. The objective was to determine the influence of oxygen, ozone and iodine concentration as well as that of radiation intensity on the possible formation of iodine oxide aerosols from elemental iodine gas. The total number of the experiments was 26.

Table 1: Matrix of the iodine oxidation experiments. The parameters varied were oxygen volume fraction, ozone generator power, UVC radiation intensity and flow rate. Iodine concentration was also varied, but it could be determined only after the experiments.

Exp.	Atmosphere	Flow rate [lpm]	O ₃ generator power [#]	UVC	Other
1A	Moist, 50% O ₂ + 50% N ₂	6	-	-	
1C	Moist, 50% O ₂ + 50% N ₂	6	3	-	
2A	Dry, 50% O ₂ + 50% N ₂	6	6	-	Revaporisation, no sample
2B	Moist, 50% O ₂ + 50% N ₂	6	8	-	
2C	Moist, 50% O ₂ + 50% N ₂	6	2	-	
2D	Moist, 50% O ₂ + 50% N ₂	6	10	ON	
3A	Dry air	6	-	ON	Revaporisation, no sample
3B	Moist air	6	-	ON	
3C	Moist air	6	-	ON	
3D	Moist air	6	-	-	
4A	Moist air	6	5	-	
4B	Moist air	12	7	-	
4C	Moist air	24	10	-	
5A	Moist air	6	8	-	
5B	Moist air	6	5	-	
5C	Moist air	12	8	-	No sample
5D	Moist air	6	-	-	
6A	Moist, 10% air + 90% N ₂	6	10	-	
6B	Moist, 10% air + 90% N ₂	6	5	-	
6C	Moist, 10% air + 90% N ₂	6	1	-	
7A	Dry, 10% air + 90% N ₂	6	10	-	Revaporisation
7B	Moist, 10% air + 90% N ₂	12	1	-	
7C	Moist, 10% air + 90% N ₂	12	10	-	
8A	Dry, 10% air + 90% N ₂	6	-	ON	Revaporisation
8B	Moist, 10% air + 90% N ₂	6	-	ON	
8C	Moist, 10% air + 90% N ₂	12	-	ON	

The atmosphere was either air or a mixture of nitrogen and oxygen. The volume fraction of oxygen in a gas flow was 50%, 21% or 2%. Experiments were conducted primarily in moist gas flow. The moisture came from the iodine production reaction. Four revaporisation experiments, where the only source of iodine was the layer deposited previously on tube surfaces, were conducted in dry gas flow. In these experiments, the aim was to study the effect of ozone and radiation on the possible evaporation and subsequent nucleation of iodine.

Ozone concentration in the experiments could be varied by changing oxygen concentration, ozone generator power or UVC radiation intensity. It was considered to be important that ozone concentration was independent on radiation and that it could be monitored online. Iodine concentration depended on the production procedure and could be verified from the filter and bubbling bottle samples only after the experiments.

In the experiments the total gas flow through the flow furnace ranged from 6 l/min to 24 l/min (NTP). The total flow rate was varied in order to study the effect of residence time on iodine reaction products.

4 Results

The results of the experiments are presented in table 2. The first two columns present iodine masses collected in aerosol filters and gas bubblers. Total gaseous iodine concentration fed into the facility is determined by means of summing the filter measurement and the bubbler bottles measurements. It is presented in table 2 in ppm:s. Iodine concentration can thus be directly compared with the ozone concentration measured using FTIR. It should be noted though that total iodine concentration is underestimated, because retention in the facility could not be taken into account. Possible decrease in ozone concentration due to dissociation and reaction with iodine was not considered either. The last column presents the gaseous iodine factor (it corresponds the fraction of gaseous iodine transported through the facility), $f_{I_2(g)}$, which is defined in equation 1:

$$f_{I_2(g)} = \frac{m_{I_2(g)}}{m_{I_2(g)} + m_{I(s)}} \quad (1)$$

where $m_{I_2(g)}$ is the amount of gaseous iodine and $m_{I(s)}$ is the amount of iodine aerosols.

When aerosol and gaseous fractions of iodine are compared, it can be seen that iodine is transported either almost completely as aerosols or almost completely as gas.

Experiments 1A, 3D and 5D were experiments with iodine feed and no ozone. As a result, iodine was transported in gaseous form, $f_{I_2(g)}$ is close to 1. Very little trapping of gaseous iodine was observed in the aerosol filter. In experiment 3D the amount of iodine in analysis was fairly low. Therefore, the accuracy of the measurement was not as good as in 1A or 5D. Probably, the amount of iodine transported as gas in that experiment was in reality higher than the value presented here.

In most experiments, when ozone concentration exceeded 8 ppm, it resulted almost complete conversion of gaseous iodine to aerosol particles, see figure 3. The most notable exceptions were experiments 2B and 2C, in which iodine retained on the tube surfaces in the previous experiment most probably influenced the results. Also in experiments 4C and 7B the conversion was not complete likely because of the shorter residence time for the reaction.

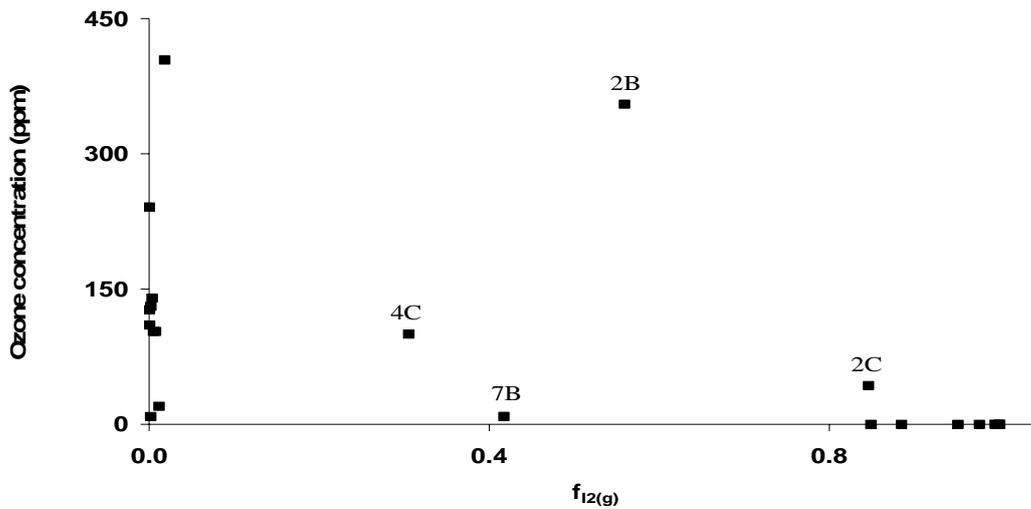


Figure 3: The effect of ozone on the fraction of gaseous iodine in the system. In most of the cases the gaseous iodine fraction $f_{I_2(g)}$ is close to zero while O_3 and I_2 are present together in the facility. The four experiments 2B, 2C, 4C and 7B are exceptions from the others.

Table 2: The mass of iodine collected on filters and in bubbling bottles during the oxidation experiments. Based on the collected mass, aerosol and gaseous iodine fractions are calculated. Total iodine concentration fed into the system can be compared with the measured ozone concentration. The residence time in the facility is calculated using the known flow rate.

Exp.	I_2 on filter [mg]	I_2 in bottle [mg]	O_3 [ppm]	I_2 [ppm]	f_{I_2} [$I_2/(I_2 + \text{iodine particles})$]
1A	0.004	43.64	0	97	1
1C	1.61	0.003	8.6	3.6	0.002
2A	-	-	206	NA	-
2B	0.005	0.006	355	0.02	0.56
2C	0.008	0.045	43	0.12	0.85
2D	0.027	0.0005	404	0.06	0.02
3A	-	-	0.1*	NA	-
3B	0.006	0.036	0.07*	0.09	0.85
3C	0.002	0.039	0.03*	0.09	0.95
3D	0.024	0.19	0**	0.47	0.88
4A	0.40	0.001	140	0.90	0.003
4B	0.17	0.0004	131	0.37	0.002
4C	0.24	0.11	100	0.78	0.31
5A	2.63	0.0008	241	5.83	0
5B	2.06	0.0007	127	4.6	0
5C	-	-	137	NA	-
5D	0.029	5.81	0.16**	13	1
6A	0.54	0.0003	110	1.2	0.001
6B	0.54	0.003	103	1.2	0.01
6C	0.40	0.005	20	0.9	0.01
7A	-	-	87	NA	-
7B	0.16	0.11	8.8	0.61	0.42
7C	0.15	0.001	103	0.32	0.01
8A	0.0002	0.008	0.03*	0.02	0.98
8B	0.00004	1.13	0.04*	2.5	1
8C	0.00007	2.39	0.04*	5.1	1

* The measurement accuracy was not good, because of the low ozone concentration.

** The column of FTIR or the volume of the facility was not completely free of ozone,

even though ozone was not fed into the facility.

In experiments 3B, 3C, 8B and 8C the only source of ozone was UVC radiation. Radiation intensity was highest in experiment 3B with three UVC lamps on. In experiments 3C, 8B and 8C only one UVC lamp was applied. In addition, oxygen concentration was 21 %-vol in experiment 3 and 2 %-vol in experiment 8. Radiation intensity and oxygen concentration had a direct impact on ozone concentration, which seemed to influence the formation of iodine oxide particles. UVC radiation alone with low oxygen concentration was not efficient in producing iodine containing particles.

The effect of residence time in the facility was studied in the experiments 4A, 4B, 4C, 7B, 7C, 8B and 8C by increasing the gas flow rate. With shorter residence time the effect of finite reaction kinetics can be observed as larger fraction of iodine is transported in gaseous form. Other effects of residence time are discussed in the next chapter about aerosol particles.

Experiments 2A, 3A, 7A and 8A were dedicated for studying revaporisation of iodine from surfaces. Filter and bubbling bottle samples were however collected only from experiments 7A and 8A. In those experiments, the amount of iodine was very low and the measurement accuracy is not at normal level. However, based on results from experiment 8A, it seems that iodine evaporates from the surfaces and is transported primarily as gaseous iodine again. A small fraction of evaporated iodine reacted with ozone and formed aerosol particles as well. It should also be noted that the concentration of ozone, produced only with UVC radiation, was very low in this experiment.

The effect of ozone concentration on iodine concentration transported through the facility is presented in figure 4. The results are from experiments 1 and 5. While the ozone concentration is low (~0 ppm) iodine is transported as gas through the facility efficiently. When ozone concentration increases, particles are formed and the amount of transported iodine decreases. The fraction of iodine retained in the facility ranged from 55% to 80%. Such retention can not be explained by aerosol deposition processes. It seems that a significant fraction of iodine reacts with the inner surfaces in the system. The presence of ozone in the system seems to promote the iodine adsorption on the surfaces.

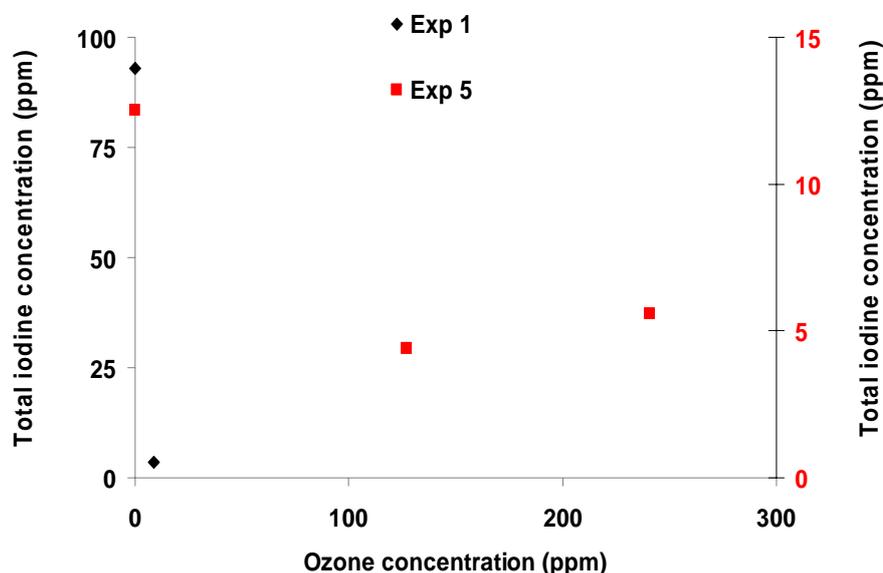


Figure 4: The effect of ozone concentration on iodine concentration.

4.1 Nucleated aerosol particles

During the experiments it was observed that the formation of aerosol particles was almost instant, when iodine feed was on and the ozone production was started. There was a remarkable difference in ozone concentration depending on the method used for generation of ozone. However, it seemed that even low ozone concentration was able to produce an enormous concentration of particles ($\sim 10^{6-8}$ #/cm³).

4.1.1 Aerosol size distribution properties

According to measured aerosol number size distributions the primary particles, formed in the reaction of iodine and ozone, were very small. The diameter of the smallest particles measured was less than 10 nm. The number median diameter of particles ranged from 60 - 120 nm depending on initial iodine concentration, ozone concentration and residence time within the facility.

Particle growth took place primarily by agglomeration. An example of the effect of residence time on particle number size distribution is presented in figure 5. It can be seen clearly that the particle size increases and their number concentration decreases with increasing residence time. Such behaviour is typical for agglomeration growth.

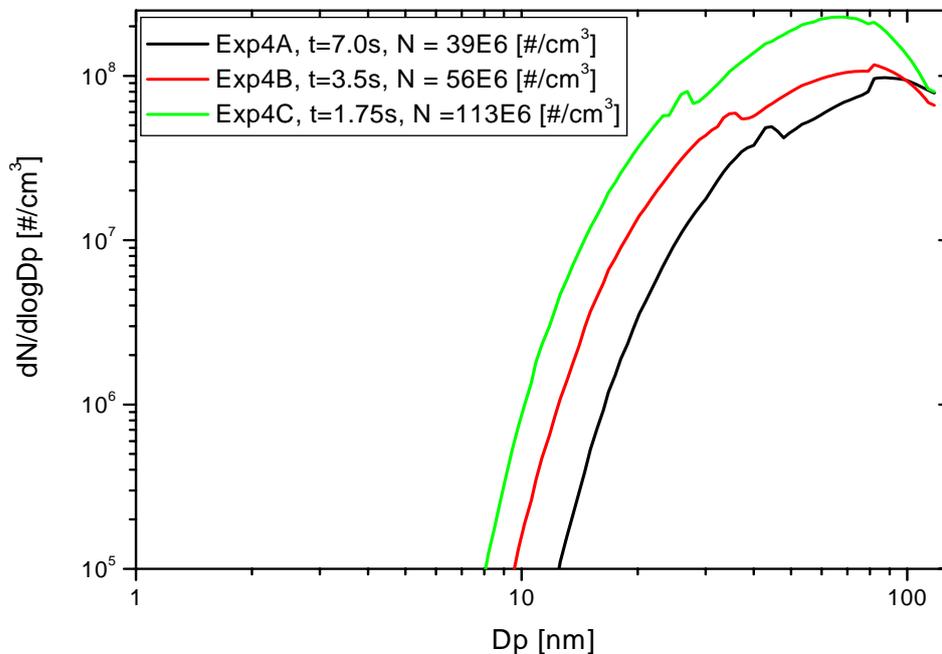


Figure 5: The effect of residence time (t) on aerosol size (D_p) and concentration (N).

The effect of initial iodine concentration on the size of the formed particles is presented in figure 6. In experiments presented in the figure the ozone concentration was almost constant ranging from 100 to 140 ppm. It can be seen that increasing iodine concentration leads to

increasing number median diameter and decreasing number concentration of particles. This is another proof of agglomeration growth as fast nucleation rate and initially high particle number concentration would lead to much higher agglomeration growth rate. On the other hand, substantially increased size of the smallest particles with high iodine concentration also indicates particle growth by reaction of iodine on particle surfaces. This would be a secondary growth mechanism in the experiments. It should be noted that data from experiment 7C can not be directly compared with other experiments in figure 6. It is measured with another DMA-analyser in order to extend the measurement range to larger particle diameter. However, at small particle size diffusion losses in that analyser are much greater than in the analyser applied in other experiments distorting the real particle size distribution. The main result from experiment 7C was to verify that the particle size distribution is log-normal and fairly narrow.

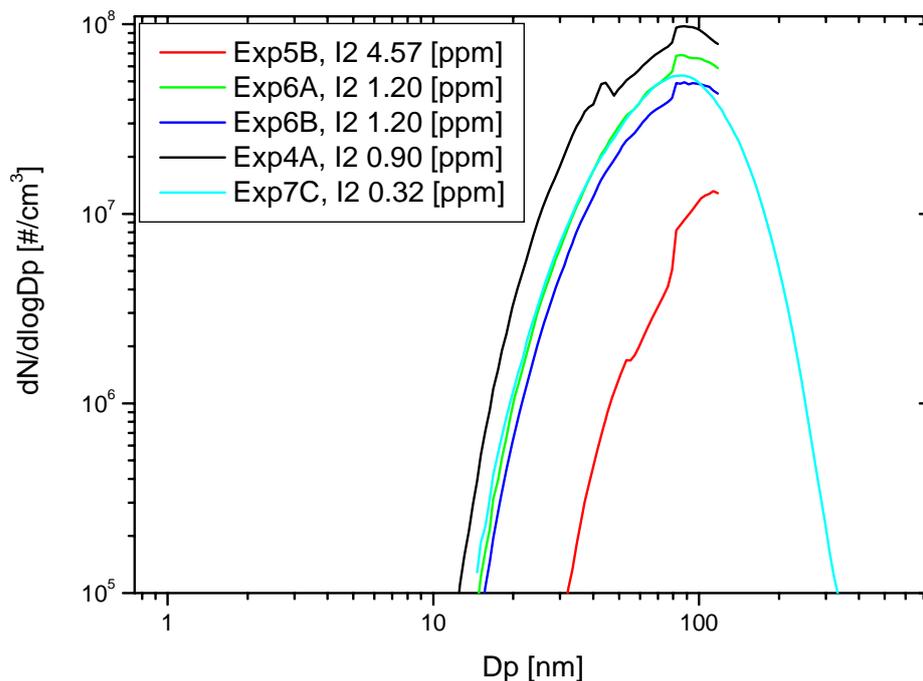


Figure 6: Aerosol number size distributions measured with varying initial iodine concentration. During the experiments the concentration of ozone was in a range 100-140 ppm.

4.1.2 SEM (EDX) analysis of particles

The formed aerosol particles were also collected with a suction sampler on a copper-carbon grid in order to conduct analysis with SEM. In addition to particle morphology, their elemental composition was studied.

Micrograph of particles collected from experiment 4A is presented in figure 7 together with results from Energy Dispersive X-ray spectroscopy (EDX) analysis. It can be seen that particles on the carbon foil appear to be either liquid or at least partially melted. This is not a surprise as iodine oxide particles are known to vaporise easily under the electron beam. Particle size also appears to be larger than that measured in the gas phase. It is likely that melting particles fuse together on the carbon foil. According to the elemental map presented in figure 7 as well as the EDX spectrum presented in figure 9, particles on the carbon foil contain both iodine and oxygen.

Unlike particles on top of carbon foil, particles deposited on copper grid appear to be crystalline. According to elemental map in figure 7 as well to EDX spectrum in figure 8, these particles do not contain essentially any oxygen. The likely reason for the difference in particle morphology and composition is that iodine oxide particles deposited on copper have reacted to copper iodide. This can not definitely be attested, because the copper signal would always be present from the grid underneath the particles. The possible formation of metal iodides from deposited iodine oxide particles is however interesting as such reactions would likely to take place also in containment building.

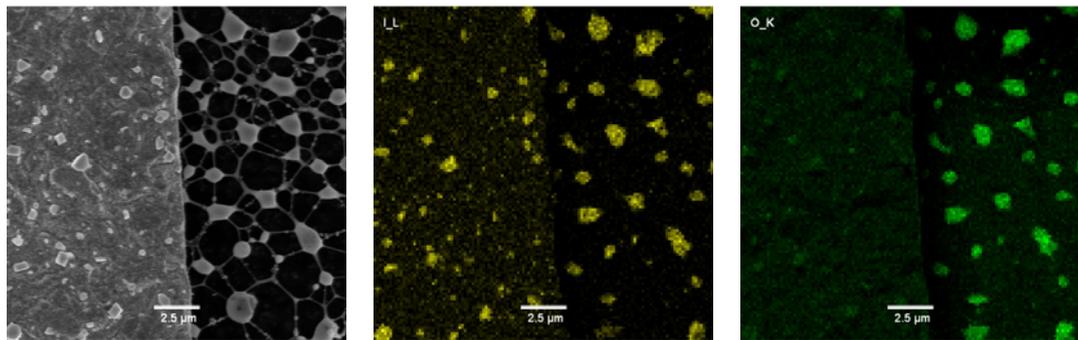


Figure 7: The EDX analysis of iodine and oxygen in collected particles on copper/carbon grid.

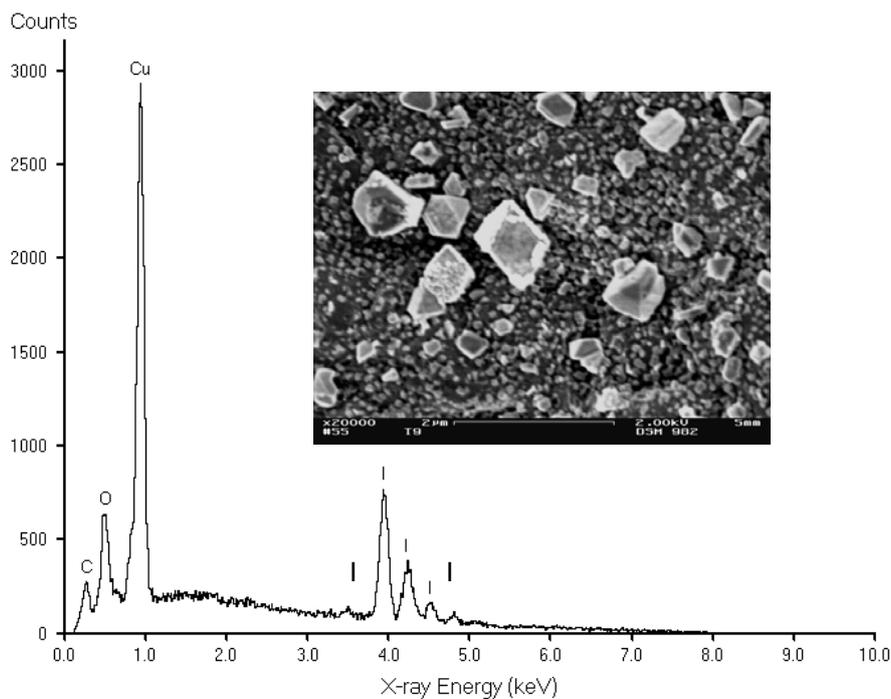


Figure 8: The X-ray spectra of particles on copper grid.

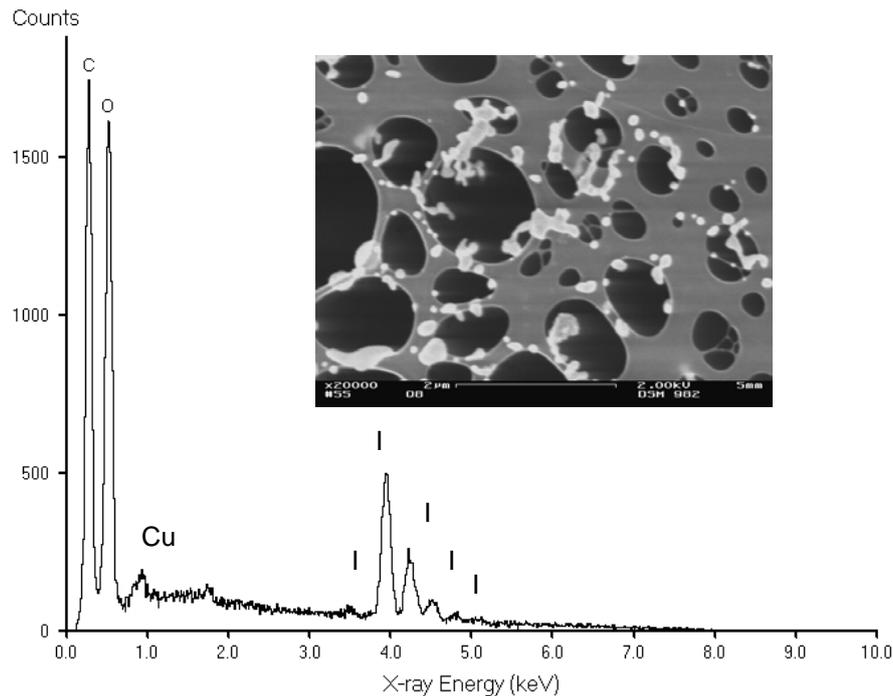


Figure 9: The X-ray spectra of the particles on carbon foil.

5 Conclusions

Experimental study on oxidation of elemental iodine in containment conditions was carried out at VTT in co-operation with Chalmers University of Technology as a part of the SAFIR2010 and the NKS-R programs. The facility, used for the experiments, built at VTT and the measuring technology is sophisticated and unique in the area of nuclear research as well as in the field of aerosol science.

It was found out that the nucleation of aerosol particles was almost instant when ozone and iodine were present in the facility. Even very low concentration of ozone produced high concentration of particles. The diameter of the nucleated primary particles was less than 10 nm. The most important particle growth mechanism was agglomeration. The number median diameter of the agglomerates ranged from 60 to 120 nm depending on initial concentration of iodine and on residence time.

The transport of gaseous iodine through the facility was very low when ozone was present in the gas. This result would indicate that gaseous iodine would most probably form aerosol particles also in reactor containment as ozone concentration is expected to be substantial during a severe accident. In re-vaporisation tests, iodine retained in the facility in previous experiments was observed to evaporate from the surface. If gaseous iodine would be released from the surfaces of the containment, it would form very small particles with low settling velocity. Such process could even lead to persistent steady-state concentration of iodine in the gas phase.

The analysis of particles with SEM and TEM was difficult. Particles seemed to evaporate under electron beam. However, it was found out that particles contained iodine and oxygen. According to literature study, there are three probable iodine oxide species what to expect – I_2O_4 , I_2O_5 and I_4O_9 . When iodine oxides are in contact with water they form hydrated species and the final product is likely to be iodic acid [12, 13]. During a severe accident it is very likely that iodic acid (HIO_3) would form, but that was not verified in this study.

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Title	Experimental study on iodine chemistry (EXSI) – Containment experiments with elemental iodine
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Abstract The behaviour of iodine during a severe accident has been studied in several experimental programs, ranging from the large-scale PHEBUS FP tests and intermediate-scale ThAI tests to numerous separate effect studies. Oxidation of iodine in gas phase has been one of the greatest remaining uncertainties in iodine behaviour during a severe accident.

In this study the possible formation of iodine oxide aerosol due to radiolytic oxidation of gaseous iodine is experimentally tested and the reaction products are analysed. The experimental facility applied in this study is based on the sampling system built at VTT for ISTP program project CHIP conducted IRSN. The experimental facility and the measuring technology are sophisticated and unique in the area of nuclear research as well as in the field of aerosol science.

The results from the experiments show an extensive particle formation when ozone and gaseous iodine react with each other. The formed particles were collected on filters, while gaseous iodine was trapped into bubbler. The particles were iodine oxides and the size of particles was approximately 100 nm. The transport of gaseous iodine through the facility decreased when both gaseous iodine and ozone were fed together into facility.

Experimental study on radiolytic oxidation of iodine was conducted in co-operation between VTT and Chalmers University of Technology as a part of the NKS-R programs.

Key words Iodine, nuclear safety, severe accident, containment, ozone