THE NEED FOR SUMP BUFFERING

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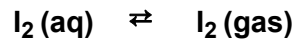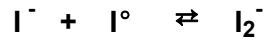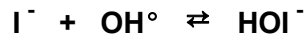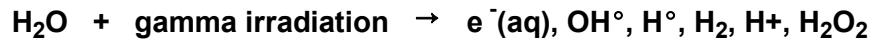**U.S. Nuclear Regulatory Commission**

Abstract

The results of the Phébus-FP tests revealed that controlling the sump pH neither prevented nor greatly affected the development of a gaseous iodine concentration in the model containment. Based on the test data, sump buffering may have no significant effect on gaseous iodine evolution in the reactor containment for at least 96 hours. Confirmatory analysis will provide iodine models that could be used to quantify iodine behavior in a pressurized-water reactor (PWR) containment.

Background

Radioisotopes of iodine are of particular safety concern because of their high radiotoxicity. Consequently, the U.S. Nuclear Regulatory Commission (NRC) has sponsored research, which has established that iodine will enter the reactor containment as a mixture of gaseous and particulate material [Ref. 1]. Both forms can leak from the containment and constitute a hazard to both onsite personnel and the public. The concentration of particulate forms of iodine in the containment atmosphere will decrease with time as a result of both natural processes (such as gravitational sedimentation) and the effects of engineered safety systems (such as containment sprays). Nonetheless, the concentration of gaseous iodine can evolve to a steady-state as a result of iodine partitioning back into the atmosphere from aqueous solutions (such as the waters found in containment sumps). Iodine in the atmosphere may be either molecular iodine (I_2) or a volatile organic iodide such as methyl iodide (CH_3I).

Figure 1 illustrates a typical reaction scheme leading to iodine partitioning from aqueous solution back into the containment atmosphere. It is known that this partitioning is profoundly affected by the total iodine concentration of the liquid, the radiation dose rate to the solution, and the solution pH. At very low iodine concentrations or very high pH (>8), little iodine will partition back into the atmosphere. High solution pH will also inhibit the formation of volatile organic iodides and partitioning of these species into the containment atmosphere. To maintain a low, steady-state concentration of gaseous iodine in containment atmospheres following reactor accidents, sumps in some reactors are fitted to disperse buffers so that the sump liquids are maintained at high pH. Typically, trisodium phosphate is used as the buffering agent. However, rather high concentrations of buffering agents are required to counter the effects of air radiolysis (which produces nitric acid) and radiolytic decomposition of cable insulation (which yields both hydrochloric acid and sulfuric acid).

$$H_2O \ + \ \text{gamma irradiation} \ \rightarrow \ e^-(aq), \ OH^\circ, \ H^\circ, \ H_2, \ H+, \ H_2O_2$$

$$I^- \ + \ OH^\circ \ \rightleftarrows \ HOI^-$$

$$HOI^- \ \rightarrow \ OH^- \ + \ I^\circ$$

$$I^- \ + \ I^\circ \ \rightleftarrows \ I_2^-$$

$$2 \ I_2^- \ \rightarrow \ I^- \ + \ I_3^-$$

$$I_3^- \ \rightleftarrows \ I^- \ + \ I_2 \, (aq)$$

$$I_2 \, (aq) \ \rightleftarrows \ I_2 \, (gas)$$

$$I_2 \, (aq) \ + e^-(aq) \ \rightarrow \ I_2^-$$
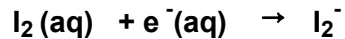
**Figure 1. A Radiolytic Reaction Scheme
Leading To Partitioning of Iodine from Aqueous Solution**

A Canadian research program [Ref. 2] has also shown that radiolysis of ketones leached from paint exposed to sump waters can cause acidification that must be counteracted by the buffering agents.

As might be expected of a non-equilibrium radiolytic reaction process, the partitioning of iodine from aqueous solution is not thoroughly understood. This chemistry has been one topic of study in the Phébus-FP tests [Refs. 3–5] conducted by an international partnership under the auspices of the French Institut de Radioprotection et de Sûreté Nucléaire (IRSN). (Figure 2 shows a schematic diagram of the Phébus experimental facility.) These tests have involved the in-pile degradation of irradiated reactor fuel. In the Phébus tests, fission products and other aerosol and vapor species released during the degradation of the irradiated fuel rods transport down a model reactor coolant system, which includes a model of a steam generator U-tube. Vapors and aerosols that successfully negotiate passage through the model reactor coolant system vent into a model containment.
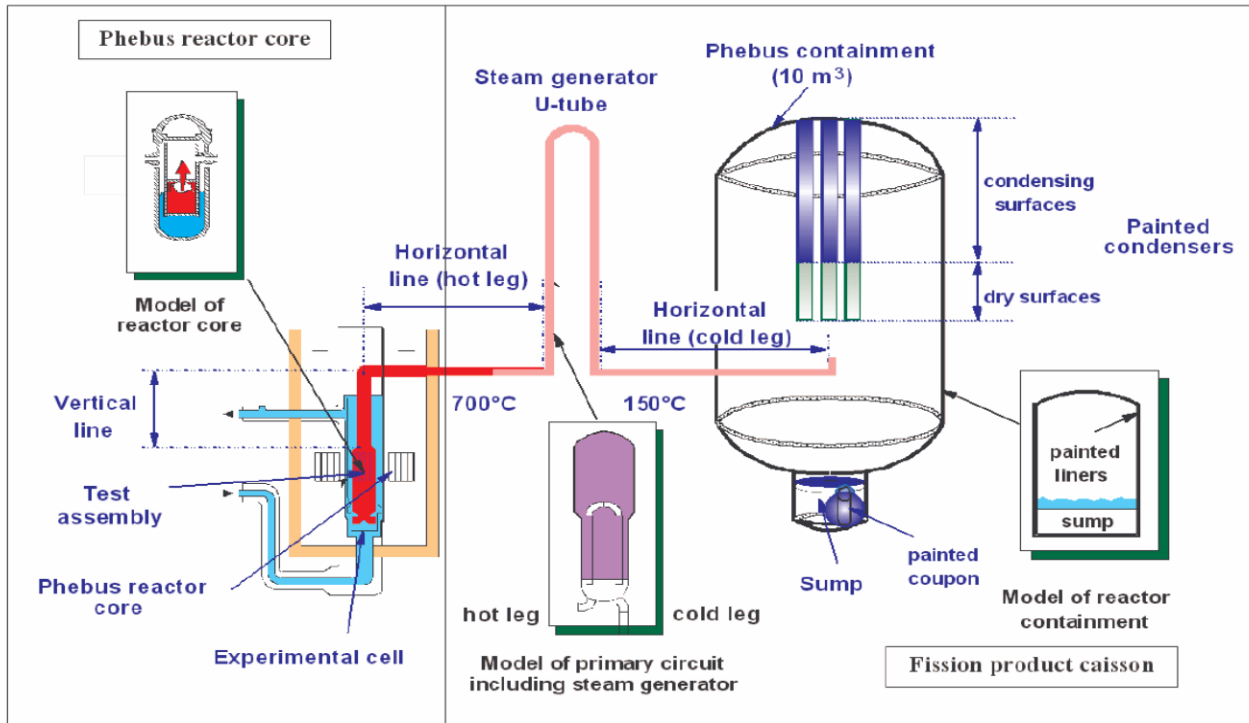
Figure 2. Schematic Diagram of the Phébus-FP Test Facility

The Phébus model containment includes a water-filled, circulating sump and condensers. The sump is maintained at selected temperatures and pH values in a test.

In a sense, the condenser simulates the effects of cool structures within the containment, where steam can condense. Surfaces of the condensers are painted and include portions that are dry, as well as portions that become covered by water films. The pH of the water films, of course, cannot be controlled by buffers in the tests, just as buffers in reactor sumps will not control the pH in condensate films on structures within a reactor containment. Aerosols settle gravitationally in the containment, or they deposit by diffusiophoresis on the condensers. Vapors can interact chemically with the dry and wet surfaces of the painted condensers.

Tests in the Phébus-FP program involve four phases. The first phase, which lasts about 1 hour, involves active fuel degradation and release of steam, fission products and other materials to the containment model. Following this first phase, is second a phase called the "aerosol phase," during which aerosol settling and deposition within the containment model is monitored. Then, in the third phase, known as the "washing phase," the lower head of the containment is sprayed with water to move deposited materials into the sump. Finally, the so-called "chemistry phase" is intended to monitor the behavior of gaseous iodine in the containment. In fact, gaseous iodine concentrations in the model containment are monitored throughout each Phébus-FP test.

Table 1 summarizes the conditions of four pertinent Phébus-FP tests. Three of the tests (FPT-0, 1, 2) involved the degradation of fuel rods along with a silver-indium-cadmium (Ag-In-Cd) control rod. The conditions of sump temperature and pH were varied among these tests to encourage either gaseous iodine accumulation in the sump or gaseous iodine partitioning from the sump. The fourth pertinent test (FPT-3) involved the degradation of irradiated reactor fuel rods in the presence of a boron carbide (B_4C) control rod.

Table 1. Conditions of Pertinent Phébus-FP Tests

Test	Fuel	Control Rod	Sump Temperature*	Sump pH
FPT-0	trace irradiated	Ag-In-Cd	90°C	5 (acid) 4 in chemistry phase
FPT-1	23GWd/t	Ag-In-Cd	90°C	5 (acid)
FPT-2	38 GWd/t	Ag-In-Cd	90°C (degradation and aerosol phases) 120°C (chemistry phase)	10 (basic)
FPT-3	23 GWd/t	B_4C	90°C (degradation and aerosol phases) 120°C (chemistry phase)	5 (acid)
* Containment pressures in all tests are about 2 bar.				

Pertinent Results of the Phébus-FP Tests

The Phébus-FP tests have yielded many findings that confirm modeling used for reactor accident analysis and development of the alternative source term (NUREG-1465). The tests have also yielded new insights, as illustrated by the following examples:

- Cesium released from the overheated reactor fuel transports as cesium molybdate (Cs_2MoO_4), rather than cesium hydroxide (CsOH). Any CsOH that reaches the containment comes from the revaporization of cesium compounds deposited in the model reactor coolant system.

- Iodine released from the overheated reactor fuel transports as both a gaseous species and particulate species. Cesium iodide (CsI) is among the chemical forms of particulate iodine. In tests with Ag-In-Cd control rods, cadmium iodide (CdI_2) is probably a more common form of particulate iodine.

- Silver vaporized from control rod alloys in FPT-0, 1, and 2 transports to the containment sumps, where it reacts with any dissolved iodine species to form insoluble AgI or $AgIO_3$. These reactions of silver limit the dissolved iodine concentration of the sump waters to very small levels that are insufficient to support substantial partitioning of iodine from the sump into the containment.

With respect to the behavior of iodine in containments, the most important observation is that, in every case, a steady-state iodine concentration developed in the containment atmosphere. Figure 3 illustrates an example of the steady-state iodine concentration in the containment atmosphere during a Phébus-FP test. In this example, as in all the Phébus-FP tests, the steady-state persisted for days. Notably, the steady-state gaseous iodine concentration in containment developed in FPT-2, even though the sump was maintained at a very basic pH so that no iodine partitioning from the sump waters would have been expected. The steady-state also developed in FPT-0 and FPT-1, even though the iodine in the sump waters was maintained at very low concentrations as a result of reactions of iodine with silver so there could be no partitioning of iodine from the sump waters even though the sump pH was acidic.

The obvious conclusion is the sump could not have been involved in the development of the steady-state observed in FPT-0, 1, and 2. The suspicion, of course, is that the steady-state arose from partitioning and deposition on water films or other surfaces of the model condenser, and these processes went on independent of the sump.

FPT-3 also yielded remarkable results. In this test, most (~80%) of the iodine that entered the containment did so as a gaseous species. Current speculation is that boric oxide (B_2O_3) produced by the steam oxidation of the boron carbide (B_4C) control material of the test reacted with all elements (such as cesium) that are capable of forming particulate material with iodine. Despite the high initial inventory of gaseous iodine, the iodine concentration rapidly decreased to the familiar steady-state concentration observed in the previous Phébus-FP tests. The rate at which the iodine concentration fell was faster (by factors of 2–4) than the rate at which the particulate material concentration declined. The rate is also much faster than would be expected if the gaseous iodine had to transport to the small surface area of the sump. Indeed, the sump was maintained at an acid pH (pH = 5) in the test, and the sump water was heated to near boiling late in the test to facilitate mass transport of molecular iodine from the sump to the containment atmosphere.

Current speculation is that the removal of gaseous iodine occurred on water films or other surfaces of condensers in the model containment. This removal was enhanced when there were higher fluxes of steam coming from the sump when it was heated. Chemistry within these water films was responsible for the development of the steady-state gaseous iodine concentration in the containment atmosphere. Increased steam flux from the evaporating sump in the later stages of the test perturbed the steady-state by augmenting the condensation on the condensers and the attendant sweepout of the gaseous iodine.
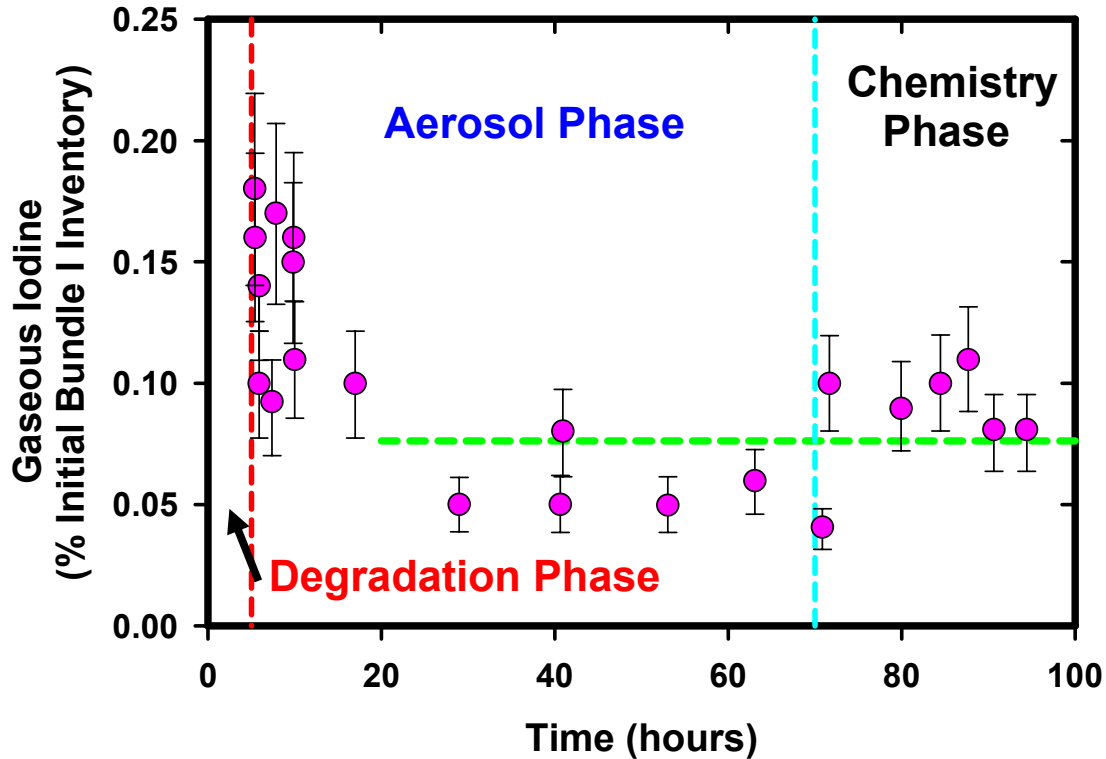
FPT-1 Gaseous Iodine in Containment

Figure 3. Steady-State Iodine Concentration in the FPT-1 Test

Interpretation of the Observations from the Phébus-FP Tests

Each of the pertinent Phébus-FP tests involved the development of a steady-state gaseous iodine concentration in the model containment atmosphere. This steady-state indicates that sources and sinks of gaseous iodine were operating simultaneously at equal rates. However, given the integral nature of the Phébus-FP tests, it is challenging to determine directly from the test results exactly what those sources and sinks might have been. Nonetheless, it is clear, that the sump was acting neither as a source of gaseous iodine nor as a sink. Consequently, whatever processes were taking place were doing so independent of the sump. The most likely region of the containment that could involve both sources and sinks would be the condensers.

Additionally, there is some evidence that the chemical form of the gaseous iodine evolved during the test. Initially, the gaseous iodine was molecular iodine (I_2). However, in some tests, the dominant chemical form of gaseous iodine appeared to evolve to become predominantly a volatile organic iodide. The appearance of this organic iodide also implies involvement of the condensers, because they were the most abundant source of organic material in the test.

In some sense, the condensers simulate the surfaces of structures and equipment that will be present in reactor containments. The pH of water films on these condensers, like water films that will form on structures within containments, cannot be affected by buffers placed in the sump. They might also be acidified by adsorption of nitric acid produced in air radiolysis, which did occur in the Phébus tests. They might also be acidified if ketone solvents in the paint were radiolytically converted to organic acids [Ref. 2]. In reactor accidents, radiolytic decomposition of polyvinyl chloride insulations on cables could also yield gaseous hydrochloric acid (HCl) and even sulfuric acid (H_2SO_4), which could be absorbed by water films [Ref. 6]. The resultant acidification of the water films would promote partitioning of iodine from the water films back into the containment atmosphere.

The sinks for the gaseous iodine have not yet been established. Certainly, one possibility is that homogeneous reaction with either ozone (O_3) or the hydroxy radical (OH) produced by air radiolysis could be responsible for destroying the gaseous iodine. The iodine-bearing product of these reactions is usually thought to be exceptionally small particles of higher iodine oxides (IO_x). These very fine particles could diffuse back to the water films, dissolve, and again undergo the radiolytic processes that produced gaseous iodine. Similarly, as organic solvents from paints on the condensers leach into the water films, opportunities could arise for radiolytic reactions that could produce volatile organic iodides.

Again, it is clear from the test results that the sump in the model containment was not involved. The atmosphere in the Phébus tests has much better access to the model containment sump than do the bulk atmospheres of reactor containments to their sumps. Even with this increased access, there seemed to be minimal involvement with the sump in the chemistry of the tests. Indeed, current interpretations of the test results indicate that the steady-state concentration of gaseous iodine decreased with evaporation fluxes of steam from the sump, and increased when steam condensed in the sumps. The iodine that did reach the sump did not have further involvement in the development of the steady-state gaseous iodine concentration in the atmosphere. Certainly, this was the case in the tests with Ag-In-Cd control rods (FPT-0, 1, and 2). Iodine in the sump either precipitated as a silver salt (FPT-0 and FPT-1) or was effectively sequestered as a result of high pH (FPT-2). Results from FPT-3 are still being analyzed. These analyses will be of interest because the sump was acidic (pH = 5) and there was no abundant source of silver in this test. Even so, all evidence from the test indicated that the sump was not a major factor in either the sharp reduction of the initially high gaseous iodine concentration or the subsequent steady-state gaseous iodine concentration.

Taken together, the results of the Phébus-FP tests show that controlling the pH of sumps in reactor containments may not significantly impact the development of a gaseous iodine concentration in the reactor containment in the immediate aftermath of an accident involving core degradation.

Confirmatory Research

There is still much to learn from the results of the Phébus-FP tests. Numerous additional technical questions have been raised that were not anticipated during development of models of gaseous iodine in reactor containments. Separate-effects test programs are now underway in the Phébus-Source Term Separate Effects Test (Phébus-STSET) program. These tests (known as EPICUR tests) are examining the interactions of gaseous iodine partitioned from aqueous solutions with paints and other materials.

Separate, complementary tests are also being planned by Atomic Energy of Canada Limited (AECL) as part of the Behavior of Iodine Project (CSNI BIP), sponsored by the Organization for Economic Cooperation and Development Committee (OECD), Committee on the Safety of Nuclear Installations (CSNI). In addition, the NRC is sponsoring mass transport and iodine chemistry modeling. These activities are being undertaken to confirm and augment the understanding of iodine behavior, especially with respect to water films on structures within the containment. Particular needs include the following:

- Establish the identities of both sources and sinks responsible for the steady-state gaseous iodine concentrations in the Phébus-FP tests.

- Determine how these sources and sinks will behave in reactor accidents, and whether other sources and sinks may be operational.

- Determine the rates of iodine mass transfer to and from sumps in both the tests and reactor accidents.

- Determine the extent and causes of the compositional evolution of gaseous iodine from molecular iodine (I_2) to volatile organic iodine (CH_3I) and whether this evolution will occur in reactor accidents.

- Understand how containment sprays will perturb the gas phase iodine concentration if the spray is drawing suction from an unbuffered sump.

Once the experimental data on these phenomena are obtained (from the Phébus-STSET program and the CSNI BIP), they will be used to validate specific models of iodine behavior. Thereafter, the iodine models can be assessed against Phébus-FP tests. The iodine models should also be subjected to peer review to provide the credibility that these models can be scaled and used to quantify iodine behavior in a PWR containment.

Conclusion

The Phébus-FP test results show that controlling the pH of sumps neither prevented nor greatly affected the development of a gaseous iodine concentration in the model containment. Thus, on the basis of the test data, sump buffering may not significantly affect gaseous iodine evolution in the reactor containment for at least 96 hours. Confirmatory research will provide iodine models that could be used to quantify iodine behavior in a PWR containment.

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