

CHAPTER II

LITERATURE REVIEW

2.1 CANDU Primary Coolant Loop

The CANDU (CANada Deuterium Uranium) is a power reactor that uses deuterium oxide (D_2O), heavy water, for the moderator and coolant systems, and natural uranium (UO_2) for the fuel in order to generate the energy by the fission reaction.

Generated heat from the fission reaction is carried by the coolant system. There are two coolant loops in a CANDU reactor, the primary coolant loop and the secondary coolant loop. The primary coolant D_2O carries heat from the reactor core, so-called calandria, to the steam generator where the secondary coolant, which is the light water, is converted into the saturated steam by the recovered heat from the primary coolant.

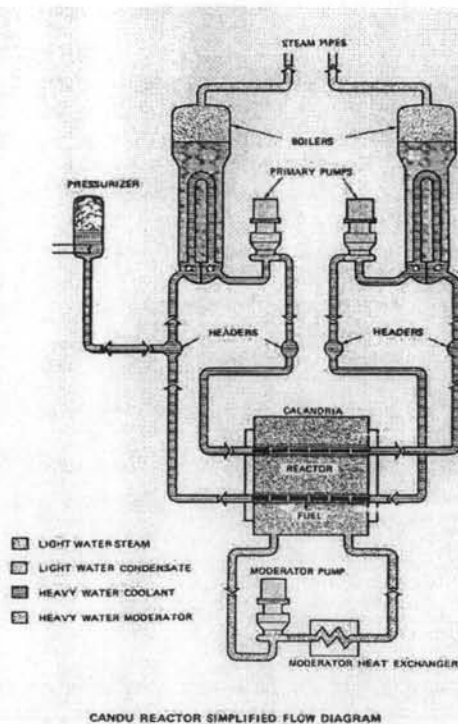


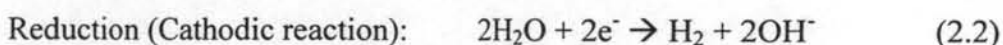
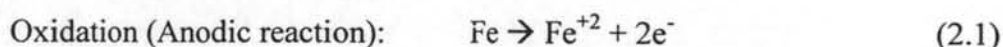
Figure 2.1 Primary coolant system of CANDU reactor (Silpsikul, 2001).

The CANDU primary coolant loop is comprised of three major components: the reactor core, the piping system and the steam generator as shown in Figure 2.1. The reactor core consists of 380 fuel channels, 190 inlet feeders and 190 outlet feeders, holding Zr-2.5%Nb pressure tubes. Each pressure tube contains twelve Zircaloy-4 fuel bundles with natural UO₂. The connection between end fittings of feeder and pressure tubes are made by Grayloc connectors. The generated heat is transferred by the primary coolant D₂O from the reactor core at 310°C with steam qualities ranging up to 6%. The steam quality increases slightly in transit due to the pressure drop along the pipes, through the piping system, header and steam generator is returned to the reactor core at 265°C. An average linear velocity of the coolant in the outlet feeders ranges from 8 m/s to about 16 m/s. To maintain the chemistry of the coolant, 3 to 10 cm³/kg (STP) of hydrogen is added to control the amount of dissolved oxygen. The alkalinity of the coolant is kept within the range of pH 10.3 to 10.8 at room temperature by adding lithium hydroxide (Lister *et al.*, 1998).

2.2 Corrosion Mechanisms

Corrosion is defined as the destruction of a material resulting from the reaction with its environment (Fontana, 1986). In modern corrosion science, it is accepted that corrosion is an electrochemical process.

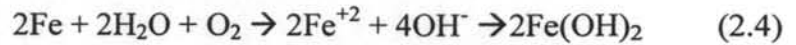
Electrochemical reactions are also used to determine the mechanism of metal corrosion in an aqueous solution.



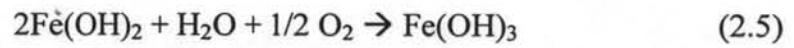
In the absence of oxygen, metal is oxidized to ferrous ion (Fe²⁺) on anodic surface. Water in the solution is reduced by the electrons from the anodic reaction and generates a hydrogen molecule on the cathodic surface. Both reactions must occur at the same rate and the same time, otherwise the metal surface would become electrically charged. However in a solution containing dissolved oxygen, the cathodic reaction can be accelerated by oxygen.



The overall reaction can be obtained by adding equation (2.1) and (2.3)



Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, is unstable in an oxygenated solution and is oxidized to rust, $\text{Fe}(\text{OH})_3$.



In slight alkaline and in the absence of oxygen; the condition in the primary coolant system of a CANDU reactor, the oxide of metal is predominately magnetite, Fe_3O_4 .

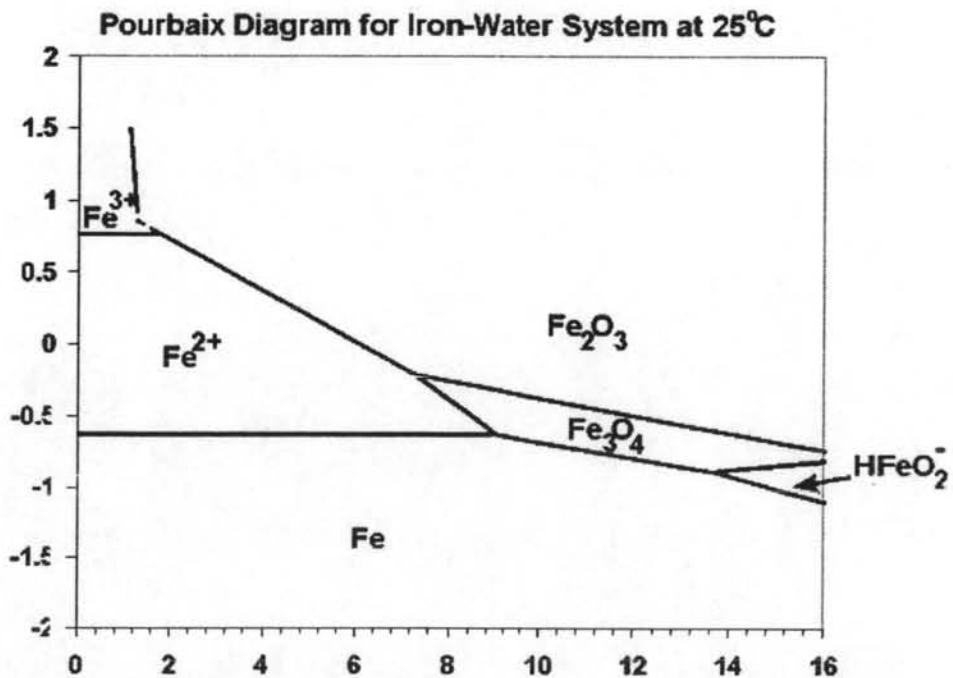
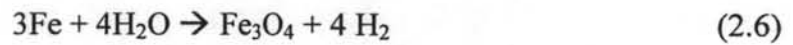
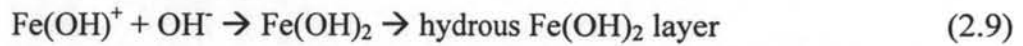
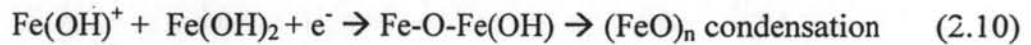


Figure 2.2 Pourbaix Diagram for Iron-Water system.

Cheng and Steward *et al.* (2004) reported that a hydrous $\text{Fe}(\text{OH})_2$ layer is formed on the metallic surface in an alkaline solution.



When the temperature rises above 150°C , polycondensation of iron hydroxide begins and magnetite is promoted via the “Schikorr reaction”.



This magnetite is stable under reducing condition. Therefore, it has protective properties and decreases the dissolution rate of steel significantly.

2.3 Mechanism of Oxide Film Growth

It is generally accepted that corrosions of low alloy carbon steel in high-temperature water, in the absence of oxygen, involves the transportation of oxygen-bearing species to the metal/oxide interface and the outward diffusion of metal ions into the bulk solution. When the solution becomes saturated, metal ions start to precipitate and grow on the outer magnetite layer. Therefore, a protective duplex oxide layer is formed on metal surface.

Cheng and Steward *et al.* (2004) proposed that the oxygen-bearing species involving the magnetite formation must be water, which was proven to act as binder between oxide chains. The diffusion through the oxide layer in a high-temperature environment occurs via short circuit routes, such as micro-pores or grain boundaries.

Hydrogen atoms diffuse toward the metal surface and are reduced by the electrons from the anodic reaction of the metal while ferrous ions diffuse outward and grow the oxide layer.

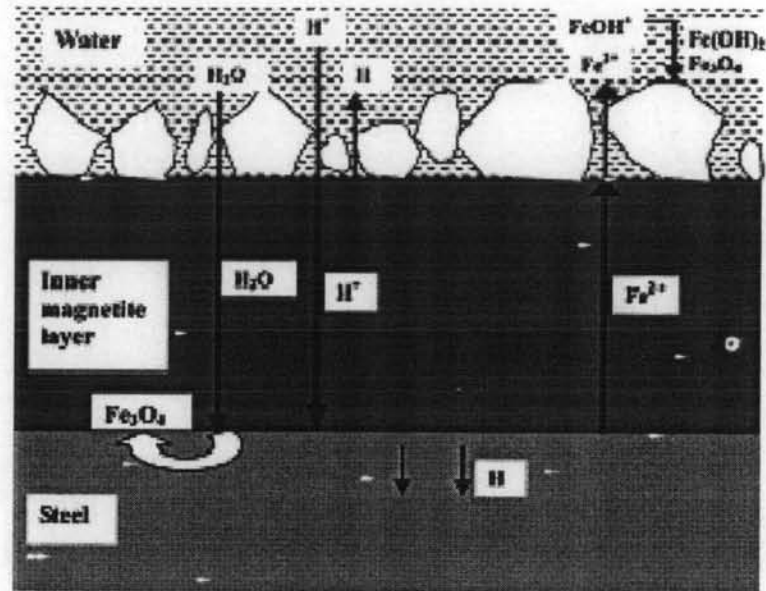


Figure 2.3 Schematic diagram of the magnetite formation on the steel surface in high temperature water (Cheng and Steward, 2004).

Figure 2.3 shows the mechanism of oxide film growth in a high temperature water solution. Water molecules and hydrogen atoms diffuse inward through the oxide film and reduce the metal at oxide/metal interface. The ferrous ions diffuse outward through the oxide film as $\text{Fe}(\text{OH})^+$ before being hydrolyzed to hydrous $\text{Fe}(\text{OH})_2$. Therefore, outer magnetite is formed via the Schikorr reaction, as shown in equation (2.7)-(2.11). Properties of the protective oxide film are also affected by environmental factors, such as chemical composition, pH, temperature and the velocity of the solution.

2.4 Oxide Film Characterization

2.4.1 Structure and Morphology

Under the alkaline and reducing conditions in high-temperature water, as in primary coolant system in CANDU reactor, the corrosion product of carbon steel is primarily in the magnetite form. The structure of magnetite is inverse-spinel which consists of 32O^{2-} , 8Fe^{2+} , and 16Fe^{3+} ions. O^{2-} ions formed in a closed pack

structure while Fe^{2+} ions occupy 8 octahedral holes, Fe^{3+} ions occupy 8 tetrahedral holes and 8 octahedral holes.

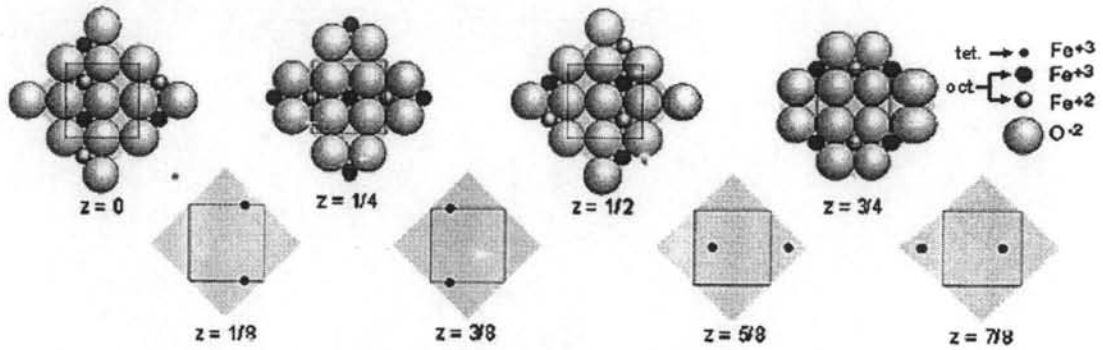


Figure 2.4 Inverse-spinel structure of magnetite.

As described in the previous sections, magnetite film formed on carbon steel gives corrosion resistance due to protective properties of the double layers, so-called a duplex of magnetite or Potter and Mann layer (Potter and Mann, 1962), as shown in Figure 2.5.

1) The inner oxide layer consists of compact fine crystals, sizes range from 10 nm (Mayer, 2001) to one half of the layer thickness. These results in the nucleation and growth within a confined space adjacent to the metal/oxide interface, replacing the volume of metal corroded (Potter and Mann, 1962).

2) The outer oxide layer consists of large octahedral crystals, sizes range from 100 nm to the complete layer thickness in intervals of 10 nm. It is precipitated from a saturated solution at the oxide /solution interface. Its properties are also affected by solution properties, such as chemical composition and velocity.

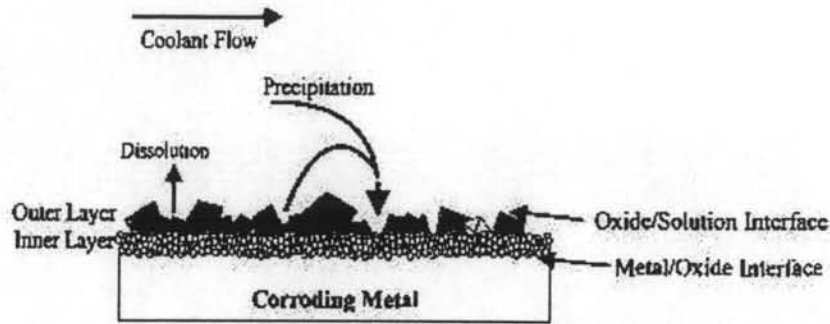


Figure 2.5 Duplex structure of magnetite or Potter and Mann layer.

2.4.2 pH Effect

Corrosion of carbon steel can be exacerbated by lowering pH. Acidity in the solution induces porosity in the magnetite film. Porosity allows easy access of the corrosive solution to the metal/oxide interface. The corrosion rate becomes limited by an interfacial reaction rather than diffusion control. The pH value also has an effect on magnetite solubility (Tremaine and LeBlance, 1980).

2.4.3 Temperature Effect

The temperature of the solution can affect the solubility of the magnetite film. Sweeton and Baes (1970) reported that under reducing condition in the primary coolant system in CANDU reactors, the magnetite solubility increases with the increase in temperature. Therefore, the coolant flowing through reactor core becomes unsaturated. As a result, the outer oxide film on the outlet feeders can dissolve into the bulk solution and yields a decrease in the corrosion resistance of the oxide film.

In terms of reaction rate, an increasing temperature can accelerate the corrosion rate. However, in an open system, dissolved oxygen content in solution is also reduced. In a closed system, where the oxygen content is kept constant in the solution, the corrosion rate increases with increasing temperature. Figure 2.6 illustrates the relationship and the corrosion rate of iron in an open system and a closed system vs. temperature (Jones, 1992).

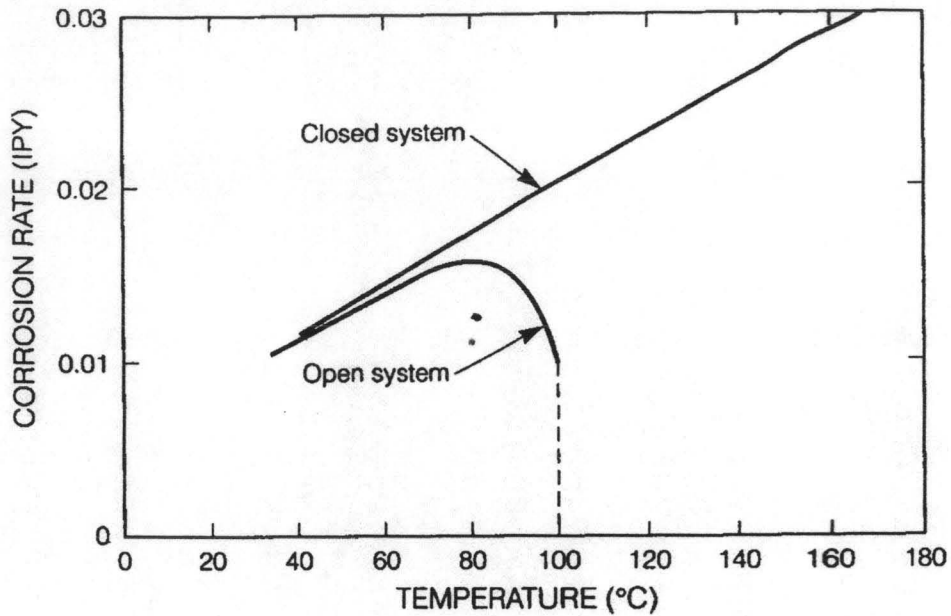


Figure 2.6 Effect of temperature on corrosion rate of iron in water containing dissolved oxygen (Jones, 1992).

2.4.4 Alloying Effect

Chemical content in the metal also has an important role on oxide film quality, which relates to protective properties. Therefore, alloying is an effective way to inhibit corrosion. This can be done by adding the following metals.

Chromium (Cr): an increase in Cr content can reduce the corrosion rate of steel at high temperatures due to the higher packing density and smaller particle sizes of the oxide layer (Taenumtrakul, 2005). It enhances the formation rate and the stability of the magnetite film.

Nickel (Ni): the combination of Ni and Cr not only improves the resistance to high temperature oxidation but also increases the thermal cyclic during the high temperature oxidation of stainless steel.

Silicon (Si): Si can improve corrosion resistance, especially at low-temperatures by forming its own oxide film or in conjunction with Cr.

Molybdenum (Mo): the main purpose of Mo in carbon steel is to increase strength and hardness.

Carbon (C): C is always used to strengthen steel. However, the precipitation of carbide can reduce corrosion resistance. To maximize corrosion resistance, heat treatment is then required.

Platinum (Pt) and Palladium (Pd): small amounts of Pt and Pd improve the catalytic efficiency for hydrogen and oxygen recombination in high-temperature water (Kim *et al.*, 1996).

2.4.5 Flow-Assisted Corrosion (FAC)

Flow-Assisted Corrosion (FAC) is defined as the acceleration in the rate of deterioration or attack on the metal because of the relative movement between the corrosive fluid and the metal surface. Metal is removed from the surface as dissolved iron, or forms a solid corrosion product that is mechanically swept from the metal surface (Fontana, 1986). It has been confirmed that FAC is the corrosion mechanism within feeder pipes in CANDU reactors. A higher coolant flow rate is believed to yield higher mass transfer of iron into the bulk coolant, resulting in thinner oxide films.

Lister *et al.* (1998) stated that FAC is influenced by the combined action of both electrochemical and mechanical effects. This mechanism has been described by a two-stage process:

- 1) Magnetite film dissolution.
- 2) Mass transfer of dissolved iron into the bulk coolant.

It was confirmed by an analysis of the accelerated corrosion rates. A dependence of the corrosion rate on the outlet feeder coolant velocity to the power 1.52 (Beshara, 1997), which implies a complex set of mechanisms. If only mass transfer was involved, the velocity dependence should be less than one. The Berger and Hau correlation for mass transfer in pipe flow showed a velocity dependence to the power 0.86 (Berger and Hau, 1977), and dissolution alone cannot explain the magnitude of the corrosion rate. Figure 2.7 illustrates correlation between coolant velocity and thinning rate of feeder pipes in the CANDU reactor at Point Lepreau.

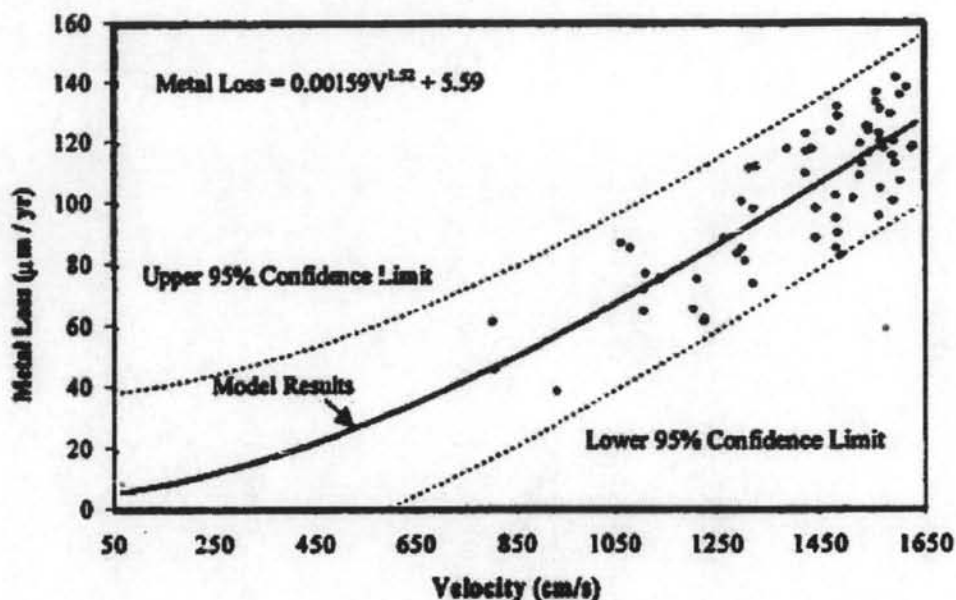


Figure 2.7 Feeder thinning correlation developed at Point Lepreau nuclear generating station (Beshara, 1997).

FAC will therefore affect the oxide film formed on carbon steel when the high-temperature water solution is undersaturated, such as in outlet feeders. If the coolant is not saturated in dissolved iron, the oxide film can dissolve into the bulk solution at a rate depending on the concentration gradient. The mass transport of iron ions to the bulk coolant can be enhanced by increasing coolant velocity. Thus, if mass transfer of the iron ions to the bulk coolant at the oxide/solution interface is faster than oxide precipitation, then outer oxide will no longer exist.

In the primary coolant of the CANDU reactor, the outlet feeders, in which coolant is undersaturated due to the increase of temperature after flowing through the reactor core, undergo more FAC effect than inlet feeders, in which coolant is saturated in dissolved iron. Therefore, the inlet feeders have a lower corrosion rate and a relatively thick oxide film compared with the outlet feeders.

Erosion also plays an important role in the corrosion of the metal surface. It is defined as an impingement attack on the oxide film resulting from water, steam, particle or a combination on the metal surface. This mechanism is caused by the mechanical effect of shear stress exerted by the fluid on the oxide

surface. Part of the oxide film, so-called spalling, is removed by fluid-induced shear stress. It can be seen as etching, scalloping or wallowing out of certain areas.

2.5 Fluid Flow Modeling

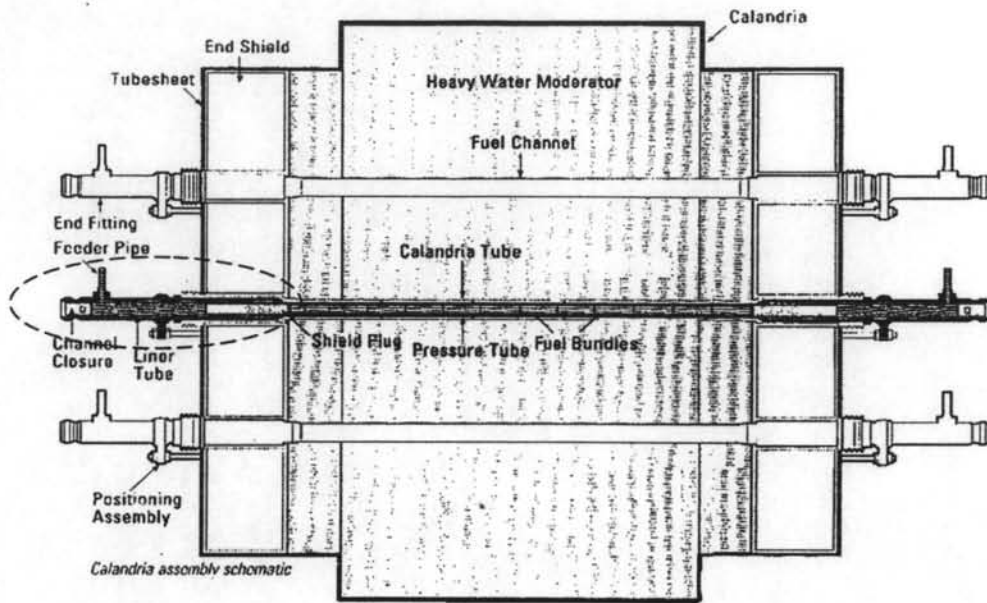
2.5.1 Introduction to Computational Fluid Dynamic (CFD)

It was believed that fundamental physics of a flowing fluid can be represented by a set of differential equation derived from the following relations: 1) mass conservation; 2) Newton's second law (momentum changing rate equals to sum of force on fluid); and 3) energy conservation (First Law of Thermodynamic).

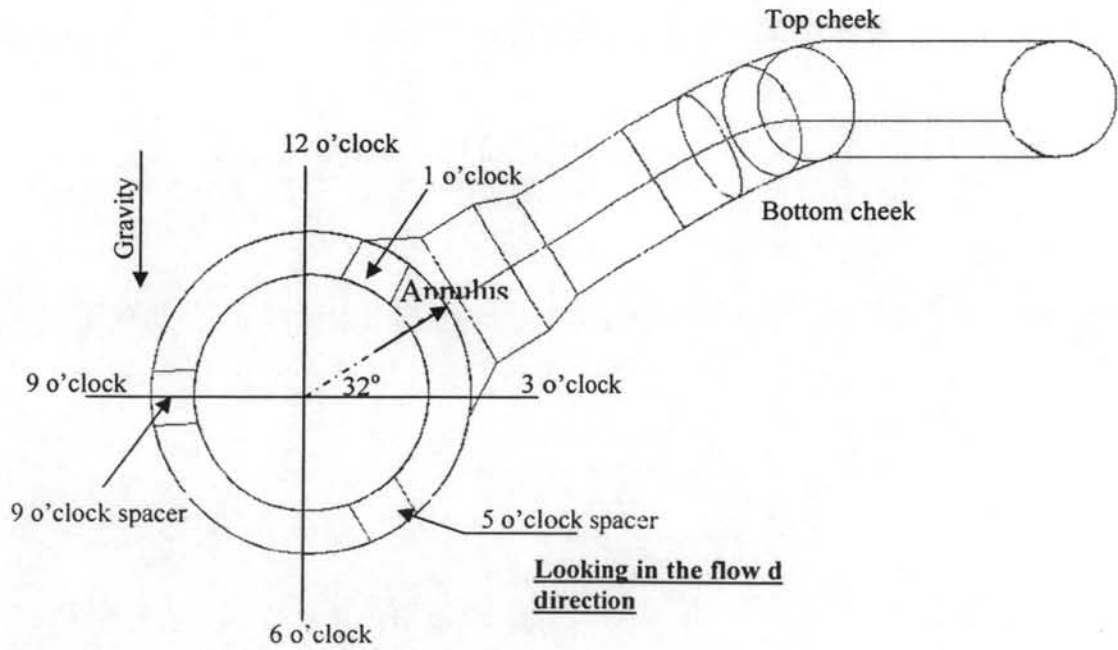
Computation Fluid Dynamic (CFD) is the science of determining a numerical solution of flow, based on the Navier-Stokes equations, to obtain a numerical description of the complete flow field of interest by using calculation tool (Supa-Amornkul (2001)). It offers a combination of theory with empirical information in a single calculation. It can be completed with experimental results when available.

CFD is an effective method to simulate fluid flow, especially for the cases where physical systems are dangerous or difficult to obtain in a physical data are not available. These advantages of CFD have made it widely used in many industries; for example: power plant, aerospace, biomedical, chemical and petrochemical processing. Many computational fluid dynamic programs have been developed in the last decade. Each software has its own advantages in solving fluid flow problems. Fluent is one of the well-known CFD software. Fluent 6 was selected to be used in this thesis in order to study the relationship of wall shear stress with the oxide thickness of an outlet feeder from a CANDU reactor.

For identification, every feeder in a CANDU reactor is labeled. The S08 feeder pipe is a double bend outlet feeder in a CANDU reactor. The rate of metal loss and oxide thickness was determined in detail for the first bend of S08 removed from the CANDU reactor at the Point Lepreau station.



(a)



(b)

Figure 2.8 S08 feeder pipe in CANDU reactor (Supa-Amornkul, 2006).

(a) S08 pipe position in CANDU reactor. (b) End-view of S08 feeder pipe.

2.5.2 Computational Fluid Dynamic by Fluent

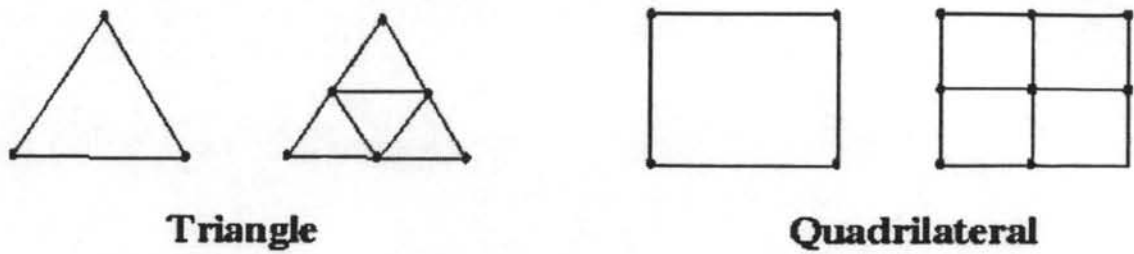
Fluent is a CFD program for fluid flow and heat transfer modeling in various geometries. In order to simulate the desired geometry, the control volume of interest is divided into sub-divisions, the so-called grid structure. The distinct point of the grid is where the equations are solved, the so-called nodes. Fluent software allows the users to input problem parameters and to examine the result via three main processes: 1.) a pre-processor, 2)-a solver and 3) a post-processor. The pre-processor allow users to define the domain parameter of the flow problem and generate the appropriate grid for the flow modeling. The solver is the part where the governing equations of fluid flow are defined and solved. The post-processor allows users to interface with the result solved by the solver.

In the CANDU reactor, coolant media consists of heavy water and heavy steam. Therefore, the Eulerian model or two-fluid model was selected for this study. The continuous phase coolant solution, heavy water, is considered as a primary phase and the discrete phase, heavy steam, was considered as a secondary phase. The following assumptions were made: 1) a single pressure is shared by both phases; 2.) the momentum and continuity equations are solved for each phase; 3.) the secondary phase consists of uniform spherical bubbles dispersed in a continuous liquid phase; 4.) the turbulent flow is everywhere isotropic; 5.) a two –equation turbulent model is solved for the mixture; and 6.) the physical properties of the two fluid are uniform throughout.

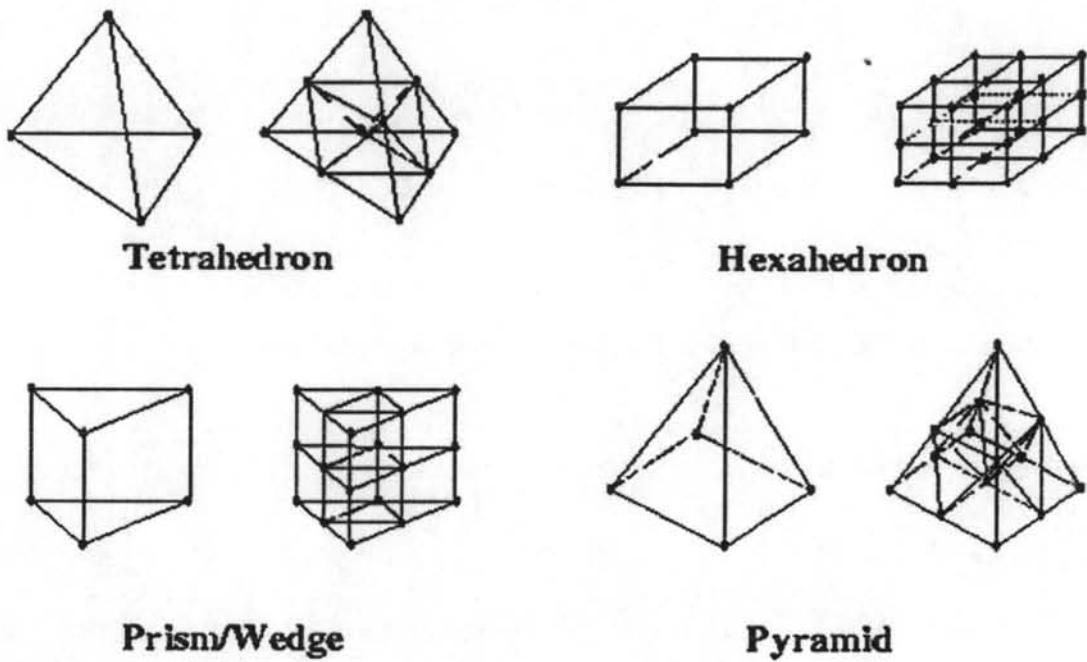
2.5.3 Grid Generation

Computational mash (or grid) quality has a significant effect on accuracy and stability of the numerical simulation. The finer quality of grid in a three-dimensional model may give more accuracy; however, it also consume more memory and computation time. Therefore, it is important to choose the appropriate grid system for each flow problem.

Gambit is a Computer Aided Design (CAD) software used in Fluent to generate the grid for a given geometry. Several kinds of grid cell can be generated in the Fluent solver, such as tetrahedral, hexahedral, pyramidal and hybrid mash, to allow users to construct a well-fitting gird system for each geometry.



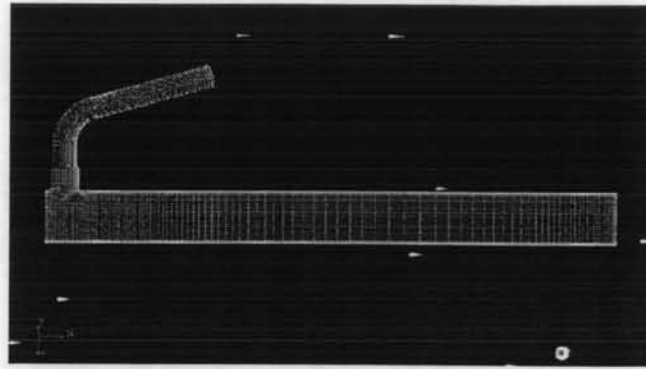
(a) 2D cell type



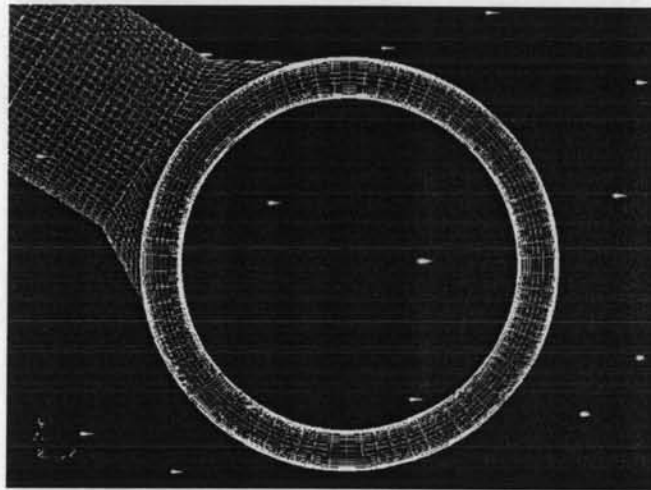
(b) 3D cell type

Figure 2.9 Cell types in Gambit.

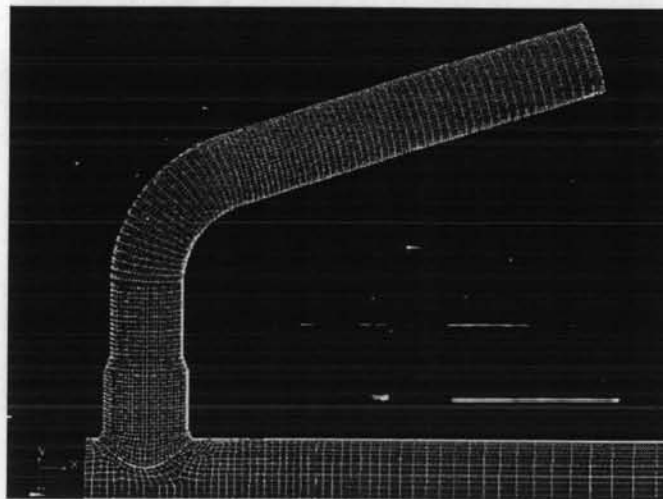
Figure 2.10 shows the 3-dimensional grid system of the first bend of the outer feeder (S08) of a CANDU reactor that is used to simulate a wall shear stress (Supa-Amornkul, 2006).



(a)



(b)



(c)

Figure 2.10 3D grid structure of S08 feeder pipe in CANDU reactor.
(a) Entire domain. (b) End view of end fitting. (c) S08 feeder pipe.