IMPROVING THE PREDICTION OF ACTIVITY TRANSFER IN NUCLEAR WATER CIRCUITS BY INTEGRATING COLLOIDAL BEHAVIOUR: MODELLING AND EXPERIMENTAL ADVANCES FOR THE OSCAR CODE

C. CHERPIN
CEA, DES, IRESNE, DTN
F-13108 Saint-Paul-lez-Durance, France
Email: chloe.cherpin@cea.fr

F. DACQUAIT
CEA, DES, IRESNE, DTN
F-13108 Saint-Paul-lez-Durance, France

1. Introduction

Understanding the mechanisms underlying the transport of activity in the primary circuit in water-cooled reactors by Activated Corrosion Products (ACPs) is crucial for reactor operation and design. Indeed, as ACPs are responsible for the majority of the dose absorbed by workers during operation and maintenance, predicting their behaviour is of paramount importance to limit the radiation fields they generate. Hence, the CEA (French atomic energy commission), in cooperation with EDF and Framatome, has developed a unique simulation tool OSCAR [1] which relies on the upgrade of models to improve its prediction abilities.

Because of general corrosion of the surface of the primary circuit, ionic and particulate corrosion products (CPs) are released and transported in the coolant, forming ACPs if they are activated. ACPs become associated with spinel-type oxides and accumulate in the corrosion-product layers formed on system surfaces or create volume contamination if they remain dissolved or suspended. It has been established that a consequential portion of the CPs is transported as particles [2]. Filtrations campaigns performed on the primary coolant of operating PWRs have shown that particles range in size from several micro-meter to sub-micrometer (or colloidal) [3]. Therefore, when modelling particulate transfer, it is essential to take into account surface interactions by considering particle-surface interactions and particle adhesion through the zeta potential ζ values (i.e. the potential at the slipping plane of the surface). The literature reports ζ values for various oxides in the conditions of the secondary circuit (i.e., up to 250 °C) [4] obtained using the streaming potential method; however, no values were obtained in the conditions of the primary circuit of PWRs.

This paper presents the experimental campaign which was performed to obtain high temperature zeta potential values of representative corrosion products and the improved deposition model implemented in the OSCAR code which includes surface interactions, as well as the consequential improvements of the OSCAR simulations using this model.

2. High temperature zeta potential determination

In order to determine ζ values for the chemical conditioning and temperatures of the primary system of a PWR, a test section was developed [5] (adapted from the design of the EPRI [6] and VTT [4] apparatuses). The streaming potential method, which involves packing the particles as powder inside a column through which a solution is flowing, was used. Each end of the column is closed by a porous membrane to contain the powder and to let the solution

flow through. As the flow is imposed through the column, the diffuse layer of ions around the particles is carried toward the low-pressure side. From the movement of these charges, a streaming current is created. Due to the accumulation of charges towards the low-pressure side, an electric field arises, resulting in a conduction current, in the opposite direction to the streaming current. A potential is thus created between the two ends of the column; it is called the streaming potential and can be measured. Eq. **Erreur ! Source du renvoi introuvable.** relating the streaming potential ΔE and the pressure drop across the column ΔP, allows the determination of the zeta potential ζ [6]:

$$\frac{\Delta E}{\Delta P} = \frac{\varepsilon_0 \varepsilon_r R r^2}{4\eta L} \zeta \qquad (1)$$

where ε_0 is the permittivity of free space, ε_r the relative permittivity of the solution flowing through the column, R the electrical resistance across the column, r the radius of the column, η the dynamic viscosity of the solution and L the length of the packed bed.

The test section described elsewhere [5] enabled the determination of the zeta potential of magnetite particles (purchased from Sigma-Aldrich, 95 % purity) and synthesized nickel ferrite particles [7] up to 240 °C for twelve different boron/lithium coordinations representative of a PWR fuelling cycle. The influence of the temperature, boron concentration and lithium concentration on the zeta potential values of magnetite and nickel ferrite were studied and are presented elsewhere [8]. The main results are as follows:

- As the temperature increases, the zeta potential increases for all boron/lithium coordinations, for both magnetite and nickel ferrite particles. A similar trend was observed by Velin et al. [4] for magnetite particles in secondary coolant conditions. The test section arrangement in the high-temperature loop would not allow experiments to continue at temperatures above 240 °C; however, if it is assumed that the linear correlation is valid for higher temperatures (see Fig. 1.), the zeta potential values (for a fixed boron/lithium coordination) can be predicted for the temperatures of the primary system.
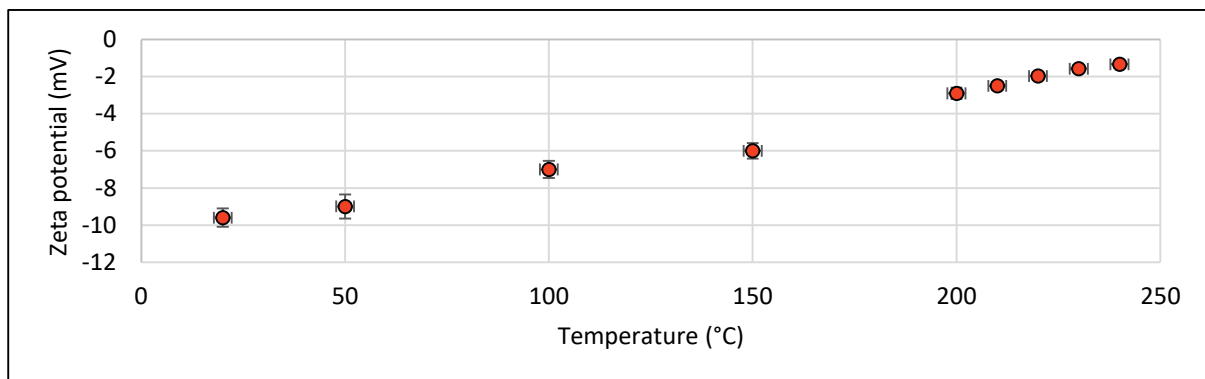

FIG. 1. Variation of the zeta potential of magnetite with the temperature up to 240 °C (for [B]=1800 ppm and [Li]=3.5 ppm).

- For a fixed temperature, an increase in boron concentration leads to a decrease in the zeta potential value for magnetite and nickel ferrite. This is explained by the adsorption of boron on the surface of particles, forming a negative co-ordination sphere [9], leading to the decrease in the zeta potential value as the borate concentration increases;

- For a fixed temperature, an increasing lithium concentration leads to a decrease of the zeta potential. Indeed, as lithium is introduced as lithium hydroxide, a strong base, hydroxide ions will predominate in the Helmholtz layer, in which the pH increases, and thus leads to a decrease of the zeta potential value.

3. Modelling particle deposition

The deposition of particles is considered to be the succession of two successive steps: the transport and the attachment steps. In the transport step, mass transfer propels the particle across the boundary layer toward the surface of a pipe, for example. The attachment step consists of the potential-driven adhesion of the particle on the surface, involving short-ranged physicochemical interactions. Eq. (2) gives the deposition velocity $V_{deposition}$ as a function of h' the mass transfer coefficient (taking into account thermophoresis arising from any temperature differences), p the attachment probability and V_{part} the velocity of the particle when it reaches the surface:

$$\frac{1}{V_{deposition}} = \frac{1}{h'} + \frac{1}{p.V_{part}} \tag{2}$$

The attachment probability p is determined by using the DLVO theory with hypothesis formulated by Urrutia [2] and Rudolph [10]. The DLVO theory enables to quantify the total interaction potential between a surface and a particle by adding the potentials deriving from attractive force and repulsive forces. In the classic DLVO theory, the attractive forces consist of the Van der Waals forces and the electrical double layer force (if the particle and the surface have surface charges of opposite signs). In the case of the particle and surface having surface charges of same sign, the repulsive term is composed of the electrical double layer force and the Born repulsive force (related to the repulsion of the atomic orbitals of the particle and the surface).

The zeta potential values measured previously enable the calculation of the electrical double layer interaction. The solid speciation of the outer oxide and of the particles is determined in the OSCAR code through the chemistry code PhreeqCEA; the average zeta potential values of the surface (outer oxide) and particles are computed.

Using the DLVO theory, the potential barrier between a particle and surface is calculated, if it exists. According to the deposition condition established by Urrutia [2], the particle will deposit only if its kinetic energy, when it reaches the surface, is sufficient to overcome the potential barrier. The ratio P_S can be defined by Eq. (3), where K_P is the kinetic energy of the particle when it reaches the surface and K the potential barrier computed from the DLVO theory:

$$P_S = \frac{K_P}{K} \tag{3}$$

The formulation of the attachment probability is borrowed from Rudolph [10] (see Eq. (4)):

$$\begin{cases} p = 0 \; if \; P_S < 1 \\ p = \frac{1}{1 + Ae^{BP_S}} \; if \; P_S \geq 1 \end{cases} \tag{4}$$

Where A and B were chosen to fit experimental data. This attachment probability profile was chosen so that:

- If $P_S < 1$, meaning that the potential barrier is too high for the particle to overcome it, the attachment probability is null;
- If $P_S \geq 1$, the attachment probability decreases as the particle kinetic energy increases. This constitutes a key assumption for this model, being that as mass transfer increases with fluid velocity, so does the shear stress at the surface, meaning that if particles are more likely to reach the surface, they are also more likely to "bounce off" or be "swept away" and will not deposit.

Calibration and validation of the previously described deposition model were performed using experiments performed on the CIRENE loop in the CEA and will not be presented here [11].

4. Simulation results

The case of a 1300 MWe French PWR (Reactor A) is used to illustrate how this new deposition model improved OSCAR simulations. At the end of cycle 22, the reactor underwent a Steam Generator Replacement (SGR) and during the shutdown one cycle later, an EMECC campaign [11] was performed to measure the surface contamination in different regions of the primary loops. These measurements showed that the crossover legs were 10 times more contaminated than the hot legs. Fig. 2. shows the measured surface contamination in [58]Co in the crossover legs and in the hot legs alongside the simulation results obtained using the OSCAR code with the previous deposition model and the new deposition model.
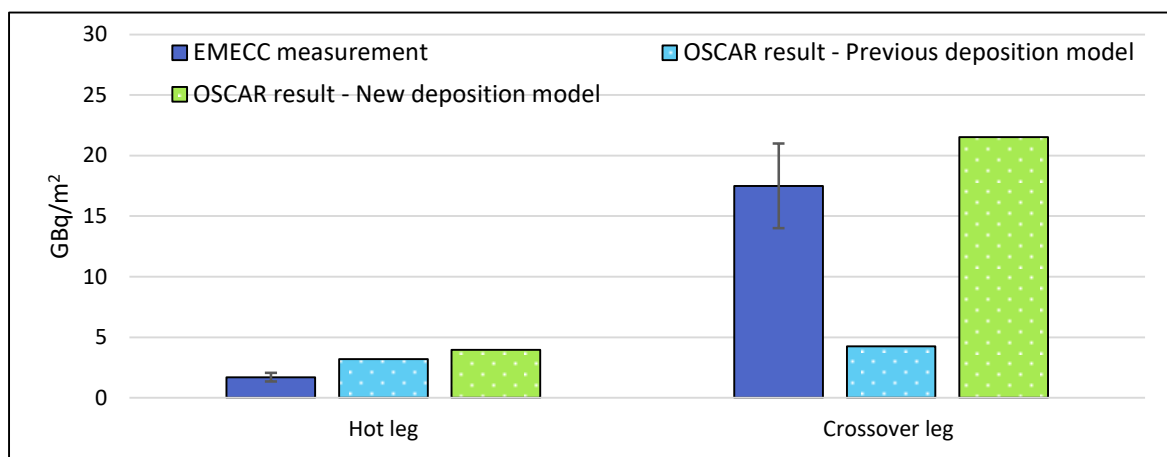

FIG. 2. Comparison between the [58]Co surface contamination measured in the hot legs and crossover legs in Reactor A with the simulation results obtained with the OSCAR code using the previous and new deposition model.

The new deposition model, which takes into account surface interactions, gives surface contamination levels more representative of those measured in the hot legs and in the crossover legs of this reactor. It is even slightly overestimating the surface contamination in both regions, indeed an uncertainty remains concerning the zeta potential values of the oxides in the primary system.

5. Conclusion and perspectives

The determination of zeta potential values up to 240 °C using the streaming potential method enabled the implementation of a revised deposition model taking into account surface interactions in the OSCAR code. This new model considers the attachment probability of a particle onto a surface through the knowledge of the value of the potential barrier it has to overcome with its kinetic energy. Using this model, a preferential contamination case was reproduced with the OSCAR code, which was not the case with the previous deposition model.

As other mechanisms describe particulate transport, work remains to fully integrate surface interactions in the OSCAR kernel. Also, an improved set up is being developed in the CEA to determine zeta potential values of oxides for temperatures ranging between 280 and 340 °C.

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