



Study on redox stability of iron oxide-based corrosion products formed in the secondary circuit of Pressurized Water Reactors

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As for many other industrial facilities, corrosion is an important issue for nuclear reactors. Iron oxides, as the major compounds of corrosion products in the secondary circuit of Pressurized Water Reactors (PWRs), are then involved in numerous phenomena. Thus, these corrosion products can reach the steam generators (SGs) following the water flow and deposit or precipitate in SGs. Both these phenomena give rise to fouling on tube surface, to clogging of water flow channel and to the formation of hard sludge. These phenomena can decrease the heat transfer efficiency and disturb the water flow distribution. During operation on PWR, several parameters (temperature, pH, oxygen, hydrazine concentration, etc.) are controlled in order to limit the corrosion and to ensure the plant safety and efficiency. However, it remains unclear how these parameters affect the iron speciation which in turn has an impact on corrosion. Industrial feedback has shown the occurrence of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) in the circuits, the latter being largely predominant. Since hematite has generally a lower solubility than magnetite, a dense layer of hematite protects the surface from flow accelerated corrosion (FAC). However, hematite increases the local electrochemical potential and therefore the risk of stress corrosion cracking (SCC) for Inconel. Since iron speciation depends greatly on transient phases during the operation of the nuclear power plants, characterized by redox variations, the kinetics of redox reaction of iron oxides becomes a key element. Thus, our objective is to understand the mechanisms and kinetics of redox transformation between iron oxides under typical secondary circuit conditions.

For the study of magnetite oxidation, synthetic magnetite was exposed to oxygen saturated alkaline solution at different temperatures from 80°C to 275°C for different reaction times. Through analysis of solid samples using XRD, SEM, Raman spectroscopy and spectrophotometric method, it is clearly demonstrated that the oxidation of magnetite leads to the formation of hematite above 80 ° C and goes through an intermediate product which is maghemite ($\gamma\text{-Fe}_2\text{O}_3$). Below 80°C no oxidation was identified. Oxidation kinetics increased with temperature from 120°C to 180°C and decreased from 180°C to 275°C, indicating a transition temperature furthermore confirmed by microscopic observations. Oxidations between 120°C and 180°C were successfully modeled, based on solid phase diffusion.

Reduction of hematite is in progress, and a setup was developed where alkaline solutions containing hydrazine circulates through a titanium reactor containing synthetic hematite. The device allows to keep stable the hydrazine concentration at 275°C. pH and redox potential of solution in the reactor at 275°C were measured in situ and the output solutions were analyzed to follow the reaction kinetics through the evolution of hydrazine and ammonium concentrations.