Elimination of sulfate ions in water by addition of an acidified calcium carbonate suspension

Abstract

This study focuses on the elimination of excess sulfate ions in drinking water under controlled stirring and by adding an acidified calcium carbonate suspension. Experimental parameters such as the mass of calcium carbonate and the concentration of hydrochloric acid are studied in order to follow the mechanism of elimination of sulfate ions. Kinetic monitoring of the residual sulfate concentration by nephelometry shows a progressive drop in the sulfate ion concentration. The variation of calcium carbonate is indifferent on the quantity of sulfates eliminated. The influence of the concentration of hydrochloric acid studied shows a maximum elimination when this concentration is 0.2 mol/L. X-ray diffraction analysis of the solids obtained revealed the presence of gypsum, thus supporting that sulfate ions are eliminated by a process that involves its formation.

Keywords: calcium carbonate, sulfate, hydrochloric acid, gypsum.

I. Introduction:

Water is a natural resource that, with population growth and development, faces pollution problems. Drinking water has become a public health issue (Levallois., 2006). The number of people relying solely on groundwater to meet their drinking water needs is estimated at nearly 2.5 billion (Gronwall and Danert 2020). Sulfate (SO_4^{2-}) is a ubiquitous anion in natural waters. It is not considered toxic, but it can be harmful to freshwater species at high concentrations (Runtti and *al.*, 2018). Sulfated waters produce a significant amount of sulfide (Daumas 1987), especially hydrogen sulfide, which gives the water an unpleasant odor and taste. They also accelerate biological corrosion and impair disinfection due to the proliferation of sulfate-reducing bacteria in stagnant areas of the water distribution network (INtCtMIS and *al.,* 1994). Several techniques are used to reduce excess sulfates in drinking water, such as reverse osmosis (Tansakul , 2009), nanofiltration (Bannoud , 2001), ion exchange (Monzie, 2003), and precipitation (Alimi and *al.,* 2003). Precipitation is one of the most widely used techniques for the removal of excess sulfates in water because it is simple to apply, pH tolerant, and inexpensive (Tait and *al.,* 2009). In this study, we reexamine the removal of sulfates by addition of a suspension of acidified calcium carbonate. The use of calcium carbonate is explained by its abundance in the natural environment.

II. Materials and methods

II.1. Preparation of the sulfate solution

Synthetic solutions, Na_2SO_4 salt crystals were dissolved in distilled water with stirring until a clear solution was obtained.

II.2. Preparation of acidified calcium carbonate suspension

In 500 mL Erlenmeyer flasks, 1 g of $CaCO_3$ wetted with 5 mL of hydrochloric acid of concentration 0.1 mol/L was introduced and stirred for 4 min to release the Ca^{2+} ions after release of carbon dioxide $CO_{2.}$ All calcium carbonate suspensions were prepared by the same procedure.

II.3. Stabilized $BaCl_2$ solution

The stabilized BaCl $_2$ solution is prepared with 25% Tween 20 solution. It is a commercial solution with an atomic molar mass of 1228g/mol and density 1.1 in a volume of one liter. It consists of taking 25 mL of this solution and diluting it with 75 mL of distilled water. Dissolve 10 g of BaCl $_{2\ \text{crystals}}$ in 20 mL of Tween 20 solution in a 100 mL flask and then top up with distilled water.

II.4. Test procedure for the elimination of sulfate ions by adding an acidified calcium carbonate suspension

First, the acidified suspension of calcium carbonate is obtained by pouring 5 mL of HCl onto $CaCO_3$ which produces effervescence. After stirring for 4 min, 500 mL of sulfated water with a concentration of SO_4^{2-} ions of 500 mg/L was added. The mixture is further stirred using a magnetic bar for 0 to 30 min. The pH was checked and samples were taken to monitor the evolution of sulfate ions. For all manipulations, at each 5 min time interval, 1 mL of the solution is taken using a 5 mL syringe minimum from the 0.45 micron filter and then introduced into a 50 mL flask.

II.5. Method for the determination of sulfates

The determination of the concentration of the remaining sulfates in the water is done with the 1 mL of the solution taken after each 5 min then diluted 50 times. It is introduced 1 ml of HCl at 1/10, 5 ml of the stabilized $BaCl_2$ solution. Shake vigorously then let stand for 15 min, shake again and take the reading on the spectrophotometer at the wavelength 650 nm. First make the control with distilled water.

III. Results and discussion

III.1. Effect of acidified $CaCO_3$ suspension

Figure 1 illustrates the variation over time of sulfate concentration by changing the amount of acidified calcium carbonate suspension.

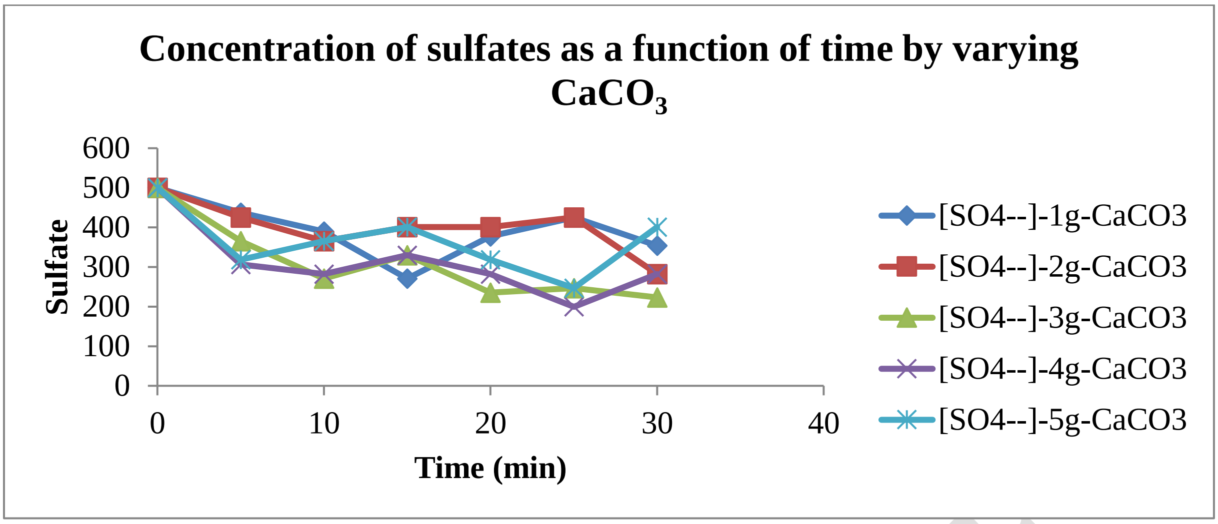

Figure 1: Sulfate concentration as a function of time by varying the mass of $CaCO_3$ for the initial sulfate concentration of 500 mg/L with 0.1 mol/L of HCl.

The analysis of Figure 1 shows a decrease in the concentration of sulfate ions with all the masses of the acidified calcium carbonate suspensions used between 0 and 10 min. This phenomenon is due to the availability of free Ca^{2+} ions from the dissolution of calcite and could combine with sulfate ions to precipitate calcium sulfate illustrated by equation 4. Beyond 10 min, an increase in the concentration of sulfate ions in the medium is observed. This increase can probably be due to the redissolution of calcium sulfate.

III.1.2. Evolution of the pH by varying the acidified $CaCO_3$ suspension

Figure 2 shows the variation over time of the recorded pH by changing the amount of acidified calcium carbonate suspension.

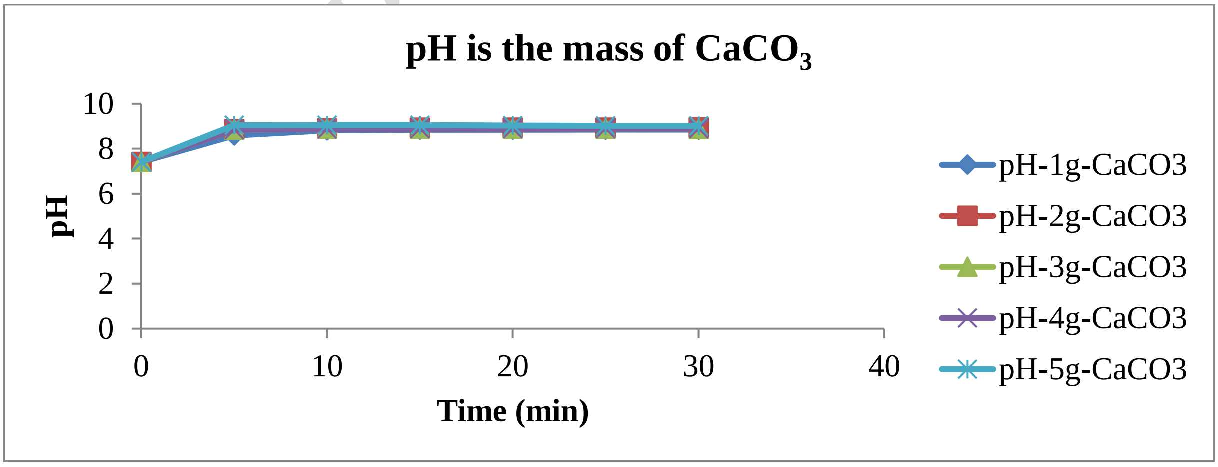

Figure 2: Variation of pH as a function of time by varying the mass of calcium carbonate.

When the synthetic sulfate solution is brought into contact with the acidified calcium carbonate suspension, an increase in pH is observed during the first five minutes, which stabilizes until the end of the manipulation. This increase could be linked to the dissociation of carbonic acid supported by equation (2) and (3). This variation in pH is independent of the quantity of acidified calcite.

III.2. Effect of HCl concentration when preparing 3 g of acidified $CaCO_3$

III.2.1. Evolution of the concentration of sulfate ions

Figure 3 illustrates the variation over time of the sulfate concentration by changing the hydrochloric acid concentration per 3 g of the calcium carbonate suspension.

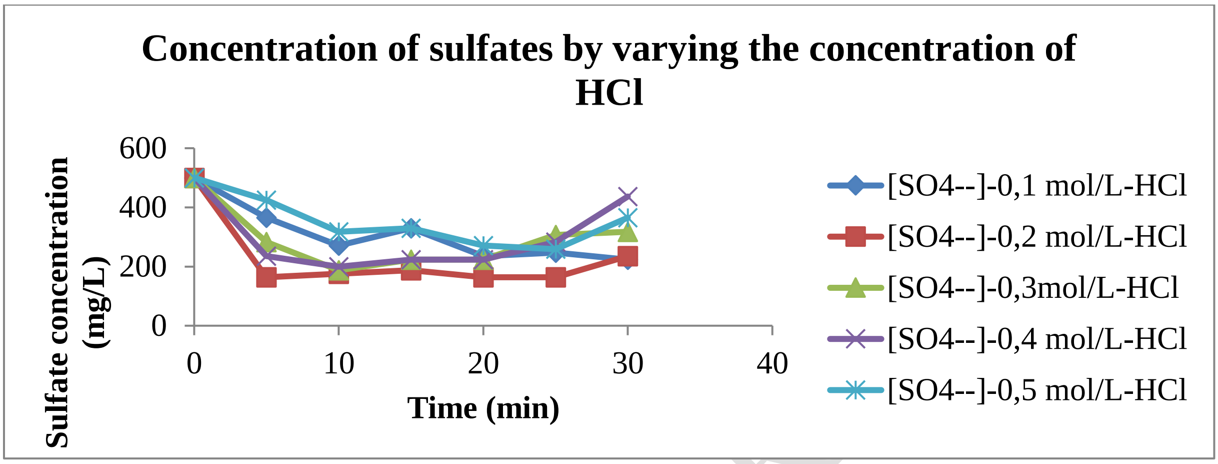

Figure 3: Concentration of sulfates as a function of time by varying the concentration of HCl, for a quantity of 3g $CaCO_3$ with initial sulfate concentration of 500mg/L.

The analysis of Figure 3 shows a sudden drop in the concentration of sulfate ions (SO_4^{2-}) for all concentrations of hydrochloric acid (HCl) used to obtain the suspension of acidified calcium carbonate, particularly between 5 and 10 min. From 10 min of stirring, a slight increase in sulfate ions is observed. Good elimination of sulfates is obtained for 0.2 mol/L of HCl. This drop in the concentration of sulfate ions would seem to be associated with the precipitation of calcium sulfate.

III.2.2. Evolution of the pH by varying the concentration of HCl

Figure 4 illustrates the variation in pH over time by changing the concentration of hydrochloric acid per 3 g of the calcium carbonate suspension.

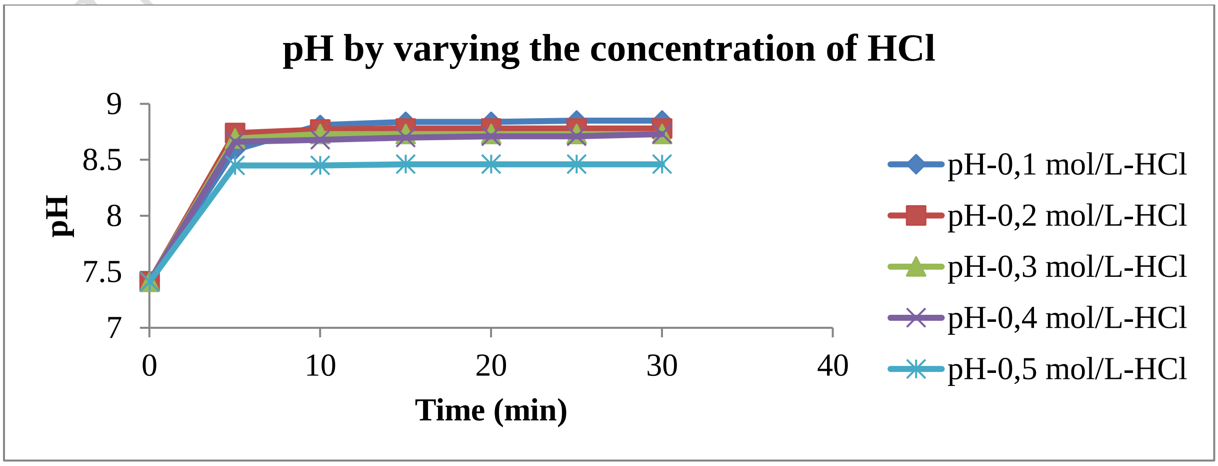

Figure 4: Variation of pH as a function of time by varying the concentration of HCl .

At the pH level, a rise in pH is recorded between 0 and 5 min which becomes slightly stable until the end of the manipulation. Whatever the concentration of HCl used to obtain the acidified calcium carbonate suspension, the variation in pH remains identical.

III.3. Study of the mechanism of elimination of sulfate ions

In fact, in an acidic medium, the dissolution of $CaCO_3$ can be developed as follows:

$$\mathrm{CaCO_3 + 2HCl \rightarrow Ca^{2+} + 2Cl^- + CO_2^{\uparrow} + H_2O} \text{ Equation 1}$$

The remainder of the CO_2 hydrolyzes in an aqueous medium, transforming into H_2CO_3, which dissociates according to the following equations:

$$H_2CO_3 + H_2O \leftrightarrow HCO_3^- + H_3O^+ \; Equation\ 2$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \; Equation\ 3$$

The drop in sulfate ion concentration is directly associated with the mechanism of calcium sulfate precipitation ($CaSO_4 .nH_2O$) according to the reaction in equation 4:

$$\mathrm{Ca^{2+} + SO_4^{2-} + nH_2O \rightarrow CaSO_{4.}nH_2O} \text{ Equation 4}$$

This result is similar to that of the work of (Booth et *al.*, 1997) when they propose for the formation of gypsum an instantaneous germination type mechanism from the hypothesis that there is homogeneity of crystal size. According to (Zarga and *al.*, 2013), the germination time of gypsum varies from 4 minutes for simple precipitations to 9 minutes for mixed precipitations. In this case, the parameter of major influence on the rate of gypsum production is without context the acidity of the solution.

III.4. X-ray diffraction (XRD) analysis results

Figure 5 illustrates the XRD analysis result of the solid deposit obtained after removal of sulfate ions by addition of an acidified calcium carbonate suspension. Analysis of this diffractogram shows peaks corresponding to gypsum thus supporting our mechanism suggested above.

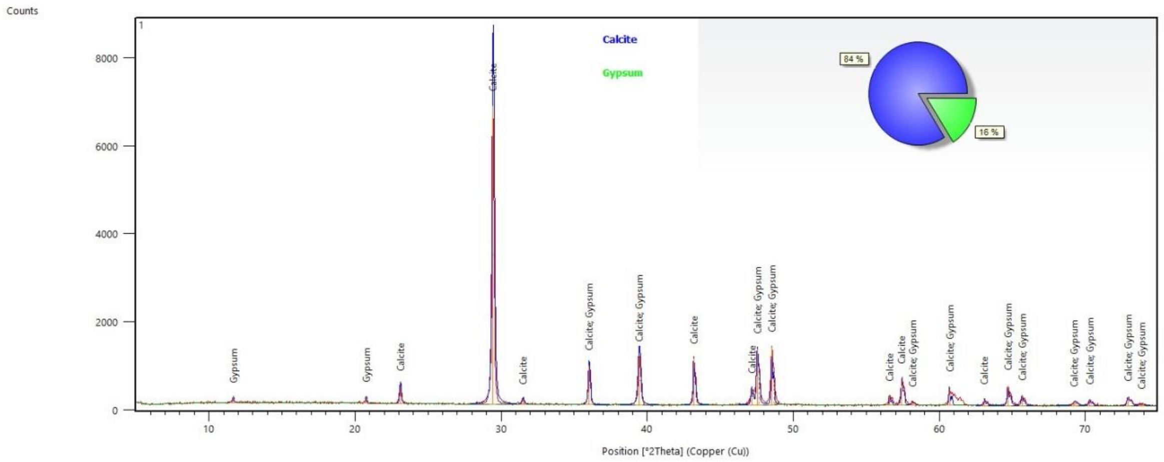

Figure 5: DRX image of the precipitated solid for an initial sulfate concentration of 500 mg/L.

IV. Conclusion

The use of calcite in the treatment of sulfate-rich waters allows to record satisfactory results concerning the elimination of sulfates. The variation of the pH is linked to the dissolution of calcium carbonate with formation of HCO_3^- ions following the injection of hydrochloric acid. A drop in the sulfate concentration was recorded from the beginning of the analysis which lasts a maximum of 10 min followed by the precipitation of gypsum as shown by the XRD.

References

Alimi , F., Elfil , H., & Gadri , A. (2003). Kinetics of the precipitation of calcium sulfate dihydrate in a desalination unit. *Desalination* , *158* (1-3), 9-16.

Bannoud , AH (2001). Removal of hardness and sulfates from water by nanofiltration . *Desalination* , *137* (1-3), 133-139.

Booth, J., Hong, Q., Compton, R.G., Prout , K., & Payne, R.M. (1997). Gypsum overgrowths passivate calcite to acid attack. *Journal of colloid and interface science* , *192* (1), 207-214.

Daumas , S. (1987). Bacterial corrosion in low-temperature geothermal energy: Corrosion mechanisms by *sulfate -reducing bacteria* (Doctoral dissertation, ANRT).

Grönwall , J., & Danert , K. (2020). Regarding groundwater and drinking water access through a human rights lens: Self-supply as a norm. *Water* , *12* (2), 419.

INtCtMIS , L., SERVI, U., & LA TIUI, PI (1994): Risk of pollution of freshwater tables due to geothermal exploitation of the Dogger aquifer in the Paris Basin.

Levallois, P. (2006). Drinking water and public health: current and future challenges. *Water Sciences Review* , *19* (2), 127-135.

Monzie, I. (2003). *Ion exchange for the production of very pure water: study of kinetic limitations by the micro-column method: extension to electrodeionization (* Doctoral dissertation, Institut National Polytechnique de Lorraine).

Runtti , H., Tolonen , E.T., Tuomikoski , S., Luukkonen , T., & Lassi , U. (2018). How to tackle the stringent sulfate removal requirements in mine water treatment—A review of potential methods. *Environmental research* , *167* , 207-222.

Tait, S., Clarke, W.P., Keller, J., & Batstone , D.J. (2009). Removal of sulfate from high-strength waste water by crystallization . *Water Research* , *43* (3), 762-772.

Tansakul , C. (2009). *Hybrid membrane processes for seawater pretreatment before reverse osmosis desalination* (Doctoral dissertation, National Institute of Applied Sciences of Toulouse).

Zarga , Y., Boubaker , HB, Ghaffour , N., & Elfil , H. (2013). Study of calcium carbonate and sulfate co-precipitation. *Chemical Engineering Science* , *96* , 33-41.