FISSION PRODUCT RELEASE MECHANISMS: RESEARCH IN CANADA

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Abstract

Research and development activities in Canada on fission product release and fuel behaviour during normal and reactor accident conditions is outlined in support of industry and regulatory requirements. An overview of key mechanisms and phenomena identified which impact the fission product release behaviour highlighting the contribution of Canadian research is reviewed. The structure of the research program, target research areas as well as the available facilities in Canada is also described.

1. Introduction:

Atomic Energy of Canada Limited (AECL) developed the concept of the CANadian Deuterium Uranium Pressurized Heavy Water Reactor (CANDU-PHWR) in the early 1960's based on the use of natural uranium and also provided the necessary infrastructure, research and technical support for the implementation of this reactor design. The natural uranium fuel cycle means that there is no requirement for uranium enrichment making this design of interest for countries with natural uranium resources but without uranium enrichment capability. The use of natural uranium requires a large reactor core and, to avoid the need to manufacture a large pressure vessel, a pressure tube design was implemented. This design also means that reactivity control devices do not need to be associated with the fuel assembly, thus simplifying fuel assembly design. Today, the CANDU-PHWR is a successful commercial design with units built in Canada, Argentina, China, India, Pakistan, South Korea, and Romania.

In the CANDU-PHWR fuel design,[1] the number of fuel rods in the bundle has increased from seven in early assemblies for the Nuclear Power Demonstration reactor (NPD), nineteen for the later NPD fuel and Douglas Point commercial prototype, twenty eight for the Pickering reactors, thirty seven for Bruce, Darlington, and early CANDU 6 reactors, and forty three for CANFLEX fuel.[2]

Since the first commercial CANDU reactor operation in 1971 until today more than 800,000 fuel elements have been irradiated in all PHW reactors. The general fuel performance in PHW reactors has been very good.[3-5] For example, operating CANDU plants have an average fuel assembly defect rate of less than 0.02%.

In the 900 MW CANDU reactors, the fuel bundles are operated at about 970 kW maximum power which renders a fuel element maximum linear power of about 60 kW/m with UO_2 pellet centerline temperature around 1700°C. The fuel bundle discharge burnup is less than 10 MWd/kgU. Because these conditions can be associated with substantial fission product release, the release characteristics of fuel elements during normal operation and under accident conditions is an important area of research for the CANDU design.

CANDU reactors have the flexibility to use a number of fuel cycles. This capability is the driver for advance fuel cycles which provide significant economic or environmental benefits. [3,6-8] Between them the most promising options are:

- Use of slightly enriched uranium;
- Use of spent PWR fuel and mixed-oxide fuel cycles;
- Destruction of military plutonium and other actinide wastes;
- Use of burnable poisons to reduce core void reactivity; and
- Use of thorium.

The assessment of each of these options requires additional fission product release research directed to support fuel design verification, failure mechanisms and fuel performance evaluations.

In each country, the drivers for applied research depend upon the relationship between the regulatory environment, nuclear industry organization and overall technology development efforts.

This paper describes the Canadian regulatory environment, industry organization, research activities in fission product release, application of this research and future areas of interest.

2. Canadian Regulatory Environment

The Canadian Nuclear Safety Commission (CNSC) is the nuclear regulatory body in Canada. The mission of the CNSC is to regulate the use of nuclear energy and materials to protect health, safety security and the environment and to respect Canada's international commitments on the peaceful use of nuclear energy. This is accomplished by the work of a Commission, a quasi-judicial tribunal comprising of up to seven members, and an organization of over 500 staff.

The Canadian regulatory philosophy is based on two accountability principles:

The licensees are directly responsible for ensuring that their licensed activities are managed so as to protect health, safety, security and the environment, and to respect Canada's international commitments on the peaceful use of nuclear energy.

The CNSC is responsible to the Canadian public for regulating licensees to assure that they are properly discharging their responsibilities, as stated above.

The licensees are expected to fulfill their responsibilities by:

- Implementing a managed system for controlling the risks associated with operation of the facility.
- Developing an organizational culture that is committed to ensuring the safe operation of the facility.
- Defining and operating within the safe operating limits for the facility's systems, structures and components.
- Monitoring both human and facility performance to ensure that the facility and the personnel perform as expected.

The CNSC fulfils its responsibilities by:

- Establishing the regulatory framework and ensuring that stakeholders understand it

- Establishing and implementing programs to ensure high levels of regulatory compliance by Licensees and conformity to international commitments
- Cooperating effectively at both the national and international levels.

Consistent with the Canadian regulatory philosophy, it is the industry (i.e. the Nuclear Power Plant operators and the government of Canada, acting through its agent Atomic Energy of Canada Ltd.) that is responsible for performing nuclear safety research. The Canadian Nuclear Safety Commission (CNSC) has a relatively small regulatory R&D program to obtain knowledge and information needed to support its regulatory mission, which they use mainly to perform specific independent confirmatory or investigative work in support of further understanding the status of various potential safety issues and concerns. There is a formal regulatory requirement (under the provisions of regulatory document S-99) for the power reactor licensees to report periodically on their Nuclear Safety R&D. Comprehensive information (R&D Reports, Data Reports and Progress Reports) is provided to the regulator as required in the course of resolving specific outstanding issues. The regulator strongly influences the scope and objectives of the industry's Nuclear Safety R&D program through a number of means, including participation in an annual R&D seminar with industry, quarterly meetings with the CANDU Owners Group Nuclear Safety Committee, establishment of regulatory Action Items (including Generic Action Items applicable to all plants) and by defining closure criteria as part of the Action Item resolution process.

3. The Canadian Nuclear Industry

Currently the nuclear industry in Canada has five main participant organizations. They are:

Atomic Energy of Canada Ltd.: AECL is the reactor design and research organization. It provides technical support to the existing reactors, develops advanced fuel and new reactor designs.

Ontario Power Generation: Owned by the province of Ontario, it is the largest electrical utility in Ontario and operates 10 nuclear reactor units and several hydroelectric and fossil fuelled plants.

Bruce Power L.P.: It is the largest privately owned nuclear electrical utility (Ontario) and operates 6 reactors. Bruce Power is currently refurbishing 2 additional reactors expected to resume operations by 2010.

Hydro Quebec: Owned by the province of Quebec, It has a very extensive hydroelectric generation capacity and operates one nuclear reactor.

New Brunswick Power: Owned by the province of New Brunswick, it operates one nuclear reactor together with a number of hydroelectric and fossil fuelled plants.

These five organizations co-ordinate and fund diverse activities that are coordinated by the CANDU Owners Group (COG). COG directs its efforts to provide programs for cooperation, mutual assistance and exchange of information for the support, development, operation, maintenance and economics of CANDU technology. In addition to the Canadian participants, COG membership includes organization in 6 countries: Argentina, China, India, Pakistan, Romania and South Korea.

Under the COG Research and Development Program, research on fission products release and its application to both station support and safety analysis are performed.

Chalk River Laboratories

AECL's major research and development efforts take place at the Chalk River Laboratories (CRL). The National Research Universal (NRU) reactor has been operating at CRL since 1957. NRU is Canada's only major materials and fuel testing reactor used to support and advance the CANDU design. The fuel testing is performed in the two pressure and temperature controlled irradiation loops in NRU. In particular the BTF, Sweep-Gas test series and other US sponsored tests (i,e,.FLHT series) were performed in the NRU reactor. CRL also has a wide range of laboratories and fabrication facilities that support the in-reactor test programs. The hot-cell facilities have been extensively used in support for out-of-pile experiments dedicated to the study of fission product release from CANDU fuel in a variety of environmental conditions.

In these out-of-pile experiments, seven different types of experimental rigs have been used at CRL, depending on the temperature range and size of specimen to be heated. For all experiments, monitoring and control of the gas environment have been a priority; in particular, control of the oxygen potential to which the fuel is exposed. One of the key features of the CRL program has been on-line measurement of the oxygen potential in the gas stream, which allows for the fuel oxidation kinetics to be calculated. Another key feature of these tests has been a direct measurement of the fission-product release rates, using a gamma-ray spectrometer, which views the heated specimen through a collimated aperture. A second spectrometer is used to monitor activity in the exhaust gas swept out of the furnace.

University Network of Excellence in Nuclear Engineering (UNENE)

The University Network of Excellence in Nuclear Engineering (UNENE) is an alliance of universities, nuclear power utilities, research and regulatory agencies for the support and development of nuclear education, research and development capability in Canadian universities.

Industrial Research Chairs (IRC) at seven universities in the province of Ontario (i.e., University of Toronto, McMaster University, University of Waterloo, University of Western Ontario, Queen's University, University of Ontario Institute of Technology (UOIT) and Royal Military College of Canada (RMC)) are being supported by the nuclear industry as part of the UNENE partnership in collaboration with the Natural Sciences and Engineering Research Council of Canada to promote research and development in nuclear engineering by bringing together Canadian industrial needs and interests, together with university talent and facilities. The RMC IRC is in the field of Nuclear Fuel that focuses on: (i) physical chemistry and basic science of nuclear fuels; (ii) the development of techniques for defective-fuel monitoring and location of defective fuel bundles; (iii) modeling of nuclear fuel and fission product release behaviour during normal and reactor accident conditions (for improved operational support, fuel performance prediction and reactor safety code analysis); and (iv) advanced fuel designs for low void reactivity fuel and next Generation IV reactors. A Chair in Nuclear Fuel at the UOIT is also being supported by the uranium company CAMECO Corporation, in which the Chair focuses on nuclear fuel conversion and nuclear waste management.

4. Research Selection Process

In Canada, safety research is almost entirely funded and carried out by the industry. As indicated previously, the CNSC has a relatively small regulatory research program, which they use mainly to perform specific independent confirmatory or investigative work programs on safety issues. However, the CNSC has the power to require that answers to specific safety questions be provided by the industry - through research when necessary - and through this mechanism has a direct influence on the issues addressed in the nuclear safety research program conducted by industry. While regulators and industry share a common goal of performing research to support safe plant operation differences can exist between industry and regulator viewpoints on the need and purpose of research. While industry recognises the importance of research in assuring safe plant operation, it also performs research to reduce operating costs and to improve efficiency and reliability of operation. In contrast, regulators, consistent with their mandate, are often interested in performing research in greater depth or for a wider range of conditions, as a means to confirm the robustness of the safety case.

The process for selecting nuclear research programs to be undertaken in Canada on behalf of power reactor licensees is based on a top-down process to identify overall needs and strategies for issue resolution from an industry perspective and a bottom-up process that incorporates needs of individual participants and defines specific potential work activities to address the overall requirements. In the area of nuclear safety, the CANDU Owners Group establishes and maintains a strategic plan for collaborative research to be performed in this area. The principal strategic objectives of the program are safe plant operation and regulatory compliance. The plan identifies strategic focus areas, which currently include closure of CNSC Generic Action Items, Improvement in Operating and Safety Margins, Plant Aging Management, Support for Plant Design Improvements and enhanced Plant Reliability.

Within each strategic focus area, research issues are identified based on direction provided by the COG Nuclear Safety Committee, whose mandate includes development of common strategies and plans to resolve issues that are common across the industry. These issues, and the associated resolution strategies, form the basis for developing Statements of Requirements for individual work packages. The Statements of Requirements are reviewed during the annual research planning cycle by the Technical Committees and discipline-specific working groups to ensure that the overall needs are met, and the COG Board of Directors approves the resulting research program.

5. Research on Fission Product Release

The purpose of the research on fission product release has evolved during the years. Initially, research was directed to the basic understanding of the main mechanisms that control the releases. All performed experiments can be roughly grouped under the following categories:

- Basic release phenomena
- Governing phenomena during normal operation conditions
- Failed fuel release behavior (NOC)
- Governing phenomena during accident conditions
- Sheath failure mechanisms
- Release of noble gases and volatile fission products
- Release of less-volatile fission products
- Impact of fuel stochiometry and volatilization
- Fission product transport
- Code validation

In addition of the experiments performed in Canada, results obtained in other countries were also included in the knowledge base for each of these categories, in particular, the experimental series HI and VI performed at ORNL and the Heva and Vercors performed at Caradache.

The results of the research on these categories were used in the following areas:

- Understanding and ranking of release and transport phenomena
- Develop codes for the prediction of releases under NOC and accidents
- Fuel design
- Establish safety and operation limits
- Reactor licensing

Below, some of these areas of research will be detailed for both normal and accident conditions.

5.1 Normal Operating Conditions

Under operating conditions, the fission gas release experimental results were mainly used on model development, model validation and fuel design. Many irradiations performed in the NRU reactor were applied for the increase the phenomena knowledge basis and to code development/validation. Validated codes are employed in the development of advance fuel designs and assessment of pre-accident fuel conditions in safety analysis. Also determination of iodine behavior in containment and water pools were incorporated directly in operational limits and safety analysis.

Due to the on-power refueling capability of the CANDU reactors, failed fuel detection and localization systems have been implemented in the reactors to expedite the removal of failed fuel. To support reactor operation with failed fuel and to decrease occupational dose, in-pile studies of the activity release mechanisms from failed fuel were completed and the investigation of the impact of fuel stoichiometry changes on fission product releases was initiated. The degree of development of these two areas is described below.

In-reactor failed fuel behavior

With the occurrence of a fuel sheath failure during normal reactor operation, coolant can enter into the fuel-to-sheath gap and fission products (i.e., notably the volatile species of noble gas and iodine) will be released into the primary coolant.[9-13] With the entry of high-pressure coolant through the defect, the fuel may be oxidized which can potentially enhance the fission product release.[14] Iodine release can also occur on reactor shutdown when the temperature in the fuel-to-sheath gap drops below the saturation temperature, permitting liquid water to dissolve the soluble iodine species in the gap resulting in an "iodine-spiking" phenomenon.[15-17] Iodine-rich water remaining in the gap on the subsequent startup can also be released as the size of the gap is reduced with fuel expansion.[18] It is therefore desirable to discharge defective fuel bundles as soon as possible since the release of fission products and fuel debris into the primary heat transport system can increase the circuit contamination and radiation exposure during maintenance.[19] Hence, a better understanding of defective fuel behaviour is required in order to develop an improved methodology for fuel-failure monitoring and coolant-activity prediction.

Previous models have been developed for fuel-failure monitoring in both light water reactors and the CANDU reactor based on a steady-state coolant activity analysis.[11,20-22] These models employ an empirical "Booth-diffusion" type model[23] for release from the fuel matrix into the fuel-to-sheath gap and a first-order kinetic model to account for the transport, holdup and release of the short-lived fission products from the gap into the primary coolant. In these tools,[11,20-22] a fission product release model is fit to coolant activity data and the fitted parameters are compared to well characterized values where the defect state is known in order to ascertain the fuel-defect condition. The application of these previous models specifically requires that steady-state (equilibrium) conditions have been met. On the other hand, a preponderance of coolant activity data involves a time dependence that can be associated with reactor shutdown/startup and bundle shifting operations, particularly in the CANDU reactor design with its ability for on-power refueling. Hence, a more general finite-element numerical treatment, i.e., the Steady-state and Transient Activity Release (STAR) code, has been developed, which is able to predict the time-dependent activity behaviour of the volatile fission products in the fuel grain, fuel-to-sheath gap and primary coolant for defective fuel elements.[24] This treatment is applicable for all volatile isotopes of interest incorporating effects of radioactive decay and neutron transmutation. It further respects the overall mass balance for a time-varying fission product generation and coolant purification flow history under all reactor operating conditions.

Changes in Fuel Stoichiometry

With defective fuel, the sheath no longer provides a barrier between the fuel and primary coolant so that oxidation of both the fuel and inner surface of the sheath may occur. The presence of water vapour in the fuel-to-sheath gap can lead to degradation in the thermal performance of the fuel element.[14] For instance, the gap heat transfer coefficient will change as steam and hydrogen replace the helium fill gas.[14,25] The fuel oxidation process itself can lead to a degraded thermal conductivity in the hyperstoichiometric fuel and a lower incipient melting temperature.[26-28] The release behaviour of fission products from the fuel element may also be enhanced due to a greater mobility of fission products in the hyperstoichiometric fuel.[29] Limited measurements of the oxygen-to-metal (O/M) ratio have been carried out on irradiated fuel specimens from defective commercial fuel rods.[30-32]

Although simple models have been developed to describe the fuel oxidation kinetics in operating defective fuel rods,[14,27] these treatments specifically ignore the axial migration of steam/hydrogen in the fuel-to-clad gap (i.e., gap oxygen potential). Moreover, these analyses neglect the effect of interstitial oxygen migration due to axial diffusion and thermo-diffusion in a temperature gradient. However, more recent mechanistic treatments have been proposed to predict fuel-oxidation behaviour in operating defective fuel elements in order to better assess the thermal performance of defective fuel.[33,34] The latter model has been benchmarked using recent O/M measurements for pellet samples taken from spent defective fuel elements based on a coulometric titration method as performed at the Chalk River Laboratories.[32,34] These theoretical developments therefore provide a better understanding on how defective fuel behaves and what parameters control this behaviour.

5.2 Accident Conditions

During postulated CANDU accidents the reactor fuel is estimated to be exposed to a variety of conditions. These conditions are dynamic and, during the course of an accident, the fuel could be exposed to temperatures ranging between 600 to 2400°C and from highly oxidizing to mildly reducing environments.

The exposure of fuel to these environments and temperatures will affect its release performance. For example the exposure of fuel to oxidizing environments will increase the oxygen potential of the fuel after the Zircaloy sheath is totally oxidized. As a result, the fuel stoichiometry will increase, changing the thermal and material properties as mentioned above. This stoichiometric modification will also have an effect on the fission product chemical speciation and consequently, the release characteristics.

In reducing environments, due to the low oxygen concentration in the coolant, the Zircaloy sheath may extract oxygen for the UO_2. This attack will produce a reduction in the fuel stoichiometry that will also affect the fuel thermal-mechanical properties and fission product speciation.

In the assessment of the source term to containment, individual release calculations for about 800 fission product and actinide radionuclides are not practical. This is due in part to the significant amount of computer time needed for a full core analysis. Since many isotopes have similar release characteristics, the concept of fission product release groups has been used in safety analysis to reduce necessary computation requirements.

Several experimental in-pile and out-of-pile research programs are actively studying the fission product release characteristics of all observable fission products. These programs provide evidence of the release characteristics of certain fission products and help in the integration of release groups. Also, equilibrium thermodynamic calculations are very powerful tools in the assessment of the most likely chemical speciation and consequently, in the expected release behaviour.

In the following sections, details of the knowledge obtained from these research programs are summarized.

Diffusion in the Fuel Matrix

The intrinsic mobility will depend on the charge state of the atomic species that migrates by volume diffusion through the lattice of the fuel. When fission product atoms reach a free surface they may form thermodynamically-favoured compounds. The chemical form will determine the subsequent gas-phase mass transport (*i.e.*, vaporization). The mobility in the fuel is also determined by the solubility of the fission product in the UO_2 lattice. In oxide fuels, the chemical state can be typically grouped as; volatile fission products (Kr, Xe, Br, I); metallic precipitates (alloys) (Mo, Tc, Ru, Pd, Ag, Cd, In, Sb, Te); ceramic precipitates (oxides) (Rb, Cs, Ba, Zr, Nb, Mo, Te); and oxides dissolved in the fuel (Sr, Zr, Nb, La, Cr, Pr, Nd, Pm, Sm).[35] During irradiation, the noble gases are distributed dynamically between a fission-induced solution within the oxide lattice and their precipitation into intragranular and intergranular bubbles.

The release of short-lived fission gases from uranium dioxide during irradiation has been extensively studied in a number of experiments with single and polycrystalline fuel specimens,[36-39] and with swept assemblies in which fuel-to-sheath gap of an intact operating fuel element was continually purged.[40-43] These experiments generally demonstrate the diffusion of noble gas atoms and iodine in UO_2 is the rate-determining mechanism for release during steady-state operation. At lower fuel temperatures (<1000°C) diffusion is independent of temperature (athermal) but is enhanced as a result of the fission process;[38,44] however, for the shorter-lived isotopes, recoil effects can also become important. [19,45] As shown in these various experiments, the diffusion coefficients of krypton, xenon and iodine were found to be similar in magnitude and in their temperature-dependent behaviour. Both thermally-activated and athermal diffusion are implicated as the main release mechanisms in these studies since the release-to-birth rate (R/B) ratio is observed to vary inversely as the square root of the decay constant. This type of behaviour was predicted over thirty years ago by Booth using diffusion theory.[46-48]

An increase in the oxygen-to-uranium (O/U) ratio results in the direct enhancement of the diffusional release of fission products from the fuel matrix.[29,49-52] Experimental work has indicated that xenon diffusion occurs as a neutral tri-vacancy in uranium dioxide, in agreement with the theoretical calculations of Grimes and Catlow.[53] These calculations also indicate that in hyperstoichiometric fuel (UO_{2+x}), the most stable solution site is the uranium vacancy.[53] This finding supports the model of Killeen and Turnbull for the noble gas diffusion coefficient in UO_{2+x} (for x in the range of 0.005 to 0.1), where it has been assumed that the gas atom mobility is influenced by the presence of the uranium cation vacancies in which Frenkel and Schottky equilibria govern the isolated point defects.[52] This model for the diffusion coefficient in agreement with annealing test results in CO/CO_2, and with the experimental work of Lindner and Matzke.[49,52] The model has been used to describe the in-pile steady-state release of fission gas from defective fuel rods.[14] This treatment has also been successful in describing the cesium release kinetics in out-of-pile experiments conducted at high temperature in steam, i.e., a reduced release from Zircaloy-clad fuel specimens, compared to that with bare fuel fragments, can be attributed to limited fuel oxidation, arising from a lower oxygen potential due to hydrogen production from metal-water reaction.[54,55]

A diffusional release of volatile fission products (e.g., Kr, I, Cs, Te) has been observed in a number of high-temperature, post-irradiation, annealing experiments with trace-irradiated polycrystalline UO_2 fuel samples,[56] and high-burnup specimens taken from commercial spent fuel rods.[57-66] In an annealing experiment with spent fuel that was conducted in a hydrogen atmosphere, the measured release kinetics (and hence diffusivities) of I, Cs and Ba were similar; in a steam test, where the Zircaloy cladding had been completely oxidized, similar release kinetics were observed for I, Cs, Xe and Te.[67] An idealized model originally introduced by Booth,[46] has been used extensively to interpret the diffusive release of the more volatile fission products in these post-irradiation annealing experiments. A square-root behaviour is theoretically predicted for the release fraction as a function of the anneal time. The equivalent-sphere model has been extended for a non-uniform distribution that develops in the fuel grains during the irradiation period when the fuel temperature is sufficiently high to allow for diffusion to occur.[68] The model has also been generalized to account for a time-dependent diffusivity that may arise form changing temperature and fuel stoichiometry conditions.[55,60,65] Several empirical models, based on a diffusion treatment and annealing test data, have been developed for source-term analysis.[60,65,69,70] However, in many out-of-pile experiments, the release kinetics are found to be much more rapid than that expected from diffusion theory alone; for example, enhanced kinetics, observed during temperature ramp-up, may result from a release of the stored inventory on the grain boundaries.[55,61-63,71] Following the initial release, a slower diffusional component is typically observed.

Fission Product Vaporization from Fuel Surface

The release kinetics of the volatile or relatively volatile fission products (Xe, Kr, Cs, I, Te, Sb) can be described by a rate-limiting process of solid-state diffusion through the UO_2 fuel matrix.[60,67,72] However, for less-volatile fission products (*e.g.*, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ba, La, Ce, Pr, Nd), their escape from free surfaces into the gas phase may be so difficult that the surface or gas-phase transport processes can control the overall kinetics. This rate-limiting step is related to the chemical state of the fission products (*i.e.*, vapour pressure of the thermodynamically-favoured compounds) that are formed at the fuel surface, and to the mass transfer from the free surface of the fuel to the bulk, hydrogen-steam, and gas flow.[67,69,72] The chemical state of the fission products will depend on the temperature and oxygen potential of the gas environment. The oxygen potential can change as a result of hydrogen production from the steam oxidation of structural materials (Zircaloy) within the damaged core. The equilibrium chemical composition can be obtained (where thermodynamic data permit) by a minimization of the free energy for a multi-component system consisting of a condensed phase (i.e., fuel plus fission products) and a gas phase (steam, hydrogen and gaseous fission product species).[72-75] The vapour species released into the bulk environment may, typically, be found in either an elemental/compound form, or as an oxide or hydroxide.

The chemical form (e.g., metal versus oxide) of the fission product can significantly affect its volatility. The oxygen potentials required for the formation of fission product oxides can be obtained from an Ellingham diagram.[35,67,73] Here, the most stable oxides (e.g., Ce_2O_3 and La_2O_3) are formed at low oxygen potentials. Also quite stable are the oxides BaO, SrO and Eu_2O_3. On the other hand, oxides requiring relatively high oxygen potentials for formation include the species TeO_2, Sb_2O_3 and RuO_4. Consequently, for typical, high-temperature, reactor accident conditions (with atmospheric ratios of H_2/H_2O of ten to one-tenth), the La, Ce, Eu, Sr, and Ba fission products should be in the form of oxides, while the Ru, Te, and Sb fission products should be found as metals.

Small releases of Ba, Sr and Eu are therefore expected in a steam environment for the low-volatility oxides in the fuel. For example, in the Vertical Induction (VI) tests at the Oak Ridge National Laboratory, small releases of Eu have been observed in steam ($<0.01\%$).[76] Releases of Ba, Sr and Eu measured in the Severe Fuel Damage tests in the Power Burst Facility and Three Mile Island Unit 2 accident were also small (typically 1% or less).[77] In contrast, much higher Eu releases (19-57%) were observed in the VI hydrogen tests, under similar temperature conditions, where higher-volatility metallics may have formed.[76] Similarly, in-pile measurements of fission product releases in the ST-1 and ST-2 hydrogen experiments at the Sandia National Laboratories indicate much higher Ba and Sr releases of several percent and up to 15% for Eu.[77,78]

For the refractory metals, Ru and Mo, the oxides (RuO_4 and MoO_2) are much more volatile than the elements, so that high releases would be expected only under strongly oxidizing conditions (high oxygen potentials). In the VI-3 test (2700 K in steam) only 5% of the Ru was released from the fuel, while at 1600 K almost 100% of the Ru was released in experiments conducted in air at the Chalk River Laboratories following significant oxidation of bare fuel samples.[79] The observed Ru releases are consistent with thermodynamic arguments.[80]

Matrix Stripping (Volatilization)

Alexander[81] has observed that in oxidizing environments at temperatures of 2100 K or higher, the volatilization of diverse species like Mo, Y, La and Ba exhibited the same activation energy for release. Neither the nature of the species nor the nature of the solid state in the UO_2 matrix showed a significant effect. Cox *et al.*[82] also reported significant weight loss of UO_2 in steam after a certain period of time. The weight loss increased with increasing temperature. These two observations indicate a volatilization of uranium mass which, in turn, will result in a release of fission products from the fuel matrix.

If the Zircaloy sheath is severely oxidized, the oxidizing environment can react with UO_2, and, under these conditions, the UO_2 will incorporate excess oxygen to form hyperstoichiometric UO_{2+x} or be converted to a higher oxide. At temperatures above 1800 K, UO_{2+x} is the stable condensed phase in both air and steam. A significant vapour pressure of uranium bearing species is predicted at equilibrium. Since the gases in contact with the fuel do not constitute a closed system, the condensed phase is vaporized at a relatively rapid rate due to incongruent vaporization of the UO_{2+x} matrix. As the matrix is volatilized, the remaining noble gases (Xe, Kr) and volatiles Cs, I, Br, Rb) will be released from the volatilized fuel volume. The low volatile fission products become concentrated at the fuel surface. At this location they can accumulate, vaporize or entrain in the flowing gases as particulates. This process has been described by Alexander[81] as "matrix stripping" or by Cox *et al.* as volatilization.[82,83]

UO_3 or $UO_2(OH)_2$ were identified at the most likely uranium-bearing species in the volatilization process. However, the maximum calculated rate of volatilization for both UO_3 and $UO_2(OH)_2$

(using a Langmuir formalism), exceeded the measured rate of mass loss. The vapour pressure of $UO_2(OH)_2$ (and volatility of this species) exhibit less of a sensitivity to temperature than UO_3 (in stoichiometric steam). In fact, the temperature dependence of the observed mass loss process shows better agreement with calculations based on UO_3. As the Langmuir formalism over-predicts the observed behaviour, phenomena such as re-condensation and mass transport effects are also believed to be important. Conditions close to the fuel, like flow velocity and oxygen partial pressure, become important for the mass transfer calculation.

Ceramographic examination of both irradiated and un-irradiated samples showed that volatilization and pore growth occurred preferentially along some grain boundaries, while other boundaries do not participate as readily in the reaction.[83] This preferential reaction at localized sites is an indication that a surface-sensitive process is limiting the overall kinetics of formation of gaseous UO_3 at the UO_{2+x} surface.

For the case of high-volatility fission products, in which the release process is controlled by diffusion through the fuel grains, the volatilization will decrease the time required for these fission products to reach the open surfaces. An instantaneous release of the volatile fission products contained in the volatilized UO_2 volume is supported by the observations.

In the case of the low-volatile fission products, for which the controlling process is vaporization from open surfaces, the volatilization process will increase the concentration of these fission products in the open surfaces. However, the effect of this increased concentration of low-volatile fission products on the uranium volatilization rate has not yet been determined.

UO_2/Zircaloy Interaction

Uranium and zirconium can form an alloy. The melting point of the alloy varies with its composition, and can be as low as ~1150°C. This alloy can be formed through reduction of the UO_2(to UO_{2-x} + U) by Zircaloy which is still in the solid state.

With contact between Zircaloy and UO_2, a series of metallographic structures will develop,[84,85] i.e., outward from the fuel pellet surface one observes: (i) a mixture of Zr_x(U) and U, Zr); a layer of (U, Zr); (iii) a layer of Zr_x(O); and (iv) the remaining of the Zircaloy sheath. It has been shown that the presence of a CANLUB layer can inhibit the chemical attack of UO_2 by the Zircaloy. In this process, some fuel "liquefaction" may result in the fuel element, well below the melting point of UO_2. The occurrence of this liquified fuel can contribute to an enhanced fission product release as a consequence of the fuel reduction.

UO_2 Dissolution by Molten Zircaloy

If fuel heatup in an accident is sufficient to produce molten Zircaloy, the Zircaloy can act to reduce the UO_2 producing a liquid (U, Zr)O + $(U, Zr)_{O2-x}$ mixture. The (U, Zr)O is a liquid at temperatures which are significantly below the melting point of UO_2 (~1150°C). This dissolution and liquefaction of the UO_2 matrix will result in large fission product release of all isotopes which either have a large partial pressure or which can form volatile compounds in the prevailing environment.

Many experiments have been carried out using unirradiated UO_2 to investigate this phenomenon. Dienst *et al.*[84] and Nikolopoulos *et al.*[85] give the results of crucible experiments in argon for temperatures in the range 1800°C to 2000°C. In these experiments, the chemical attack of the UO_2 was sufficient to disintegrate the crucibles. This large-scale chemical attack of the UO_2 by the Zircaloy required intimate contact between the fuel and the molten cladding for a period of >100 seconds. This requirement is due to the fact that O-poor Zircaloy does not wet the UO_2. Therefore, the molten Zircaloy must be oxidized by the UO_2 before it can wet the UO_2, penetrate along cracks and over the entire available surface area and significantly affect the UO_2 morphology. Oxidation of the Zircaloy by the UO_2 occurs as quickly as oxidation of Zircaloy by steam, since the rate-limiting step is diffusion of the oxygen in the Zircaloy.

Kim *et al.*[86] reports the results of experiments similar to those described above. These experiments confirm that the chemical attack of UO_2 by Zircaloy acts along exposed surfaces and cracks so that the wetting behaviour of the molten Zircaloy is important. The interaction therefore develops in layers for simple geometries, and the layer growth can be described using parabolic rate kinetics. These experiments also confirm the expected result that, while O-rich Zircaloy wets the UO_2 more completely, the dissolution rate is reduced due to the fact that the molten Zircaloy already contains some O and so the reaction with O from the UO_2 is less energetically favourable.

Rosinger *et al.*[87] and Hayward *et al.*[88,89] report experiments that are intended to more closely represent CANDU fuel. These experiments examine dissolution of unirradiated UO_2 by molten Zircaloy for temperatures of 1970°C to 2350°C. These experiments indicate that, if heatup is slow enough (i.e., the Zircaloy oxidation is sufficient to allow it to wet the fuel element), the molten Zircaloy will not drip off of the fuel element and will then reduce the UO_2. The reduction of the UO_2 will dissolve a percentage of the fuel element which depends on the temperature of the melt and the initial oxygen content of the Zircaloy. These experiments indicate that O-free Zircaloy will dissolve ~60% more UO_2 than $Zr_x(O)$ if it is able to wet the fuel.

Indications of dissolution of UO_2 by molten Zircaloy in fission product release experiments have been limited to experiments in reducing environments. This is due to the fact that, in oxidizing environments, experiments which have heated up to temperatures sufficient to melt Zircaloy in an oxidizing environment have heavily oxidized Zircaloy cladding before reaching these high temperatures. ZrO_2 does not reduce UO_2. Only in experiments in which Zr or $Zr_x(O)$ are present in significant quantities at the time of melting does significant UO_2 dissolution take place.

The ST-1[90] and VI-4[91] experiments were both LWR fuel experiments in which fuel was heated to 2400-2500 K in a H-rich gas flow. These experiments showed evidence of attack of UO_2 by molten Zircaloy and formation of the low melting point (U,Zr) eutectic. The attack was sufficient that macroscopic dissolution of the UO_2 matrix occurred. These processes occur at such high temperature, however, that any additional fission product release is swamped by the already high release rate associated with high temperatures for volatile fission products and noble gases. Release of non-volatiles did not seem to be affected, except in the case of Eu, which had its release enhanced, and Sb and Te, which were released in much lower amounts than would be expected in an oxidizing environment in which molten Zircaloy-UO_2 interaction does not take place. The reduced release of Sb and Te is not directly related to attack of the UO_2 by molten Zircaloy, but to the presence of metallic Zircaloy to react with. The enhanced release of Eu is attributed to the reducing chemical environment and not to the attack of the UO_2 by molten Zircaloy.

Fuel Frothing

Various processes have been described which "liquify" the UO_2, that is, they result in a significant disruption of the UO_2 matrix. They will lead to a release of fission gases and volatile fission products which are retained in the fuel matrix at the time of "liquefaction".

The pressure of fission gases and highly volatile fission products in the intact fuel matrix can be very high. If the matrix is suddenly disrupted, these fission products can form large bubbles since the restraint of the UO_2 matrix is no longer available to restrict the fission product volume. This process results in a large increase in the volume of the fuel, a phenomenon that is referred to as fuel frothing.

Fuel frothing has been observed in experiments with irradiated fuel in which the fuel has been liquified either by melting or by dissolution of UO_2 by molten Zircaloy. The amount of UO_2 affected by the UO_2/Zircaloy solid state interaction is sufficiently small that the fuel frothing does not occur. Dissolution of UO_2 by molten Zircaloy has been observed in significant quantities in tests in a reducing environment, such as ST-1[90] and VI-4[91] since these tests had significant amounts of non-oxidized Zircaloy available to wet the UO_2 at temperatures above the Zircaloy melting point. Most experiments which heat up to such high temperatures in an oxidizing environment do not result in fuel frothing[92], since these tests are of long duration and the Zircaloy is fully oxidized by the time the melting temperature is reached.

An exception to this general trend is BTF-107[93]. In this test, a flow blockage occurred which resulted in rapid temperature escalation for the fuel sheaths to temperatures well in excess of the Zircaloy melting point. The escalation was sufficiently rapid that the Zircaloy was not fully oxidized before reaching the melting temperature. Therefore, molten metallic Zircaloy was available to wet the UO_2 and reduce it to UO_{2-x}. Post-test examination of the fuel shows that the molten Zircaloy wetted the UO_2 along all exposed surfaces, including the cracks, and formed the molten (U, Zr)O eutectic phase. Large scale dissolution of the UO_2 matrix appears to have occurred, resulting in fuel frothing.

Because of the smaller fission gas production in the relatively low burnup CANDU-type fuel used in BTF-107, the amount of fuel frothing was less in BTF-107 than in ST-1 and VI-4. The volume expansion in BTF-107 can be estimated at ~10%, as compared to 50-100% in the higher burnup LWR experiments. As would be expected in CANDU fuel, this is due to the lower gas quantity generated in the fuel matrix during irradiation.

Fuel frothing is a mechanism whereby a small amount of highly volatile fission products can be retained in the fuel, trapped in the bubbles. At these high temperatures, most of the volatile fission products would be released even in an oxidizing or inert environment, so the dissolution of the fuel matrix does not have as large an effect on fission product release as would initially be expected. However, the volume increase associated with fuel frothing could have an impact on the accessibility of coolant to the fuel, which could result in more severe temperature transients than would be the case if frothing did not occur. These high temperatures could also have a feedback effect on fission product releases. Therefore, it is important that this process be considered in accident scenarios in which it is possible for Zircaloy to exceed its melting temperature of 1760°C.

Less-Volatile Fission Products

The fission product release behaviour observed in various in-pile and out-of-pile tests has been reviewed.[94] Consistent release behaviour of the volatile (Xe, Kr, I, Cs, Te and Sb), semi-volatile (Mo, Rh, Ba), low volatile (Ru, Ce, Np, Sr and Eu) and less-volatile (Zr, Nb, La and Ne) fission products was observed in the annealing experiments at the Oak Ridge National Laboratory (ORNL), Centre d'Études Nucléaire de Grenoble of the Commissariat à l'Energie Atomique (CEA), and Chalk River Laboratories (CRL) of Atomic Energy of Canada Limited.[70,76,95-99] Similar results to the annealing experiments were also observed in various in-pile tests except for the release of barium, where a reduced volatility was observed in the in-reactor experiments compared to the annealing tests due to thermochemical effects as a result of the presence of iron and zirconium oxides.[100] As mentioned, the prevailing local atmospheric conditions (i.e., oxygen potential) particularly influence the release characteristics of the low-volatile fission products.[72,97] Moreover, the non-coherent nature of melt progression tends to mask individual release mechanisms as identified in the out-of-pile experiments.[94] A significant enhancement of release due to fuel liquefaction is not typically observed in the separate effects experiments.

High temperature annealing experiments in the VERCORS test program at the CEA confirmed a nearly total release of such volatile species as Cs, I, Te and Sb; however, the Te and Sb fission product were observed to be trapped in the unoxidized cladding although their level of release eventually reached that of the volatile ones.[98] The semi-volatile fission products included Mo, Rh and Ba, whose chemical forms inhibit their release to nearly half that of the volatiles, exhibiting a sensitivity to the atmospheric conditions. The Mo release was observed to increase in oxidizing conditions while, in contrast, Ba and Rh releases are enhanced in reducing conditions. The low-volatile fission product and actinide species consisted of Ru, Ce, Np, Sr and Eu with releases between 3 to 10%. The Np and Ce release increased in reducing conditions. There was no measurable release of the non-volatile fission products of Zr, Nb La and Nd under the temperature range studied in the VERCORS 1 to 6 experiments. In the VERCORS 6 test performed with high burnup fuel, although early fuel collapse and partial liquid corium was observed, there was no significant enhancement in release, where the liquid phase retained a fraction of semi and low-volatile fission products.[98,99]

Impact of environment (steam, air)

In the CRL experiments, the release rates of volatile fission products from clad fuel samples after complete clad oxidation are almost independent of temperature in the range 1670 to 2140 K.[101] These experiments show that releases of volatile fission products (Kr, Xe, I, Cs and Te) are relatively low in inert or reducing atmospheres but increase significantly after clad oxidation in oxidizing atmospheres. In some of the high temperature tests on unclad fuel samples, large fractions of the UO_2 fuel was volatilized in highly oxidizing environments, leading to releases of low-volatile fission products (e.g., Zr, La, Ba, Ce, Pr, Eu) via the “matrix stripping” process, where these products are normally soluble in the UO_2.[83,102] The low-volatile fission products released in hydrogen-rich atmospheres (Eu, Ba, etc.) are different from those released in steam (Mo, Ru, Nb, etc.) due to chemical effects on the fission product volatility. For example, smaller releases of barium and strontium are observed in steam experiments where the prevailing atmosphere typically hinders the formation of the more volatile metallic species but favours low-volatility oxides and hydroxides. Since the oxygen potential of the environment is known in the CRL tests, it has been possible to develop models for steam and air oxidation of UO_2.[103] Significant release of fission products such as Ru and Nb have been observed only in oxidizing (air) environments and after the UO_2 has oxidized to an equilibrium state.[104]

6. Areas of Research on Fission Product Release

Fuel oxidation

It has been shown by many investigators that the fuel oxidation process is rate-controlled by steam dissociation at the fuel surface in experiments at atmospheric pressure.[103,105,106] A square-root dependence of the fuel oxidation rate on the steam pressure has been observed for experiments with thin disks of UO_2 with steam-argon and steam-helium mixtures at steam partial pressures ranging from 0.01 to 1 atm.[76,106] Although experiments in the temperature range 773 to 873 K with pure steam at higher pressures of 7 and 70 atm also suggests a similar pressure-dependence,[27] experiments at ~100 atm should be considered for the development of fuel oxidation models applicable to operating defective fuel elements. The effect of coolant radiolysis on fuel oxidation kinetics in operating defective rods is also not clearly understood.[27,107,108]

When the gas stream is switched from pure steam to Ar/H_2 in experiments with polycrystalline and single crystal UO_2 specimens conducted in steam-hydrogen mixtures at 1273 to 1623 K, the return to stoichiometry is much more rapid compared to the initial rate of oxidation.[106] The faster fuel reduction kinetics (i.e., as compared to that of fuel oxidation), suggest a different rate-determining mechanism, which may be controlled by either solid-state diffusion of oxygen through the solid, hydrogen mass transport through the surface-boundary layer or chemical reaction/mass transfer at the fuel surface.[106] It is important to model this process since the fuel could reduce, especially during a transient as a result of hydrogen generation from enhanced metal-water reaction. Hydrogen is also formed in the fuel cracks and fuel-to-clad gap of operating defective fuel elements due to the fuel and sheath oxidation reactions. Hence, additional experiments in varying hydrogen/steam mixtures at different temperatures are needed at the Chalk River Laboratories to study and model the fuel reduction kinetics.

Oxygen partial pressure in the fuel/sheath gap

During reactor accident conditions, steam that enters into a fuel element will interact with the Zircaloy sheath at high temperature and produce significant quantities of (molecular) hydrogen gas as a result of the metal-water reaction. The incoming steam must therefore diffuse against an outgoing current of hydrogen gas produced from the (internal) Zircaloy corrosion reaction as well as from the fuel oxidation reaction itself. In addition, at higher fuel temperatures there is a greater release of fission gas (i.e., xenon and krypton) into the fuel-to-sheath gap from the fuel matrix and therefore a greater outflow current of fission gas. These processes give rise to multi-component transport in the gap, which is particularly important because it can inhibit the fuel oxidation process in the early stages of the accident. Any hydrogen production will significantly reduce the oxygen potential in the gap. Thus, in addition to a physical barrier, the sheath also acts as a chemical barrier while oxidation of the sheath is occurring.[109-111] For example, this phenomenon is observed indirectly in annealing experiments with mini-length fuel elements at the Chalk River Laboratories, where significant cesium release does not occur until the sheath is completely oxidized.[111] Thus, for the high-temperature transient, a gas mixture can exist where the relative concentrations of the steam, hydrogen and fission gases are of the same order of magnitude. This transport process must therefore be described by a more complicated Maxwell-Stefan treatment for multi-component diffusion in the gap as opposed to simple binary diffusion for assessment of the oxygen potential in the fuel-to-sheath gap.[112-114]

Fission product release under reducing conditions

The fission product release behaviour is dependent on the prevailing atmospheric conditions that dictate the chemical form and volatility of the fission products.[72,115,116] Although the fission product release behaviour has been investigated in reducing condition in several separate-effects annealing experiments at high temperature at the ORNL and CEA, experiments in hydrogen need to be considered for CANDU fuel at the Chalk River Laboratories for comparison to earlier experiments conducted in steam where the oxygen potential was well qualified. In particular, since a segmented furnace tube was used in the ORNL and CEA tests to allow for rapid heating, there was not a good containment of the test environment in steam where there is evidence of oxidation of the graphite susceptor.[76] Hence, this condition provides some uncertainty in the control of the environment and subsequent estimation of the atmospheric oxygen potential for the comparative tests in steam.

Burnable poisons

With aim to increase the robustness of safety margins by reducing core void reactivity, the additions of burnable poisons is considered in new fuel designs. One of these designs is the replacement of the current 37-element fuel bundle by the Low Void Reactivity Fuel (LVRF)[8] fuel bundle. Also, the new AECL reactor design ACR-1000[117], makes use of the advantages offered by the use of burnable poisons. Research on the behavior of doped fuel elements during NOC and accident conditions is needed for both in-reactor and out-of-reactor experimental facilities.

7. Summary

1. Research and development (R&D) activities in Canada to address regulatory requirements have been reviewed. This R&D is carried out by the nuclear industry through the partnership of the commercial utilities, reactor designer and national laboratory within the CANDU Owners Group framework. In addition, the industry also supports research activity through a network of excellence of universities with programs in Nuclear Engineering. The facilities used to support the R&D effort have also been discussed.
2. The areas of research on fission product release are specifically outlined. Moreover, the mechanisms and phenomena that affect fission product release behaviour during normal and reactor accident conditions are identified and detailed, which include: fission product diffusion; effect of temperature ramps on release; the impact of atmospheric conditions and oxygen potential on the vaporization and release behaviour of volatile and low volatile fission products; fuel/sheath interaction and fuel dissolution by the Zircaloy sheathing; fuel oxidation (and reduction) behaviour; and fuel volatilization, frothing and melting.
3. Future research that is needed to better understand fission product release behaviour is suggested.

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