PhD Dissertation

Modeling the behavior of colloidal corrosion products in the primary circuit of Pressurized Water Reactors

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Defended on January 20, 2022

Extended summary

In the wake of the COP26, the question of producing decarbonized electricity remains a burning issue. With the ageing of nuclear reactors, the French nuclear industry has to prove its legitimacy both to the authorities and the public to legitimize the renewal of its fleet. In this context, it is essential to improve tools for the prediction of the contamination of circuits by radioactive substances, for the radioprotection of workers and for the availability of reactors.

In Pressurized Water Reactors (PWRs), accounting for the totality of the commercially operated reactors in France, the uniform corrosion of the primary circuit surface leads to the formation of oxide layers and to the release of ionic species in the coolant [1]–[3]. Due to the erosion of oxides or to local solubility differences, particles are also present in the coolant. These corrosion products whether they are ions or particles are transported in the coolant and can get activated thus forming Activated Corrosion Products (ACPs), which can be troublesome. For instance, ^{60}Co causes major radioprotection issues as it is long-lived (half-life 5.2 years) and emits high-energy gammas (1.17 and 1.33 MeV). It is the result of the activation of ^{59}Co, which is an impurity in the major alloys in the primary circuit and a constituent of high-cobalt alloys. ACPs become associated with spinel-type oxides and accumulate in the corrosion-product layers formed on system surfaces, creating radiation fields, thus inducing surface contamination and volume contamination if they remain dissolved or suspended in the primary coolant.

For more than 50 years, the OSCAR code standing for tOol for Simulating ContAmination in Reactors [4], [5] has been developed by the CEA. This multiphysics simulation tool aims at accurately predicting contamination levels by activated corrosion products, fission products and actinides in nuclear systems. It relies on the development of comprehensive models to fully describe the numerous and complex interactions underlying activity transport. At the heart of this PhD, the current deposition model, based on the Beal model developed in the 1970s [6], [7], shows results in good agreement with the field experience. However, the Beal model does not take into surface interactions, which are known to be predominant for the deposition of small particles [8].

A non-negligible proportion of particles in the Reactor Cooling System (RCS) of PWRs exists under colloidal size (by definition within a size inferior to 1 µm), exhibiting specific behaviour as surface interactions are decisive for their deposition [9]. Such interfacial interactions are outside the scope of the Beal model and should be included in an updated comprehensive deposition model. Thus, an inclusive deposition model taking into account surface interactions was developed, using the classic DLVO (Derjaguin, Landau, Vervey and Overbeek) theory. This theory relies on the knowledge of the zeta potential value of the particle and of the surface to predict if deposition will occur [10]. The zeta potential is, by definition, the potential at the slipping-plane of the

particle in the fluid, ie the plane at the interface separating mobile fluid from fluid that remains attached to the surface, which is often used as an approximation of the surface. Measuring the zeta potential of particles and surfaces in the primary circuit under operating conditions is challenging and the literature does not report any values of zeta potentials in the chemical conditions of the primary coolant above 70 °C [9].

The first step of this PhD was to synthetize representative corrosion products (CPs) found in the primary circuit conditions. In order to identify the main phases existing in operating primary conditions, an adaptation of the geochemistry code PhreeqC (developed by the US Geological Survey) to the temperatures of PWRs produced by the CEA as well as a specific thermodynamic database were used [11]. Among the main components of the outer oxides and particles in the primary circuit under normal operating conditions, magnetite (Fe_3O_4) and nickel ferrite ($NiFe_2O_4$) were chosen for this research work. Nickel ferrite particles were synthesized using an optimized solid-state route, relying on the following reaction $NiO + Fe_2O_3 \rightleftarrows NiFe_2O_4$ occurring at 1000 °C. This route led to the production of pure nickel ferrite particles within colloidal size range, verified by SEM imaging, Raman spectroscopy and X-Ray diffraction measurements.

As no data for zeta potential values of typical CPs in the RCS are available in the literature, the second step of this PhD was to design and manufacture a test-section for their measurement. The technique employed [12], [13], measuring the streaming potential by flowing water through a packed bed of particles, involved constructing a tube of temperature-resistant polymer that insulated the particles from the containing steel pressure boundary. The bed was contained between porous ceramic membranes while platinum wires, insulated from contact by oxidized zirconium, served as electrodes upstream and downstream of the bed to measure the potential difference and electrical resistance [14]. Installed in a high-pressure and -temperature recirculating loop, the test section permitted the measurements of the zeta potentials of commercially purchased magnetite and synthesized nickel ferrite between 20 and 240 °C for 12 different boron/lithium coordinations, representative of the chemical conditions of the primary circuit (operation cycle and cold shutdown process). These measurements are the first ever measurements of zeta potential of magnetite and nickel ferrite in the chemical conditions of the primary circuit up to 240 °C. The influence of the temperature, boron concentration and lithium concentration on the zeta potential values were studied and the following conclusions were obtained:

- As the temperature in the system increases, the zeta potential increases (for a fixed boron and lithium coordination),
- As the boron concentration increases, the zeta potential decreases, resulting from the adsorption of borate species on the particle surface, creating a negatively charged complexation sphere,
- As the lithium concentration increases, the zeta potential decreases, due the increase of the pH of the system (as lithium is introduced as lithium hydroxide, a strong base).

An extrapolation of the measured zeta potential values was used to cover the range of operating conditions of the primary circuit. A new inclusive deposition model to predict the deposition of both colloidal and inertial particles was developed and coded in the OSCAR calculation kernel. It enables to compute the deposition rate for each radionuclide in a given region of the circuit as a function of time. This improved model describes the deposition of particles as the succession of two steps in series: the transport step followed by the attachment step. In the transport step, the particle is transported by mass transfer, diffusion (Brownian and turbulent) and sedimentation should it be in a horizontal pipe. A new expression for the attachment probability was developed

to describe the attachment step. Its value depends on the ratio of the particle kinetic energy to the height of the potential barrier to overcome for deposition to happen (computed using the DLVO theory).

The model was calibrated using experiments performed on the CIRENE loop operated in the CEA. Its goal is to reproduce the conditions of the primary circuit and to study the deposition kinetics of particles following their injection in the loop using an in-line particle counter. By reproducing the CIRENE experiments in an entry dataset for the OSCAR code, the new inclusive deposition model was able to reproduce with satisfying accuracy experimentally measured deposition.

The calibrated model was then used to predict contamination in a 1300 MWe PWR and the simulation results were compared with measurements performed on an operating 1300 MWe PWR using the EMECC device [15]. The OSCAR code was able to reproduce preferential contamination in ^{58}Co in the cold regions of the circuit, which marks the first time that the code is able to reproduce this measurement.

This PhD has paved the way for further work concerning activity transport under colloidal form. Indeed, a new test section is being designed and built in the CEA to conduct more zeta potential measurements. Also, other mechanisms ruling particulate transfer in nuclear circuits are being improved to include surface interactions. The R&D field regarding high temperature colloidal transport is relevant to many nuclear reactor technologies including pressurized water reactors, boiling water reactors, CANDU reactors as well as fusion reactors (ITER). At the end of the day, the integration of colloidal behavior in the OSCAR aims at improving the prediction ability of the code in order to provide the industry with a reliable tool to limit the contamination of nuclear circuits.

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