Business from technology

Transport and chemistry of fission products (TRAFI)

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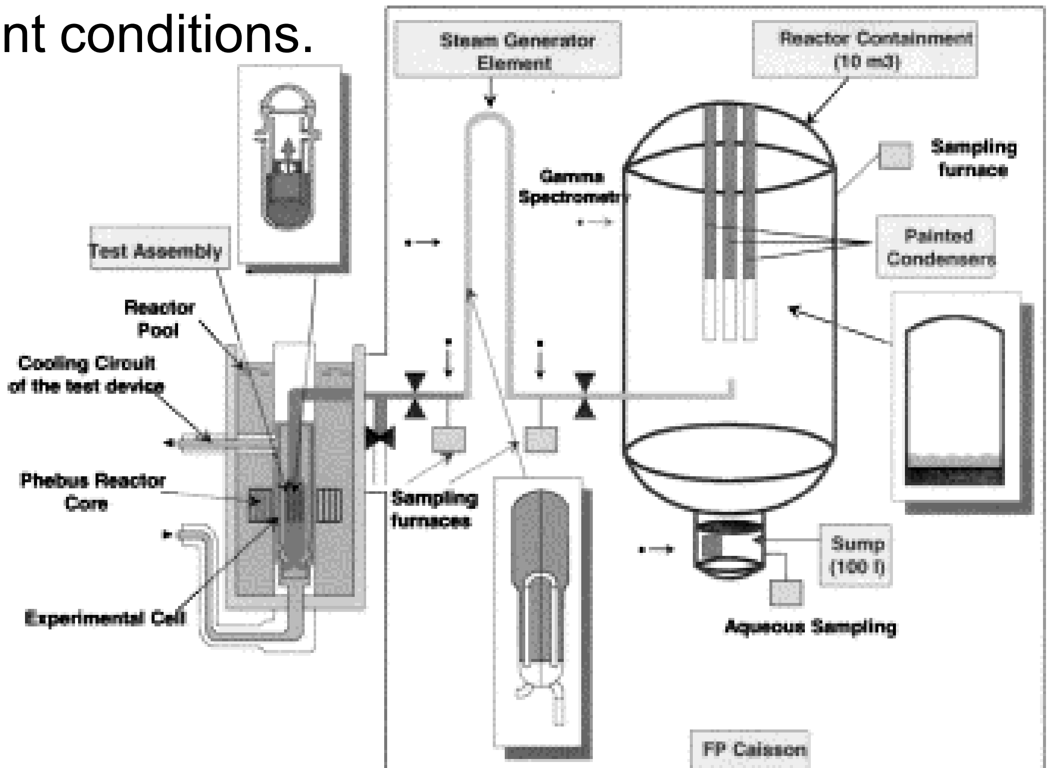
Background

- Fukushima Daiichi nuclear accident took place on 11th of March, 2011. Since the cooling of three reactor units could not be restored in time, fission products were partly released from the damaged fuel.
- As expected in a such severe accident, the highest contribution to the source term to the environment was from iodine isotopes.

[1]

Background

- The behaviour of fission products have been studied in several research programs. Phébus FP international program [2] has been one of the largest experimental program focusing on the release of FPs from real fuel samples and their transport in primary circuit and containment conditions.



[2]

Background

- In Phébus FP program it was noticed as a surprise e.g.:

1) gaseous iodine depleted from the atmosphere much faster than expected in the early phase of the tests,

2) a steady-state concentration of iodine in containment atmosphere was reached in all Phébus FP tests,

3) silver iodide precipitated in the sump, when AIC control rod was applied in the tests. With B_4C control rod most iodine released in the model containment was in gaseous form.

Aim

- Based on the results from Phébus FP program a number of hypothesis on iodine behaviour were formulated [3]:

  1) Either the painted surface or the steel walls acted as the source of the gas phase iodine species in the tests.

  2) Radiolytic processes destroyed gas phase molecular iodine and organic iodide to form iodine oxide or iodine nitroxide particles.

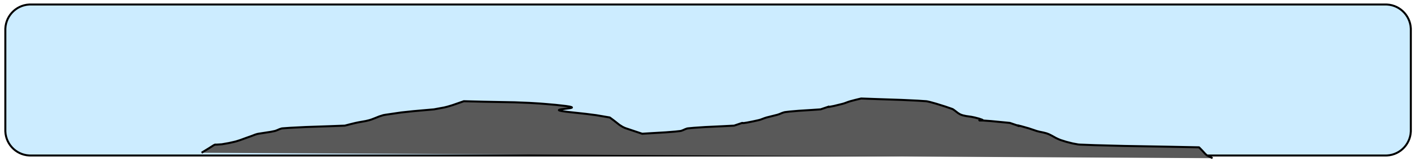
  3) The source of gaseous iodine from the circuit was either chemical reactions on the gas stream or on the surfaces of the tube walls.

- The hypothesized mechanisms were tested in TRAFI project. For example, the primary circuit chemistry of iodine has also been studied in co-operation with IRSN (ISTP program, CHIP).

Primary circuit chemistry of iodine

- The work has concentrated on quantifying the effect of surface reactions on gaseous iodine release from the primary circuit.
- The possible influence of surface reactions on iodine speciation has a direct effect on nuclear safety. At the moment, they are not considered at all in the analysis of severe accidents.

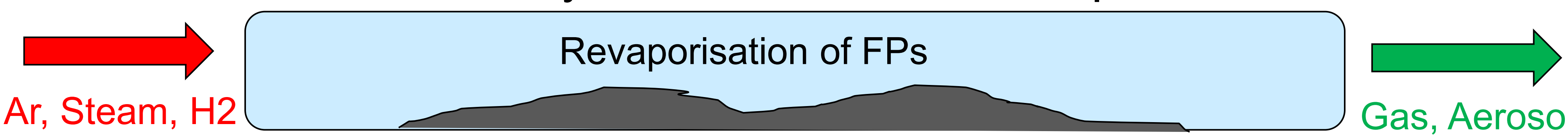
Primary circuit tube with FP deposition



Primary circuit chemistry of iodine

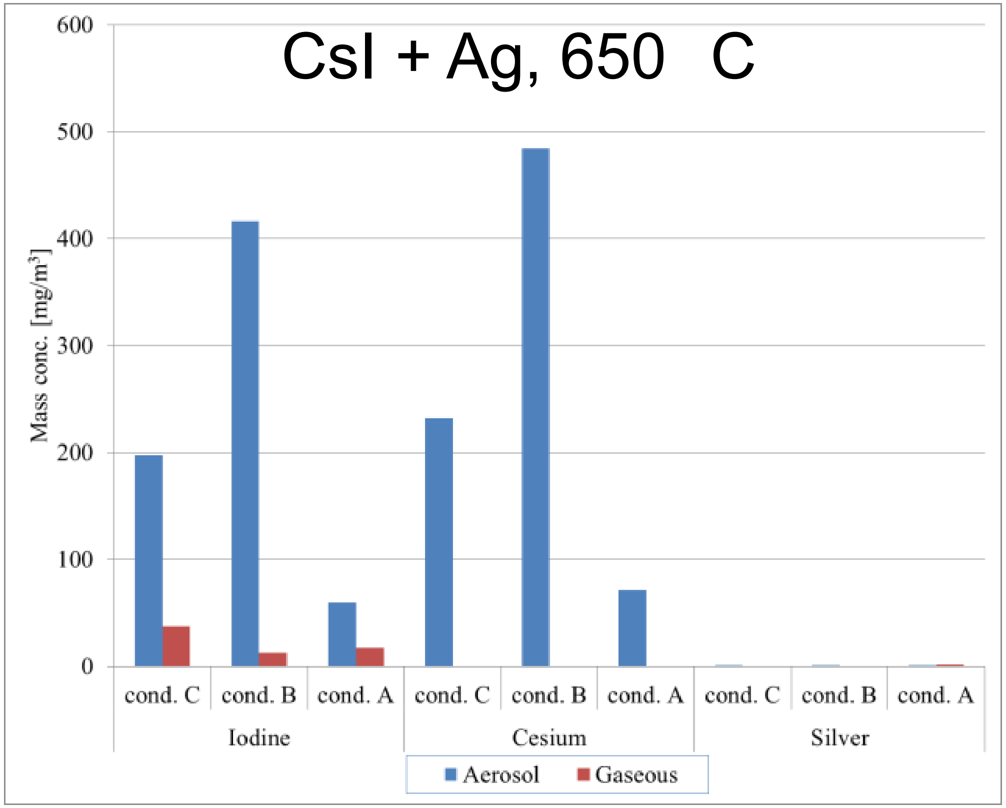
- In the experiments, the source of iodine was CsI or AgI powder. The precursor was vaporised at 400 - 650 °C in a mixture of Ag, MoO_3 or B_2O_3.

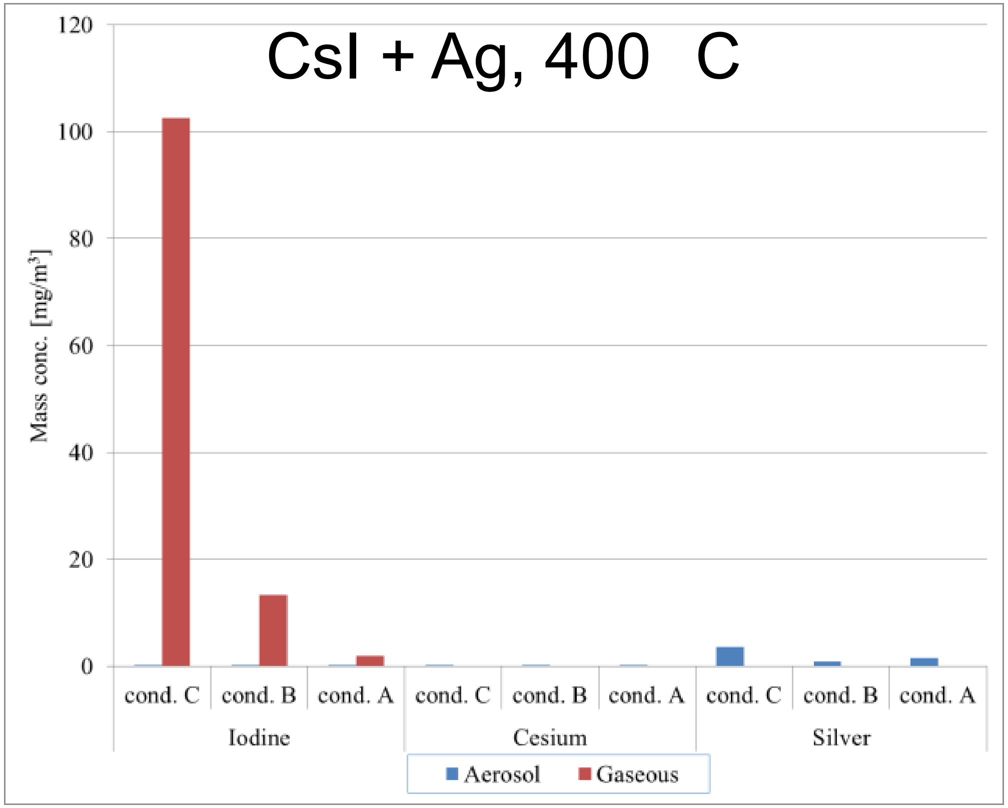
Primary circuit tube with FP deposition



		Condition		
		A	B	C
Argon	Gas vol-%	90	88.3	79.2
Steam	Gas vol-%	10	10	10
Hydrogen	Gas vol-%	0	2.7	10.8

Primary circuit chemistry of iodine

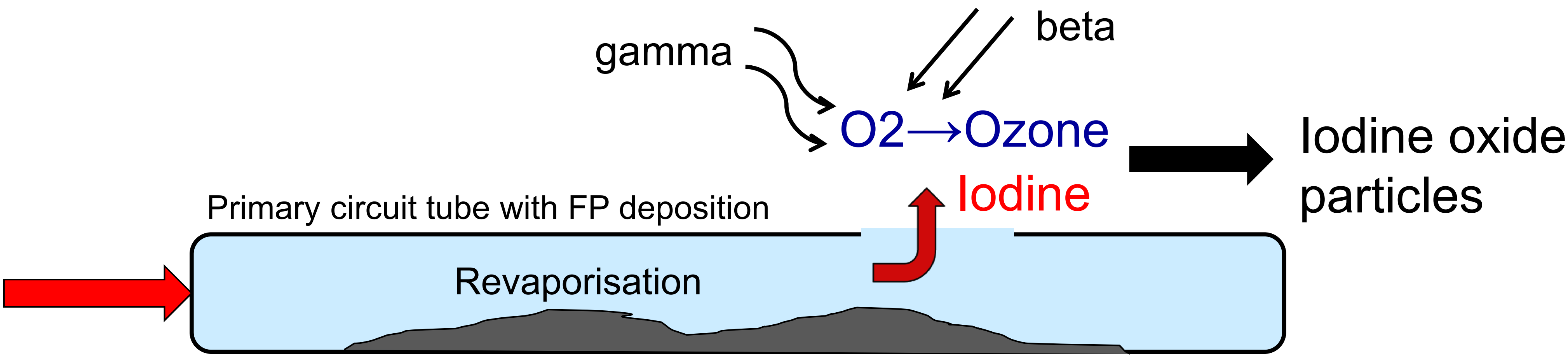




- Significant releases of gaseous iodine from PC surfaces even at conditions simulating late phase of accident.

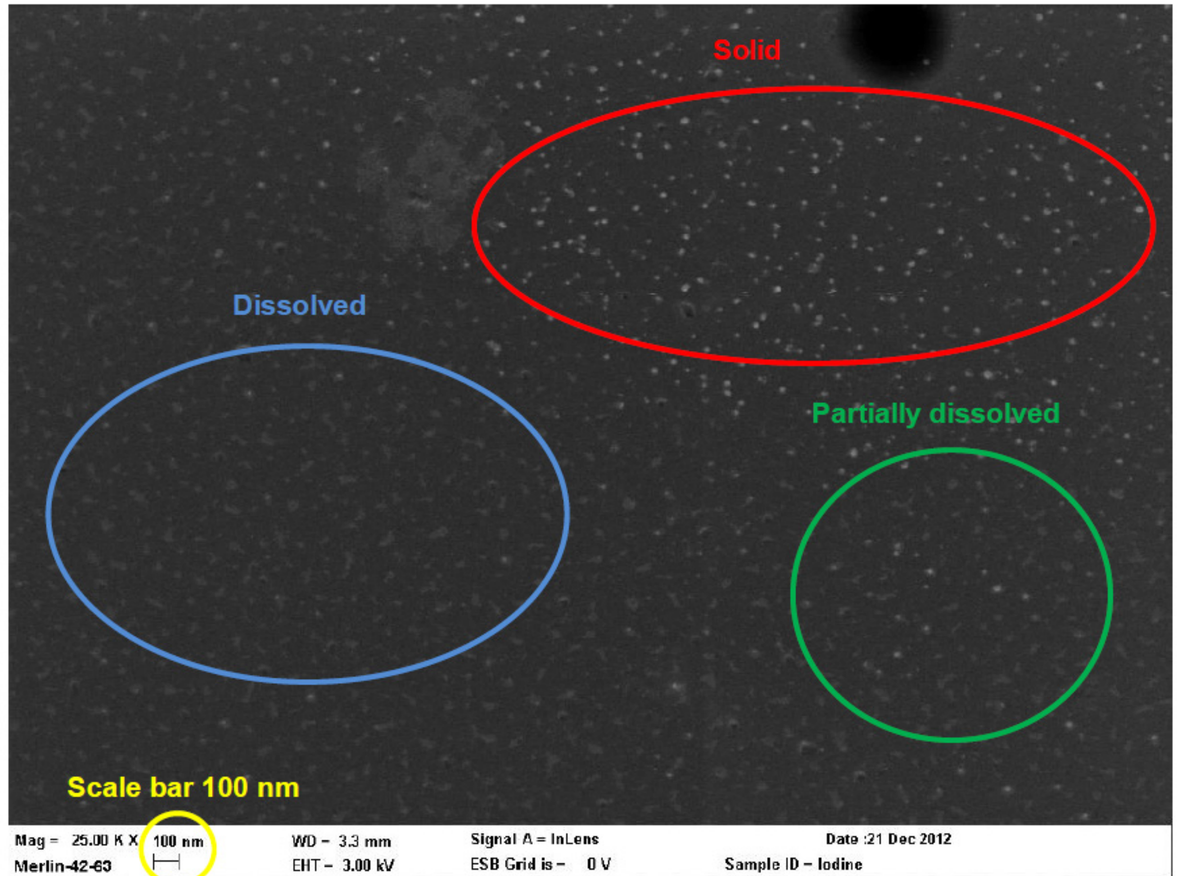
Radiolytical oxidation of gaseous iodine by beta radiation

- When gaseous iodine is released e.g. through a break in a primary circuit to the containment atmosphere, it will react with air radiolysis products such as ozone.
- Previously, the radiolytical oxidation of gaseous iodine by UV and gamma radiation has been studied in CHEMPC project [4].
- Since beta decay corresponds mainly for the dose rate in the gas phase of containment [5], its effect on the reaction product speciation of organic iodine was studied within TRAFI project.



Radiolytical oxidation of gaseous iodine by beta radiation

- When gaseous methyl iodide (CH_3I) was exposed to beta radiation in oxygen the formation of IOx particles took place.
- The diameter of particles was small, c.a. 10-50 nm.
- IOx particles seemed to react with the humidity of air and dissolve/de-compose very rapidly forming HIO3.
- Leads to a depletion of gaseous iodine in the containment atmosphere.

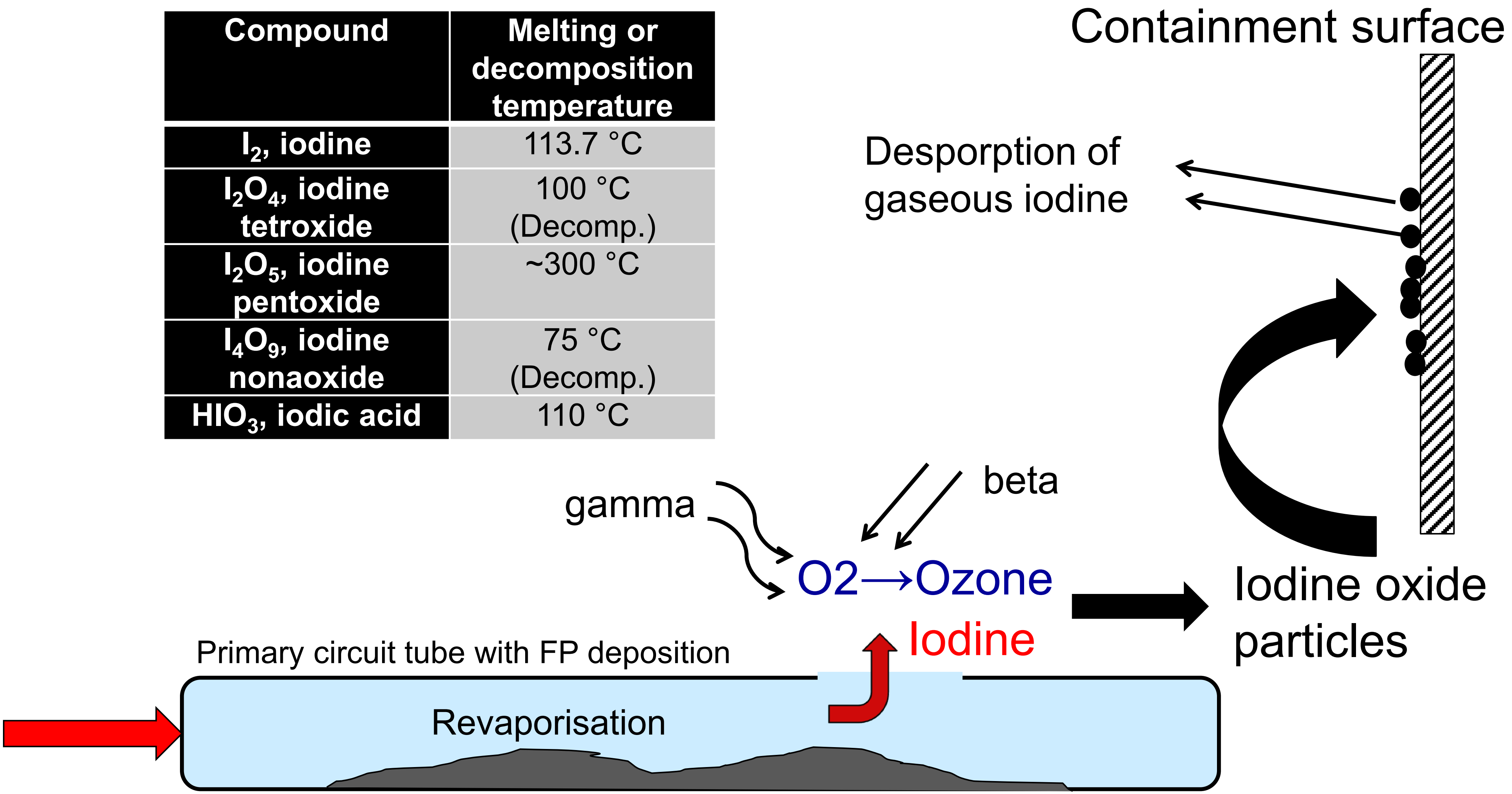


Analysis of iodine oxide deposits on containment surfaces (NKS-collaboration with Chalmers (Sweden))

- As a consequence of e.g. turbulent deposition, the iodine oxide particles in the containment atmosphere will deposit on the various surfaces of containment building.
- In order to validate the source of gaseous iodine in the containment gas phase, samples were prepared for iodine desorption studies.
- The surfaces exposed to IOx particles were paint (Teknopox Aqua V A), stainless steel (316), copper, zinc and aluminium.
- TRAFI project has also participated in OECD/STEM program where similar experiments with painted surfaces are conducted.

Analysis of iodine oxide deposits on containment surfaces

Compound	Melting or decomposition temperature
I_2, iodine	113.7 °C
I_2O_4, iodine tetroxide	100 °C (Decomp.)
I_2O_5, iodine pentoxide	~300 °C
I_4O_9, iodine nonaoxide	75 °C (Decomp.)
HIO_3, iodic acid	110 °C



Analysis of iodine oxide deposits on containment surfaces

- When IOx particles were exposed to **humid air**, they decomposed to a mixture of iodic acid (HIO_3) and elemental iodine (I_2).

- Iodic acid or partially hydrated $I_2O_5 \bullet HIO_3$ were observed on all the studied surfaces with some adsorbed elemental iodine.

Compound	Solubility in water
I_2, iodine	slightly soluble
I_2O_4, iodine tetroxide	decomp. to $HIO_3 + I_2$
I_2O_5, iodine pentoxide	decomp. to HIO_3
I_4O_9, iodine nonaoxide	decomp. to $HIO_3 + I_2$
HIO_3, iodic acid	very soluble

- IOx particles reacted with the metal surfaces forming water soluble ZnI_2 and water insoluble CuI.

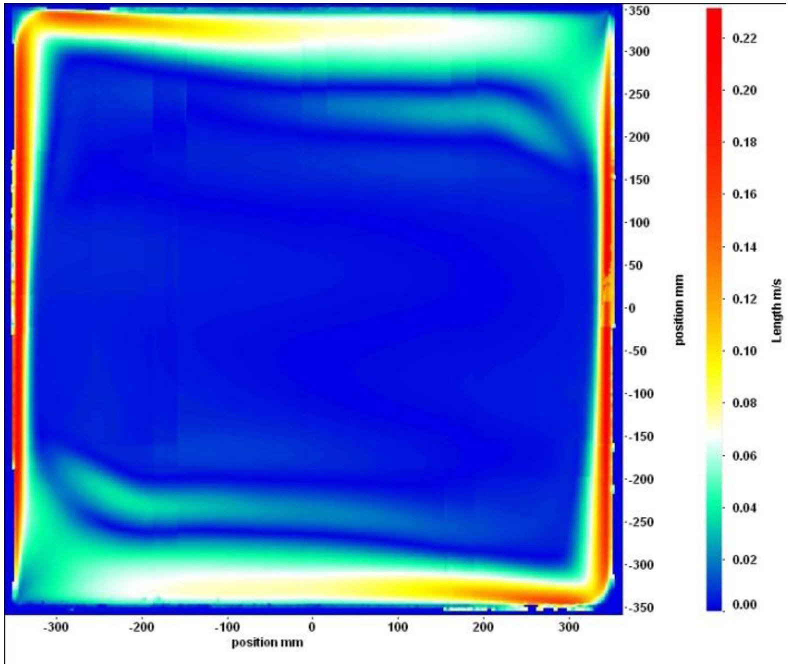
- Iodine was released from all the surfaces back into gas phase when deposits were exposed to humidity, heat and gamma radiation.

Turbulent deposition of fission products

- The deposition of fission products on the containment walls was significantly higher than expected in Phébus FP program.
- One hypothesis to explain the high deposition was that turbulent flow might have increased the fraction of wall deposition within the model containment. Turbulent natural convection flows will develop in real containment building due to temperature gradients.
- The effect of turbulence on particle deposition is tested at PSI by modelling the flow using DNS and LES tools. These models are validated against experiments carried out at TRAFI –project.

Turbulent deposition of fission products

- **DI**fferentially heated cavity with **A**erosol in turbulent **NA**tural convection (**DIANA**) facility was constructed for measurements of particle depositions on a turbulent natural convection.
- The temperature and flow velocity fields inside the facility are measured.
- Preliminary results verified the formation of turbulent flow next to the walls of the facility.



- This could explain the observed wall deposition of FPs in Phebus program.
- Experiments on the turbulent deposition of aerosol particles are on-going.

Conclusions

- Effects on nuclear safety:

1) Iodine seemed to be released almost completely in gaseous form from primary circuit at low temperature (400 °C) despite the used precursor mixtures.

2) Radiolytical oxidation of gaseous organic iodine by beta radiation produces iodine oxide particles. The formed particles were highly water soluble and volatile.

3) In humid conditions during a severe accident, iodine oxide particles would decompose to a mixture of HIO_3 and $I_2O_5 \bullet HIO_3$ particles and I_2. In case iodine oxide particles react with metal surfaces, metal iodides could be formed as is suggested in this study.

4) The desorption of iodine from iodine oxide deposits on paint and metal surfaces was observed to take place when the samples were exposed to heat, humidity and gamma irradiation.

Future

- The information on the iodine chemistry developed in CHEMPC and TRAFI projects have been utilized e.g. in the development of electric filtration technique for gaseous and particulate iodine species.
- The efficiency of this Finnish innovation is currently evaluated in EU PASSAM project. This project aims at studying different techniques to trap iodine inside the containment building and to mitigate the possible releases of FPs to the environment.
- The experimental data on the release of iodine from primary circuit and on the oxidation and desorption of iodine in the containment conditions will be utilized in the development of severe accident analysis codes (e.g. ASTEC).

References

- [1] www.dailymail.co.uk
- [2] M. Schwarz, B. Clement, A. V. Jones, Applicability of Phebus FP results to severe accident safety evaluations and management measures, Nuclear Engineering and Design, Vol. 209, Issues 1-3, pp. 173–181, 2001.
- [3] R.Y. Lee and M. Salay, Phébus-FP Findings on Iodine Behaviour in Design Basis and Severe Accidents, Presented to the Advisory Committee on Reactor Safeguards 8.5.2008, U.S.NRC
- [4] T. Kärkelä, J. Holm, A. Auvinen, T. Kajolinna, H. Glänneskog, C. Ekberg, J. Jokiniemi, EXSI facility – Experiments on radiolytical oxidation of CH_3I by gamma radiation, VTT-R-00527-11, 2011.
- [5] L. Bosland, L. Cantrel, N. Girault, Evaluation of the dose rate inhomogeneities in PHEBUS containment during FPT1 and FPT3 tests, 31th CCIC meeting, 2010.