



Progress with Iodine Chemistry Studies in SARNET2

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ABSTRACT

The EU SARNET project (Severe Accidents Research NETwork of excellence) unites the research efforts of 47 organisations from 24 countries worldwide to help to resolve the most important remaining uncertainties and safety issues on severe accidents (SA) in existing and future water-cooled nuclear power plants (NPP). The SARNET2 project started in April 2009 for 4 years in the 7th Framework Programme (FP7) of the European Commission. One of the most important parts of SARNET concerns evaluation of the “source term”, involving the development of methods to calculate the time, history, and chemical and physical forms of radionuclides that could be released to the environment, following containment breach and/or venting in the course of a severe accident.

A major part of the source term research concerns iodine, in view of its high radiotoxicity. Relevant work performed in this part of SARNET2 concerns firstly small-scale experiments to examine the behaviour of iodine in the circuit and reactor containment with a view to developing relevant computer models such as those in the European reference code ASTEC; followed by development and improvement of such models, and finally their assessment using independent data, such as those from the integral test series Phébus FP and THAI. An important parameter is the amount of organic iodide present in the containment, as this cannot easily be removed by filtration when using containment venting. Research has concentrated on the following important aspects: the behaviour of iodine oxides, interaction of iodine in the containment atmosphere with paints (as this can generate organic iodide), iodine interactions in the sump and exchanges with the atmosphere, and iodine transport in the primary circuit particularly concerning kinetic limitations, which mean that the relative compositions of material arriving at and in the containment may not reflect an equilibrium state. This paper summarises the progress made in SARNET2 to date in the iodine chemistry area, and indicates what results are to be expected at the end of the project next year, 2013.

1 INTRODUCTION

Research into the behaviour of iodine under severe accident conditions forms an important part of the source term studies in the SARNET2 network of excellence [1] in the EC 7th Framework programme, on account of that element’s volatility and high radiotoxicity. The overall aim of the source term work is to reduce the uncertainties associated with

calculating the potential release of fission products to the atmosphere, particularly using the European severe accident analysis code ASTEC, developed by IRSN and GRS.

Following a review of research priorities at the end of the previous SARNET project [2], emphasis was placed as follows: iodine transport in the circuit (kinetics of iodine chemical reactions, speciation of re-vaporised iodine), and iodine behaviour in the containment (association with painted surfaces, radiolytic destruction of gaseous iodine species to form nucleate particles, sump chemistry/iodine partitioning). This research work covers both experimental and modelling studies. While use is made of existing experimental data supplied by project partners and in past and ongoing external research programmes such as those under the auspices of OECD, emphasis here is placed on work performed specifically in the SARNET2 framework, indicating the progress made to date from the start of the project in April 2009, and what results are likely to be obtained by the end of the project at the end of March 2013. The partners involved in the circuit and containment work reported here are IRSN (France, coordinator of WP8-2 on iodine source term), VTT (Finland, overall coordinator of WP8 on source term), AECL (Canada), Chalmers University (Sweden), CIEMAT (Spain), EdF (France), GRS (Germany), EC/JRC/ITU (EC, Germany), KINS (Korea), National Nuclear Laboratory (NNL, UK), Newcastle University (UK), PSI (Switzerland) and USNRC.

2 PRIMARY CIRCUIT CHEMISTRY

2.1 Experimental studies

Due to strong thermal gradient and short residence time in the reactor coolant system, the usual assumption, which is to calculate the gaseous species at thermochemical equilibrium can be false; such disequilibrium will promote the persistence of a gaseous iodine fraction at a coolant system break as shown in [3]. In integral experiments such as Phébus FPT1 [4] an early presence of gaseous iodine in the containment has been observed, which could result from iodine kinetic limitations through the RCS. Thus, *IRSN* have conducted iodine chemistry experiments in primary circuit conditions using a small-scale facility [5] and the larger CHIP PL line [6], examining the kinetics of reactions involving iodine. Tests performed with the (Cs, I, Mo, O, H) system confirmed that gaseous iodine is persistent at 150°C as soon as Mo was in excess compared to Cs with up to 70% of iodine released under gaseous form at the outlet of the experimental lines. Molecular iodine has been identified as the main species, but the existence of other gaseous species (HI, HOI) cannot be excluded [5]. The first test in CHIP PL line, with concomitant injection of I, Cs and B at 1600°C showed that the fraction of gaseous iodine released at 150°C was less than 1 % of the total iodine transported. A large quantity of I and Cs was detected in the aerosol filters with an excess of Cs.

At *VTT*, fifteen primary circuit chemistry tests were conducted using the EXSI-PC facility. The precursor of iodine was CsI powder which has been heated up to 400°C, 550°C or 650°C in a flow furnace [7]. In addition, Mo, MoO₃, B₂O₃ or Ag was added to the precursor. When only CsI precursor was applied in the tests, a significant amount of gaseous iodine was always released especially in pure steam flow. The fraction of gaseous iodine decreased with increasing temperature and hydrogen concentration. As expected Mo, MoO₃ and B₂O₃ all increased the fraction of gaseous iodine. Silver decreased the gaseous iodine release at 650°C, but surprisingly increased the release rate substantially at 400°C. Six further experiments will be conducted during 2012 including e.g. first tests with AgI precursor.

While not directly concerning iodine, re-vaporisation tests performed at *JRC/ITU* on Phébus FP primary circuit (vertical line) samples provide some insight into possible iodine

speciation in the circuit. In SARNET2, revaporisation tests performed on FPT3 samples [8] added to the data already obtained from similar samples from FPT1, and showed the dependence of caesium volatilisation on heat-up rate and on temperature, with evidence of different chemical forms volatilising, and the possibility of reactions with the substrate.

2.2 Model development and assessment

IRSN is developing kinetic modelling of gaseous reactions under circuit conditions, involving iodine, caesium, oxygen and hydrogen. Kinetic schemes have been determined and implemented in the ASTEC/SOPHAEROS code [9]. The main difficulty is to obtain the kinetic rate constants for each elementary reaction which is part of the kinetic scheme. Most of them are not available in literature and need to be calculated. Two approaches are used to calculate the rate constants. The first one is a rough empirical method in which the interest is to get an approximate indication of the temperature dependence. This first assessment enables sensitivity analyses to identify the most relevant reactions under some typical representative boundary conditions. The second step is, by theoretical chemistry, to re-calculate the rate constants of these relevant reactions with greater accuracy. For this, the Transition State Theory (TST) is used and the challenge is to localise the reactive complex on the potential energy surface (PES). This work has been completed for iodine [3] and is ongoing for caesium. The kinetics were mainly validated on tests carried out in the small-scale GAEC facility [5]. For oxidising conditions simulations agree well the experimental results, whereas for reducing conditions some assumptions still need to be confirmed. Further work will extend to boron chemistry, notably to reactions leading to formation of caesium borates.

3 CONTAINMENT CHEMISTRY

The main lines of research here concern iodine interactions with paints, iodine oxide formation and behaviour, and sump chemistry/iodine partitioning,

3.1 Experimental studies

The EPICUR programme at *IRSN* allows on-line measurement of the kinetics of release of the volatile iodine species formed either in solution or on surfaces.

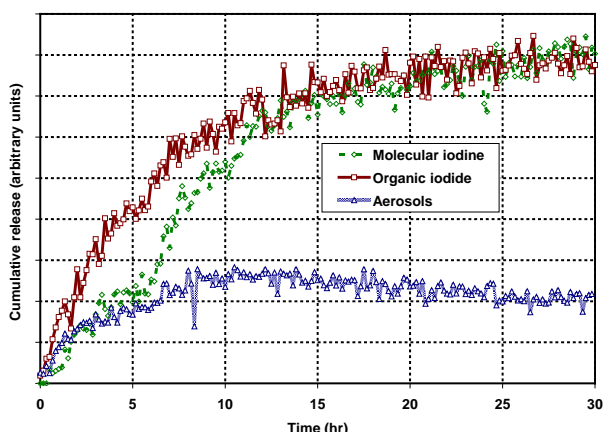


Figure 1: On-line measurements for a 30 hour duration irradiation test in EPICUR

The temperature in the irradiation vessel is regulated and can range from 40 to 130°C. Tests were performed to study the formation of organic iodide from painted coupons (steel, surface area of 50 cm² with a diameter of 56 mm and thickness of 3 mm) loaded with iodine and placed in the containment atmosphere. To simulate paint ageing, the painted coupons were preheated at 130°C in a dry atmosphere for 96h prior to labelling and irradiation. They were loaded with molecular iodine from the gaseous phase.

Three main parameters were investigated to evaluate their impact on the formation of organic iodide: the initial concentration of iodine on the coupon ($[I]_i$ in mol of iodine per m² of paint; between $\sim 1.10^{-4}$ and 1.10^{-2} mol.m⁻²), the temperature (80°C or 120°C) and the

relative humidity (e.g. at R.H.: 0%, 20%, 60%) in the irradiation vessel. The irradiation phase lasted for about 8-100 hours. The gas flow in the irradiation vessel was usually regulated at $0.25 \text{ l}\cdot\text{min}^{-1}$ (leading to a residence time of about 20 minutes). After each irradiation phase, the atmosphere of the vessel was swept towards the Maypack filter device (which allows discrimination amongst aerosol, molecular iodine and organic iodide) for gamma-counting of the volatile species produced.

Results show that the initial concentration of iodine on the coupon mainly influences the molecular and aerosol production rate. Figure 1 shows the on-line γ -measurements obtained on each filter for a long irradiation phase. For the Knitmesh and the charcoal filter stages, one can observe that the volatilisation increases with time but does not follow a linear law, whereas the activity measured on the quartz fibre filter reaches a plateau. This figure also highlights that there is still volatilisation of iodine after 8 hours of irradiation but with slower kinetics. It is concluded that at least two different iodine release kinetics exist (fast during the first hours of irradiation and a remaining slower one afterwards).

VTT and *Chalmers* carried out EXSI tests on radiolytic oxidation of gaseous organic iodine in containment conditions. Ozone and UVC radiation was used to simulate the radiolytic reaction of methyl iodide. Up to March 2012, sixteen experiments on radiolytic oxidation of methyl iodide were performed within the NROI project (a Nordic collaboration studying iodine chemistry in the containment). The parameters varied in the experiments were temperature, residence time, ozone concentration, UV-radiation intensity, methyl iodide concentration and humidity [10].

The particle formation was rapid when methyl iodide was exposed to ozone and/or UV-radiation. No particles were formed when only methyl iodide was present in the system. The mass of the formed particles at dry conditions, presented in Figure 2, varied between 20-500 mg/m^3 depending on ozone concentration, UV-radiation intensity and temperature. Particle size increased with temperature and with increasing ozone concentration. Particle growth took place primarily by agglomeration, which was enhanced by increased mass and number concentration of nucleated particles. Increasing flow rate decreased the particle size as the residence time for agglomeration was limited. Another conclusion is that ozone and UV were more effective together in oxidising methyl iodide than either of them alone. In humid conditions the particle formation was even more extensive, especially when ozone concentration was high. High particle concentration caused some problems with clogging of the tubes. Particle mass concentrations as high as $1200 \text{ mg}/\text{m}^3$ were measured in some tests with humidity. Methyl iodide concentration decreased when particle mass concentration was increased with increasing temperature, ozone concentration and UV-radiation intensity. The most significant gaseous reaction species from decomposition of methyl iodide were formaldehyde and methanol. The particles were composed of iodine and oxygen, but it was impossible to determine an exact speciation.

It should be noted that in reactor accident conditions there will be a different radiation type (ionising) leading to a larger variety of reactive species, not just O_3 . Good understanding of all the processes involved is necessary to apply these results reliably in such situations.

Chalmers completed preliminary tests on absorption of I_2 on fresh paint, which will be compared with the real paint from Barsebäck NPP. The behaviour of different iodine species, including elemental iodine and low molecular weight alkyl iodides (methyl and ethyl iodide) has been studied. Their distribution between containment air and water pools, their removal from gas streams by wet-scrubbing in Venturi scrubber safety systems and their interactions with various surfaces such as epoxy paint films have been investigated. The distribution and hydrolysis of methyl iodide between an aqueous and a gaseous phase were studied

experimentally for aqueous pools of pH = 4 - 10 from room temperature to 70°C. It was concluded that a decrease in the pH or an increase in the temperature causes the partitioning coefficient (aqueous phase/gas phase) to decrease. The results are summarised in [11].

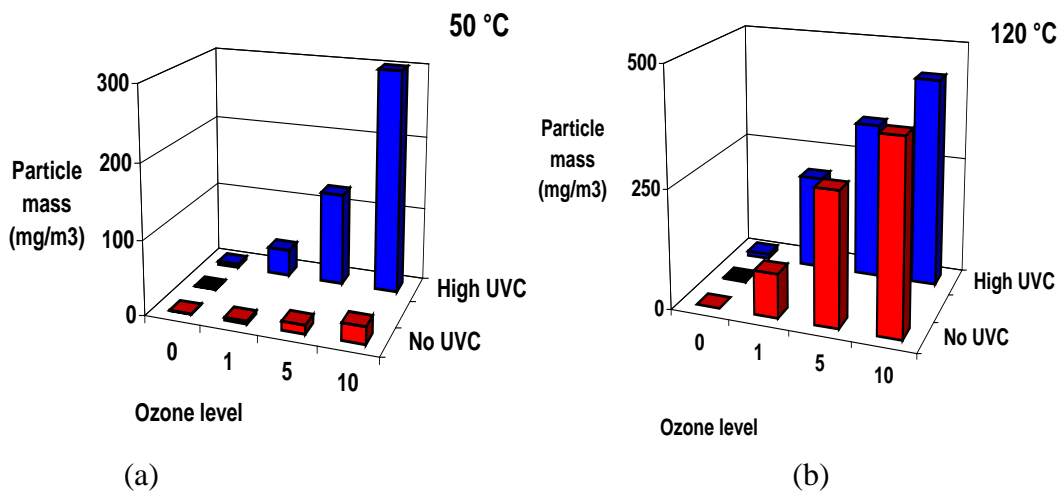


Figure 2: The particle mass at different temperatures, UV-intensities and ozone levels measured in the EXSI facility

Since 2000 the technical-scale THAI test facility (THAI = Thermal hydraulics, Hydrogen, Aerosols, Iodine) [12] has been operated by *Becker Technologies* at Eschborn, Germany, in close co-operation with *AREVA NP* and *GRS* in order to provide an experimental data base for the development and validation of lumped-parameter and CFD containment codes. One focus of THAI is the investigation of coupled containment phenomena between the areas of thermal hydraulics, hydrogen, iodine and aerosols. Data from the iodine tests Iod-9, Iod-11, Iod-12, Iod-13 and Iod-14 have been released by the German Federal Ministry for Economics and Technology (BMWi) to SARNET for further evaluation and code validation. In particular, the last two of these tests study iodine oxide aerosol production at different iodine/ozone ratios. Further details are given in [11].

The Radioiodine Test Facility (RTF) [13] was built at *AECL's* Whiteshell Laboratories to study the time-dependent concentration of airborne iodine ^{131}I in the reactor containment, an important parameter used to evaluate radiological impacts of a reactor accident. Data from Phase 9 Test 3 (P9T3) were provided to SARNET members; this examined iodine behaviour in an electropolished stainless steel vessel in the presence of a ^{60}Co radiation source. Although initially 25°C, the temperature was increased in stages (first to 60°C, and then to 80°C) to investigate the effect of temperature on iodine volatility. Details of the test results are given in [11]; the results can be used to develop or validate containment iodine codes.

Iodine chemistry studies at *PSI* [14] aimed at quantification of the effects of nitrate, nitrite and chloride ions on iodine radiolysis reactions. The results clearly showed that nitrate and nitrite ions in argon-sparged and irradiated iodide solutions (conc., 10^{-4} mol.dm $^{-3}$) containing boric acid lower % I_2 yields up to an initial NO_3^- concentration of $\sim 5.0 \times 10^{-3}$ mol.dm $^{-3}$. Using a low CsI concentration (4.0×10^{-5} mol.dm $^{-3}$) estimated in the containment sump during a severe-accident, an initial nitrate concentration (10^{-3} mol.dm $^{-3}$) and pH 7.1, ~ 3.6 % I_2 was produced by argon sparging at a dose of 20.5 kGy. In contrast, 80% I_2 was formed at a dose of 12 kGy in the absence of nitrate ions. The differences in the obtained yield under use of different sparging gases are explained by the level of net oxidation of the system determined by the sparging gas type.

3.2 Model development and assessment

IRSN analysed new EPICUR tests together with Phébus FP and OECD/BIP experimental results and has proposed new insights for iodine interaction with paints. Instead of a purely empirical approach based on fitted correlations, some further understanding was required to be able to predict well organic iodide formation during a severe accident. The mechanistic approach is based on a representation of the epoxy monomer including amide, amine and alcohol functional groups. It is assumed that iodine adsorption rate depends on the active sites and the organic iodide released from paint with a kinetic in two steps can be explained by the existence at least of two sites which contribute to the organic iodine (Org-I) formation. Based on these assumptions, which need to be consolidated with theoretical chemistry tools, to develop a model after developing a suitable methodology, the parameters are mainly fitted on EPICUR experiments as being the most prototypic. This model applied to Phébus FP tests gives reasonable agreement except for FPT1 where experimental Org-I data are much higher than the calculated values. Interpretations of OECD/BIP results are ongoing, but the first trend shows discrepancies. It means that either the model has to be revised or some other significant parameters are not considered. The OECD/BIP2 and OECD/STEM programs (see [11]) will furnish additional data which could be used to enhance these models.

CIEMAT also analysed ISTP/EPICUR and OECD/BIP experiments with ASTEC/IODE. Organic iodide formation from painted walls was modelled considering dose rates, loading conditions, total doses, and the initial concentration of iodide adsorbed in the painted surfaces. The P10T2 and P11T1 BIP-RTF tests were also analyzed, on organic iodide generation from aqueous iodine solutions contacting painted surfaces and with aqueous iodide solutions in which some organic compounds are dissolved. Results seem to indicate that organic iodide formation in the aqueous phase might be faster than predicted and that some of the organic iodides formed might be less volatile than CH_3I , the organic species assumed in IODE. A simplified iodine model for organic iodide formation has been developed in *KINS* in their iodine code RAIM, using data from ISTP/EPICUR and PARIS experiments. It has been validated using other EPICUR data with mixed results so far. MELCOR/RAIM has been tested by trial plant calculations against Phébus FPT3 data to show its applicability. *GRS* carried out COCOSYS/AIM code validation particularly on the basis of Phébus FPT2 and FPT1 data, focussing on uncertain iodine model parameters. Study of wet deposition of I_2 (THAI Iod-24) is on-going. *NNL* performed preliminary calculations using the mechanistic IODAIR model to simulate the EXSI tests on gaseous methyl iodide oxidation by ozone or UV irradiation. The products predicted by the model were qualitatively in agreement with the experimental observations. The results suggested that there may be a direct reaction between O_3 and CH_3I for which kinetic data have not previously been reported.

Chalmers have developed a model to describe their data on distribution and hydrolysis of methyl iodide between an aqueous and gaseous phase for aqueous pools of $\text{pH} = 4 - 10$ from room temperature to 70°C . Calculations of the impact of pH and redox potential of iodine solutions on volatility of different iodine species have been compared with on-line data, with good results, for example on time-dependent methyl iodide concentration in the gas phase and liquid phase, and that of I^- in the aqueous phase. *Newcastle University* is developing a Computational Fluid Dynamic (CFD) model for the agglomeration of iodine oxide (IOx) polydisperse aerosols generated by the radiolytic reaction of I_2 gaseous species with ozone in the THAI Iod-13 and experiments. The models are implemented in the SATURNE CFD code with the cooperation of *EdF*. The work started with a study of agglomeration of aerosol particles in a 2-dimensional vertical rectangular cavity flow of air driven by natural convection. Future work includes the validation of the model with data from THAI Iod-13/14 and the extension of the model to inertial particles. Analysis of *PSI* tests on

iodine volatility from irradiated solutions was carried out in *NNL* with the *INSPECT* code and compared with earlier Harwell tests. Good agreement was found for tests without impurities, but not yet for tests with nitrate. *PSI* interpreted their own results using their *PSI*iodine code [15]. *USNRC* carried out work on thermal aqueous reactions of iodine and documentation is underway. Work on adsorption of aqueous iodide and iodate is continuing. Modelling of aqueous molybdate and borate ions is complete and documentation is being prepared. Modelling of boric acid vaporization from aqueous solution continues.

4 CONCLUSIONS

Containment iodine experiments in *SARNET2* have been discussed in [11] on a thematic basis, noting that the three main safety-related topics were: (i) iodine interaction with paints; (ii) iodine oxide formation in the gas phase of the containment atmosphere; and (iii) iodine volatility in the sump, in the presence of impurities. It was shown how collaborative experimental and theoretical work in these areas was and is leading to improvements in major severe accident codes such as *ASTEC* and *MELCOR*, and hence in reducing uncertainties in the prediction of the potential iodine source term to the environment in the event of a severe accident. Similarly, knowledge being gained in separate-effects experiments is being used to improve the modelling in primary circuit codes, such as *ASTEC/SOPHAEROS*, where considerable progress has been made in implementing kinetic modelling of reactions involving iodine; work is continuing both experimentally and theoretically. Consolidation of these activities is under way, with the aim of publishing the main findings concerning the three containment chemistry topics, and circuit chemistry, following the end of the *SARNET2* contract in March 2013.

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