

## **Study on the Effect of pH, Ionic Strength and Pressure on the Solubility of CaSO<sub>4</sub>-NaCl-H<sub>2</sub>O System**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. Authors DB and UK performed all the experiments. Authors PPS and MKB designed, analyzed and interpreted data and wrote the whole manuscript. All authors read and approved the final manuscript.*

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### **ABSTRACT**

The present study investigates the solubilities of calcium sulphate (CaSO<sub>4</sub>) in NaCl-H<sub>2</sub>O solutions at 5 and 10 Kg/cm<sup>2</sup> pressures respectively under boiling water temperature. As no previous work has been carried out to account for the effect of very low concentrations of NaCl the solubility of on calcium sulphate over a wide acidic pH range, various concentrations of NaCl (0.001-0.1 M) were used and the experiments were performed at different pH values (3.0 – 6.0) under hydrothermal conditions using an autoclave. Dissolved sulphates were determined by the turbidity measurement. Dissolved sulphates in each experiment were calculated from the respective absorbance datum at 420 nm wavelength recorded from a UV-Visible spectroscopy using the standard calibration curve. Highest soluble sulphate (14.58 x 10<sup>-3</sup> moles L<sup>-1</sup>) is observed at pH 5.0 when the concentration of NaCl is 0.05 M at 5 Kg/cm<sup>2</sup> pressure. At NaCl concentration of 0.01 M, highest soluble sulphates

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( $12.50 \times 10^{-3}$ ,  $13.33 \times 10^{-3}$  and  $13.33 \times 10^{-3}$  moles L<sup>-1</sup> at pH 3.0, 3.5 and 4.0), respectively has been found at lower pH range. Upon increasing the concentration of NaCl to 0.05 M, the sulphates with the highest solubilities, i.e.,  $13.33 \times 10^{-3}$ ,  $14.58 \times 10^{-3}$  and  $13.33 \times 10^{-3}$  moles L<sup>-1</sup> appeared at pH values (4.0, 5.0 and 5.5, respectively). A further increase of the concentration of NaCl to 0.1 M, the highest sulphates solubilities ( $13.33 \times 10^{-3}$  and  $14.37 \times 10^{-3}$  moles L<sup>-1</sup>) have been found at pH values of 4.5 and 6.0, respectively. However, almost similar solubility values ( $12.91$ - $13.33 \times 10^{-3}$  moles L<sup>-1</sup>) at different NaCl concentrations have been observed at pH 4.0. Comparatively the solutions with less soluble sulphate containing ionic strengths of NaCl at different pH values, were obtained when the experiments were performed under 10 Kg/cm<sup>2</sup> pressure. In this case, the highest soluble sulphate ( $12.08 \times 10^{-3}$  moles L<sup>-1</sup>) was obtained at 0.05 M NaCl solution at pH 4.0. The values of soluble sulphate are lower at lower pH values (3.0, 3.5 and 4.0) in all the concentrations of NaCl, whereas above the pH of 4.0, the values of soluble sulphate are insignificant. The results of this study are valuable in the assessment of calcium sulphate solubilities over a broad pH range and low concentrations of NaCl under boiling water temperature conditions at two different pressures.

*Keywords: Solubility; pH; ionic strength; calcium sulphate.*

## 1. INTRODUCTION

Calcium sulphate is present in natural water and causes permanent hardness. In addition, it is a byproduct of a number of industrial processes such as flue gas desulphurisation, the phosphoric acid and hydrogen fluoride production, etc. Most of the ground water sources, which are considered safe for drinking may be rich in Ca<sup>2+</sup> [1] since calcium does not show any adverse effect on human health. Calcium sulphate is a salt that occurs abundantly in different natural environments.

Calcium sulphate has been known in three forms – anhydrite (CaSO<sub>4</sub>), Plaster of Paris (CaSO<sub>4</sub>.0.5H<sub>2</sub>O) and gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O).

Solubility of calcium sulphate and its hydrates in presence of sodium chloride over a wide range of temperatures and concentrations has been studied by various workers [2-4]. These investigations can be correlated with the solubility of the minerals in sea water, i.e., sea salt solutions behave like sodium chloride solutions of identical ionic strength. These workers observed that above 45°C approximately, anhydrite form is the stable form and that below this temperature gypsum is stable. Above 93°C the hemi-hydrate form is more stable than the dehydrate (gypsum), though it is less stable than anhydrite. Small increases in solubility occur at low pressure and temperature [5,6] and Blount & Dickson [5] measured anhydrite solubility to 1000 bar and 450°C in pure H<sub>2</sub>O and in NaCl solutions up to 26 wt %. They observed substantial increase of solubility with salinity. The importance of studying solubility of calcium sulphate in NaCl solution is

that in salt solutions of higher ionic strength, the calcium sulphate solubility product is considerably increased. An increase in ionic strength reduces the activity of the species. According to Loewenthal & Marais [7], calcium sulphate has extremely low solubility, i.e., 1290 ppm at 0°C. High degree of ionization in alkali chloride solutions may facilitate the formation of the solute CaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub>, which could form by the reaction of CaSO<sub>4</sub> and NaCl [8].

This study focuses on the investigation of the solubility of calcium sulphate in NaCl-H<sub>2</sub>O solutions at different pH and ionic strengths. The extent of solubility would also be measured under the same conditions (pH and ionic strength) at boiling temperature of water and different pressures.

## 2. MATERIALS AND METHODS

To study the solubility of calcium sulphate in water at different pH, ionic strength of NaCl and pressure, the following reagents and methods have been considered:-

Preparations of different solutions and reagents are as follows

200 ml of NaCl solutions of 0.001, 0.005, 0.01, 0.05 and 0.1 M were prepared by dissolving the required amount of the salt in distilled water.

For the preparation of standard sulphate solution, Na<sub>2</sub>SO<sub>4</sub> salt was dried at 110°C in an oven for about one hour and then after cooling, the salt was kept in a desiccator. 0.3678 g of the dried Na<sub>2</sub>SO<sub>4</sub> was taken in a 250 ml volumetric flask,

dissolved in distilled water and made up to 250 ml. 1 ml of the  $\text{Na}_2\text{SO}_4$  solution contains 1.0 mg  $\text{SO}_4^{2-}$ .

Barium chloride solution was prepared by dissolving 16 g of the salt in 250 ml distilled water.

A conditioning reagent containing glycerol, hydrochloric acid, ethanol and sodium chloride was prepared. For this purpose, 25 ml glycerol, 15 ml concentrated hydrochloric acid, 50 ml of 95% ethanol were mixed and the mixture was added to the sodium chloride solution prepared by dissolving 37.5 g NaCl in distilled water. All the compounds were mixed thoroughly, kept in a volumetric flask and made up the final volume to 250 ml using distilled water.

Preparation of standard curve was made by using standard sulphate solution. Six 100 ml glass stoppered flasks were taken. 10 ml of the standard sulphate solution was added to the first flask, 20 ml to the second, 30 ml to the third, 40 ml to the fourth, 50 ml to the fifth and 60 ml to the sixth. To each flask containing standard sulphate solution, 5 ml of the conditioning reagent was added and stirred well. Then the volumes of the flasks were made up to 100 ml mark using distilled water. The whole solution was transferred to 250 ml volumetric flask, shaken well and during shaking 5 ml barium chloride solution was added. After one minute of shaking, the solution was poured immediately to the 4 cm sample cell and the measured the absorbance at 420 nm wavelength by using UV-visible Spectrophotometer. Distilled water was used for blank and the spectrophotometer was set to zero. The standard calibration curve was drawn by plotting concentration of sulphate in mg against absorbance.

Experiments of solubility of calcium sulphate were performed using the hydrothermal process at the boiling point of water under two different pressures (5 and 10  $\text{Kg/cm}^2$ ) conditions. Initially seven glass stoppered bottles (500 ml) were taken and to each bottle, 300 ml distilled water was added. The pH of the distilled water in each bottle was maintained at 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0 using very dilute hydrochloric acid.

In one set of experiment at a constant pressure and temperature, five dry beakers (250 ml) were taken. 35 ml of a either pH solution was added to each beaker. 10 ml of 0.1 M sodium chloride solutions to the first beaker, 10 ml of 0.05 M to

the second, 10 ml 0.01 M to the third, 10 ml of 0.005 M to the fourth and 10 ml of 0.001 M to the fifth were added. 0.4304 g  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was added to each beaker with slow shaking and then kept in an autoclave. Definite pressure and water boiling temperature was maintained for two hours. After cooling to room temperature, the solid undissolved materials were centrifuged out. The filtrate of the respective beaker was collected in five 100 ml dry beakers, 5.0 ml of the conditioning reagent was added to each beaker and shake well. Then 5 ml barium chloride solution was added. After maximum one minute of shaking, the absorbance of the turbid solution was measured immediately at 420 nm wavelength by using the UV-visible Spectrophotometer. Dissolved sulphate was calculated from the respective absorbance datum using the standard calibration curve. Similarly, a number of sets of experiment were performed at two different pressures and at various pH conditions.

The amount of dissolved sulphate is first converted into gram, then into moles. The total volume of the solution was 50.0 ml in each experiment. In this study, the amount of dissolved sulphate is expressed in moles per litre.

### 3. RESULTS AND DISCUSSION

As majority of the workers studied solubility of  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  system at high ionic strengths, high pressure and temperature and even presence of sulphate ions [9,10], the present study was undertaken at very low ionic strengths of NaCl (0.001-0.1 M) at the boiling temperature of water. Some interesting results have been obtained. For the results obtained from experiments performed at 5  $\text{Kg/cm}^2$  pressure and at boiling temperature of water are presented in Figs. 1-7.

At pH 3.0, highest soluble sulphate ( $12.50 \times 10^{-3}$  moles  $\text{L}^{-1}$ ) is observed at 0.01 M NaCl solution while the lowest value ( $8.53 \times 10^{-3}$  moles  $\text{L}^{-1}$ ) is found at 0.1M NaCl solution (Fig. 1). The soluble sulphate ( $13.33 \times 10^{-3}$  moles  $\text{L}^{-1}$ ) is found to increase at 0.01 M NaCl solution which is the highest soluble sulphate at pH 3.5 but the lowest soluble sulphate at the same pH is ( $10.41 \times 10^{-3}$  moles  $\text{L}^{-1}$ ) in the 0.001 M NaCl solution (Fig. 2). At pH 4.0, the soluble sulphate is  $13.33 \times 10^{-3}$  moles  $\text{L}^{-1}$  in all concentrations of NaCl solution except 0.1M solution, where the soluble sulphate has been found to be lower, i.e.,  $12.91 \times 10^{-3}$

moles L<sup>-1</sup> (Fig. 3). In the ionic strength of 0.1 M NaCl solution at pH 4.5, highest soluble sulphate (13.33 x10<sup>-3</sup> moles L<sup>-1</sup>) is observed while it is lowest (10.41 x10<sup>-3</sup> moles L<sup>-1</sup>) in 0.05 M NaCl solution; in other ionic strengths, minor variation of soluble sulphate (12.08-12.71 x10<sup>-3</sup> moles L<sup>-1</sup>) is observed (Fig. 4). An exceedingly high soluble sulphate (14.58 x10<sup>-3</sup> moles L<sup>-1</sup>) in the 0.05 M NaCl solution at pH 5.0 but exceedingly low soluble sulphate (4.17 x10<sup>-3</sup> moles L<sup>-1</sup>) in 0.01 M solution is observed (Fig. 5). At pH 5.5, highest soluble sulphate (13.33 x10<sup>-3</sup> moles L<sup>-1</sup>) in the solution of 0.05 M NaCl has been found while the lowest value of soluble sulphate is recorded in the 0.1 M NaCl solution (Fig. 6). In the 0.01, 0.005 and 0.001 M ionic strengths of NaCl

solutions at pH 6.0, minor variation of soluble sulphate (13.33 – 13.75 x10<sup>-3</sup> moles L<sup>-1</sup>), highest soluble sulphate (14.37 x10<sup>-3</sup> moles L<sup>-1</sup>) in 0.1 M and lowest soluble sulphate (11.25 x10<sup>-3</sup> moles L<sup>-1</sup>) in the 0.05 M NaCl solution have been observed (Fig. 7).

On increasing the pressure under similar conditions to 10 Kg/cm<sup>2</sup>, although some significant results of soluble sulphate at pHs 3.0, 3.5 and 4.0 have been noticed but at other pHs (pH 4.5, 5.0, 5.5 and 6.0), the values are almost insignificant. The results are presented in Figs. 8-14. Highest value of soluble sulphate (12.08 x 10<sup>-3</sup> moles L<sup>-1</sup>) is observed at pH 4.0 in the 0.05 M NaCl solution is found.

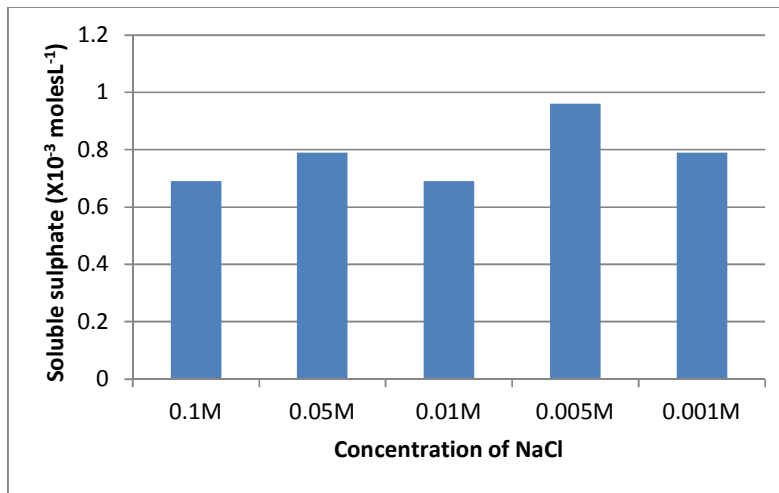


Fig. 1. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 3.0 under pressure 5 Kg/cm<sup>2</sup> at different ionic strengths

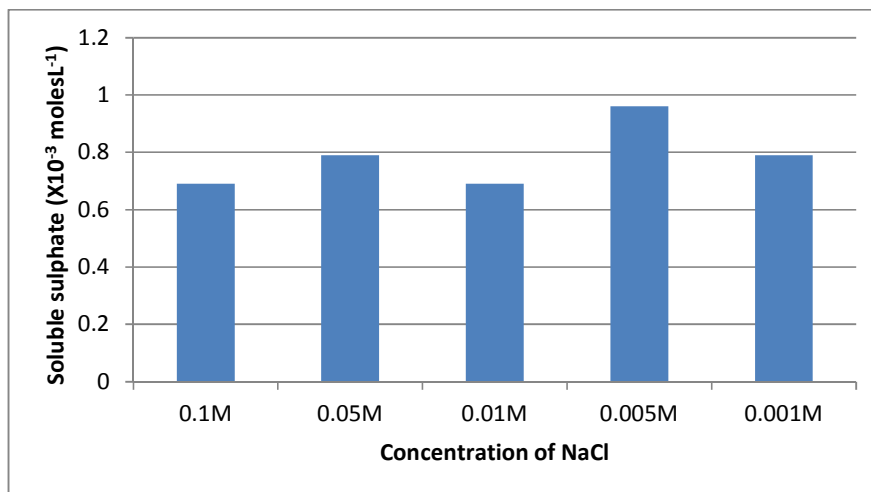


Fig. 2. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 3.5 under pressure 5 Kg/cm<sup>2</sup> at different ionic strengths

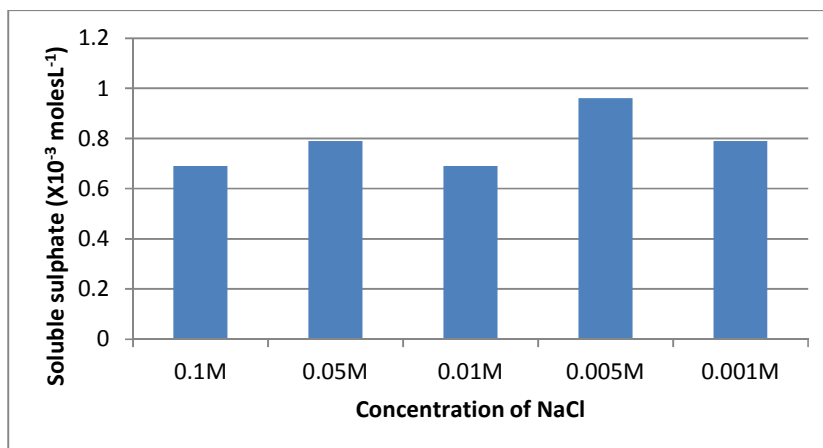


Fig. 3. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 4.0 under pressure 5 Kg/cm<sup>2</sup> at different ionic strengths

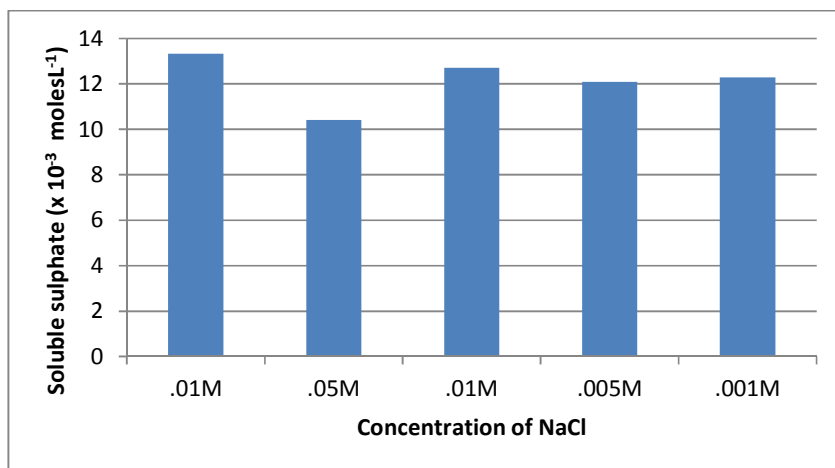


Fig. 4. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 4.5 under pressure 5 Kg/cm<sup>2</sup> at different ionic strengths

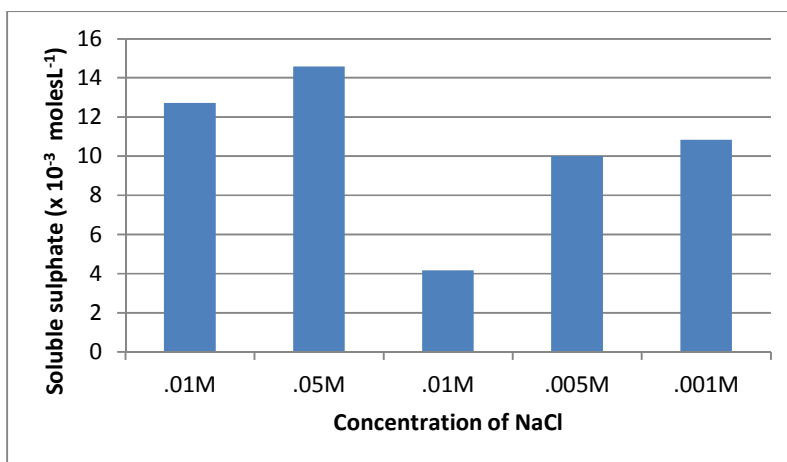


Fig. 5. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 5.0 under pressure 5 Kg/cm<sup>2</sup> at different ionic strengths

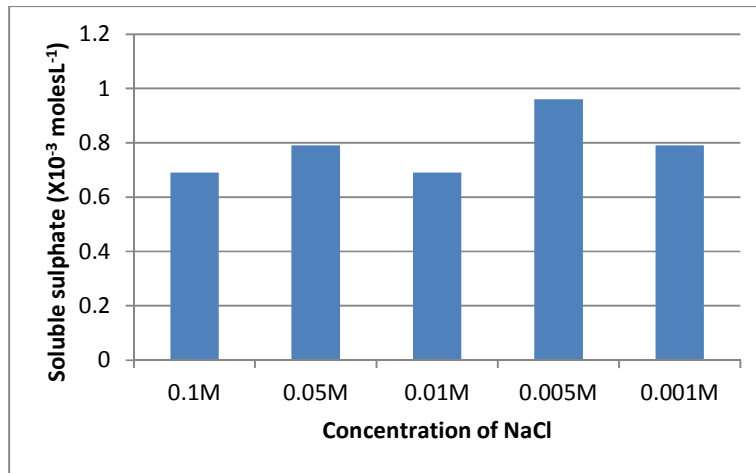


Fig. 6. Amount of soluble sulphate produced from solubility of  $CaSO_4$  at pH 5.5 under pressure  $5 \text{ Kg/cm}^2$  at different ionic strengths

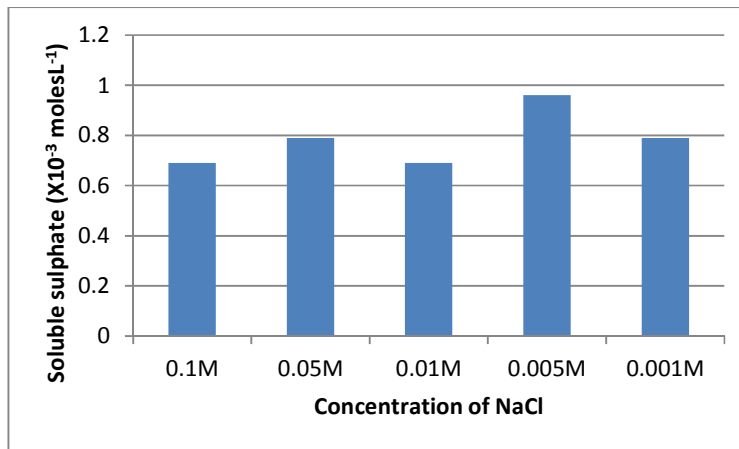


Fig. 7. Amount of soluble sulphate produced from solubility of  $CaSO_4$  at pH 6.0 under pressure  $5 \text{ Kg/cm}^2$  at different ionic strengths

The results obtained from experiments boiling temperature of water are presented in performed at higher pressure ( $10 \text{ Kg/cm}^2$ ) and at Figs. 1-7.

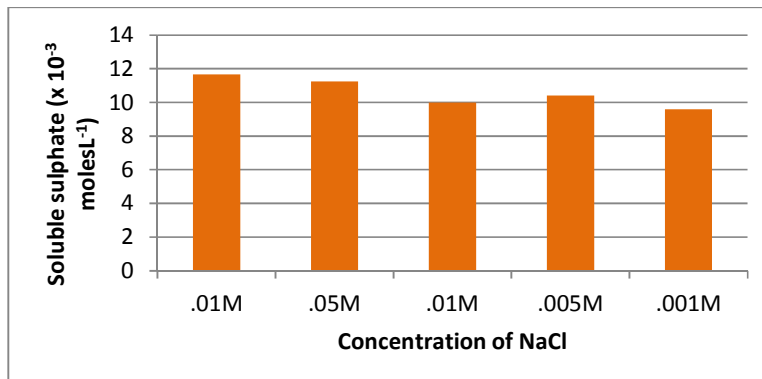


Fig. 8. Amount of soluble sulphate produced from solubility of  $CaSO_4$  at pH 3.0 under pressure  $10 \text{ Kg/cm}^2$  at different ionic strengths

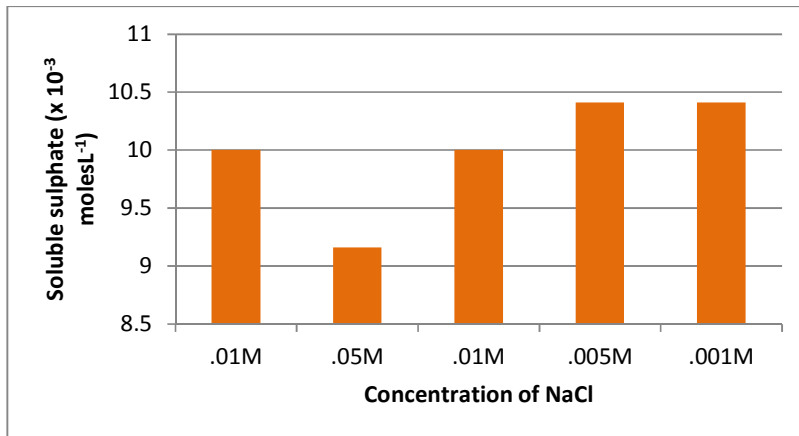


Fig. 9. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 3.5 under pressure 10 Kg/cm<sup>2</sup> at different ionic strengths

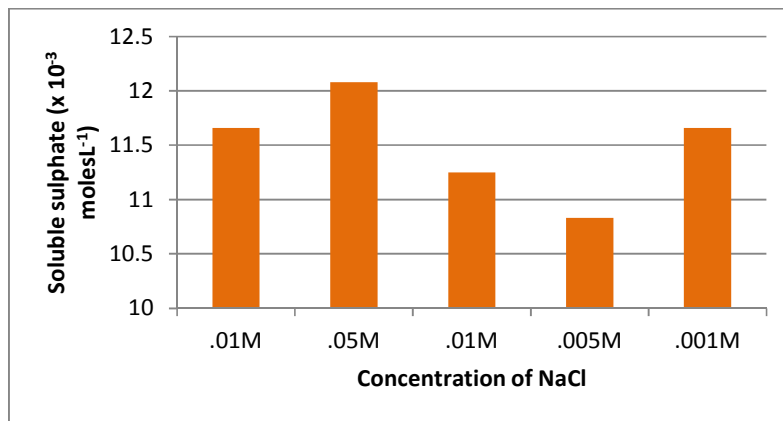


Fig. 10. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 4.0 under pressure 10 Kg/cm<sup>2</sup> at different ionic strengths

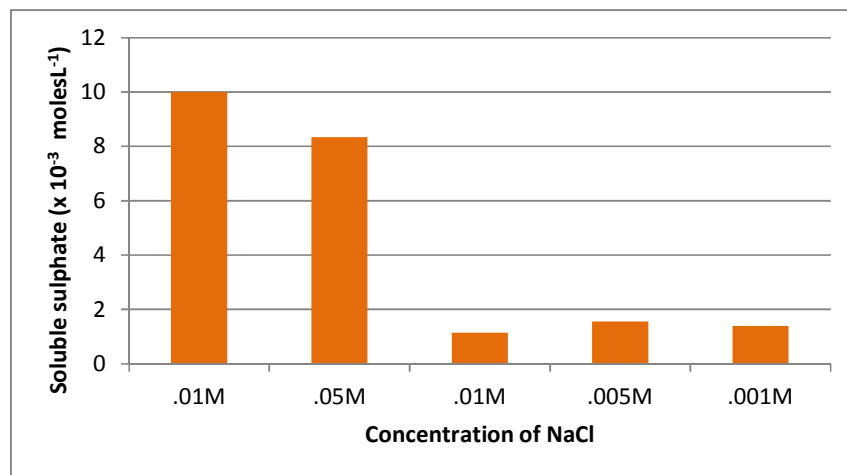


Fig. 11. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 4.5 under pressure 10 Kg/cm<sup>2</sup> at different ionic strengths

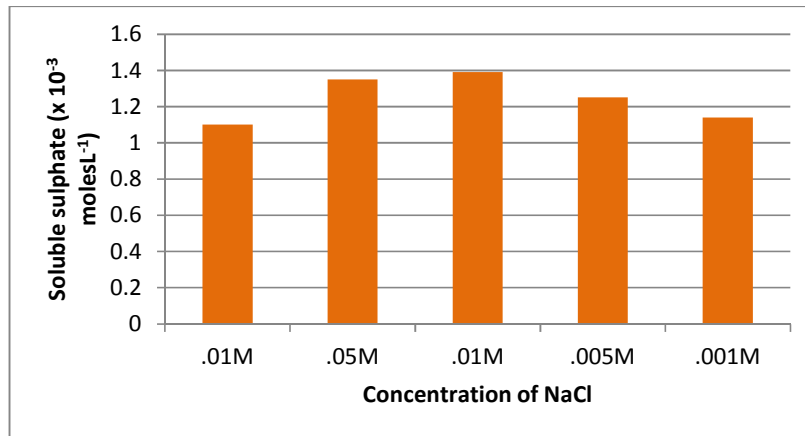


Fig. 12. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 5.0 under pressure 10 Kg/cm<sup>2</sup> at different ionic strengths

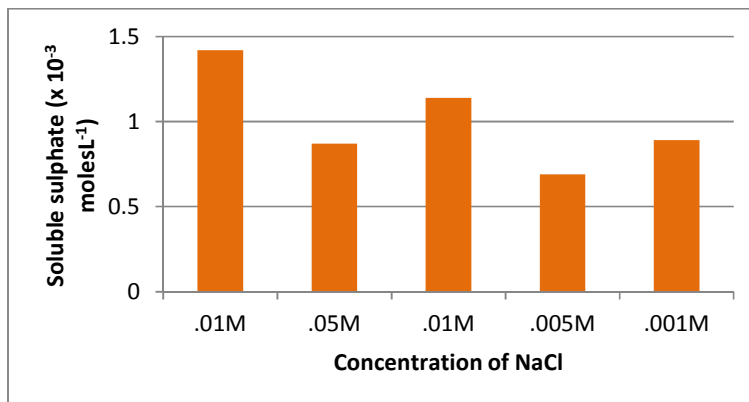


Fig. 13. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 5.5 under pressure 10 Kg/cm<sup>2</sup> at different ionic strengths

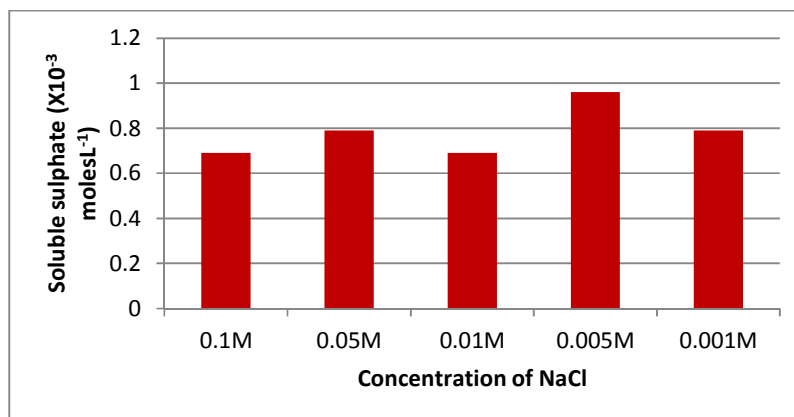


Fig. 14. Amount of soluble sulphate produced from solubility of CaSO<sub>4</sub> at pH 6.0 under pressure 10 Kg/cm<sup>2</sup> at different ionic strengths

Flint [11] observed variation of solubility of calcium sulphate at different brine concentrations which follows a similar pattern and a decrease in solubility, after a concentration twice that of



natural sea water (19% Cl sea water). In the present study, at a particular ionic strength of NaCl solution, the pattern of soluble sulphate is more or less similar in the pH range 3.0 – 6.0. Little variation of CaSO<sub>4</sub> solubility with increase of NaCl concentration has also been noticed. However, comparatively higher values of soluble sulphate are found when the experiments were performed at lower pressure.

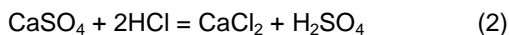
In studying the solubility of CaSO<sub>4</sub> in the presence of NaCl, some calcium chloride and sodium sulphate are formed.



where  $\Delta G_{293}$ , the free energy of reaction, is +15.5 Kcal/mole. The positive value of  $\Delta G$  suggests a non-spontaneous reaction and in fact, the reverse reaction might occur with precipitation of CaSO<sub>4</sub>. Consequently, little variation in solubility of CaSO<sub>4</sub> with increase in NaCl concentration has been found. Our assumption is strongly supported by Flint [11], who found very little increase in solubility with increase in NaCl concentration both in distilled water and sea water.

Another important observation was that during adjustment of the solution at a particular pH, very little dilute hydrochloric acid was added. There might be an effect of HCl solution on the solubility of CaSO<sub>4</sub>. In this work, a pH range 3.0-6.0 was considered and to adjust the pH 3.0, highest amount of the acid was added. If HCl has any influence on the solubility of CaSO<sub>4</sub>, highest quantity of soluble sulphate would have been observed at pH 3.0. But it is not observed at pH 3.0 because highest soluble sulphate has been noticed at pH 5.0 when the pressure is 5 Kg/cm<sup>2</sup>. This reveals that the presence of HCl did not have any influence on the solubility of CaSO<sub>4</sub>.

It has been shown that reaction of CaSO<sub>4</sub> with HCl forms calcium chloride and sulphuric acid (equation 2) [11].



where  $\Delta G_{293}$  is +19.5 Kcal/mole which suggests that no increase in solubility of calcium sulphate would be observed; in this case also, the reverse might occur with precipitation of the compound. The positive free energy in equations 1 and 2 are less energetic and results in a lower dissolution of calcium sulphate. Thus it is evident from the positive  $\Delta G$  values that the presence of NaCl and

HCl did not influence largely on the dissolution of CaSO<sub>4</sub> at different pH values and ionic strengths of the solutions.

#### 4. CONCLUSION

In this study, it is clear that accurate solubility experiment is important to depict the behaviour of calcium sulphate in aqueous medium in the presence of different concentrations of NaCl at the boiling temperature of water under pressures of 5 and 10 Kg/cm<sup>2</sup>. At lower pH (pH 3-6), hydrochloric acid is also present, although very little amount. The solubility of calcium sulphate was determined from the amount of soluble sulphate. In aqueous medium, release of sulphate reaches a maximum at pH 5.0 when the concentration of NaCl was 0.05 M in the experiment performed under pressure 5 Kg/cm<sup>2</sup> while at pressure 10 Kg/cm<sup>2</sup>, highest soluble sulphate was recorded at pH 4.0 at 0.05M concentration of NaCl. An interesting observation is that the difference of highest to lowest values of soluble sulphate in the pH range 3.0-6.0 at 0.001M NaCl solution is 2.92 moles L<sup>-1</sup>, at 0.005 M is 2.08 moles L<sup>-1</sup>, at 0.01 M is 9.58 moles L<sup>-1</sup>, at 0.05 M is 3.96 moles L<sup>-1</sup>, and at 0.1 M is 5.0 moles L<sup>-1</sup> under 5 Kg/cm<sup>2</sup> pressure while under 10 Kg/cm<sup>2</sup> pressure, difference of sulphate content is more than 10 moles L<sup>-1</sup> in the concentrations of NaCl, studied here. At either pressure, however, the solubility of calcium sulphate increases from pH 3.0 to 4.0 in all the concentrations of NaCl. As the report on solubility of calcium sulphate at different pH and very low concentrations of NaCl is not known, the results obtained in this study will help to further understanding on the extent of the solubility of calcium sulphate under different parameters, used here.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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