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# APPENDICES

## Nomenclature

| | |
|---|---|
| $a_i$ | activity of cation/anion |
| $C_{Ba^{2+}}$ | concentration of $Ba^{2+}$ |
| $C_{SO_4^{2-}}$ | concentration of $SO_4^{2-}$ |
| $\Delta P_0$ | constant pressure drop before the deposition is detected |
| $\rho_{BaSO_4}$ | density of $BaSO_4$ (4.5 g/mL) |
| $R_{new}$ | final radius/calculated radius of capillary |
| $R_0$ | initial radius of capillary |
| $R$ | ion ratio |
| $L$ | length of capillary |
| $\Delta P$ | pressure drop across the capillary |
| $r$ | radius of capillary |
| $K_{sp}$ | solubility product of barium sulfate |
| $S_a$ | supersaturation ratio |
| $m$ | uniform deposit mass |
| $\mu$ | viscosity |
| $Q$ | volumetric flow rate |

**Appendix A  Cleaning System**

As mentioned in section 5.2.1, barium sulfate formation is an instantaneous reaction. Thus, after $BaCl_2 \cdot 2H_2O$ and $Na_2SO_4$ solutions are mixed, barium sulfate can deposit at any part in the system. The main part which barium sulfate can easily deposit is the mixing tee. Figure A.1 shows the deposition of barium sulfate in the mixing tee. If there is barium sulfate deposit in the mixing tee, the deposited barium sulfate can affect to the mixing system of two solutions. Thus, after an experiment is finished, every part in the experimental system has to be cleaned.
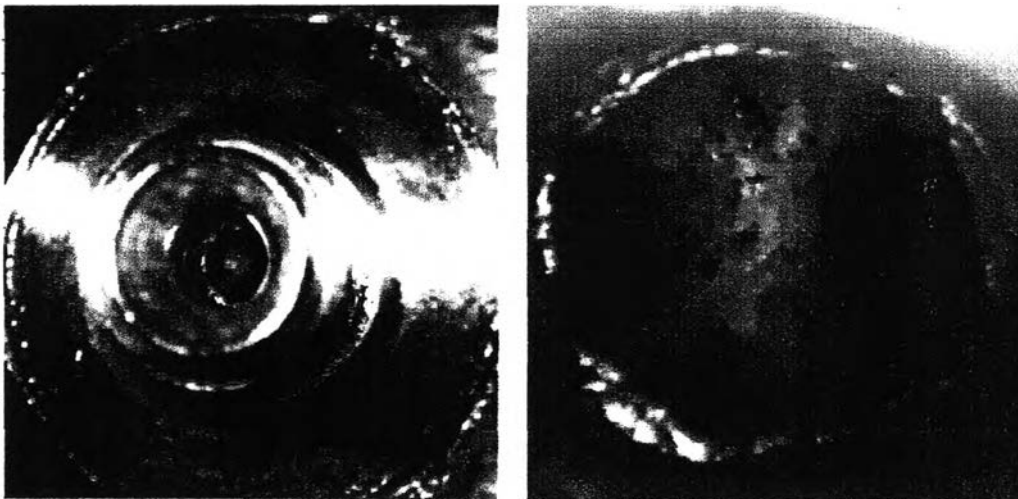


**Figure A.1** Barium sulfate deposition in the mixing tee.

## Appendix B Morphology and Particle Size of Barium Sulfate

According to barium sulfate formation is an instantaneous reaction and barium sulfate can be formed at after two solutions, $BaCl_2 \cdot 2H_2O$ and $Na_2SO_4$, are mixed. An experiment was conducted by mixing $BaCl_2 \cdot 2H_2O$ and $Na_2SO_4$ solutions at different concentration in a beaker. After 5 second, samples were taken and examined by microscope. Figure B.1 shows the morphology and particle size of barium sulfate after two solutions at different concentration were mixed for 5 second. Micrographs show that, after 5 second, all particles are in spherical shape. However, the particle size for 1 mM is smaller than 3 and 5 mM. From the micrographs, it can be seen that barium sulfate has not completed their growth yet. Thus, the micrographs can be used to confirm that when two solutions were flowed through the capillary, residence time is about 1 sec; barium sulfate is in the growth step.
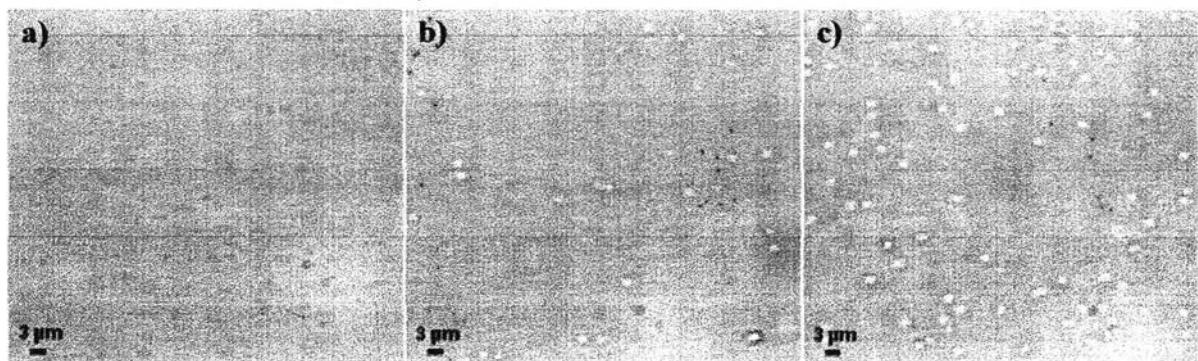


**Figure B.1** Micrographs showing the morphology and particle size of barium sulfate after $BaCl_2 \cdot 2H_2O$ and $Na_2SO_4$ solutions were mixed for 5 sec. a) 1 mM b) 3 mM and c) 5 mM.
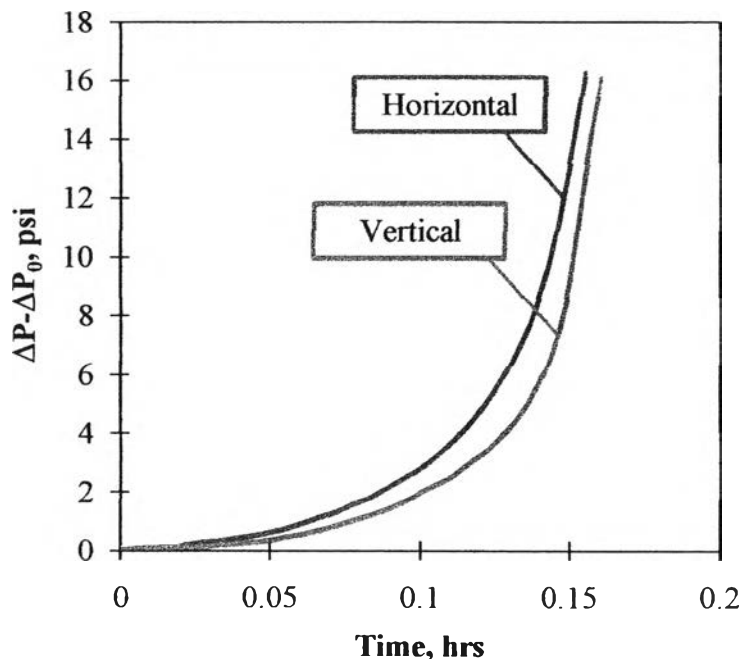
## Appendix C  Capillary Position

The position of a capillary is one of the major issues for investigation of the barium sulfate deposition. Initially, capillary was mounted in horizontal position. Precipitated barium sulfate solution was prepared by mixing 100 ppm of $BaCl_2 \cdot 2H_2O$ and $Na_2SO_4$ solutions at 200 rpm for 13 hours. Then, the precipitated solution was flowed through the capillary. Result, as shown in Figure C.1, shows that pressure drop increases as a function of time. However, when DI water was flowed through the capillary at about 13 hours, pressure drop fell down to almost the same as initial pressure drop. This indicates that most of barium sulfate particles were flowed out from the capillary. Moreover, in order to determine the final radius of the capillary, solution flasks have to be replaced with DI water flasks. When the tube was moved from one flask to another flask, there was an air bubble went to the tube and the air bubble could remove most of the settling particles inside the capillary and in the
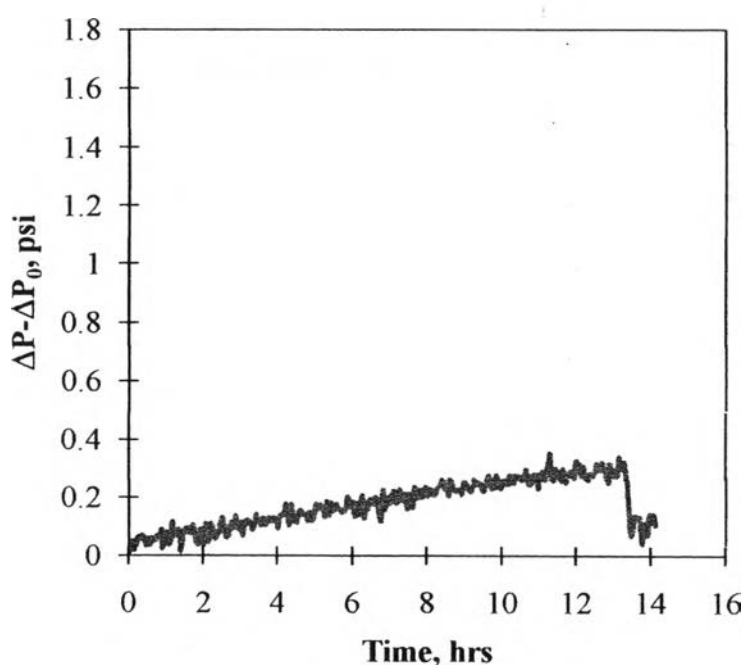


**Figure C.1** Pressure drop as a function of time when a capillary was mounted in horizontal position.

effluent tube out. This visual observation can be seen because the effluent tube is translucent and when there was an air pocket passed through the tube, it swept all particles out to the effluent flask. Thus, the capillary has to be mounted in vertical position in order to prevent the settling down of particles in the capillary.

Not only the position of a capillary was investigated for flowing precipitated barium sulfate solution through the capillary but it was also investigated when $BaCl_2 \cdot 2H_2O$ and $Na_2SO_4$ solutions were mixed in the mixing tee and flowed through the capillary as described in section 3.4.1. Figure C.2 shows that the deposition is almost the same either the capillary was mounted in horizontal or vertical position. Due to the residence time is about 1 second, barium sulfate particles, which are in growing step, are not big enough so that there is less effect of gravity on the particles. Hence, for flowing two solutions through the capillary, capillary can be mounted either in horizontal or vertical position.



**Figure C.2** The deposition of flowing two solutions, 3 mM, through horizontal and vertical capillary.

## Appendix D  Dissolution Technique

In order to quantify the deposited mass of barium sulfate inside a capillary, DTPA solution which is a chelating agent has been used. Although DTPA solution is an effective chelating agent to dissolve barium sulfate but residence time which is a time for DTPA to form a complex with barium is also important. Therefore, three methods were conducted in order to determine an appropriate method for dissolving barium sulfate from the capillary. For the first and second method, DTPA solution was flowed through the capillary at 1 and 2 mL/min, respectively. For the third method which is flow and soak, DTPA solution was flowed through the capillary at 2 mL/min after that it was allowed to stay in the capillary for 1 hour and this method was repeated until the accumulated mass of barium sulfate got constant. Total dissolution time and volume of DTPA solution, which was used to dissolve all barium sulfate from the capillary, were used to determine the dissolution technique. Table D.1 shows that the shortest total dissolution time is when DTPA solution was flowed at 2 mL/min. However, for flowing DTPA solution at 1 mL/min, the lowest volume of DTPA solution which was used is observed. According to the total dissolution time is a major concern for this work so that an appropriate method for dissolving barium sulfate from the capillary would be flowing DTPA solution at 2 mL/min.

**Table D.1** Comparison of the total dissolution time and volume of DTPA solution at different flow rate

|  | 1 mL/min | 2 mL/min | Flow and soak |
|---|---|---|---|
| Total dissolution time (hours) | 17 | 15 | > 23 |
| DTPA solution (L) | 1 | 1.5 | > 1.1 |

## Appendix E  Supersaturation Ratio and Ion Ratio

A change in salt concentration, $BaCl_2 \cdot 2H_2O$ and $Na_2SO_4$, leads to change in supersaturation ratio and ion ratio. In this work, the salt concentration was varied from 100 ppm to 40 mM. Thus, supersaturation ratio and ion ratio were calculated by using Eq. (3) and (4), respectively. Table E.1 shows the supersaturation ratio and ion ratio of salt solution at different concentration.

**Table E.1** Supersaturation ratio and ion ratio at different salt concentration

| $[Ba^{2+}] = [SO_4^{2-}]$ | 100 ppm | 1 mM | 3 mM | 5 mM | 40 mM |
|---|---|---|---|---|---|
| R | 0.59 | 1 | 1 | 1 | 1 |
| $S_a$ | 50 | 74 | 150 | 258 | 613 |

# CURRICULUM VITAE

**Name:**              Mr. Ratchapum Charoenthaipanich

**Date of Birth:**      May 14, 1987

**Nationality:**        Thai

**University Education:**

2005 – 2008  Bachelor Degree of Science (First Class Honors, Gold Medal) in Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand.

**Work Experience:**

2008              Position:   Project Based Internship Student

Company: Thaioil Public Company Limited, Thailand

**Proceedings:**

1. Charoenthaipanich, R., Fogler, H.S., and Malakul, P. (2011, April 26) Development of Capillary Flow Technique to Investigate the Mechanism of Barium Sulfate Deposition. Proceedings of The 2$^{nd}$ Research Symposium on Petroleum, Petrochemicals, and Advanced Material and The 17$^{th}$ PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.