SULPHATE REMOVAL RESULTS USING BARIUM-CARBONATE AND THEIR ANALYSIS FOR REACTOR SYNTHESIS

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ABSTRACT

The reaction rate of sulphate removal from acid mine drainage using barium carbonate was studied for various pH, calcium concentration, and $BaCO_3/SO_4^{2-}$ feed ratios using batch studies. Process synthesis concepts were used to investigate the interaction between the optimum regions for reactor operation and the experimental results. The effect of various process objectives on the optimal operating region was also investigated, and its implication for the process design and further experimental program was considered.

1. INTRODUCTION

The CSIR patented alkali barium and calcium (ABC) process uses the barium technology to remove sulphate from acid mine drainage (AMD) and other industrial effluents. The primary core of the process focuses on the sulphate removal. The sulphate removal process involves precipitation of sulphate present in mine wastewater mainly as $CaSO_4$ to generate $BaSO_4/CaCO_3$ sludge:

$$Ca^{2+}\,(aq) + SO_4^{2-}\text{-}\,(aq) + BaCO_3\,(s) \rightarrow BaSO_4\,(s) + CaCO_3\,(s) \qquad (1)$$

This work focused on the interaction between the optimum regions for reactor operation and the experimental results.

2. MATERIALS AND METHODS

Feedstock

Pre-treated AMD containing about 2000 mg/l SO_4^{2-} was used as feed water in this study. $BaCO_3$ produced in the CSIR laboratories was used for SO_4^{2-} removal.

Experimental Procedure

Batch studies on SO_4^{2-} removal from pre-treated AMD using $BaCO_3$ were carried out by using 3 l completely stirred tank reactors, containing about 2000 mg/l SO_4^{2-}. The pH of pre-treated AMD was raised to above 12 to remove Mg^{2+}. SO_4^{2-} removal tests with $BaCO_3$ were conducted in the high pH water and after reducing the pH to below 8 with CO_2 gas.

Analytical Procedure

The reduction in the sulphate concentration was monitored by sampling at 5 min, 15 min, 30 min, 60 min, 90 min, 120 min, 180 min and 240 min intervals. Sulphate was determined in the filtered samples using a Hach DR/2010 data logging spectrophotometer. The pH for the samples was determined using a Metrohm 691 pH meter.

3. RESULTS

The experimental data were used to calculate the rates of SO_4^{2-} removal using $BaCO_3$ at various experimental conditions. The concentrations of SO_4^{2-} and $BaCO_3$ represent those in the reactor. The sulphate concentration in the reactor was measured and the corresponding barium carbonate calculated. The rate of sulphate removal (mg/L.min), was determined from the slopes to the concentration profiles at different residence times using Matlab© (Levenspiel, 1972)

The set of sulphate concentration and barium carbonate concentration for a fixed molar feed ratio and varying reaction time are given in Figure 1 for the reaction temperatures of 25 °C. The points with the same molar fixed feed ratio composition are indicated by a line that has no other significance, to help group them for ease of interpretation. The composition of the feed gas is shown for each set. The measured rates of sulphate removal at the associated concentrations are the numbers indicated on the graph. In particular, we considered the influence of concentrations and feed ratios of $BaCO_3:SO_4^{2-}$ on the rate of sulphate removal. To illustrate the application of process synthesis to optimizing the reactor design, we initially considered a first simple objective (which is possibly quite unrealistic).

We considered that we wish to remove a given amount of sulphate as specified by the South African Department of Water Affairs and Forestry (DWAF) in the smallest possible reactor. To do this, we needed to consider the rate of sulphate removal and factors on which it depends.

The values of the concentrations of sulphate and barium carbonate are the result of varying the feed ratio of the loading materials and hence the conversion in the reactor. We observed that, by increasing the feed molar ratio, the rate of sulphate removal increases. At low sulphate removal conversion (high molar feed ratio), the overall rate of sulphate removal is high. In contrast, high conversion (low molar feed ratio) resulted in a low overall rate of sulphate removal.

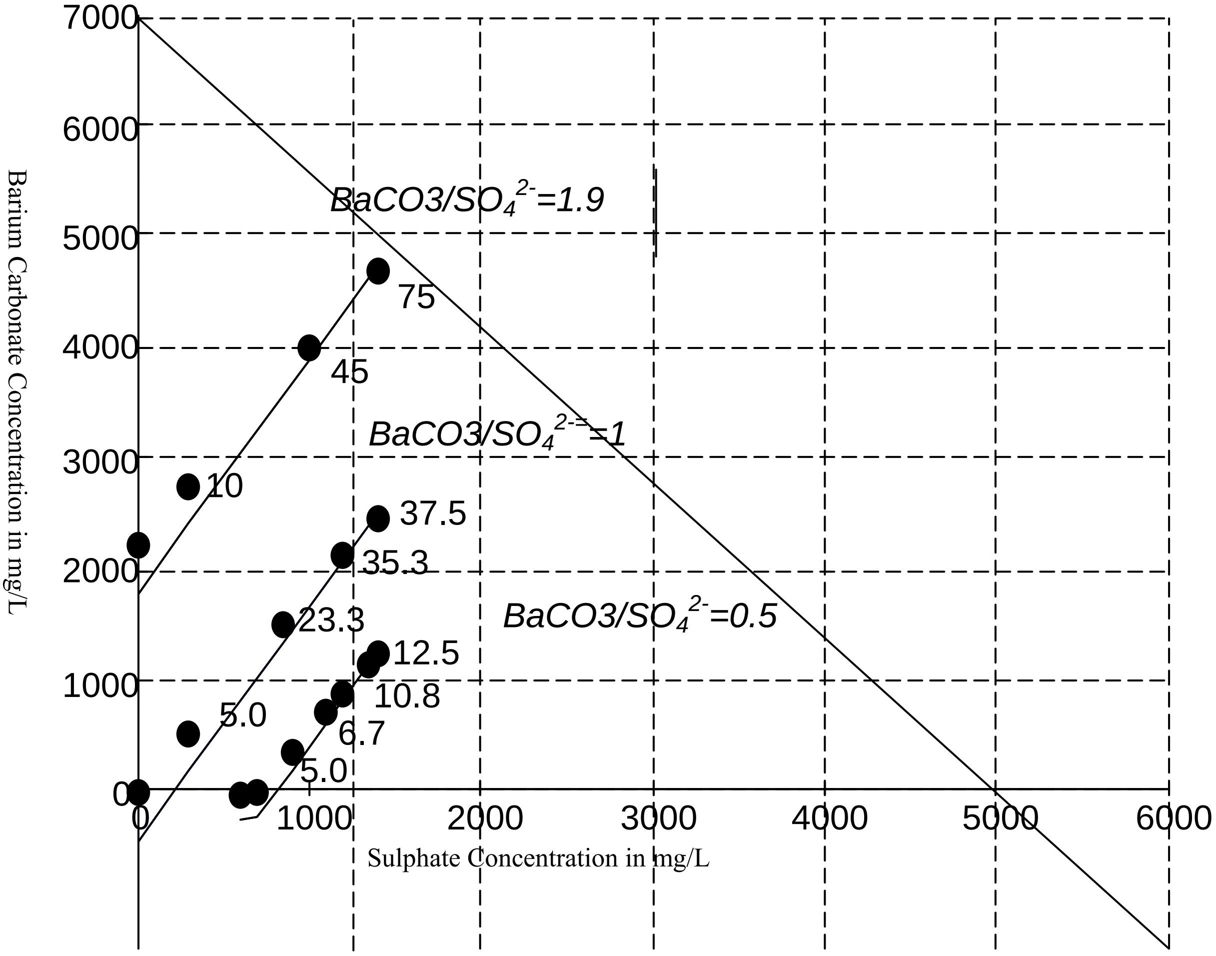

Figure 1. Rate of Sulphate Removal at 25 °C at various concentrations of sulphate and barium carbonate for three different feed ratios. The numbers indicate the rate of sulphate removal in mg sulphate/L.min. The feed ratio for each set of experiments is indicated on the associated line

The trend shown in Figure 1 is that, for each set of experiments with fixed $BaCO_3$/ SO_4^{2-}feed ratio, the rate of sulphate removal decreases monotonically as the concentrations of $BaCO_3$ and SO_4^{2}- decrease. Furthermore, an increase in the concentration of $BaCO_3$ and a decrease in the concentration of sulphate favour high rates of sulphate removal as shown in Figure 2.

If we now consider the objective function that we proposed, namely, to remove a given amount of sulphate in the smallest reactor, we can see that this would be equivalent to operating the reactor at the highest rate of sulphate removal. The highest rates of sulphate removal for a fixed feed composition are obtained at high concentrations of $BaCO_3$ and SO_4^{2-}.

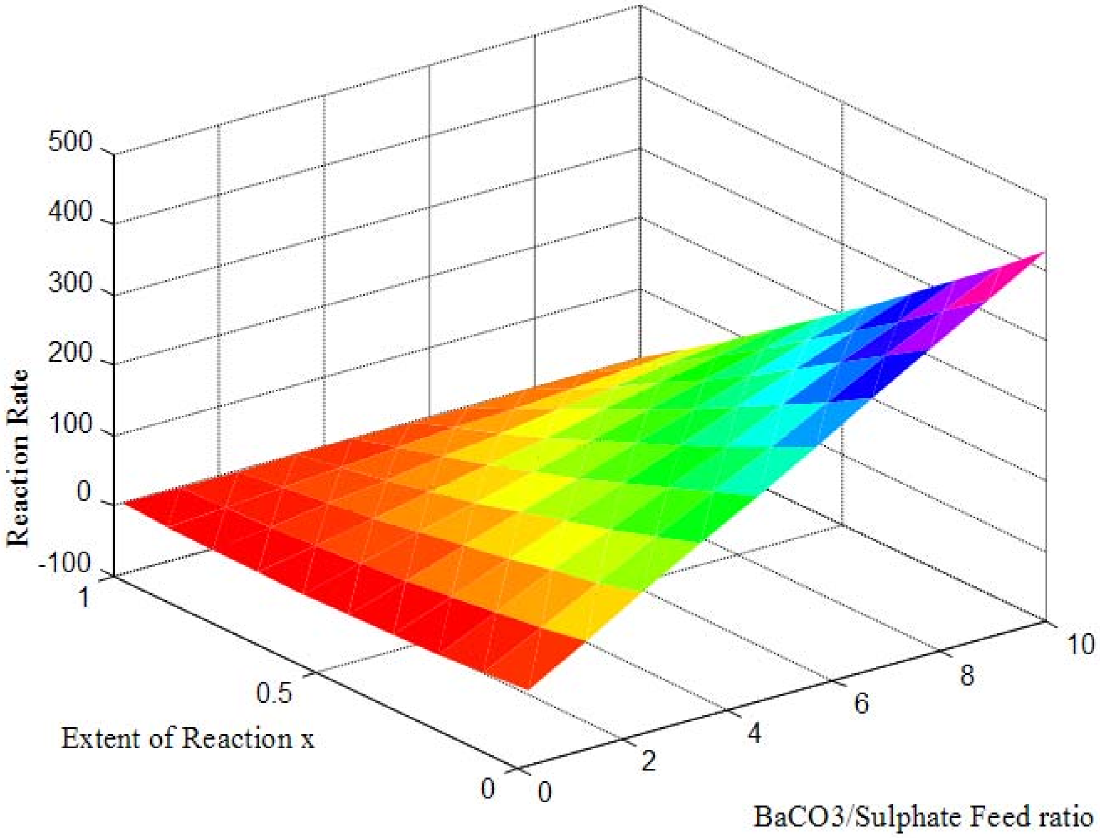

Figure 2. Surface Reaction Rate (Sulphate Removal) as a function of the extent of reaction and the $BaCO_3$/Sulphate feed ratio

The reactor should thus be operated at low conversions and higher total number of moles. If the above objective is applied in a situation where there is flexibility of changing the $BaCO_3/\ SO_4^{2-}$feed ratios, the reactor should rather be operated in a region of high $BaCO_3/\ SO_4^{2-}$ feed ratios. For the data shown, this would correspond to a $BaCO_3/\ SO_4^{2-}$ feed ratio of 1.9. For the purpose of answering the question of how to remove a given amount of sulphate in the smallest possible reactor, we plotted the reciprocal rate of sulphate removal (*1/-rate*) at various sulphate concentrations and at different $BaCO_3/\ SO_4^{2-}$ feed ratios as indicated in Figure 3. It can be seen from Figure 3 that *1/-rate* increases monotonically as the concentration of sulphate decreases (because the conversion increases) for each of the experimental sets with different $BaCO_3/\ SO_4^{2-}$ feed ratios. This trend indicates that the optimum reactor structure to be used is a plug-flow reactor (Glasser et al. 1999)

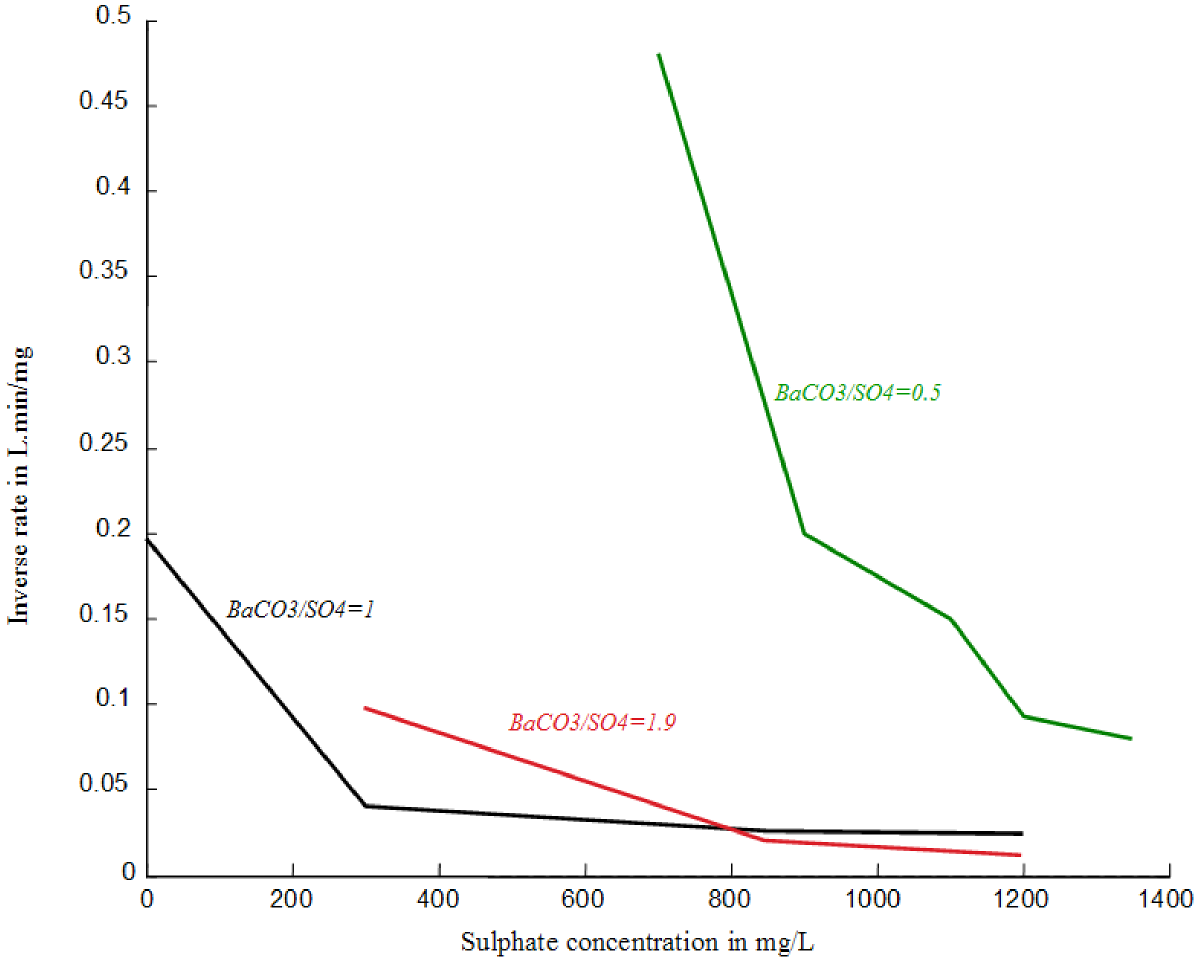

Figure 3. Plot of 1/rSO42- versus Sulphate Concentration at 25o C. Each curve corresponds to a different feed ratio of BaCO3/SO42- as indicated in the legend. The dimensions of the rate of SO42- removal are mg SO42-/L.min

High rates of sulphate removal are obtained in the region of high concentrations of $BaCO_3$ and low concentrations of sulphate; thus, a plug-flow reactor with a $BaCO_3$-rich feed would give the optimum reactor structure for this simple objective. This could be achieved by designing a process with a large $BaCO_3$-rich recycle stream around a plug-flow reactor as shown in Figure 4.

There are two factors that need to be considered at this stage. At first sight, it seems we would need to do further experiments at even higher $BaCO_3$/ SO_4^{2-}feed ratio, lower conversions, in order to see if the trend of the reaction rate continues to increase and where the highest rates occur.

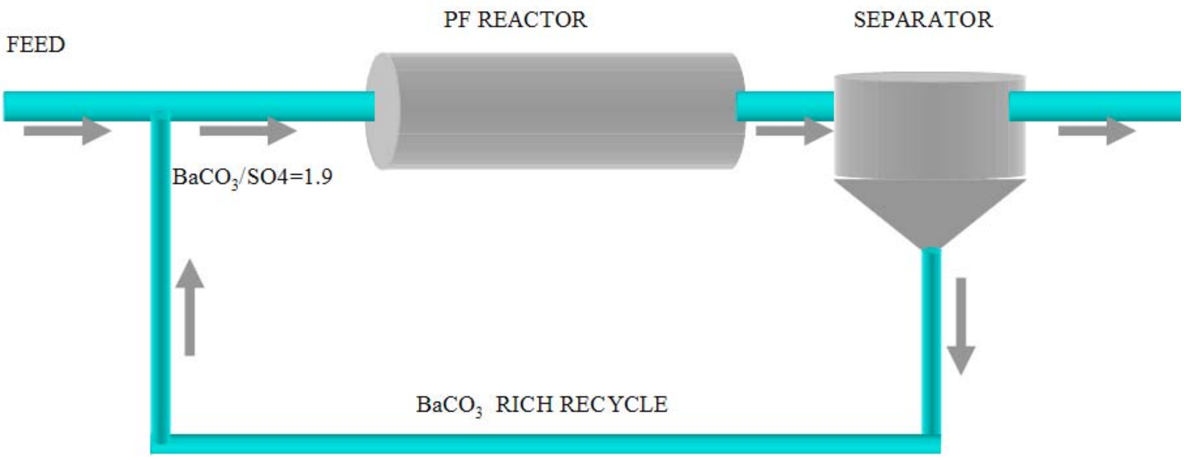

Figure 4. Process Configuration for removing a given amount of sulphate in the smallest reactor

At this stage, we would need to do calculations to examine the trade-off between reducing the reactor volume and increasing the recycle cost. The results of these calculations could modify the decision as to where to perform further experiments. Hence, we can see that we should design an experimental program so that the interpretation of the experimental results and implications on the design are incorporated into the planning. However, the objective of minimizing the reactor volume is going to result in a process with a large BaCO3-rich recycle stream as described in Figure 4. Its implication on the process is that we will need tight separation constraints as to eliminate (recover) the toxic (expensive) barium in the separator effluent. Thus, although the reactor volume may be minimized, it may be somehow at the expense of the process itself. However, rather than continue with this objective, we shall instead consider the effect on the reactor design, experimental program, and process design when we change the objective function.

4. FUTURE QUESTIONS

Let us assume that we change the objective and now wish to minimize the production of $CaCO_3$. To consider this new objective, we need to consider the rate of $CaCO_3$ production and, in particular, what it depends on. We know that the reaction product is the $BaSO_4/CaCO_3$ sludge which needs to be processed further by thermal reduction. Logically if we have sludge with less $CaCO_3$ we will save a considerable amount of energy lost in processing an undesired product. So we need to look at the rate of production of $CaCO_3$. We therefore foresee a challenge of where further experiments need to be performed.

5. CONCLUSIONS

The optimal region for the operation and design of a sulphate removal reactor in the barium process differs for different objectives. Therefore, one need to be sure about what one is trying to optimize and set as system parameters. To be able to do this, one needs to choose the operational objectives and system parameters properly. Furthermore, the influence of the system parameters on the optimal operating region needs to be understood. This can only be done if the kinetics and process design are done iteratively. This suggests that it would be desirable to integrate the experimental program with the process design. However, probably one of the most important results in this work is that implementing the optimal reactor operating conditions results in a process with somehow large excess feed. Hence, one should not optimize the reactor independently of the process in which the reactor is going to be used.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

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