CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Instruments and Apparatus

1. Atomic Absorption Spectrophotometer (AAS), PERKIN-ELMER 2380.

2. Scanning Electron Microscope (SEM)

3. pH meter, HACH D/R 2800.

4. Digital camera

3.1.2 Plaster of Paris ($CaSO_4.\frac{1}{2}H_2O$)

Plaster of Paris is calcium sulfate hemihydrate, $CaSO_4.\frac{1}{2}H_2O$ and is defined by the Canadian Standard Association as a calcined gypsum having a purity of not less than 66% $CaSO_4 \cdot \frac{1}{2}H_2O$ by mass. It is a generic name for a family of powdered cementitious products consisting primarily of calcined gypsum with additives to modify physical characteristics, and having the ability, when mixed with water and aggregate, to produce a plastic mortar or slurry which can be formed to the desired shape by various methods and will subsequently set to a hard, rigid substance.

Plaster of Paris was chosen as the substrate for these experiments as it presents many advantages. For example, plaster of Paris is easily cast to a suitable size and shape, furthermore it is inexpensive and replacement of the test sections can be easily made. Moreover, the solubility of the plaster in water is reasonable and significant results can be obtained in a short period of time. Coney *et al.* (1982) have used it to predict the effects of hydrodynamics on the dissolution of pipe walls.

Plaster of Paris, which was used for this project, is a plaster from United States Gypsum Company (USG) containing impurities such as sand particles. The plaster is composed of more than 70% of $CaSO_4 \cdot \frac{1}{2}H_2O$ and less than 30% of crystalline silica (sand) and expanded perlite.

When plaster is mixed with water, a reaction takes place and water is absorbed by the calcium sulfate hemihydrate to form the dehydrate generally referred to as gypsum.

$$CaSO_4 \cdot {}^{1}/_2 H_2O + {}^{3}/_2 H_2O \longrightarrow CaSO_4 \cdot 2H_2O$$

Plaster of Paris   *Gypsum*
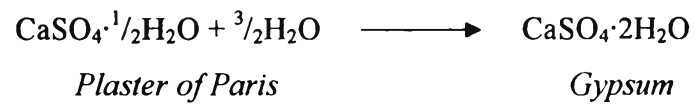
The final product is a coherent mass of needle-shaped gypsum crystals as shown in Figure 3.1.
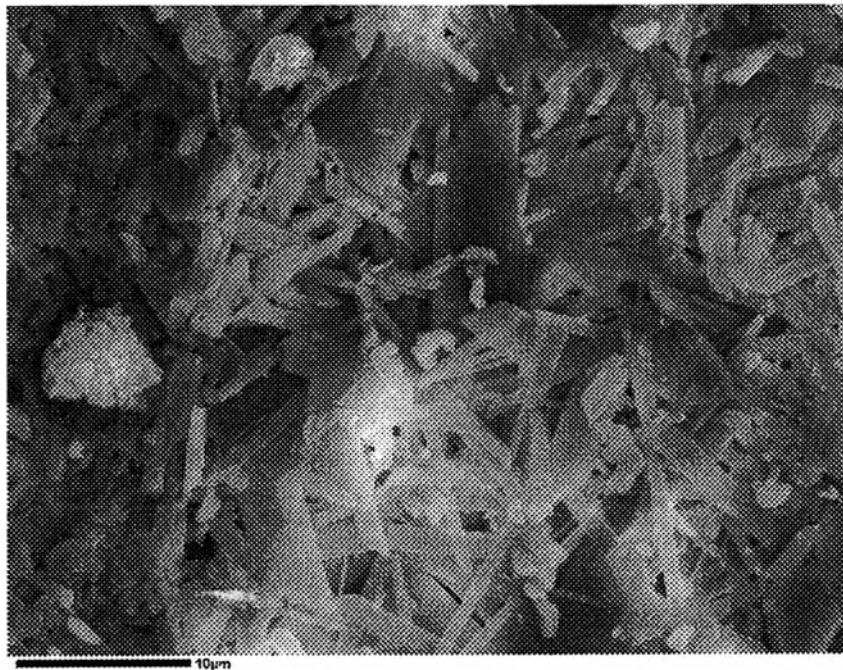

Figure 3.1 SEM of the plaster structure.

3.1.3 Water and Chemicals for Controlling pH and Temperature

- Water supply, Fredericton City Water
- Nitric acid (HNO_3)
- Sodium hydroxide (NaOH)
- Deionized water

3.2 Methodology

3.2.1 Mixing of the Plaster

The reaction between water and plaster of Paris normally requires 18.6 wt% water for hydration but, for practical reasons, an excess of water was added to allow a higher fluidity and an easier casting of the plaster. The porosity of plaster of Paris is important because of 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 more brittle. Therefore, to minimize the formation of large pores and air bubbles, the plaster was thoroughly mixed with water in a vacuum chamber, see Figure 3.2. The slurries obtained under vacuum were significantly more compact than the ones prepared under atmospheric conditions.
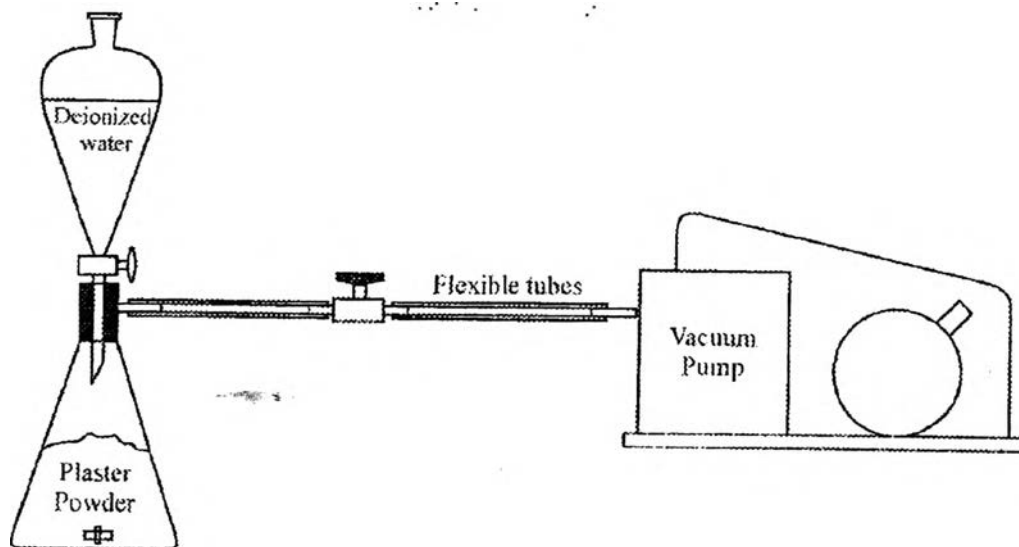

Figure 3.2 Schematic of the mixing apparatus.

The mechanical properties of the plaster of Paris depend on the water-to-powder ratio R_o ($R_o = M_{water}/M_{plaster}$). The final consistency was optimized by varying the ratio R_o during the mixing. A small R_o led to a very compact and dense material but the plaster was too thick to be cast. At larger R_o the fluidity of the plaster increased but the final plaster was more brittle. A compromise had to be found to

obtain a satisfactory consistency for the plaster. Finally, the $CaSO_4 \cdot \frac{1}{2}H_2O$ powder was mixed with deionized 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, see Appendix A for the details.

3.2.2 Test Section

Continuing the work of Villien *et al.* (2005), similar experiments were designed. A transparent test section had been designed to allow visual observation of the formation and evolution of scallops. The test section consisted of two 75 cm-long half-cylinders made of transparent and chemically inert acrylic, that are bolted together every five cm 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 3.3. A 1-inch outside diameter stainless steel rod was used as a mould to obtain the inside shell shape. A layer of plaster was molded in the bottom half-cylinder so as to make the two halves coincide exactly.
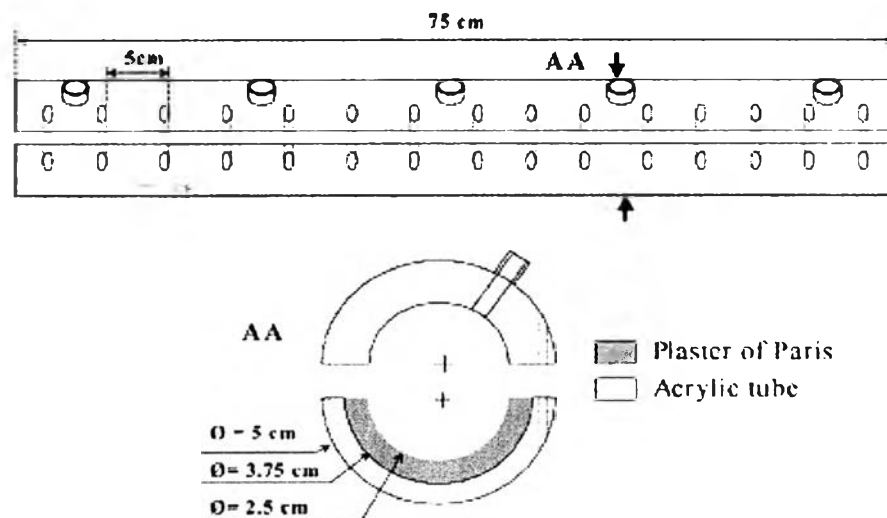

Figure 3.3 Schematic of the test section. (Villien, *et al.*, 2005)

Once the test section was cast, the plaster of Paris was allowed to dry for five days at room temperature under atmospheric pressure.

3.2.3 Test Loop

The test section was installed within a water loop, as shown in Figure 3.4. There are two reservoir tanks (600 liters per each tank) to store the water for mixing with the chemical to control pH. The fluid flows along the pipe and passes through the test section for studying the scallop surface and dissolution rates under various pH and temperature conditions. The fluid is discharged and can be sampled at the end of the test section to measure calcium concentration and calculate the dissolution rates 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, see Appendix A. Sulfuric acid or calcium hydroxide was added to the reservoir to adjust the pH. The flow rate was adjusted with a valve and measured with a rotameter. The temperature was recorded at the inlet of the test section during all tests. Samples of the solution were taken at the end of the test section for analysis.
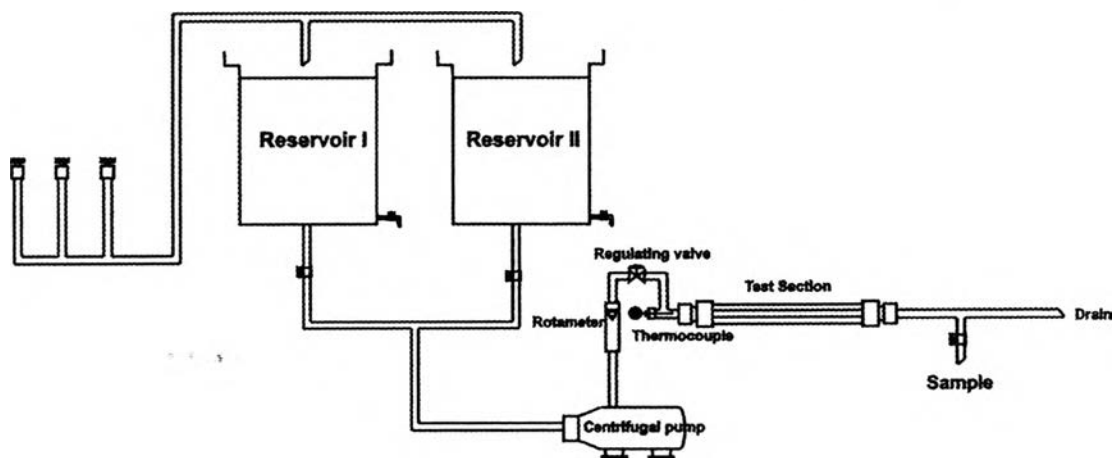
Figure 3.4 Schematic of the experimental loop.

Different parameters were recorded to indicate the dissolution of the plaster of Paris. The calcium concentration of the samples was measured by using an Atomic Absorption Spectrophotometer (AAS) and used to calculate the dissolution rates. The pH and temperature were measured with a pH meter and a thermocouple, respectively, during each test. The scallop surfaces were examined with a digital camera for each run.

3.2.4 Test Runs and Conditions

From measuring the water flow from the taps, the maximum flow rate was 35 liters per minute (LPM). In order to achieve Reynolds numbers in the range of 18900 to 44200 as in previous work, another flow rate was chosen in this work, 25 LPM. These flow rates give Reynolds numbers 29709 and 21220.

Nitric acid (HNO_3) and sodium hydroxide (NaOH) were mixed in the water to obtain a pH of 3 and 10, respectively. Different flow rates were operated under different pH. There were two different temperatures, which are 10 and 25 °C. Table 3.1 shows all the parameters in this work.

Table 3.1 Test conditions

Condition of fluid No.	Flow rate (LPM)	pH	Temperature (°C)
1	25	3	25
2	25	7	25
3	25	10	25
4	35	3	25
5	35	7	25
6	35	10	25
7	25	3	10
8	25	7	10
9	25	10	10
10	35	3	10
11	35	7	10
12	35	10	10

3.3 Analytical Techniques

3.3.1 Dissolution Rate Analysis

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

1. Dissolution rate from mass variations

By measuring the weight of plaster lost by dissolution at the end of the test, this mass loss was transformed to rate of dissolution $(g/m^2.min)$

$$R = \frac{\left((m_o - m_f)\frac{MW_{Ca}}{MW_G}\right)}{t \cdot A} \tag{3.3.1a}$$

where m_o and m_f are the weight of the plaster tube before and after a run respectively (g), MW_{Ca} and MW_G are the molecular weight of calcium and gypsum respectively, t is running time (min), A is the nominal surface area (m^2).

2. Dissolution rate from using atomic absorption spectrophotometer

The atomic absorption spectrophotometer (AAS) was used to measure calcium concentration directly. This method determines the dissolution rate at every 30 minutes.

$$R = \frac{(C_{f,i} - C_o)U \times 10}{A} \tag{3.3.1b}$$

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).

The dissolution rate is calculated from mass variation for checking the dissolution rate from using AAS.

3.3.2 Characterization of Scalloped Surface

The morphology of the scalloped surface was determined by using a digital camera. The formation of scallops is large enough to take a photograph at any given time and after each experiment. In addition, a scanning electron microscope (SEM)/EDX was used to analyse the structure of the plaster at the micrometre scale and the composition of plaster after each experiment. Laser Raman Spectroscopy (LRS) was used to analyse the plaster surfaces. The vernier was used to determine the thickness of plaster wall.