CHAPTER II
LITERATURE REVIEW

2.1 Crud Deposition in PWRs

2.1.1 Crud Composition

In 1979, Sandler investigated crud samples from various PWRs, and x-ray diffraction patterns showed that the predominant constituent was an inverse spinel with a cubic lattice parameter between that of Fe_3O_4 and stoichiometric nickel ferrite $NiFe_2O_4$, suggesting that the main constituent was a non-stoichiometric nickel ferrite. Aluminium was also found in combination with silicon, forming an amorphous alumino-silicate.

According to Cohen (1980), the composition of in-pile fuel-rod crud was found to be 58 wt %Fe (46.3% of this as Fe_3O_4), 5.8 wt %Ni, 1.9 wt %Mn, and 2.2 wt %Cr. Polley and Pick (1986) calculated the composition of crud in Westinghouse PWR fuel crud. The iron-nickel ratio was about 2-3, corresponding to an elemental composition of 68±7 wt %Fe, 29±6 wt %Ni, 3±2% wt Cr and 0.17±0.17 wt %Co.

Samples of crud from Callaway, the plant experienced AOA, were examined by Frattini et $al.$ (2000). By using Mössbauer spectroscopy, x-ray and electron diffraction, EDX, inductively-coupled plasma spectroscopy and scanning and transmission electron spectroscopy they found that the deposit samples contained predominantly nickel in a form of NiO, with a minor component of nickel ferrite. Surprisingly, the samples were also rich in zirconia, as monoclinic ZrO_2. This suggested the dissolution and re-deposition of cladding material. Moreover, a considerable weight fraction of a boron-rich compound in the form of long, slender needles known as bonaccordite, Ni_2FeBO_5, was also found in the deposit samples. Once formed, boaccordite is relatively insoluble and it may persist in the deposits over a wide range of chemistry conditions. Furthermore, it was found that the concentration of [10]B in crud flakes had depleted to 10.2±0.2%, as compared to its

20% natural isotopic abundance and its 17% end-of-cycle abundance in the bulk coolant (Sawicki, 2002).

2.1.2 Crud Formation

Corrosion product release and subsequent deposition depend greatly on their solubility in the coolant. The study of magnetite-nickel-ferrite solid phase equilibria in the PWR primary conditions was performed by Lambert et $al.$ (1983). The results of solid phase analysis showed the existence of the simultaneous reactions:

$$3NiFe_2O_4 + 4H_2 \leftrightarrow 3Ni + 2Fe_3O_4 + 4H_2O \qquad (2.1)$$

$$xNiFe_2O_4 + (1-x)Fe_3O_4 \rightarrow Ni_xFe_{3-x}O_4 \qquad (2.2)$$

where x is a number between 0 and 1.

In 1986, Lambert et $al.$ reported that the minimum solubility of magnetite and nickel ferrite occurred at around 300°C in a solution of H_3BO_3 and LiOH. According to Rühle and Riess, (1989), the minimum solubility for Ni was reached at $pH_{300°C}$ 7.2 and ranged from 50 to 100 ppt. Another investigation from Walker and Thornton (1989) showed that the pHs at which nickel solubility from both NiO and $Fe_{3-y-z}Ni_yCo_zO_4$ was a minimum were fairly close (7.3-7.7 at 573K) and were higher than those for iron solubility minimum from magnetite or nickel ferrite (6.9-7.0) at the same temperature.

Mathur and Venkataramani (1998) studied surface charge and surface chemical characteristics of magnetites substituted with nickel, cobalt and chromium, which are the principal corrosion products in water-cooled nuclear reactors. They found that with an increase in the concentration of the substituting cation the mixed oxide sorbed more water (became more hydrophilic) as the amount of strong sorption sites increased above a specific composition. However, as the concentration of the substituting cations in the primary heat transport system will be small as compared to the large quantity of iron present in the system, they were expected to be more hydrophobic. In order to perform chemical contamination, a suitable wetting agent was required. The relationship between compositions of the substituting cations and their surface charge were also reported. Furthermore, it was found that under the

reducing conditions of the reactor, rearrangement of Ni-rich Fe_3O_4 takes place expelling Ni as NiO, which may be subsequently reduced to metallic nickel (Allen *et al.*, 1988).

2.1.3 Effect of Coolant Chemistry

There is substantial evidence of the benefit from increasing pH and maintaining it constant during the operating cycle. Results have included reductions in the specific activity of deposits, resulting in lower radiation fields, as well as reductions in the amount of crud deposited on fuel. It was observed by EPRI (EPRI NP-1254, 1979) that operation under low pH chemistry conditions led to heavier deposits on heated surfaces than that under higher pH conditions. This conclusion was confirmed by Burrill and Shaddick (1980) and Large *et al.* (1986) that the pH was the dominant variable. However, the possibility of accelerated cladding corrosion is increased in regions of the core where subcooled boiling occurs and lithium concentrations increase locally (Polley and Evans, 1992; Millett and Wood, 1998).

2.1.4 Effect of Boiling

There are several studies reporting the effects of boiling on the deposition of corrosion products, and it appears that AOA was associated with high boiling duty in PWR cores (Millett and Wood, 1998). It was noted by Sandler (1979) that in the chemical environment of the reactor Ni, but not NiO, is expected to be the thermodynamically stable phase. However, at higher temperature or lower hydrogen concentrations, NiO could form. NiO might form under nucleate boiling, which would reduce the local hydrogen concentration and thus increase the degree of oxidizing conditions. This creates the possibility for NiO to form on high-performance cores.

It was observed by EPRI (EPRI NP-1254, 1979) that the weight of deposited iron was greater at higher surface heat flux. The deposition mechanisms were believed to depend on the change in solubility of crud induce by evaporation and temperature changes in the coolant.

Basset (1999) demonstrated the importance of bubble trapping mechanisms in magnetite particle deposition under subcooled boiling conditions at atmospheric pressure. The deposition mechanism was controlled by microlayer evaporation and by the process of bubble nucleation and bubble growth. The average deposition rate was dependent on the square of the heat flux.

Crud deposition experiments under boiling condition at high crud levels produced heavy deposits with steam "chimneys" (Kondratova and Lister, 2000). This morphology resulted from bubble nucleation at preferred sites on the heated surfaces. These sites remained crud-free, but mass transfer of deposited particles around the sites was increased due to the boiling, and chimneys were formed. The present of chimneys with boiling, so-called wick boiling, can lead to precipitation of boron components within the crud and initiate AOA.

2.2 Interaction of Boron with Deposits

2.2.1 Proposed Mechanisms of Boron Pickup

In 1980, Cohen suggested four possible mechanisms of boron accumulation within the core: direct precipitation of boric acid or its salts on surfaces or within crud deposits; adsorption on core deposits from solution in the bulk coolant; concentration within the pores of crud deposits due to boiling; and, adsorption on crud from local high concentrations produced by boiling. Moreover, addition of LiOH as the alkaline additive introduces the possibility of lithium borate to be present as deposit. Interaction between crud and boric acid was carried out by Fletcher in the 1960s – as summarized by Cohen (1980). The results showed that boric acid adsorbed by synthetic crud increases with temperature as well as boric acid concentration.

A model developed by Frattini and coworkers (2000) predicted that adsorption of boric acid is the principal hideout mechanism for boron on fuel deposits and suggested that lithium metaborate is not the hideout species. The results of this model were in reasonable agreement with observed AOA data. In the model, corrosion product deposition from soluble species was based on two principal processes:

■ Thermodynamics: the solubility difference resulting from higher coolant temperature at the surface of the fuel clad than in the bulk coolant. It is known that the solubility of some iron and nickel compounds decreases with increasing temperature. Thus, precipitation is most likely to occur at fuel surfaces

■ Liquid-phase mass transfer: the transport of species from the bulk to the cladding surface is proportional to its concentration difference. The buildup of fuel deposits via this mechanism is therefore limited by the kinetics of mass flux toward the cladding surface.

It was found by the model that mean deposit mass correlated well with steaming rate, being highest for the highest power bundles, and matched within roughly 30% the measured mass loading determined from fuel scraping following plant shutdown. The calculations also showed that it is unlikely that $LiBO_2$ will precipitate under existing plant conditions.

2.2.2 Boron Desorption from Crud

Cohen (1980) described the study of reversible of boron absorption in synthetic crud by Fletcher. Boron, absorbed on crud at high solution concentration, was removable at low solution concentration within a short time, indicating that at the end-of-core life, when boron concentration is low, there would be significant boron desorption. However, irradiation effects were not taken into account in these findings. This conclusion was confirmed by Picone's observation (also reported by Cohen, 1980) on boron content of naturally-formed crud deposits on fuel irradiated in high-temperature boric acid solution. Very low irreversible deposition was observed and was found to be independent of exposure period in the reactor over the range of one to three months.

However, there was evidence from plants that experienced AOA of irreversible pickup of boron with crud deposition (NRC Information Notice 97-85, 1997). The reactor power was reduce to 30% in the hope of releasing lithium borate from the crud, thereby creating a more positive AO when power was returned to 70%. However, this manoeuvre was unsuccessful. It was found that after 24 hours

at 30% power, only 25% of the boron had been released from the crud. When power was increased to 70%, approximately 70% of the boron that had been released during the power reduction was reabsorbed into the crud. And the AO after the manoeuvre was greater than before. It was surmised that the worsening AO was caused by the release of depleted boron during power reduction, followed by absorption of fresh, undepleted boron into the crud during the return to 70% power.

2.2.3 Solute Concentration Mechanisms in Crud

It was suspected by Najibi *et al.* (1997) that the local chemistry at the deposit/cladding interface could differ substantially from that of the bulk coolant, thereby affecting both the nature and extent of the deposition process. Concentrating lithium ions and boric acid in this region modified the pH of the near-clad coolant, which in turn altered the solubility/precipitation characteristics of the water-borne species. When bubbles formed on a heat transfer surface, the local concentration increased significantly at the gas/liquid/solid interface and deposits formed (Najibi *et al.*, 1997).

Pan *et al.* (1985) developed the model of concentration levels of solutes in porous deposits with chimneys under wick boiling conditions. They postulated that solutes in the bulk liquid were carried into the porous deposit by liquid flow which was induced by the evaporation at the chimney wall and driven by capillarity. Then the non-volatile solutes might be concentrated near the chimney wall, especially in the region near the heating surface. They found that the maximum concentration factor increased with decreasing porosity, with increasing chimney population and with increasing system pressure (in the range of interest to light water reactors). Moreover, maximum concentration factor increased exponentially with heat flux and crud thickness. According to this model, the bulk concentration of LiOH at 2ppm, corresponding to PWR conditions, could lead to concentrations in crud as high as 8.5M, which actually exceed the solubility limit.

2.2.4 Surface Interaction

A protective borated layer on crystallite surfaces may be the possible mechanism responsible for the low solubility of nickel and iron from nickel ferrite.
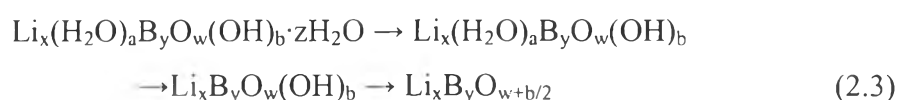
Sandler and Kunig (1981) investigated the effect of simulated PWR shutdown conditions on the solubility of nickel and iron in 2160 ppm boron as boric acid at different temperatures. The solubility of both nickel and iron reached a maximum in the region between 50 and 100°C and the ratio of the solubility throughout the entire temperature range lay between 4 and 5, which was roughly congruent to their concentration ratio in the solid. The authors noted that the solubility of iron obtained at low temperature in borated solution was apparently lower than that obtained for magnetite in HCl solution in the same pH conditions. The presence of a protective borated layer formed on the ferrite, which prevented establishment of equilibrium with the bulk phase, was attributed to this effect. However, it seemed likely that the protective film at low temperature was provided by compound formation which occurred at high temperature.

Thornton (1986) experimented on the dissolution of magnetite in boric acid solution and found that the solubility of magnetite is slightly lower than that reported by previous studies at the same pH. However, the magnetite solubility in the previous reports was studied in dilute HCl or base. The reason was tentatively explained by the inhibitive effect of a borated surface layer formed on the magnetite. However, the presence of a borated layer would be difficult to detect, since the analysis procedure might decompose the layer.

2.2.5 Chemistry of Lithium Borates

Lithium metaborate, $LiBO_2$, is expected to be the hideout species in crud because it has retrograde solubility at high temperature (Cohen, 1980).

Touboul and Bétourné (1996) synthesized the following compounds: $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$, $Li_3B_5O_8(OH)_2$, $Li(H_2O)B_2O_3(OH)$ and $Li(H_2O)_3B_5O_6(OH)_4$. Their dehydration mechanism and crystal structure were studied. They found that the hydrated lithium borates can be obtained from an aqueous solution of a stoichiometric mixture of $LiOH \cdot H_2O$ and H_3BO_3 by the evaporation under constant stirring and heating. They also proposed the following scheme of dehydration for hydrated lithium borates:

$$Li_x(H_2O)_aB_yO_w(OH)_b \cdot zH_2O \rightarrow Li_x(H_2O)_aB_yO_w(OH)_b$$

$$\rightarrow Li_xB_yO_w(OH)_b \rightarrow Li_xB_yO_{w+b/2} \quad (2.3)$$

in which the final amorphous product can be decomposed.

It was of interest that the final dehydration step from $LiB(OH)_4$ to $LiBO_2$ occurs at 170°C and a high-temperature phase, β-$LiBO_2$, occurs at 470°C but transforms to α-$LiBO_2$ on cooling.

In 1998, nine compounds, namely Li_3BO_3, α-$Li_4B_2O_5$, β-$Li_4B_2O_5$, $Li_6B_4O_9$, α-$LiBO_2$, $Li_2B_4O_7$, $Li_3B_7O_{12}$, LiB_3O_5 and $Li_2B_8O_{13}$ in the Li_2O-B_2O_3 system were synthesized and studied by Mathews and coworker. The densities of the compounds were found to be in the 1.90-2.50 g/cm^3 range, while their solubility in water at room temperature was in the 0.91-8.64×10^{-2} g/cm^3 range. The solubility of these compounds decreased with increase in B_2O_3 content up to 70 mol% (corresponding to the compound $Li_3B_7O_{12}$). Beyond this composition, the solubility of the compounds increased with increase in B_2O_3 content. Their thermal behavior showed that except for the congruently melting α-$LiBO_2$ and $Li_2B_4O_7$, the rest of the compounds undergo phase transition, decomposition or incongruent melting below their liquidus temperatures in air. High-temperature studies indicated that all of these compounds were stable at temperatures up to about 600°C.

2.3 Effect of Zinc on Corrosion Product Deposition

Zinc addition has been implemented successfully in BWRs in terms of dose rate reduction for many years, and this strategy is also employed in PWRs. In 1990, the effect of dissolved zinc on the transport of corrosion products in PWRs was studied by AECL (EPRI NP-6975-D, 1990). It was found that the Co-60 pickup on both stainless steel and Inconel was reduced by factors of 8-10. Oxide film thickness were reduced, but by lesser amounts, indicating that the oxide properties were changed by zinc, becoming resistant to cobalt incorporation. The effect of zinc on corrosion release seemed to be unclear.

The effect of zinc addition on PWR corrosion product deposition on Zircaloy-4 was studied between 1995 to 2001 (Walters *et al.*, 2002). An in-pile loop was made of Inconel, stainless steel and Zircaloy in proportion to typical wetted surface areas in a plant. Corrosion products were divided into two types: loose crud

particles, removed by water flushing, and deposited oxide, removed by acid leaching. They reported that, on the Zircaloy surface, loose crud was less with 10-ppb zinc addition than that without zinc by a factor of six. However, the amount of deposited oxide was greater in the experiment with added zinc by a factor of three. Overall, the effect of zinc addition was a small increase (less than a factor of two) in the amount of total oxide found on the Zircaloy surface. On the other hand, it was observed that zinc addition significantly reduced the deposited oxide on Inconel and stainless steel surfaces.

The chemical form of added zinc may affect pH in the coolant (Beverskog, 2004). Zinc is added as zinc oxide (ZnO) to BWR coolant, while in PWRs zinc is added as zinc acetate or zinc borate. The net effect of zinc addition in BWRs is that the coolant is more alkaline below the hydrolysis temperature (167°C); above that, the pH of the coolant is unaltered (neutral). In PWRs, zinc addition causes the decrease in pH, and consequently increases the solubility of the surface oxides. The higher content of metal in the coolant results in the increase of fuel crud deposition. Beverskog (2004) also noted that zinc addition causes the reduction in radiation dose rate contributed mainly by active cobalt. Zinc competes with radiocobalt to absorb on the surfaces and then can be incorporated into the oxide layer. Moreover, zinc reduces the diffusion rate of other species through the oxide, and consequently reduces the oxide growth rate. On the PWR fuel cladding surface, zinc does not form a new solid phase, since nickel ferrite is the most stable solid. However, zinc is incorporated into the crystal structure mostly as interstitials. The net effect of zinc addition is slightly increased deposition rate of fuel crud.

Stellwag *et al.*, 2004, reported the effects of zinc injection at a concentration of 5 ppb in the reactor coolant for radiation control implemented in Siemens PWRs for 8 years. It was observed that zinc injection resulted in an increase of Co-58 and Co-60 level in the reactor coolant system, consequently causing a considerable decrease of the dose rate level. Zinc injection also resulted in an increase of the iron concentration level which, in turn, increased the tendency of crud formation on fuel rods. It should be noted, however, that zinc injection was not found to have any effect on the visual appearance or crud loading of the fuel assemblies.

The effect of zinc addition on crud deposition on fuel rod surfaces in BWRs was investigated by Uruma and colleges (2004). The presence of 5-10 ppb zinc was found to accelerate crud deposition by changing the pH slightly. It should be noted that small pH changes in the bulk might affect local pH on the heated surfaces greatly and result in crud deposition. It was also reported, by Turnage (2004), that most plants with zinc addition have observed more extensive crud area coverage over almost all of the fuel assembly surfaces. However, most of those crud layers have been quite thin and have no known fuel performance effects.

2.4 Boron Measurement by Neutron-Based Techniques

Neutrons can be used for measuring boron due to its high absorption cross-section at thermal energies (3840 barns). Since most neutron-emitting sources emit fast neutrons, a moderating material is used to slow them down. If boron is surrounded by a medium that can slow neutrons down, the source can directly be made incident on the medium. Otherwise, the boron-containing sample can be inserted into a moderating assembly. In either case, a neutron detector can be placed in the proximity of the interrogated sample to measure the change in the thermal-neutron flux. Alternatively, the prompt gamma-rays emitted, at 478 keV energy, upon the absorption of neutrons by boron can be measured using a detector located farther away from the sample, since gamma-rays can usually travel larger distance than thermal neutrons. In general, one can state that there are three different ways to measure boron by neutrons: (1) slowing down followed by absorption, (2) flux depression within a slowing-down assembly and (3) prompt gamma-ray activation analysis.

Boron analysis by neutron absorption was used to measure boric acid concentration in a nylon intermediate process (Charlton, 1986). A fast neutron source and a slow-neutron detector were arranged in the backscattering mode. Fast neutrons from the source were slowed down by collision with hydrogen and the detector continuously monitored slow neutrons which diffused out through the pipe wall. The reduction in the detector count rate resulting from slow-neutron absorption by boron nuclei was directly related to the concentration of boric acid.

The boron content in heat resistant material was determined by the flux depression method (Hussein, 2003). This method is designed to use an isotopic source, and requires a thermalization assembly to create a thermal neutron cloud inside an inspection facility. The presence of boron, a strong thermal neutron absorber, causes a depression in the neutron flux. The amount of flux depression corresponds to the concentration of boron in the object. This method was also applied to determine the boron concentration in metal alloys, glass and detergents (Hussein, 2003).

Prompt gamma-ray activation analysis (PGAA) has been used to measure boron concentration, by monitoring the 478 keV prompt gamma-rays after neutron absorption. Baechler *et al.* (2002) and Byun *et al.* (2004) reported the use of this method to determine the boron concentration with a detection limit of the order of 1 ppm. Neutrons used to irradiate borated samples were extracted from a neutron generator and moderated to obtain high intensity thermal neutrons at the sample position. Samples were contained in specific containers, such as thin Teflon bags, which do not interfere with the analysis.

One of the goals of the work reported in this thesis was to develop a technique to determine the change in boron concentration in a circulating-flow autoclave, which was operated at high temperature and pressure. The use of a radioisotopic source was most practical for this situation. Neutron slowing-down followed by absorption is possible since a slowing-down assembly can be used to create a thermal neutron cloud inside an autoclave, and a detector can be located in the proximity of the inspected medium. On the other hand, PGAA associated with a radioisotopic source is another possible alternative. In this work, both methods were investigated.