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Simulation of stable and metastable sea-type carbonate systems for optimization of $MgCO_3 \cdot 3H_2O$ precipitation from waste sea brines

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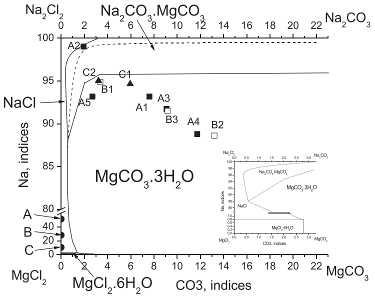
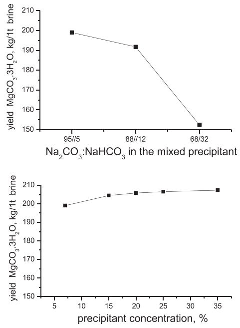
HIGHLIGHTS

- Thermodynamic modeling of stable and metastable sea-type four component carbonate systems
- Thermodynamic simulation of alkaline precipitation of metastable $MgCO_3 \cdot 3H_2O$ from waste sea brines
- Design of the purified $MgCO_3 \cdot 3H_2O$ precipitation from waste sea brines

GRAPHICAL ABSTRACT



Thermodynamic modeling



Design of $MgCO_3.3H_20$ precipitation from waste brines (initial Mg^{2+} content 2.72%)

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ABSTRACT

The thermodynamic simulation of the systems $Na^+, Mg^{2+}/Cl^-, CO_3^{2-}//H_2O$ and $Na^+, Mg^{2+}/SO_4^{2-}, CO_3^{2-}//H_2O$ using the Pitzer method at 25 °C revealed that both stable and metastable crystallizations take place in these systems. $MgCO_3 \cdot 3H_2O$ is always a metastable phase. Thermodynamic modeling of Mg^{2+} removal as a part of desalination of hyper-saline sea-salt waste brines, which can be described by these systems, pointed to the co-precipitation of various salts. Ensuing from the obtained data and considering the crystal chemistry and kinetic crystallization of the co-crystallizing salts we designed the precipitation of $MgCO_3 \cdot 3H_2O$ from sea-salt brines avoiding its further transformation to metastable $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ and stable $MgCO_3$. Our experimental studies confirmed the designed method and optimized the conditions for precipitation of high-purity $MgCO_3 \cdot 3H_2O$ with good filtration characteristics.

1. Introduction

Sea water is a complex multicomponent system where almost all chemical elements are present in different concentrations (macro, micro and trace) and forms (simple and complex ions, dissolved gases, etc.). Therefore, sea water can be used as a source for the extraction of useful substances, also resulting in sea water desalination. Different desalination processes such as membrane desalination [1], reverse osmosis [2], evaporation processes, and evaporation–cooling processes [3] are applied. The extraction of NaCl and production of sea-salt, based on solar sea water evaporation, are the most widespread methods

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in the countries with a hot or temperate climate. All these technologies generate hyper-saline waters as waste products. The desalination of hyper-saline waters is an important issue with respect to the environment. Macro elements are mainly of interest from a practical point of view for preparation of different salts. The development of easy and non-expensive technologies is an economic and environmental issue. According to the macro element composition, sea waters and brines can be defined as a seven-component system Na^+, K^+, Mg^{2+}, Ca^{2+}/Cl^-, SO_4^{2-}, $CO_3^{2-}//H_2O$, called sea-type system. This system, as well as its sub-systems, has been a subject of extensive experimental and theoretical studies. The six-component sub-system Na^+, K^+, Mg^{2+}, Ca^{2+}/Cl^-, $SO_4^{2-}//H_2O$ has been partially investigated mainly in the crystallization field of NaCl [4–6]. The most investigated five-component sub-system is Na^+, K^+, Mg^{2+}/Cl^-, $SO_4^{2-}//H_2O$ [4–10], while the most investigated reciprocal four-component sub-systems are Na^+, Mg^{2+}/Cl^-, $SO_4^{2-}//H_2O$ [4–9,11–13] and K^+, Mg^{2+}/Cl^-, $SO_4^{2-}//H_2O$ [4–9,14,15]. There are scarce literature data on the systems Na^+, Mg^{2+}/Cl^-, $CO_3^{2-}//H_2O$ and Na^+, Mg^{2+}/SO_4^{2-}, $CO_3^{2-}//H_2O$. The latter two systems have been partially investigated at 25 °C [16] and crystallization of eitelite ($Na_2CO_3 \cdot MgCO_3$), northupite ($Na_2CO_3 \cdot MgCO_3 \cdot NaCl$) and $2Na_2CO_3 \cdot 2MgCO_3 \cdot Na_2SO_4$ has been reported; however, their crystallization fields have not been determined. Crystallization of $MgCO_3 \cdot 3H_2O$ has been established in a chloride–carbonate system in the presence of CO_2 [17,18]. The most studied sub-systems are the three-component and the two-component ones for which complete data over a wide temperature range are compiled.

The removal of the macro elements from sea waters and brines is based on the knowledge of the above systems. In this study we elucidate the removal of Mg^{2+} ions from hyper-saline waste sea-salt brines and the precipitation of $MgCO_3 \cdot 3H_2O$ on the base of solubility/crystallization in Na^+, Mg^{2+}/Cl^-, $CO_3^{2-}//H_2O$ and Na^+, Mg^{2+}/SO_4^{2-}, $CO_3^{2-}//H_2O$ systems. The literature data on the precipitation of $MgCO_3 \cdot 3H_2O$ from sea-salt brines are limited, focusing mainly on $MgCl_2$-rich brine. Wu et al. [19] used purified $MgCl_2$-rich brine and optimized the conditions for precipitation of $MgCO_3 \cdot 3H_2O$ with dilute (1 M) solution of NH_4HCO_3. Toyozo [20] started from waste sea-salt brine containing Ca^{2+} ions and first precipitated them as $CaCO_3$ with $(NH_4)_2CO_3$ or Na_2CO_3. Then, after membrane purification of the solution, $MgCO_3 \cdot 3H_2O$ crystallized. More literature studies deal with different raw materials rich in magnesium. Thus, Wang et al. [21] studied the homogenous, non-seeded precipitation of $MgCO_3 \cdot 3H_2O$ from $MgCl_2$ solution with $(NH_4)_2CO_3$ as a precipitant and found that the initial $MgCl_2$ concentration (0.5–4 M) and the temperature (15–60 °C) have a strong effect on the composition and morphology of the precipitated product. Other studies [22–24] reported the precipitation of pure $MgCO_3 \cdot 3H_2O$ to occur without co-crystallization of $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ at a stoichiometric ratio of $MgCl_2$ and Na_2CO_3 and a temperature below 40 °C. Judd [25] precipitated high-purity $MgCO_3 \cdot 3H_2O$ starting from a $Mg(OH)_2$ suspension using step-by-step carbonization with CO_2, followed by decarbonization of the $Mg(HCO_3)_2$ solution. Hiroshi [26] carbonized the same system consecutively with $(NH_4)_2CO_3$ and CO_2. Pohl et al. [27] obtained $MgCO_3 \cdot 3H_2O$ as an intermediate phase in the process of $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ precipitation starting from magnesium oxide and its further transformation into $Mg(OH)_2$.

The aim of the present work was to design, on the base of theoretical considerations, the removal of Mg^{2+} ions from waste sea-salt brines of salinity varying in a wide range, as $MgCO_3 \cdot 3H_2O$ of low impurity content and good filtration characteristics.

For this purpose a thermodynamical simulation of the stable and metastable equilibria in the four-component sea-type systems Na^+, Mg^{2+}/Cl^-, $CO_3^{2-}//H_2O$ and Na^+, Mg^{2+}/SO_4^{2-}, $CO_3^{2-}//H_2O$ at 25 °C was performed. As $MgCO_3 \cdot 3H_2O$ was found to precipitate as a metastable phase in both systems, the saturation indices (SI) of all eventually co-precipitated solid phases were calculated and their crystal chemistry and kinetics were also considerated. Further, the designed process was experimentally optimised.

2. Methods and experiments

2.1. Computational methods

2.1.1. Thermodynamic simulation of carbonate sea-type systems

A thermodynamic ion-interaction Pitzer model, PHREEQCI computer program, version 2.14.3, was used for simulation of the stable and metastable equilibria in the four-component systems Na^+, Mg^{2+}/Cl^-, $CO_3^{2-}//H_2O$ and Na^+, Mg^{2+}/SO_4^{2-}, $CO_3^{2-}//H_2O$ at 25 °C. The standard Pitzer approach was used [28]. The values of the binary parameters ($\beta^{(o)}$, $\beta^{(1)}$ and C^{φ}) and of the ternary parameters (Θ and Ψ), as well as the values of the standard chemical potentials of the solution species and the solid phases were taken from Harvie, Moller and Weare [29]. The database was extended by adding the solubility products of eitelite ($Na_2CO_3 \cdot MgCO_3$) [30] and northupite ($Na_2CO_3 \cdot MgCO_3 \cdot NaCl$) [31] crystallizing in these systems.

2.1.2. Thermodynamic simulation of the precipitation of high-purity $MgCO_3 \cdot 3H_2O$ from waste sea brines

The precipitation of $MgCO_3 \cdot 3H_2O$ from waste sea-salt brines was simulated using the Pitzer model. Because of the system complexity, the SI of six solid phases, which may precipitate under the experimental conditions, were calculated according to Eq. 1 and were further used as an indicator for possible co-precipitation.

$$SI = lg(IAP/K) \tag{1}$$

where IAP is the ion activity product, and K is the solubility product.

The calculations were done for three compositions of waste sea-salt brines by varying the precipitant composition and keeping the initial molar ratio $Mg^{2+}:CO_3^{2-}$ equal to 1:1 or 1:1.1.

2.2. Experiments

2.2.1. Materials

Starting waste sea-salt brines—three Black Sea waste brines with different compositions (Table 1), typical for the sea-salt production, were used in the laboratory experiments. The pilot-plant experiments were performed with only one of them (Brine A).

Precipitant—a mixture of technical grade Na_2CO_3 and $NaHCO_3$ in different ratios (95:5; 88:12 and 68:32), in the form of solid phase, suspension or solution (7, 10, 15, 20, 25 and 35%) was used in the experiments.

2.2.2. Laboratory studies

The laboratory experiments were designed on the base of the solubility diagrams of the Na^+, Mg^{2+}/Cl^-, $CO_3^{2-}//H_2O$ and Na^+, Mg^{2+}/SO_4^{2-}, $CO_3^{2-}//H_2O$ systems and aimed at optimizing the conditions for precipitation of $MgCO_3 \cdot 3H_2O$ of good filtration ability and low impurity content. Thus, the effects of brine and precipitant composition and concentration, amount of seeds used, reaction time and temperature were investigated. The precipitation of $MgCO_3 \cdot 3H_2O$ was carried out with the above alkaline carbonate/hydroxycarbonate precipitants at an initial molar ratio $Mg^{2+}:CO_3^{2-}$ of 1:1 or 1:1.1. The precipitant was quickly added to the waste brine under intensive mixing followed by adding of $MgCO_3 \cdot 3H_2O$ seeds in a quantity of 0.5% of the theoretical yield. The system was allowed to re-crystallize in a static regime for various times depending of the temperature and then was filtered. The solid phase was washed with water 4–5 times, dried at 50–70 °C and analyzed.

2.2.3. Pilot-plant studies

Pilot-plant studies were performed in order to optimize the technological processes. As the laboratory studies showed that the composition and concentration of the three studied brines did not influence the quality, but only the quantity of the final product, only brine A was used as a raw material in our pilot studies. Eight cycles were