PRELIMINARY STUDY OF THE EFFECT OF DISSOLVED ZINC IN PWR COOLANT ON IN-CORE CRUD DEPOSITS

P. Srisukvatananan, PhD Candidate
Supervisor: Dr. D.H. Lister
Department of Chemical Engineering, University of New Brunswick
PO Box 4400, 15 Dineen Dr., Fredericton, NB E3B 5A3

ABSTRACT

While zinc addition to the primary coolant is used to reduce radiation fields in Pressurized Water Reactors (PWRs), further investigations of its effects on in-core deposition are required to determine if crud-induced power shift is increased or lessened. In this work, PWR chemistry operating at high-temperature and high-pressure subcooled boiling condition is simulated to study the effects of pH and 10-ppb zinc addition on the deposition of corrosion product, non-stoichiometric nickel ferrite, onto Zircaloy-4 heated surfaces. Preliminary results revealed the deposit morphology of chimneys and thick deposit on the boiling surfaces, whereas very small amounts of deposit were observed on non-boiling surfaces. Without zinc, the deposit thickness is greater at the lower pH (10 and 1.3 μm at $pH_{300°C}$ of 6.8 and 7.0, respectively). With 10 ppb zinc at $pH_{300°C}$ of 7.0, the deposition increased by about 60%.

INTRODUCTION

Higher fuel burnup conditions have been performed in modern Pressurized Water Reactors (PWRs), giving rise to higher fuel duty and longer residence times. This results in high crud build-up on fuel cladding, higher cladding oxidation than anticipated and, in some cases, the axial offset anomaly (AOA) or also known as crud-induced power shift (CIPS). Axial offset occurs when the neutron flux is displaced towards the bottom of the core, probably because of boron sequestration in crud deposits at the top of the core (Frattini *et al*., 2000).

Zinc addition has been implemented in BWRs for more than ten years and more recently in PWRs. It has been shown to have a beneficial effect in terms of radiation field reduction (Lister *et al*., 2002; Uruma *et al*., 2004). It is understood that zinc makes spinel oxide films more protective and inhibits cobalt, a major activity source, from being incorporated. This lowers radiation fields and radiation doses in the plant. However, the effects of zinc addition on the deposition of corrosion products on Zircaloy fuel cladding are not fully understood.

In this work, PWR primary coolant conditions were simulated in an out-reactor loop to study the deposition of corrosion products on a heated Zircaloy surface. Subcooled boiling, controlled by a cartridge heater in a length of Zircaloy-4 fuel cladding, was imposed inside an autoclave in the loop circuit. Nickel ferrite,the principal primary-system corrosion product, was synthesized and injected into the autoclave as crud. To obtain, in a reasonably short time, deposits that were thick enough to be examined, high concentrations (~500 ppb) of crud were employed. The effects of pH and zinc addition were investigated.

EXPERIMENTAL

• Nickel Ferrite Synthesis

Non-stoichiometric nickel ferrite, $Ni_{0.8}Fe_{2.2}O_4$, was synthesized with a solid-state method via the following reaction:

$$0.8NiO + 0.8Fe_2O_3 + 0.2Fe_3O_4 \rightarrow Ni_{0.8}Fe_{2.2}O_4$$

The crystal structure of the synthesized nickel ferrite was determined with XRD analysis. The microstructure and composition of particles were examined with scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis, respectively.

• Nickel Ferrite Deposition

A schematic diagram of the experimental loop is shown in Figure 1. The coolant chemistry was monitored and adjusted via hydrogen purging and additions of lithium and boron in the reservoir in the cold, low-pressure section of the loop. The coolant leaving the reservoir was pressurized and pumped through an interchanger and preheater to raise the temperature. A heater jacket on the autoclave ensured that the bulk temperature as indicated by a thermocouple was 300°C. The coolant entered the autoclave and flowed upward over the electrically-heated Zircaloy tube simulating a fuel element. The coolant was then recirculated back to the reservoir via the interchanger and cooler, undergoing filtration and ion-exchange on the way.

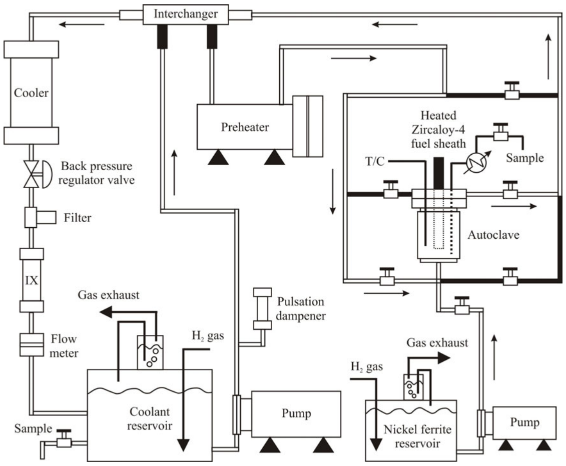

Figure 1 Schematic diagram of the experimental loop.

The heat flux in these experiments was controlled at 90% of the maximum to 160 kW/m^2. With a flow of 0.72 L/min and a bulk temperature of 300°C, this gave an estimated subcooled boiling rate at the top of the tube of 114 $g/m^2 \cdot s$. Two sets of removable Zircaloy-4 sample bands in the form of split cylinders were positioned on the heated region, a set of two at each end, to observe the effect of surface boiling on the deposition. Both the morphology and the amount of the deposits at either the top or the bottom of the tube could be examined at the same time.

In order to obtain observable deposits in a reasonable experiment time, high crud concentration of 500 ppb was generated in the autoclave by injecting a suspension of the nickel ferrite particles. The conditioned suspension was prepared in another reservoir and injected directly into the coolant entering the autoclave.

In the experiment with zinc addition, zinc solution was prepared by dissolving ZnO in lithiated-borated solution. The proper amount of zinc stock solution was added to the corrosion product reservoir and injected, together with nickel ferrite particles, to obtain a zinc concentration of 10 ppb inside the autoclave.

At the end of an experiment, the top bands of each set were examined for the amount of deposit. The bottom bands of each set were characterized for particle morphology and composition by SEM and EDX, respectively.

Three runs of duration 130-140 hours, with two values of $pH_{300°C}$ at one concentration of boron and with and without added zinc, were completed. The experimental parameters are presented in Table 1. It should be noted that in Run1, the pump used for slurry injection failed in the middle of the run. Nickel ferrite injection, therefore, was stopped for 90 hours; after its resumption, the run was prolonged to complete the target duration. In Run2, there was an electric power interruption of 10 hours towards the end of the experiment.

Table 1 Experimental conditions

Parameters	Run		
	1	2	3
pH at 300°C (calculated)	6.8	7	7
Li concentration (ppm)	1.5	2.4	2.4
B concentration (ppm)	1100	1100	1100
Zinc concentration (ppb)	0	0	10
Heat flux (kW/m^2)	160	160	160
Nickel ferrite concentration (ppb)	500	500	500
Pressure (psi)	1500	1500	1500
Bulk temperature (°C)	300	300	300
Flow rate (L/min)	0.72	0.72	0.72
Oxygen concentration (ppb)	<30	<30	<30
Duration of nickel ferrite injection (hours)	140	130	130
Total duration of Run (hours)	230	130	130

RESULTS AND DISCUSSION

- **Nickel Ferrite Synthesis**

The synthesized nickel ferrite was analysed to be $Ni_{0.72}Fe_{2.28}O_4$. Scanning electron microscopy showed the morphology of the particles, as in Figure 2. The size of the nickel ferrite particles varied between 1 and 2 μm.

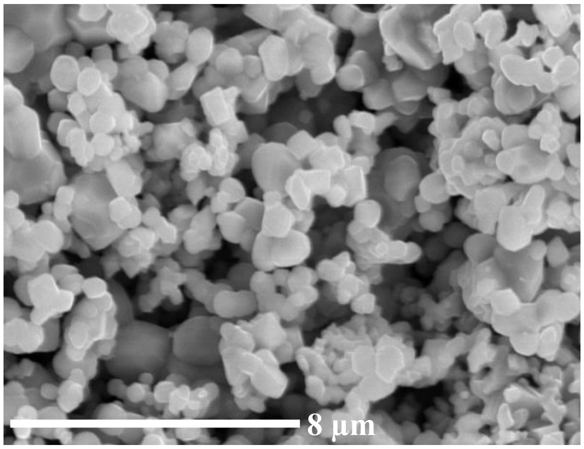

Figure 2 Scanning electron micrograph of $Ni_{0.72}Fe_{2.28}O_4$.

- **Nickel Ferrite Deposition**

There was significantly more deposit on the top bands than on the bottom bands; the differences could be distinguished with the naked eye. The Scanning Electron Microscope (SEM) revealed the deposit morphology from the three experiments, as depicted in Figures 4 and 5. The morphology indicated "chimneys", typical of wick boiling, in the deposits on the whole surface of the top bands. The chimneys were about 20-25 μm in diameter. Only scattered clumps of deposit were observed on the bottom bands. Particle sizes in all deposits were about 1-2 μm, similar to those of the injected nickel ferrite.

The deposit composition analyzed with Energy Dispersive X-ray (EDX) is presented in Table 2. Because of the sparse nature of deposits on the bottom bands, zirconium contributed considerably to the analysis. Percentages of iron and nickel in the deposits analyzed with EDX were similar to those of synthesized nickel ferrite; although, there were variations between the top and bottom sample bands. According to the particle size and the composition, then, the deposits were predominantly injected nickel ferrite.

Table 3 shows the amounts of deposit per unit area as elemental iron and nickel and the calculated deposit thicknesses. The deposit thicknesses were calculated from the amount of deposit by assuming elements present as nickel ferrite and a crud density of 2 g/cm^3 (assumed from plant experience of the fuel deposits).

It was postulated by Basset *et al*. (2000) that deposition in boiling is controlled by microlayer evaporation and by the process of bubble nucleation and bubble growth at preferred sites on the heated surface. Such sites often remained crud-free, but mass transfer of particles adjacent to the sites was increased, resulting in small rings of deposit. It was suggested that chimneys would develop later on. Since the temperature at the bottom of the heated tube in these experiments was too low to sustain boiling, deposits on the bottom bands were sparse.

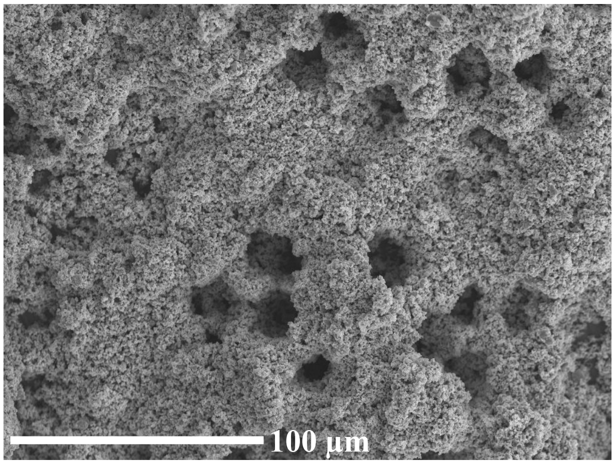

Figure 3 Deposits on the top band, Run1.

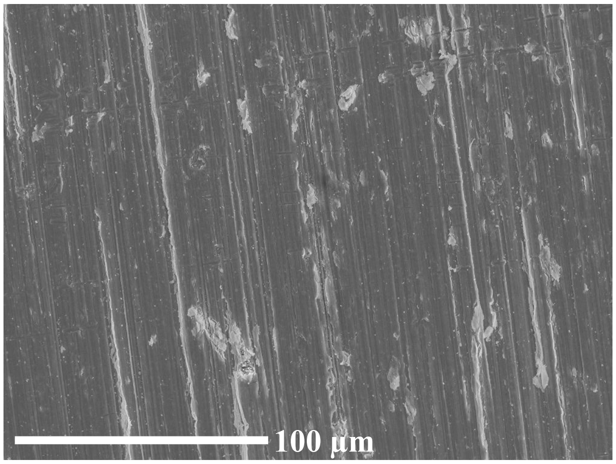

Figure 4 Deposits on the bottom band, Run1.

The deposits on the heated surface were thicker at lower lithium concentration (and therefore lower pH) – see Table 3. The surface charges of the nickel ferrite particles and the zirconium oxide on the Zircaloy-4 may be partly responsible. Thus, Mathur and Venkataramani (1998) reported the PZC (pH of zero charge) of magnetite substituted with nickel ($Ni_{0.72}Fe_{2.28}O_4$) to be 6.0, while Regazzoni *et al*. (1983) reported the PZC of zirconium oxide to be in the range 6.0-6.5. Although these determinations were made at low temperature, they suggest that the repulsive forces between the like charges on the particles and the surface were higher at the higher pH. The sub-cooled boiling may serve to concentrate the additives locally and increase the effect.

Table 2 EDX analysis of the deposits

Run	Sample band	Weight %			
		Fe	Ni	Zr	Zn
1	Top	74.87	25.13	-	-
	Bottom	55.31-60.85	21.58-22.60	16.56-23.11	-
2	Top	74.74	25.26	-	-
	Bottom	53.96-62.35	24.70-26.04	11.26-21.33	-
3	Top	73.46	26.23	0.30	-
	Bottom	59.97	25.05	13.64	1.34

Table 3 Amounts of deposit as elements on the sample band surfaces

Run	pH	Zinc addition	Sample band	Amount of deposit (mg/cm^2)			Deposit thickness (μm)
				Fe	Ni	Zn	
1	6.8	-	Top	1.018	0.376	-	9.86
			Bottom	0.098	0.035	-	0.93
2	7.0	-	Top	0.130	0.049	-	1.28
			Bottom	0.031	0.011	-	0.30
3	7.0	10 ppb	Top	0.195	0.081	0.003	2.02
			Bottom	0.047	0.012	0.001	0.38

Zinc addition to give 10 ppb in the coolant had an effect on the deposition, as shown in Tables 2 and 3. With zinc addition, the amount of iron and nickel was increased by about 60%. Walters *et al*. (2002) reported a small increase in the amount of total oxide found on Zircaloy surfaces with zinc addition in the in-reactor experiment. Moreover, as reported by Turnage (2004), more crud coverage was observed over fuel assembly surfaces with zinc addition, but most of those crud layers were thin and had no effect on the fuel performance. It is believed that when zinc is added to a coolant system, it displaces soluble species from oxide crystallites and may also release particles from surfaces. Coolant concentrations, therefore, increase and promote deposition. In this work, however, solid nickel ferrite was injected at a fixed concentration. It may be concluded, then, that zinc affects particle deposition. No change in pH was observed during the experiment with zinc addition.

The zinc content of the deposits was very small according to the EDX analysis in Table 2. This is consistent with the fact that trevorite (nickel ferrite) is more stable than franklinite ($ZnFe_2O_4$) and is not likely to incorporate zinc very strongly.

CONCLUSION

After 5-6 days, with high coolant concentration of nickel ferrite particles, substantial amounts of deposit were observed on heated Zircaloy-4 surfaces where sub-cooled boiling occurred. The deposit morphology indicated “chimneys”, typical of wick boiling. Increasing the lithium concentration to increase the $pH_{300°C}$ from 6.8 to 7.0 decreased the deposition in boiling. Adding zinc to 10 ppb in the coolant at $pH_{300°C}$ 7.0 increased the deposition by about 60%.

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