

Relations for the determination of the polymorphic composition of calcium carbonate precipitated in saturated sodium chloride solutions

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The purification of concentrated sodium chloride solutions from calcium and magnesium ions is realized by precipitating them in the form of calcium carbonate and magnesium hydroxide using a reagent solution composed of sodium carbonate and sodium hydroxide. The functioning of the industrial process depends on the polymorphic composition of the precipitated calcium carbonate. The classical experimental design method is used to obtain quantitative relations and graphical presentations expressing the polymorphic composition of the precipitated calcium carbonate as a function of stoichiometric ratios between calcium and magnesium ions and their respective precipitation reagents. These relations can be used in practice for the determination of operating conditions permitting the well functioning of industrial installations of brine purification.

Introduction

Many industrial processes are used to purify concentrated (saturated) sodium chloride solutions from calcium and magnesium ions by precipitating them as calcium carbonate and magnesium hydroxide, respectively. Calcium carbonate can precipitate in three crystalline forms: vaterite, aragonite and calcite. During the purification processes, the aragonite is undesirable, because this polymorph generates many operational problems (very small particles, difficult liquid-solid-separation processes, etc.). On the contrary, the precipitation of calcium carbonate as calcite sensibly ameliorates the functioning of the purification process. In addition, we can note that the presence of vaterite does not pose any problem, because it is a metastable phase of calcium carbonate at ambient conditions at the surface of the earth. Therefore, once vaterite is exposed to water, it is transformed principally to calcite (Dandeu et al., 2005). Many previous studies are interested in the formation of calcium carbonate polymorphs (Zhon and Mucci, 1989; Tai and Chen, 1998; Chen and Xiang, 2009), but until now no any study is published

about the polymorphic composition during the precipitation of calcium carbonate in saturated sodium chloride solutions. In this context, the aim of our study is to find some mathematical relations and graphs expressing the polymorphic composition of the precipitated calcium carbonate as a function of operating conditions in order to determinate the operation domain where the produced precipitate is in majority composed of calcite.

Experimental

Experimental set up and operation mode

The precipitation of calcium carbonate and magnesium hydroxide is carried out at 60°C (generally the temperature of the industrial process) in a standard batch reactor of 2.5L under nitrogen atmosphere. The reactor has a diameter of 15cm and four baffles of 1.5cm. It is equipped with a four pitched blade turbine with a stirring speed of 700rpm (Fig. 1). Also, nitrogen is bubbled for many hours in all reagent solutions in order to eliminate dissolved carbon dioxide before precipitation. The brine used in all experiment is a concentrated sodium chloride solution 5M containing 1.5 gL⁻¹ of Ca²⁺ and 0.050 gL⁻¹ of Mg²⁺. The precipitating agent is a prepared sodium chloride solution 5M where sodium carbonate and sodium hydroxide at variable concentrations are added (so the initial sodium chloride solution containing Ca²⁺ and Mg²⁺ will be not diluted after mixing).

First, the reactor is filled with brine and heated in order to obtain the temperature value of 60°C. After that, a fixed small quantity of the reagent solution is rapidly added in the reactor (injection time less than 2s). After 2 min the precipitation of calcium and magnesium ions is finished and samples of suspension are taken from the reactor.

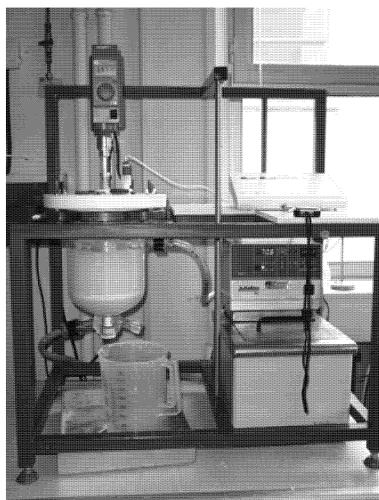


Fig.1. Experimental set-up

The samples are filtered and the solid phase is washed and dried for the determination of the polymorphic composition by Raman spectroscopy according to an original methodology. More about this methodology can be found in Dandeu et al., 2006 and Carteret et al., 2009. Many solid samples are observed by scanning electron microscopy in order to valid the data obtained by Raman spectroscopy.

Experimental design

The aim of our work is to clear up the influence of sodium carbonate and sodium hydroxide initial concentrations on the polymorphic composition at the end of the precipitation process after 2 min of the injection of reagents solution.

If the solid phase stays more time in the reactor, the polymorphic composition can vary due to the phase transformation phenomenon (Dandeu et al., 2005).

At today level of knowledge, it is impossible to predict theoretically the polymorphic composition of precipitated calcium carbonate from concentrated brines in the presence of magnesium ions, so the experimental design method is used to obtain some empirical relations for predicting the polymorphic composition of the precipitated calcium carbonate as a function of reagents stoichiometric ratio M and R defined by following expressions:

$$M = \frac{n_{\text{CO}_3^{2-}}}{n_{\text{Ca}^{2+}}} \quad \text{and} \quad R = \frac{n_{\text{OH}^-}}{2 \cdot n_{\text{Mg}^{2+}}} \quad (1)$$

where "n" is the number of moles corresponding to subscript ions.

A 3^2 experimental design is used to obtain the empirical expressions of the calcium carbonate polymorphic composition as a function of M and R. Table 1 shows the level variations of the experimental design, while in Table 2 corresponding real values are presented.

Experimental results

The experimental results of polymorphic composition of precipitated calcium carbonate obtained by Raman spectroscopy are presented in Table 3. In some cases, the sum of percentages of calcite and aragonite does not give exactly 100%, but is some % lower. This is principally due to the error of determination by Raman spectroscopy, which is several % (Dandeu et al., 2005). On the contrary, in the case of experiments 6 and 8, it is a great difference between the sum of percentages and 100%. We thought that this is due to the formation in appreciable quantities of vaterite. To valid this assumption, the corresponding solid samples are observed by scanning electron microscopy, which showed qualitatively an important presence of vaterite.

Two relations expressing the percentage of calcite and aragonite as a function of precipitation parameters "M" and "R" are obtained by the mathematical treatment (Minitab package) of the experimental data according to the experimental design method. These expressions are:

Table 1. The 3^2 experimental design used to obtain the empirical relations

N° of experiment	R	M
1	1	1
2	-1	1
3	1	0
4	0	-1
5	-1	-1
6	0	0
7	-1	0
8	1	-1
9	0	1

Table 2. Real values of initial reagents concentrations in the reactor after mixing and corresponding "M" and "R" values.

	-1	0	1
OH ⁻ concentration, mol L ⁻¹	4.20·10 ⁻³	6.05·10 ⁻³	7.94·10 ⁻³
CO ₃ ²⁻ concentration, mol L ⁻¹	3.02·10 ⁻²	3.78·10 ⁻²	4.53·10 ⁻²
M	0.80	1.00	1.20
R	1	1.46	1.92

$$\% \text{ of calcite} = 10.5 + 6.08 \cdot R - 13.7 \cdot M - 4.52 \cdot R^2 + 18.4 \cdot M^2 - 1.03 \cdot M \cdot R \quad (2)$$

(correlation coefficient $r = 0.88$)

$$\% \text{ of aragonite} = 84.0 - 10.2 \cdot R + 19.6 \cdot M + 3.58 \cdot R^2 - 19.5 \cdot M^2 + 7.55 \cdot M \cdot R \quad (3)$$

(correlation coefficient $r = 0.96$)

These equations clearly show the influence of each reagent in the formation of calcium carbonate polymorphs in the presence of magnesium ions. So, the excess of sodium carbonate increases the presence of aragonite, while the insufficiency of this one increases the presence of calcite. On the contrary, the excess of sodium hydroxide favours the production of calcite, but the global influence of hydroxyl ions on the polymorphic composition of precipitated calcium carbonate is sensibly lower than the influence of carbonate ions. The above experiments are carried out in relatively restrictive intervals of parameter values variation ($0.80 < M < 1.20$ and $1 < R < 1.92$). In a new experimental campaign, the parameters "M" and "R" are varied from 1.2 to 1.6 for M, and from 1.9 to 2.5 for R. In addition, two supplementary experiments at very low sodium carbonate concentration corresponding to $M = 0.50$ and $M = 0.60$ keeping "R" constant ($R = 1.9$) are carried out in order to extrapolate the results in a domain of lower importance for industry. The synthesis of all experimental results allows to obtain a 2D graph with iso-percentage lines representing the calcite and aragonite percentage (Figs. 2 and 3) as a function of "M" and "R".

Table 3. Experimental data of calcium carbonate polymorphic composition as a function of the reagents stoichiometric ratio "M" and "R".

N° of experiment	R	M	% of calcite	% of aragonite
1	1	1	22	78
2	-1	1	7	90
3	1	0	11	85
4	0	-1	56	39
5	-1	-1	22	72
6	0	0	5	82
7	-1	0	7	92
8	1	-1	41	30
9	0	1	8	92

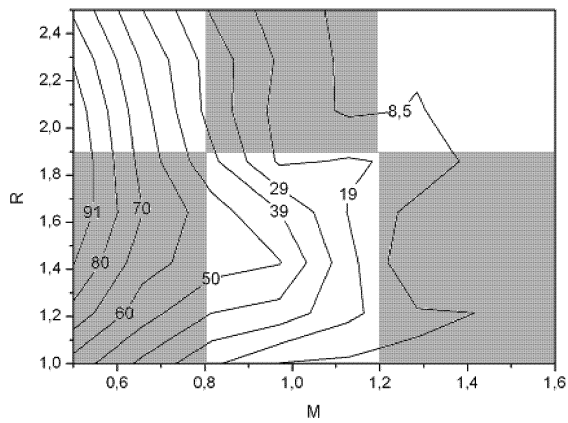


Fig.2. Calcite iso-percentage lines as a function of "M" and "R".

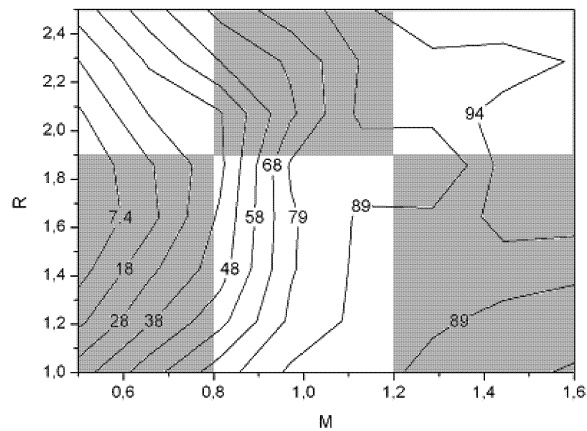


Fig.3. Aragonite iso-percentage lines as a function of "M" and "R".

In these figures, zones in grey are not investigated; the iso-percentage lines are plotted by extrapolation only using the mathematical expressions experimentally obtained of other zones.

In Figs. 2 and 3 it is clearly shown that the sodium carbonate stoichiometric ratio "M" sensibly influences the polymorphic composition of precipitated calcium carbonate. For $M > 0.9$, aragonite is predominant, while for $M < 0.8$ calcite is in larger quantity. In addition, for $0.8 < M < 0.9$, polymorphic mixtures of about 50% of calcite and 50% of aragonite can be obtained. Figs. 2 and 3 also show that sodium hydroxide stoichiometric ratio slightly influences the polymorphic composition of precipitated calcium carbonate. The results especially presented in Figs. 2 and 3 are very important for the industrial process. Firstly, the slight influence of sodium hydroxide stoichiometric ratio on polymorphic composition of precipitated calcium carbonate is a valuable information; the excess of hydroxyl ions in the process will be determined only in relation to the

desired outlet concentration of magnesium ions in concentrated sodium chloride solution. Secondly, a very low (desired) concentration of calcium ions can be attained only when an excess of sodium carbonate is used ($M > 1$). Our study has shown that under this condition the precipitated calcium carbonate is composed in majority of aragonite, which is, as mentioned above, not appreciated by the industrialists. Calcite is produced when "M" is low (less than 0.8). According to this information the question is: how to design a process providing a sodium chloride solution of high purity (excess of sodium carbonate at the outlet of the installation, i.e. $M > 1$) and simultaneously producing a solid phase composed in majority of calcite? At first glance, this seems incompatible, but it is easy to be realized by adding the reagents solution gradually. In this manner, during the precipitation, most of the time the stoichiometric ratio "M" will be less than 0.8 (producing calcite), and only in the end period of precipitation it will increase to be more than 1 (producing a small quantity of aragonite). Based on these considerations, an industrial continuous process is designed, but its description is out of the scope of this paper.

Conclusion

The purification of brines from Ca^{2+} and Mg^{2+} is realized by precipitating them with sodium carbonate (for Ca^{2+}) and sodium hydroxide (for Mg^{2+}). In spite of the fact that no any theory can predict the polymorphic composition of calcium carbonate precipitated under these conditions, an experimental design method can be successfully used to obtain the polymorphic composition (Figs. 2 and 3) as a function of reagents stoichiometric ratio "M" and "R". Based on these results, operating conditions can be established in industrial scale in order to obtain the desired calcium carbonate polymorph.

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