



CHAPTER II LITERATURE REVIEW

2.1 Flow Accelerated Corrosion (FAC)

It is understood that Flow-Accelerated Corrosion (FAC) is the chemical dissolution of surface oxide and metal, accelerated by flow and flow impingement. FAC is also called Flow-Assisted Corrosion or Erosion-Corrosion and is a mechanism of piping degradation that causes a loss of material from the inside of the pipe and thinning of the wall. The FAC of steels depends strongly on such factors as the flow passage geometry, temperature, water chemistry, flow rate, steel composition and the oxygen content of the water.

FAC is governed by two major mechanisms: chemical corrosion involving a mechanism that dissolves the oxide layer on the carbon steel pipe wall and mechanical erosion accelerated by fluid flow inside the pipe or high-velocity liquid droplets impinging on the wall. Experimental observations or plant measurements strongly reveal that FAC also depends on the piping layout, local distributions of flow properties, flow chemistry, etc. (Yuh-Ming *et al.*, 1998)

FAC can occur in both single-phase (liquid), and two-phase (steam and water) systems. High flow rates, turbulence, and especially flow impingement enhance the water-steel contact and thereby increase the rate of iron dissolution and corrosion. Liquids or gases that have suspended solid particles will wear or remove the oxide protective film and leave alloy exposed and more susceptible to corrosion. Corrosion rates are usually higher on the outside of pipe bends and tees and at turbulence promoters such as irregular welds or changes in pipe diameter (Shao, 2006).

The FAC in outlet feeders of a power plant can be described as a combination of dissolution-controlled and erosion-controlled corrosion. Dissolution and mass transport may act together and involve convective diffusion, while the erosion component is characterized by the combined action of flow-induced mechanical forces (shear stresses, pressure variation by high flow velocity and particle impact in multi-phase flows) and electrochemical processes (Villien *et al.*, 2001)

The accelerated thinning can lead to a scalloped surface which has a distinctive wave-like appearance with a smooth bottom and sharp crests. The scalloped surface supporting a thin oxide layer is observed in many situations involving FAC. Figure 2.1 shows a scalloped surface on the inner surface of a carbon steel feeder pipe.

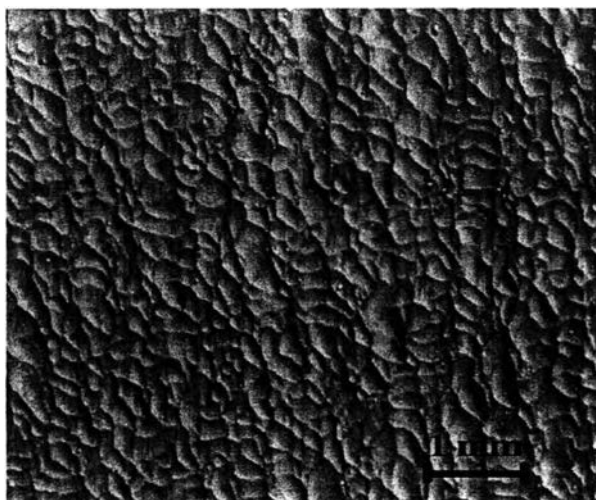


Figure 2.1 Scallop on the inner surface of a carbon steel feeder pipe (Villien *et al.*, 2001)

2.2 Flow-Accelerated Corrosion (FAC) of CANDU Feeder Pipes

The CANDU reactor, which stands for "CANada Deuterium Uranium", is a Canadian-designed Pressurized Heavy Water Reactor (PHWR) which uses heavy water, deuterium oxide (D_2O), as a moderator and coolant and natural uranium (UO_2) for the fuel in order to generate the energy by the fission reaction.

For the CANDU feeder pipes, it has been found that the corrosion is not only uniform corrosion but also susceptible to erosion, and therefore called flow-accelerated corrosion or flow-assisted corrosion (FAC). It has been identified in CANDU primary coolants as the loss of metal from the walls of reactor outlet feeder pipes with high flow velocities.

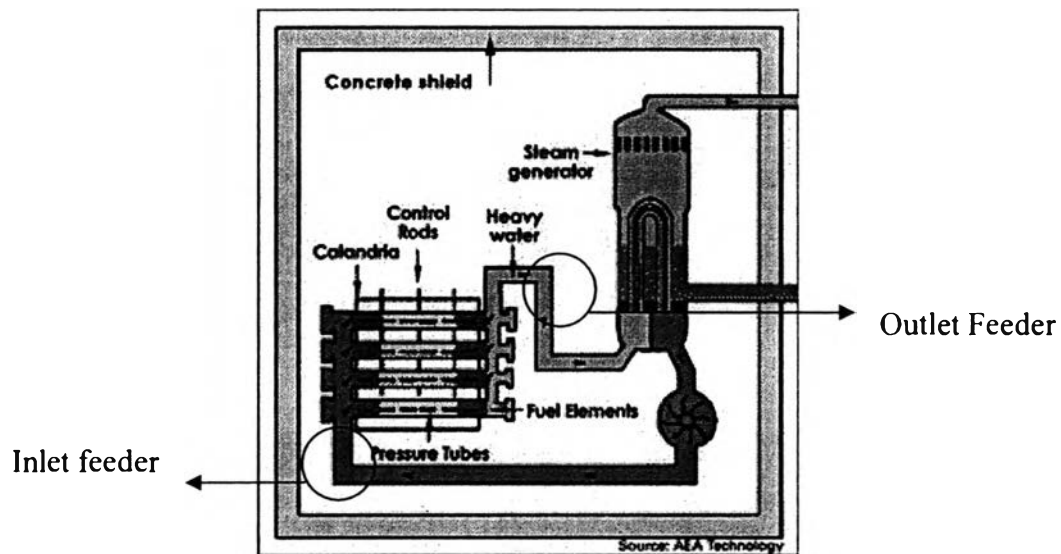


Figure 2.2 Schematic of primary coolant in a CANDU reactor

As shown in Figure 2.2, fuel channels are fixed horizontally in a tank called a calandria. Heavy water coolant is pumped through the channels containing the fuel assemblies to pick up the heat generated from the nuclear reaction. Then the coolant moves to the steam generators to produce steam from ordinary water and returns to the reactor. The heavy water is expensive but it permits the use of natural uranium as fuel.

After the inspection of the outlet feeders at Point Lepreau during 1995-1996 at places close to the reactor face, it was found that excessive thinning of the first few meters of the outlet feeders was widespread due to FAC. Since the discovery there have been many attempts to understand the mechanism of this FAC and correlate the corrosion rate with operating variables. (Lister *et al.*, 1998)

A sample of outlet feeder pipe was removed from the Point Lepreau reactor and scanning electron microscope (SEM) images show clearly that the roughness pattern consists of the scallops typically found on secondary side piping that has experienced FAC. Some outlet feeder pipes in Point Lepreau were found to have cracks on the inside surface. Near the cracks, scallops can be clearly seen.

2.3 Scalloped Surface

Surface scalloping is typical of the attack by FAC of carbon steel. It is also found in the sculpting of clay, mud or rock river beds by fast flowing streams (Allen, 1971**). In general, the crest-to-crest spacing is eight times longer than the peak-to-valley height of scallops. Basically, the scallops are produced from turbulent flow of a solvent over a soluble surface.

Villien *et al.* (2001 and 2005) found that the size of defects in the surface of plaster also influenced scallop formation. At a given flow rate, smaller sand particles embedded produced smaller scallops. Moreover, the size and number of scallops depended on the water flow rate. The number of scallops increased with the flow rate whereas the average size of a scallop decreased with the flow rate. Some defects are erased from the surface after a given time and only scallops bigger than a critical size, set by the flow conditions, remain at the surface.

Burrill and Cheluget (1998) compared the characteristics of scallops formed on corroded metal with those formed on plaster of Paris. Due to the similar profile, they concluded that the scalloping is the result of hydrodynamic phenomena and little influenced by the properties of the solid.

Curl (1974) explained the characteristic scaling of scallops such that if the velocity is low, transition to turbulence (Point 3 in Figure 2.3) will occur further along the scallop and reattachment will impinge on the next crest. The higher corrosion rate at that point will reduce that crest and, in effect, lengthen the scallop. On the other hand, if the velocity is high, transition and reattachment will occur sooner. In this case, the distance between the reattachment (Point 4) and the next crest will be increased and an irregularity in this region could be the origin of a new scallop, thereby reducing the average scallop size. See Figure 2.3.

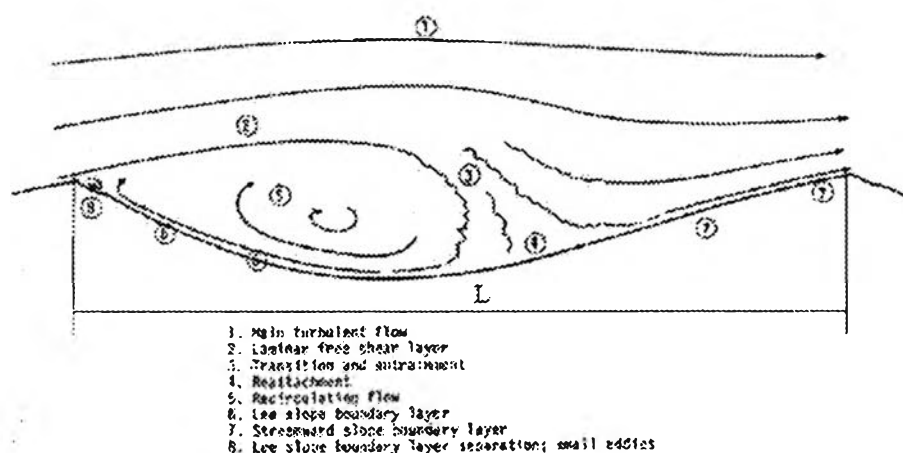


Figure 2.3 Flute hydrodynamics (Blumberg, 1970)

2.3.1 Geological Studies

Erosional processes have been studied in a variety of disciplines like geomorphology, geology, aeronautics and civil, mechanical and chemical engineering. The reason is that the several processes of erosion are physically analogous and often lead to similar surface markings.

Geological investigations have found the formation of erosion marks similar to those observed on the steel feeders (Lister *et al.*, 1998). As shown in Figure 2.4, there are two alternative theories about the spacing, size and shape that come from these studies:

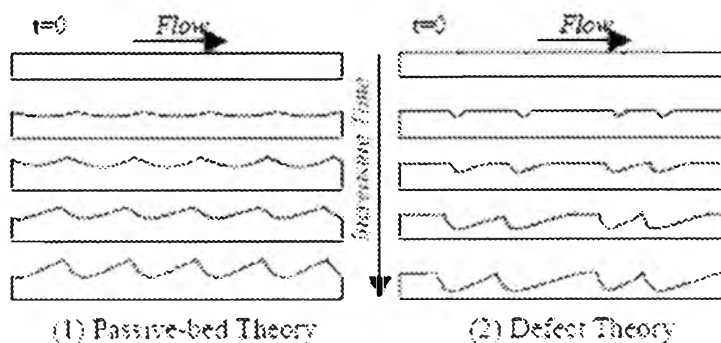


Figure 2.4 Evolution of a surface according to (1) passive-bed theory and (2) defect theory

The passive-bed theory of erosion marks postulates that the characteristics of the erosion marks are entirely determined by the dynamic properties of the fluid in contact with the surface. The properties of the material have therefore no influence on the formation of the scallops. The length of the erosion marks is thus assumed constant with time. Sharp (1947) and Leighly (1948) proposed that the characteristics of scallops on ice surfaces were controlled by the properties of vortices in the adjacent air. Henderson and Perry (1958) support the same idea with studies of meteorites and limestone caves, respectively (Villien *et al.*, 2001).

The defect theory postulates that the position of each erosion mark is due to the initial presence of an irregularity or a defect at the surface. It assumes an independent evolution for each mark and an increase of length and amplitude with time up to a limit set by the initial spacing of defects. Therefore, the characteristics of any assemblage of erosion marks depend on the duration of the eroding process, the spatial distribution, shape and dimensions of the defects, and the character of the flow (Villien *et al.*, 2001).

Villien *et al.* (2001) found that the presence of an initial defect at the surface is responsible for the formation of a scallop. Therefore, it supports the defect theory that no scalloping can occur if there is no driving force for the dissolution process. In 2005, they continued their work and finally found that scallops are difficult to develop on the surface of reference plaster due to the absence of physical defects initially. It demonstrates as well that hydrodynamics of the surrounding fluid alone cannot initiate the scalloping phenomenon at the surface but may influence it afterwards once the process has already started, presumably by dissolution. Moreover, the size of the scallops generated increases with increasing defect size.

Shao studied the origins of scallops and found that a scallop originated from a surface imperfection (probably air bubble or impurity material). Actually, Allen (1971) even proposed a defect model. The model postulates that there is a population of surface flaws on the surface. Under certain flow conditions, these flaws will grow and evolve into scallops.

2.3.2 Flute

In nature, the scallops can occur most frequently with water dissolving limestone or air subliming ice. In either case, surface irregularity may lead to the flow situation in Figure 2.3 as above.

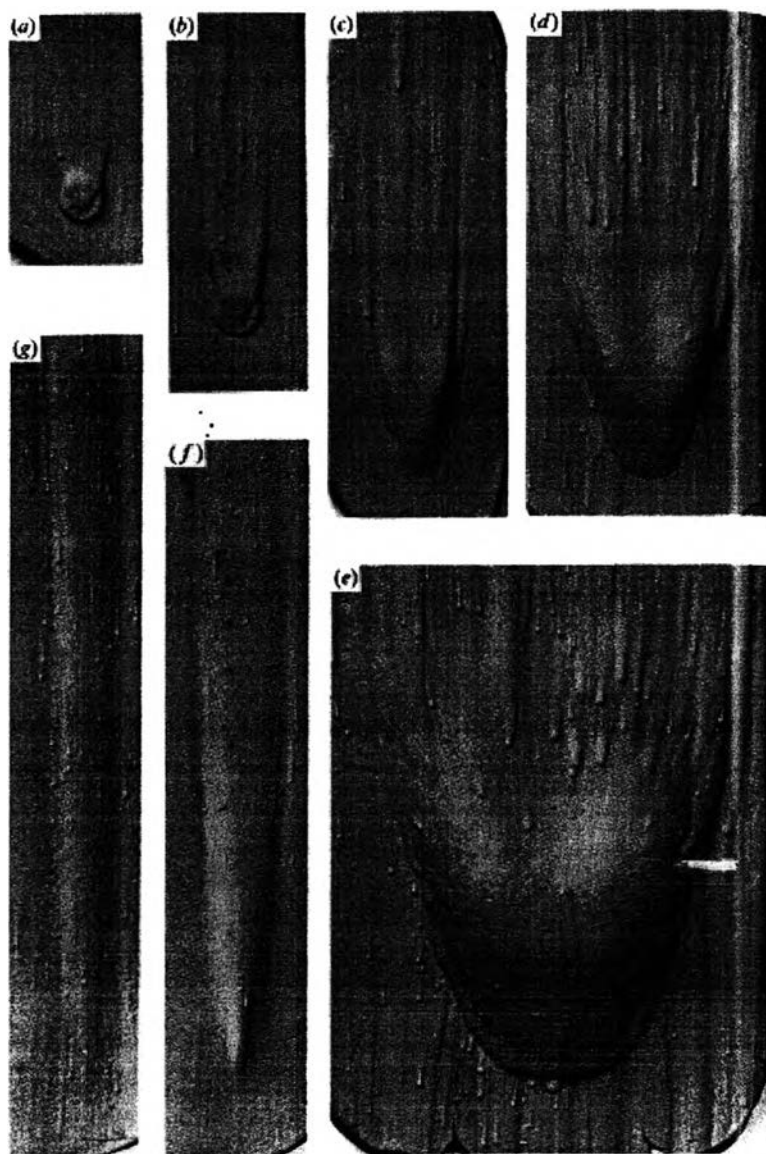


Figure 2.5 Stages in the development of experimental Flutes (a-e) and grooves (f), (g) from defects introduced into Plaster of Paris beds. Flow from bottom to top. (e) is 10 cm wide. (Allen, 1971*)

A flute is a defect that exceeds a certain critical dimension set by flow conditions and grows by length, breadth and depth into a heel-shaped hollow with a parabolic plan. Allen (1971)** found that flutes on the surface resulting from defects change into scallops.

Blumberg (1970) studied the hydrodynamic factors affecting the original propagation of the flute. He tried to obtain a stable fluted surface and found that by using a knife to create a series of grooves perpendicular to the flow direction, a stable dissolution profile flute could be created. Another important conclusion is that there is a stability wavelength Reynolds number for flute stability which is about 23,000 (Blumberg and Curl, 1974). This agrees with that obtained from ice and limestone. They proposed that the number 23,000 could be a universal Reynolds number for an equilibrium erosional surface.

2.4 Dissolution of Plaster

The dissolution rate of a solid into an aqueous solution without any further reaction between the formed ions is controlled by the chemical reaction at the surface or by molecular diffusion through boundary layer. In both cases, mass flow resulting from the dissolution of the surface, is, at steady state, equal to the rate of solute transport through the boundary layer.

Two extreme cases exist. When the diffusion transfer is high enough to ensure that the surface concentration of the dissolved species is close to that in the bulk flow, the rate of dissolution is controlled by the reaction rate at the surface. On the other hand, when the diffusion transfer is relatively low and/or the rate of dissolution of the surface is high, molecular diffusion becomes the limiting step. An increase in the fluid velocity will thus enhance mass transfer (Villien *et al.*, 2001 and 2005).

Dissolution of plaster in water has been studied extensively. Early studies showed that the dissolution kinetics is transport-controlled and a first-order rate equation for the dissolution rate is often proposed (Liu and Nancollas, 1971; Christoffersen and Christoffersen, 1974; James and Lupton, 1987; Opdyke *et al.*, 1987).

$$R = k_t (C_s - C_b) = \frac{D}{\varepsilon} (C_s - C_b) \quad (1)$$

where R is the overall dissolution rate, C_s is the concentration at the surface, C_b is the concentration of dissolved species in the bulk, k_t is the mass transfer coefficient, ε is the diffusion layer thickness and D is the diffusion coefficient through the boundary layer. This has been supported by the observed dependence of the overall dissolution rate on the thickness of the diffusion layer. A thinning of the layer at the dissolving surface results in higher dissolution rates. An increase of the fluid velocity will decrease the thickness of the boundary layer, and the concentration gradient in the boundary layer becomes steeper.

Recently, Raines and Dewers, (1997) and Jeschke *et al.* (2001) argued that the dissolution of gypsum is jointly controlled by the surface reaction and the diffusion transport through the diffusion layer. The effective gypsum dissolution rate is then determined by “mixed” kinetics. Assuming a second-order reaction, the dissolution rate of gypsum is expressed by (Raines and Dewers, 1997)

$$R = k_t \left[1 - \Omega^{1/2} + \zeta \left[1 - \left\{ 1 + \frac{2(1 - \Omega^{1/2})}{\zeta} \right\}^{1/2} \right] \right] \quad (2)$$

where k_t is the transport coefficient for purely transport control, ζ is the transport reaction factor and $\Omega = C_b/C_s$. The factor ζ measures the relative influence of transport and reaction processes and is expressed as:

$$\zeta = \frac{Dm_{eq}}{2\varepsilon k_t} \quad (3)$$

where m_{eq} is the molal equilibrium concentration.

Raines and Dewers, (1997) suggested that there is 5-step process to chemically interact minerals with moving fluids. First, reactants in the fluid must cross a hydrodynamic boundary layer to reach the mineral surface. Second, reactants must

be adsorbed onto the mineral surface. Next, a chemical reaction must take place. Finally, the products must be transferred across the hydrodynamic boundary layer and into the bulk solution. For the case of the gypsum-water system, the reactants are H_2O and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The products are Ca^{2+} and SO_4^{2-} ions.

Villien *et al.* (2005) studied the dissolution rates of plaster with four different liquid flow rates and found that the dissolution rates of gypsum decreased approximately exponentially as the concentration of Ca^{2+} increased. As shown in Figure 2.6, the gypsum dissolution is under mixed transport/reaction control, where the transport-controlled kinetics dominate the initial dissolution, and surface reaction kinetics become more important as the concentration of Ca^{2+} increases, which is in agreement with Raines and Dewers, (1997).

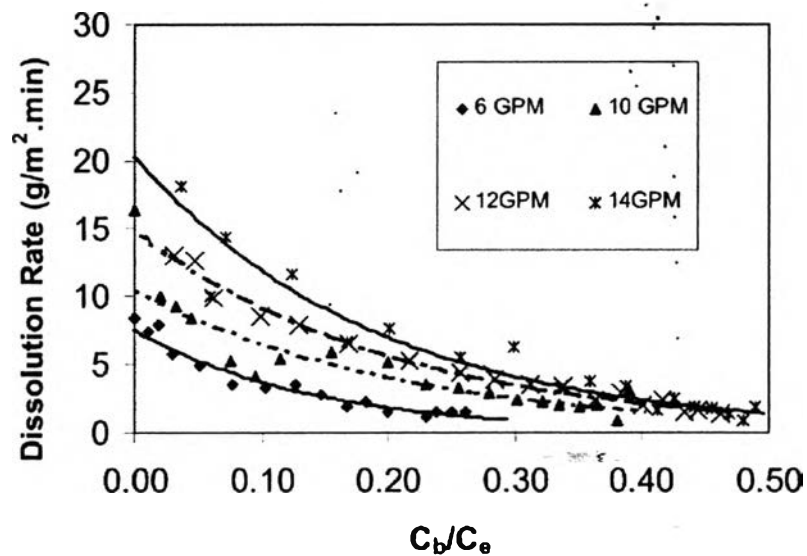


Figure 2.6 Dissolution rates of gypsum as functions of flow rates. (Villien *et al.*, 2005)

In addition, with the assumptions of first-order and second-order reactions at the surface of gypsum, expressions (1) and (2) respectively, their results showed that equation (2) or a second-order reaction was found to describe better the kinetics of dissolution for plaster of Paris, but seems to overestimate the dissolution rate as the solution approaches saturation.

Raines and Dewers, (1997) found that the rates of dissolution of two alabaster gypsum samples are similar, while the “porous” gypsum and anhydrite samples display lower steady-state concentrations and consequently lower dissolution rates, as shown in Figure 2.7. From their results, it can be seen that the experiments achieved a steady state after about 4 hours. Different lithologies of gypsum, which differ in amounts of impurities and porosity, in general dissolve at a faster rate than anhydrite.

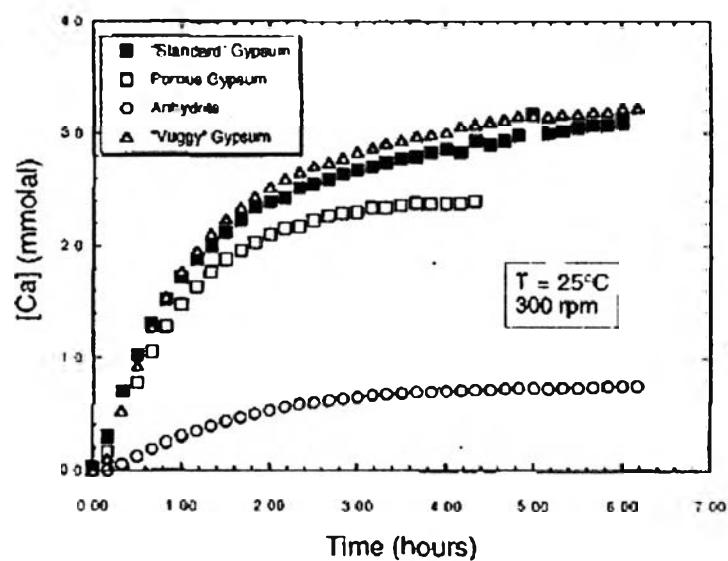


Figure 2.7 Concentration of calcium ion vs time for four experiments, each run at 300-rpm spinning rate and 25°C (Raines and Dewers, 1997)

Shao (2006) found that scallops developed very fast at the beginning of the test (plaster of Paris, within 1 hour), which corresponded to a quick increase of water conductivity. He suggested that a higher driving force for mass transfer occurred in the beginning of the test, which was reduced when the dissolution of plaster of Paris increased the Ca^{2+} and SO_4^{2-} ion concentrations. In addition, he found that the inlet and outlet for fluid flow in the pipe had different scalloping types, which suggested that the scalloping profile is related to the dissolution rate and the higher turbulence within the entrance length may induce higher dissolution.

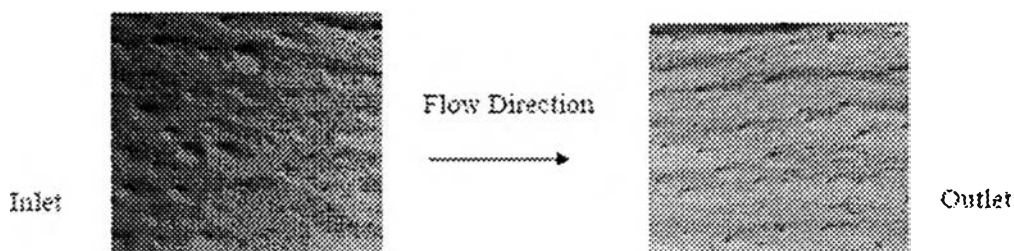


Figure 2.8 Schematic of different scallop types at inlet and outlet (Shao, 2006).

2.4.1 The Effect of Temperature

Lebedev and Lekhov (1989) studied the dissolution kinetics of natural gypsum in water at 5-25 °C and found that the temperature dependence of the rate constants fits an Arrhenius equation. The activation energy of 10-11 kcal/mol appears to correspond to mixed dissolution kinetics. Moreover, the rate constants seem to be proportional to the temperature, as in Liu and Nancollas's (1971) work where the rate constants were analysed from the Arrhenius equation at temperatures between 10° and 30°C. The activation energy was found to be $E_a = 10 \pm 1.5$ kcal/mole, which is larger than the value of 4.5 kcal/mole, to be expected on the basis of pure mass transport control for which only the temperature dependence of the diffusion coefficient should be important. Although much of the evidence points to film diffusion as being the rate controlling step in the dissolution of calcium sulfate dihydrate, it is not possible in the light of this relatively large activation energy. It is possibly a more complicated mechanism.

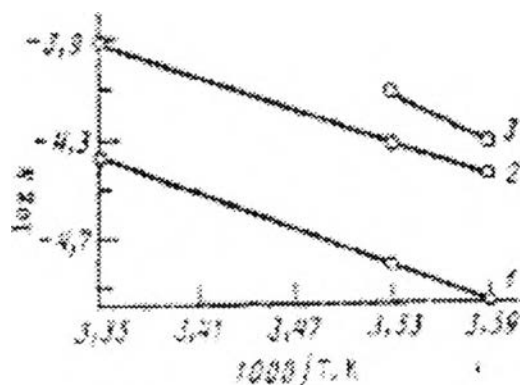


Figure 2.9 The 1000/T dependence of log k (dissolution rate constant) at different specimen or different kind of gypsum (Lebedev, *et al.* 1989).

2.5 Pressure Drop

Shao, (2006) studied the effect of scalloping on pressure drop. He found that the pressure drop increased at the beginning and became stable for Run 1 but decreased in Run 2, as shown in Figure 2.10.

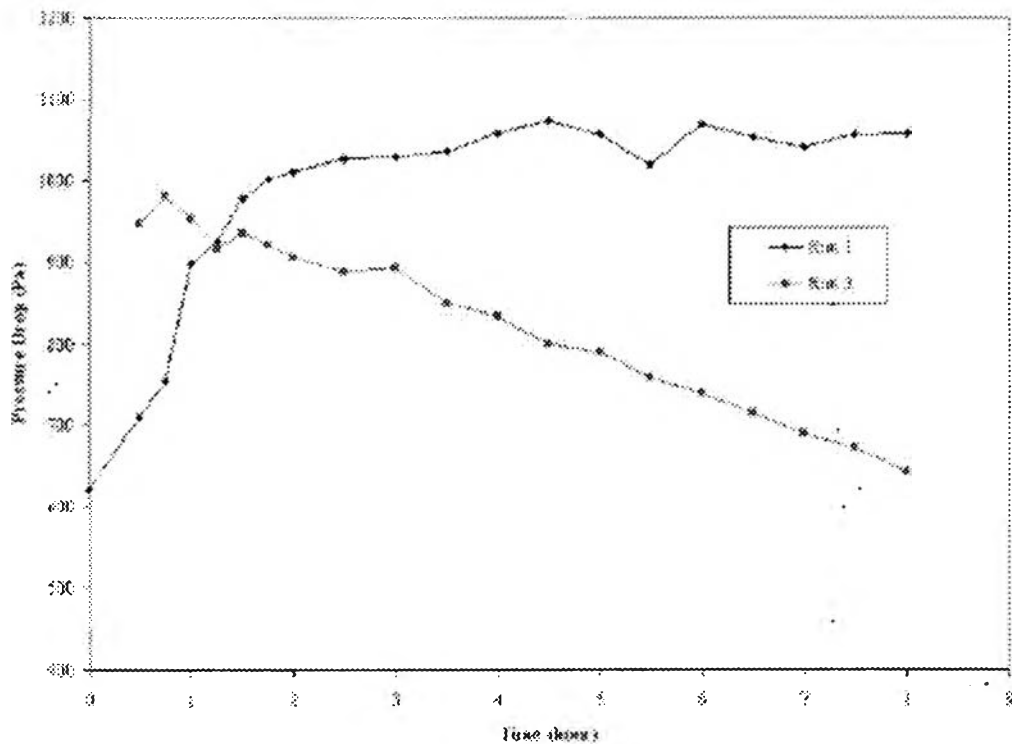


Figure 2.10 The pressure drop versus time (Shao, 2006)

These two runs operated at the same conditions but had different types of plaster of Paris; Run 1 is a pure plaster of Paris (98% $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and Run 2 is commercial plaster of Paris containing impurities such as sand. It seems that Run 2 gives high scalloping but less resistance. It appears that hydrodynamic forces could make the plaster surface less resistant. However, the difference between Run 1 and Run 2 was not explained.

Shao (2006) proposed that if the scalloping can make the surface smoother, a scalloped surface could be the best candidate to give the highest ratio of k/f (mass transfer coefficient to friction factor) for a given roughness height. This ratio can

make the scalloped surface a desired choice for high mass transfer with a low pressure drop.

Lertsurasakda (2007) investigated the effect of scallop distribution on pressure drop and found that the pressure drop mainly depends on the surface geometry, not the position. The pressure drop of a scalloped surface depends on the scallop surface area and is almost unaffected by the scallop distribution. He also studied the effect of scallop surface area with forward and backward flow on the pressure drop. He found that the friction factors obtained from backward and forward flow are not the same, even though they have the same roughness height. The friction factors calculated from the experiment are not equal to those calculated from the Von Karman equation for fully rough surfaces in turbulent flow, which give a constant value of the friction factor at high Reynolds numbers.