



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Certified A.C.S. grade of barium chloride dihydrate,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , and sodium sulfate,  $\text{Na}_2\text{SO}_4$ , supplied by Fisher Chemical were used to study barium sulfate deposition. Diethylenetriaminepentaacetic acid, DTPA, 98% total solids,  $\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_{10}$ , supplied by Thermo Sci Acros Organics and certified A.C.S. grade of potassium hydroxide, KOH, supplied by Fisher Chemical were used to study barium sulfate dissolution. Concentrated trace metal grade hydrochloric acid, HCl, supplied by Fisher Chemical was used to create a surface roughness inside a capillary. Deionized water (Ultrapure Milli-Q<sup>TM</sup> water system (18 M $\Omega$ )) was used as a solvent for preparing all aqueous solutions.

### 3.2 Equipment

- 3.2.1 Two HPLC 510 water pumps
- 3.2.2 MasterFlex peristaltic pump Model 7543-60 with pump head Model 7021-24 from Cole-Parmer Instrument Company
- 3.2.3 Stirrer Model PC-410D from Corning
- 3.2.4 Syringe pump Model 55-2222 from Harvard Apparatus
- 3.2.5 Norm-ject<sup>®</sup> syringe 60 mL from Henke Sass Wolf
- 3.2.6 Stainless steel type 316 tubing with OD 0.0625" and ID 0.020" from Fisher Scientific Inc.
- 3.2.7 Stainless steel fittings from Upchurch scientific
- 3.2.8 The differential pressure transducer model Z with a range of 25 psi from Honeywell International Inc.
- 3.2.9 USB-6009 14 bit, 48 kS/s Multifunction Data Acquisition system from National Instruments
- 3.2.10 Inductive-coupled plasma spectroscopy/mass spectroscopy (ICP/MS) for elemental analysis from Perkin Elmer (Model ELAN

DRC-e)

3.2.11 Nikon Eclipse E600 optical microscope

3.2.12 Olympus SZX12 stereo microscope

### 3.3 Software

3.3.1 LabVIEW by National Instruments – used for data acquisition and logging

3.3.2 ELAN9000 – installed with Perkin Elmer ICP/MS

3.3.3 WinTV2000

3.3.4 Image Pro

### 3.4 Methodology

As mentioned in the above section, section 2.2, deposition mechanism of  $\text{BaSO}_4$  is still unclear. Thus, in order to investigate the possible mechanisms, two mechanisms were proposed. First, since barium sulfate has nucleated and before growth has completed, barium sulfate can deposit in pipelines. Second, after barium sulfate has completed their growth, barium sulfate can deposit in pipelines.

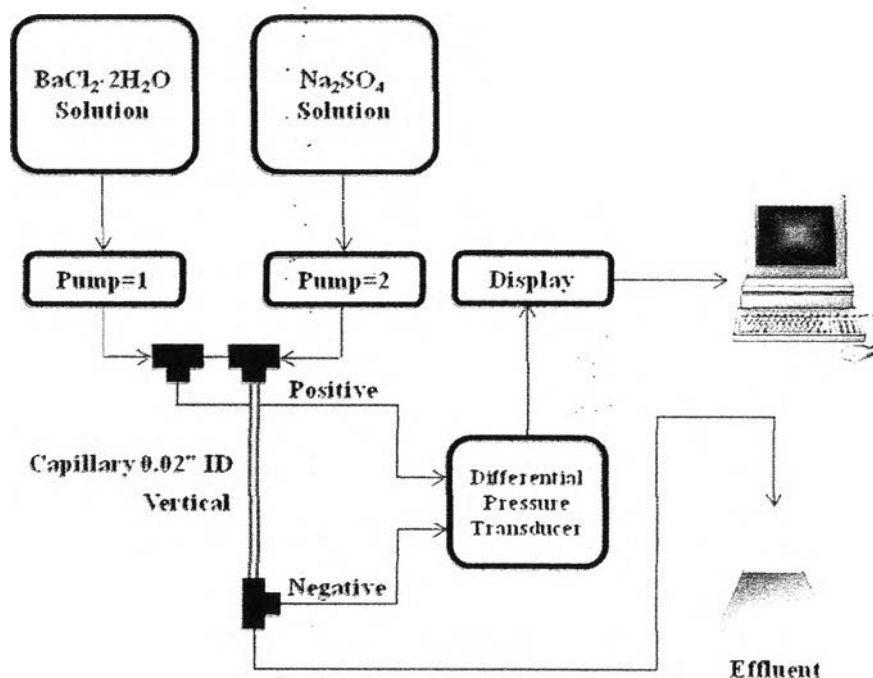
#### 3.4.1 Barium Sulfate Deposition

An experimental schematic, shown in Figure 3.1 was used to investigate the first mechanism. The experimental set up consists of two HPLC pumps, one for  $\text{Na}_2\text{SO}_4$  solution and another one for  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  solution. Both solutions were pumped at 2 mL/min and mixed in the second connecting tee then passed through 0.02 inches inner diameter capillary. The solution flowing out from the capillary was collected in an effluent flask. Due to an instantaneous precipitation of  $\text{BaSO}_4$  when two solutions were mixed,  $\text{BaSO}_4$  can plug in the flow line, so positive inlet pressure was measured before mixing of the two solutions. Negative outlet pressure was measured at the tee after the solution came out from the capillary and flowed into an effluent flask. All experiments were conducted at room

temperature and concentrations of both solutions were varied, 100 ppm (0.41 mM  $[\text{Ba}^{2+}]$  and 0.70 mM  $[\text{SO}_4^{2-}]$ ), 1 mM, 3 mM and 5 mM.

#### 3.4.1.1 Effect of Surface Heterogeneity

In an oil field, rough surface is often observed inside a pipeline due to corrosion and consequently there are more favorable sites for nucleation (Hoek *et al.*, 2006). In order to investigate the effect of an inner surface of a capillary on the barium sulfate deposition, two types of inner surfaces were used, smooth (normal) and rough surfaces. For creating a rough surface inside a capillary, the capillary was dipped in 20% hydrochloric acid and left overnight (about 13 hours). Then, the capillary was washed with DI water.



**Figure 3.1** Schematic of the experimental apparatus for barium sulfate deposition.

#### 3.4.2 Flowing Precipitated BaSO<sub>4</sub> Solution Through a Capillary

Precipitated BaSO<sub>4</sub> solution was prepared by mixing BaCl<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub> solutions at different concentrations of 100 ppm and 5 mM in 2 L Erlenmeyer flask. The solution was stirred overnight (about 13 hours) at 200 rpm. Then, the solution was pumped through a capillary at 3.6 mL/min by using peristaltic

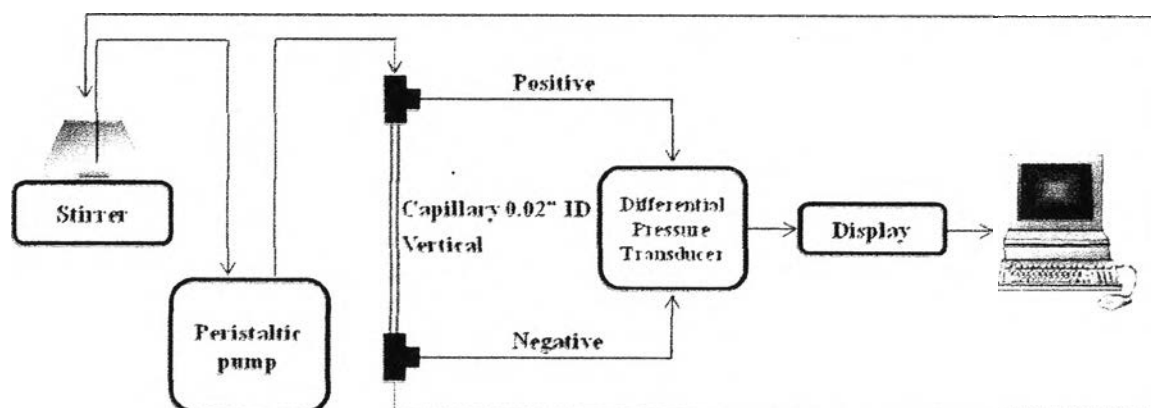
pump and the pressure drop across the capillary was measured by differential pressure transducer as shown in Figure 3.2. After forming a completely aged barium sulfate solution, samples were taken in order to determine the morphology and particle size of BaSO<sub>4</sub> particles by using microscope. All the experiments were conducted at room temperature. Moreover, in order to avoid settling down of BaSO<sub>4</sub> particles inside a capillary, the capillary was mounted in vertical position.

#### 3.4.2.1 Effect of Surface Heterogeneity

The experiment, as mentioned above, was conducted by changing three types of inner surfaces, smooth, rough and pre-scaled surfaces. In order to create a pre-scaled surface inside a capillary, BaCl<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub> solutions were flowed through a capillary. When the pressure drop reached 2 psi from the initial value, solution flasks were replaced by water flasks and the experiment was stopped when the pressure drop seemed constant.

#### 3.4.3 Quantifying the Deposit Mass

In order to determine the deposited mass of BaSO<sub>4</sub>, two techniques have been used. As known that DTPA is widely used to dissolve deposited scale out from the pipelines, DTPA has been used as the first technique to dissolve BaSO<sub>4</sub> out from the capillary. The second technique is based on the weight difference of the capillary to determine the deposited mass of BaSO<sub>4</sub>.



**Figure 3.2** Experimental schematic for flowing precipitated particles through a capillary.

#### 3.4.3.1 *Dissolution Method*

For preparing 0.41 mM DTPA solution, 0.322 g of DTPA was dissolved in 0.5 M KOH solution (pH 11-12). After running BaSO<sub>4</sub> deposition, capillary was dried at 100 °C overnight. A syringe pump was used to inject DTPA solution to the deposited capillary at 2 mL/min then the effluent was collected at the outlet of the capillary. Afterwards, 5 mL of each collected effluent was diluted to 50 mL with DI water and barium ion concentration was measured by using ICP/MS technique. Barium ion concentration was used to calculate the collected mass of BaSO<sub>4</sub> which was deposited inside the capillary.

#### 3.4.3.2 *Gravimetric Method*

The capillary was weighed before and after deposition experiment then mass of BaSO<sub>4</sub> was calculated from the weight difference.