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PRESENT STATUS OF IODINE RESEARCH AT IPSN AND ITS APPLICATION TO REACTOR SAFETY

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Abstract :

Since several years, IPSN has conducted an effort in order to evaluate the release of radioactive iodine in case of hypothetical severe accident in a realistic manner. This source-term evaluation is performed with IODE code which is a module of the ESCADRE system of codes. This code is validated against :

- analytical experiments ; in these experiments, IPSN studies radiolytic effects and chemical processes in the sump, organic iodine formation, mass transfers, effect of spray (CARAIDAS experiment),
- the CAIMAN semi global experiment ; this experiment will allow to study the phenomena linked to iodine behavior under representative containment geometry in the presence of painted surfaces and global irradiation,
- the PHEBUS FP program.

The paper consists to describe succinctly the current status of IODE and the various experiments for its validation.

In case of hypothetical severe accident iodine can induce important perturbations of human organism. The effects are principally radiological, in particular on the thyroid. At short term, radioactive iodine is the most important contributor for the sanitary risk. It represents 55 % of effective dose and 92 % of thyroid dose at 10 km in case of controlled rejects with current assumptions. This is the reason why it must be actively studied.

In France, the safety evaluations are performed with mechanistic codes or lumped parameter codes like ESCADRE which contains a module devoted to iodine studies: IODE. The objective of the French experimental program on iodine is to understand and quantify important phenomena in order to put kinetic parameters in IODE module. The experiments can be classified in analytical experiments (mass transfer, deposition, spray washout...), the semi-global experiment CAIMAN which takes into account different phenomena studied in analytical experiments and the global experiment PHEBUS PF, not only devoted to iodine behavior study.

In the following text we will present the needs of IODE code and these different experiments [(1)].

1 - IODE CODE

1.1. - INTRODUCTION

For iodine behavior studies we use IODE 4.0 code which is a module of ESCADRE 1.0. Reactor geometry, gaseous and liquid phase volumes in containment, exchange surfaces, painted surfaces are taken into account in the code. Initial conditions like species concentrations, pH, dose rate, temperature and pressure are also used to perform calculations.

Only 15 chemical reactions have been introduced because the code approach is:

- semi-mechanistic if the phenomena are well-known
- empirical if the phenomena are too complex to be described by elementary reactions.

The code is developed by IPSN (CADARACHE).

1.2 - DESCRIPTION OF THE CODE

The iodine is assumed to be mainly released in the containment in the form of non-volatile CsI aerosols which is ultimately located in the sump water. The different phenomena which are described in the code can be divided in two aspects:

- physical aspects:
  - exchanges of volatile iodine species between the sump water and the containment atmosphere,
  - steam condensation on the containment walls and on the water surface,
  - gas phase leakage from the containment (in case of accidental leak or a purge of the containment atmosphere),

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(1) a part of these experiments is sponsored by EDF

- source of I^- in the sump water (CsI aerosols are I^- ion sources in the water),
- molecular iodine I_2 adsorption/desorption onto/from surfaces in containment,
- iodine removal by spray.

- chemical aspects:
  - containment atmosphere chemistry:
    - * oxidation of molecular iodine to iodate by ozone formed under radiation,
    - * formation of organic iodides.
  - sump chemistry modeled in the code:
    - * pH calculation
    - * hydrolysis of molecular iodine,
    - * HOI dissociation and disproportionation,
    - * oxidation of iodide by oxygen dissolved in sump water and under radiation,
    - * formation of methyl-iodide from I_2 and radiolytic decomposition,
    - * formation of silver iodide,
    - * hydrolysis of methyl-iodide,
    - * decomposition of iodate under radiation,
    - * formation of methyl-iodide by surface process.

For calculation, the code allows the user to activate only some of chemical reactions. It gives the user the possibility to change in an easy way the kinetic constants and activation energies of chemical reactions. The kinetics constants are calculated using Arrhenius law and most of reactions follow Van't Hoff's law.

1.3 - PRESENT STATUS AND FUTURE WORK

- *Reaction with silver : $2\,Ag + I_2 \rightarrow 2AgI$*

This reaction is extensively studied in the frame of PHEBUS FPT0 interpretation. The kinetic model has been validated on AEA and RTF3/PHEBUS experiments. A study of AgI stability in presence of radiation has begun. An experimental work has been proposed in the frame of CEC-4FP (1996-1998) with AEA and PSI.

- *Mineral species radiolysis*

The correlation which is used in IODE code has been validated on IPSN experiments and ACE/RTF experiments. IPSN tests have been performed at small scale, 40°C (one of two compartments with paint). This validation has some limitation linked to uncertainties in the determination of mass transfer in this kind of experiment. A new model has been developed taking into account pH effect and dose rate. Its validation is on-going. The effect of temperature will be studied in CAIMAN facility.

- *Organic iodine formation*

Organic iodine formation model by paint has been introduced in the code based on Deane's works. This correlation has been validated on ACE/RTF experiments but not with French paints. It will be validated on results of PHEBUS/RTF performed with French paints. A new modelisation will be develop to study organic iodine formation principal mechanisms: I_2/I^- aqueous solutions in presence of paints, I_2 gaseous phase in presence of painted surfaces, aerosols deposition on painted surfaces behavior, formation from organic materials. This work will be supported by an experimental work. These studies have been proposed in the frame of CEC-4FP (1997-1998) with AEA and VTT.

- *Mass transfer I_2*

The various models which are currently in IODE code need improvement or future development: the model for transfer between sump water and atmosphere, the model describing kinetic wall deposit (only global coefficient which is representative of convection effect and painting adsorption), the gaseous iodine transported by steam and sump evaporation. So, transfer phenomena modelisation must be improved.

The validation experiments are the following :

- Current experiments:
  - mass transfer without condensation : PHEBUS/RTF4,
  - mass transfer with condensation : PHEBUS/RTF3,
  - mass transfer in isotherm conditions : CAIMAN
- Short-term experiments needs (1996-1997) :
  - convection effect on interfacial transfer : IPSN experiment is launched,
  - painting behavior and painting trapping in reactor conditions : CAIMAN
- Long term experiments needs:
  - iodine volatilization from a sump in evaporation. This item has been proposed in the frame of CEC 4FP (1997-1998).

- *Iodine washout by spray.*

As regards the washout of iodine by spray, IPSN has decided to realize the following methodology :

- 1st step : study of different phenomena which have a function in the washout. This SOAR must lead to a spray model which must be validated,

- 2nd step : a first validation will be done using an IPSN analytical experiment. It will allow the determination of molecular iodine transfer rate for one free falling drop,
- 3rd step : the extension to high density of drops will be performed and validated if needed.

2 - ANALYTICAL EXPERIMENTS

2.1 - INTRODUCTION

Since several years a lot of analytical experiments have been made in iodine study domain. This IODE validation program has three investigation directions:

- the radiolysis phenomena and interactions with paints (mass transfer and chemical interaction),
- the gas-paint, water-paint mass transfers,
- the liquid-gas mass transfer.

This program is performed by IPSN (CADARACHE).

2.2 - RADIOLYSIS EXPERIMENTS IN PRESENCE OF PAINTED SURFACES

The objectives of these experiments are:

- the determination of iodine distribution between gaseous, aqueous phases and painted surfaces as function of :

  integrated dose (to be performed),

  temperature (on - going tests),

  initial iodide concentration,

  pH,

  painted surface location (gaseous, aqueous phase),

  surface/volume ratio (to be performed),

  other organic materials (to be performed),
- the evaluation of quantities and chemical forms of organic iodides coming from painted surfaces or any other organic materials.

The principal results are (at 43°C):

- pH effect : 60 % I_2 is produced at pH = 5 and 2 % at pH = 8.2,
- painted surfaces are a very efficient trap for iodine (80 % of I_2 produced is trapped on the epoxy),
- very few organic iodides have been found (0,4 % of initial iodide at pH = 6.4); the major compound is 2-iodo-propane,
- total volatile iodine (I_2 + R - I) in gaseous and aqueous phases, after 220 kGy irradiation is less than 4 % of initial I^- at pH = 5 and less than 0.1 % at pH = 8.2.

2.2 - RADIOLYSIS EXPERIMENTS IN TWO COMPARTMENT CELLS

The objective of these radiolysis experiments is to determine the amount of molecular iodine generated under radiation, as a function of :

- the integrated dose (60-1600 kGy), temperature (20°C - 130°C), pH (4.4 - 8.2),
- the initial iodide concentration (10^{-6} - 10^{-3} M), initial form of iodine (I^- or IO^{3-})
- the buffer effect of the solution (boric acid), perturbing ions Cl^-, NO_3^-.

The addition of perturbing ions and the initial form of iodine have no effect. The initial concentration in iodide has a clear effect which must be explained. The other parameters have strong effects, in particular temperature (studies recently completed) and integrated dose (few experimental results, possible further experiments to be performed).

2.3 - GAS-PAINT MASS TRANSFER

The objectives of the experiments are :

- the study of trapping velocity of iodine onto painted surfaces,
- the determination of mass transfer coefficients and limiting factors,
- the study of iodine desorption from the paint.

The effect of temperature depends on thermal pre-treatment of it. Without pre-treatment :

- between 28°C and 90°C, there is only chemical interaction; at 90°C there is a competition between diffusional resistance and chemical interaction,
- between 90°C and 120°C, the paint undergoes a physical transformation which implies a decrease of the reactivity with I_2,
- between 120°C and 190°C, the paint is in a stable state.

On the other hand, with a thermal pre-treatment of the paint, it is observed a decrease of trapping velocities for a treatment at 110°C and a strong decrease for a treatment at 130°C. With pre-treatment at 130°C, trapping increases with temperature between 90°C and 130°C but it remains less important than the case without pre-treatment of paint.

For the other parameters:

- I_2 trapping increases with humidity ratio and initial water content in paint (pre-treatment at 130°C),
- iodine desorption from paint depends on the initial loading in iodine and on the time spent between trapping and desorption. The release chemical form is I_2.

2.4 - LIQUID-GAS MASS TRANSFER

The goal of the experiments is to determine mass transfer coefficients and limiting factors : iodine diffusion in aqueous phase or interfacial resistance or diffusion of iodine in gaseous phase.

For I_2, the limitation is due to the diffusion in the aqueous phase but the transfer velocity increases with temperature (between 25°C - 90°C : factor 20). For organic iodides, the experiments must be performed.

2.5 - CURRENT STATUS OF THE PROGRAM

Some of experiments described previously are ongoing and will be achieved (mass transfer). New experiments will emphasize on the effect of silver (see PHEBUS FP), kinetic effects with on-line measurements and the desorption of iodine from paints under radiation.

3 - CAIMAN EXPERIMENT

3.1 - INTRODUCTION

The aim of CAIMAN program is the study of gaseous and organic iodine behavior in PWR containment during an hypothetical severe accident. The experimental results will permit :

- to validate the IODE code with several phenomena interacting,
- to estimate iodine activity in containment and different rooms.

In case of accident, the important physical parameter is radiolysis of water sump induced by fission products gamma irradiation. Consequently, CAIMAN program will be realized in an irradiator which allows to reach gamma dose rate equal 10kGy/h.

This program is performed by CEA/DRN for IPSN (CADARACHE)

3.2 - PRINCIPAL OPTIONS

The containment is simulated by a 300-liter volume vessel. This value has been chosen to have the best phenomena representativity in irradiator geometry and to be able to compare results with other experiments. The vessel is divided in two parts:

- the "containment" which is the part containing the gaseous phase (300-liter volume),
- the "sump" which is the part containing the liquid part (2-liter volume); this part undergoes irradiation.

Iodine behavior evolution is monitored in the atmosphere and on the walls by gamma spectrometry. ^{131}I is used with an initial activity of 37 MBq.

The sump is surrounded by a 5-centimeter thick lead protection. This thickness has been chosen in order to have a dose rate equal to 0.02 Gy/h on measure instrumentation (Ge-Li detectors). A dose rate equal to 10 kGy/h imposes a 74 TBq ^{60}Co source.

The irradiation duration is about 48 hours.

The vessel conception allows to realize experiments up to a maximal temperature of sump water of 130°C and an absolute pressure of 5 bar.

3.3 - DESCRIPTION OF THE FACILITY

The vessel geometry similitude is not necessary. Its surface is made with electropolished steel (against fission products trapping), with specific surfaces interacting with iodine behavior (painted surfaces, sump water surfaces,...).

The Surface/Volume proportion ratio is preserved (containment). The proportion ratios are the following :

- walls in touch with atmosphere : 0.5 m^{-1}
- walls in touch with water sump : 4.3 m^{-1}
- atmosphere/water sump interface : 1.7 10^{-2} m^{-1}

The water surface is equal to 51 cm² and the water volume is less than 2.4 l after the water evaporation linked to the vessel pressurization.

The differences between gas and wall, water and wall are reproduced during tests. The influence of vessel surfaces on surface behavior must be minimized: active surfaces are hanging from the top of the vessel and the wall temperature is controlled. Painted surfaces in atmosphere are equal to 1500 cm² and 61 cm² in liquid.

The following parameters are controlled:

- temperatures : - gas (max 130°C)
  - walls (max 135°C)
  - water (90°C - 130°C)
- pressure (max 5 bar)
- humidity rate (0 % - 100 %)
- water pH (4 - 9 at 25°C)
- dose rate (max 1 Mrad/h).

Vessel wall temperature and bottom vessel temperature are regulated between 0°C and + 5°C above water saturation temperature (against condensation) and painted surfaces temperatures are regulated between 0°C and - 5°C under water saturation temperature.

The measurement of activities on non-submerged painted surfaces is performed by gamma spectrometry through vessel wall without atmosphere modification (temperature, pressure...). Submerged painted surface activity measurement is performed at the end of each test by extraction of surfaces.

3.4 - TEST MATRIX

The tests are divided in two sets: global tests and semi-analytical tests to understand these former.

- Global tests :
  - test A : study of soda injection influence on iodine behavior (spray simulation),
  - test B : study of MCCI influence on iodine behavior with the end of test A as initial conditions (H^+ production ⇒ pH decay)

  In these two tests, the pH will vary from 5 to 9 after equilibrium of the system and will decay for the study of MCCI (test B). The dose rate will be 0.1 Mrad/h and 1 Mrad/h, the atmosphere temperature will be 130°C.

- Semi-analytical tests: three set of tests will be performed

  The aim of the first tests is to study the molecular iodine transfer between sump and atmosphere

- 1 st step: transfer kinetics of I_2 from water sump to atmosphere (pH = 5, 130°C, dose rate = 0)
- 2 nd step: transfer kinetics of I_2 from atmosphere to water sump (pH = 9, 130°C, dose rate = 0).

The aim of the second tests is to study radiolysis influence on molecular iodine transfer.

- 1 st step: radiolysis influence on transfer kinetic of I_2 from water sump to atmosphere (same conditions, but the dose rate),
- 2 nd step: basic pH influence on aqueous reactions and I_2 transfer in presence of radiation.

The last set of tests is dedicated to improve modelisation of organic iodine formation from painted surfaces.

In liquid :

- 1 st step : organic iodine production evaluation without radiation (pH = 5, T = 130°C)
- 2 nd step : dose rate influence on organic iodine production evaluation (pH = 5, T = 130°C),
- 3 rd step: I^- adsorption on paintings and organic iodine production without radiation (pH = 9, T = 130°C)
- 4 th step: same experiment with radiation.

In atmosphere:

- 1 st step: organic iodine production evaluation without radiation (pH = 5, T = 130°C),
- 2 nd step: same experiment with radiation.

3.5 - CURRENT STATUS

Two tests have been performed without irradiation. The goal of these tests was to verify the facility behavior.

The first test with irradiation (0.1 Mrad/h) will be performed next September. Three tests are planned at the end of 1996. The first "1 Mrad/h irradiation test" is expected in 1997.

4 - CARAIDAS EXPERIMENT

4.1 - INTRODUCTION

In case of a severe accident occurring in a French PWR, a reduction of containment pressure is obtained by the use of spray system allowing steam condensation on cold drops. With this thermalhydraulic function, spray depletes suspended fission product aerosols and iodine in the containment atmosphere.

Today, this spray system is taken into account in different safety codes using washout rates which have been determined during global experiments. With this approach, it is not possible to extrapolate experimental results to accident situations, which leads to very conservative hypothesis for safety evaluations. This is the reason why it is necessary to have more realistic washout rates for current reactors as well as for future reactors. It is the goal of CARAIDAS experiment. The facility will be used to study aerosol washout and, after, iodine washout. We will only describe the iodine experiment part.

This program is performed by IPSN (SACLAY).

4.2 - MAIN OPTIONS

The aim of this work is to develop experiments in order to determine the collision efficiency of iodine by a single drop. In French nuclear power plants, spray nozzles generate drops with a diameter between 100 µm and 500 µm with an initial temperature which depends of spray phase (direct spray or recirculation spray). The experimental facility has been designed with five fundamental criteria:

- thermodynamic conditions must be representative of atmosphere,
- thermodynamic equilibrium must be attained between water drops and the gaseous phase,
- the different phenomena which lead to washout must be independently studied in order to evaluate the elementary collection efficiency relative to each effect,
- operating conditions must be homogeneous and constant during each experiment,
- experimental technology must be developed to measure the particles.

For iodine the washout is due to:

- absorption with condensation of I_2; thermal effect of condensation modifies gas-liquid transfer,
- chemical reactions in drops which increase the quantity of absorbed iodine.

The iodine washout coefficient would be function of drop pH and iodine concentration.

The experiments, conducted with monodispersed drops, must take into account the following parameters:

- thermalhydraulic conditions (saturation and super-heated steam),
- pressure and temperature vessel (current or future reactors conditions),
- diameter and temperature drops (direct spray or recirculation spray),
- pH drops (direct spray with soda or recirculation spray during MCCI).

4.3 - DESCRIPTION

The previously options lead to a 4 m^3 volume vessel (5 ml useful high). Nozzle is at the top and drops collection below. The experimental conditions are the following:

- air-steam:
  - pressure: 10^5 Pa to 7 10^5 Pa,
  - temperature: 20°C to 160°C,
  - saturation rate: 0 to 95 %,
- drops :
  - diameter : 100µm to 600µm (monodispersed),
  - flowrate: 0.2 to 50 m/h,
  - temperature: 20°C to 80°C,
  - pH: 4 to 9
- iodine :
  - nature I_2,
  - concentration 20 ml/m^3.

The drops are generated by an electrostatic system. It is positioned out of the vessel in order to reduce the hot-cold interface and to permit a fast opening and a good control of injected drops. Along the vessel wall, there are 4 points of measure by camera.

The iodine generator is currently under its specification process. The iodine will be measured out with a colorimetric method (detection limit: 0.1µg/l). The collection of drops with iodine in the bottom of vessel will be made on a glass fiber impregnated by soda.

4.4 - TESTS MATRIX

The tests will be only devoted to I_2 washout since all previously performed experiments have shown that spray is not effective to wash out organic iodine.

Two cases can be distinguished:

- Direct spray :

  1 st step : reactor case without soda,
  pH = 5, I_2 concentration 20 mg/m^3, pressure = 2 bar to 8 bar, atmosphere temperature = 90°C to 160°C

  2 nd step: reactor case with soda,
  pH = 9, I_2 concentration = smallest as possible, same pressure and temperature.

  In these experiments drops temperature = 20°C and saturation rate = greatest as possible.

- Recirculation spray: ›dine is present in water, MCCI conditions,
  pH = 4, I_2 concentration in drops = 5000 mg/m^3, pressure = 5 bar atmosphere temperature = 140°C, drops temperature = 40°C to 80°C,
  saturation rate = greatest as possible

This test matrix will allow to cover all reactor situations.

4.5 - CURRENT STATUS

The aerosols washout experiments are on-going. They will be achieved at the end of this year.

Afterwards the CARAIDAS facility will be modified to perform iodine experiments which will begin in mid 1997.

5 - PHEBUS FP PROGRAM

5.1 - INTRODUCTION

PHEBUS FP is an international program, managed by IPSN (Institute for Nuclear Safety and Protection), Electricité de France (France) and the European Commission, in close collaboration with the USNRC (US), COG (Canada), NUPEC and JAERI (Japan) and KAERI (South Korea). Its objective is to investigate through a series of in-pile integral experiments, key phenomena involved in LWR severe accidents. The first test FPT0 was performed in December 1993 with trace irradiated fuel and showed some unexpected results regarding iodine behavior. The next test is FPT1 which is identical with FPT0 but the fuel will be irradiated. Six experiments are foreseen. The next two paragraphs are coming from the presentation done at CSARP meeting (may 1996) by Jacquemain and al [(2)].

5.2 - PHEBUS FPT0

During the FPT0 test, iodine was almost totally released from the fuel. In the vertical hot line above the bundle, iodine probably reacted with Cs, Rb or Ag to form a metal iodide vapor. This vapor was transported up to the steam generator tube where wall and bulk condensation of the vapor occurred. In the cold leg of the circuit, most of the iodine was transported by a homogeneous aerosol population, the aerosols being essentially composed of structural materials. A significant iodine fraction behaved differently, this fraction could be composed either of gaseous iodine or of small-size iodine aerosols.

The inventory found in the cold leg of the circuit reached the containment. The aerosols either settled on the containment bottom either deposited on the containment surfaces. Examination of the containment walls after the test showed that some iodine

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(2) Overview of the iodine behavior in PHEBUS FPT-0 - D. Jacquemain, N. Hanniet, C. Hueber, C. Poletiko; C.A. Chuaki, S. Dickinson, Y. Drossinos, F. Funke, L. Herranz - CSARP Meeting, May 96 - Bethesda MARYLAND

deposited on the painted condenser surfaces, most of it on the cooled condenser surface. There was also an unexplained deposition on non-condensing stainless steel surfaces.

About 10 hours after the aerosols reached the containment, the mass of iodine suspended in the containment atmosphere represented only a small fraction of the iodine initial inventory and remained low and constant during the long term chemistry phase. This volatile fraction of iodine is, according to the May-pack data, essentially composed of organic iodides. The most probable source for these compounds is a reaction of iodine deposits with the painted condenser surfaces.

The sump chemistry after the washing of the containment bottom was strongly influenced by the partial dissolution of the aerosol material. This dissolution resulted in a decrease of the sump pH from 5.0 to 4.0. It also resulted in a significant increase of the iodine concentration in the sump, but the levels of iodine concentration in the containment atmosphere remained low and constant. These results are consistent with the existence of an no volatile and insoluble iodine species in the sump which prevented the formation of molecular iodine by radiolysis and its subsequent volatilization. AgI is the only candidate due to a very large Ag/I ratio in the sump water. Analysis of sump liquid samples showed that elements such as Ag,U, Fe behaved as colloidal species. This behavior is confirmed by the large deposits of Ag fund on all surfaces in contact with the sump. The iodine deposition on the surfaces in contact with the sump is thus attributed to the deposition of a Ag/AgI colloidal suspension on the surfaces.

5.3 - PHEBUS FPT1

FPT1 is identical with FPT0 but the fuel is irradiated. Some improvements have been introduced concerning:

Determination of volatile iodine fraction.

Instrumentation has been modified for an improved separation efficiency of aerosols/gaseous species. Additional tests on filtering media (May-pack, quartz filters) have been performed by IPSN. There will be more measurements during the main fission product release phase, some special events like washing will be particularly studied and there will be some additional sampling.

Chemical speciation

New post-tests analysis operation will permit to characterize better the chemical species present in solid deposits, colloidal suspensions and sump samples.

5.4 - CURRENT STATUS

PHEBUS FPT1 should be shortly performed. The following test, FPT4, will be representative of a debris bed configuration.