

Activity Transport in a Supercritical Water-cooled Reactor

David Guzonas

Atomic Energy of Canada Limited
Chalk River Laboratories
Chalk River, Ontario Canada
Tel: 613-584-8811 x43154
Email: guzonasd@aecl.ca

Liyan Qiu

Atomic Energy of Canada Limited
Chalk River Laboratories
Chalk River, Ontario Canada
Tel: 613-584-8811 x43996
Email: qiul@aecl.ca

Abstract

In a supercritical water reactor (SCWR), the decrease in water density from subcritical to supercritical regions in the reactor core results in a decrease of solubility and deposition of most corrosion products. Such deposition in the reactor core can seriously affect fuel performance, thermalhydraulics and activity transport in an SCWR. In addition, the dissolution of the oxides formed by deposition or corrosion can release radioactive corrosion products into the supercritical water (SCW) coolant. In a boiling water reactor, the phase change that occurs upon boiling and the very low solubility of metal salts in steam prevents most radioactive species from being transported by the steam to the turbines. In an SCWR core, there is no phase change in the coolant, only a density change. While the solubilities of relevant corrosion products are low, they are not negligible, and ion pairs, the dominant solution species in low density SCW, can be transported by the SCW coolant to the turbines. Thus it is likely that radioactive corrosion products will be transported to the SCWR high pressure turbine where they will deposit due to the changes in temperature and pressure.

This paper reviews the solubilities of potential corrosion products in SCW and presents a semi-quantitative prediction of the amount of activity transport expected in an SCWR. Potential mitigating strategies will be briefly discussed.

1. Introduction

The transport of radioactive species from the core of a nuclear reactor and their subsequent deposition on out-of-core piping (activity transport) has been the subject of much research since the first reactors were brought into service. Activity transport leads to radiation dose to plant workers, increased shielding requirements for reactor components, and increased costs associated with waste disposal and decommissioning. While corrosion product and activity transport have been identified as key water chemistry issues for supercritical water-cooled reactor (SCWR) concepts [1, 2], the focus of most studies has been corrosion product deposition in-core (Guzonas et al. [2], Burrill [3], Cook and Olive [4]). Transport of corrosion products released by corrosion of feedtrain components into the core by the coolant could lead to deposition on in-core surfaces, especially the fuel cladding, resulting in reduced heat transfer, flow restrictions, and under-deposit corrosion. These authors highlight the need for good chemistry control in the feedtrain and optimized selection of feedtrain materials to minimize corrosion product concentrations at the core inlet. The related issue of the release of radionuclides produced in the core by neutron activation or from defected fuel into the coolant has been addressed only briefly [5]. Information on activity generation and out-of-core deposition is required not only for the SCWR design (e.g., to determine shielding requirements) but also for the planned Generation IV

International Forum fuel qualification tests; in particular it is needed for predicting the consequences of a fuel failure. While the various SCWR concepts are direct cycle plants similar to boiling water reactors (BWRs), the absence of a phase change in the SCWR core gives rise to the possibility of transport of activated metals out of the core. This is different than in a BWR, where the liquid-gas phase change in the core leaves essentially all of the non-gaseous radioactive species in the core and associated piping. However, it is well known in the fossil-fired power industry that impurities can be transported at low concentrations in steam as dissolved species or as particles transported by entrainment in the steam (mechanical carryover) [6]. Transport as dissolved species depends strongly on the temperature and pressure, as discussed below.

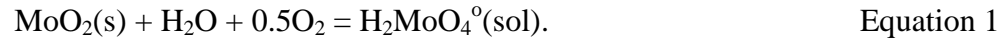
The major alloys proposed for in-core use in all SCWR concepts are composed mainly of iron, nickel, and chromium, with smaller amounts of elements such as molybdenum, tungsten, vanadium, niobium and yttrium added to impart desired mechanical or corrosion resistance properties. Little data exists on the solubilities of the oxides of most of these elements under conditions relevant to the SCWR. Qiu and Guzonas [7] recently reviewed the effects of parameters such as temperature, pressure, pH and redox conditions on the solubility of various metal oxides. Typically, the solubilities of metal oxides such as CuO [8, 9], PbO [8], Al₂O₃ [10], and ZnO [11] increase with increasing temperature and reach a maximum near the critical point. In the subcritical region, density changes are relatively small and temperature is the dominant factor affecting solubility. As the temperature approaches the critical temperature, a small temperature increment has a large effect on the water density and drastically changes the solubility of oxides and ionic compounds. Well above the critical point the solubilities of metal oxides change very slowly with temperature and density. In this region water behaves like a non-polar organic solvent in which ionic compounds and metal oxides typically have low solubilities.

The formation of neutral complexes increases with temperature, and can become important under near-critical and supercritical conditions. The most important region is from 300 to 450 °C where the properties of water change dramatically, and solvent compressibility effects exert a huge influence on solvation. This is reflected in the dielectric constant of water, which falls from 79 at 25 °C to 15 at 350 °C at 25 MPa. The low dielectric constant stabilizes neutral complexes relative to charged species. As a result, species such as $[\text{Me}^{n+}(\text{X})^n]_{(\text{aq})}^0$ ($\text{Me}^{n+} = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Cs}^+, \text{Sr}^{2+}, \text{UO}_2^{2+}$ etc., and $\text{X} = \text{OH}^-, \text{Cl}^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}$) are expected to dominate in the supercritical region. The concern for all SCWR designs is that radioactive neutral species may be sufficiently soluble in supercritical water (SCW) to be carried to the turbines. These may be transported as dissolved species, colloids [12], or larger particles.

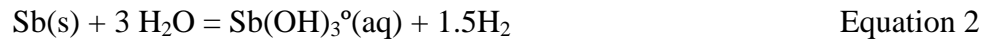
In contrast to the behavior of the metal oxides discussed above, the solubility of molybdenum and tungsten oxides increases with increasing temperature from subcritical to supercritical regions. WO₃ has a high solubility in SCW; at 500 °C and 34 MPa, for example, the solubility is 31.2×10^{-3} mol/kg, which is four orders of magnitude higher than of magnetite under similar conditions. Static autoclave testing has shown that alloying elements such as Al, Ti, Mo and W can be released into SCW at very high concentrations [13]; the release of the latter two elements is consistent with the reported solubility behavior of molybdenum and tungsten oxides [14]. Daigo et al. [15, 16] have shown that chromium released from the autoclave can migrate to the surfaces of tests specimens in the autoclave and lead to improved corrosion resistance, and proposed that dissolved Cr³⁺ species were the major species involved.

Oxidizing and reducing media also play an important role in the dissolution of oxides as observed in the solubility measurement of uranium (IV) oxide [17]. Kudrin [18] studied the effect of O₂ fugacity on the solubility of MoO₂, finding that the dissolved Mo(VI) concentration increased linearly with the

logarithm of oxygen fugacity (Equation 1), indicating that Mo(VI) is the dominant dissolved molybdenum species under oxidizing conditions:



Zotov et al. [19] investigated the solubility of metallic antimony in water as a function of hydrogen fugacity at 450 °C and pressures of 50 and 100 MPa. They found that antimony solubility decreased linearly with increasing logarithm of hydrogen fugacity (Equation 2), consistent with the formation of $\text{Sb}(\text{OH})_3^\circ(\text{aq})$:



2. Activity Transport Source Terms

There are three source terms for activity that must be considered:

1. Corrosion products transported to the core, activated and then released;
2. Release of activated elements by corrosion of in-core materials; and
3. Fission products and actinides released from failed fuel.

These processes are illustrated in Figure 1 and are discussed in the next sub-sections.

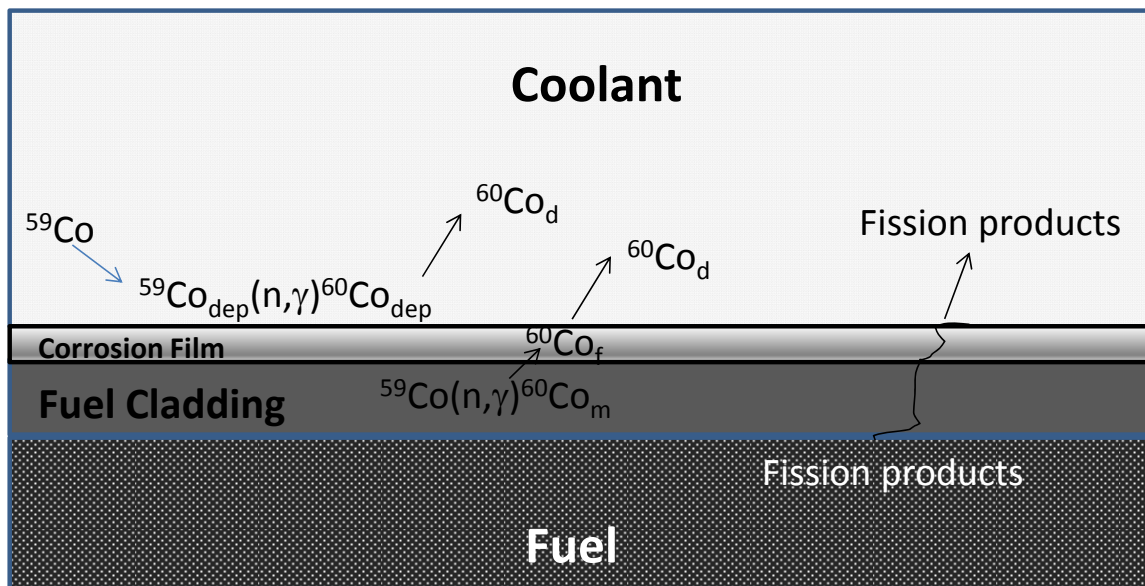


Figure 1: The three source terms for activity transport in an SCWR. From left to right the processes are: 1) deposition of corrosion products (in this example ^{59}Co) released by corrosion in the feedtrain, neutron activation and then release of ^{60}Co to the coolant; 2) neutron activation of ^{59}Co in the alloy, and subsequent diffusion of ^{60}Co into the corrosion film and release into the coolant, and 3) release of fission products into the coolant through a fuel defect.

2.1 Corrosion Products from the Feedtrain

Very small but finite concentrations of impurities (e.g., corrosion products, impurities from water treatment) will be transported by the feedwater to the reactor core even with the optimum selection of feedtrain materials and water chemistry. These impurities can be transported as dissolved species or particles. While a small amount of neutron activation of impurities will occur during the brief period that the coolant transits the core, the biggest concern is impurity deposition on in-core surfaces, either by precipitation of dissolved species or by the deposition of particles from the coolant. Once deposited, activation will occur until the material is released back into the coolant and transported out of the core.

Burrill [3] first highlighted the issues associated with in-core deposition and presented some preliminary estimates of the deposited amount. Cook and Olive [4] recently provided more detailed calculations of in-core deposition for the Canadian SCWR design, using updated thermodynamic data to calculate the high temperature solubilities. They considered the deposition of iron and nickel, for two scenarios: 1) coolant saturated in the metal species of interest at the core inlet; and 2) coolant unsaturated in the metal species of interest at the core inlet (10^{-8} kg·m⁻³ for iron and 10^{-9} kg m⁻³ for nickel). When the coolant was saturated at the core inlet, deposition started at the core inlet, reached a maximum about 1 m into the core and continued until the core outlet. When the coolant was unsaturated deposition started roughly 1 m into the core and continued until the core outlet.

Under all conditions studied, Cook and Olive predicted deposition would continue along the entire length of the core, i.e., there is no region in which the in-core oxide became soluble again because the coolant was now unsaturated in dissolved metals. Therefore during normal operation, release of activity by iron and nickel oxide dissolution is not expected. The most likely mechanism for activity release from these deposits is release during reactor shutdown, as the solubility increases by several orders of magnitude as the temperature decreases below the critical temperature. Other possible release mechanisms are mechanical wear (e.g., due to vibration of the fuel rods), erosion by the flowing coolant or spalling of the oxide from surfaces.

2.2 Activation of In-core Materials

While corrosion products transported from out-of-core sources are typically deposited and released over relatively short periods, in-core materials can reside in the core for long periods. During this time they are subjected to nearly continuous irradiation, leading to changes in alloy composition due to transmutation, various forms of irradiation damage, as well as the production of potentially hazardous radionuclides by nuclear reactions (Table 1). Some of these radionuclides can then be released into the coolant by corrosion.

Of the radionuclides listed in Table 1, ⁶⁰Co (from cobalt activation) and ⁵⁸Co (from nickel activation) have been the most troublesome in existing water-cooled reactors. Cobalt is typically present in steels as an impurity at ppm concentrations, and is also a major component of some specialty alloys such as Stellites (Co-W-Cr alloys). ⁶⁰Co is particularly hazardous as it emits two high energy (~1 MeV) gamma rays and has a relatively long half-life that allows it to build up to significant concentrations on out-of-core piping. Short-lived radionuclides do not build up on out-of-core surfaces, but can result in high doses during outages, especially if they are mobilized by chemistry transients during reactor shutdown. The behaviour of ⁵⁸Co during outages in pressurized water reactors (PWRs) is a well-known example. Antimony is also a trace impurity in many steels, and is also used in some

bearing and seal materials. Zr and Nb have been included in the table because both elements are sometimes added to steels to improve their properties, typically at concentrations on the order of 1%.

Table 1: Parent isotopes, production reactions and half-lives for key activation products.

Parent Isotope	Reaction	Half-life
^{59}Co	$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$	5.27 y
^{58}Ni	$^{58}\text{Ni}(n,p)^{58}\text{Co}$	71 d
^{59}Fe	$^{58}\text{Fe}(n,\gamma)^{59}\text{Fe}$	44.5 d
^{54}Fe	$^{54}\text{Fe}(n,p)^{54}\text{Mn}$,	312.2 d
^{50}Cr	$^{50}\text{Cr}(n,\gamma)^{51}\text{Cr}$	27.8 d
^{121}Sb	$^{121}\text{Sb}(n,\gamma)^{122}\text{Sb}$	2.7 d
^{123}Sb	$^{123}\text{Sb}(n,\gamma)^{124}\text{Sb}$	60.2 d
^{94}Zr	$^{94}\text{Zr}(n,\gamma)^{95}\text{Zr}$	64 d
^{95}Zr	^{95}Nb by beta decay of ^{95}Zr	35 d
^{93}Nb	$^{93}\text{Nb}(n,\gamma)^{94}\text{Nb}$	20,000 y

There have been only a few studies of the metal release into the coolant in SCW. Guzonas and Cook [13] reported data on the release of iron, manganese, nickel and chromium from 403 stainless steel in static autoclaves, as well as data on the release of various elements into SCW from Hastelloy C and Alloy 625 autoclaves. Han and Muroya [20] quantified the release of ^{60}Co radiotracer from irradiated 304 SS samples as a function of time and temperature in SCW by collecting the material released on ion exchange resins and measuring the amount collected by gamma spectrometry. The temperature dependence of the release showed a large decrease between 300 and 550 °C (the amount released at 550 °C was below the detection limit of the method employed). The decrease reflects the change in solubility of ionic species through the critical point, both directly by lowering the solubility of cobalt in water, and indirectly because, as the solubility of the iron oxides decrease, the thickness of the corrosion film on the surface increases, slowing down the diffusion of cobalt from the bulk metal to solution interface. One deficiency in this test methodology was the use of ion exchange resins to capture the released ^{60}Co ; as noted earlier neutral species are typically the dominant species in SCW.

Liang et al. [21] reported measurements of the solubility of $\text{Co}(\text{OH})_2$ and CoO in SCW. As expected the solubility below the critical temperature was dominated by the ionic species $\text{Co}(\text{OH})_3^-$, and above the critical temperature by the neutral species $\text{Co}(\text{OH})_{2(\text{aq})}$. The solubility of $\text{Co}(\text{OH})_2$ was between 15 and 50 ppm in the vicinity of the critical point, while the solubility of CoO was about 10 ppm at the same temperatures. However, the measurements did not extend to temperatures above 450 °C. Further measurements of the solubilities of relevant cobalt oxides are needed at higher temperatures before accurate predictions of cobalt transport can be made.

Carvajal-Ortiz et al. [22] measured the metal release from 316 SS at temperatures from 350 to 650 °C at neutral ($\text{pH}=7\pm 0.3$) and alkaline ($\text{pH}=10\pm 0.3$) pH_{25} . The concentrations of Cr were below the method detection limit (<0.7 ppb) as expected as the dissolved O_2 concentration in the water was very low and the formation of H_2CrO_4 , which has a high solubility in SCW, was not expected. With the exception of nickel at 650 °C, the concentrations of iron and nickel under alkaline conditions were lower than those found at neutral pH. The largest metal loss was for iron at 350 °C at neutral pH. At all temperatures, nickel was found at lower concentrations (<3 ppb) compared to Fe (~10-20 ppb);

under most conditions the Fe/Ni ratio in solution was much higher than the ratio in the alloy, indicating preferential release of Fe. The relatively low nickel concentration compared with iron is due to the stability of nickel oxide, NiO at high temperatures in neutral and slightly alkaline environments [23], and the low affinity of Ni for oxygen compared to chromium and iron [7]. It is worthwhile noting that there was a decrease in the nickel concentration in the effluent after the first week, especially at alkaline conditions, reflecting the initial formation of the surface oxide film and its approach to a steady-state growth rate. Luo et al. [24] reported the weight loss measurements after descaling of SS 316L coupons under similar conditions (480 °C, 25 MPa). The reported value (1.31 mg·dm⁻²·d⁻¹ (mdd)) is significantly higher than the apparent corrosion rate obtained from the metal release data (0.0091 mdd at 500 °C), indicating that almost all of the oxide (~99%) produced by corrosion at this temperature remained on the surface.

The metal release data of Carvajal-Ortiz et al. [22] can be used to estimate the ⁶⁰Co activity release from the stainless steel fuel cladding expected to be used in an SCWR. Cohen [25] discusses the activation of 304 SS fuel cladding relevant to the Yankee PWR; after 3 years irradiation (roughly the expected in-service life of the fuel cladding) in a typical PWR flux the amount of ⁶⁰Co activity in the alloy is about 2 MBq/mg; this value gives the peak ⁶⁰Co releases. A reasonable estimate for the activity release rate AR (in MBq/d) for ⁶⁰Co can be obtained using Equation 3:

$$AR = 2 \text{ MBq/mg metal} \times S_{ac} \times R. \quad \text{Equation 3}$$

where S_{ac} is the surface area of the cladding and R is the metal release rate from the surface. The value of the release rate, R , will vary with location in the core, as it depends on corrosion rate and on the solubility of the resulting surface oxide film; the latter depends on the SCW density [26], which changes with distance through the core. We can consider two limiting cases:

Case 1: At the core inlet where the temperature is low and the coolant density is high, the solubility of the oxide film is relatively high. If it is assumed that there is no transport of metal ions from the feedtrain into the core (i.e., the concentration of metal ions in the coolant is zero at the core inlet), then the metal release data [22] suggest that about 10% of the corroded metal is released into the coolant. Equation 3 can therefore be rewritten as Equation 4:

$$AR = 2 \text{ MBq/mg metal} \times S_{ac} \times 0.13 \text{ mdd} \quad \text{Equation 4}$$

The total in-core surface area of the fuel cladding in the Canadian SCWR concept is about 2000 m², giving a peak ⁶⁰Co release rate of about 50000 MBq (1.4 Ci) per day near the core inlet.

Note that in the more realistic case that the concentration of metal species in the coolant is non-zero, the dissolution of the oxide film may be very low if the coolant is already saturated with the relevant dissolved metal species. Thus the presence of a **very low** concentration of dissolved metal species in the coolant at the core inlet is not necessarily detrimental from an activity transport perspective.

Case 2: Near the core outlet where the coolant temperature is high and the coolant density is low, the solubility of the oxide film is very low and most of the metal species released by corrosion will remain on the surface. Assuming that only 1% of the metal released by corrosion enters the coolant, Equation 3 becomes Equation 5:

$$AR = 2 \text{ MBq/mg metal} \times S_{ac} \times 0.013 \text{ mdd} \quad \text{Equation 5}$$

and the peak ⁶⁰Co release rate is about 5000 MBq (0.14 Ci) per day near the core outlet.

The coolant flow rate in the Canadian SCWR concept is on the order of 1000 kg/s; using an average release rate of 2750 MBq·d⁻¹ × 1.16 × 10⁻⁵ d·s⁻¹ = 0.032 MBq·s⁻¹ gives a coolant ⁶⁰Co concentration of

about 60 Bq/kg ($\sim 1.5 \text{ nCi}\cdot\text{kg}^{-1}$), on the same order as the coolant concentration of ^{60}Co found in current generation PWRs and pressurized heavy water reactors. Note that this corresponds to a Co concentration of $\sim 10^{-14} \text{ mol}\cdot\text{kg}^{-1}$, well within the range of metal oxide solubilities at 600 °C (as low as $10^{-15} \text{ mol}\cdot\text{kg}^{-1}$ for NiO to as high as $10^{-8} \text{ mol}\cdot\text{kg}^{-1}$ for Cr_2O_3 [13]). Therefore in spite of the reduced solubilities of metal oxides in SCW, significant activity transport to out-of-core surfaces is possible as dissolved species.

More detailed predictions are not possible as the necessary solubility data are not available and the in-core chemistry conditions cannot be adequately specified. In particular, it is still unclear whether water radiolysis can be controlled, e.g., by the addition of hydrogen to the coolant at the inlet to the reactor core [2]. Yeh et al. [27] have predicted very high concentrations of oxidants in an SCWR if water radiolysis is not controlled. Mayanovic et al. [28] have recently shown that radiolysis-induced effects may cause colloidal precipitate formation from tungsten ions in SCW, and that iron species may be either oxidized, reduced, or form a precipitate depending upon the pressure, temperature and irradiation conditions.

Of particular concern is the behaviour of Cr; under oxidizing conditions, Cr oxides are soluble and ^{51}Cr could be transported from the core. While ^{51}Cr has a relatively short half-life (27.8 d), its presence on out-of-core surfaces would be a concern during maintenance outages. As noted previously, formation of soluble Cr(VI) species has been observed in SCW at 25 MPa [15, 16]. The phenomenon of chromia evaporation in mixtures of oxygen and water at temperatures above 500 °C has been well documented [29-31]. The process shows a strong dependence on flow, showing that it depends on the mass transfer of the volatile (dissolved) species away from the surface. Chromia evaporation is attributed to the following reaction:



$\text{CrO}_2(\text{OH})_2$ is chemically identical to H_2CrO_4 presented in the Pourbaix diagram for chromium [32]. Chromium oxide dissolution as H_2CrO_4 (transpassive dissolution) is noted in BWR plants that operate with normal water chemistry (i.e., no hydrogen gas addition) because of the high concentration of oxidizing species present from water radiolysis. A similar behaviour is possible in an SCWR if water radiolysis cannot be controlled [2], as suggested by Karasawa et al. [33] and Fujiwara et al. [34].

2.3 Fission Products and Actinides

To date there have been few studies of the solubilities of fission products and actinides in SCW. Zimmerman et al. [35] recently reported preliminary results of an experimental study to determine the association constants of strontium with hydroxide and chloride ions at temperatures up to 350 °C, using high-pressure flow AC conductance. The systems $[\text{Sr}(\text{OH})_2 + \text{H}_2\text{O}]$ and $[\text{SrCl}_2 + \text{H}_2\text{O}]$ were chosen because of their importance to modeling fission product transport in SCWR reactors, and because they are soluble in near-critical water and so may be used as model systems for other M^{2+} species. Under SCWR conditions the formation of SrOH^+ and $\text{Sr}(\text{OH})_2^0$ ion-pairs was established to be greater than SrCl^+ and SrCl_2^0 ion pairs, so that hydroxy complexes will be the dominant strontium species in solution. Neutral species were found to be substantial at 350 °C at concentrations above $10^{-3} \text{ mol}\cdot\text{kg}^{-1}$, for both salts. These data are an important first step in determining whether the neutral $\text{Sr}(\text{OH})_2^0$ may be sufficiently soluble in SCW to be carried to the high pressure turbines. Further work on fission product and actinide transport under expected SCWR conditions is required.

3. Summary

This paper briefly introduces some preliminary thoughts on activity transport in an SCWR. A more detailed evaluation is hindered by the lack of experimental data on metal oxide solubilities under SCWR conditions and our inability to precisely define the in-core chemistry conditions. However, simple calculations making reasonable assumptions show that the concentration of ^{60}Co in the SCWR coolant at the core outlet may not be significantly different than that found in current generation water-cooled reactors. While the solubilities of metal oxides in low-density SCW are low, they are still much higher than the solubilities of the same oxides in the lower pressure steam found in BWRs. The transport and release of particulate species, alluded to in the discussions above, must be considered in detail.

Several mitigating strategies can be suggested to reduce the impact of activity transport on out-of-core components. Optimizing feedtrain chemistry to minimize the concentration of corrosion products at the core inlet would reduce the contribution of this source term. Ultrasonic cleaning of the once-burned and twice-burned fuel during refueling outages to remove the deposited oxide would reduce this source term as well as reducing the effects of the deposits on heat transfer and flow. Zinc addition has been used with great success in BWRs and PWRs to reduce activity transport; while little is known about the effects of zinc addition in a SCWR, this option could also be explored. Optimizing reactor shutdown chemistry and procedures should also be done to ensure that in-core oxides are not mobilized during reactor cooldown due to the large increase in oxide solubility. Selection of fuel cladding and other in-core alloys should consider the possible activity transport effects of alloying elements; in particular, cobalt should not be used in alloys in contact with the primary coolant. The use of alloys with low corrosion rates in-core will reduce the release of activated corrosion products to the coolant.

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