



CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Equipment:

1. Scanning Electron Microscope (SEM)
2. Atomic Absorption Spectrophotometer (AAS)
3. pH meter.
4. Digital camera
5. Pressure Transducer.

3.1.2 Chemicals:

1. Pure Plaster of Paris (95 wt% $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$)
2. Water supply, Fredericton city water
3. Nitric acid (HNO_3)
4. Sodium Hydroxide (NaOH)
5. De-ionized water
6. Sand

3.2 Methodology

3.2.1 Mixing

3.2.1.1 *Mixing of the Plaster*

The hydration reaction between water and plaster of Paris normally requires 18.6 wt% of water in the mixture but, for easier casting and for higher fluidity, an excess of water is added. The porosity of plaster of Paris is caused by the evaporation of the excess water during the drying process. Air bubbles are often trapped in the plaster structure during mixing causing the material to be brittle, which will affect the test. Therefore, to minimize the formation of air bubbles, the plaster is thoroughly mixed with de-ionized water in a vacuum chamber, see Figure

3.1. The obtained slurries, under vacuum, are significantly denser and have fewer air bubbles than one prepared under atmospheric conditions.

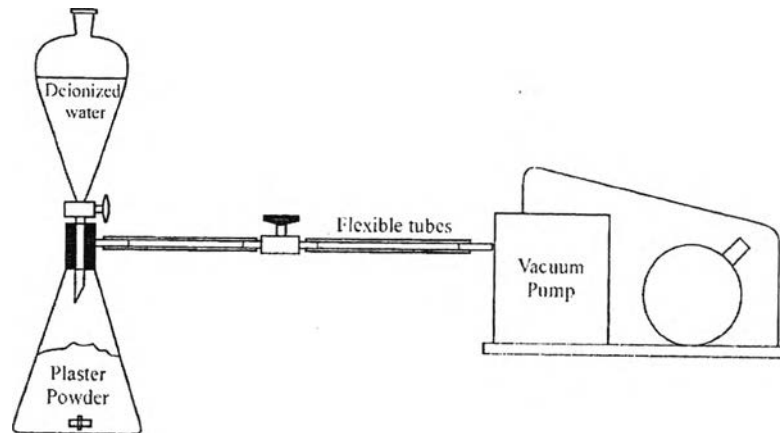


Figure 3.1 Schematic of the mixing apparatus.

The ratio of water-to-powder, R_o , ($R_o = M_{\text{water}}/M_{\text{plaster}}$) affects the mechanical properties of plaster of Paris. The final consistency is optimized by varying the ratio R_o during the mixing. A small R_o leads to a very compact and dense material but the plaster is too thick to be cast. At larger R_o , the fluidity of the plaster increases but the final plaster is more brittle. A compromise had to be found to obtain a satisfactory consistency for the plaster. Finally, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ powder was mixed with de-ionized water in the ratio 70:100 ($R_o=0.7$) as a regular procedure. The wet plaster was fluid enough to be easily injected by syringe into the test section and most of the air bubbles in the plaster were easily removed.

3.2.1.2 *Mixing sand grains with plaster of Paris (Artificially created defects)*

Sand grains were screened to separate particles of diameter ranges of 0.21 – 0.25mm, 0.420 – 0.50mm and 0.500 – 0.707mm (mean particle diameters are 0.230, 0.460, 0.604mm respectively). Plaster of Paris was mixed with the sand grains during the mixing of plaster. The sand particles were added and adjusted to obtain defect concentrations of 50 and 100 defects/cm³ of plaster.

3.3 Test Section

Villien *et al.* (2005) designed the test section, so similar experiments to theirs are used here. Loop test sections consist of two 75 cm-long and 5 cm-diameter horizontal half cylinders of transparent acrylic, bolted together every 5 cm and with a seal of plastic tape to prevent the test section from leaking. The bottom part of the test section (3.75 cm ID) has a larger inside diameter than the top part (2.5 cm ID), as shown in Figure 3.2. The bottom part has a lining of cast plaster which is allowed to dry for 5 days at room temperature and atmospheric pressure so that the inside of the test section presents a smooth circular pipe to the flowing water. Water from reservoirs in parallel is pumped through the test section and the effluent is sampled and analysed for dissolved calcium sulphate, conductivity and pH. After a run, the test section is disassembled, photographed and its surface examined to characterise the scalloping.

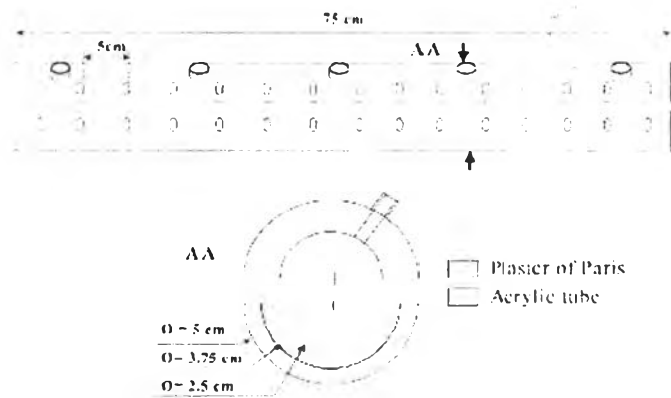


Figure 3.2 Schematic of the test section. (Villien, *et al.*, 2005)

3.4 Test Loop

The test section is installed within a water loop, as shown in Figure 3.3. Two reservoir tanks (600 liters each) are used to store the water which is mixed with sodium hydroxide or sulfuric acid to control pH. The fluid flows along the pipe and passes through the test section for studying the scallop surface and effect of

dissolution rate under different pH and flow rate conditions. Fluid is discharged and can be sampled at the end of the test section to measure calcium concentration and calculate the dissolution rate as a function of time with an Atomic Absorption Spectrophotometer.

A ratio of $R_o = 0.7$ was adopted for all runs after initial trials. Sulfuric acid or sodium hydroxide is added to the reservoir to adjust the pH. The flow rate is adjusted with a valve and measured with a rotameter. Samples of the solution are taken every 30 minutes for 5 hours for analysis, the characteristics of scallops, the thickness of deposit, defect density, dissolution rates are recorded. Pressure drop is measured with pressure transducer along the test section and pictures of scallops are taken for analysis.

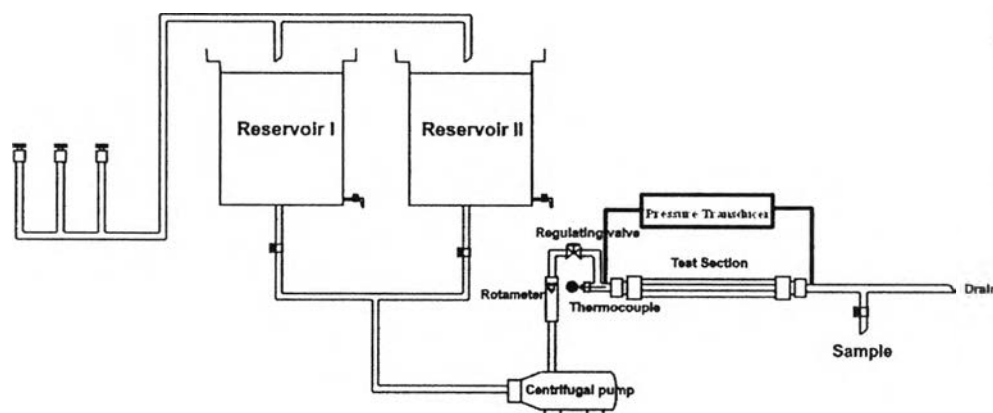


Figure 3.3 Schematic of the experimental loop.

3.5 Test conditions

Different parameters have been tested for investigating different ways of scallop initiation. Flow rates have been tested at 25 and 35 LPM, so Reynolds numbers 29709 and 21220 were obtained. pH was adjusted by adding sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) to be 3, 7 and 10. Different parameters were tested as in Table 3.1 and 3.2 below.

Table 3.1 Conditions for studying the effects of pH and flow rates (pure plaster – no defects).

Condition of fluid No.	pH	Flow rate (LPM)	Temperature (°C)
1	3	25	30 ± 2
2	7	25	30 ± 2
3	10	25	30 ± 2
4	3	35	30 ± 2
5	7	35	30 ± 2
6	10	35	30 ± 2

Table 3.2 Conditions for studying the effects of temperature, particle size, defect concentration and flow rate.

Condition of fluid No.	Particle size (mm)	Particle Concentration (Defects/cm ³)	Flow rate (LPM)	Temperature(°C)
1	0.210-0.250	50	25	25 ± 2
2	0.420-0500	50	25	25 ± 2
3	0.500-0.707	50	25	25 ± 2
4	0.210-0.250	100	25	25 ± 2
5	0.420-0500	100	25	25 ± 2
6	0.500-0.707	100	25	25 ± 2
7	0.210-0.250	50	35	25 ± 2
8	0.420-0500	50	35	25 ± 2
9	0.500-0.707	50	35	25 ± 2
10	0.210-0.250	100	35	25 ± 2
11	0.420-0500	100	35	25 ± 2
12	0.500-0.707	100	35	25 ± 2
13	0.210-0.250	50	25	10 ± 2
14	0.420-0500	50	25	10 ± 2
15	0.500-0.707	50	25	10 ± 2
16	0.210-0.250	100	25	10 ± 2
18	0.420-0500	100	25	10 ± 2
19	0.500-0.707	50	35	10 ± 2
20	0.210-0.250	50	35	10 ± 2
21	0.420-0500	50	35	10 ± 2
22	0.500-0.707	100	35	10 ± 2
23	0.210-0.250	100	35	10 ± 2
24	0.420-0500	100	35	10 ± 2

3.6 Analytical Techniques

3.6.1 Dissolution rate analysis

The average dissolution rate of the plaster of Paris was estimated in two ways.

3.6.1.1 *Dissolution rate with time from mass variations*

By weighing the plaster before and after the test the mass loss by dissolution was obtained. Then, mass loss was converted to average rate of dissolution (mg of Ca²⁺/cm².min)

$$R = \frac{\left((m_o - m_f) \frac{MW_{Ca}}{MW_G} \right)}{t \cdot A} \quad (3.1a)$$

where m_o and m_f (g) are the initial and final weight of the plaster pipe respectively, MW_{Ca} and MW_G are the molecular weight of calcium and gypsum respectively, t is testing time (min), A is the surface area (cm²).

3.6.1.2 *Dissolution rate with time by using atomic absorption spectrophotometer (AAS)*

Calcium concentration in the effluent was directly measured by using AAS and converted to dissolution rate with time. Effluent was sampled every 30 minutes.

$$R = \frac{(C_{f,i} - C_o)U \times 10}{A} \quad (3.1b)$$

where C_o is the calcium concentration in the reservoirs (ppm or mg/L) and $C_{f,i}$ is calcium concentration at every 30 minutes (ppm or mg/L), U is volumetric flow rate (L/min).

3.6.1.3 Dissolution rate along the pipe

The thickness of plaster pipe was measured at three circumferential points every centimeter at the end of the test. The thickness of the pipe was converted to average dissolution rate along the pipe.

$$R = \frac{\left((m_o - m_f) \frac{MW_{Ca}}{MW_G} \right)}{t \cdot A} \quad (3.1c)$$

where m_o and m_f (g) are the initial and final weight of the plaster pipe respectively, MW_{Ca} and MW_G are the molecular weight of calcium and gypsum respectively, t is testing time (min), A is the surface area (cm^2).

3.6.2 Pressure drop analysis

Pressure was measured at the entrance and the exit of the pipe every 30 minutes by using differential pressure transducers and converted to pressure drop.

$$P = 0.0254 \times \rho g H \quad (3.2)$$

where P is pressure at a point (Pa), ρ is the density of water (Kg/m^3), g is the gravity (m/s^2) and H is height of the water which is measured with a differential pressure transducer (metre).

3.6.3 Characterization of scalloped surface

Formation of scallops was recorded photographically at any given time and after each experiment with a digital camera.

3.6.4 Determination of the gypsum dissolution

Mass transfer coefficient (k_m) was determined at different regions along the pipe length. The integrated turbulent Leveque equation was used to determine the mass transfer coefficient in the entrance section (Berger and Hau, 1997);

$$St_d = 0.276 Re^{-0.417} Sc^{-2/3} (L/d)^{-1/3} \quad (3.3a)$$

where St_d is Stanton number for mass transfer, k_m/U , U is mean velocity (m/s), Re is Reynolds number, Sc is Schmidt number, L is length of mass transfer length (m) and d is tube diameter (m).

Mass transfer coefficients were determined in fully developed flow over the range $8 \times 10^3 < Re < 2 \times 10^5$ and at Schmidt number varying between 1000-6000 by

$$St_d = 0.0165 Re^{-0.14} Sc^{-0.67} \quad (3.3b)$$

The overall rate constant (K) was determined from the dissolution rate along the pipe length;

$$\text{Dissolution rate} = K(C_s - C_b) \quad (3.3c)$$

The dissolution coefficient (k_d) was calculated from the correlation between the mass transfer coefficient and the overall rate constant;

$$1/K = 1/k_m + 1/k_d \quad (3.3d)$$

where K is the overall rate constant (m/s), k_m is the mass transfer coefficient (m/s) and k_d is the dissolution coefficient (m/s).