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Adsorption of Iodine on Painted Surfaces in Nuclear Power Plants Containment Buildings

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ABSTRACT

The paper is focused on prediction of adsorption and desorption of iodine on painted surfaces in containment buildings during loss-of-coolant accidents. The scope is to adjust the COCOSYS computational models to available experimental data. The theoretical part of the paper contains an introduction into iodine behaviour in containment buildings, short description of the COCOSYS (COntainment COde SYStem) computational code used for analysis and a description of validation chain defined by the IAEA. The experimental part of the paper is aimed at validation of COCOSYS iodine paint deposition model in dry conditions and fine-tuning parameters of this model on selected experiments executed under the OECD NEA Behaviour of Iodine Project. The model fine-tuning aims at adsorption and desorption rate as well as the splitting factor of physisorbed and chemisorbed iodine. The selected experiments include those with Ameron Amerlock paint, which is present in the Temelin WWER-1000/V320 NPP containment. This work was conducted under the framework of the EU R2CA project.

1 INTRODUCTION

Iodine is amongst the most important ^{235}U fission products formed in nuclear reactor with high fission yield (approximately 7 %, cf. Figure 1). Iodine has a large amount of short-lived radioactive isotopes and can also form highly volatile species as molecular I_2, organic CH_3I etc. Furthermore, iodine is an essential chemical element for human organism as a part of hormones important for thyroid gland function. Iodine released during a hypothetical NPP accident may therefore lead to significant radiological consequences and can cause significant damage to human health after inhalation. Containment release of iodine depends on various processes, e.g., adsorption of I_2 on painted surfaces in containment, which may lead to reduction of iodine release to the environment and subsequently reduced radiological consequences after the accident. A detailed study and a comprehensive understanding of iodine properties and behaviour in containment buildings and primary circuit are then required. This has been the subject of numerous experimental and modelling studies for several decades. Modelling of iodine transport and chemical behaviour in NPP containment is in particular possible thanks to

COCOSYS code and the AIM model [1]. Application of the code results in the NPP safety analyses chain has been the subject of an intensive validation work on various single effect and integral tests [2].

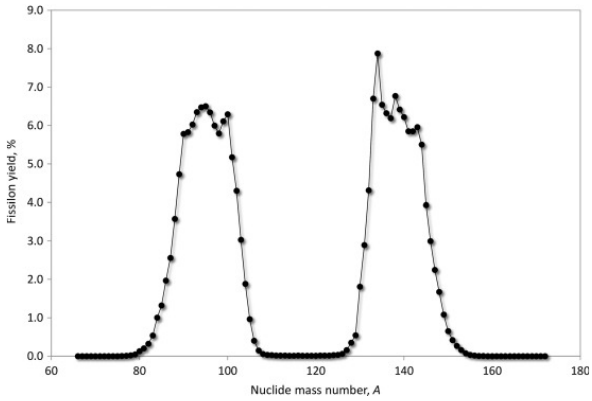

Figure 1: ^{235}U fission product yield [3]

2 IODINE TRANSPORT IN NPP CONTAINMENT

Iodine has a complex chemical behaviour in NPP containments (Figure 2). Iodine species are associated with water phase (sump), immersed surfaces, gas phase, surfaces exposed to the gas phase, and aerosols (dry particles, droplets). Water phase can contain soluble iodine species like iodides I^-, hypoiodous acid HOI and iodates IO_3^-, poorly soluble silver iodide AgI (silver issued from control rods may be an important sink for dissolved iodine), molecular iodine I_2 and organic iodides RI: both can dissolve only to certain concentrations according to Henry's law. Gas phase can also contain volatile iodine species such as I_2 and CH_3I, besides there can be caesium iodide CsI and iodates IO_3^- as soluble iodine aerosols. All these iodine compounds can participate in various radiolytic and chemical reactions in the containment. Painted surfaces which represent the most of all surfaces in the containment may serve as an important sink for volatile iodine [4].

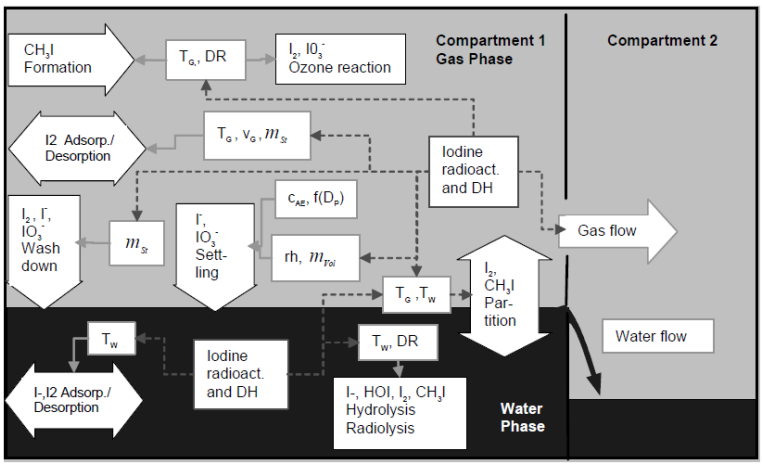

Figure 2: Modelling of iodine behaviour in NPP containment [4]

3 COCOSYS V3.0 & AIM-3 MODEL

The Containment Code System COCOSYS V3.0 is a code system based on mechanistic models for the comprehensive simulation of all relevant processes and plant states design basis accidents and severe accidents. The code system can be used for the identification of possible deficits in plant safety, the quantification of the safety reserves of the entire system, assessment of damage limiting or mitigating accident management measures and safety evaluations of new plant concepts. The inner part of the code system consists of 3 main modules: The Thermal Hydraulic Main Module (THY) for the simulation of thermodynamic behaviour and transient processes, The Aerosol Fission Product Main Module (AFP) for the simulation of fission product behaviour, decay heat release and chemical reactions, and The Core Concrete Interaction Main Module (CCI) for the simulation of the core melt behaviour, concrete erosion, releases from core melt and chemical processes inside of core melt [1].

Further programs are also coupled to COCOSYS for evaluation and visualisation of the results. Iodine behaviour is calculated by semi-mechanistic iodine model AIM-3 (Advanced Iodine Model, 3rd Version) which is a part of the AFP Module. In AIM-3, 53 chemical reactions and 18 physical processes in each compartment are considered. Iodine transport between compartments by gas and water flows is provided by the THY module and aerosol behaviour of the particulate iodine species is treated by the AFP module [1].

3.1 AIM-3 model

AIM-3 calculates concentrations of considered species resulting from many coupled processes as a function of time. General form of chemical process in COCOSYS is described in equation (1), where k_1 is the reaction rate constant for the forward reaction where the reactants are compounds A, B and C, D are the products and k_2 is for the reverse reaction (C, D are the reactants and A, B are the products) [1].

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + D \tag{1}$$

A kinetic equation is formulated in AIM-3 for each iodine species. The resulting set of differential equations is solved for each iodine compartment. To calculate reaction rate constants k_i at elevated temperatures (T [K]) the Arrhenius equation (2) is mostly applied. In equation (2) BAS_i is reaction rate constant at the temperature of 25 °C, R is the gas constant 8.3144 J mol^{-1} K^{-1} and $EAKT_i$ is an activation energy [J mol^{-1}].

$$k_i = \mathrm{BAS_i} \cdot e^{\mathrm{EAKT_i}\left(\frac{T-298,15}{RT\cdot 298,15}\right)} \tag{2}$$

The constants BAS_i and $EAKT_i$ can be, in some cases, modified by the user [1].

3.1.1 Physical behaviour of gaseous I_2 and its adsorption on painted surfaces in AIM-3

Molecular iodine I_2 is a reactive and water-soluble gas which can deposit and resuspend from surfaces. Following equations are important for iodine adsorption on dry painted surface:

- Physisorbed I_2 is weakly bounded to paint (with reaction rate constant k_{76}) and can be desorbed (resuspended) back to gas phase (k_{62}). Further equation (3) describes this reversive reaction. In COCOSYS $I_2(g)$ is for gaseous I_2 and $I_2(dep,p,g)$ is for I_2 deposited on paint from gas phase [1].

$$I_2(g) \underset{k_{62}}{\overset{k_{76}\cdot \mathrm{FSATP}\cdot \mathrm{XPHS}}{\rightleftarrows}} I_2(dep,p,g) \tag{3}$$

- Chemisorbed I_2 is strongly bounded to paint also with k_{76}. The reaction described by the equation (4) in COCOSYS is technically reversive but the value of k_{77} is set to 0 in this version of the code system. $I_2(g)$ is also for gaseous I_2 and $I_{chs}(dep,p,g)$ is for I_2 chemisorbed on paint from gas phase [1].

$$I_2(g) \underset{k_{77}}{\overset{k_{76}\cdot \mathrm{FSATP}\cdot(1-\mathrm{XPHS})}{\rightleftarrows}} I_{chs}(dep,p,g) \tag{4}$$

Schemes of both equations (3) and (4) are shown in Figure 3.

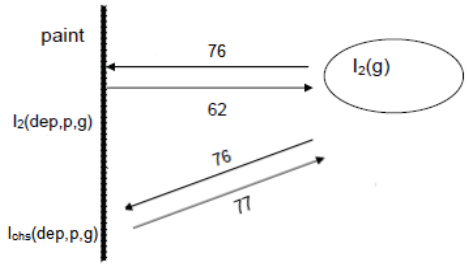

Figure 3: Interactions of gaseous I_2 with painted surface in containment

Furthermore, COCOSYS allows the user to modify the XPHS splitting factor, which determines the fraction of physisorbed and chemisorbed iodine of the total adsorbed iodine for specific kind of paint. FSATP is a dimensionless function of the absolute steam density to describe the influence of humidity and temperature, it cannot be changed by user [1].

The adsorption model is in original conditions set up for the GEHOPON paint [1].

4 COCOSYS-AIM-3 VALIDATION FROM BIP

According to IAEA Safety Standards [2], validation should be performed on all computer codes that are used for deterministic safety analysis of nuclear power plants. The purpose of validation (also referred as elsewhere as code qualification or code assessment) is to provide confidence in the ability of the code to predict, realistically or conservatively, the values of the safety parameter or parameters of interest. The major sources of information that should be used to assess the quality of computer code predictions are analytical solutions, experimental data, nuclear power plant transients and benchmark calculations (code to code comparisons).

The validation process should be conducted both on the side of the code developer as well as on the side of the code user. The validation conducted by the COCOSYS code developer GRS gGmbH can be found in [5]. Furthermore, the validation process should ideally include 4 different types of tests: basic, separate effect, integral and nuclear power plant level tests. [2]

Separate effect tests address specific phenomena that may occur at a nuclear power plant but does not address other phenomena that can occur at the same time. The BIP IA experiment [6], which is the subject of this paper, is a typical representant of a separate effects test.

The OECD (Organisation of Economic Co-operation and Development) initiated the Behaviour of Iodine Project with AECL (Atomic Energy of Canada Limited) as operating agent to achieve better understanding of iodine behaviour in NPP containments. Project performed work in 3 areas: adsorption of molecular iodine on surfaces (IA), organic iodides formation from containment paints loaded with iodine (OIF) and provision of Radioiodine Test Facility (RTF). The results of several IA experiments were used for modification of computational parameters executed for the purposes of this paper. Previous studies at AECL have determined that adsorption of gaseous molecular iodine is strongly dependent on the temperature and relative humidity of the air-steam mixture containing iodine. One of the paints used for BIP IA experiments is the Ameron Amerlock which is used on inner surface in NPP Temelin containment [6].

5 CALCULATIONS AND RESULTS

5.1 Computational model

The computational model for COCOSYS consists of three types of nodes (Figure 4). The BUFF1 to BUFF6 represent large volumes, which contain the gaseous mixture of desired pressure, temperature, humidity, and iodine concentration. The VESSEL represents the experimental cell with coupon and the ENVIRON collects the mass released from the VESSEL. The mass flow between the BUFFx and VESSEL is maintained by a corresponding ventilation component. Activating and deactivating of these ventilation systems allow precise control of gaseous mixture entraining in the experimental cell. The ventilation system FREM removes the mass from the VESSEL into the zone ENVIRON. This approach helps to keep stable thermal hydraulic conditions in the system.

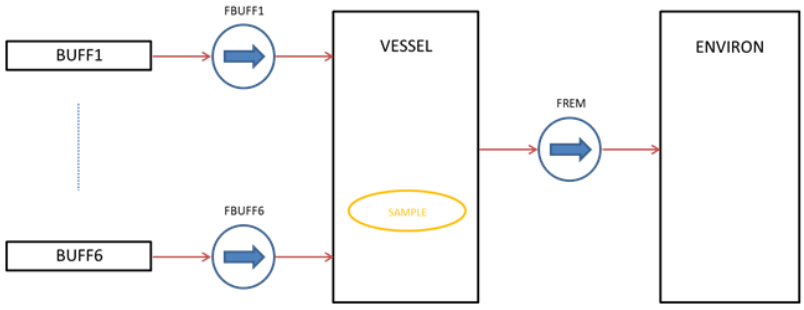

Figure 4: Nodalisation of the BIP IA experiments

5.2 Results and discussion

A typical experiment with painted coupon starts with injection of gas mixture containing iodine. This yields to adsorption (chemisorption and physisorption) of iodine onto the coupon, cf. Figure 5. At certain time point, the iodine injection stops. The physisorbed iodine is then released from the surface. This release ends at a certain point, where the adsorbed iodine is mainly composed of the strong bound chemisorbed iodine. The experimental results are labelled Coupon 1, 2, 3. The sum of the calculated physisorbed and chemisorbed iodine is labelled m_{total} (the orange curve). Physisorption and chemisorption are represented individually, where the physisorbed iodine mass is labelled $m_{I2\ paint}$ (the yellow curve), and the chemisorbed iodine mass is labelled $m_{Ich\ paint}$ (the blue curve).

The recalculation of the Ameron Amerlock experiments revealed significant underestimation of the adsorbed iodine mass. Furthermore, the desorption of physisorbed iodine was not interpreted correctly, as presented on the G-20 test, cf. Figure 5. The list of the investigated tests is presented in Table 1.

Table 1: Investigated IA tests with Amerlock coupons [6]

Test #	Coupon material	Temperature [°C]	Humidity [%]	Other information
G5	Aged Amerlock	70	15-40-60	Humidity was raised in stages
G8	Aged Amerlock	30	70	Temperature effect
G9	Aged Amerlock	50	70	Temperature effect
G12	Fresh Amerlock	70	70	1 adsorption/desorption cycle
G14	Aged Amerlock	70	15-40-60	Humidity was raised in stages
G19	Aged Amerlock	30	80	The same partial pressure of steam
G20	Aged Amerlock	50	27,5	
G21	Aged Amerlock	70	10,89	

The fine-tuning of the model parameters was done with a demand on realistic representation of the investigated phenomena for all the tests in Table 1. Calculation with modified model parameters (XPHS and BAS) led to more realistic estimate of the adsorption and desorption on dry Ameron Amerlock painted surfaces, cf. Figure 6.

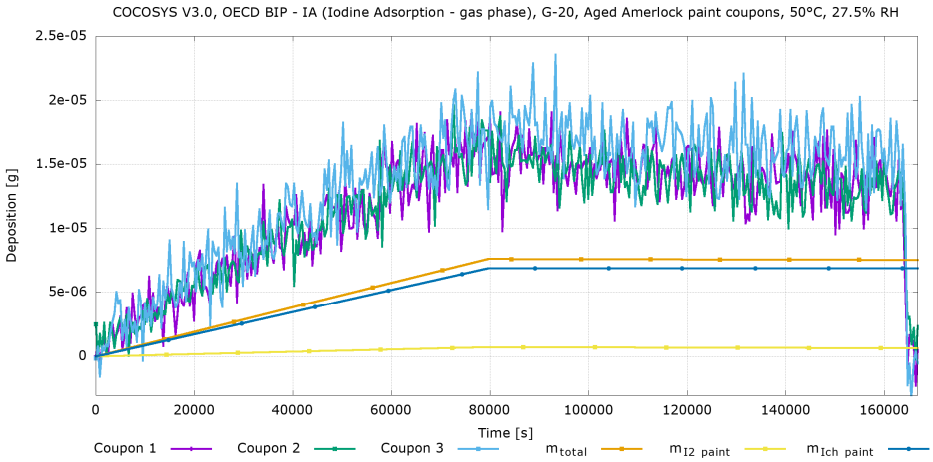

Figure 5: Prediction of iodine adsorption (original parameters)

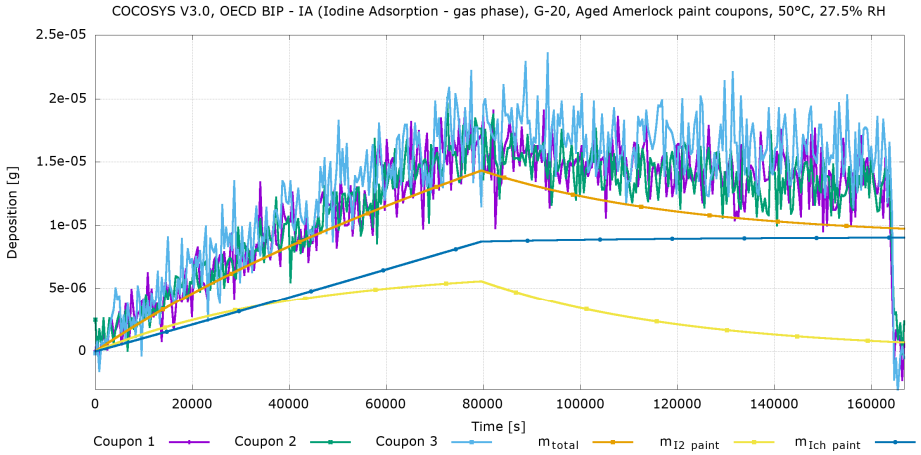

Figure 6: Prediction of iodine adsorption (modified parameters)

6 SUMMARY

The work conducted in this study proved the ability of COCOSYS V3.0 to simulate the iodine adsorption and desorption on dry painted surface. It should be noted that this type of fine tuning should be done for each investigated surface type and coating. Values presented in Table 2 are valid for the Ameron Amerlock only and may be further modified based on other experiments.

Table 2: Proposed BAS_i and XPHS parameters values for Ameron Amerlock

Parameter	$BAS_i(76)$	$BAS_i(62)$	XPHS
Modified value	7.5E-3	2.0E-6	0.6

Future work should be aimed at other single effect and integral tests and on implementation of the validation results into the models used for the NPP safety analyses and further reduction of radiological consequences. Future work will be aimed at verification of the

adjusted parameters on other experimental data. Furthermore, an extensive uncertainty study is planned for the future as well.

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