

Zinc corrosion after loss-of-coolant accidents in pressurized water reactors – Thermo- and fluid-dynamic effects



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HIGHLIGHTS

- Borated coolant supports corrosion at zinc-coated installations in PWR after LOCA.
- Dissolved zinc is injected into core by ECCS during sump recirculation phase.
- Corrosion products can reach and settle at further downstream components.
- Corrosion products can cause head losses at spacers and influence decay heat removal.
- Preventive procedures were tested at semi-technical scale facilities.

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ABSTRACT

Within the framework of the German reactor safety research, generic experimental investigations were carried out aiming at thermal-hydraulic consequences of physicochemical mechanisms, caused by dissolution of zinc in boric acid during corrosion processes at hot-dip galvanized surfaces of containment internals at lower coolant temperatures and the subsequent precipitation of solid zinc borates in PWR core regions of higher temperature. This constellation can occur during sump recirculation operation of ECCS after LOCA. Hot-dip galvanized compounds, which are installed inside a PWR containment, may act as zinc sources. Getting in contact with boric acid coolant, zinc at their surfaces is released into coolant in form of ions due to corrosion processes. As a long-term behavior resp. over a time period of several days, metal layers of zinc and zinc alloys can dissolve extensively.

First fundamental studies at laboratory scale were done at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR). Their experimental results were picked up for the definition of boundary conditions for experiments at semi-technical scale at the Hochschule Zittau/Görlitz (HSZG). Electrical heating rods with zircaloy cladding tubes have been used as fuel rod simulators.

As near-plant core components, a 3 × 3 configuration of heating rods (HRC) and a shortened, partially heatable PWR fuel assembly dummy were applied into cooling circuits. The HRC module includes segments of spacers for a suitable representation of a heating channel geometry. Formations of different solid zinc compounds (mainly borates) were observed at the heatable zircaloy surfaces and characterized in detail during the heating-up to several coolant temperatures. As a strict consequence of their proven influence on heat removal and coolant flow behavior in the PWR core, preventive water-chemical methods were defined and tested.

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1. Introduction

LOCAs are design-basis challenges for the safety of light water reactors such as PWRs. To remove the decay heat after a LOCA and to prevent the integrity of the fuel rods, the long-term behavior during LOCA in PWR is characterized by coolant discharge flow through the pipe leak in the primary cooling circuit, the collection of coolant in the containment sump and the recirculation to the

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reactor core by emergency cooling pumps as integral part of the ECCS. The decay heat removal can be influenced by the occurrence of several forms of debris materials in the sump (potentially inducing a clogging of the sump strainers upstream of the ECCS-pumps) or directly in the core. The debris materials in the sump can be heavily fragmented, like pipe insulations, occurring as particles of a fibrous substance with different settling properties. There were several attempts to differentiate between their forms of appearance and their attributes (Shaffer et al., 2003; Seeliger et al., 2004).

A precedent case took place in 1992 in the BWR plant of Barsebaeck/Sweden. As a later consequence, also for PWRs, comparable cases have been considered experimentally and simulatively (Bröcker and Pointner, 2011). Due to different external materials with varying characteristics assembled worldwide, their influence on coolant chemistry cannot be excluded for all cases. For the most part, components for realizing preventive measures were designed and installed, where their effects on thermohydraulics have been verified e.g. by complex numerical simulations (Krepper et al., 2011). A comprehensive overview of worldwide activities regarding the investigation of chemical effects (sump strainer clogging and downstream effects) is given in (Kryk et al., 2014), which provides the basis for the investigations described in the present paper. International investigations regarding LOCAs along with the release of debris like pipeline insulation material as well as sump strainer clogging issues were performed in the past. Most long-term scenarios show one coincidence: Released materials have always been present in the core after passing the sump strainers, but their release was caused by exceptional processes like jet fragmentation. A further overview is given in the introducing part of (Krepper et al., 2011).

In the case described here, foreign materials are formed directly inside the core due to chemical effects leading under certain circumstances to so-called downstream effects (e.g. in-vessel effects). Constellations of boundary conditions and parameters may lead to the formation of zinc-containing corrosion products at plant components. The according PWR LOCA scenario inside the plant is shown schematically in Fig. 1.

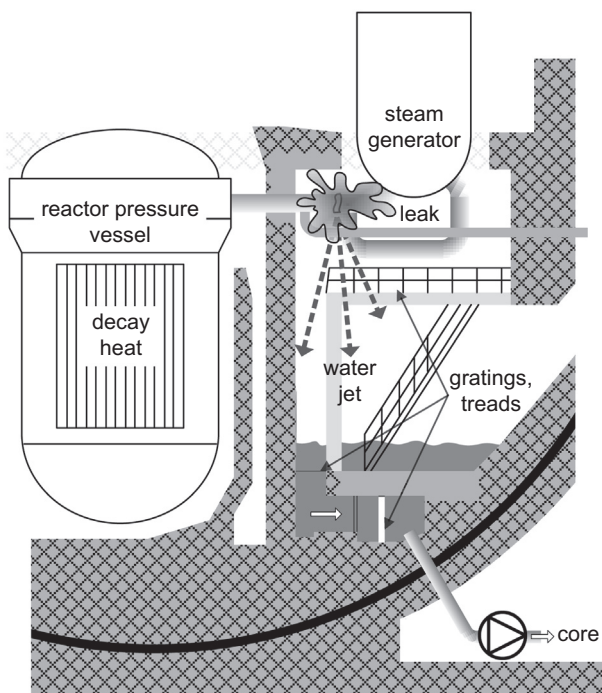


Fig. 1. Scheme of LOCA scenario inside a German PWR.

Within joint research projects between Hochschule Zittau/Görlitz (HSZG) and Helmholtz-Zentrum Dresden-Rossendorf (HZDR), generic investigations have been done regarding formation and deposition of solid corrosion products under LOCA conditions as a result of zinc corrosion processes in the presence of acidic borated water (coolant).

For first studies, potential zinc sources like containment installations of hot-dip galvanized steel (e.g. gratings, flight of stairs, inspection platforms, room divider and support grids of sump strainers) were considered. The layer structure of the hot-dip galvanized gratings (HGG), which mainly consists of pure zinc as external layer, a hard zinc layer and basic steel material, was determined by analyses of micrographs (Fig. 2). Usually, the zinc is applied to the basic structure of the HGG by hot-dipping, which produces a continuous coat of 50–150 μm thickness (Kästner et al., 2012). This coat promotes a release of zinc, causing a change of the coolant chemistry as a long-term effect. Zinc will be released in form of ions by flow-induced corrosion effects.

In German PWR the coolant in the sump can contain up to 2300 ppm boron in form of boric acid as a mixture of primary circuit coolant, coolant out of the accumulators and from the ECCS flooding tanks. The pH-value of this assumed coolant in the sump may reach values from pH = 5.2 up to pH = 6.2 depending on the amount of lithium hydroxide, which is the common pH-buffering agent in German PWR. Especially, as no alkaline substances are added during a LOCA in several European PWRs, the pH may be less than 5.2. The borated coolant with dissolved zinc can reach core regions of higher temperature (hot spots), generating layer-forming compounds (Renger et al., 2013).

To complement according experiments done at laboratory scale (Kryk et al., 2014), selected boundary conditions were performed under near-plant geometries (e.g. fuel assembly, containment sump), processes (leakage jet) and installations (grids and strainers) at semi-technical scale. For this purpose, fuel rod simulators (FRS) with zircaloy cladding tubes, internally equipped with heating cartridges, have been applied. Its maximum heating surface load was estimated based on calculations according to DIN 25463-1 considering conditions inside a generic PWR 5 h after SCRAM.

No previous scientific work is known concerning modeling and simulation of these complex physico-chemical effects of precipitation, deposition and blockage of zinc compounds as well as their influence on thermo- and fluid-dynamic behavior of coolant and the heat transfer inside the PWR core.

2. Fundamentals

First fundamental lab scale experiments are described in (Kryk and Hoffmann, 2014 and Kryk et al., 2014). The latter gives an overview of experimentally detected zinc solubility behavior at different temperature regimes of coolant in the core. Results indicate a cycle showing growing corrosion effects (viz. release of zinc ions) at lower coolant temperatures. In contrast, there are increased precipitations of solid corrosion products at higher coolant temperatures, if oversaturation occurs. The resulting solid corrosion products were identified by chemical analysis as zinc borates (general formula: $x\text{Zn} \cdot y\text{B}_2\text{O}_3 \cdot z\text{H}_2\text{O}$) where different types of zinc borates may occur depending on their forming temperature. Thus, zinc solubility scheme with the emphasis on dissolution and precipitation processes shown in Fig. 3 gave an orientation to the experimental parameterization at semi-technical scale, performed at test rigs as described in the following.

Zinc, which is released into coolant in form of ions, hereby stands as primary corrosion product (CP). Any further solid compounds (e.g. precipitations of zinc borates, ZBP), which are formed as a consequence of this release, are considered as secondary CP.

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