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REMOVAL OF SULPHATE IONS FROM MINE TAILINGS

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Abstract

Sulphates can be removed via both active and passive processes.[1-3] Some examples of active processes currently used to remove sulphates from tailings are: precipitation reactions, nanofiltration, electrodialysis, and adsorption. Precipitation and adsorption can also be used passively by designing enclosures that perform the same reactions at a slower rate. Precipitation reactions are useful for sulphate removal because the chemistry is fairly simple and easy to put into practice. In this experiment, mock tailing solutions containing an average of 10g/L $[SO_4]^{2-}$ was reacted in a CSTR as a batch process. With 2X excess of $CaCO_3$ as the precipitating reagent, the concentration of $[SO_4]^{2-}$ was reduced to 3g/L. Treating the spent solution with $BaCO_3$ decreased $[SO_4]^{2-}$ to 0.246g/L, which is below the Environmental Protection Agency (EPA) standard for sulphate.[4] The residence time and the optimal impeller speed for 2L of solution in a 5L tank were determined empirically as 3hr and 350rpm, respectively. Higher N_{Re} values led to greater turbulence and greater mixing overall. The major challenges with this experiment was heavy sedimentation of the solid precipitating reagent and product. This could have been resolved by using a larger sample volume and by the addition of axial mixing. There are numerous practical applications for this method, and simple reactor designs lead to easy maintenance and cheap overhead cost.
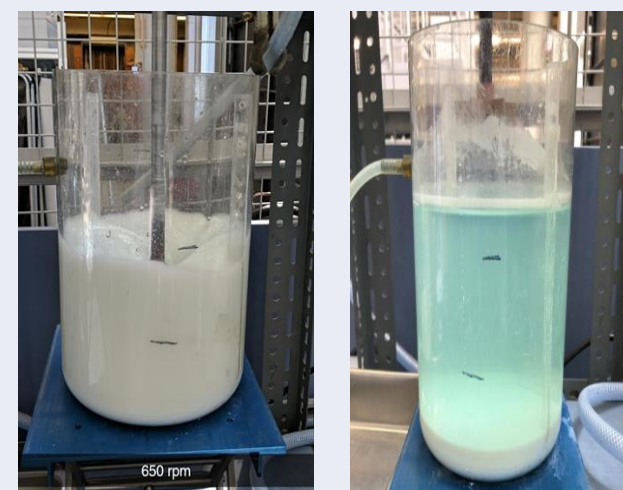
Objective

The aim of this project is to recreate the simplest of these methods- chemical precipitation and passive bed adsorption- in order to quantify the amount of sulphate actually removed from a solution containing a typical mixture of the major ions found in copper and nickel mine tailings ponds to see whether these values are achieved or even exceeded at the bench level. The amount and type of precipitating agent and impeller speeds for these processes will also be varied for analysis purposes.
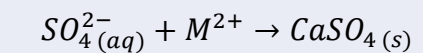

Methodology

A mock tailing solution comprising of calcium, iron, tin, nickel, copper, and zinc was created using the salts of these metals. The sulphate was supplied to the solution with copper sulphate, nickel sulphate, and sulphuric acid, which also helps simulate the acidity of tailings ponds.

To begin treatment, calcium carbonate was mixed into the mock tailings solution in the continuous stirred tank reactor (CSTR) outfitted with a six-bladed radial impeller. Agitator speed from 250rpm to 655rpm were tested at 2X excess of $CaCO_3$. The residence time for the runs was determined empirically. The second phase of treatment took place after decanting the original solution to separate the liquids and solids. After separation, the liquid was poured back into the reactor tank, and barium carbonate was added at an approximately one to one stoichiometric ratio. All trials were operated at roughly 370rpm. Testing for sulphate concentration during phase 1 and 2 trials took place roughly every 30 minutes after the initial sample at the time of origin, with three replicate samples taken and averaged to reduce precision errors. Samples were also tested before and after treatment for metals concentrations using ICP.

Results & Discussion

The overall reaction for the chemical precipitation is as follows:

$$SO_4^{2-}{}_{(aq)} + M^{2+} \rightarrow CaSO_4{}_{(s)}$$

Where M is calcium, strontium and barium, which are all suitable candidates for this reaction. The relative abundance and low cost of calcium makes it a particularly attractive choice, although its relative solubility is the highest of the three. The typical source for these metals is in the form of a carbonate. As an added bonus, less energy is typically required to remove solid particulate compared to soluble ions. One major drawback of newer separation technologies such as reverse osmosis and nanofiltration is the high energy costs. The size of the tank, relative amounts of fluid and solid, impeller size and characteristics, and residence time will all play crucial roles in determining how much sulphate can be removed. Therefore, the optimization of these parameters can greatly change the feasibility of the process. There are many factors to consider when optimizing a CSTR. These factors are essentially the same factors that affect the Reynolds number of the system, which are impeller speeds, impeller types and sizes, and the tank size.[6] The Reynolds number of the system can be determined with the Reynolds number equation designed for impellers. One of the parameters that was tested through experimentation was tested through experimentation was Reynolds number, which influences the reaction rate and residence time while minimizing the amount of energy used to ensure high efficiency and minimal wear on the unit. The optimal Reynolds number is also essential for upscaling the system, as it is one of the few variables which stays constant when upscaling. Once upscaled, the optimal Reynolds number can be used to determine the impeller diameter and rotational speed. Another important factor in optimization is the percentage of excess reactants that must be added to influence short residence times and high efficiency. The amount of excess required can be used to determine the proportion of reactants that must be used when upscaled. Its also important to consider recycle reactions to react unreacted excess reactant to increase efficiency and reduce cost. Otherwise, there is a tapering increase in reaction rate as the rate of agitation increases. It is suspected that all but 250rpm agitation rates would be sufficient for a t_R=3h, so naturally the lowest functional agitation rate of 353 rpm should be chosen for optimal energy efficiency. When examining the kinetics data for this reaction, it can be seen that the reaction has a second order rate function. The barium carbonate data kinetics data suggests that the reaction is zero order. Although the data is limited, it confirms that this compound treatment is effective. Ca/Ba carbonates can effectively remove sulphate from tailings, as concentrations were reduced to an average of 0.246 g/L, which is below the desired EPA limit of 0.250g/L.
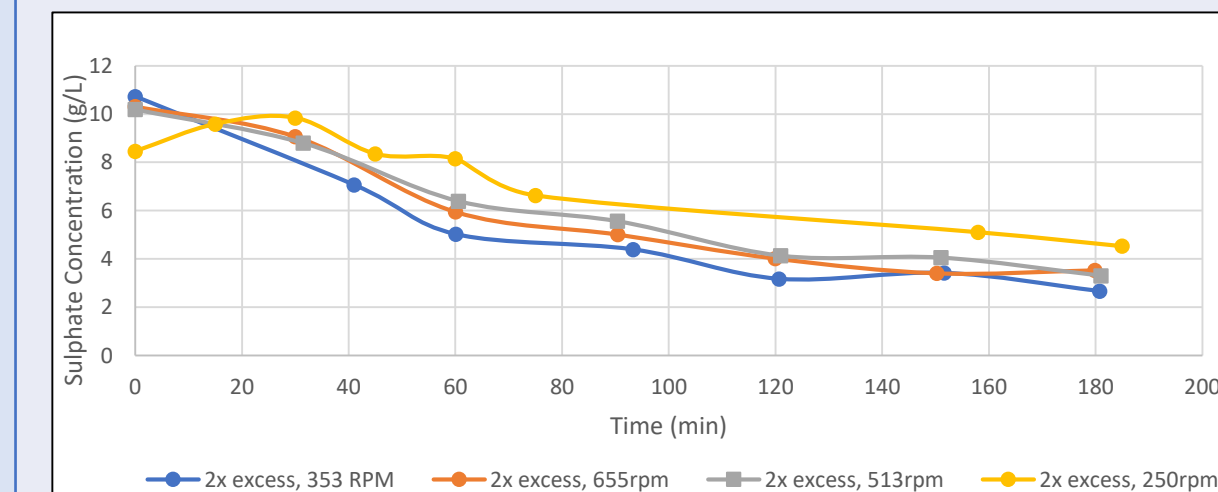

Figure 1. Concentration of Sulphate vs Time when precipitating agent is 2X excess $CaCO_3$
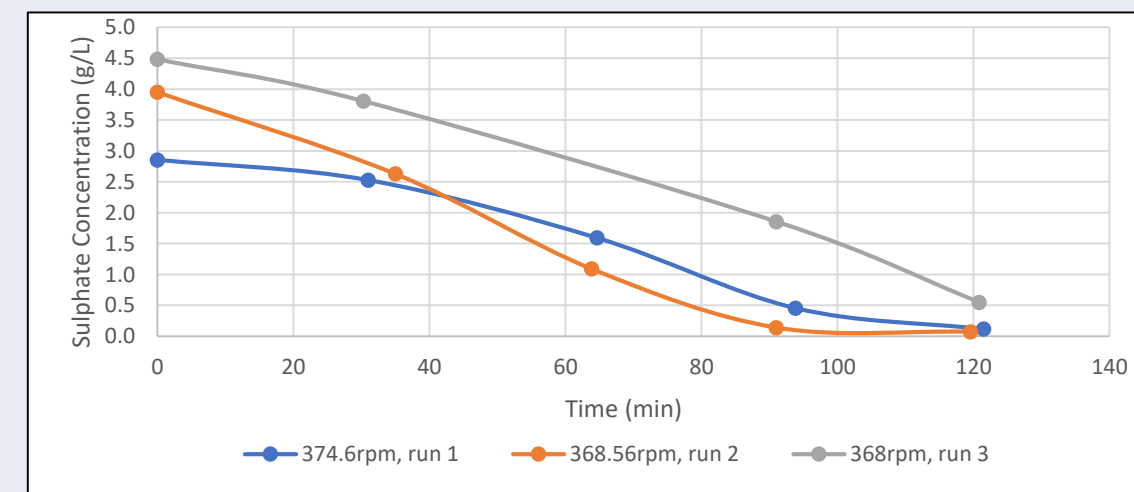

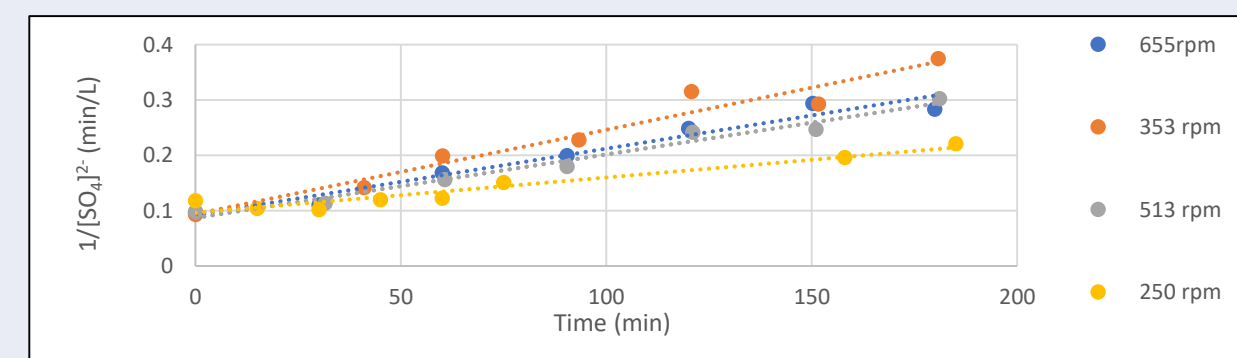Figure 2. Concentration of Sulphate vs Time for Treatment with $BaCO_3$

Figure 3. Second order kinetics data for the reaction between tailings solution and $CaCO_{3(s)}$

Industrial Applications

Sulphate removal by chemical precipitation has numerous applications in industry. Some applications for this particular methodology include:
- Wastewater treatment operations for mining and electrochemical processes involving SO_4^{2-} ions[2,5]
- SO_4^{2-} scrubbing from combustion processes
- Solid-aqueous precipitation reactions with 2nd order kinetics
- Construction of future tailings ponds with lime/limestone liners[1,3]

Conclusions

The experimental findings confirm that chemical precipitation with lime and barium carbonate is a viable method for the removal of sulphate in very acidic waste containing a high metal concentrations. Furthermore, this process was found to proceed at a reasonable rate (t_R < 3hr) and does not require a large excess of reagents to proceed. The overall average change in $[SO_4]^{2-}$ was close to 9g/L, which means that it could be effective at actual tailing concentration levels. Careful monitoring of the free barium concentration by ICP showed that less than 10ppm was added to the solution in exchange. The experiment can be improved by expanding the range of impeller speeds to verify that the conditions explored are optimal, and working at larger volumes (i.e. 5L instead of 2L) to verify that the process can be scaled up.

Recommendations

The following recommendations are suggested:
- This system could be extended as a passive treatment. This was attempted, but problem with flow through the vessel was limited, as well as the amount of packing that could be added, if this experiment was to be redesigned, a larger cross-sectional area would be desired.
- Test at lower agitator speeds, as the range obtained does not include laminar conditions.
- Comparison of axial mixing versus radial mixing and optimize the system for use with different styles of impellers
- Introduction of a filtration step after mixing to increase the total amount of gypsum precipitated for improved efficiency
- Conversion of this set-up from batch process to continuous process to simulate an industrial setting

References

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Acknowledgements