CHAPTER III
EXPERIMENTAL

A laboratory program was undertaken to study the deposition of nickel ferrite particles onto Zircaloy-4 surfaces and the hideout return of boron under subcooled boiling conditions in a high-temperature, and high-pressure loop. The effects of pH, surface boiling, and zinc addition were investigated. Boron measurement by neutron-based techniques in static and room temperature environments was also studied.

3.1 Nickel Ferrite Synthesis and Characterization

Non-stoichiometric nickel ferrite, $Ni_{0.8}Fe_{2.2}O_4$, was synthesized with a solid-state method (Ranganathan, 2001) by the following reaction:

$$0.8NiO + 0.8Fe_2O_3 + 0.2Fe_3O_4 \rightarrow Ni_{0.8}Fe_{2.2}O_4 \qquad (3.1)$$

The required quantity of NiO, α-Fe_2O_3 and Fe_3O_4 was finely ground in a mortar with a pestle in ethanol medium. After it was uniformly mixed, the mixture was vacuum sealed in a glass tube, and heated to 1,000°C for 50 hours. The mixture was then finely ground again, and was ready to be used.

The crystal structure of synthesized nickel ferrite was determined from XRD analysis, using CuK_α radiation at wavelength of 1.5406 Å. Lattice parameters were calculated and compared with those of magnetite and stoichiometric nickel ferrite, which should give a linear relationship according to Vegard's law (Ranganathan, 2001).

The microstructure and composition of particles were examined with scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis, respectively. In order to confirm the composition, three different regions in the sample were examined and then averaged.

3.2 The Experimental Loop

A loop simulating PWR conditions was used to study the deposition of corrosion products on the heated surfaces, and a schematic diagram is shown in Figure 3.1. The coolant chemistry in the primary coolant reservoir could be monitored and adjusted via the reservoir in the cold and low-pressure section of the loop. The coolant was pressurized and pumped through an interchanger and a preheater to raise the temperature to 300°C. The coolant entered the autoclave and flowed upward over an electrically-heated Zircaloy tube simulating the core of a nuclear reactor. The coolant then was recirculated back to the reservoir.

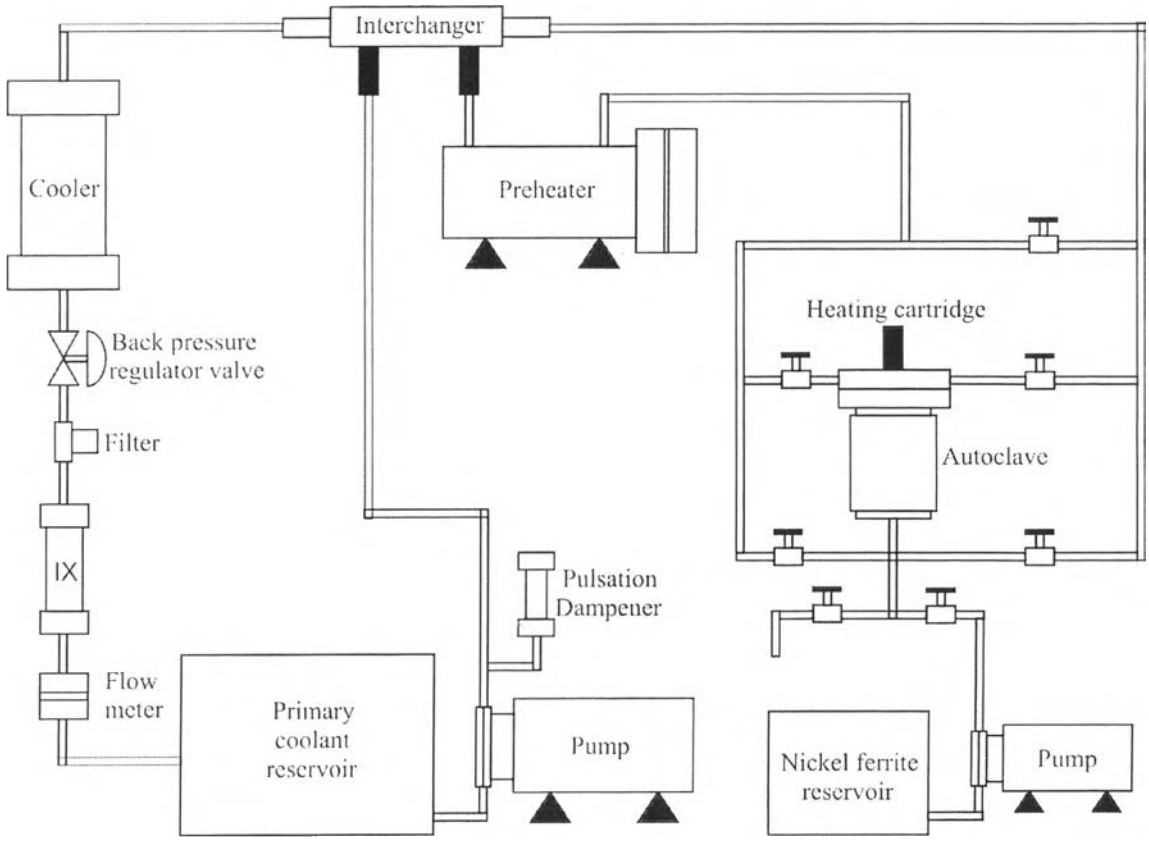

Figure 3.1 Schematic diagram of the loop.

Simulating a corrosion product, nickel ferrite particles were added in another reservoir, and injected directly into the coolant entering the autoclave. A

stirrer with a speed of 1,000 rpm was installed in this reservoir to ensure that all particles were well suspended. The nickel ferrite reservoir and the pump were placed close to the injection point in order to minimize particle deposition in the pipeline. Particulates left in the coolant exiting the autoclave were then removed out by the filter installed downstream of the loop cooler. In order to remove soluble contaminants, an ion exchange resin column was used.

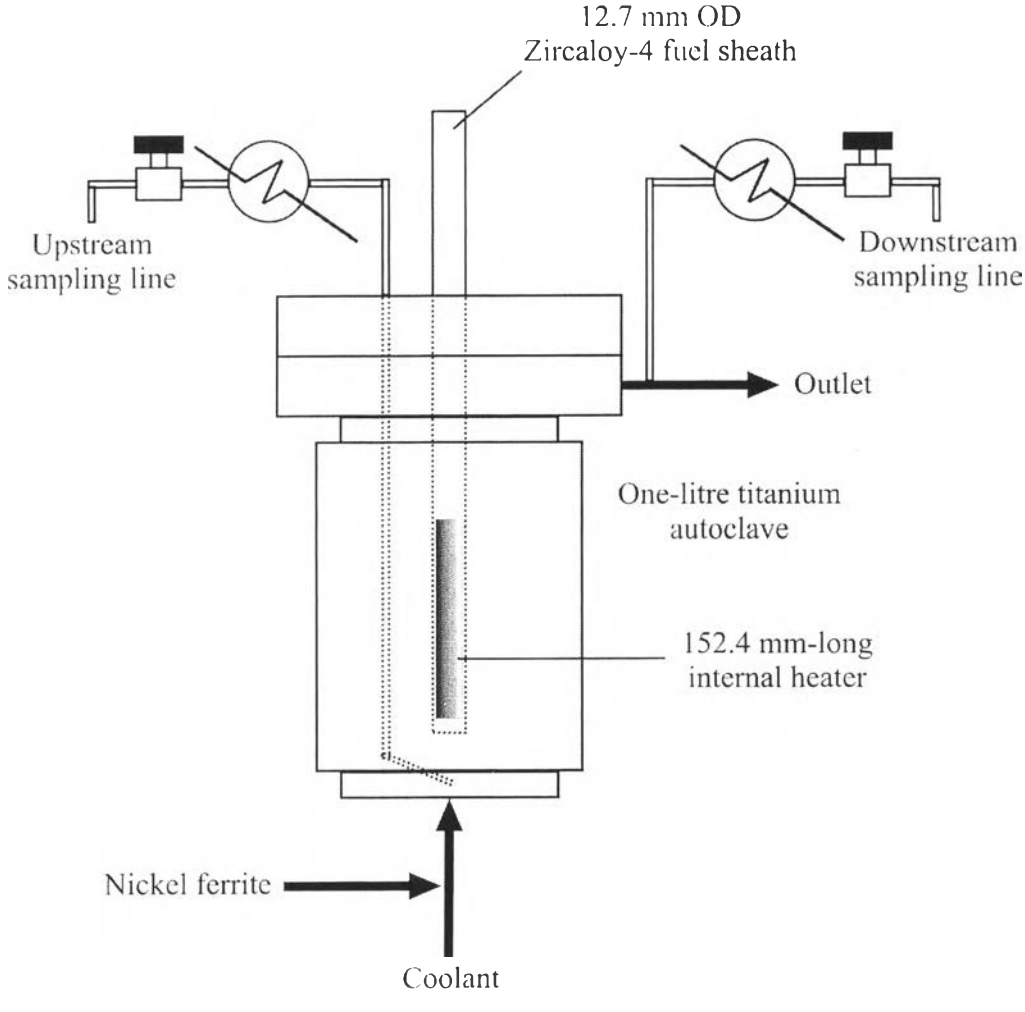

Figure 3.2 Schematic diagram of the autoclave.

A length of Zircaloy-4 fuel sheathing containing an electric heater was installed inside the autoclave to mimic a reactor core. The heat flux of the heating cartridge was controlled to give a maximum output of 18 kW/cm^2. Upstream and

downstream sampling lines of the autoclave were installed to check the chemical concentration, as depicted in Figure 3.2. Two sets of Zircaloy-4 coupons were positioned at both ends of the Zircaloy-4 sheath to observe the effect of surface boiling on the deposition. There were two coupons in each set, so that both the surface morphology and the amount of the deposits could be examined at the same time. The coupons were removed for analysis by sliding off the bottom of the sheath. Figure 3.3 shows the coupon arrangement.

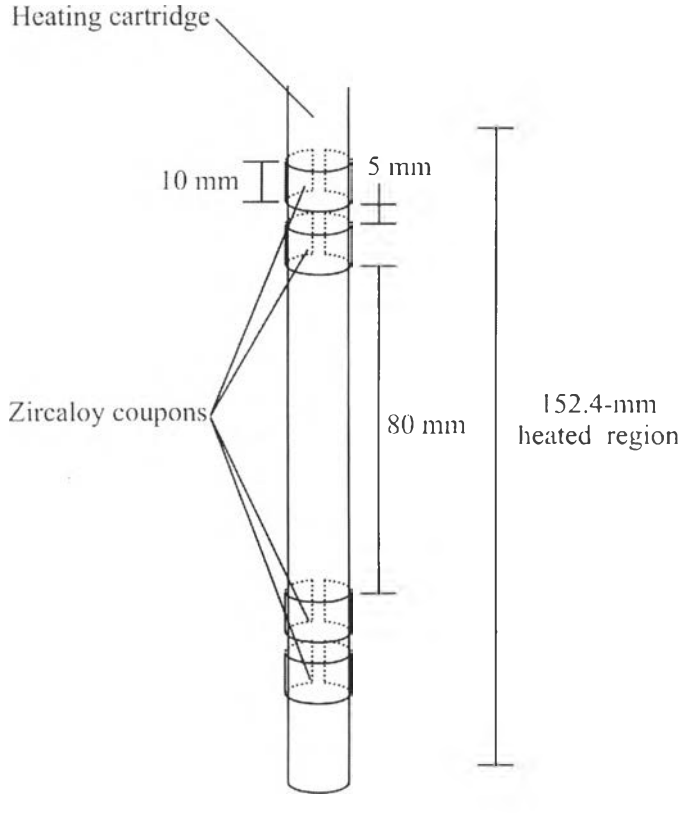

Figure 3.3 Schematic diagram of Zircaloy-4 coupon arrangement.

3.3 Nickel Ferrite Deposition and Boron Hideout Return Experiments

3.3.1 General Procedure

The loop was pressurized to 1500 psi, and the temperature raised to 300°C. Hydrogen was continuously purged through the reservoir for 24 hours before starting the experiments until the end to ensure low oxygen concentration. The

oxygen level was monitored by Chemets colorimetric indicator and kept as low as possible; generally below 30 ppb. After hydrogen purging for 24 hours, the autoclave was gradually valved in until its temperature reached 300°C. Then heat flux was applied to the heating cartridge for 24 hours to allow the Zircaloy-4 surfaces to become oxidized.

The water in the nickel ferrite reservoir was also purged with hydrogen throughout the experiment and had the same chemistry as in the primary coolant reservoir. After the heat flux had been applied for 24 hours, the proper amount of synthesized nickel ferrite particles was added to the nickel ferrite reservoir and injection to obtain the desired nickel ferrite concentration inside the autoclave was begun. The injection rate of nickel ferrite was chosen not to be too low to avoid particle plug-up in the pipeline and to obtain a constant flow rate. In this work, the flow rate was set at 10 ml/min and the nickel ferrite concentration in the reservoir of 36.5 ppm gave a concentration in the autoclave of 500 ppb.

During the experiment, 50 ml of samples were taken from coolant reservoir, upstream and downstream of the autoclave every day to check the chemistry. Samples taken from the same spot were expected to be identical. Therefore, samples were randomly selected and analyzed.

At the end of each run, the heating cartridge was turned off, the flow was diverted to the by-pass line, and the autoclave was allowed to cool down. After isolation, 25 ml of samples were taken from the autoclave at different times; 0, 5, 10, 30, 60, and 180 minutes, to observe any boron hideout return. At about 50°C, the autoclave lid was removed together with the heating cartridge. The Zircaloy coupons were then carefully slid off the bottom of the heating cartridge, and prepared for analysis. The loop filter was removed, and particulates were collected for analysis.

3.3.2 Analysis

Lithium, iron, nickel and zinc concentrations in coolant samples were determined with ICP-OES. To dissolve nickel ferrite particles in the sample solution, hydrochloric acid was used. Two ml of 36% hydrochloric acid were added to each 40 ml sample solution. The solution was then heated almost to dryness on a

heating plate and de-ionized water added to dissolve precipitated salts. Iron and nickel concentrations then could be determined.

Boron concentration in the loop was determined quantitatively by titration with standardized sodium hydroxide. Since boric acid is a weak acid, before the titration mannitol was added to form complexes with boric acid. Phenolphthalein was used as an indicator. Details are described in Appendix D.

For the Zircaloy-4 coupons, the top coupons of each set were examined for the amount of deposit. These coupons were kept in isopropyl alcohol, and sonicated for 30 minutes in a water bath at 50°C to remove deposited particles. In the same time, alcohol was allowed to evaporate to almost dryness. The deposits were then dissolved in 36% hydrochloric acid to determine the concentration of iron and nickel with ICP-OES. The concentration was calculated back to the amount of deposit per unit area. The bottom coupons of each set were characterized for crystal structure, surface morphology and composition by XRD, SEM and EDX, respectively.

Particulates from the filter downstream of the loop cooler were removed by sonication and characterized by SEM and EDX. This was done to determine any phase change of injected nickel ferrite during its passage through the loop.

3.3.3 Experimental Parameters

There are three parameters that play an important role in the deposition of corrosion product; pH, corrosion product concentration and heat flux. The last is particularly important when it induces subcooled boiling. Basset (1999) and McCrea (2001) reported that the amount of deposit increases with heat flux and corrosion product concentration. In this work, the heat flux was set at 90% maximum of the output of the heater in the Zircaloy-4 sheath, and nickel ferrite concentration was at 500 ppb, which was almost three orders of magnitude higher than that in a typical plant condition. These conditions were expected to create deposits on the heated surfaces in a conveniently short time. The effect of zinc on the deposition of corrosion product under PWR operating condition was studied.

Therefore, the pH at 300°C, based on lithium and boron concentration, was set to be 7. All experimental parameters are tabulated in Table 3.1.

Table 3.1 Parameters of nickel ferrite deposition experiments

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/cm^2)	16	16	16
Nickel ferrite concentration (ppb)	500	500	500
Pressure (psi)	1500	1500	1500
Bulk temperature (°C)	300	300	300
Flow rate (ml/min)	0.72	0.72	0.72
Oxygen concentration (ppb)	30	30	30
Duration of nickel ferrite injection (hours)	140	130	130

In the experiment with zinc addition, zinc solution was prepared by equilibrating ZnO for 8 hours in lithiated-borated solution. The solution was then filtered through a 0.45-μm pore-size filter to give a stock solution with a concentration of 13 ppm. 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.

It should be noted that in Run1, the pump used for nickel ferrite injection was damaged in the middle of the run. Nickel ferrite injection, therefore, was stopped for 90 hours, and then restarted to complete the target duration. In Run2, there was an electric power interruption of 10 hours prior to the end of the experiment. Therefore, boron hideout measurements could not be made.

In this work, the effect of surface boiling can be deduced from observations of the top and the bottom coupons. The effects of pH and zinc addition can be investigated by comparing Run1 with Run2, and Run2 with Run3, respectively.

3.4 Boron Measurement with Neutron-Based Techniques: Experimental Apparatus

3.4.1 Neutron Slowing-Down Followed by Absorption

Static experiments at room temperature were carried out in order to determine the effect of boron on neutron fluxes. The apparatus was designed to detect the accumulation of boron in the middle of the autoclave, where a boron hideout at the surface of the heated Zircaloy-4 sheath was expected to occur. Both the transmission and scattering of neutrons could be monitored. However, with the transmission arrangement, better contrast was more likely to be obtained. This is because transmission can detect the effect of both fast-neutron attenuation and scattered-neutron absorption, while scattering can detect only the effect of scattered-neutron absorption. Although the neutron absorption cross section decreases with increasing neutron energy, boron can still absorb high-energy neutrons to some extent. Hence, transmission was investigated in this work. Figures 3.4 and 3.5 show schematic diagrams of the experimental setup and electronic assemblies, respectively.

Californium-252 (^{252}Cf) was employed as the fast neutron source in the experiment. This radioisotope decays by alpha-particle emission (97%) and spontaneous fission (3%), yielding an average of 3.75 fast neutrons per fission, and the effective half-life is 2.65 years (Hussein, 2003). This source and its activity were 2 μg and 40 MBq, respectively, in 1986. Its current activity is estimated to be 361 kBq, giving about 361,000 neutrons per second.

Helium-3 and BF_3 gas proportional counters were used as neutron detectors. When a ^3He nucleus absorbs a neutron, it releases a proton, which gives rise to an electronic signal. In a BF_3 detector, the electric signal is produced via a (n,α) reaction with ^{10}B. Helium-3 and boron-10 have absorption cross-sections of

5330 and 3840 barns, respectively, for thermal neutrons, but the values decrease with neutron energy. Cadmium, which has a neutron cut-off energy of 0.5 eV, was used in the form of a sheet to wrap around the wall of the detector to ensure that most of the counted neutrons came from the front. The neutron source and detector were kept as close to the autoclave as possible since the intensity of the neutron beam decreases with distance. Both the neutron source and detector were placed at the same vertical level, at the mid-height of the autoclave.

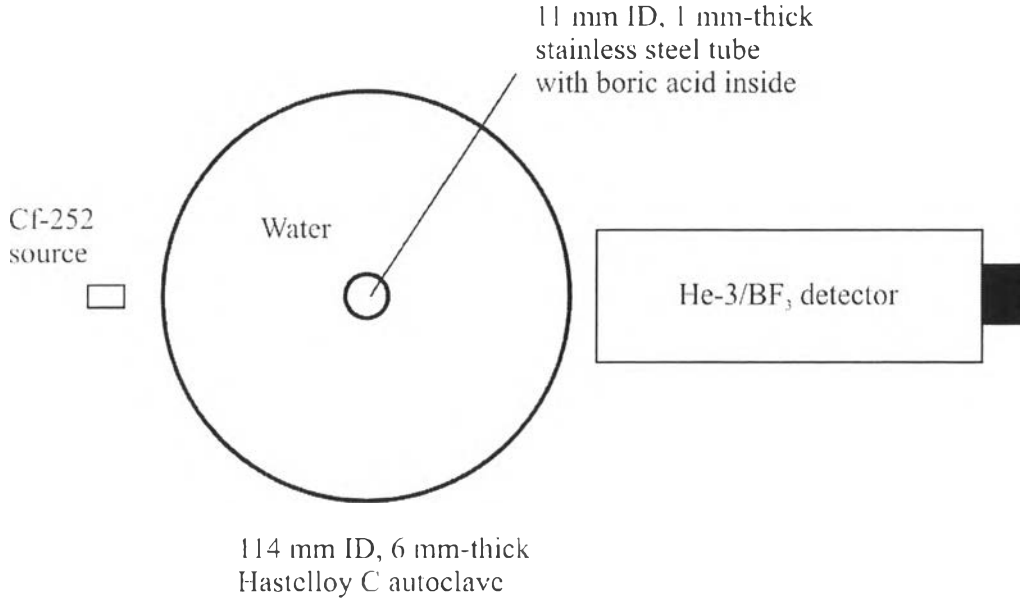

Figure 3.4 Schematic diagram of the neutron slowing-down followed by absorption experimental apparatus.

The counting system used in this experiment was a pulse-type consisting of a high-voltage power supply, a preamplifier, an amplifier, a Multichannel Analyzer (MCA), Single Channel Analyzer (SCA) and a counter, as shown in Figure 3.5. Voltages of 1560 V and 1350 V were supplied to the He-3 and BF_3 detectors, respectively. Detection instruments and their purposes are given in details in references: Knoll (1989); Tsoulfanidis (1995) and Hussein (2003).

Since hydrogen is the best moderating material, the hydrogen in the water served as a neutron moderator. In this low temperature experiment, paraffin wax ($C_{30}H_{62}$) was used when moderation and/or shielding were required.

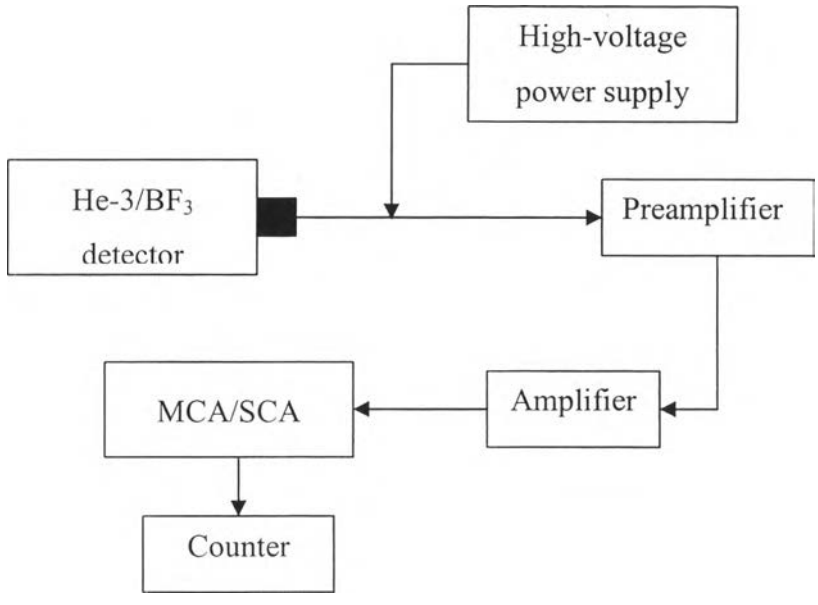

Figure 3.5 Neutron slowing-down followed by absorption electronic trains.

3.4.2 Prompt Gamma-Ray Activation Analysis

A ^{252}Cf source was applied in this experiment to irradiate boric acid powder in the tube in the middle of the autoclave with neutrons to give prompt gamma rays. The ^{252}Cf source itself also releases a gamma ray, which can disturb the counting system. Hence, direct exposure of the gamma-ray detector to the source had to be avoided. The source and the detector were arranged in the scattering mode, with lead bricks placed in between to prevent gamma ray from the source reaching the detector, as shown in Figure 3.6.

A thallium-activated sodium iodide scintillator, NaI (Tl), was used as a gamma-ray detector. It had a built-in preamplifier. The energy loss from gamma rays as they travel through NaI (Tl) crystal is converted to visible light, which can be measured with photomultiplier tube. The voltages applied to the detector in this experiment were 650 V and 1000 V.

The electronic assembly for the PGAA experiment is shown in Figure 3.7. Paraffin wax was employed as a neutron slowing-down material.

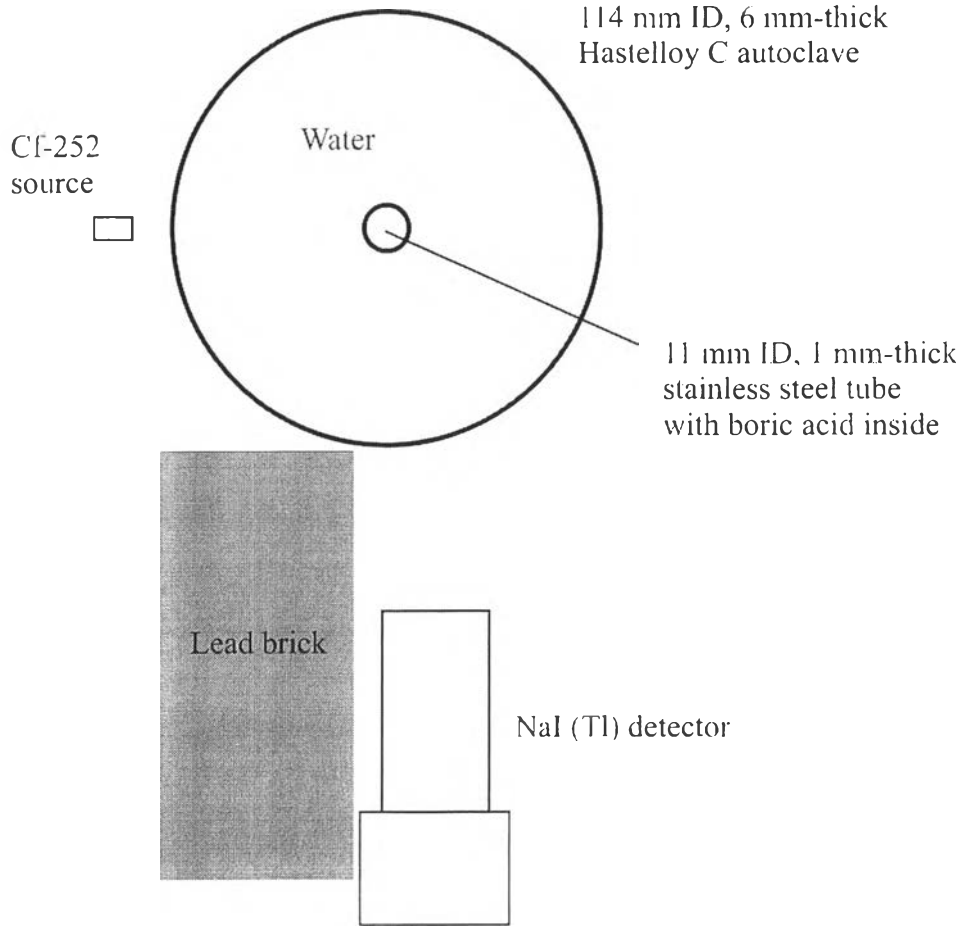

Figure 3.6 Schematic diagram of the PGAA experimental apparatus.

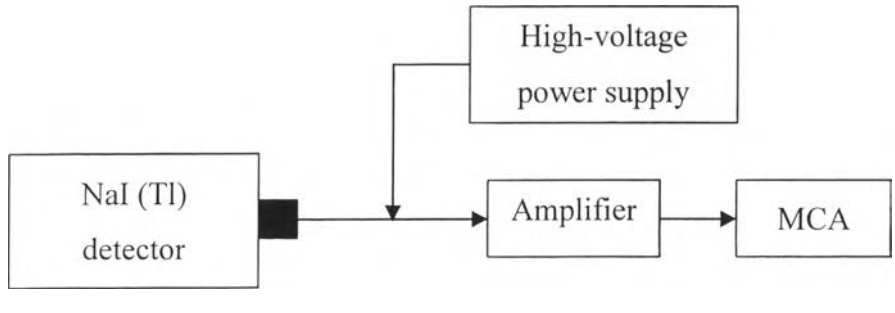

Figure 3.7 PGAA electronic trains.

3.5 Boron Measurement with Neutron Based Techniques: Procedures

3.5.1 Neutron Slowing-Down Followed by Absorption

Boric acid powder inside a stainless steel tube was placed in the middle of the autoclave, which was filled with water. To compare the signals with and without boric acid, measurements were also made with an empty tube. The ratio of counts without and with boric acid was reported: the higher the ratio, the better the contrast.

First, an experiment was performed with the He-3 detector (because of its higher efficiency than that of the BF_3 detector) without any shielding or source modulation. The counting period for this stage was one minute, and counting was repeated 10 times. Then, the system was optimized by using the MCA, which gave the neutron energy distribution. A thirty-minute counting period was set and three measurements were made to attain an error less than 2% (Hussein, 2003). The amplification (gain) was adjusted. The system was optimized further by using paraffin wax placed in front of the detector and beside and on top of the autoclave to moderate and reflect neutrons. Experimental conditions with different arrangements are tabulated in Table 3.2. The illustrations of the side arrangements of wax are given in Figures 3.8 and 3.9. It should be noted that the thickness of the side and top shielding did not affect the system optimization, because only neutrons reflected off the surface of these shields affect the counts. On the other hand, wax in front of the source moderates neutrons; therefore, its thickness is important.

The best setup as deduced from the MCA results was analyzed further with the SCA because it was more convenient to use, as it provided a single reading rather than a distribution. The SCA scanning was performed with a 10-minute counting period. The lower-window energy was first fixed at the proper value, and the upper-window energy was varied. Then, the upper-window energy was fixed at the setting that gave the best contrast ratio, and the lower-window energy was varied. Subsequently, the lower and the upper windows were set to provide the maximum contrast. As well as the powder, boric acid solutions in the tube with various concentrations were used: 8000, 4000, 2000, 1000 ppm B. Since radioactive decay of a radioisotopic source is a random process, and any measurement based on such a

source is subject to some degree of statistical fluctuation, estimations of errors were made. The statistical calculations of radiation counting are shown in Appendix G.

Table 3.2 Experimental conditions for the MCA in neutron slowing-down followed by absorption

Run	Wax thickness in front of source (mm)	Top shielding	Side shielding
1	None	None	None
2	15	None	None
3	15	Yes	Both sides and cover the whole autoclave, as shown in Figure 3.8
4	15	Yes	Both sides and cover only half of the autoclave, as shown in Figure 3.9
5	30	Yes	Both sides and cover only half of the autoclave, as shown in Figure 3.9

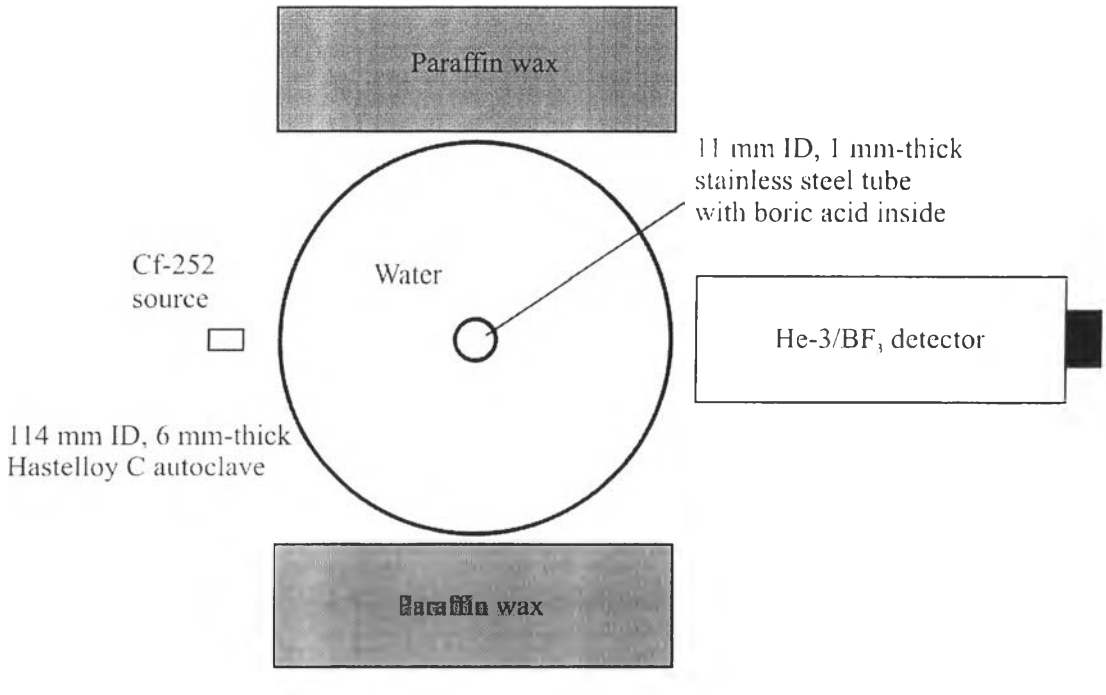

Figure 3.8 Schematic diagram of side arrangement of wax for Run3.

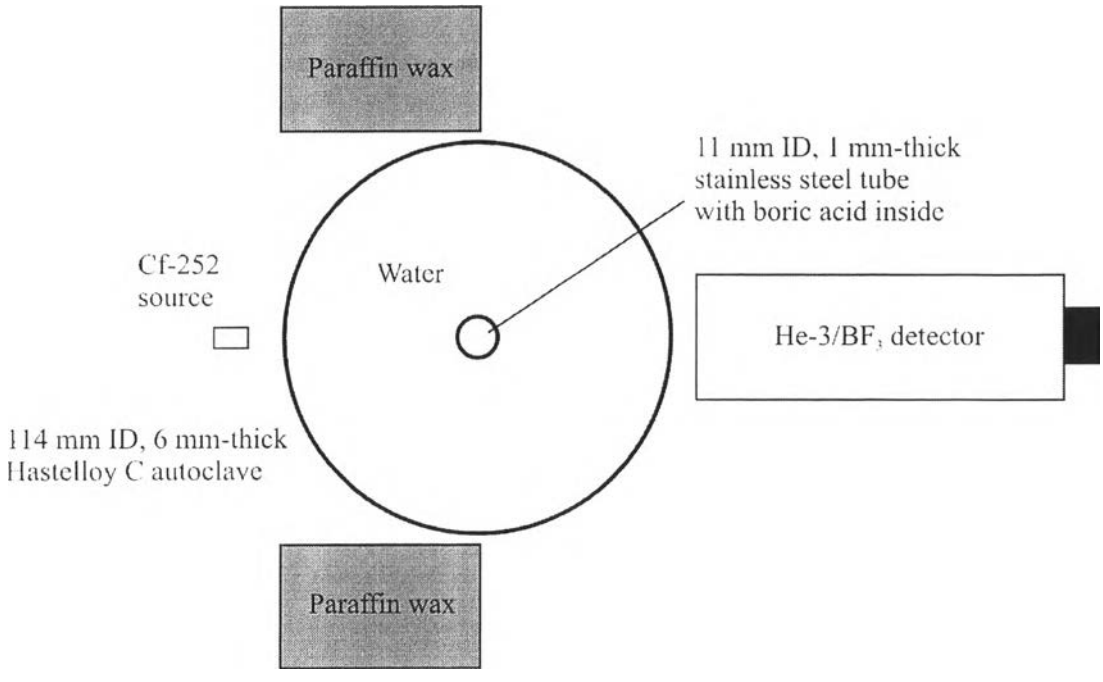

Figure 3.9 Schematic diagram of side arrangement of wax for Run4 and 5.

If the lower-window energy was set at the proper position, it can be concluded that the thermal neutron cloud was maximized. In order to prove that, a cadmium sheet was placed between the He-3 detector and the autoclave. No tube was inside the autoclave. Cadmium has a neutron cut-off energy of 0.5 eV (thermal energy range). Therefore, one should be able to see a significant change in counts with and without the cadmium sheet. The proper upper-window energy was set using the previous results. The SCA scanning with different lower-window energies was performed with 15 minutes counting period and three measurements. The ratios of counts without and with cadmium sheet were recorded and compared.

With the same position and arrangement, a BF_3 detector was used instead of a He-3 detector. The BF_3 detector is less sensitive to gamma rays, and the efficiency is relatively low (Hussein, 2003). The MCA was used to analyze the pulse-height distribution with and without boric acid powder and, because of the low efficiency, one-hour counting periods and three measurements were applied. Then the SCA analysis was performed following the same procedure as those with the He-3 detector; the energies of the upper and lower window were set and a cadmium

sheet was inserted to test the thermal neutron cloud. One-hour counting periods and three measurements were applied to the SCA analysis.

3.5.2 Prompt Gamma-Ray Activation Analysis

The MCA was employed to show the pulse-height distribution. Since the prompt gamma rays at 478 keV were emitted after neutron absorption, energy calibrations were required. Cesium-137 and Co-60 were used as gamma-ray calibration sources. The former gives gamma-ray energy at 662 keV, and the latter gives energy at 1173 and 1333 keV (Hussein, 2003). The gamma sources were placed 6 inches away in front of the detector for 30 seconds, and pulse-height distributions were obtained. The peaks on the distributions were related to the gamma-ray energy. Once the energy was calibrated, gamma rays emitted during neutron absorption on boron could be observed. Re-calibration was required if voltage applied to the detector and/or amplification were changed.

The voltage of 650 V was applied to the detector with two different amplifications: 200 and 500. The tube with and without boric acid powder was placed in the middle of the autoclave to observe the contrast in counts, especially at energy of 478 keV. A thirty-minute counting period was employed, and three measurements were taken and averaged in each condition. A voltage of 1000 V was then applied to the detector with Gain 100 and 200 to see if the contrast could be improved.

When neutrons irradiate substances, photons are released at different energies. Such photons can lose energy by scattering with other atoms or molecules; more scattering, more energy loss. In this experiment, a metal autoclave was used and filled with water. Lead brick was placed beside the detector to avoid direct exposure to the neutron source. If the amount of scattering were reduced, better contrast with and without boric acid might have been obtained. Therefore, with the best amplification, two arrangements of lead brick were investigated: (1) brick placed beside the source instead of beside the detector and (2) no brick between the source and the detector. The MCA was employed in this stage with a 30-minute counting period for three measurements.