Morphology of carbonates particles precipitated from saline waste solution: Influence of magnesium

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Abstract. The role of a very low concentration of Mg on the nature, morphology and surface of carbonate particles during soda-ash residual brine carbonation has been studied. The Mg concentration of 200 mg/kg in brine slows down the kinetic of carbonation, modifies the shape of precipitated particles and new carbonated phases are precipitated. The existence of aragonite and (Ca, Mg) hydrated phases is supposed for Ca:Mg ratio equivalent to 24:1 in solid fraction.

1. Introduction

The ammonia soda process is used to produce sodium carbonate and bicarbonate from two raw materials, lime and NaCl brines. The by-products are residual brines, they are now landfilled and the surnageant is sent to the nearest river or the sea. Efforts have to be done on brine treatments to decrease their environmental impact. In this study, by-products are carbonated by bubbling to avoid unsuitable phase formation during landscape storage. This method has two environmentally advantages: the precipitation of stable carbonates and the carbon dioxide sequestration. During carbonation of brines, initial chemical composition and contained mineral phases affect precipitated carbonates nature and reactions kinetics. Availability of calcium and magnesium [1]seems to be significant factors influencing carbonation with pH, temperature and CO₂ pressure [2]. The main components of brine are chlorine, calcium, potassium and sodium. Four carbonatable phases are identified: Ca(OH)₂, Mg(OH)₂, CaOHCl and CSH [3,4,5]. Competition between ions present in solution can influence the nature of precipitated carbonates: a high concentration in Ca⁺ favors calcite formation [6]. Contrary to Ca, the ions of Mg stabilize amorphous, unstable and hydrated phases [1,7] and so decrease the quantity of well crystallized carbonates. Magnesium incorporation also inhibits carbonate growth and seems to change their morphology, from rhombohedral to spindle-like shape [8,9,1]. Magnesium influence is well known in sea water or in brine with a Mg:Ca ratio superior to 1:1.

The Mg:Ca ratio is generally inferior or equivalent to 1:3000 in liquid fraction of residual brines from soda-ash process. Thus, the aim of this study is to understand the role of a very low concentration of Mg on brine carbonation.

Infrared spectroscopy and electronic microscopy are applied to study the role of Mg on the nature, morphology and surface carbonates. The final objective is to establish a relation between low Mg concentration in brine and properties of carbonated phases.
2. Experimental procedure
To study the role of Mg on carbonation, brines from ammonia-ash process were filtrated (<10μm) to eliminate solid fraction (>100μm). Indeed, solubilization of solid phase could add new ions in liquids and so perturb the initial equilibrium. Resulting liquids are then carbonated by bubbling (15%CO₂ - 85% air, total flowrate: 67 L/h) in a 30 L reactor at 55°C. The same experiment is done with different concentrations of added soluble magnesium (MgCl₂.6H₂O, Merk). Four Mg concentrations have been studied: 0, 25, 100 and 200 mg/kg of brine. During brine carbonation, pH decreases from 10.3 to 5.7. Thus, monitoring the pH is used to control the carbonation progress. The pH value is measured continuously during experiments. Samples are taken at three stable pH values: 9.5, 8 and 7.2. Samples are then filtrated at 0.45 μm in a Teflon Millipore compressed air system (2 bar). Liquids are acidified for analyses. Solids are frozen and lyophilised to eliminate free water. Chemical compositions of solid and liquid phases have been determined by inductively coupled plasma mass spectroscopy (ICP-MS) excepted for CO₃²⁻ done by ACA and Ca. Solid samples have been studied by diffuse reflectance infrared Fourier transform spectroscopy. Infrared spectra were recorded with a Fourier Transform Infrared (FTIR) spectrometer (BRUKER IFS 55) equipped with a large band (5500–600 cm⁻¹) mercury–cadmium telluride (MCT) detector cooled at 77K. Solids were investigated morphologically by scanning electron microscopy (SEM), with a Hitachi S-4800. Dispersed solid powder was deposited on a carbon ribbon and examined at 5 kV. For particles analyses, a high-resolution transmission electron microscope (TEM), a CM 20 Philips was used at 200 kV with energy dispersion spectroscopy (EDS). In TEM, the powder was dispersed in alcohol and deposited on a copper grid.

3. Results and discussion
3.1. Chemical analysis
Chemical composition of solid fraction shows significant evolution of carbonate composition in function of Mg content. Initial CO₃ concentration at pH 10.3 is considered near to 0 mg/kg. The carbonate concentration in filtrated brines without added Mg (Figure 1) is around 380 mg/kg and does not evolve between pH 9.5 and pH 7.2. It signifies that most of the carbonation occurs between initial pH 10.3 and pH 9.5. When a weak quantity of Mg (25 mg/Kg) is added, carbonation rate is not affected. On the contrary, CO₃ concentration continuously raises (125 to 350 mg/kg) from pH 10.3 to 7.2 for 200 mg/kg of Mg.

![Figure 1. Evolution of CO₃ content in the solid fraction during carbonation of filtrated brine in the presence of different concentrations of additional Mg.](image-url)
According to the literature [8,9,1], Mg adsorbed on carbonates inhibits their growth and so decreases carbonation rate. The new results of this study concern the non-linear influence of Mg on carbonation rate. Indeed low Mg concentrations (25 mg/kg) do not influence carbonate precipitation rate whereas higher Mg quantities (100-200 mg/kg) decrease significantly the carbonation rate. The Mg concentration can reach 120 mg/kg in the non filtrated brines, the influence of Mg ions on carbonate rate can not be considered as negligible in these conditions.

The Ca:Mg ratios have been calculated in liquid and solid fractions. Figure 2 presents the evolution of Ca:Mg ratio during carbonation in function of Mg quantity. At alkaline pH (9.5), the additional Mg is precipitated immediately in a non soluble stable Mg(OH)₂ phase. Between pH 9.5 and 8, Mg is solubilized and the ratio Ca:Mg is decreasing in liquids. For the three first samples (0, 25 and 100 ppm Mg) a stabilization is observed for pH values inferior to 8 (Figure 2a). The solubilization rate of Mg seems to be comparable to the rate of Mg incorporation in carbonates, the Ca:Mg ratio is then stabilized. For higher Mg concentration (200 ppm) is magnesium solubilized in solution faster than its incorporation in carbonates.

![Figure 2. Evolution of Ca:Mg ratio in liquid (a) and solid (b) fraction during carbonation of filtrated brine in the presence of different concentration of Mg.](image)

Figure 2b shows that the Ca:Mg ratio in solid fraction increases during carbonation. It means that Ca is more carbonated than Mg in all samples. Considering the low Mg concentrations and the slow Mg solubilization rate, this result is not surprising. At stable neutral pH (7.2), Mg(OH)₂ should be completely solubilized, then Mg present in solid fraction can be associated exclusively to carbonates. Without additional Mg, less than 0.1 wt% of Mg is present in carbonates. For 25 and 100 ppm of added Mg, the capture of Mg by carbonates is estimated at 1%. These values are coherent with adsorption of Mg ions on calcite lattice for advanced carbonation (pH 7.2). In the last solid sample (200 ppm Mg), Ca:Mg ratio is equal to 24:1 for neutral pH values. Are all Mg ions (5 wt%) adsorbed at the surface of calcite or are others carbonated phases precipitated?

3.2. FTIR spectral analysis

The all diffuse reflectance FTIR spectra of carbonated brine samples are almost similar at pH 9.54 (Figure 3a). Main peaks 875, 1462 and 713 cm⁻¹ correspond respectively to ν₂, ν₃ and ν₄ of calcite CO₃ vibrations [10]. Peaks at 2513, 2875 and 2987 cm⁻¹ are attributed to calcite harmonics. Gypsum is identified by 1134-1162 cm⁻¹ doublet and 1637 cm⁻¹ corresponding respectively to ν₃(SO₄), and
ν₂(H₂O). A detailed observation of spectra between 3600 and 3800 cm⁻¹ (Figure 3b) indicates a peak at 3698 cm⁻¹ assigned to the infrared active hydroxyl stretching vibration of Mg(OH)₂. At pH 9.5, this peak is present in the three samples with added Mg. The Mg(OH)₂ band disappears at pH 8 for 25mg/kg of Mg. When carbonation is advanced (pH 7.2), this band is only visible for higher Mg concentrations (200 mg/kg of added Mg). Thus, more brine is carbonated, less Mg(OH)₂ band is visible. Others absorption features at 3639 and 3656 cm⁻¹ are observed at pH 9.5 and 200 mg/kg of added Mg (Fig.3b). The first peak corresponds to OH stretching vibration of Ca(OH)₂ and is visible in this condition only. A pure sample of Ca(OH)₂ (Merk) presents a peak in diffuse reflectance at 3645 cm⁻¹, the 6 cm⁻¹ of difference in the studied Mg-sample is attributed to the substitution of Ca by Mg in portlandite lattice. The other band (3656 cm⁻¹) may be attributed to OH stretching vibration of a hydrated magnesium carbonate, Hydromagnesite Mg₅(CO₃)₄(OH)₂•4(H₂O) [10].

IR-spectra of carbonated brines at pH 7.2 are almost identical to the precedent spectra at pH 9.5 excepted little features. Detailed spectrum of 800-950 cm⁻¹ vibrations (Figure 4) shows three peaks. The major peaks at 871 and 712 cm⁻¹ correspond to ν₂(CO₃) and ν₄(CO₃) of calcite. A third feature is observable at 854 cm⁻¹ for 200 mg/kg of Mg and could be assigned to ν₂(CO₃) of aragonite or to an hydrated Mg carbonate, Nesquehonite (MgCO₃.3H₂O) [10]. The hypothesis of aragonite presence is reinforced by an anomaly at 1082 cm⁻¹ only present in the sample carbonated in presence of 200 mg/kg of Mg.

A model of phases evolution during brine carbonation in presence of a low but non negligible Mg concentration can be proposed. Calcium hydroxides present initially in brine disappear at pH 9.5 excepted for higher Mg concentration. Without additional Mg, Ca(OH)₂ is carbonated at the beginning of bubbling, between pH 10.3 and 9.5. Magnesium presence changes the equilibrium, Mg²⁺ competes with Ca²⁺ and so inhibits calcite precipitation [11,12]. Contrary to Ca(OH)₂, Mg(OH)₂ seems to be solubilized and carbonated continuously from pH 9.5 to pH 7.2.

Figure 3. FTIR spectra of carbonated brine (pH 9.54) with different Mg concentrations (a) and (b) 3500-3800 cm⁻¹ detailed spectra.
Figure 4. Detailed FTIR spectra (3500-3800 cm\(^{-1}\)) of carbonated brine (pH 7.18) with different added Mg concentrations.

In non filtrated brines, Mg is slowly liberated by Mg-minerals (silicates, hydroxides...) and its concentration in liquids can exceed 100 mg/kg for neutral pH. The proportion of Mg liberated in solution increases as pH decreases. IR results indicate that hydrated Mg hydroxy-carbonates can be precipitated at the beginning of carbonation. And then, in neutral pH, Mg adsorbed at the carbonate surface seems to stabilize unstable calcium carbonates (aragonite) as confirmed by Figure 3 that corroborates with result of Folk [8].

3.3. Microscopic observations

Photos presented in Figure 4 show the consequences of Mg addition on the morphology of carbonate particles. With low Mg concentration, the size of calcite particles (Figure 4a) can reach 7µm with rhombohedral and sharped extremity. Many ramifications are observed. Magnesium presence on carbonate surface leads to decrease particles size (3-4µm maximum for 200 mg/kg of Mg) and particles extremities become round. The number of particle ramifications falls significantly. In theory this morphologic changes are explained by the difference of Ca and Mg ions diameters.

Figure 4. Particle photos (SEM) of filtrated brines solid fraction carbonated until pH 7.2 without added Mg (a) and with 200 mg/kg of added Mg (b).
SEM photo (Figure 4b) also reveal the presence of a film at the surface of carbonate particles for highest Mg concentrations. It can correspond to the precipitation of amorphous phase by a dissolution-reprecipitation process at the interface carbonate-brine solution and later the interface air-carbonate during liophylisation[1]. Analyses with TEM-EDS indicate that only 2-3% of Mg are incorporated near particle extremities, it is sufficient to radically change calcite morphologies.

4. Conclusion
This study demonstrates that low Mg concentrations (200 mg/kg) have an influence on brine carbonation.

- In residual brines, Mg(OH)2 is solubilized for pH values inferior to 9.5. The incorporation of Mg in portlandite particles stabilizes hydroxide phases and decreases the availability of Ca at basic pH (9.5).
- Mg has an influence on carbonation of calcite. Magnesium slows down the kinetic of carbonation and modifies precipitated particles shape.
- At 200 mg/kg of additional Mg, new carbonated phases have been precipitated. Hydrated magnesium carbonates and an intermediate polymorph of CaCO3 (aragonite) have been detected by infrared spectroscopy. Amorphous carbonated phases are observed on calcite surface in presence of Mg.

This study reveals the importance of Mg parameter to control the carbonation of low Mg:Ca brines. Higher Mg concentrations have to be tested in further works as well as higher CO2 flow rates to confirm findings results and envisage a better control of precipitated phases.

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