The Effect of Initial Iron Concentration and pH on theRadiolytic Formation of γ-FeOOH Nanoparticles

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Summary

The formation of iron oxyhydroxide nanoparticles under gamma irradiation is a process in the infancy of its understanding. Herein we present work to describe how initial iron concentration and pH impact the growth of radiolytically formed nanoparticles. These results can be used to better understand the activity transport processes occurring within a reactor environment which may pose both environmental and safety concerns. Preliminary results suggest that the final particle size is proportional to the initial dissolved iron concentration, while experiments probing the effect of solution pH are ongoing.

1. Introduction

Corrosion of steel piping in a nuclear reactor, and particularly within the reactor coolant systems, is a major concern. There are issues associated with bulk corrosion and potential impacts on piping integrity. There are also issues with corrosion product radioactivity transport in the coolant system. As a consequence of a corrosion process, metal ions may dissolve into the heat transport system and circulate throughout the reactor. These ions, if transported into the reactor core, may form colloids due to reactions with water radiolysis products, and these solid metallic species can become neutron activated, generating radioactive species which can then circulate with the coolant and deposit elsewhere in the heat transport system (activity transport). Corrosion product deposits of this type may not only act as nucleation sites for further corrosion, but they can also pose a serious hazard to employees who may be exposed to elevated levels of radiation.

Activity transport is controlled by water purification systems that are designed to remove dissolved metal ions and particulates. The efficacy of these systems depends on the nature of the ions and particles that are present. To design and operate purification systems, we need to understand the challenges that they face.

Corrosion is nuclear reactor systems is complex on its own. However, in many systems, and particularly the reactor coolant system, substantial levels of ionizing radiation can be present. Ionizing radiation drives water radiolysis and this generates reactive oxidizing and reducing species [1] (1):

$$H_2O \rightarrow \bullet OH, \bullet e_{aq}^-, \bullet H, HO_2\bullet, H_2, H_2O_2, H^+ (1)$$

These radiolysis products can have a significant impact on the chemistry of dissolved corrosion products and can lead to the formation of small (nano-scale) particles that may be challenging for purification systems to remove. A solid understanding of how these corrosion product nanoparticles form and behave in different chemical environments is necessary. Some of the ground work in this area has already been completed [1], but there are still work to be done to understand how the different parameters in coolant water can affect nanoparticle behaviour. This paper provides preliminary results on the impact of dissolved iron ion concentration on particle formation.

2. Experimental

Previous studies featured argon-purged solutions prepared at an initial pH of 5.5 with a dissolved ferrous sulfate concentration of 5×10^{-4} M[1].Those samples were irradiated in a ^{60}Co gamma cell at anabsorption dose rate of 6.7 kGy $h^{-1}$and were removed at specific time intervals for chemical analysis of the gas phase concentrations of hydrogen and oxygen (gas chromatography), the aqueous phase speciation of iron(II) and iron(III) (ferrozine UV-Visible spectrophotometric method [2]), the size and morphology of any particles present (transmission electron microscopy, TEM) and finally the identity and chemical phase of the nanoparticles (Fourier transform infrared (FTIR) spectroscopy and selected area electron diffraction, SAED).

3. Proposed Mechanism

A synthetic mechanism has been proposed to describe the formation and growth of ironoxyhydroxide colloids in irradiated water. The mechanism has three main stages (illustrated below): 1) nucleation and primary particle growth, 2) growth of γ-FeOOH particles, and 3) establishment of phase equilibrium. The dominant chemistry occurring within the each stage is different. By manipulating variables it should be possible to resolve the factors most important to each stage and how those factors ultimately affect the particle formation.

3.1 Nucleation and Primary Particle Formation

The first stage, nucleation and primary particle formation, is the result of the pseudo-equilibrium statebetween the hydroxyl radicals and solvated electrons which forces the establishment of a pseudo-equilibrium between the ferrous and ferric states within the solution.This occurs within the first milliseconds of irradiation. The solubility of ferric species is a several orders of magnitude lower than that of ferrous and any appreciable conversion of ferrous ions to ferric ions leads to the solution being effectively supersaturated with ferric ions. The Fe^{3+} species then condense and dehydrate out of the solution into a solid phase of $Fe(OH)_3$ (possibly with partially hydrated Fe^{3+} present as well). These condensate particles form nucleation sites on which Fe^{2+} ions can adsorb and where ongoing oxidation of this adsorbed Fe^{2+} to Fe^{3+} can occur, thereby growing the oxide particles.

3.2 Growth of γ-FeOOH Particles

The second stage, the growth of the γ-FeOOH particles, is characterized by slow conversion of Fe^{2+} to Fe^{3+}. The slower conversion rate in this phase is attributed to the increased importance of heterogeneous reactions in determining the dominant chemistry of the solution. During this stage the establishment of particle size and identity is determined. Under the conditions studied the final phase of the iron species was determined to be γ-FeOOH species.

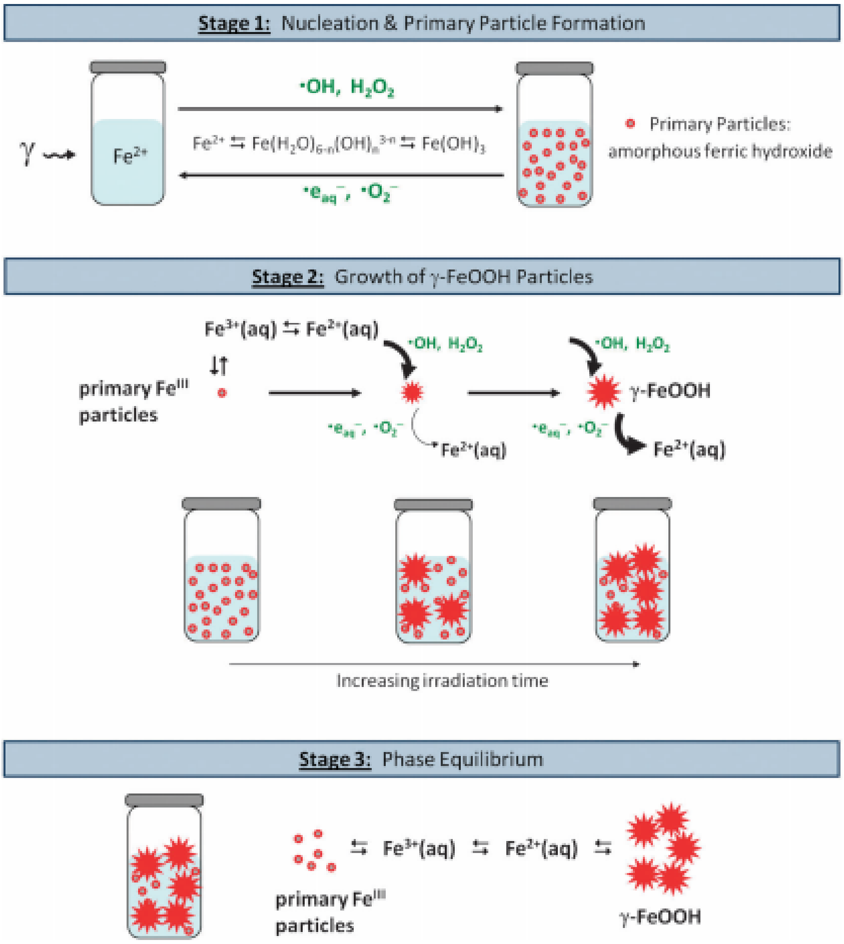

Figure 1 Proposed mechanism for the formation of γ-FeOOH nanoparticles [1].

3.3 Phase Equilibrium

The third and final stage, phase equilibrium, occurs when the molecular kinetics within the bulk solution reach equilibrium. This stage allows the γ-FeOOHparticles to grow to their final size which, in theory, is determined by the initial parameters of the solution.

4. Discussion

Below are the TEMs of particles collected from two tests where the conditions differed only in the initial $FeSO_4$ concentrations. The images show that the higher concentration Fe^{2+} solution led to the formation of fewer and much larger particles. The particles are roughly spherical, with a dendritic surface structure and have a relatively uniform size of about 40-60 nm. The particles formed in the lower concentration solution are also spherical and have a uniform size distribution, but they are much smaller (<10 nm in size). It is hard to determine whether these smaller particles also have a 'crystalline' morphology, but they do appear to be irregular and not smooth spheres.Experiments are ongoing at even lower initial Fe^{2+} concentrations and the interim results are that the nanoparticle size is smaller.

The preliminary results of our work indicate that that not only the initial concentration but also the reaction time influences the final size of the nanoparticles that are formed.The model presented above provides an explanation for our observations. A higher initial concentration of dissolved iron(II) species pushes the phase equilibrium towards larger nanoparticles by accelerating the rate at which the nanoparticles are formed.

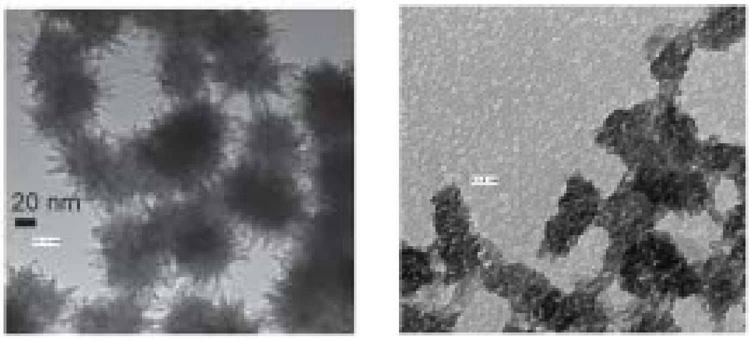

Figure 2 TEM of iron nanoparticles after 300 min of irradiation. The initial $FeSO_4$ concentrations were $5x10^{-4}$ M (left image) and $1x10^{-4}$ M (right image). Both images are to the same scale [1].

5. Conclusion

This study provides additional information on which a model to predict the propagation of iron nanoparticles in a heat-transfer system can be validated. Refinement of the model will require an understanding of how these nanoparticles behave not just in static conditions, but along gradients of concentration, pH, dose rate and other such factors. Understanding how these nanoparticles behave will allow nuclear plants to become more efficient, by controlling the variables which form these nanoparticles through metal dissolution. It will also allow nuclear plants to become safer for their workers, by reducing activity transport and exposure to radiation.

6. Acknowledgements

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7. References

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