



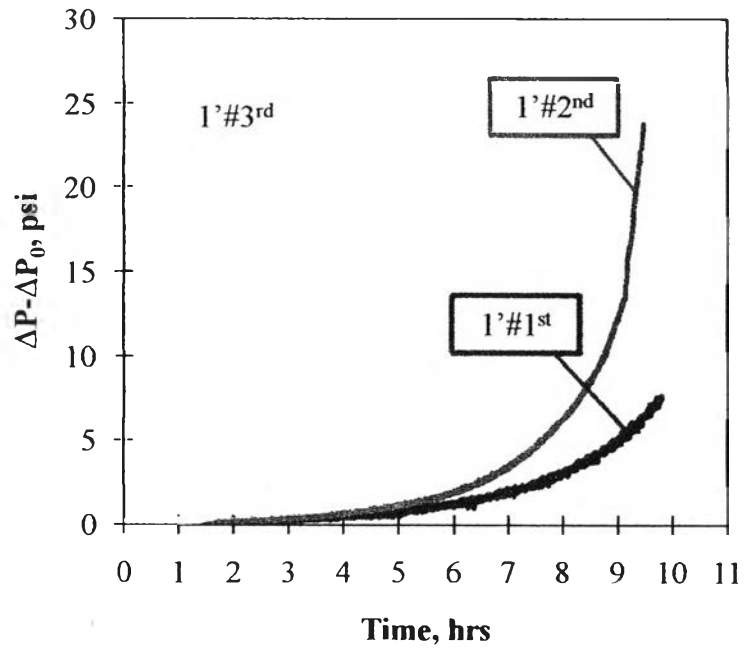
## CHAPTER IV

### RESULTS AND DISCUSSION

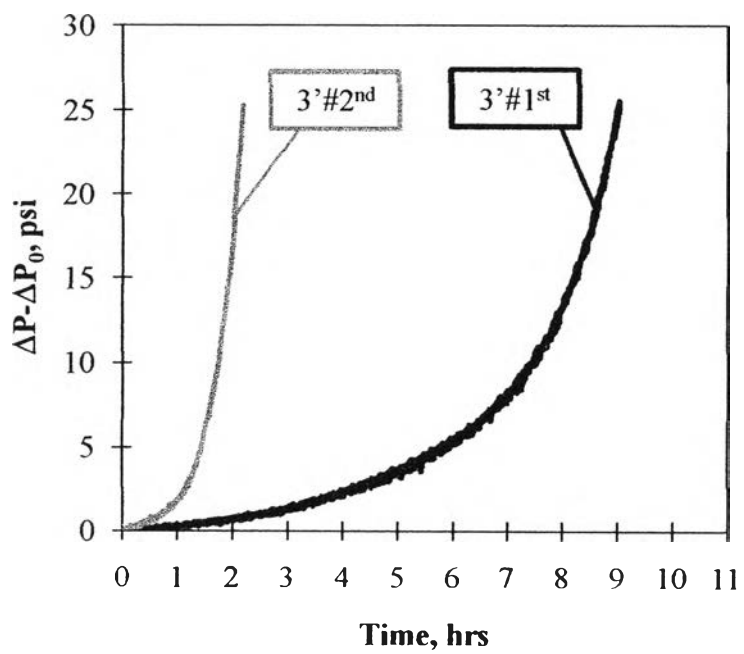
#### 4.1 Barium Sulfate Deposition

##### 4.1.1 Reused Capillary

According to Eq. (5), a slightly change in the radius of a capillary will bring a significantly change in the pressure drop across the capillary. In order to ensure a constant radius of the capillary, capillary was reused. Initially, a new capillary was used to run BaSO<sub>4</sub> deposition at 100 ppm of BaCl<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub> solutions. The BaSO<sub>4</sub> deposited inside the capillary was dissolved out by flowing DTPA solution through the capillary, as mentioned above. After that, the same capillary was reused for the next BaSO<sub>4</sub> deposition experiment. The results are shown in Figure 4.1 where x-axis is time in hours and y-axis is pressure drop minus pressure drop zero measured in psi, pressure drop zero is a constant pressure drop before pressure drop starts to increase. For a fresh capillary, 1<sup>#1<sup>st</sup></sup>, at almost 10 hours the pressure drop was still increasing but when BaSO<sub>4</sub> which was deposited inside the capillary was dissolved and the same capillary was reused again to run BaSO<sub>4</sub> deposition experiment for the second time and the third time, 1<sup>#2<sup>nd</sup></sup> and 1<sup>#3<sup>rd</sup></sup>, the deposition occurred faster. Similar results can also be seen in a 3 feet length capillary as shown in Figure 4.2. One possible reason that can be used to explain these results is DTPA solution might not be able to dissolve all BaSO<sub>4</sub> out from the capillary. BaSO<sub>4</sub> sites which are still inside the capillary can cause faster deposition in the next experiment (Ostvold *et al.*, 1993; Quddus *et al.*, 2000). Further explanation on these results is given in the next section. Thus, from these results, it was concluded that capillary cannot be reused for the next BaSO<sub>4</sub> deposition experiment.



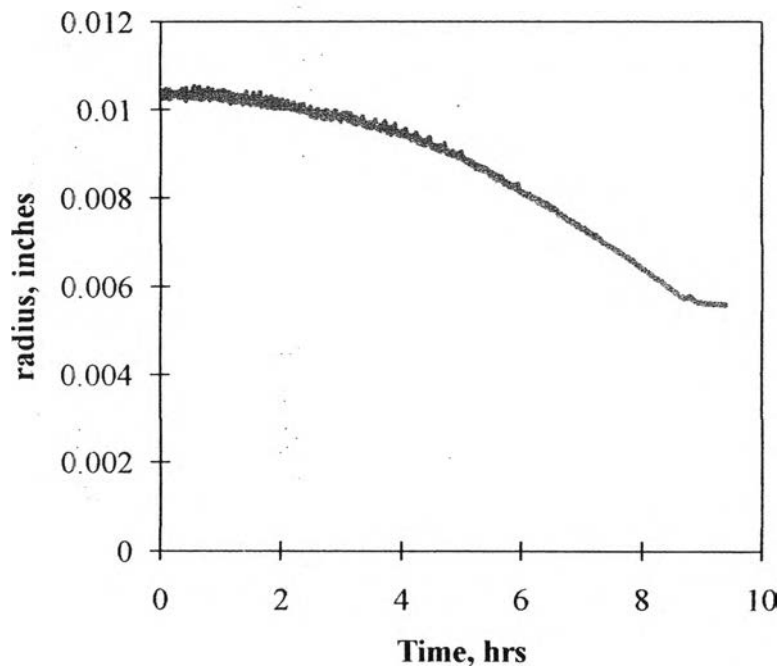
**Figure 4.1** BaSO<sub>4</sub> deposition in 1 foot length reused capillary.



**Figure 4.2** BaSO<sub>4</sub> deposition in 3 feet length reused capillary.

#### 4.1.2 Decreasing Radius of Capillary

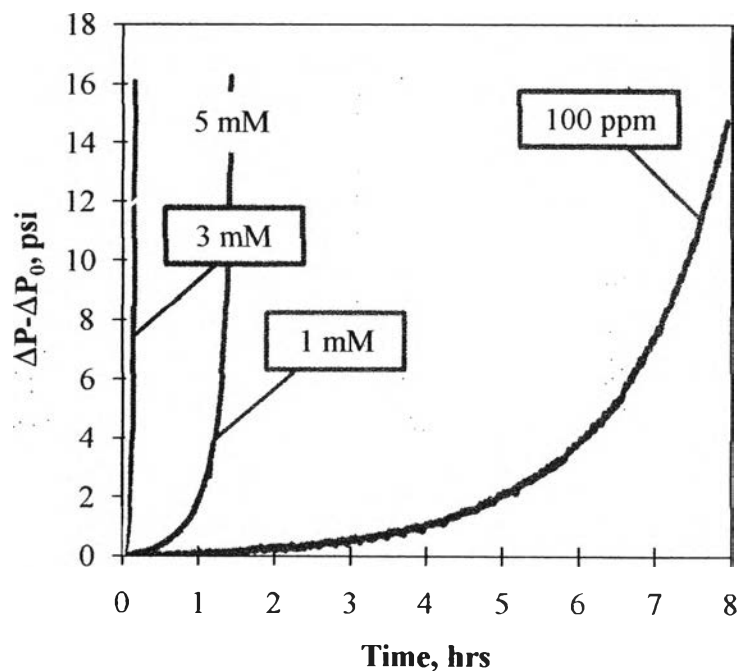
Radius of the capillary can be calculated from Hagen-Poiseuille equation (Eq. (5)) by using the increase in pressure drop based on the assumption that  $\text{BaSO}_4$  is uniformly deposited inside the capillary. Figure 4.3 shows the radius of capillary as a function of time. The initial calculated radius of the capillary is 0.0105 inches but when  $\text{BaSO}_4$  starts to deposit inside the capillary, radius of the capillary decreases. Before finishing the experiment, salt solutions were replaced by water to measure the final radius of the capillary.



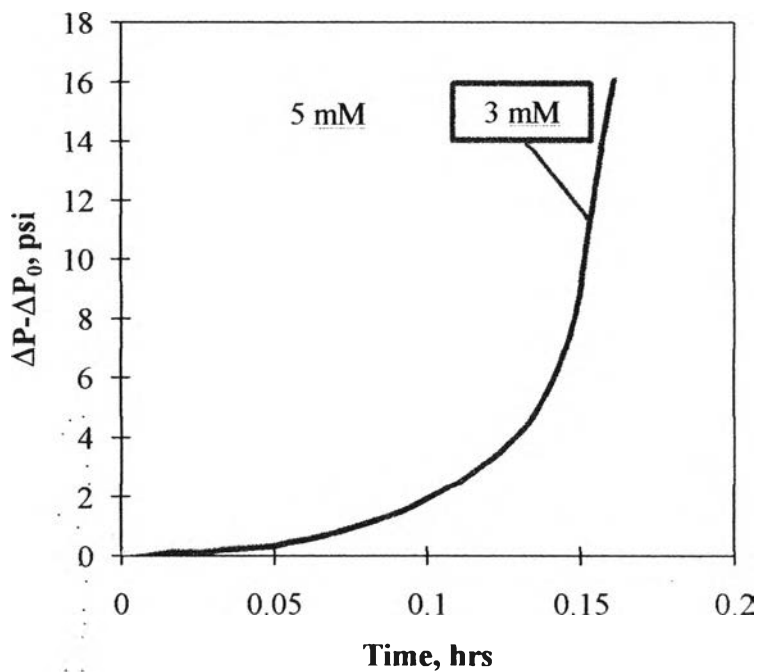
**Figure 4.3** The radius of capillary as a function of time.

#### 4.1.3 Effect of Salt Concentration

Barium sulfate deposition experiments were conducted by changing the concentration of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions, 100 ppm, 1 mM, 3 mM and 5 mM. Figure 4.4 and 4.5 shows that barium sulfate deposition occurs faster when the salt concentration increases. Results can be explained by two reasons. First, when the salt concentration increases, there is a higher amount of barium sulfate passing through a capillary and leads to faster deposition. Second, supersaturation ratio which is a driving force for barium sulfate deposition increases as the salt concentration increases.



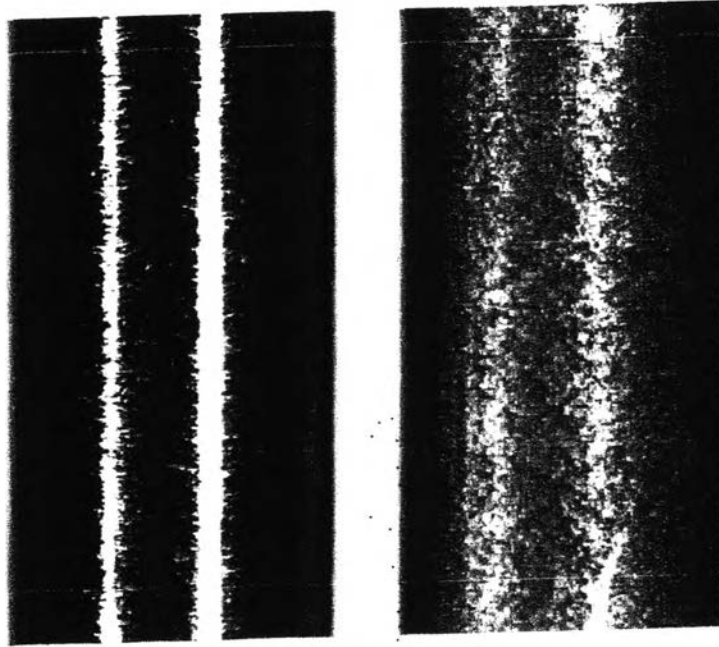
**Figure 4.4** Effect of salt concentration on the deposition.



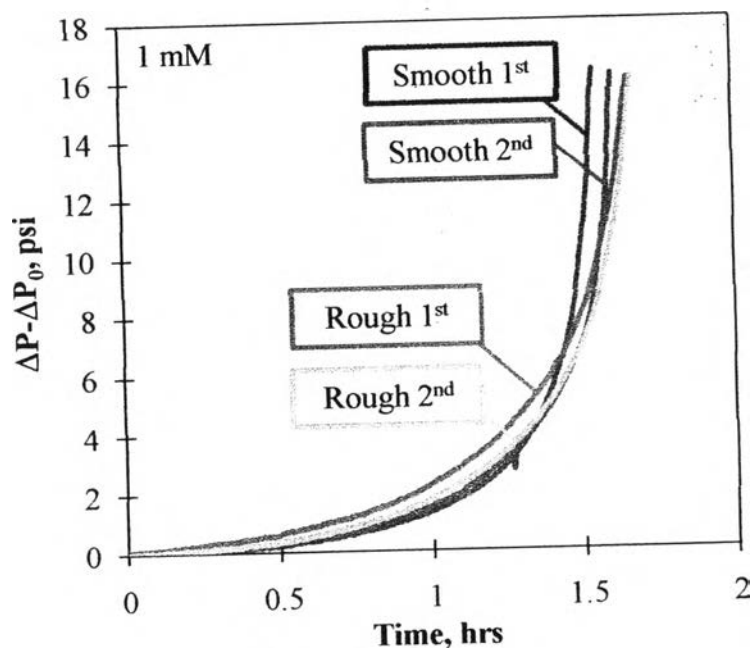
**Figure 4.5** Zoom of Figure 4.4 for 3 mM and 5 mM.

#### 4.1.4 Effect of Surface Heterogeneity

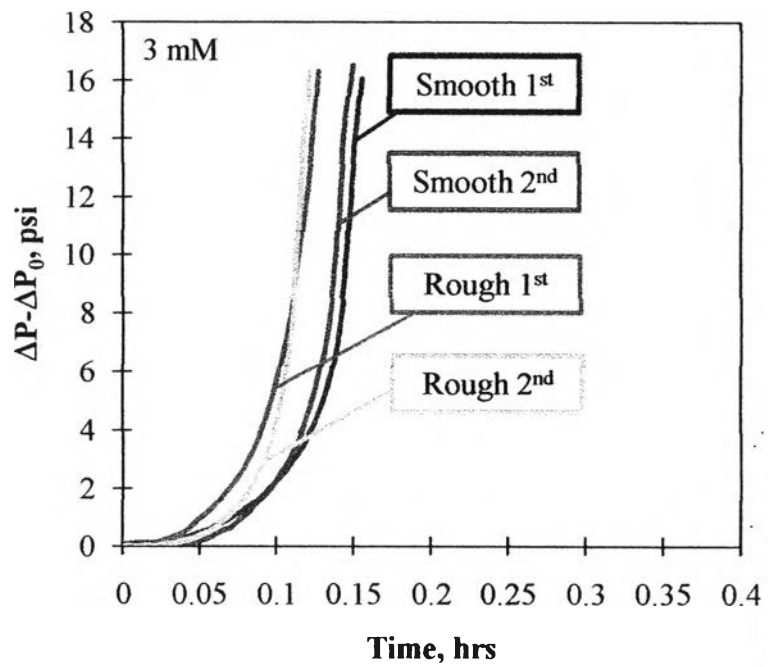
A capillary was dipped in 20% hydrochloric acid for 13 hours. After that the capillary was washed with DI water and morphology of outside capillary surface was examined by stereo microscope. The comparison of smooth and rough surfaces is shown in Figure 4.6. As mentioned, surface heterogeneity might affect the deposition of barium sulfate. However, results as shown in Figure 4.7-4.9 show that the deposition is almost the same in rough surface as compared to smooth surface. Moreover, as the concentration of salt solution is changed, the same deposition trend is observed. The possible reason to explain these results is that since the residence time is about 1 second, barium sulfate (which is still in growing step) will deposit inside the capillary at the same rate even the surface is smooth or rough. In addition, all experiments were repeated, 2<sup>nd</sup>, and reproducible results were obtained for all conditions studied.



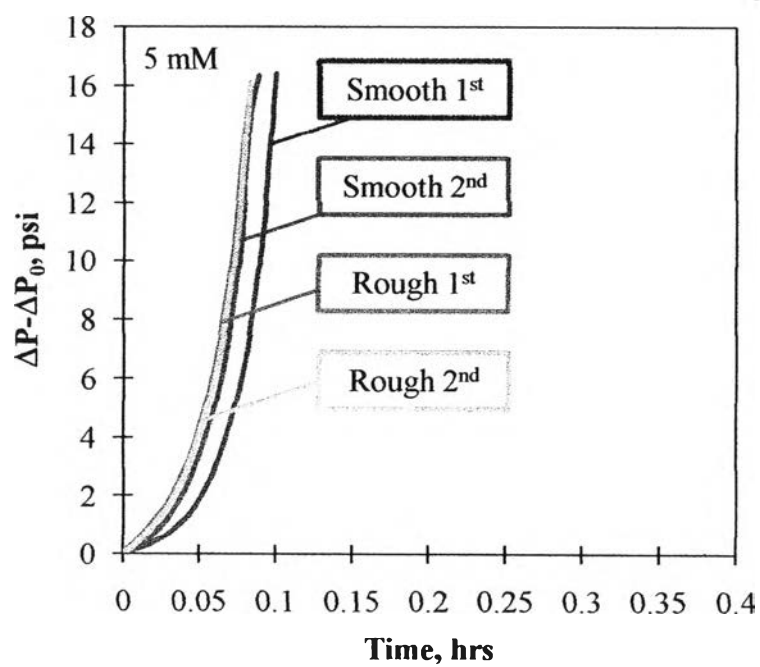
**Figure 4.6** Outside surface of a capillary. Left: smooth (normal) surface. Right: rough surface.



**Figure 4.7** BaSO<sub>4</sub> deposition in smooth and rough surfaces, [Ba<sup>2+</sup>] = [SO<sub>4</sub><sup>2-</sup>] = 1 mM.



**Figure 4.8**  $\text{BaSO}_4$  deposition in smooth and rough surfaces,  $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 3$  mM.



**Figure 4.9**  $\text{BaSO}_4$  deposition in smooth and rough surfaces,  $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 5$  mM.

#### 4.2 Comparison of Techniques to Quantify Deposit Mass

As mentioned in the previous section, two techniques can be used to determine the deposit mass and in order to compare the two techniques, new capillaries were used in every experiment. Moreover, experiments were conducted by using 100 ppm of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions and results are shown in Table 4.1. As can be seen from the percent difference in Table 4.1, the deposit mass from the two techniques are moderately in agreement.

#### 4.3 Barium Sulfate Dissolution

According to Figure 4.1 and 4.2, to confirm that capillary cannot be reused,  $\text{BaSO}_4$  dissolution was conducted to measure the collected mass of  $\text{BaSO}_4$  inside reused capillary. Both experiments, 1'#1<sup>st</sup> and 1'#2<sup>nd</sup>, were finished at around 10 hours but as shown in Table 4.2, the collected mass and total dissolution time that was spent to dissolve  $\text{BaSO}_4$  out from the capillary increased when capillary was reused. Thus, not only pressure drop but also collected mass and total dissolution time can confirm that capillary cannot be reused and can lead to erroneous results.

**Table 4.1** Deposit mass from dissolution method and gravimetric method

	1' (run A)	1' (run B)	1' (run C)
Deposited mass from ICP/MS, g	0.0111	0.0164	0.0183
Weight difference between before and after deposition, g	0.0080	0.0166	0.0147
% difference	27.82	1.06	19.65



**Table 4.2** Collected mass and total time for fresh capillary and reused capillary

Length (ft)	Collected mass (mg)	Total dissolution time (hrs)
1' #1 <sup>st</sup>	18.21	20
1' #2 <sup>nd</sup>	32.43	46

#### 4.4 Non-uniform Deposition

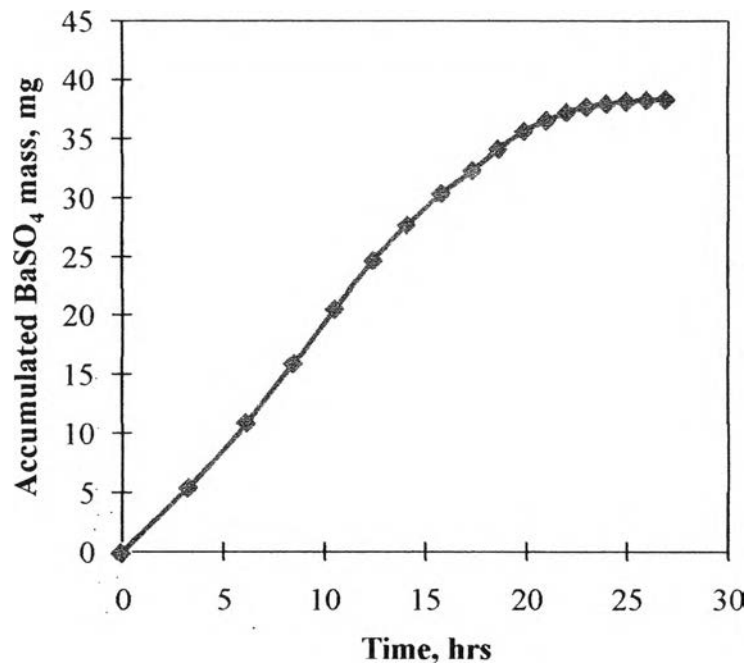
In order to investigate the uniformity of BaSO<sub>4</sub> deposition, uniform mass and collected mass have to be compared with each other. After initial radius and final radius were calculated as mentioned in the previous section, section 4.1.2, uniform mass can be calculated from both values by using Equation 7 as shown below.

$$m = \rho_{BaSO_4} \pi L (R_0^2 - R_{new}^2) \quad (7)$$

Where

- m is the uniform deposit mass (g)
- $\rho_{BaSO_4}$  is the density of BaSO<sub>4</sub> (4.5 g/mL for BaSO<sub>4</sub>)
- L is the length of capillary (m)
- R<sub>0</sub> is the initial radius of capillary (m)
- R<sub>new</sub> is the final radius/calculated radius of capillary (m)

As mentioned in BaSO<sub>4</sub> dissolution section, DTPA solution was flowed through the capillary then the effluent was collected and barium ion concentration in each collected effluent was measured by using ICP/MS so collected mass can be calculated. Figure 4.10 shows the collected mass/accumulated mass of BaSO<sub>4</sub>. The graph shows that at around 25 hours, almost all of BaSO<sub>4</sub> was dissolved out from the capillary. Moreover, comparison of the uniform mass and collected mass of 1 foot length capillary and 3 feet length capillary are shown in Table 4.3. Results show that uniform mass and collected mass is not equal so the deposit is non-uniform.



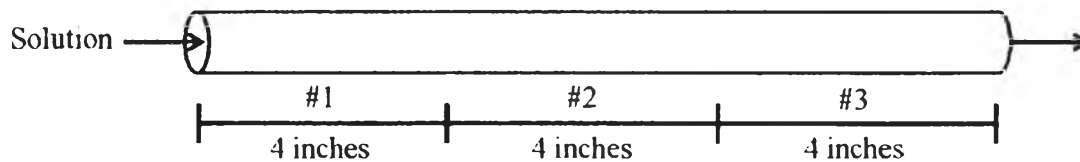
**Figure 4.10** Accumulated mass of BaSO<sub>4</sub> as a function of time of 3 feet length capillary.

**Table 4.3** Comparison of uniform mass and collected mass

Length (ft)	Initial radius, $R_0$ ( $\mu\text{m}$ )	Calculated radius, $R_{\text{new}}$ ( $\mu\text{m}$ )	Uniform mass, $m$ (mg)	Collected mass (mg)
1	266.12	166.22	189.60	18.21
3	268.84	157.77	612.52	38.39

#### 4.5 Deposit Location

In order to determine the deposit location, the experiments were conducted in a 1 foot length capillary by using 100 ppm of BaCl<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub> solutions. At the end of the experiment, capillary was cut into 3 sections, 4 inches per each section as shown in Figure 4.11. Afterwards, the deposited mass in each section was



**Figure 4.11** Capillary section schematic.

dissolved by DTPA solution as described in section 3.4.3.1. The results, as shown in Table 4.4, show that there was more deposition at the beginning of the capillary. One possible reason might be that after the two solutions,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$ , were mixed together, supersaturation ratio is reached and there is a greater driving force which propels barium sulfate deposition at the beginning of the capillary. Moreover, when the deposition occurred at the beginning of the capillary, concentration of  $\text{BaSO}_4$  solution decreased along the length of the capillary causing less deposition at the end of the capillary.

#### 4.6 Flowing Precipitated $\text{BaSO}_4$ Solution Through a Capillary

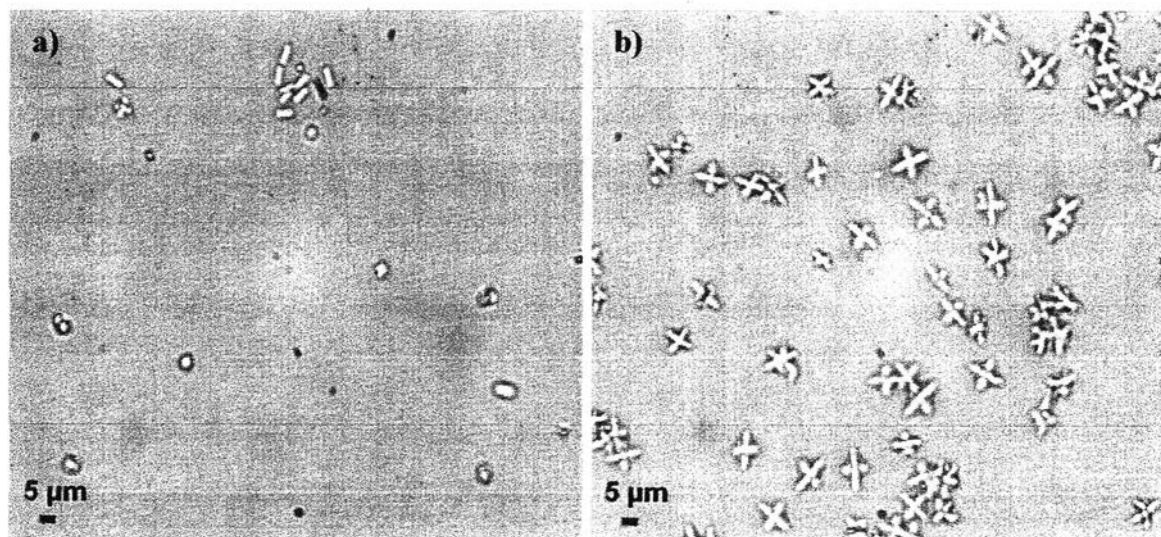
As mentioned in section 2.2, there are many possible ways in which barium sulfate can deposit in pipelines. An experiment, shown in Figure 3.2, was designed to investigate the mechanism: barium sulfate precipitates, grows in the bulk solution and after barium sulfate has completed their growth, barium sulfate can deposit in pipelines.

**Table 4.4** The collected mass in each capillary sections

Capillary sections	Collected mass (mg)
1	10.90
2	6.00
3	4.50

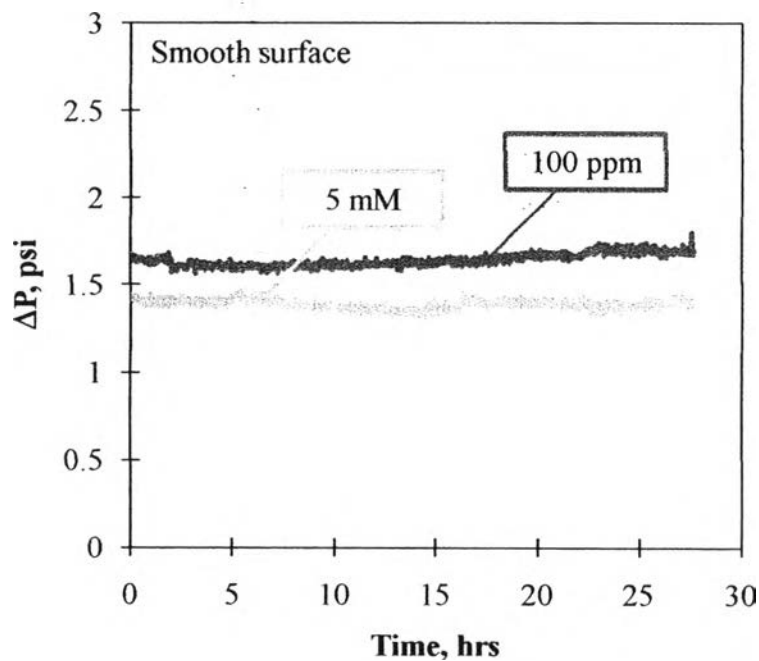
Initially, the solution was prepared by mixing  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions at 200 rpm for 13 hours. Then, the solution was pumped through the capillary and the experiment was repeated for different salt concentrations. A change in concentration of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions leads to change in particle size and morphology of barium sulfate particles. Thus, after the solutions were prepared for 13 hours, samples were taken and analyzed by optical microscope. The morphology and particle size are shown in Figure 4.12. At low salt concentration, 100 ppm, most of the particles are rectangular while some have spherical and dendrite shapes. However, at high salt concentration,  $[\text{Ba}^{2+}] : [\text{SO}_4^{2-}] = 5 : 5$  mM, dendrite shape is dominant. As can be seen when the salt concentration increases, the particle size is bigger as compared to lower salt concentration. Furthermore, it can be seen that there is a particle size distribution in the solution. These results are consistent with Nancollas *et al.*, 1976, Kind *et al.*, 2004, and Steyer *et al.*, 2009.

Figure 4.13 and 4.14 show the deposition of precipitated barium sulfate solution when it was flowed through a capillary. Results indicate that when barium

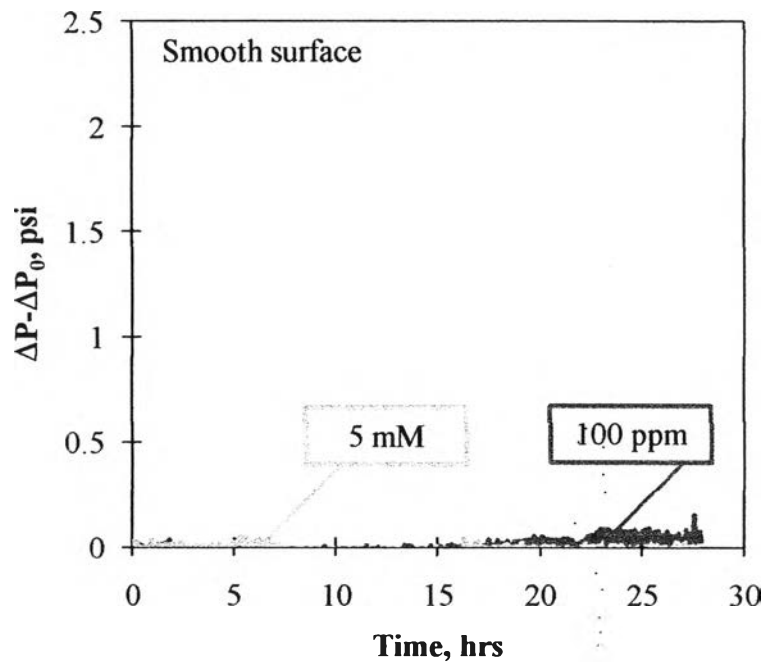


**Figure 4.12** Micrographs showing the morphology and particle size of  $\text{BaSO}_4$  at different salt concentration,  $[\text{Ba}^{2+}] : [\text{SO}_4^{2-}]$ , in mM: a) 0.41 : 0.7 and b) 5 : 5.

sulfate particles have completed their growth, they will not deposit in a capillary as can be seen from the pressure drop which is constant as a function of time. A possible reason for these results is that contrary forces between precipitated barium sulfate solution-particle and surface-particle. According to the size of barium sulfate particles, micron size, drag force which is a force applied from the solution to the surface of particles might overcome an attraction force between particles and surface, Van der Waals force. Consequently, barium sulfate particles will not deposit on the surface of a capillary. In addition, although the concentration of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions are changed, there is no barium sulfate deposition occurs in a capillary. These results imply that the amount of barium sulfate particles, particle size and particle shape may not affect to the deposition when growth has finished and barium sulfate particles are bigger than some certain size. However, it must be noted that a residence time of precipitated barium sulfate solution which pass through a



**Figure 4.13** Flowing precipitated barium sulfate solution through a smooth surface capillary at different concentrations.



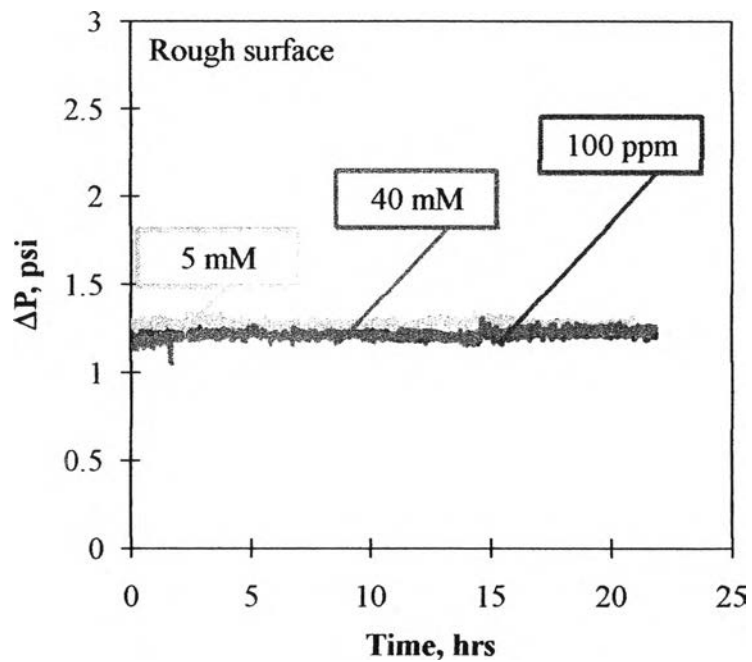
**Figure 4.14** Comparison of barium sulfate particles deposition in smooth surface capillary at different concentrations.

capillary is 1 second and might not be sufficient for barium sulfate particles to deposit in a capillary.

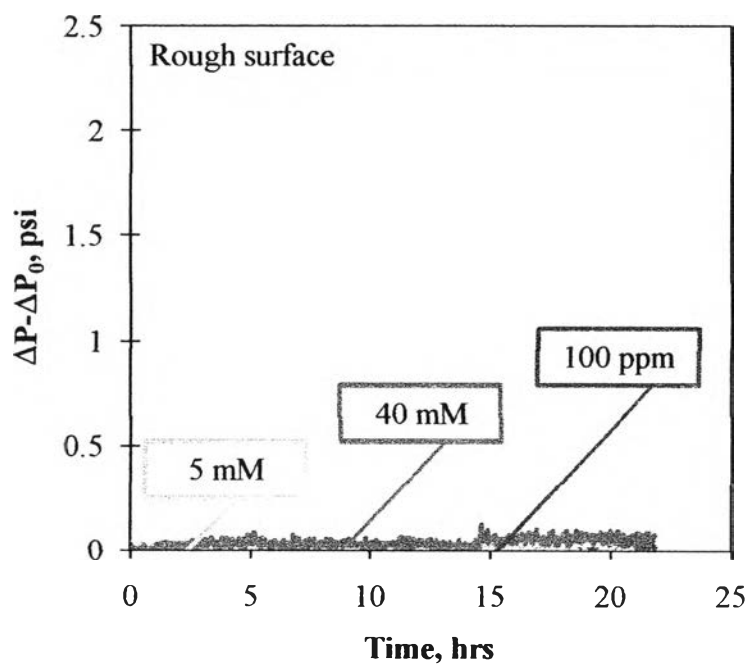
#### 4.6.1 Effect of Surface Heterogeneity on Barium Sulfate Particle Deposition

In the previous section, smooth inner surface capillaries were used. However, in order to investigate the effect of surface heterogeneity when barium sulfate particles are flowed through a capillary, two more types of inner surfaces capillary were used, rough and pre-scaled surfaces.

The deposition study of barium sulfate particles in rough surface was conducted and results are shown in Figure 4.15 and 4.16. Nevertheless, results for 100 ppm and 5 mM of both  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions are the same as compared with smooth surface. Figure 4.15 and 4.16 show that there is no deposition of barium sulfate in a capillary. In order to confirm the results, higher salt concentration was used. 40 mM of each salt solution were mixed at 200 rpm for 13 hours and the solution was flowed through a capillary. Results, as shown in Figure



**Figure 4.15** Flowing precipitated barium sulfate solution through a rough surface capillary at different concentrations.



**Figure 4.16** Comparison of barium sulfate particles deposition in rough surface capillary at different concentrations.

4.15 and 4.16, show that although the concentration of both solutions increase to 40 mM, there is no deposition occurring in the capillary. One possible reason might be because of the corrosion in a capillary is not enough to create a deep pit on the inner surface for trapping barium sulfate particles. Due to the volume of hydrochloric acid in a capillary is  $0.0681 \text{ cm}^3$ , calculated from a volume inside the capillary, and the acid is stagnant, despite there is a corrosion occurs in the capillary but it might not enough for creating a deep pit on the inner surface of the capillary. Moreover, corrosion rate decreases with time owing to the formation of corrosion products thin film such as ferrous chloride ( $\text{FeCl}_2$ ) on the surface. This film will act as protective coating and reduce the corrosion rate significantly (Corrosion Engineering: Principles and Practice). During the corrosion experiments, a thin film of corrosion products was observed as a black layer coated on the surface. These results indicate that after the growth of barium sulfate has finished, not only the amount of barium sulfate particles, particle size and particle shape but also surface heterogeneity of the capillary may not affect to the deposition.

The next inner surface of a capillary which was used is pre-scaled surface. Initially,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions were flowed through a capillary in order to create a barium sulfate layer inside the capillary. In order to confirm that barium sulfate layer was formed, after the pressure drop reached 2 psi, both solutions were replaced with DI water and the experiment was finished when the pressure drop was constant. Figure 4.17 shows comparison between the deposition of 1 mM solutions which were flowed through a capillary (normal run) and the experiments which were stopped when the pressure drop reached 2 psi. In addition, as can be seen from the normal run, after the pressure drop is higher than 2 psi, it will drastically increase. Thus, the experiment was finished when the pressure drop reached 2 psi. Precipitated barium sulfate solution was prepared by mixing 1 mM of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions at 200 rpm for 13 hours. Then, the solution was flowed through a pre-scaled capillary. Figure 4.18 shows an increasing of pressure drop as a function of time which means there is barium sulfate particles continuously deposit in the pre-scaled capillary. However, the deposition of barium sulfate particles is quite slow as



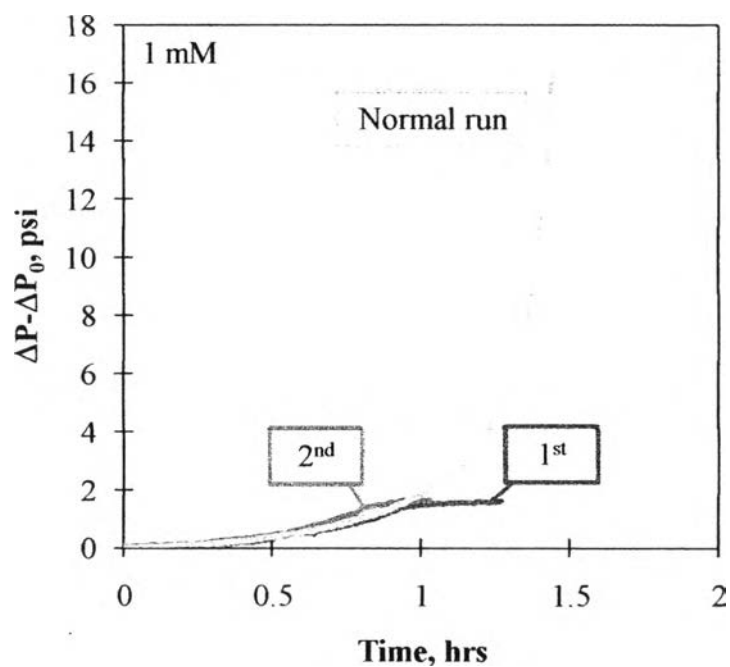


Figure 4.17 Creating a pre-scaled surface for 1 mM salt concentration.

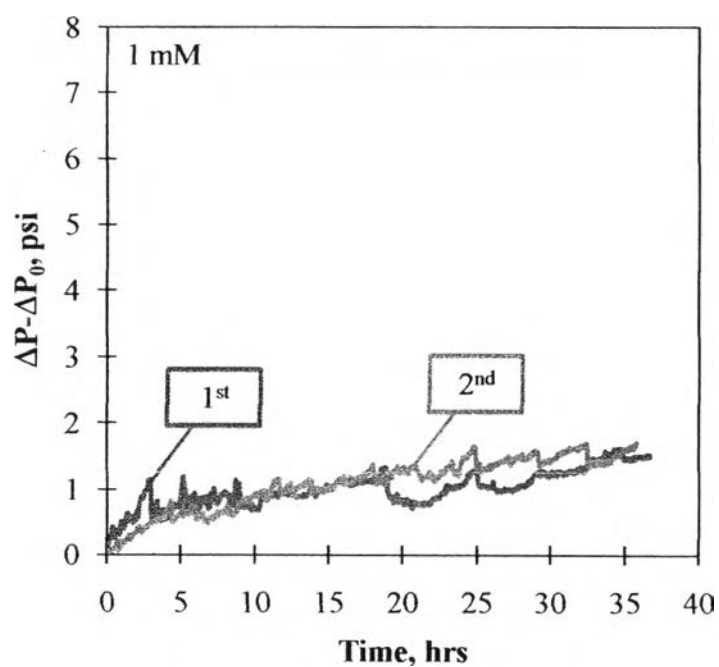
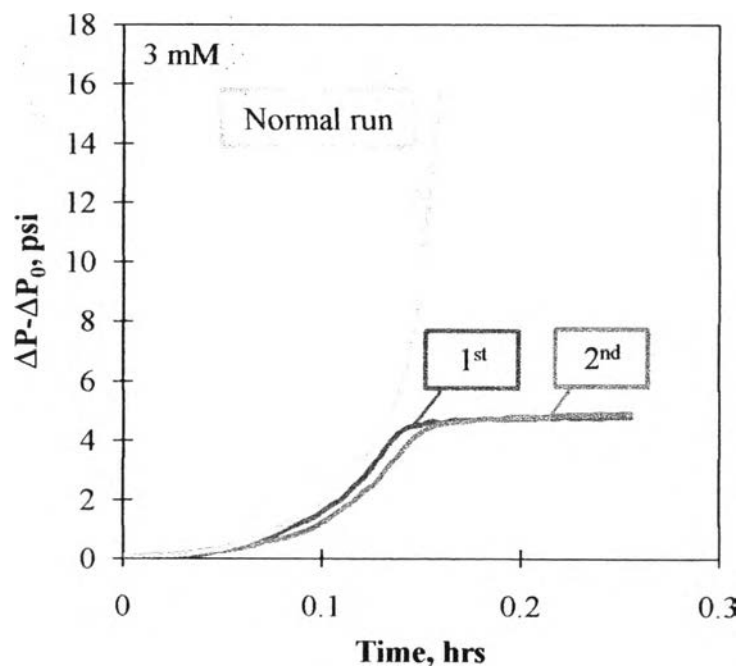


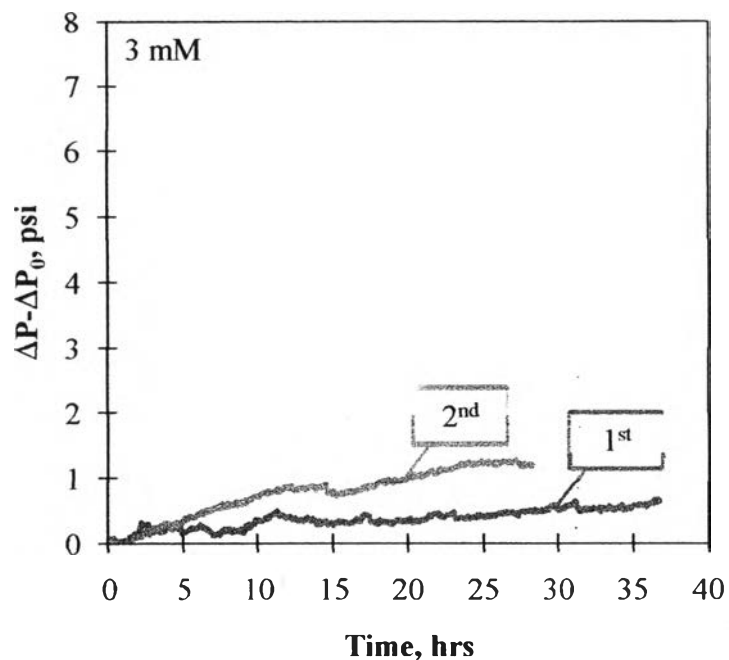
Figure 4.18 The deposition of barium sulfate particles in the pre-scaled capillary at 1 mM of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions.

compared with the deposition of barium sulfate whose growth has not completed yet. As can be seen from Figure 4.17 for the normal run of 1 mM both solutions, pressure drop shot within about 1.5 hours but Figure 4.18 shows that at 35 hours, pressure drop was gradually increasing. The experiment was repeated for the second time, 2<sup>nd</sup>, and results indicate that this experiment can be reproduced.

Barium sulfate particles deposition experiment in a pre-scaled capillary was also conducted at higher salt concentration, 3 mM. Results are shown in Figure 4.19 and 4.20. For creating a pre-scaled capillary, the same experiment was conducted for 3 mM of both salt solutions. Although the solution flasks were replaced by DI water flasks when pressures drop reached 2 psi, the pressure drop was increasing until about 5 psi. At high concentration, 3 mM, supersaturation ratio which is a driving force for the deposition is higher as compared with the low concentration, 1 mM. Thus, even both solutions were replaced at 2 psi but the residual supersaturation ratio can cause an increasing in pressure drop (Boodhoo *et al.*, 2007). After the pre-scaled layer was created, 3 mM of precipitated barium



**Figure 4.19** Creating a pre-scaled surface for 3 mM salt concentration.



**Figure 4.20** The deposition of barium sulfate particles in the pre-scaled capillary at 3 mM of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  solutions.

sulfate solution was flowed through the pre-scaled capillary. Figure 4.20 shows that barium sulfate particles deposit in the pre-scaled capillary as seen with 1 mM salt solutions. Due to the pre-scaled surface inside the capillary, barium sulfate layer will act as preferential sites for subsequent barium sulfate particles to deposit on those sites (Ostvold *et al.*, 1993; Quddus *et al.*, 2000). Thus, it must be noticed that, for a 1 second residence time, precipitated barium sulfate particles will deposit on the barium sulfate layer but will not deposit on smooth and rough surfaces.