

5.5. Release of fission products during a core melt accident

This section deals with releases of fission products (FPs) from degraded fuel or corium during an in-vessel or ex-vessel core melt accident. In the latter case, the accident is considered to lead to vessel failure and relocation of corium into the containment. It also discusses the transfer of FPs from the reactor to the containment via the gas mixture produced during the progression of the accident in the core (mixture of steam and hydrogen; this hydrogen is produced primarily by oxidation of the zirconium [Zr] in the cladding) in the event of an RCS break. Lastly, it describes the behaviour of FPs in the containment.

Figure 5.52 summarises the sequence of the processes involved in the release and transfer of FPs to the environment during a core melt accident. The main parameters governing these processes are also listed in Figure 5.52. Their effects on the release of FPs from the reactor core, their transport in the RCS and their behaviour in the containment are discussed in greater detail in the following sections.

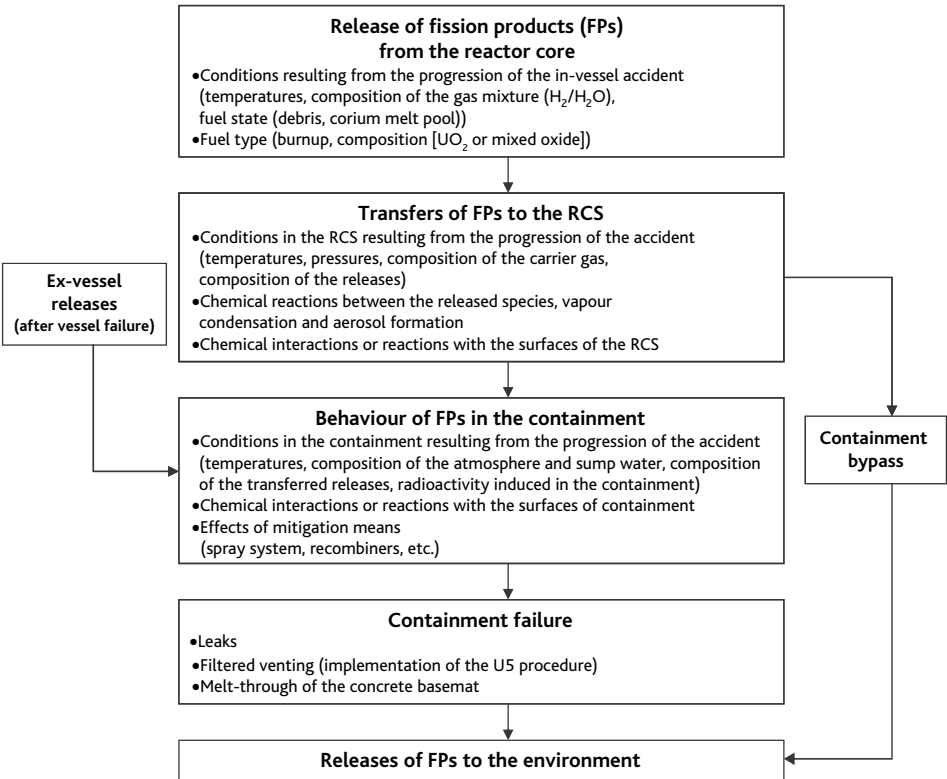


Figure 5.52. Summary description of the processes involved in the release and transfer of FPs to the environment during a core melt accident.

OECD/CSNI reports published in 1994 [1] and 2000 [2] provide an overview of the matter. More recent state-of-the-art reports are available on iodine chemistry [3] and nuclear aerosols [4].

5.5.1. *Inventory and relative importances of FPs*

Fission products are produced during fission reactions caused by the effect of neutrons on fuel. Each FP has a specific yield that depends on the type of fission (thermal neutrons for ^{235}U or ^{239}Pu , fast neutrons for ^{238}U , etc.). It should be noted that, fission yields of some FPs, such as ruthenium (Ru), can differ greatly from one isotope to another depending on whether fission concerns ^{235}U or ^{239}Pu . For example, the fission yield (in percent) of ^{103}Ru is 5.8% from ^{239}Pu and 3.0% from ^{235}U . However, the yield of ^{106}Ru is 5.0% from ^{239}Pu but only 0.38% from ^{235}U .

The inventory of FPs in terms of mass or number of atoms increases virtually in a near-linear fashion depending on the burnup rate (around 75 kg/(GWd/t)) to around 2 tonnes of FPs in the core of a 900 MWe PWR at balance. Table 5.9 lists this inventory for each fission product and each heavy nucleus together with the change in total core activity from the time of reactor shutdown to one month later.

Under nominal burnup conditions of a PWR, the FPs in the fuel matrix are at various chemical states [5]:

- in the form of *dissolved oxides* for nearly half and in particular strontium (Sr), yttrium (Y), zirconium (Zr), lanthanum (La), cerium (Ce) and neodymium (Nd);
- in the form of *oxide precipitates* primarily for barium (Ba) and niobium (Nb);
- in the form of *metal precipitates* for molybdenum (Mo), technetium (Tc), ruthenium (Ru), rhodium (Rh) and palladium (Pd);
- mainly in the form of *dissolved atoms* for the volatile FPs: bromine (Br), rubidium (Rb), tellurium (Te), iodine (I) and caesium (Cs). However, the chemical state of these FPs is not fully known. Above a certain temperature, they can migrate radially into the fuel pellets and condense in the colder sections, where they form more complex compounds with fuel elements or other FPs. For example, caesium can form compounds such as caesium molybdates and uranates;
- in the form of *dissolved atoms or intergranular or intragranular gas bubbles*: xenon (Xe) and krypton (Kr) in the case of the fission gases. It should be noted that gases that accumulate at the grain boundaries are more easily released during accident situations.

Radioactive FPs, especially those with short half-lives, have a smaller mass but generate most of the radioactivity and residual heat. Their relative importance can be assessed using two main criteria:

- their dosimetric impact if released to the environment: this impact varies depending on the half-life and type of radiation emitted. For example, Figure 5.53 shows the relative importance of FPs and actinides on the dose to the lungs. Figure 5.54

Table 5.9. Change in the activities of the FPs and actinides in a 900 MWe PWR (1) after reactor shut-down (RT = reactor trip).

| Fission products | Total mass at RT, in kg (2) | Activities as a fraction of the total activity | | | |
|------------------|-----------------------------|--|-----------|----------|------------|
| | | at RT | at 1 hour | at 1 day | at 1 month |
| As | 7.39E-03 | 0.20% | 0.01% | 0.00% | 0.00% |
| Se | 3.14E+00 | 0.58% | 0.02% | 0.00% | 0.00% |
| Br | 1.16E+00 | 1.17% | 0.20% | 0.00% | 0.00% |
| Kr | 2.21 E+01 | 2.32% | 1.46% | 0.03% | 0.06% |
| Rb | 2.03E+01 | 3.22% | 0.84% | 0.01% | 0.00% |
| Sr | 5.51 E+01 | 4.50% | 3.85% | 2.57% | 6.10% |
| Y | 2.89E+01 | 5.84% | 5.11% | 3.40% | 8.16% |
| Zr | 2.10E+02 | 4.73% | 3.83% | 4.63% | 10.30% |
| Nb | 3.24E+00 | 7.09% | 5.68% | 5.93% | 13.18% |
| Mo | 1.84E+02 | 4.28% | 2.28% | 2.90% | 0.01% |
| Tc | 4.52E+01 | 4.82% | 2.50% | 2.77% | 0.01% |
| Ru | 1.37E+02 | 1.85% | 3.11% | 3.67% | 10.27% |
| Rh | 2.36E+01 | 2.30% | 3.42% | 4.96% | 10.26% |
| Pd | 5.93E+01 | 0.19% | 0.33% | 0.18% | 0.00% |
| Ag | 3.97E+00 | 0.14% | 0.11% | 0.12% | 0.05% |
| Cd | 4.00E+00 | 0.03% | 0.02% | 0.01% | 0.00% |
| In | 8.20E-02 | 0.13% | 0.03% | 0.01% | 0.00% |
| Sn | 2.65E+00 | 0.66% | 0.15% | 0.02% | 0.01% |
| Sb | 8.98E-01 | 1.76% | 0.68% | 0.17% | 0.06% |
| Te | 2.62E+01 | 3.85% | 4.16% | 2.88% | 0.69% |
| I | 1.27E+01 | 5.70% | 8.94% | 6.39% | 0.65% |
| Xe | 3.07E+02 | 4.33% | 3.60% | 5.12% | 0.41% |
| Cs | 1.61 E+02 | 3.82% | 1.27% | 0.46% | 1.61% |
| Ba | 8.21 E+01 | 4.67% | 3.75% | 3.46% | 3.45% |
| La | 6.99E+01 | 4.71% | 5.22% | 3.57% | 3.25% |
| Ce | 1.63E+02 | 3.61% | 5.04% | 7.41% | 16.01% |
| Pr | 6.21 E+01 | 3.10% | 4.63% | 5.49% | 11.76% |
| Nd | 2.07E+02 | 0.68% | 1.07% | 1.25% | 0.82% |
| Pm | 1.24E+01 | 0.65% | 1.22% | 1.65% | 1.48% |
| Sm | 3.57E+01 | 0.21% | 0.46% | 0.54% | 0.00% |
| Eu | 8.90E+00 | 0.08% | 0.19% | 0.29% | 0.36% |
| Actinides | | | | | |
| U | 6.99E+04 | 9.37% | 3.91% | 0.00% | 0.00% |
| Np | 3.15E+01 | 9.37% | 22.76% | 29.86% | 0.02% |
| Pu | 5.89E+02 | 0.05% | 0.11% | 0.19% | 0.80% |
| Am | 6.18E+00 | 0.00% | 0.00% | 0.00% | 0.00% |
| Cm | 2.09E+00 | 0.01% | 0.03% | 0.06% | 0.21% |

(1) 900 MWe PWR with UO_2 fuel enriched to 3.70% of ^{235}U , 72.5 tons of initial uranium, with the fuel loaded into four regions of the core (burnup rate of the assemblies: 10.5 GWd/tU for the first region [one burnup cycle], 21 GWd/tU for the second region [two cycles], 31.5 GWd/tU for the third region [three cycles] and 42 GWd/tU for the last region [four cycles]).

(2) Total mass of the stable isotopes and the radioactive isotopes.

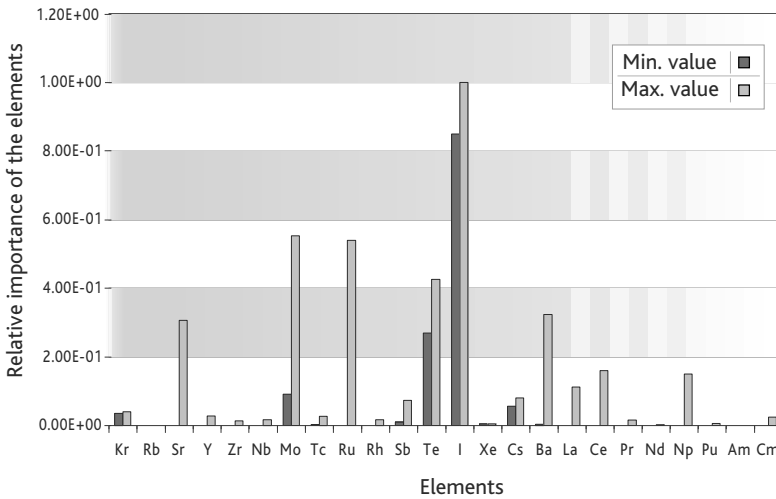


Figure 5.53. Relative importance of the elements released during a PWR core melt accident (100% core melt) on the dose to the lungs.

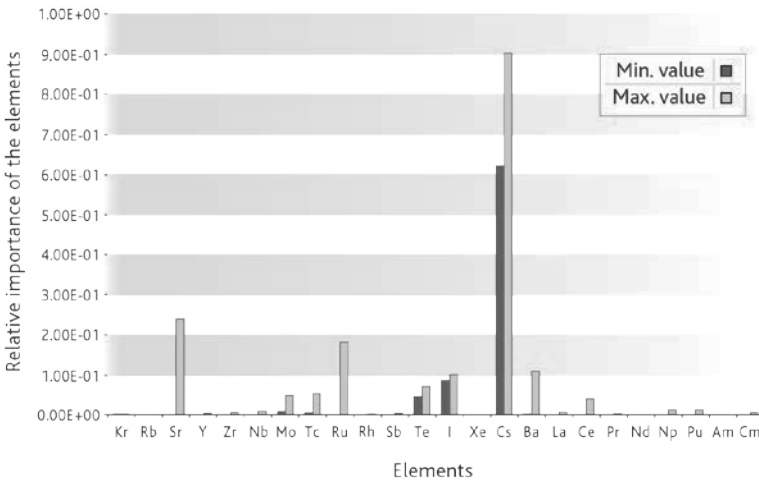


Figure 5.54. Relative importance of the elements released during a PWR core melt accident (100% core melt) on latent cancers (long-term exposure).

shows the same information, but for the long-term consequences (latent cancer). The relative importance indicated for each element are derived from studies conducted by the US NRC [6]. The minimum and maximum values shown on the graphs are derived from studies conducted by IRSN on the variability and uncertainty of the release rates;

- their contribution to the residual heat generated in fuel or corium, which is illustrated by Figure 5.55. Residual heat influences accident progression, such as the moment of vessel failure or the moment of corium melt-through of the containment basemat.

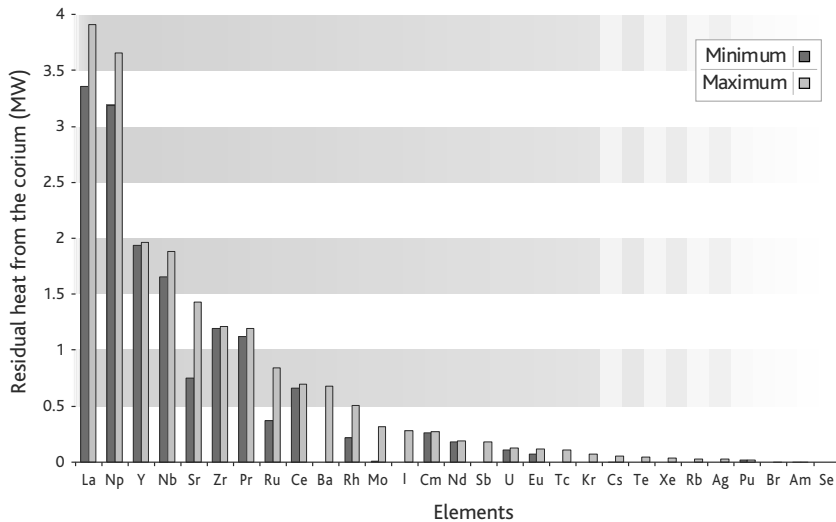


Figure 5.55. Minimum and maximum residual heat associated with the elements in corium at the time of vessel failure during a large-break LOCA in the RCS.

Stable FPs, which have a higher mass, can influence core degradation because the formation of eutectic mixtures of uranium dioxide-fission product (UO_2 -FP) seems to lower the fuel-melting temperature [7]. The concentration of FPs in the fuel is not negligible at high burnup (they may account for more than 10% of the total number of atoms beyond 50 GWd/t). Furthermore, under oxidising conditions, the hyperstoichiometry of the fuel (oxygen content greater than the stoichiometric content UO_2) lowers its melting temperature [8].

5.5.2. Release of FPs into the reactor vessel

The chemical state of the FPs initially present in the fuel matrix in the form of dissolved atoms or oxides, oxide precipitates and metal precipitates is not permanent. Some FPs may shift from one chemical state to another depending on the temperature of the fuel, the oxygen content in the fuel (which increases with the burnup rate) and the burnup rate (increase in the concentration of FPs in the fuel matrix). This is especially true for molybdenum, which precipitates in fuel mainly in metal form but can also be in oxidised form (especially on the surface of MOX fuel pellets), and for niobium and strontium, whose oxides may be partly dissolved and precipitated in the fuel.

5.5.2.1. Physical phenomena involved in the release of FPs

► Fission gases

During fuel irradiation, fission gases form as atoms in the grains of UO_2 . These atoms of gas either diffuse toward the grain boundaries or precipitate into nanometre-sized intragranular bubbles, slowing down their rate of migration towards the grain boundaries. The bubbles may then redissolve under the influence of fission spikes (defects

created along the path of the fission fragments just after their formation), which speed up the rate at which gas is supplied to the grain boundaries. Once on the grain surface, (mainly by atomic diffusion, but also by bubble migration), the fission gases accumulate to a point where they coalesce to form larger bubbles and fill the boundaries. These bubbles are then capable of moving into the free volume of the rod [9].

At the onset of the accident, the gases consist of:

- gas atoms dissolved in the fuel matrix;
- intragranular gas bubbles with little mobility;
- gases accumulated in the grain boundaries (intergranular bubbles).

Their release is governed by a number of mechanisms. The first release phase (often referred to as “burst release”) corresponds to the *release of gases accumulated in the intergranular spaces*. The fraction already released into the rod plenum during normal irradiation must also be taken into account, ranging from a few percent to 10%, depending on the burnup, the irradiation power and the fuel type. Such releases occur at the beginning of the temperature rise at around 1000 °C, though this is sometimes lower for high burnup fuels.

The second phase involves the *release of the intragranular gases via a thermally activated diffusion process* that begins with dissolved atoms. The *gases trapped in the intragranular bubbles* (which are of nanometre size) are the last to be released, which generally occurs when the fuel melts.

It is therefore important to correctly quantify the respective fractions of these three phases when modelling gas releases, which depend on their radial position in the pellet and on the fuel type (high burnup fuels [the granular structure on the periphery of the pellets is degraded, resulting in more pores where the gases can accumulate] and heterogeneous MOX fuels have a higher intragranular fraction).

During a core melt accident, all the fission gases are released from the fuel when it melts.

► Non-gaseous FPs

It is generally accepted that the release of non-gaseous FPs follows a two-phase process: (1) the FPs in solution in the matrix (or the precipitates when the solubility limit has been reached) diffuse as far as the grain boundaries, and then (2) a mechanism of mass vaporisation transfers the FPs from the grain surface outside of the fuel matrix. This mechanism also involves a number of chemical aspects. The potential formation of species (such as molybdates, uranates, zirconates) can determine transfers of FPs (caesium, barium and strontium) in the fuel. Likewise, oxidation or reduction of FP precipitates by water vapour or hydrogen has a significant impact on transfers of these species in the fuel. It should be noted that the basic thermodynamic data on the formation and destruction of these species currently are subject to high uncertainties that affect the

calculation of FP chemistry – and thus FP transport – in the fuel and, consequently, affect the calculation of FP releases from fuel. The predictive capability of the release models is discussed in Section 5.5.2.3.

Outside the fuel matrix, chemical interactions with the cladding or elements of the core structures can then reduce the volatility of some elements through the formation of more refractory species.

Lastly, once released from the core, a significant fraction of the FPs condenses in the colder sections of the upper core structures before even reaching the hot legs of the RCS or the containment. This is especially true for low-volatile FPs.

Qualitatively speaking, the main physical parameters influencing the release of FPs are as follows:

- the fuel *temperature* is the main parameter, at least until loss of integrity of the fuel assemblies in the core leads to loss of core geometry;
- the *oxidising-reducing conditions* have a significant impact on fuel. The release kinetics of volatile FPs are particularly accelerated under oxidising conditions. Furthermore, the overall release of certain FPs is very sensitive to the oxidising-reducing conditions. For example, the release of molybdenum increases in steam, whereas that of ruthenium can be very high in air. Conversely, the release of barium (as for strontium, rhodium, lanthanum, cerium, europium [Eu] and neptunium [Np]) increases under reducing conditions;
- *interactions with the cladding and/or elements of the core structures* can play a major role. For example, the presence of tin in the cladding delays the emission of the volatile elements tellurium and antimony (Sb). Barium significantly contributes to the decay heat (*via* its daughter product ^{140}La) and is also partially trapped in both the cladding (probably due to the formation of zirconates) and in the steels of the structures.
- the *burnup* accentuates releases, in terms of both the kinetics of volatile FPs, and the magnitude of release of low-volatile species such as niobium (Nb), ruthenium, cerium and neptunium (Np);
- The *fuel type* also has a significant impact: MOX releases tend to be higher than those of UO_2 . This phenomenon is probably related to its heterogeneous microstructure, with the presence of plutonium (Pu)-rich agglomerates where the local burnup can be very high;
- Last of all, the *physical state of the fuel* (fragmented, solid, liquid) during its in-vessel degradation has a significant influence. The transition from a “degraded rod” geometry to a “debris bed” geometry also involves an increase in releases *via* the increase in the surface-to-volume ratio. Conversely, the transition from a debris bed to a molten pool slows down the release of FPs as a solid crust forms on the surface of the molten corium pool.

► Degrees of volatility of the various FPs

The current state of knowledge, obtained in particular thanks to the analytical experiments of the VERCORS programme and the integral tests of the Phebus programme (Section 7.3), make it possible to schematically classify FPs and fission gases into four categories of decreasing volatility (Figure 5.56):

- *fission gases and volatile FPs* (Kr, Xe, I, Cs, Br, Rb, as well as Te, Sb and silver [Ag]): almost all of these products are released even before reaching molten pool conditions. The release kinetics of these elements are accelerated under oxidising conditions and are slightly retarded for Te and Sb than for the other volatile FPs due to interactions with tin in the cladding;
- *semi-volatile FPs* (Mo, Ba, Y, Rh, Pd, Tc): their release rates can be very high and are sometimes equivalent to those of volatile FPs yet are highly sensitive to the oxidising-reducing conditions and result in significant retention in the upper vessel internals;
- *low-volatile FPs* (Sr, Nb, Ru, La, Ce, Eu, Np): they are characterised by low but significant levels of release, ranging from a few percent to 10% during the fuel-rod degradation phase (prior to loss of fuel rod geometry). Nevertheless, some of these releases can reach much higher levels for fuels with very high burnups under specific conditions (this is especially the case of Ru in air). Retention of these FPs is nevertheless expected to be significant in the upper vessel internals;
- *non-volatile FPs* (Zr, Nd): to date, no significant release of these two elements has been demonstrated experimentally. These are the two most refractory FPs.

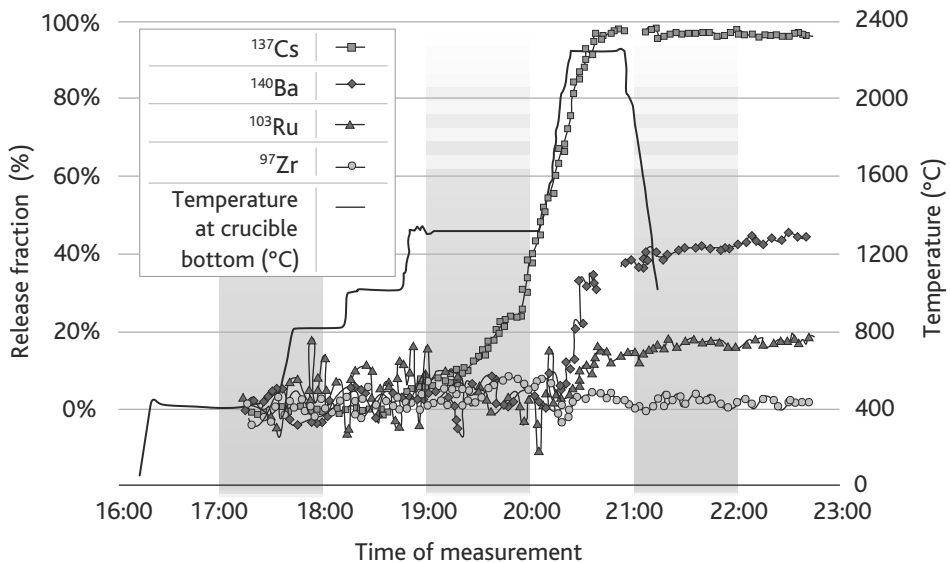


Figure 5.56. Illustration of the four volatility categories for FPs according to the results of a VERCORS test [10].

► Actinides

Most of the quantitative data on releases of actinides during a core melt accident come from the VERCORS programme [10]. The behaviour of uranium and neptunium is similar to that of low-volatile FPs whereas the behaviour of plutonium is rather more similar to that of non-volatile FPs.

5.5.2.2. Experimental programmes

Experimental programmes on FP releases have mainly relied on analytical experiments performed on sections of irradiated fuel. They were eventually supplemented by integral tests performed on reduced-scale fuel assemblies particularly to study the effects of changes in core geometry (particularly debris bed and molten pool formation) during core degradation on the release of FPs.

► Analytical experiments

Five major analytical programmes have been conducted since the late 1970s: SASCHA in Germany [11], HI/VI in the United States [12], CRL in Canada [13], VEGA in Japan [14] and HEVA/VERCORS [15] in France. The HEVA/VERCORS programme is described in greater detail on account of its significant contributions to the development and validation of the FP release models developed by IRSN (Section 5.5.2.3):

- the first analytical experiment of its kind, the SASCHA programme was performed by FZK on *unirradiated* UO_2 fuel under various atmospheres, including argon, air and steam. The UO_2 pellets were specially manufactured *with additives that simulate FPs*. Although the SASCHA programme was not really representative of the real location of the FPs in fuel during irradiation, it did provide a series of preliminary estimates for iodine and caesium releases up to 2000 °C;
- ORNL conducted the HI/VI programme between 1981 and 1993 (13 tests in total). The experimental configuration, at least for the VI tests, was similar to that of the VERCORS programme, i.e., a test loop equipped with thermal-gradient tubes (TGT) to collect condensable gases (these samples were used to determine the condensation concentrations and temperatures), a series of filters to trap aerosols and a condenser and cartridges to trap fission gases. The fuel samples were cladded sections of irradiated UO_2 measuring around 15 cm in length and sealed at the ends. A hole was drilled in the cladding at midplane height. This programme provided *highly representative results on the release of FPs, but only in relation to long-lived FPs* (mainly ^{85}Kr , ^{106}Ru , ^{125}Sb , ^{134}Cs , ^{137}Cs , ^{144}Ce and ^{154}Eu) as the samples were not re-irradiated prior to the tests;
- AECL's CRL programme was a highly analytical programme conducted to study CANDU fuels. It consisted of many tests on fragments of irradiated fuel (from 100 mg to 1 g) and on short sections of cladded fuel. The resistive furnace used during the tests limited temperatures to a maximum of 2100 °C. Some samples were pre-irradiated to measure the release of short-lived FPs. One of the

important results of this programme was the first quantification of the very *high release of ruthenium in air*;

- performed by JAERI (Japan), the VEGA programme was very similar to the VERCORS programme in terms of its experimental configuration and conditions, especially the VERCORS HT series (see next paragraph). A total of 10 tests were carried out: eight on UO_2 fuel and two on MOX fuel. Some of the tests were carried out in a *steam atmosphere up to fuel melting temperatures*. Some of the samples were re-irradiated prior to the tests but under less than optimal conditions. The irradiation time, which was shorter than the in-reactor irradiation time, and the long decay time did not result in a sufficient quantity of short-lived FPs. A unique feature of these tests was the inclusion of *tests at a pressure of 10 bar*, which notably demonstrated a reduction in caesium releases;
- the HEVA/VERCORS programme, performed by the CEA and financed by IRSN (IPSN at the time) and EDF, aimed at quantifying releases of FPs and actinides (kinetics and total release rates) from irradiated nuclear fuel under conditions representative of a core melt accident. These tests were performed in a high-activity cell on different types of fuel sample irradiated in a PWR (around 20 g of fuel) under a range of experimental conditions. Most of the samples were re-irradiated for a few days at low power in an experimental reactor in order to build up an inventory of short-lived FPs. These samples were then heated in an induction furnace under a variable atmosphere of steam and hydrogen simulating core melt accident conditions (Figure 5.57). FP releases from the fuel samples were measured by gamma spectrometry of the decrease of the FPs in the fuel samples during the test. Twenty-five tests were carried out between 1983 and 2002 in three phases: (1) eight HEVA tests (release of volatile and semi-volatile FPs up to 2100 °C); (2) six VERCORS tests (release of volatile and semi-volatile FPs and some low-volatile FPs up to 2300 °C, the limit for the onset of fuel collapse in the sample), (3) eleven HT/RT tests (release of all types of FP until the melting point was reached). These tests resulted in the compilation of an extensive database on the release of FPs: the parameters that varied during these tests were the maximum temperature reached (below or above fuel melting temperature), the oxidising-reducing conditions, the burnup, the fuel type (usually UO_2 , although MOX was used in two tests) and the initial fuel geometry (intact fuel or fuel debris to simulate the formation of a debris bed during a core melt accident).

There still are, however, uncertainties about the release of FPs. This is particularly the case for very-high-burnup UO_2 fuels (70 GWd/t and beyond), MOX fuels, and accidents with in-vessel ingress of air or in-vessel fuel reflooding.

The VERDON programme, conducted at the CEA facility of the same name as part of the International Source Term Programme (ISTP) [16], aims to address these issues, apart from aspects related to reflooding. Tests on FP releases from samples of high burnup fuels, MOX fuel samples and fuel samples in an air atmosphere have been conducted since 2011 at a facility similar to that where the VERCORS HT tests were carried out.

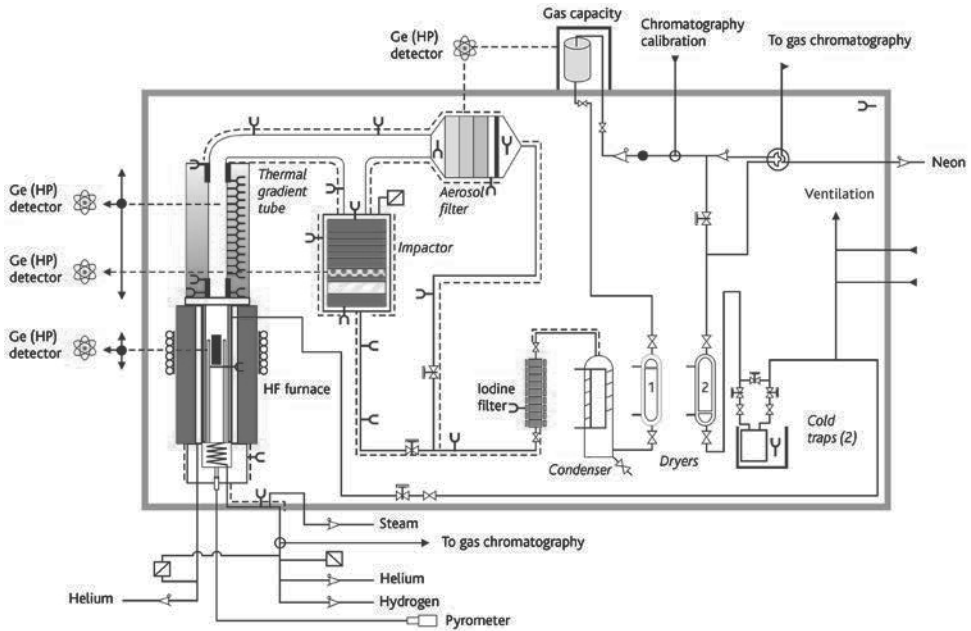


Figure 5.57. The VERCORS HT loop [15].

► Integral tests

Among the experimental programmes devoted to fission product releases, the Phebus FP programme is one of the most representative of core melt accident conditions, particularly with regard to releases from fuel, transport in the RCS and the behaviour of FPs in the containment [16]. Four bundles of 20 fuel rods (three of which were re-irradiated in order to obtain inventories representative of the short-lived FPs) with burnup of between 20 and 40 GWd/tU were brought to fuel melting conditions. In three tests, the bundles were brought to molten pool conditions. A specific test was conducted to study degradation of a debris bed up to molten pool conditions. The programme and the lessons learnt are described in Section 7.3.

In terms of in-vessel FP releases, the Phebus FP programme made a huge contribution in addition to the analytical tests by providing better understanding of two aspects: (1) releases of FPs depending on the progression of the accident in the vessel and (2) the effect, on such releases, of the chemical interactions with the cladding material or structural steels in the core. For example, lower FP releases were observed with molten corium melt pools than with releases from solid fuels. In-core fuel collapse during degradation (collapse of the fuel rods with the formation of debris and the relocation of corium to the cool areas at the bottoms of the bundles) results in spikes in FP releases. The case of barium is a good example in terms of the effects of the chemical interactions, with these releases being much lower than those recorded

in the analytical tests. This difference in behaviour is ascribed to interactions with the fuel rod cladding and possibly iron from the molten structural steels of the core, which reduced the volatility of the barium.

For the other fission products, the total releases were highly consistent with those obtained from the analytical tests.

5.5.2.3. Physical models and simulation codes

Two approaches are used in computer codes to model FP releases: (1) a simplified approach that allows models to be easily integrated into integral codes (see Chapter 8), and (2) a mechanistic approach that describes, at best, all the physical phenomena that come into play. Both approaches can be illustrated by two tools used at IRSN: (1) the Franco-German ASTEC code, which uses semi-empirical release models, and (2) the MFPR mechanistic code developed jointly by IRSN and the Russian institute IBRAE.

► Simplified approach used in the ASTEC code

The ASTEC code [17] models releases of FPs according to three categories:

- so-called *volatile* FP releases (Xe, Kr, I, Br, Cs, Rb, Sb, Te) are governed by their *diffusion* in fuel grains. Their diffusion coefficient is a function of the temperature and oxygen content of fuel. This coefficient is the same for all FPs, excepting Sb and Te, for which a release delay is applied to take into account their retention in the cladding provided the latter has not oxidised completely;
- so-called *semi-volatile* FP releases are governed by *mass transfers* induced by their vaporisation at grain boundaries. Their vapour pressures are determined using thermodynamic correlations made with the GEMINI2 (Sr, Ru, Ba and La) or FACT (Mo, Ce and Eu) solvers, which calculate the equilibrium state of the chemical system involved by minimising its free enthalpy (Gibbs free energy). The same mass-transfer mechanism is applied to all FPs released from a molten corium pool;
- so-called *non-volatile* FP releases are governed by the *vaporisation of UO_2* when it becomes hyperstoichiometric (UO_{2+x} with an oxygen content higher than that of stoichiometric UO_2) and oxidises until UO_3 forms. This category also covers the actinides U, Np, Pu, Am and Cm.

► Mechanistic approach of the MFPR code

MFPR [18] is an 0-D mechanistic code designed to simulate FP releases from solid UO_2 fuel. FPs are assumed to be present in fuel in atomic or oxide form. Two types of modelling are performed: one for fission gases, the second for other FPs.

Modelling of FPs includes all the physical phenomena described in Section 5.5.2.1: intragranular diffusion of atoms and bubbles to the grain boundaries with modelling of the bubble formation (nucleation, growth) and destruction (return to solution form)

mechanisms. Releases from the grain boundaries occur after coalescence and interconnection of the gas bubbles.

In 2015, modelling of other FPs involved 13 elements: Cs, I, Te, Mo, Ru, Sb, Ba, Sr, Zr, La, Ce, Nd and Eu. They are assumed to diffuse to the surface of the grain boundaries, with some oxidation occurring during their transfer to the fuel matrix. They then form three distinct phases: a metallic phase, a ternary phase (known as the grey phase and composed of FP oxides) and a specific phase for CsI (caesium iodide). Releases from fuel are governed by the thermodynamic equilibrium of these three phases, with the gas contained in spaces between the grains (grain boundaries).

Much progress has been made in the validation of the simplified and mechanistic release models. The experimental observations are well reproduced by the calculated releases of the volatile FPs. However, the ASTEC results slightly underestimate the releases at intermediate temperature (between 1000 and 1500 °C) because the model does not take into account the intergranular inventory. The greatest uncertainties relate to the results for the semi-volatile and low-volatile FPs and are due in particular to the difficulty in properly addressing the chemical reactions with the structural elements of the core (control rods, reactor core internals, etc.).

5.5.2.4. Releases of structural materials

The radioactivity of structural materials, due mainly to their activation, is relatively low. Nonetheless, it is important to evaluate releases of these materials for two reasons: (1) they may chemically react with FPs, such as iodine with the silver in silver-indium-cadmium (SIC) control rods or tellurium with the tin in cladding, and (2) they significantly contribute to the quantity of aerosols released into the containment. Structural materials agglomerate with FP-laden aerosols, increasing the average size of the particles and contributing to increasing their gravitational settling.

Releases of components from SIC control rods (rods in French 900 MWe reactors and in many other PWRs of Western design) depend primarily on their degradation mechanisms described in Section 5.1.1.2. When the cladding and guide tubes of SIC rods fail, the liquid SIC alloy inside comes into contact with the surrounding fluid and vaporises. The release rates then depend on the vapour pressures of these three metals. This is well known and correctly modelled. What remains uncertain is the degradation phenomena of the control rods and guide tubes. Depending on the level of degradation of these components, the liquid alloy may remain at high temperature for a variable period of time before flowing to the colder sections in the lower end of the core and solidifying. This has an effect on the quantities that are vaporised.

The boron carbide in other types of control rod (those used in French 1300 MWe reactors along with SIC rods, also in BWRs, and in VVERs (PWRs of Russian design)) begin to oxidise when it comes into contact with the surrounding fluid, i.e., after cladding and guide-tube failure. The resulting oxidation products are boric oxide and carbon monoxide or carbon dioxide (depending on the oxidising potential of the fluid). The boric oxide is converted into boric acid as it is transferred from the RCS to the containment.

Theoretically, the carbon monoxide could turn into methane in the RCS if reducing conditions prevail there. In practice, the formation of methane in the RCS remains negligible at low pressure and is very low at high pressure because the reactions that allow it to form are too slow to achieve a significant yield.

In the case of Zircaloy fuel-rod cladding, significant amounts of tin are released (tin is a minor component of Zircaloy). It is the form SnO_2 (tin dioxide) that is volatile and released. The degradation mechanisms of the cladding govern the releases of tin. Satisfactory models are obtained by taking into consideration that the release kinetics of tin follow those of the oxidation of Zircaloy cladding.

5.5.2.5. Summary and Outlook

The experimental database of analytical tests performed on sections of irradiated fuel is relatively broad in the case of UO_2 fuels with average burnups. It is supplemented by integral Phebus FP type tests. These experiments have helped improve understanding of the effects of the different parameters influencing releases, such as temperature, oxidising-reducing conditions, interactions with structural materials (especially cladding), burnup and the type (UO_2 or MOX) and state of the fuel (solid or liquefied).

These results have made it possible to develop and validate two types of model. Mechanistic models are used to describe most of the interactions in the fuel and above all to interpret the tests. Simplified models describing the main phenomena can be derived from these mechanistic models and used in integral codes such as ASTEC (see Chapter 8).

The hypotheses formulated to interpret the tests are based mainly on the physico-chemical changes in the fuel and make it possible to correctly reproduce the influence of the various parameters on releases (temperatures, burnup, composition of the atmosphere surrounding the fuel). Apart from predicting the behaviour of fission gases, the MFPR code is used to determine variations in the composition of the different phases containing FPs inside the fuel as well as the chemical species of the elements involved. However, these hypotheses still lack sufficient validation. Such validation should be made possible by the fuel sample microanalysis performed in one part of the ISTP (the aim is to determine FP distributions and, if possible, the chemical species of FPs in matrices of fuel-samples obtained from fuel degradation tests conducted as part of the VERCOR and VERDON programmes).

The experimental database has been extended to cover MOX fuel (two tests) and high-burnup UO_2 fuel (one test) in the VERDON programme, which is part of the ISTP and which ended in 2014.

Releases during reflooding of solid high-burnup fuels were experimentally studied in the QUENCH-ISTC programme. This programme did not provide any significant lessons about releases.

The case of accidents with air ingress into the vessel, such as when the reactor is shut down, is also explored. The available data, primarily Canadian, show that in such

accidents ruthenium behaves like a volatile FP and may be almost completely released from fuel [19]. Models have been developed and in 2012 a specific test in the VERDON programme was conducted to study releases in air from MOX fuel, another one in 2015 will study releases in air from high burn up UO_2 fuel.

5.5.3. Fission product transport in the reactor coolant system and secondary loops (fission gases excluded)

FPs and structural materials are released primarily as gases or vapours. These vapours cool in the vessel upper head and then in the RCS. A number of phenomena occur during this cooling:

- the vapours condense on nuclei and form fine particles in a phenomenon commonly known as homogeneous nucleation;
- the vapours condense on pre-existing particles in a phenomenon commonly known as heterogeneous nucleation;
- the vapours condense on the walls, forming deposits.

The temperatures at which these phenomena occur depend on the chemical form of the FPs and structural materials. Fission product chemistry is discussed in Section 5.5.6. After the vapours condense, the FPs and structural materials are entrained into the RCS primarily in aerosol form. Notable exception are iodine and ruthenium, which can in some circumstances remain in gas form. The main processes involved in such transfers are shown in Figure 5.58.

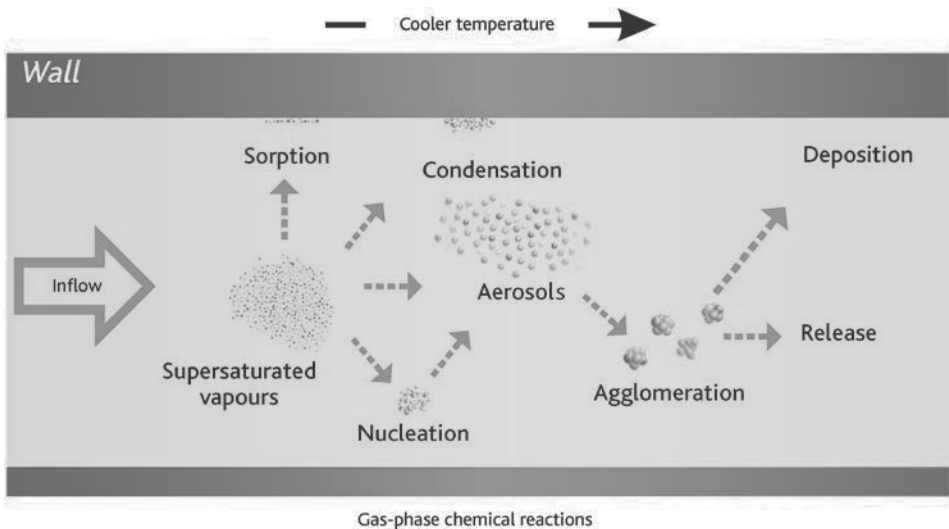


Figure 5.58. Process determining FP transfers to the RCS in aerosol form.

5.5.3.1. Physical phenomena involved in aerosol transfers

► Nucleation phenomena

The formation of particles through homogeneous nucleation can be described at the scale of the atoms and molecules produced or at a more macroscopic scale by directly taking into account particle formation. This macroscopic description is easier to model and yields results similar to those of the atomic-scale description. As a result, it is generally used in computer codes to analyse homogeneous nucleation.

In heterogeneous nucleation, vapours condense on existing aerosol particles consisting of less-volatile elements that have condensed at higher temperatures. The existing models, which analyse the diffusion of molecules in a carrier fluid, are considered to be satisfactory.

► Coagulation (or agglomeration) phenomena

The motion of aerosols formed through nucleation is relative to the fluid carrying them and due especially to Brownian diffusion, turbulence and gravitational settling (sedimentation). This motion leads aerosol particles to collide with each other and stick together (agglomeration). The aerosols grow as they are carried and typically reach a size of a few micrometres in the RCS.

These phenomena are well understood and the available models yield computational results that are satisfactory for the experimental conditions. It should be noted however that some parameters of the models, such as the form factor of the particles (which indicates their deviation from sphericity) are poorly known. However, this lack of understanding does not give rise to any significant uncertainties.

► Deposition by vapour condensation

Part of the FPs and structural materials released as vapours from the reactor core will condense and deposit on the cool walls. This deposition phenomenon is generally modelled using an analogy of mass transfers and heat transfers whereby the values of the dimensionless numbers governing these transfers (Sherwood and Nusselt numbers) are considered to be the same. This assumes that the properties of the vapour species involved, especially their saturation pressure, are known. The associated chemical aspects are discussed in Section 5.5.6.

Prior to the Phebus FP integral tests, there was a high degree of confidence in the deposition-by-condensation models. But these tests have shown that deposition by condensation was underestimated by a factor of as much as two. A number of assumptions have been explored by CFD calculations. These calculations have made it possible to conclude that this underestimation was caused by effects related to the fact that the flow of fluid in the system was neither thermally nor hydraulically stable [20]. In such situations, the heat-exchange and mass-transfer coefficients are increased, leading to a corresponding increase in the deposits.

► Deposition by gravitational settling (sedimentation)

Aerosols move under the action of gravity and settle on horizontal surfaces. This deposition phenomenon is only significant when the carrier fluid velocity is low and thus the system transit time is long.

This phenomenon is well understood and the available models yield computational results that are satisfactory under the experimental conditions.

► Deposition by Brownian or turbulent diffusion

Brownian motion of particles, particularly those with a diameter of less than $0.1\ \mu\text{m}$, can cause particles to collide with and deposit on walls. This phenomenon is significant only in laminar flows. At high flow rates, aerosols deposit on walls by means of turbulent diffusion. These phenomena are well understood and the available models give computational results that are satisfactory under the experimental conditions.

► Deposition by impaction

This phenomenon occurs especially where there are changes in system geometry: elbows, changes in cross-section, obstacles, etc. The inertia of the particles moves them away from the lines of flow and can cause them to collide with the walls. Aerosol size is an important factor. Deposition by impaction occurs primarily with large aerosols.

In the RCS, most deposition by impaction occurs in elbows and where there are changes in cross-section (e.g., steam generator tube inlets). This deposition is modelled using physical correlations that generally yield satisfactory results. The case of deposition on the secondary side following an SGTR is discussed below.

► Deposition by thermophoresis

When aerosols are carried by a hot fluid into a system where the walls are cooler than the hot fluid, the temperature gradient between the centre of the hot flow and the cooler flow along the walls results in more collisions between the molecules of the carrier fluid and the aerosols at the centre of the flow than in the vicinity of the walls. This causes the aerosols to move towards the walls, favouring deposition there. Many theoretical and experimental studies have made it possible to establish widely accepted formulae for deposition rates by thermophoresis [21]. Examples of past experimental studies include the TUBA thermophoresis tests carried out by IPSN [22].

The models have been satisfactorily validated by the calculation of the TUBA thermophoresis experiments. Nonetheless, the Phebus FP integral tests revealed significant differences between the calculation results and the experimental results for deposition by thermophoresis in steam generators. The calculations overestimate this deposition by a factor of around two. This is true for all the codes used to calculate core melt accidents. A number of areas have been investigated to explain these differences, including

the influence of the differences between the Phebus tests and those used to validate the models (e.g., the temperature differences between the fluid and the wall or the differences in aerosol concentrations). CFD calculations following the trajectories of aerosols have also been conducted [24], but a convincing explanation has yet to be found. In the case of core melt accidents following a large RCS break, the differences between the calculation results and the experimental results have little impact on the releases calculated in the containment because the retention in the RCS is low. However, retention in pipes has a strong impact on the possible releases in the case of accidents with containment bypass (e.g., V-LOCA; see Section 4.2.1.3).

► Deposition by diffusiophoresis

Condensation occurs when the walls of the RCS are cooler than the saturation temperature of the steam. This condensation causes a flow of gas that carries particles towards the walls [23]. The models available for calculating deposition by diffusiophoresis are based in particular on the results of the TUBA-diffusiophoresis tests performed by IPSN [25]. They yield satisfactory results for calculating deposition in the RCS.

► Mechanical resuspension

A number of phenomena, such as the production of steam during core reflooding, may lead to significant flows in the pipework. Deposited particles may then be mechanically entrained. This entrainment may be high in the case of a highly turbulent flow and dry deposits. Resuspension phenomena are quite complex. To simplify, resuspension occurs when the aerodynamic forces exerted on aerosols deposited on walls are stronger than the forces causing them to adhere to walls. A number of models have been developed, including one that considers a single layer or several layers of aerosol deposits. The validation of these models is based primarily on the results of the STORM tests [26] conducted at the Joint Research Centre in Ispra, Italy.

A state of the art study on aerosol resuspension, conducted as part of the European SARNET network, found that the validation of the models was insufficient, particularly regarding the evaluation of releases from accidents with containment bypass (V-LOCA or SGTR) for which aerosol retention in pipes is an important factor in reducing releases.

► Revolatilisation

This phenomenon is the opposite of deposition by vapour condensation. When the thermodynamic conditions in the RCS (temperature of the fluid carrying the aerosols, oxidising-reducing conditions and vapour concentration in the fluid) change, deposited vapours can revolatilise. Due to the importance of the associated chemical aspects, revolatilisation is discussed in Section 5.5.6.

It should be noted that this phenomenon was clearly demonstrated during the Phebus FP integral tests and in the VERCORS tests.

► Deposits in the secondary loop (steam generators and tubes)

During an SGTR (initial or induced rupture), the secondary side of the affected steam generator may be dry or flooded. This can have a significant effect on aerosol deposits in the secondary loop and thus on releases. Considering that very few experiments have been conducted under representative conditions, lower-bound deposition assumptions are currently being used to evaluate aerosol retention in the secondary side of damaged steam generators (these assumptions thus increase the calculated releases). A more realistic assessment of aerosol retention in the secondary side of damaged steam generators was therefore deemed necessary. As a result, the ARTIST experimental program [27] was conducted at the Paul Scherrer Institute (PSI) in Switzerland as part of an international consortium project. The programme led to the development of a new model of aerosol retention usable for cases where the secondary side of a steam generator is flooded.

5.5.3.2. Experimental programmes, physical models and simulation codes

The aerosol physics phenomena have been the subject of many experimental and theoretical studies often conducted outside the field of nuclear engineering, which have led to the creation of basic models. These models show a good consensus and have been implemented in computer codes used to analyse core melt accidents, such as the SOPHAEROS module of IRSN's ASTEC integral code.

SARNET identified two additional priority areas regarding transfers of aerosols in the RCS and the secondary loop:

- mechanical resuspension: efforts were made to better assess the validity of the models using existing data [28] (the STORM programme conducted by the JRC/IE [Joint Research Centre/Institute for Energy]) in the late 1990s;
- deposition in the secondary sides of damaged steam generators: as mentioned above, this topic was explored in the ARTIST programme conducted by PSI, a partner of IRSN [29]. The design of the experimental steam generator was representative of the design of Framatome steam generators, but with a reduced height of 3.8 metres. The steam generator internals and upper structures (separators and dryers) were of the same scale as that of a real steam generator used in the Beznau nuclear power plant in Switzerland. The experiments studied the aerosol retention in broken tubes near and beyond the break, in the separators and dryers, under dry secondary side conditions. Retention in a flooded steam generator was also investigated. The retention factors deduced from these experiments (dry or flooded secondary side) are used to assess the validity of the models of retention in the secondary side of a damaged steam generator.

5.5.3.3. Summary and Outlook

The phenomena associated with the transport of aerosols in the RCS are now generally well understood and satisfactory models, often based on data from fields other than nuclear engineering, have been developed to describe them. The main deposition

phenomena, such as thermophoresis and diffusiophoresis, have been the subject of specific experimental programmes conducted to validate the corresponding models.

The models describing the phenomena of mechanical resuspension of deposited particles due to high flow rates are less well validated. An effort is being made to improve these models.

Because aerosol retention in the secondary sides of steam generators remains poorly quantified, lower-bound retention coefficients are used in safety studies. This matter is the subject of supplementary studies based on the findings of the international ARTIST programme.

5.5.4. Ex-vessel fission product releases

Ex-vessel releases of FPs and aerosols can be caused by several phenomena that can occur inside the containment:

- releases of aerosols from boiling sump water;
- releases during MCCI;
- resuspension of aerosols deposited on containment walls.

The specific aspects of iodine and ruthenium, both of which have a complex chemistry, are discussed in section 5.5.6.

5.5.4.1. Physical phenomena

► Releases from boiling sump water

Aerosols released into the containment during a core melt accident end up primarily in the sump water after settling. Resuspension of these aerosols may occur if the sump water begins to boil. The results of past REST tests [30] carried out by FzK (Germany) have been used to develop semi-empirical models for both soluble and insoluble aerosols.

► Releases during MCCI

Such releases primarily relate to semi-volatile FPs and low-volatile FPs, as volatile FPs are released beforehand during in-vessel degradation and core melt. The release rates depend on the composition of corium and particularly its metallic zirconium content, which determines the oxygen potential of the corium and influences the chemical form of the FPs and thus their volatility. The concrete composition (siliceous concrete or silico-calcareous concrete) also plays a role, particularly because of differences in the production of gases during erosion of the concrete.

Releases during MCCI can be estimated from the FPs vapour pressures calculated using a thermodynamic code such as GEMINI for different corium compositions and concrete types. The highest values are obtained for zirconium-rich corium and siliceous

concrete. The only elements with significant releases (greater than 1%) are barium and strontium.

As the release rates are low, it has not been considered necessary to conduct R&D programmes to refine the results.

► Resuspension of aerosols deposited on the containment walls

Some events, such as hydrogen combustion or corium-water interaction may result in high gas velocities near the containment walls and allow resuspension of deposited aerosols. Such resuspension is not addressed by existing models, but experiments are planned to assess if it can have a significant radiological impact on the environment.

5.5.4.2. Experimental programmes, physical models and simulation codes

The effect of possible releases from a boiling sump and during MCCI on releases during core melt seems to be relatively low. Specific models for assessing these releases exist, but they are not implemented in the ASTEC integral code presented in Chapter 8.

5.5.4.3. Summary and Outlook

Ex-vessel releases of FPs can occur if sump water boils (aerosol releases) or during MCCI. Studies conducted on these two issues have revealed only low release rates, which are lower than those in-vessel.

Nor has the possible resuspension of aerosols deposited on containment walls during violent events (such as hydrogen combustion) been investigated in detail. The reason is that such resuspension is not expected to significantly contribute to releases to the environment.

5.5.5. Behaviour of aerosols in the containment

Aerosols released into the containment are subjected to the phenomena of agglomeration, deposition and, in some cases, resuspension. The basic physical phenomena are the same as those governing the transport of aerosols in the RCS. They depend on thermal-hydraulic conditions in the containment (humidity rate, condensation or non-condensation of steam). The main deposition phenomena are gravitational settling and diffusiophoresis. Some safety systems, such as sprays, can also have a major influence on aerosol concentrations in the containment.

5.5.5.1. Physical phenomena

► Hygroscopicity and agglomeration phenomena

Aerosol agglomeration phenomena are the same as those at play in the RCS. They cause the particles to increase in size, accelerating their deposition by gravitational settling.

Hygroscopicity can play a major role. Some compounds, such as caesium hydroxide, are able to absorb water molecules and form droplets. This, too, causes aerosol particles to increase in size and accelerate their gravitational settling.

Models for calculating the size of the droplets formed at equilibrium as a function of temperature and relative humidity are available.

A difficulty in using such models lies in the limited knowledge of the chemical species formed by FPs. Prior to the *Phebus* FP tests, it was generally accepted that caesium was released into the containment in highly hygroscopic hydroxide form. The first two *Phebus* FP tests showed that this was not the case. Thermodynamic calculations taking account of the molybdenum releases show that the most likely chemical form of caesium is caesium molybdate. This is consistent with the caesium volatility measured during the tests. However, this finding cannot be directly extrapolated to all possible accident situations because the formation of caesium molybdate depends on the oxidising-reducing conditions in the RCS. Furthermore, the same tests show that the aerosols were agglomerates composed of released structural materials and FPs, the majority of which are poorly soluble. These agglomerates are much less hygroscopic than caesium hydroxide.

Aerosol hygroscopicity and assessments of aerosol settling rates in the containment must therefore be considered with caution. Nonetheless, these uncertainties probably have very little effect on the estimation of releases outside the containment.

► Washout of deposits by water vapour condensation

Aerosols deposited on the containment walls can be washed away by water condensed from vapour and be drawn down into the sumps. A simplistic approach to studying this phenomenon in the computer codes considers that insoluble aerosols are not washed out but that soluble aerosols are. However, the difficulty is the same as that described above regarding aerosol hygroscopicity, i.e., uncertainties exist as to the type of chemical species making up the aerosols and thus their solubility. As most of the chemical species of barium and caesium are soluble, both elements are considered to be soluble.

► Spray removal of aerosols in the containment

The main purpose of the containment spray system in France's PWRs is to prevent excessive pressure from building up in the containment. It also significantly lowers the concentration of suspended aerosols in a matter of hours. In the past, airborne concentrations were assessed using simple time-constant models. More recent studies allow current computer codes to obtain a better physical description of the phenomena involved.

Spray removal of aerosols in the containment depends on the characteristics of the droplets, particularly their masses, velocities and temperatures as they fall. Changes in these characteristics depend on evaporation and condensation phenomena as well as coalescence of the droplets.

The trapping of aerosols by droplets involves the following mechanisms:

- inertial impaction and interception, mechanisms that primarily apply to large aerosols;
- Brownian diffusion, a mechanism that is particularly effective in the case of small particles near droplets;
- phoretic capture, which is associated with movements of particles in a temperature field. This mechanism is particularly effective in the upper part of the containment before the droplets reach thermal equilibrium with the atmosphere.

5.5.5.2. Experimental programmes, physical models and simulation codes

The basic mechanisms involved in aerosol deposition in the containment (deposition by diffusiophoresis and thermophoresis on the containment walls, deposition by gravitational settling) are well known. Models have been developed to describe these basic mechanisms, often using data from outside the field of nuclear engineering. Where necessary, these basic models were validated by specific experiments such as the PITEAS experiments, which were conducted at Cadarache by IPSN to study of the behaviour of aerosols in the containment [31].

More recently, R&D work conducted in the 2000s have made it possible to explore more deeply issues relating to spray removal of aerosols in order to quantify the kinetics and efficiency of removal of aerosols and gaseous iodine in the containments of France's PWRs. This work includes:

- the CARAIDAS [32] tests conducted by IRSN in a cylindrical enclosure measuring 5 metres high and 0.6 m in diameter. The tests made it possible to determine the individual efficiencies of various mechanisms for collecting aerosols and gaseous iodine species by drops under steady-state conditions, under various conditions representative of a core melt accident (temperature, pressure, humidity, pH of the drops, iodine concentration);
- in terms of modelling, the development of a detailed description of the physical change in the drops during their fall as well as the various aerosol capture mechanisms. This description was implemented in the ASTEC integral code. Its thermal-hydraulic aspects were validated using the results of the CSE [33] tests conducted in the USA and its aerosol aspects were validated using the results of the CARAIDAS tests.

5.5.5.3. Summary and Outlook

The various phenomena governing the behaviour of aerosols in the containment are generally well understood and physical models have been developed to describe them, often using data from outside the field of nuclear engineering. The main deposition phenomena, such as diffusiophoresis and gravitational settling, have been the subject of specific experimental programmes conducted to validate the corresponding models.

5.5.6. Fission product chemistry

During a core melt accident, FPs are released from fuel as vapours. The chemical form in which they are released depends on the equilibrium with their condensed phase in the fuel. This equilibrium varies during the course of an accident, mainly due to variations in temperature and oxidising-reducing conditions. Once released, FPs soon find themselves in a different environment during their transport in the RCS, with variations in temperature and in the composition of the carrier fluid and changes in their chemical speciation in the RCS. Most of the chemical reactions take place in the gas phase, but the vapours may also interact with pipe walls. The structural materials released to outside the core also play a role (SiC and/or boron carbide control rod materials, tin in the Zircaloy cladding, etc.).

Most of the FPs are released into the containment either in condensed form (aerosols) or rapidly condense there. The behaviour of aerosols in the containment atmosphere is determined primarily by the deposition processes described in Section 5.5.5.1. The chemistry of the FPs has little effect on these processes. A large fraction of the aerosols is washed down into the sump water, where they dissolve depending on their respective solubility.

Iodine [3] and ruthenium are two FPs that exhibit specific behaviour and can be present in significant quantities as gases in the containment. These two highly radiotoxic elements (Section 5.5.1) have a complex chemistry in both their gas and liquid phases and can react with painted surfaces and metal surfaces in the containment. Their interactions with the water and air radiolysis products, formed under the radiation emitted by the FPs in the atmosphere and sumps of the containment, also play an important role.

5.5.6.1. Physical phenomena

► Chemistry of gaseous FPs in the RCS

The chemical speciation of FPs in the RCS during a core melt accident can be estimated by assuming, as a first approximation, that the chemical reactions have reached thermodynamic equilibrium, with understanding of the concentrations of the various chemical elements and of the thermodynamic properties of the various chemical species likely to be formed. However, given the complexity of the chemical systems involved, particularly due to the large number of elements involved in the chemical reactions (FPs, elements released by degradation of the control rods and core structures, hydrogen and oxygen in the carrier gas molecules), the existing thermodynamic databases are not comprehensive enough. Furthermore, some of these databases contain significant uncertainties. It is for these reasons that the chemical species of FPs in the RCS cannot be determined with certainty by thermodynamic calculations.

Furthermore, the thermodynamic equilibrium is not always reached. This is particularly true when chemical reactions occur at a rate too slow for equilibrium concentrations of the species formed to be obtained. While thermodynamic equilibrium is most probably reached at high temperature in the vessel near the core (chemical reactions occur very quickly at high temperature), this is most likely not to be the case in the cold legs,

where the temperatures are lower, and for some species in the parts of the RCS where the temperature of the carrier fluid drops quickly (the steam generators in particular). Thus, in the parts where the temperature drops quickly, the reaction rates become sufficiently slow to have an effect on the final speciation of the FPs. As a result, the species found are not always those that would have been formed at thermodynamic equilibrium.

Studies conducted to determine the species formed initially looked at the volatile elements (particularly iodine) and the simple reaction system limited to the elements Cs, I, O, H [34], while taking into consideration the influence of boric acid. These studies led to the conclusion that, in the absence of boron, iodine is transported as caesium iodide (CsI) with the remaining caesium in hydroxide form (CsOH). The presence of boron may lead to the formation of caesium borate, which is less volatile than CsOH, and where part of the iodine converts to hydroiodic acid (HI), which is more volatile than CsI [36]. These studies are based on the results of experiments conducted with simulated FPs, such as the British FALCON programme [35].

The results of these preliminary studies led developers of computer codes such as MELCOR (an American code; see Chapter 8) to set the chemical forms of the transported elements without taking the chemical reactions into account. The computer codes, such as SOPHAEROS (a module of the ASTEC integral code; see Chapter 8), for which modelling of the transport of FPs in the RCS was developed more recently, calculate the chemical speciation of FPs. These are not thermodynamic calculations of the complete reaction systems. Rather, they are simplified calculations limited to reaction systems most important for the chemical speciation of FPs and which were carried out using a thermodynamic database that was as comprehensive and validated as possible.

The chemical forms selected based on the aforementioned preliminary studies were challenged primarily by the results of the Phebus FP programme (Section 7.3). One strong point of this programme is that the source of the FPs and structural materials is the most realistically achievable both in terms of its composition and the release kinetics. This is because the source comes from an irradiated fuel rod cluster undergoing degradation.

In the Phebus FP tests, the chemical forms are not determined directly, owing to the detection limits of the various techniques for low amounts of radioactive materials. However, indirect indications are provided by the volatility of the elements (their condensation temperatures) and their solubility in water or acid.

Regarding caesium, the results of the Phebus FP programme (Section 7.3) showed that in the presence of a carrier gas rich in water vapour, caesium was primarily in the condensed phase at 700 °C. This is incompatible with caesium hydroxide, which is in the vapour phase at this same temperature. These tests also showed that with a steam-rich carrier gas, two things occur: (1) molybdenum releases are higher than initially expected and (2) molybdenum is present in the RCS at a much higher concentration than caesium, thus promoting the formation of caesium molybdate, a less-volatile species than caesium hydroxide. The concentration of this species is correctly calculated by the ASTEC code, which uses thermodynamic data for the species involving molybdenum. After

reviewing the results of the Phebus FP tests, the developers of the MELCOR (US NRC) code modified it to take into account the formation of caesium molybdate.

In the case of iodine, calculations made with the ASTEC code predict the formation of caesium or rubidium iodide (equivalent properties). The Phebus tests, particularly FPT2, showed that this is not always the case. Depending on the oxidising-reducing conditions and the concentration of elements from the control rods in the RCS (Ag, In and Cd or B), caesium iodide and at least one more-volatile species may be present or absent. This chemical speciation is not currently predicted by the models. The aim of the CHIP experimental programme, conducted at Cadarache by IRSN and devoted to iodine chemistry in the RCS in event of a core melt accident, is to provide indications on the chemical reactions involved and the species formed. This programme is discussed more in detail in Section 5.5.6.2.

► Interactions of FPs with the walls of the RCS

Fission product vapours can react with the walls of the RCS. Elements such as tellurium can also be chemisorbed, increasing deposition. However, this does not seem to occur if sufficient amounts of tin (a component of Zircaloy) are transported with tellurium to form tin telluride. If degradation of Zircaloy cladding leads to a significant release of tin, higher amounts of tellurium may be transported by the aerosols in the containment.

The FP vapours condense on the metal walls and react with them. This is particularly the case with caesium in the hot leg of the RCS. This interaction has been demonstrated by many experimental programmes, including the DEVAP programme [37] conducted for IRSN at CEA's centre in Grenoble, and the Phebus FP programme. Deposit reevaporation tests conducted on hot-leg samples from the FPT1 test of the Phebus FP programme showed that interactions between caesium and steel may lead to the formation of several different volatile species [38]. Revolatilisation of deposited FPs may occur after their main release from the core during a core melt accident. This can lead to long-term releases, particularly in the case of delayed containment failure (failure occurring at least 24 hours after the onset of the accident *via* mode δ or mode ε , for example; see Section 4.3.3.3). Such releases are determined by the volatility of the species in the deposits.

► Iodine chemistry in the RCS

In the RCS, iodine is likely to combine with many other elements (FPs or structural materials), particularly caesium, rubidium, silver, indium and cadmium. Iodine may also be present in the RCS as atoms (I), molecules (I₂) or hydroiodic acid (HI). These species have the particularity of being in the gas phase in the conditions that prevail in the RCS during a core melt accident.

Following the studies conducted after the TMI-2 accident, it was generally accepted in the 1980s and 1990s that iodine was transported primarily as caesium iodide (CsI). In 1995, the US NRC conducted a new set of studies aimed at better estimating releases

to the containment during a core melt accident. These studies were summarised in benchmark report NUREG-1465 [40], which indicated that a significant fraction (5%) of volatile iodine (I and HI) may be released into the containment. This percentage was not determined based on experimental results but rather on calculations, for several accident sequences, of the thermodynamics of the Cs, I, O, H simple system supplemented by assessments of the speeds of the chemical reactions for the iodine speciation. As mentioned above, when the reaction rates are sufficiently low, iodine does not have time to fully react with the caesium in the RCS. As a result, non-negligible fractions of volatile iodine (I and HI) remain.

The results of the Phebus FP tests show that the behaviour of iodine in the RCS is in reality more complex. Iodine is not always present primarily in the form of caesium iodide, but rather forms species with other elements released during degradation of fuel and structural materials. In particular, thermodynamic assessments have shown that the silver and cadmium in SIC control rods can affect the iodine chemistry in the RCS depending on the oxidising-reducing conditions and temperature levels. Thermodynamic data of the species that may be present in the RCS were compiled and verified. This considerable task has made it possible to implement extensive databases in computer codes such as ASTEC. Despite this work, however, the thermodynamic calculations still do not make it possible to reproduce the iodine behaviour observed during the tests of the Phebus FP tests.

Another notable result of the Phebus FP tests is that the presence of gaseous iodine in the containment at the onset of fuel degradation cannot be explained by chemical reactions in the containment. This presence is attributed to an influx of gaseous iodine from the RCS. The fractions of gaseous iodine transported in the RCS at a given moment in relation to the total iodine (gaseous iodine and iodine aerosols) reached 30% during the FPT-0 test and 4% during the FPT1 test [39, 41]. It should be noted that:

- during these tests, the maximum fractions of gaseous iodine were measured when the hydrogen content in the RCS was at its highest (approx. 50%);
- these are estimates for a cold-leg break; the results of the FPT1 test seem to show that the fraction of gaseous iodine is higher for a hot-leg break;
- the difference in iodine concentrations between the two tests (30 times less iodine during test FPT0, which was conducted with only very slightly irradiated fuel) suggests that the reaction rates for the formation of iodine compounds have an influence on the fraction of gaseous iodine;
- the relationship between the fraction of gaseous iodine and the hydrogen concentration is less clear for the FPT2 test;
- the FPT0 test is a special case in that the test fuel was very slightly irradiated and, as a result, the iodine concentrations were not representative of an actual accident sequence.

Phebus tests FPT0, FPT1 and FPT2 were conducted using a SIC control rod like those used in French 900 MWe PWRs (also in most PWRs of Western design) for example. On

the other hand, Phebus test FPT3 was conducted using a boron carbide (B_4C) control rod, like the ones used in 1300 MWe and 1450 MWe PWRs. The iodine fraction in the gaseous phase measured in the containment during this test was significantly higher (more than 80% [43]) than during the other tests in the programme. This result can be explained by a number of assumptions, including the absence of silver, indium and cadmium (which reduces the number of elements with which iodine can chemically combine) and the presence of high concentrations of boric acid from oxidation of the control rod (boric acid can combine with caesium, preventing the formation of caesium iodide). The combination reactions of iodine with other elements may be lower and more iodine may remain in gaseous form. The CHIP experimental programme conducted at Cadarache by IRSN aims to test these assumptions.

Nevertheless, caution should be exercised in extrapolating these experimental results to real accident sequences in a power reactor. Although studies conducted around the year 2000 on possible releases during core melt accidents took into account the results of the FPT0 and FPT1 tests (by taking a 5% fraction of gaseous iodine in the fluid leaking from an RCS break), supplementary studies are necessary to take into account the implications of the results of the FPT3 test for power reactors.

► Iodine chemistry in the containment sump

Iodine released in aerosol form in the containment behaves like the other aerosols (Section 5.5.5) that are primarily entrained into the sump water. With the notable exception of silver iodide (AgI), most of the metal iodides (CsI , RbI , CdI_2 , InI) are soluble. The soluble iodides dissolve in water, forming I^- and IO_3^- ions.

The large amount of FPs in the containment sump create significant dose rates in the sump water, leading to the formation of water radiolysis products including reactive molecules and radicals such as $\cdot OH$, $\cdot O_2^-$, H_2O_2 , etc. Many chemical reactions take place, the net result of which is radiolytic oxidation of the iodide ions (I^-) into volatile molecular iodine (I_2). The formation of I_2 depends on many parameters, the most important being water pH. If the pH is kept basic, the I_2 production rate is very low.

The sump water also contains organic compounds primarily from submerged paintwork. The iodine reactions with the organic radicals formed through decomposition of these organic compounds due to the dose rates produce volatile organic iodides such as methyl iodide (CH_3I) or low-volatile organic iodides such as compounds of higher molecular weight.

These reactions in the liquid phase (see Figure 5.59) have been studied in depth both experimentally and theoretically, and the associated phenomena are reasonably well understood [45, 46]. However, there remain uncertainties about the effect of some impurities, such as the NO_3^-/NO_2^- ions produced by radiolysis of the gases in the containment atmosphere (a product of radiolysis is nitric acid [HNO_3], which is drawn into the sump by the condensing water vapour), the Fe^{2+}/Fe^{3+} ions from the steel surfaces in contact with the liquid phase in the sump (these ions are formed by corrosion reactions), or the Cl^- ions that may come from cable pyrolysis during an accident involving fire in

the containment. The effect of these impurities is still being investigated by experimental programmes conducted in Canada and Switzerland, primarily as part of the OECD's international *Behaviour of Iodine Project* (BIP).

During the first Phebus FP tests, it was noticed that the silver released from the SIC control rods reacted with the iodine in the sump to form insoluble silver iodide. If there is sufficiently more silver than iodine (since this is a reaction between silver particles and iodine solubilised in the form of iodide (I^-) or iodine (I_2), the number of active sites on the surface of the silver particles must be high enough to react with most of the iodine) the concentration of iodide ions (I^-) drops sharply in the sump, leading to very little production by radiolysis of gaseous iodine (I_2). These phenomena have been quantified and models have been developed from the results of dedicated experiments, particularly the Phebus RTF tests conducted by AECL to study the reactions of iodine with silver in the sump [47] and the tests conducted by PSI, under the Phebus FP programme, to study the stability of silver iodide (AgI) [48].

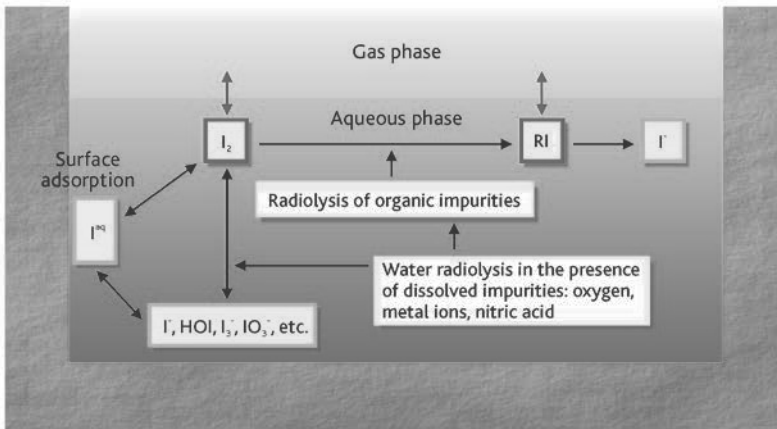


Figure 5.59. Main reactions involving iodine in the liquid phase in the containment sump (taken from [3], reproduced by courtesy of the OECD).

► Iodine chemistry in the containment atmosphere

Gaseous iodine in the containment atmosphere has two origins:

- gaseous iodine exiting the break in the RCS;
- gaseous iodine produced by radiolytic reactions in the sump water.

Transfers of gaseous iodine from the sump obey classic laws of mass transfer. Mass-transfer models exist that can be applied to a sump with and without evaporation of water vapour to the containment atmosphere.

Iodine in the gas phase of the containment reacts with the surfaces in the containment, mainly those made of metal or covered by paint, in physical and chemical adsorption and desorption reactions. These reactions are a function of the temperature and dose rate.

Existing data on iodine adsorption and desorption are derived from laboratory-scale experiments or more integral tests such as those conducted in the RTF [49] in Canada and the CAIMAN facility [50] in France. The experimental parameters investigated were primarily the type of paint, its ageing, temperature and dose rate. The derived correlations correspond to first-order kinetics.

In safety terms, the iodine-paint interactions are highly significant because they lead to the formation of gaseous organic iodides that are not retained by the filters, especially when the containment filtered venting system is opened (U5 procedure in France, see Section 4.3.3.3). Organic iodide production rates were established from the results of a large number of small-scale tests that involved taking painted surfaces on which iodine had been deposited and irradiating them in an atmosphere representative of the containment atmosphere. These tests show that radiation has a greater effect than temperature and their results have been used to develop semi-empirical models. However, given the dispersion of the results and the difficulty in distinguishing the influence of the various parameters, the models are only capable of reproducing the experimental results to within about one order of magnitude.

When exposed to radiation, molecular iodine (I_2) is oxidised by the radiolysis products of the gases in the containment atmosphere (ozone and nitrogen oxides) to form iodine oxides and nitroxides. These compounds are less volatile than molecular iodine particularly because they react with the water vapour to form compounds that are entrained down to the sump. Several reactions occur simultaneously (Figure 5.60):

- the oxidising species (ozone and nitrogen oxides) are formed and destroyed by irradiation;
- the oxidising species interact with the metal surfaces and painted surfaces;
- the oxidising species react with the iodine;
- the iodine reacts with the metal surfaces and painted surfaces.

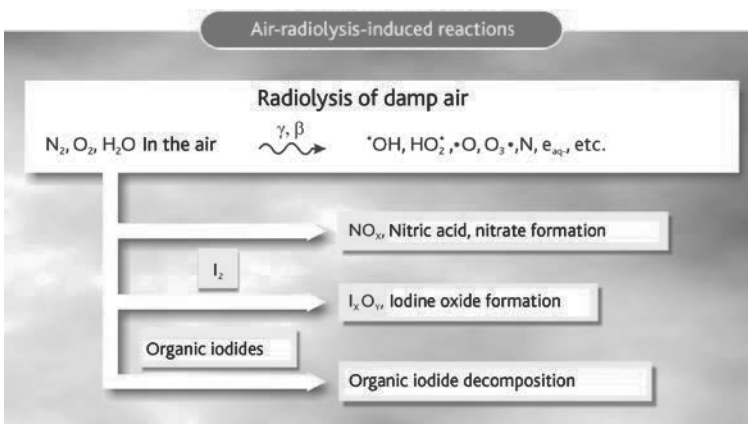


Figure 5.60. Main reactions involving iodine and radiolysis products in the containment atmosphere sump (taken from [3], reproduced by courtesy of the OECD).

The tests conducted during the preliminary studies on the effect of air radiolysis products, particularly ozone, found high iodine concentrations. The models derived from these tests could not be easily extrapolated to the conditions of a core melt accident in a power reactor. More recent tests (PARIS project [51]) have made it possible to gain a better understanding of the phenomena and identify the most influential parameters.

Organic iodine (CH_3I) is also destroyed by reactions with air radiolysis products. The tests carried out show that the destruction rate of organic iodine is proportional to the dose and that temperature has little effect on the rate of the destruction reaction.

An important mechanism that lowers the concentration of gaseous iodine in the containment is its capture by the spray droplets [32]. This mechanism involves the following process:

- transfer of the iodine from the gas phase to the droplets;
- transfers at the gas-droplet interface and within the droplets;
- in-ump liquid-phase chemical reactions.

Capture of gaseous molecular iodine depends on the pH of the droplets. It is more efficient when the pH is basic, which is the case when the containment spray system (CSS) is used in direct mode. Unlike molecular iodine (I_2), organic iodine (CH_3I) is not efficiently scavenged by the droplets.

The RECI tests [52] conducted by IRSN in the early 2000s studied the possible interactions of iodine in the recombiners. The following phenomena are involved in these interactions:

- heating of the metal halide aerosols (CsI , AgI , CdI_2 , etc.) as they pass between the plates of the recombiners;
- vapourisation and dissociation of the iodides, leading to the formation of dissociated gaseous iodine in the hottest sections;
- quenching at the outlets of the recombiners, with the formation of gaseous molecular iodine and fine aerosols by nucleation.

The small-scale RECI tests have more recently been supplemented by larger-scale tests using real recombiners and conducted as part of OECD/NEA THAI project [53]. The production of gaseous iodine by iodide dissociation in the recombiners has been quantified and its impact on iodine releases during a core melt accident has been assessed. Although this impact is not zero, it is lower than that of other phenomena, such as gaseous iodine injected into the containment from the RCS.

► Ruthenium chemistry

As mentioned in Section 5.5.2, large amounts of ruthenium may be released from fuel during an accident with fuel degradation in the presence of air. Such an accident may be a core melt accident caused by vessel melt-through, a spent fuel handling accident, or a spent fuel pool uncover accident [54]. If released to the environment, the dosimetric impact of ruthenium may be high and similar to that of iodine in the short term and caesium in the medium term [6]. Furthermore, ruthenium has a very complex chemistry.

Ruthenium is in metal form in the fuel. However, in the presence of air, it is released primarily as ruthenium(IV) oxide (RuO_2). When it reaches the colder sections of the RCS, RuO_2 can either condense on the walls or oxidise to form gaseous ruthenium tetroxide (RuO_4). This gaseous RuO_4 can then react with the walls and deposit on them in the form of RuO_2 . Due to its kinetics, this last reaction may not be complete in the colder sections of the RCS, allowing ruthenium to persist in the form of gaseous RuO_4 . The behaviour of ruthenium in the RCS was investigated during the RUSSET tests [55-57] conducted by AEKI (Hungary) and tests conducted by VTT [58] in Finland. Conducted under various oxidising-reducing conditions, these ruthenium vaporisation tests revealed, despite significant deposits on the walls of the loops, the existence of gaseous ruthenium in the coolest sections of the loops. During the RUSSET tests, partial pressures of gaseous ruthenium corresponding to the equilibrium between the gaseous RuO_4 and the deposited dioxide were measured at temperatures of around 600-700 °C.

As mentioned above, the gaseous RuO_4 can react with the walls of the pipes and remain trapped there. These effects were studied experimentally by VTT [58] in Finland. The ruthenium deposition (in the form of RuO_2 , as the RuO_4 had been reduced during the reactions with walls) was measured on aluminium oxide and steel pipes. This deposition was light on the aluminium oxide pipes but heavy on the steel pipes except in the presence of water vapour. No explanation was given for this result. The conclusion drawn from these tests is that a significant fraction of ruthenium can be released in gaseous form in the containment.

The behaviour of gaseous ruthenium in the containment was the subject of experiments conducted at IRSN [59-63] as part of the "containment ruthenium" section of the ISTP. These experiments investigated three areas: (1) adsorption and desorption phenomena of gaseous ruthenium on steel walls and painted surfaces; (2) radiation effects that lead to the formation of air radiolysis products such as ozone; and (3) reactions of ruthenium deposited on the containment walls or dissolved in the sump water with these products, which can lead to revolatilisation of gaseous ruthenium.

The results of these tests suggest that, if gaseous RuO_4 is present in the containment, a significant portion of this gaseous ruthenium can remain suspended in the containment atmosphere despite being deposited on its walls. These results also suggest that the ruthenium deposited on the walls or dissolved in the sump water can be revolatilised by radiation. Having been established, the kinetics of these reactions are used to build viable models for determining the quantities of gaseous ruthenium present in the containment of a power reactor during a core melt accident.

5.5.6.2. Experimental programmes, physical models and simulation codes

► Fission product chemistry in the RCS

Regarding the behaviour of FPs in the RCS, the calculation and experimental results are compared primarily for deposition of FPs on the walls of the RCS and for quantities of FPs released to the containment. Work in interpreting these results, especially for

the Phebus FP and VERCORS HT tests with the ASTEC code, made it possible to supplement the thermodynamic databases used for relative calculations of the chemistry of the FPs in the RCS. The results obtained using the supplemented thermodynamic databases, now integrated into the ASTEC software, are satisfactory, except for simulating the behaviour of the iodine measured during the Phebus FP tests.

In particular, the ASTEC calculations do not correctly predict the fractions of gaseous iodine present in the RCS. As a result, the CHIP experimental programme was launched in 2005 to obtain additional data on the iodine chemistry in the RCS, both in terms of its thermodynamics and its chemical kinetics. This programme consists of two types of tests conducted at Cadarache by IRSN:

- analytical tests that study chemical systems consisting of, in addition to hydrogen and oxygen (elements that make up the carrier gas), iodine and only one other element in order to obtain data on the kinetics and thermodynamics of the chemical reactions involving iodine;
- larger-scale studies for studying more complex chemical systems having a higher number of elements (representative of the FPs, control-rod components and core structures) in order to obtain data on the amounts of volatile iodine in the RCS as a function of the elements present and the boundary conditions (oxidising-reducing conditions, element concentrations, temperatures, carrier gas flow rates).

These tests are supplemented by literature reviews to establish kinetic and thermodynamic databases for developing kinetic models. When this data are missing or too uncertain, they are obtained using methods of theoretical chemistry (*ab initio* calculations). The models are then validated by comparison with results of the CHIP tests and progressively integrated in the ASTEC code.

The behaviour of ruthenium is studied in the experimental programmes led by AEKI and VTT described in the previous section (5.5.6.1). The results obtained confirm that a significant portion of ruthenium is transported as metastable gaseous RuO_4 to the free volume of the containment even if the gaseous ruthenium deposits onto the steel pipes.

► Fission product chemistry in the containment

Research on this topic primarily covers iodine and ruthenium chemistry in both experimental and modelling terms.

Iodine chemistry in the containment during a core melt accident has been the subject of many research programmes in several countries since the 1980s. There are detailed reviews that present the main advances made in this area (see [3] in particular).

Until the mid-1990s, before the first results of the Phebus FP tests had been analysed, the research programmes conducted on iodine chemistry in the containment during a core melt accident primarily focussed on studying volatilisation of molecular iodine from the sump and its adsorption on the metal and painted surfaces in the containment.

This was because it was assumed that iodine was released in the containment exclusively in the form of CsI aerosols, that these aerosols were drawn down to the sump and that they led to the formation of iodides (I^-) through solubilisation of the CsI.

The research programmes conducted at the time made it possible to satisfactorily understand and model the kinetics of the chemical reactions involving, with or without radiation, the inorganic iodine species in the sump (primarily iodides [I^-], iodates [IO_3^-] and molecular iodine [I_2]) [45, 46]. The main parameters that influence the kinetics of the reactions and the volatilisation of molecular iodine from the sump are the pH, the dose rate, the temperature and the oxidising-reducing conditions in the liquid phase. The effect of each of these parameters on iodine volatility has been studied in detail (up to an in-sump temperature of 80-90 °C). It turns out that pH is the parameter that has the greatest influence: a basic pH (in the sump or spray droplets) sharply reduces volatility of iodine in the containment.

Based on the results of these programmes, the conclusion was made that the effect of high temperatures (beyond 90 °C) and of the presence of impurities in the sump on iodine volatility had to be quantified. The aim of the EPICUR programme (conducted by IRSN as part of the ISTP and described in detail below), and the OECD BIP (conducted by CNL, formerly AECL) is to obtain sufficient data to be able to model these effects. It should be noted that PSI has conducted a programme complementary to the OECD BIP to study the effect of the presence of impurities in the sump on iodine volatility.

Research programmes have also made it possible to obtain a database for assessing the adsorption rates of molecular iodine on the metal walls and painted walls of the containment in order to obtain preliminary results for assessing the production of organic iodides from painted surfaces (see, for example, [49, 50], which present the results obtained during the RTF integral tests conducted by AECL and the CAIMAN tests conducted by the CEA for IRSN).

However, the results obtained from the Phebus FP tests showed that iodine volatility in the containment could be affected by other processes, particularly:

- releases of gaseous iodine from the RCS. This gaseous iodine, which is not produced by the chemical reactions occurring in the sump, can react directly with the painted walls of the containment and ultimately lead to releases of organic iodides. Furthermore, gaseous iodine can also react with gas radiolysis products in the containment atmosphere. Until the mid-1990s, all these chemical reactions in the containment atmosphere had been studied very little;
- releases of silver through degradation of the SIC control rods. The silver that ends up in the sump forms silver iodide, which sharply reduces the volatilisation of gaseous iodine from the sump. Like the reactions in the containment atmosphere, the influence of silver on the iodine chemistry in the sump had not been studied as part of specific research programmes.

Since then, research programmes studying the influence of silver on iodine volatility in the containment have been conducted by AECL, as part of the international Phebus FP

programme, and by PSI [48, 49]. These programmes have made it possible to model the reactions involving silver. This model is integrated in most integral codes for core melt accidents, particularly ASTEC. These models allow a satisfactory understanding of the influence of silver on iodine volatility.

A research programme studying the reactions between gas radiolysis products in the containment atmosphere and gaseous iodine was recently conducted by AREVA-NP in collaboration with IRSN [51]. The results of these tests have increased understanding and modelling of chemical reactions that affect iodine volatility. However, they do not make it possible to precisely quantify this effect. It should be noted that iodine volatility is reduced by the reactions between air radiolysis products and gaseous iodine in the containment atmosphere. The reason is that the products thus formed react with the water vapour and form compounds that are entrained down to the sump.

In 2005, IRSN launched the EPICUR programme as part of the ISTP. The programme aims to study more particularly the processes whose effects on iodine volatility in the containment were insufficiently quantified:

- the formation of organic iodides in the containment atmosphere from painted surfaces;
- in-sump iodine radiolysis, particularly at high temperatures (beyond 90 °C);
- iodine radiolysis in the containment atmosphere.

The EPICUR facility (see diagram in Figure 5.61) consists of a vessel that can hold a liquid phase in its bottom section. This vessel can be exposed to irradiation by ^{60}Co source. Small painted specimens can be placed in either the liquid phase or the gas

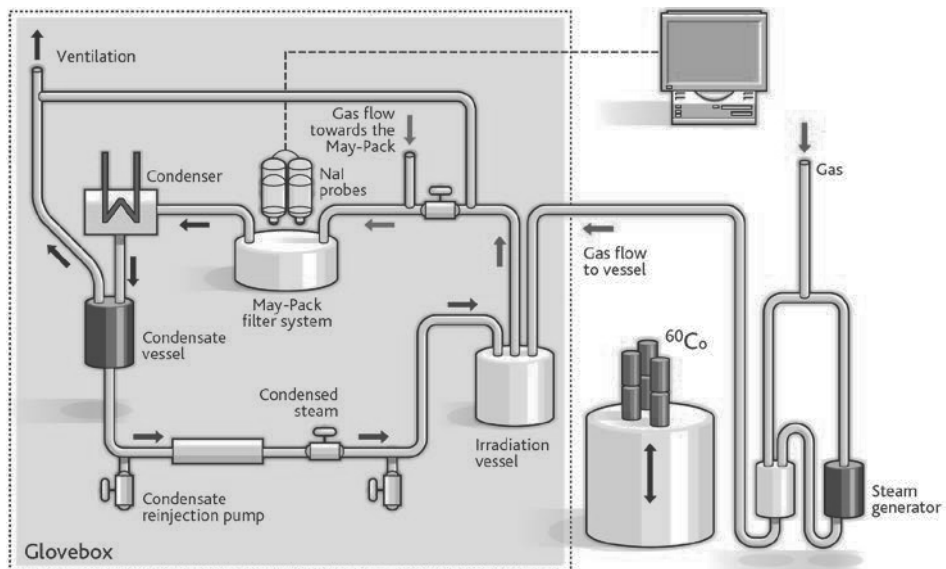


Figure 5.61. Schematic view of the EPICUR facility.

phase of the vessel. The liquid phase can hold iodide ions or molecular iodine solubilised according to its pH. Likewise, iodine can be deposited on the painted specimens before they were placed in the vessel.

Volatile iodine (molecular and organic) produced by radiation from either the liquid phase or the painted specimens, as well as the iodine oxide aerosols produced by radiation in the vessel atmosphere, are continuously entrained by a gas flow and collected in selective filters that separate the iodine, molecular iodine and organic iodine aerosols. The use of iodine containing iodine-131 (^{131}I) makes it possible during a test to perform gamma spectrometry measurements at each filtration stage and determine the kinetics of the processes of volatile iodine production.

The ASTEC code is used at IRSN to interpret these tests. The first part of the programme, which looked at iodine radiolysis in the liquid phase, was fully implemented and made it possible to improve the in-ump iodine radiolysis models. The results obtained also showed that releases of organic iodine from the liquid phase are low but that releases of organic iodine from the painted specimens placed in the vessel atmosphere are high. It remains to be examined whether this mechanism of organic iodine production on the painted surfaces in the containment atmosphere can have an effect on the possible releases during a core melt accident.

It should be noted that, in addition to the tests of the influence of the presence of in-ump impurities on iodine volatility, some of the OECD BIP tests, complementary to the EPICUR tests, investigate the formation of organic iodides from painted surfaces in the containment for the purposes of validating the reaction models involving organic iodides and developed using the results of the EPICUR programme.

At the same time, work on interpreting the Phebus FP tests is continuing, with the participation of a number of partners from outside the programme. The results of the Phebus FPT3 test are drawing special attention. Analyses of these results show that the concentration of gaseous iodine in the containment, very high at the start of the test, decreased quickly and that much iodine is trapped on the painted surfaces of the containment.

In 2010, IRSN published a summary detailing the model of the iodine chemistry in the containment during a core melt accident implemented in the ASTEC code and its use for interpreting the Phebus FPT2 test [65].

An experimental programme on the behaviour of ruthenium in the containment was conducted at IRSN between 2004 and 2008 [59, 63]. This programme investigated a number of areas, including:

- adsorption of gaseous ruthenium by the metal surfaces and the painted surfaces in containment and its desorption from these surfaces;
- revolatilisation of the ruthenium deposited on the surfaces of the containment under the action of ozone and radiation;
- revolatilisation of the ruthenium from the liquid phase of the sump under the action of ozone and radiation.

The results of this programme made it possible to develop models of ruthenium chemistry in the containment during a core melt accident.

5.5.6.3. Summary and Outlook

► Fission product chemistry in the RCS

The Phebus FP integral tests have prompted a review of a number of assumptions on the chemistry of FPs – particularly caesium and iodine – in the RCS. Recent studies of degradation in air of fuel have also shown that a review of ruthenium chemistry was necessary.

Contrary to assumptions prior to the Phebus tests, caesium is not necessarily in the form of CsOH but can be in the form of caesium molybdate, which is less volatile. The models now take this into account. Phenomena of revolatilisation from deposition in the RCS have also been observed and may lead to delayed releases, after the main release phases associated with fuel degradation, in the containment.

Iodine chemistry is more complex. Iodine is not always in the form of caesium iodide in the RCS. The Phebus FP tests show that, apart from the gaseous forms, at least two other species could be present depending on the conditions prevailing in the RCS (other elements present, oxidising-reducing conditions, temperature in the RCS). Part of the iodine is also in gaseous form in the RCS until its release in the containment. Exploitation of the results of the Phebus FP tests as well as of the results of the specific studies using the entire set of available experimental data resulted in using a gaseous iodine quantity of 5% in relation to the total iodine released in the containment for studies on releases during core melt accidents. However, the percentage observed during the last test in the Phebus FP programme (Phebus FPT3) exceeded 80%. This percentage was probably due to highly different chemical conditions in the RCS during the test resulting from the absence of species from degradation of a SIC control rod and the presence of species from degradation of a boron carbide control rod (for this test, the SIC control rod had been replaced by a boron carbide rod). That said, there are two reasons why caution should be exercised in relation to the consequences of this result in terms of the possible releases during a core melt accident:

- the control rods in 1300 MWe and 1450 MWe power reactors are not made solely of boron carbide but are composed in part of a silver-indium-cadmium alloy;
- during the Phebus FPT3 test, the concentration of gaseous iodine in the containment decreased rapidly and much of this iodine was trapped on the painted surfaces.

As regards more specifically iodine chemistry in the RCS, critical reviews of the thermodynamic data for the various possible chemical species have been conducted and have enabled chemical speciation calculations to be made. However, these calculations do not make it possible to fully reproduce the iodine behaviour observed in the RCS during the Phebus FP tests, particularly the existence of several non-gaseous species of metal iodide. A possible hypothesis is that the thermodynamic calculations are

insufficient for modelling iodine chemistry in the RCS, particularly in the sections where the temperature falls sharply (at the core outlet and the inlets of the steam generators), and that they must be supplemented by calculations of the kinetics of the chemical reactions. Indeed, if they are sufficiently slow, the kinetics of some reactions can lead to incomplete reactions of iodine with metallic elements (such as caesium, silver or cadmium) and gaseous iodine. The CHIP experimental programme is continuing to identify the important chemical reactions of iodine with silver, indium and cadmium and determine the kinetic data needed to conduct chemical kinetics calculations.

Experiments conducted in Hungary and Finland have shown that, during a core melt accident with vessel melt-through and air ingress, the ruthenium released from the fuel can be transported as metastable gaseous RuO_4 to the free volume of the containment although a significant amount of the ruthenium remains on the pipes. Additional data on the behaviour of ruthenium in the RCS were collected during a test conducted at the CEA's VERDON facility as part of the ISTP (Section 5.5.2.2) to study in-air degradation of the irradiated fuel, FP releases and associated transfers to the RCS and are collected as part of the OECD STEM project.

Lastly, the experimental data on revolatilisation of FPs deposited in the RCS are insufficient for quantifying the possible effect of this process on releases during a core melt accident. Additional experiments aimed at allowing this quantification are being conducted as part of the OECD STEM project conducted by IRSN and which began in 2011.

► Fission product chemistry in the containment

During a core melt accident, the two FPs whose chemistry in the containment can strongly influence radioactive releases and their consequences are iodine and ruthenium¹². This is due to the fact that both FPs can exist in gaseous form under the conditions prevailing in the containment. These gaseous species may be released to the environment by either direct or indirect leaks from the containment or during implementation of the containment filtered venting procedure.

Iodine

Many experimental and theoretical studies have been conducted on iodine chemistry in the containment during a core melt accident. These studies have looked at iodine chemistry in the sump and the containment atmosphere, its interactions with the surfaces of the containment and the influence of radiation on these various processes [3]. The available models describing this chemistry are either mechanistic, spanning several hundred reactions, or simplified to cover a smaller range of reactions. The latter type of model is generally used in the integral codes such as ASTEC [65].

12. Other FPs, such as caesium, may significantly contribute to the radiological consequences of a core melt accident with containment failure. However, their chemistry in the containment has not a strong influence on their behaviour during releases.

Despite these research efforts, substantial uncertainties remain about the estimation of radioactive iodine releases during a core melt accident. This was brought to the fore during the OECD International Standard Problem (ISP) exercises, which compare the results of calculations and experiments. ISP 41 dealt with iodine chemistry in the containment for an RTF experiment conducted by AECL. ISP 46 dealt with iodine chemistry in the RCS and the containment for the *Phebus* FPT1 experiment. This is particularly true for the formation of organic iodides in the containment atmosphere. The EPICUR, OECD STEM, and OECD BIP experimental programmes aim to provide new data on this matter as well as certain aspects related to liquid-phase and gas-phase iodine radiolysis.

The effect of spraying, which enables partial capture of iodine in droplets, has been quantified and validated models are available.

Analytical experiments have revealed that the interactions between iodine aerosols and the plates of hydrogen recombiners could lead to the formation of gaseous iodine in the containment. A larger-scale experiment was conducted as part of the OECD/NEA THAI project led by Becker Technology in Germany [53]. The transposition of these results to the recombiners in the containment shows that the production of gaseous iodine by the recombiners in the containment is not zero but lower than that due to other sources such as gaseous iodine from the RCS.

Another source of gaseous iodine in the containment is related to radiation-induced decomposition of the metal halides (e.g., caesium iodide) and iodine oxides deposited on the walls of the containment. This is one of the themes of the experimental studies of the OECD STEM project conducted by IRSN which began in 2011.

Ruthenium

Regarding ruthenium chemistry in the containment during a core melt accident, the experiments conducted show that part of the ruthenium can be in gaseous form in the containment. Experiments have made it possible to study adsorption of gaseous ruthenium on the surfaces of the containment and its desorption from the surfaces as well as revolatilisation of ruthenium deposited or trapped in the liquid phase of the sump under the action of radiation [59, 63]. The kinetics of the various processes have been established so that it is possible to assess gaseous ruthenium concentrations in the containment during a core melt accident. Ruthenium transport in the RCS is being studied as part of the OECD STEM project.

5.5.7. Conclusion

Releases and transfers of FPs in the RCS during a core melt accident has been the subject of many research programmes. Releases of FPs from fuel inside the reactor core are in overall terms well understood. Nevertheless, improvements in physical modelling are expected between now and late 2015 on the basis of the results of a few additional tests (VERDON programme conducted by the CEA as part of the ISTEP). The current state of knowledge of releases from corium outside the vessel seems satisfactory.

Transfers and behaviour of FPs in the RCS and the containment are governed by physical processes that depend primarily on aerosol physics and chemical processes. Aerosol physics is well established and the corresponding models seem satisfactory. Nevertheless, it would be desirable to have additional data in order to better analyse some complex situations, such as aerosols in the secondary sides of steam generators during an accident with steam generator tube rupture. The situation is different for the chemical processes. Although the analysis of the results of the programmes conducted between 1990 and 2010, particularly those of the Phebus FP programme, have made it possible to improve understanding and modelling of the most important processes, additional programmes remain necessary to reduce the uncertainties, particularly regarding iodine chemistry. Improvements in modelling are expected to be made by late 2015 on the basis of the experimental results of the ISTP programmes (CHIP, EPICUR) and OCDE BIP-2, THAI-2 and STEM. The research conducted on this topic brings aspects of chemical kinetics into play in complex reaction systems.

The models developed are implemented in computer codes, such as ASTEC. These codes play a role in the capitalisation of knowledge and are used to conduct safety studies for power reactors.

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