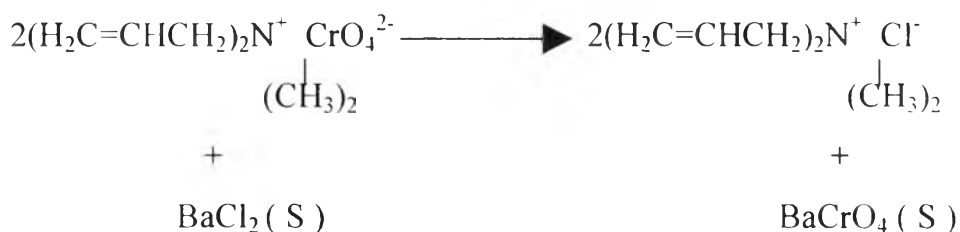# CHAPTER IV
RESULTS AND DISCUSSION

4.1 Equilibration Time

The equilibration time of chromate precipitation was determined by setting feed barium to chromate concentration ratio at 2 to 1 and concentration of QUAT at 0. 0.2, 0.3, and 0.4 M. The reaction of barium chromate in the presence of QUAT is shown below

$$2(H_2C=CHCH_2)_2N^+ \ CrO_4^{2-} \longrightarrow 2(H_2C=CHCH_2)_2N^+ \ Cl^-$$
$$(CH_3)_2 \qquad\qquad\qquad\qquad (CH_3)_2$$
$$+ \qquad\qquad\qquad\qquad\qquad +$$
$$BaCl_2\,(\,S\,) \qquad\qquad\qquad\qquad BaCrO_4\,(\,S\,)$$

Where (S) refers to solid, all other species being dissolved. The reaction was run with an excess of $BaCl_2$ to complete precipitation of residual chromate in the supernatant. The data are given in Appendix A and the results are shown in Figure 4.1. It was found that in the absence of QUAT, the average chromate concentration in the supernatant was 0.16 ppm. In the presence of 0.2. 0.3, or 0.4 M QUAT, the plot shows the decrease of chromate concentration when the time increases from 0 to 0.5 hours. and chromate concentration seems to reach the equilibrium after 0.5 hours. After equilibration. the average chromate concentration (after 0.5 hours) in the supernatant was 1.54, 1.54. and 1.64 ppm when the QUAT concentration was 0.2. 0.3. and 0.4 M. respectively.
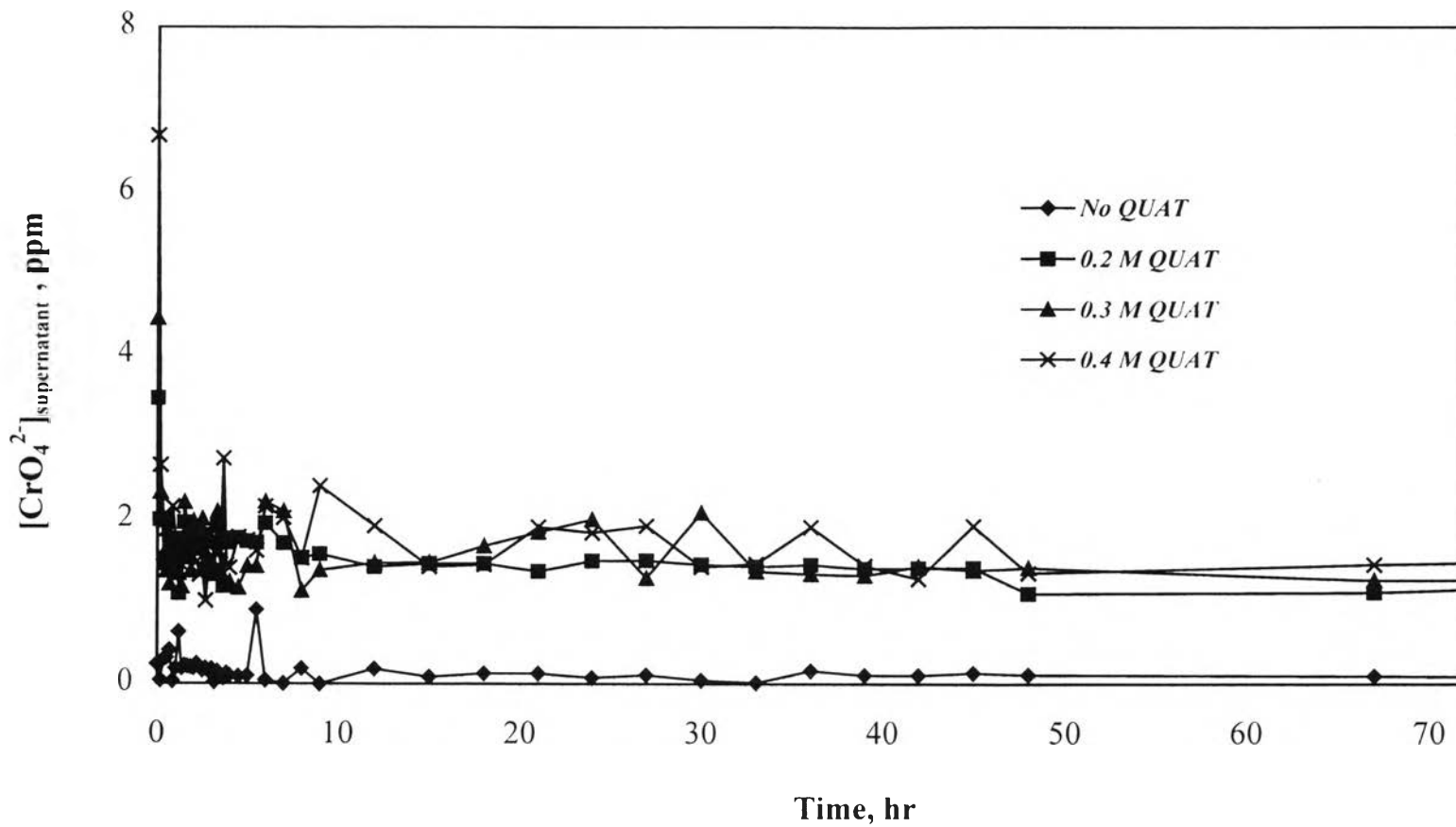
Figure 4.1   Supernatant concentration of barium chromate in Equilibration Experiments.

4.2 Semi-Batch Process

4.2.1 Effect of Flow Rate on Precipitation

Experimental data of the fraction of CrO_4^{2-} in the barium chromate particles. barium and QUAT concentrations at the outlet are shown in Appendix B.1A. These experiments were operated in the semi-batch mode at the highest outlet port (83 cm from bottom). Barium and chromate solutions were fed into a small reservoir which was connected to the crystallizer inlet to improve the efficiency of mixing before the feed solution reached the crystallizer. Flow rates were varied from 4 to 14 mL/min while holding the concentration of QUAT constant at 0. 0.2, 0.3 and 0.4 M. The amount of CrO_4^{2-} in the $BaCrO_4$ particles at the overflow solution was determined relative to the initial chromate concentration at the inlet. The plots of barium chromate particles as a function of flow rate are demonstrated in Figure 4.2. The results showed that in the absence of QUAT. as the flow rate increases from 4 to 14 mL/min, the fraction of CrO_4^{2-} in the barium chromate particles slightly increased from 0.51% to 3.53%. In the presence of QUAT. at all concentrations, there were about 20% - 40% CrO_4^{2-} in the barium chromate particles at the flow rates between 8 mL/min and 12 mL/min and more than 40 % CrO_4^{2-} in the barium chromate particles when the flow rate was 12 mL/min and beyond. At flow rate 10 mL/min and below, the difference of QUAT concentrations showed significantly different in the percent of CrO_4^{2-} in the barium chromate particles. however the percent difference decreases as the flow rate increased to 12 mL/min and 14 mL/min. The result shows that the dispersion of barium chromate particles at low flow rate and low QUAT concentration was high.

Figure 4.3 illustrates the chromate concentration in overflow. In the absence of QUAT, the average concentration of chromate over the entire range of flow rate was 0.44 ppm (or 0.02% of chromate in supernatant to
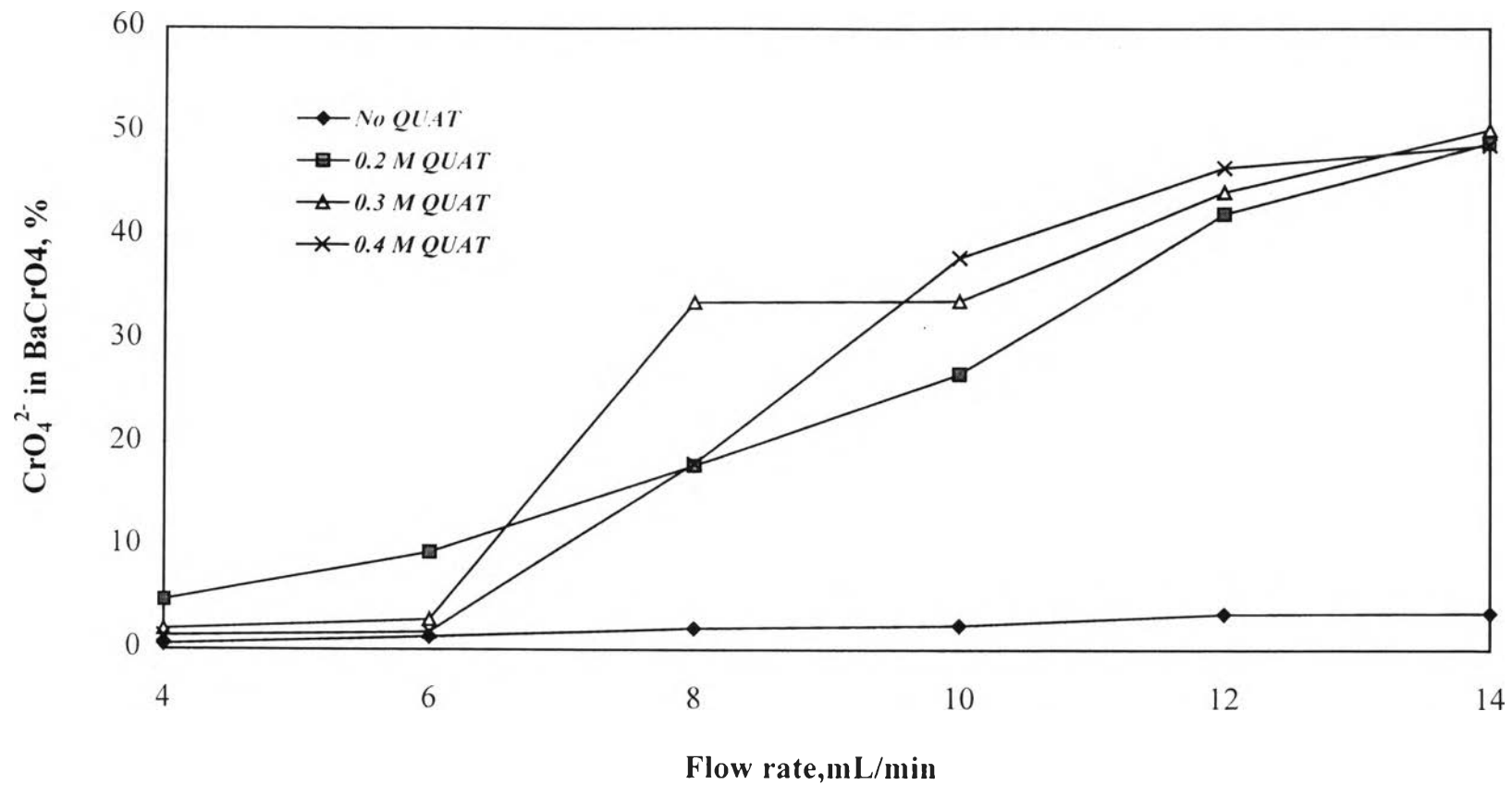
Figure 4.2 Ratio of chromate concentration in precipitate in overflow to chromate concentration in feed as a function of flow rate, crystallizer outlet 83 cm, semi-batch operation.
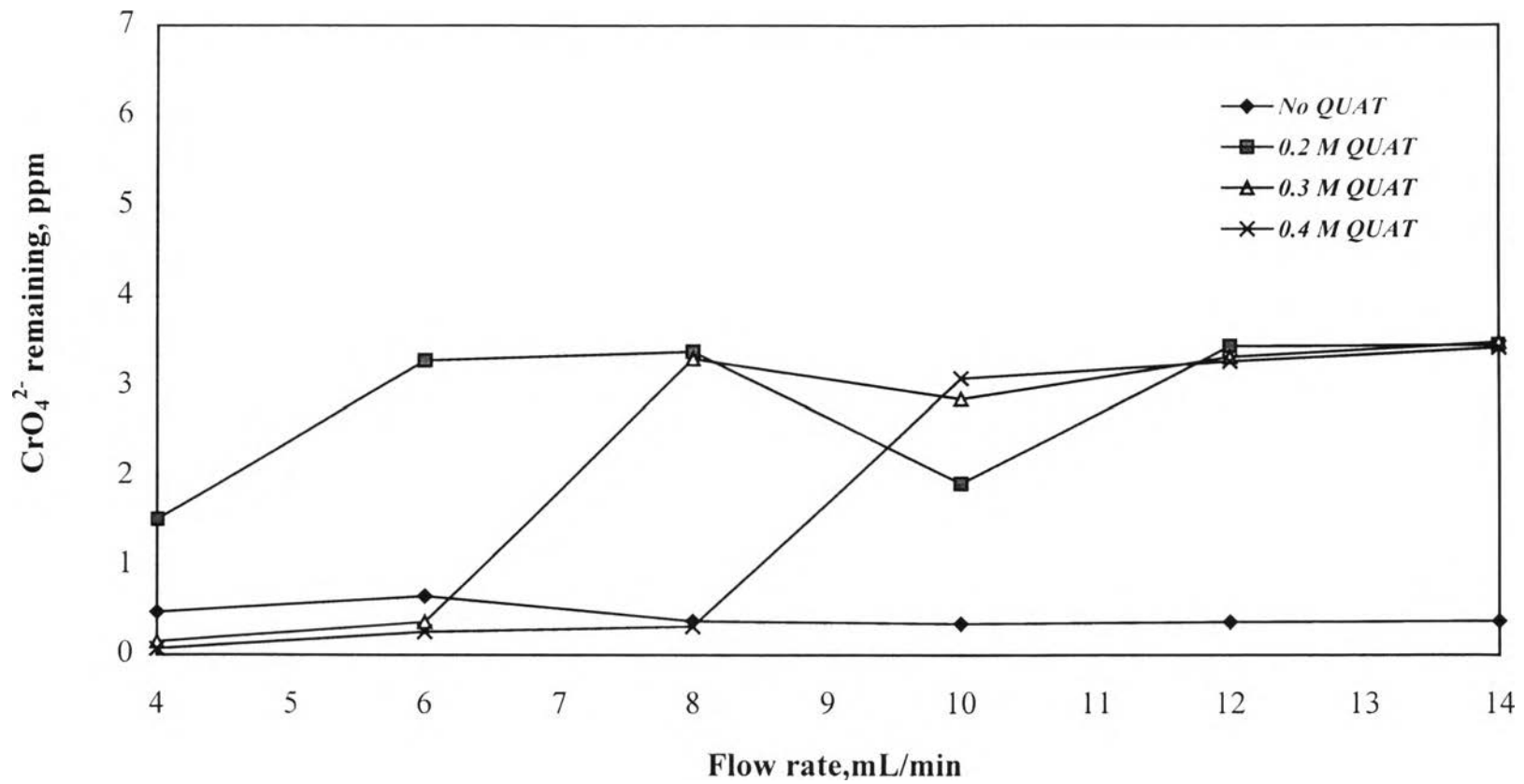
Figure 4.3   Chromate concentration in overflow as a function of flow rate, crystallizer outlet 83 cm, semi-batch operation.

chromate in feed) with less than 30% variation. In the presence of 0.2 M QUAT. the percent of chromate was 0.02% at flow rate 4 mL/min, and the average percent of chromate at 6 - 14 mL/min was 0.15% with less than 3% variation. In the presence of 0.3 M QUAT, at 6 mL/min and above, the percent of chromate was less than 0.02%, and the average percent of chromate was 0.14% with less than 2% variation. Finally in the presence of 0.4 M QUAT. at 8 mL/min and above, the fraction of chromate was less than 0.02%, and the average percent of chromate was 0.14% with the deviation less than 5 %. Therefore. the concentration of CrO_4^{2-} ions as a function of flowrate were dependent of the QUAT concentration in the feed solution.

The fraction of QUAT in the supernatant to QUAT in feed are shown in Figure 4.4. as a function of flow rate. The result showed higher dissolution of QUAT occurring with the feed solution containing 0.2 M QUAT than the solution containing 0.3 or 0.4 M QUAT at all flow rates. Therefore. the feed containing 0.2 M QUAT gave the highest percent of QUAT (43% at 14 mL/min) in the overflow solution. The QUAT dissolution in the overflow solution decreased as the QUAT concentration in the feed increased. However, percent of QUAT in the supernatant largely increased when the flow rate was 8 mL/min and beyond for all concentrations of QUAT in the feed solutions.

Viscosity of the solution increases as the QUAT concentration increases. When QUAT increased and the flow rate decreased, QUAT blocked the precipitate area of barium chromate. There was more time for QUAT to adsorb with barium chromate precipitate. As the result, there was minimum % QUAT in the supernatant solution from the feed containing 0.4 M QUAT and increase flow rate allowed dissolution of QUAT to increase.
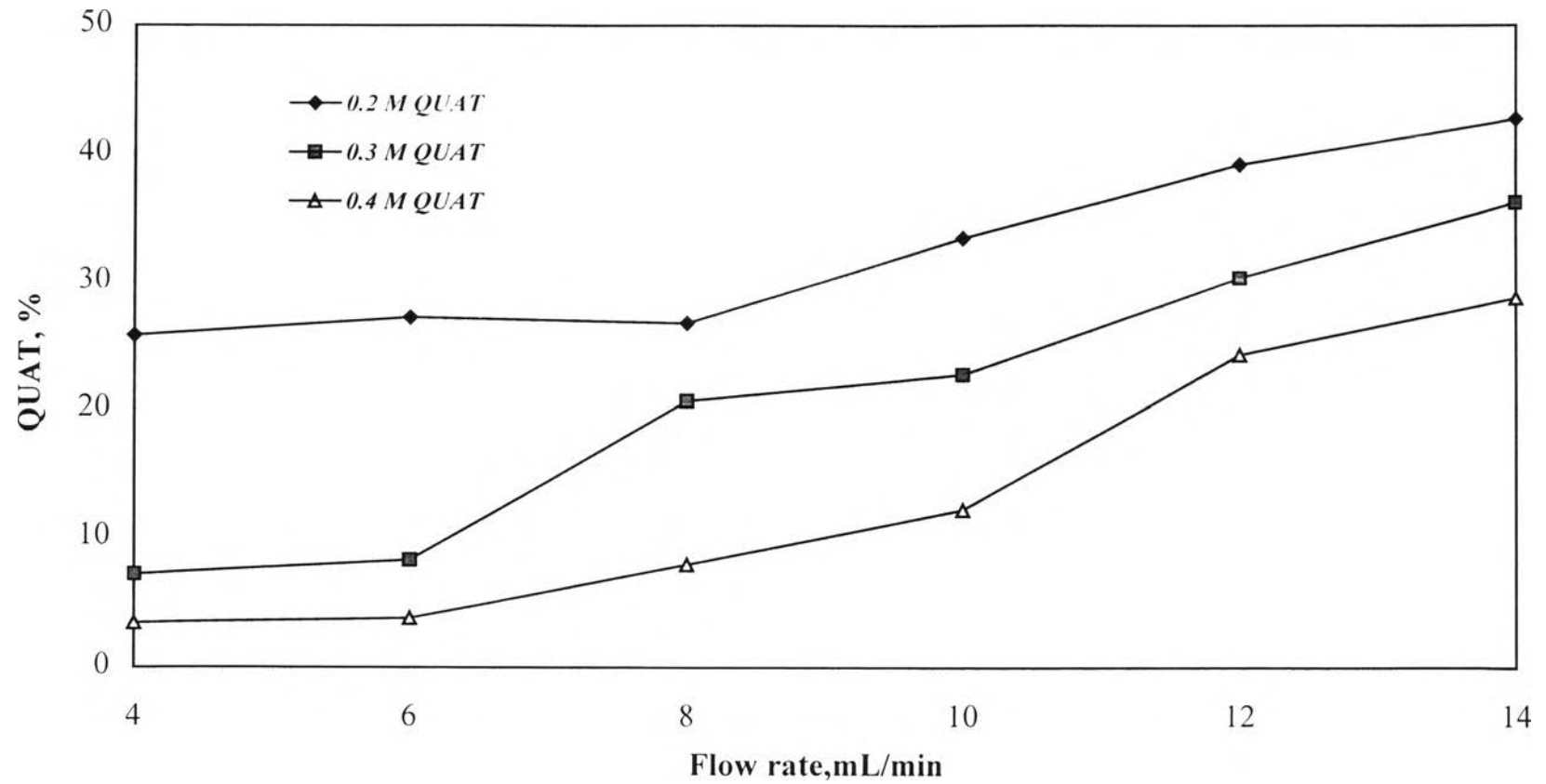
Figure 4.4   Ratio of QUAT concentration in supernatant to QUAT concentration in feed
as a function of flow rate,crystallizer outlet 83 cm,semi-batch operation.

4.2.2 Effect of Heights on Precipitation

Figure 4.5 - 4.8 show the effect of outlet height on the barium chromate precipitation at different flow rates (4 to 14 mL/min) and constant QUAT concentrations (0, 0.2. 0.3, and 0.4 M). At all conditions of QUAT, the percent of CrO_4^{2-} in the barium chromate particles slightly decreased as the crystallizer outlet height increased from 33 cm to 83 cm. Figure 4.5, in the absence of QUAT, the results of all flow rates show less than 6% CrO_4^{2-} in the barium chromate particles remaining in the overflow solution at the crystallizer outlet height of 33 cm.
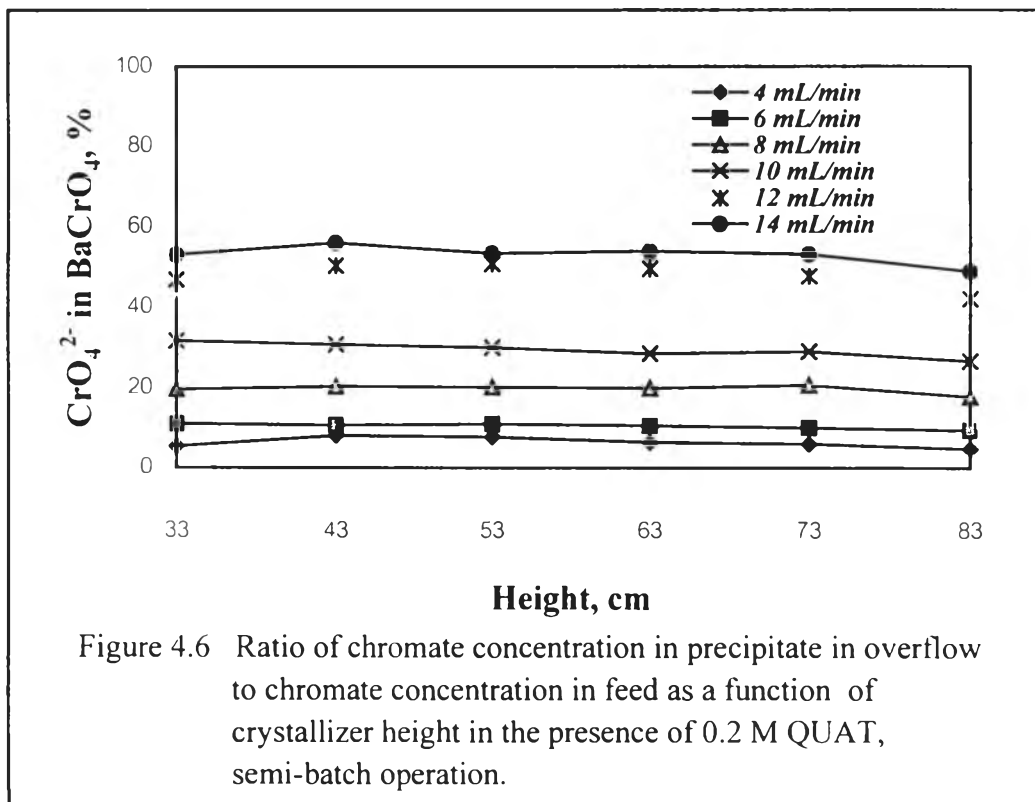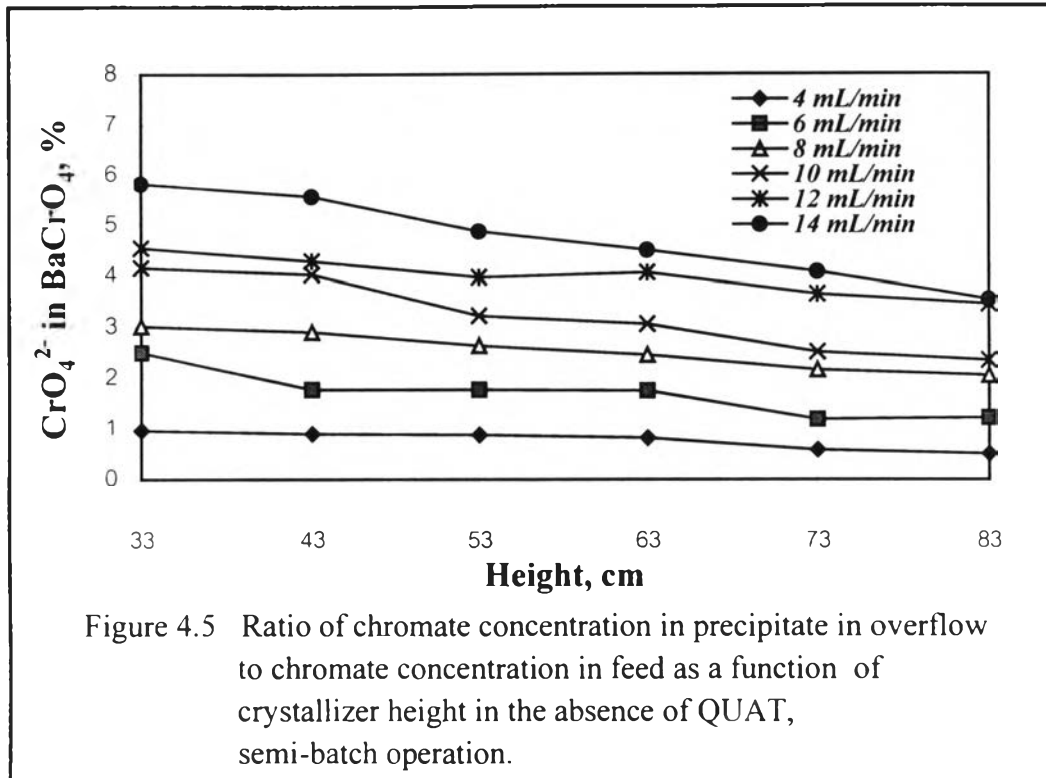
Figure 4.6, in the presence of 0.2 M QUAT, the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed varied little at all outlet heights and at each flow rate. Comparison of the percent of CrO_4^{2-} in the barium chromate particles at higher flow rate ($\geq$ 8 mL/min) with the lower flow rate (< 8 mL/min) showed that the former contained much higher percent of CrO_4^{2-} in the barium chromate particles in the overflow solution than the latter. Similarly, the results of the solution containing 0.3 M QUAT (Figure 4.7) and 0.4 M QUAT (Figure 4.8) showed higher % CrO_4^{2-} in the $BaCrO_4$ particles at higher flowrate (> 8 mL/min) than at lower flow rate.
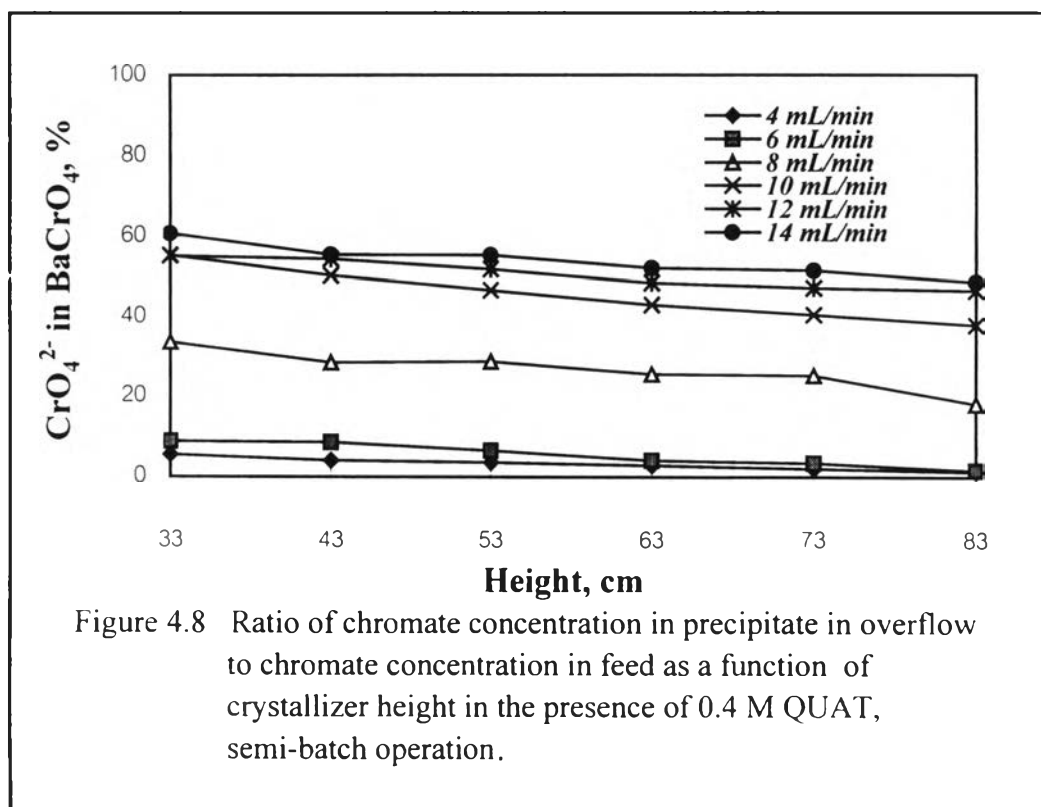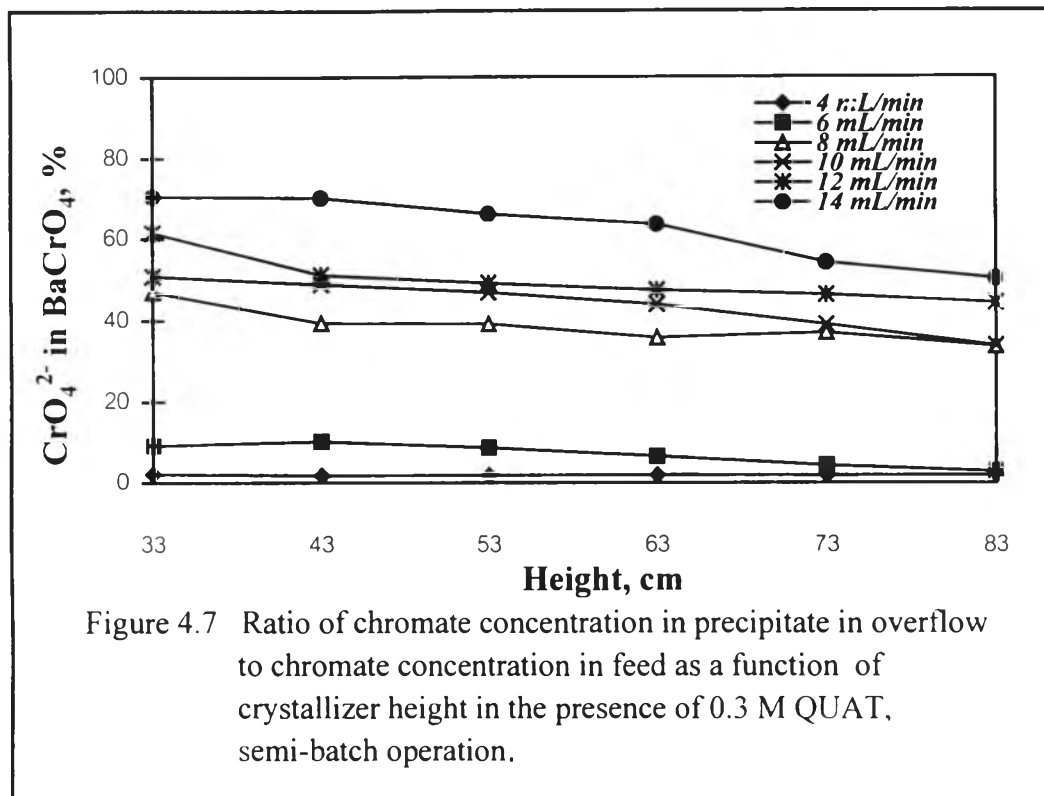
At all concentrations of QUAT, increasing outlet height for the overflow solution leaving the crystallizer resulted in a decrease in the percent of barium chromate particles. In addition, the presence of QUAT has strong effect on the decrease percent of barium chromate particles.

4.2.3 Effect of Concentration Ratio on Precipitation

Precipitation of chromate ions in the presence of different QUAT concentrations was done by varying concentration ratio of barium to chromate from 1.0 to 2.5. The data are shown in Appendix B.3 and the results are shown in Figure 4.9. At the ratio equals to 1, the result showed that chromate concentrations were 2.38 ppm (or 0.10%), 4.78 ppm, 11.08 ppm, and 12.27

Figure 4.5   Ratio of chromate concentration in precipitate in overflow
to chromate concentration in feed as a function of
crystallizer height in the absence of QUAT,
semi-batch operation.

Figure 4.6   Ratio of chromate concentration in precipitate in overflow
to chromate concentration in feed as a function of
crystallizer height in the presence of 0.2 M QUAT,
semi-batch operation.

Figure 4.7   Ratio of chromate concentration in precipitate in overflow
to chromate concentration in feed as a function of
crystallizer height in the presence of 0.3 M QUAT,
semi-batch operation.

Figure 4.8   Ratio of chromate concentration in precipitate in overflow
to chromate concentration in feed as a function of
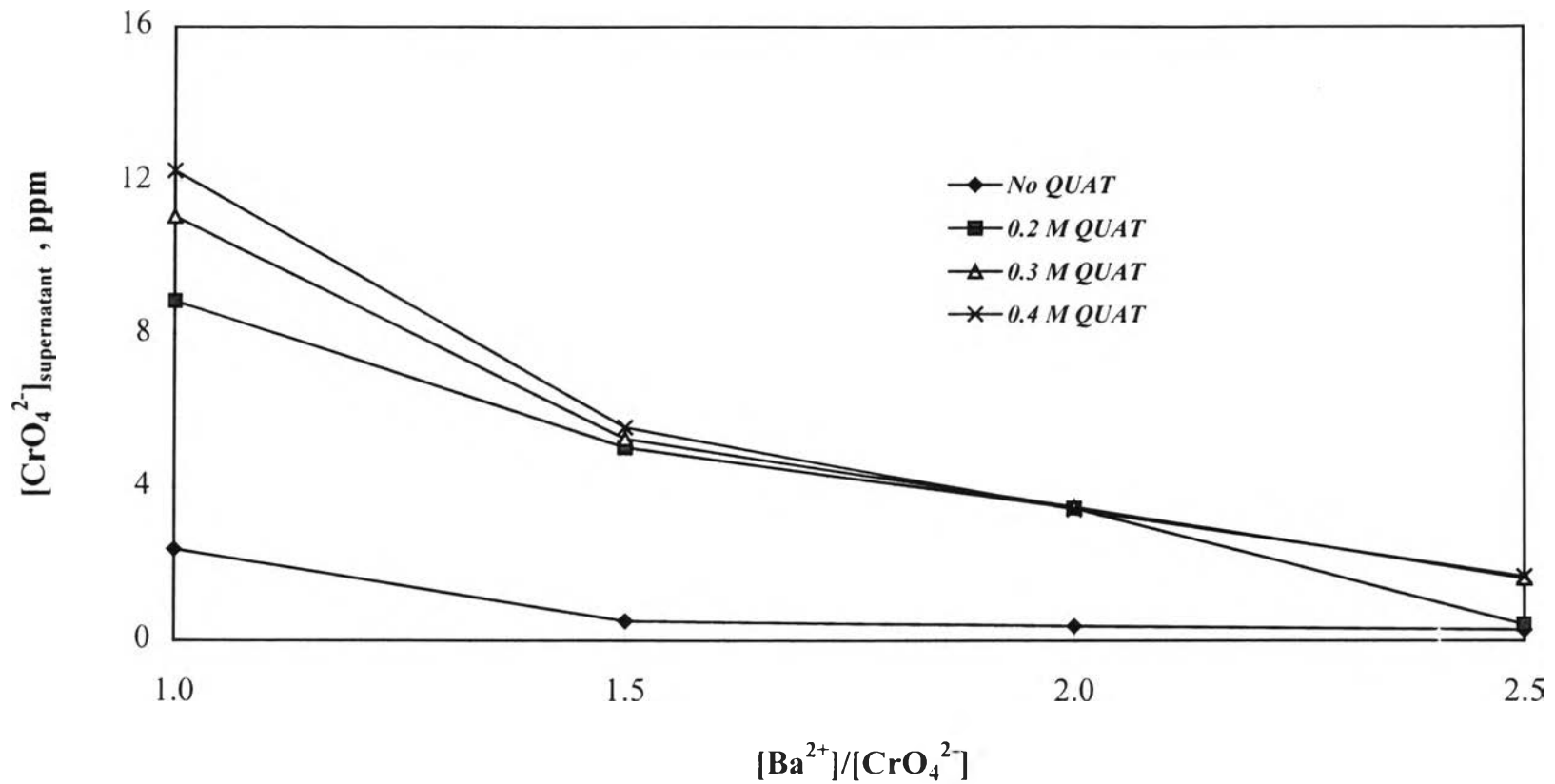crystallizer height in the presence of 0.4 M QUAT,
semi-batch operation.

Figure 4.9   Chromate concentration in supernatant as a function of concentration ratio
of barium to chromate on BaCrO4 precipitation, semi-batch operation.

ppm(0.53%) when the QUAT concentrations were at 0, 0.2, 0.3, and 0.4 M, respectively. Further increase the ratios to 2.0 and 2.5 of the solutions containing 0.4 M QUAT, the chromate remaining in the solution were 3.45 ppm (or 0.15%) and 1.67 ppm (or 0.07%), respectively.

4.3 Continuous Process

4.3.1 Effect of Flow Rate on Precipitation

Flow rates were varied from 4 to 14 mL/min while holding concentration of QUAT constant at 0, 0.2, 0.3 and 0.4 M and the crystallizer outlet 83 cm. The fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed at the outlet was determined relative to the initial chromate concentration.

The experimental data, the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed, barium and QUAT concentration at the outlet are shown in Appendix C.1A. The plots of the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed as a function of flow rate are shown in Figure 4.10. The results showed that in the absence of QUAT and the flow rate increasing from 4 to 14 mL/min, the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed slightly increased from 0.66% to 2.23%. In the presence of QUAT, and 4 - 6 mL/min flow rate, the 0.2 M QUAT solution showed the highest fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed and 0.4 M gave the lowest increase. It was noted for the 0.2 M QUAT solution that the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed largely increased when flow rate was greater than 4 mL/min, but very slightly increased when flow rate was greater than 12 mL/min. In the presence of 0.3 M QUAT, the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed increased largely when the flow rate was greater than 6 mL/min and slightly changed after 10 mL/min. In the presence of 0.4 M QUAT, large change of the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed began at
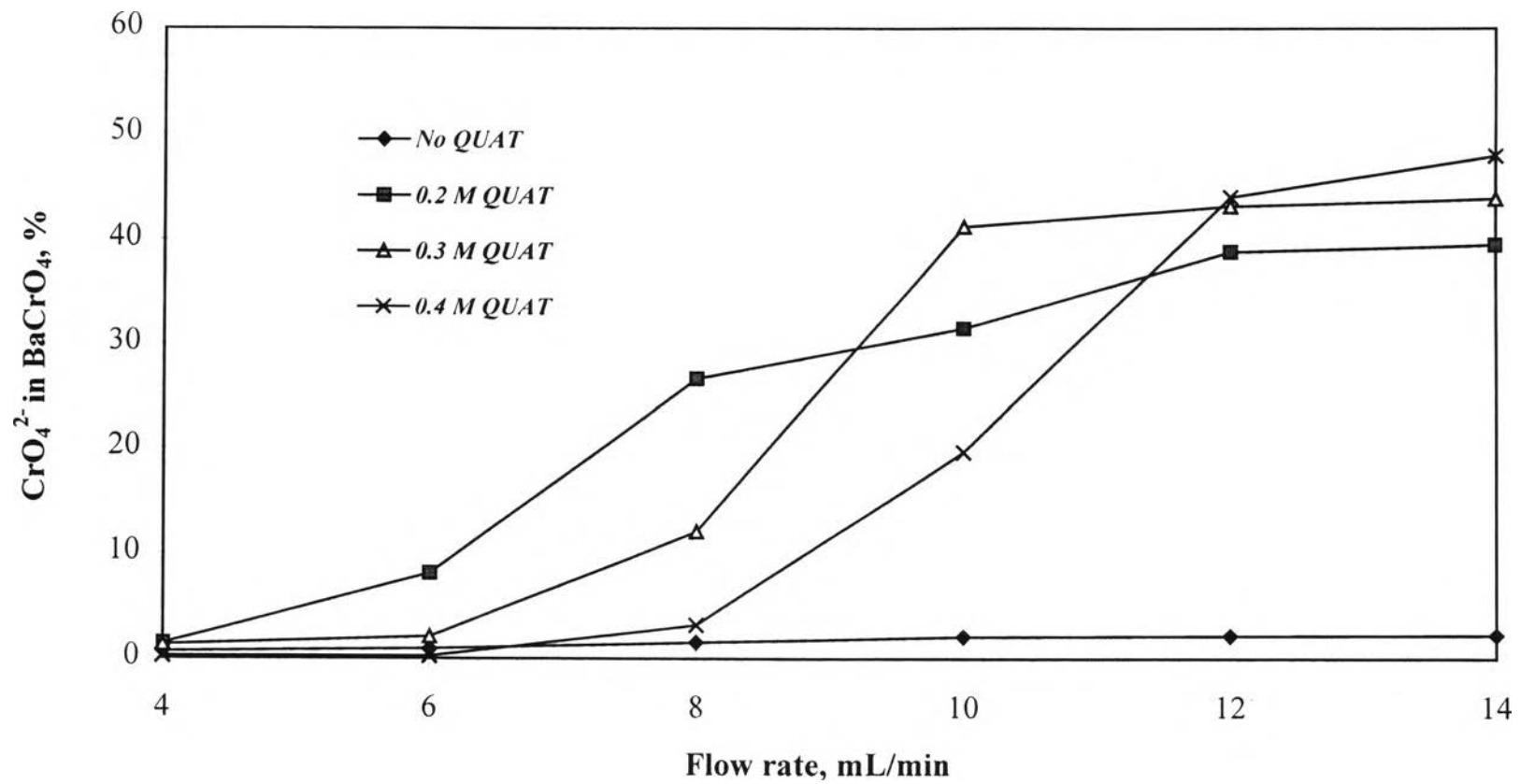
Figure 4.10 Ratio of chromate concentration in precipitate in overflow to chromate concentration in feed as a function of flow rate, crystallizer outlet 83 cm, continuous operation.

8 mL/min to 12 mL/min and slightly increased beyond 12 mL/min. Comparison of three QUAT concentrations below 12 mL/min flow rate , the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed were significantly different, while at 12 mL/min and above, the percents of barium chromate particle were less different.

Figure 4.11 illustrates the chromate ions in the overflow solution. In the absence of QUAT, average chromate concentration remaining was 0.31 ppm (0.01%) with less than 30% deviation over the entire range of flow rate. Similarly. in the presence of 0.2 M and 0.3 M QUAT and 4 - 14 mL/min flow rate, the average chromate concentrations remaining were 0.44 ppm (0.02 %) and 0.30 ppm (0.01%), respectively, and the variation was less than 30% for both cases. Similar result was also obtained for the 0.4 M QUAT condition, and its average chromate concentration was 0.29 ppm (0.01%). Therefore, the change of CrO_4^{2-} ion was independent of flow rate and the QUAT concentration when the barium to chromate ratio was 2.

The concentration of QUAT remaining in the supernatant as a function of flow rate is shown in Figure 4.12. When the system contained 0.2 M QUAT, the result showed that the QUAT concentration was 23.09 % at 4 mL/min flow rate, gradually increased to 32.23% at 6 mL/min. 36.96% at 8 mL/min and 39% at 10 mL/min and higher flow rate. At 0.3 M QUAT, the result showed that the fraction of QUAT in supernatant to QUAT in feed (12%) remained unchange at 4 to 6 mL/min flow rate, largely changed from 12% at 6 mL/min to 35% at 10 mL/min, and remained unchange beyond 10 mL/min. Similar changes were also observed for the 0.4 M QUAT solution, but the percent of QUAT was less than for the 0.3 M solution and the change was rather constant at 12 mL/min and higher flow rate. The conclusion of the result as shown in Figure 4.12 indicates that the percent of QUAT at the crystallizer outlet decreases as the QUAT concentration in the feed increases, and higher flow rate gives higher percent QUAT leaving the crystallizer outlet.
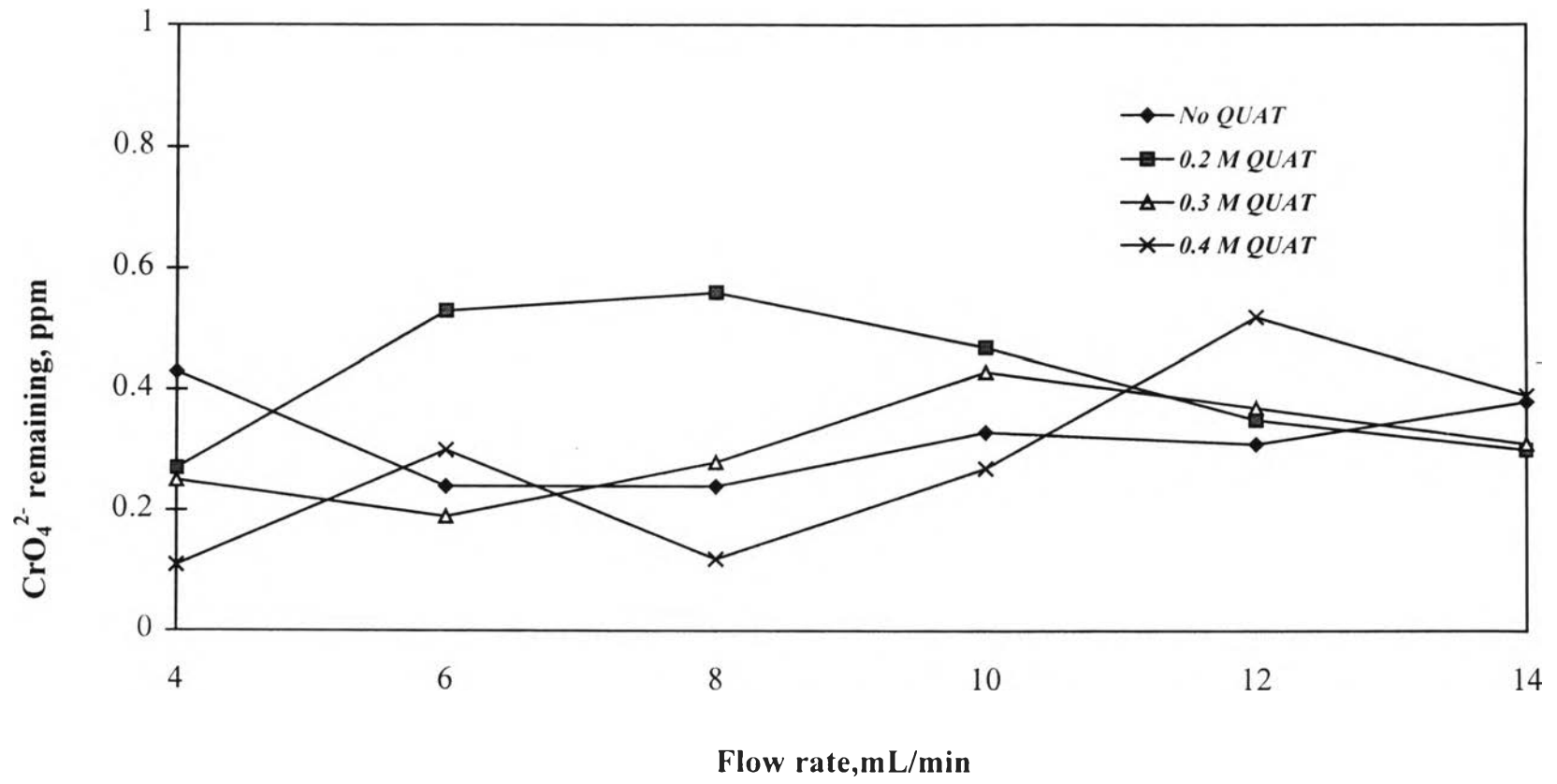
Figure 4.11   Chromate concentration in overflowas a function of flow rate, crystallizer
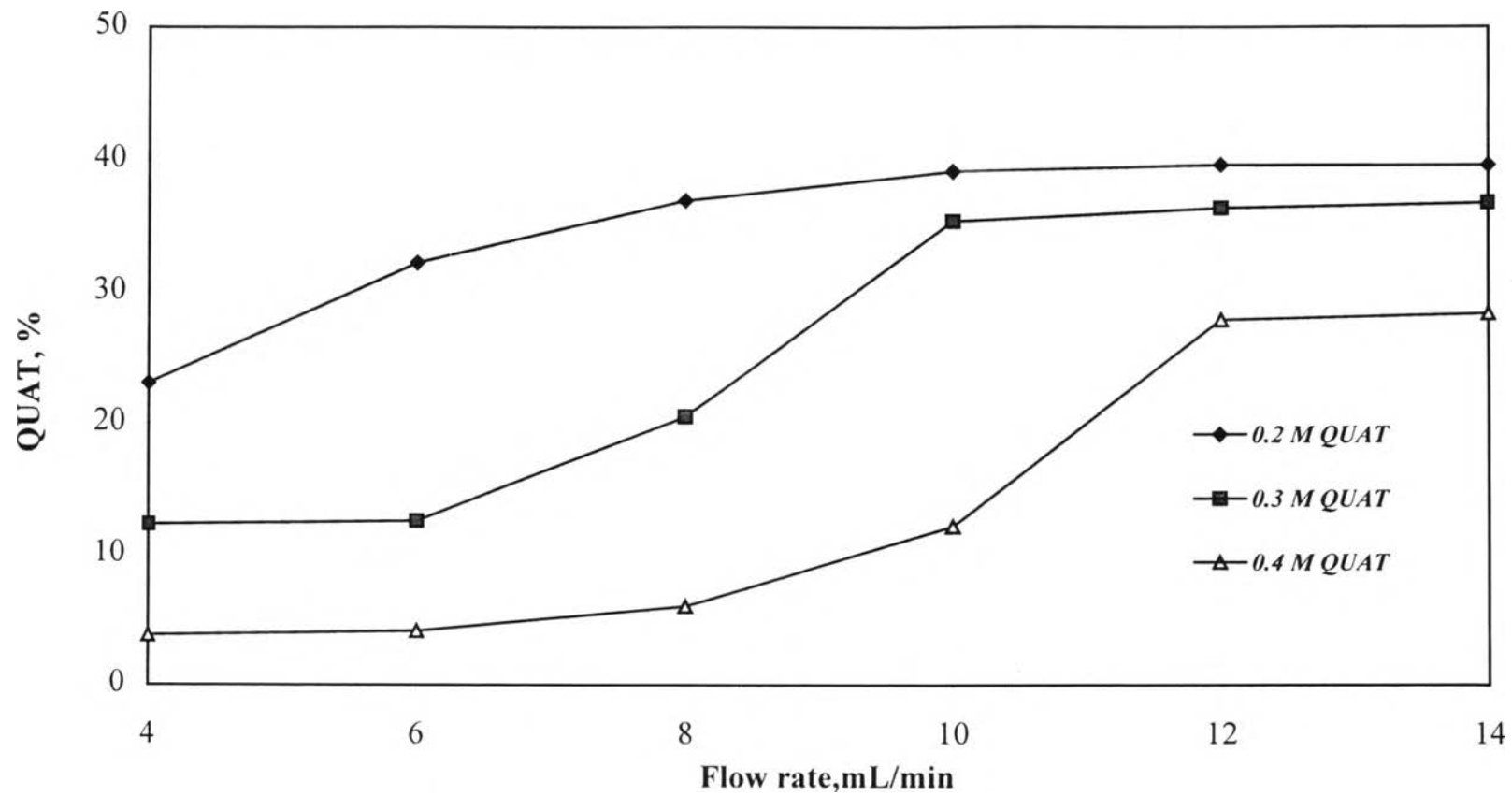outlet 83 cm, continuous operation.

Figure 4.12   Ratio of QUAT concentration in supernatant to QUAT concentration in feed
as a function of flow rate,crystallizer outlet 83 cm, continuous operation.
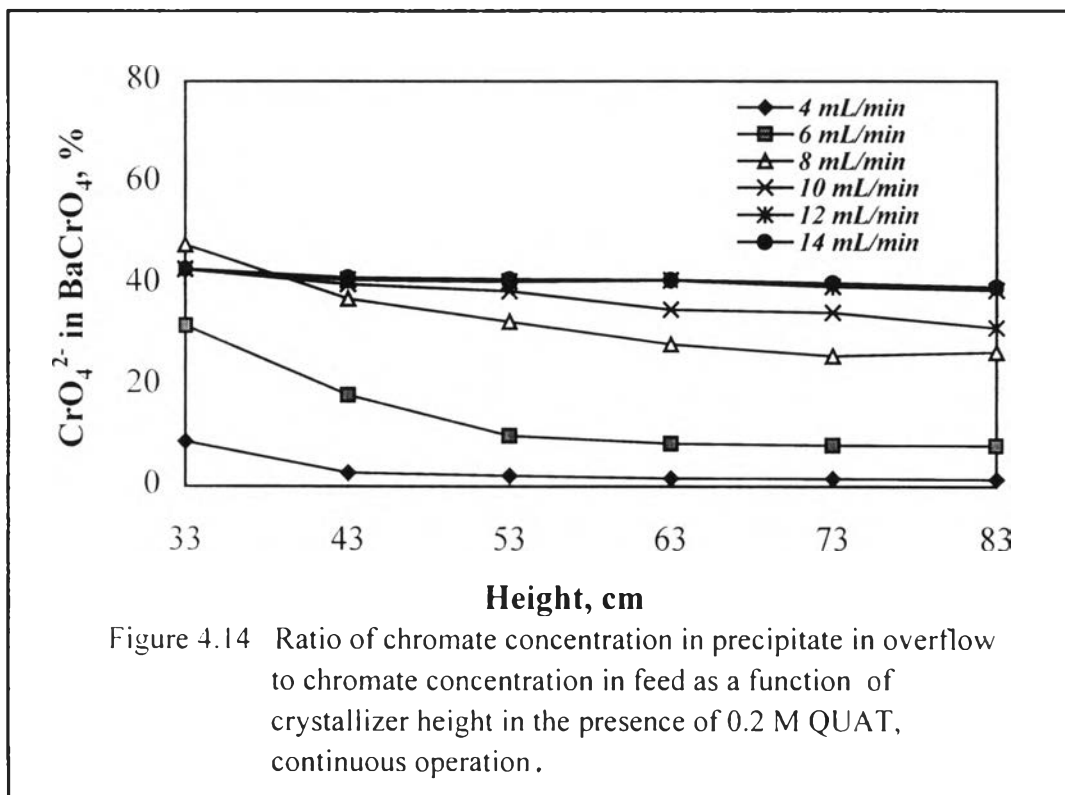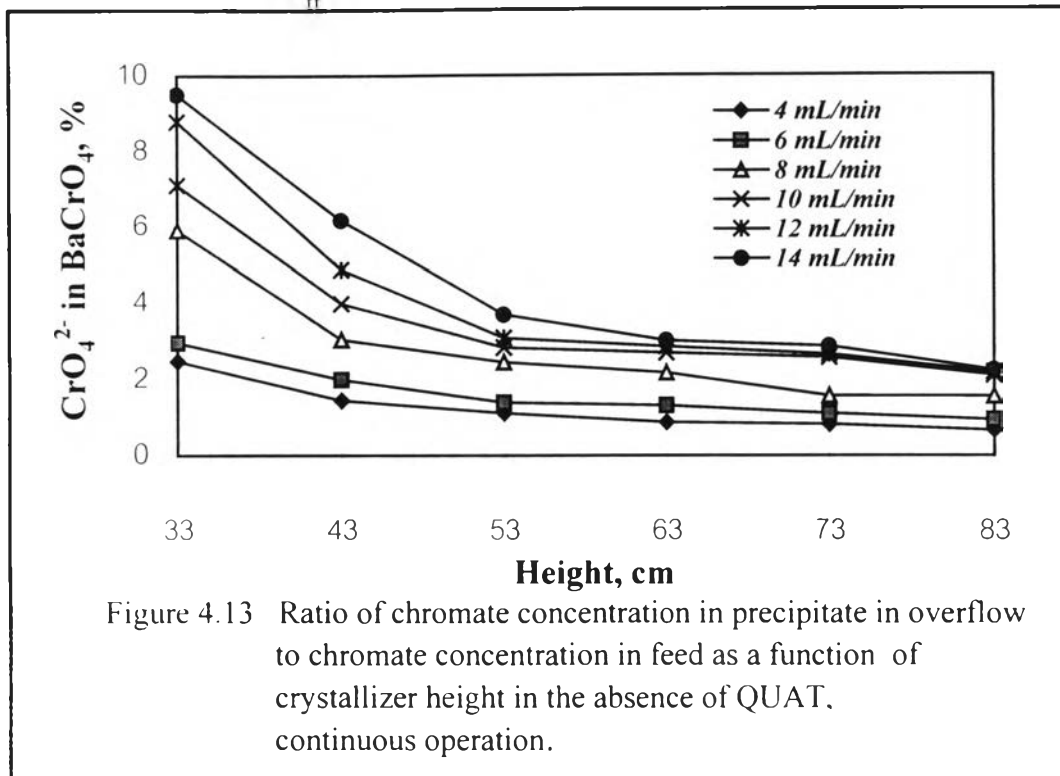
QUAT increases viscosity of the solution and decreases the movement of ions so QUAT has more time to adsorb on barium chromate particles and settles together with barium chromate precipitate. The QUAT 's behavior was very obvious at low flow rate, as the QUAT concentration increased. the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed decreased. and the percent of QUAT decreased. Increase flow rate reduced time for QUAT to adsorb on barium chromate particle and resulted in increase of barium chromate particle and the QUAT concentration leaving the crystallizer.

4.3.2 Effect of Heights on Precipitation

When the flow rates were fixed at 4, 6, 8, 10, 12, and 14 mL/min, and QUAT concentrations at 0, 0.2, 0.3, and 0.4 M, the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed remaining in the overflow solution were determined at different crystallizer outlets. The results showed in Figures 4.13 to 4.16. demonstrate the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed as a function of the crystallizer outlet height. Figure 4.13, in the absence of QUAT, the results of all flow rates show less than 10% of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed remaining in the overflow solution at outlet 33 cm, and as the outlet height increased the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed further decreased. At 83 cm crystallizer outlet, the 4 and 14 mL/min flow rates showed 0.66% and 2.23% chromate particles, respectively. In addition, all flow rates showed that the percent of chromate particles remained unchange at 53 cm and higher crystallizer outlet.

Figure 4.14, in the presence of 0.2 M QUAT, the results show large decrease of the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed at the flow rate of 8 mL/min and lower, and small decrease above 8 mL/min at crystallizer outlet 53 cm and lower. Above 53 cm, the results were slightly changed. Comparison of the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed above 53 cm, at higher flow rate (> 8 mL/min) with lower flow rate

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Figure 4.13 Ratio of chromate concentration in precipitate in overflow to chromate concentration in feed as a function of crystallizer height in the absence of QUAT, continuous operation.

Figure 4.14 Ratio of chromate concentration in precipitate in overflow to chromate concentration in feed as a function of crystallizer height in the presence of 0.2 M QUAT, continuous operation.

(< 8 mL/min) showed that the former contained much higher fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed in the overflow solution than the latter. For example. at 63 cm and the flow rate less than 8 mL/min, % CrO_4^{2-} were 1.59% (at 4 mL/min), and 8.50% (at 6 mL/min), and at flow rate higher than 8 mL/min, the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed were 35.02% (at 10 mL/min), 40.80% (at 12 mL/min), and 40.48%(at 14 mL/min). respectively.

Figure 4.15, in the presence of 0.3 M QUAT, the results of the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed are similar to those in the presence of 0.2 M QUAT (Figure 4.14). At outlet 53 cm and below, the results showed large decrease of the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed below 8 mL/min and small decrease for the flow rate above 8 mL/min, and at outlet above 53 cm. the fraction of chromate was rather constant for all flow rates. Comparison of chromate particles at the higher flow rate (> 8 mL/min) with lower (< 8 mL/min) flow rate above 53 cm outlet indicated that the former contained much higher fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed than the latter. For example, at outlet 63 cm, the flow rates less than 8 mL/min showed the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed 1.08% (at 4 mL/min), 2.60% (at 6 mL/min). and the flow rate higher than 8 mL/min showed the percent of barium chromate 43.16% (at 10 mL/min), 42.50% (at 12 mL/min), and 44.41% (at 14 mL/min).

In the presence of 0.4 M QUAT (Figure 4.16), at all flow rates, as the outlet height increases, the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed decrease slightly. However. above 53 cm crystallizer outlet. the fraction of chromate particles remained unchange at all flow rates. Comparison of chromate particles at the higher flow rates (> 8 mL/min) with the lower flow rates (< 8 mL/min) showed the former having much higher fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed than the latter. It was noted for outlet above 53

Figure 4.15   Ratio of chromate concentration in precipitate in overflow
to chromate concentration in feed as a function of
crystallizer height in the presence of 0.3 M QUAT,
continuous operation.

Figure 4.16   Ratio of chromate concentration in precipitate in overflow
to chromate concentration in feed as a function of
crystallizer height in the presence of 0.4 M QUAT,
continuous operation.

cm that the 10 mL/min flow rate was intermediate that gave the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed between low and high flow rate.

At all concentrations of QUAT, increase outlet height for the overflow solution leaving the crystallizer decreased the fraction of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed. and further increase in outlet height beyond 63 cm had no effect on decreasing barium chromate particle. The outlet at 63 cm should be minimum height for all flow rates and all concentrations of QUAT.

4.3.3 Effect of Concentration Ratio on Precipitation

Figure 4.17 shows the concentration of chromate ions remaining in the supernatant solution as the ratio of barium to chromate is varied. At the stoichiometric ratio of barium to chromate (1 : 1), the result showed that the chromate concentrations in the equilibrium were 1.18 ppm (or 0.05%). 3.63 ppm, 5.55 ppm. and 6.68 ppm (or 0.29%) when QUAT concentrations were at 0. 0.2. 0.3. and 0.4 M. respectively. When the ratio of barium to chromate increased to 1.5, the result showed the fraction of chromate less than 4 ppm (0.20%) for all concentrations of QUAT. Furthermore increase barium to chromate ratio showed chromate concentration remaining less than 1 ppm at all QUAT concentrations.

4.4 Comparison of Semi-Batch and Continuous Process

At all concentrations of QUAT and lower flow rate (< 8 mL/min). the fractions of CrO_4^{2-} in precipitate to CrO_4^{2-} in feed obtained from the continuous process were lower than those of the semi-batch process. At the higher flow rate (> 8 mL/min). both processes gave very similar %CrO_4^{2-}. Furthermore. at 12 mL/min flow rate and above, both processes showed more than 40% chromate in barium chromate particles for all QUAT concentrations.
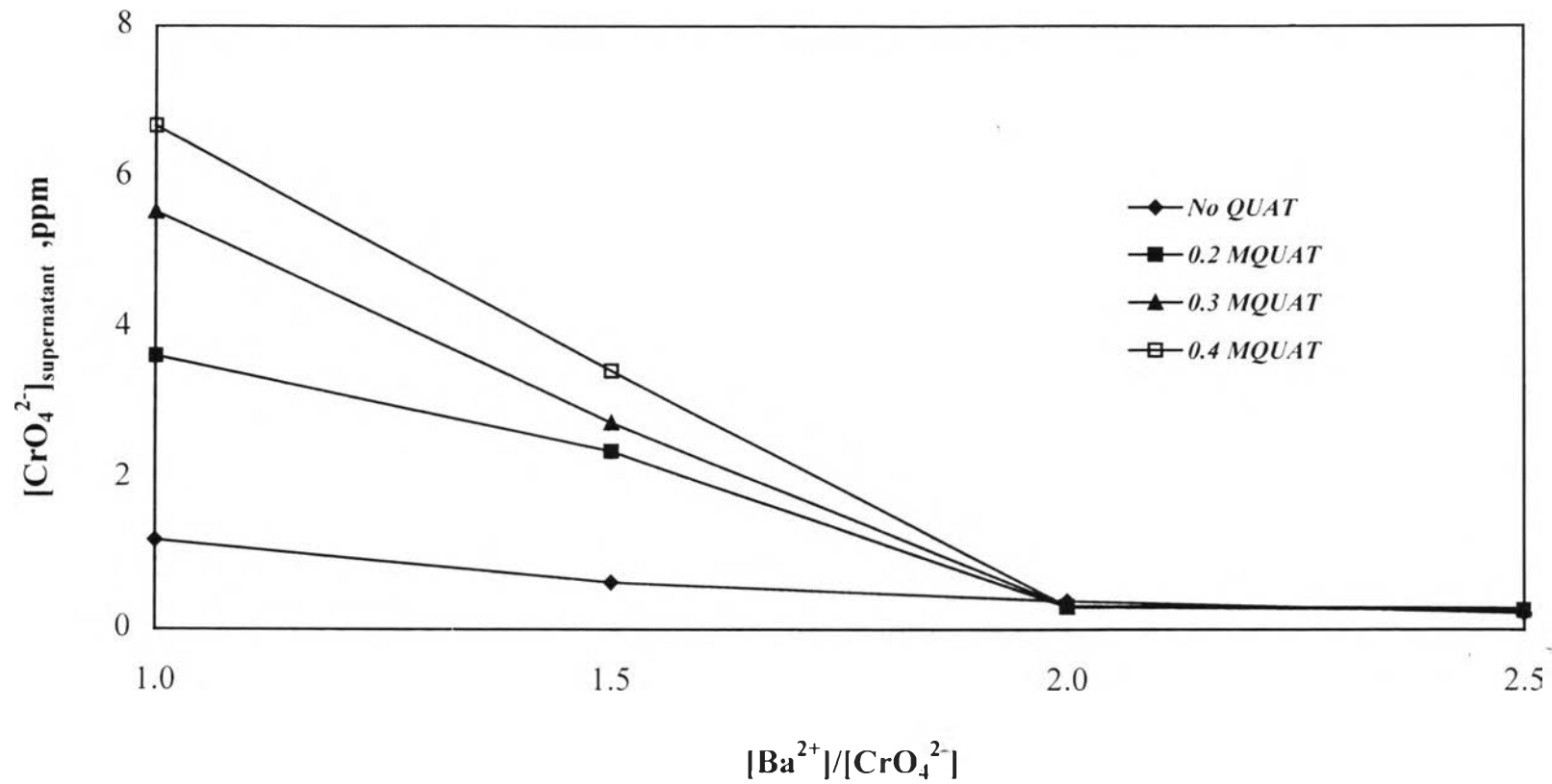
Figure 4.17 Chromate concentration in supernatant as a function of concentration
ratio of barium to chromate on BaCrO4 precipitation, continuous operation.

It was noted that the fractions of chromate ions at all flow rates were less than 0.02% with 5% variation in the continuous process, while the semi-batch process, at lower flow rate (< 6 mL/min) showed 0.02% CrO_4^{2-} with 40% variation and at higher flow rate (>6 mL/min) showed 0.13% CrO_4^{2-} with 40% variation. Both systems showed the percent of QUAT in the overflow solution to be high, when the flow rates were high. Also, high concentration of QUAT in the initial feeding solution resulted in high percent of QUAT in the overflow solution. Furthermore, the results showed that at all flow rates, the chromate in barium chromate particle decreased when crystallizer height increased from 33 to 53 cm. Above 53 cm, the results showed no effect of height on the barium chromate precipitation. Increasing barium to chromate concentration ratio to greater than 1.0 showed insignificant decrease of chromate concentration in the supernatant.