

**STUDY OF THE CONVERSION OF  $\text{CaSO}_4$  TO  $\text{CaCO}_3$  WITHIN THE  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$  FOUR-COMPONENT WATER-SALT SYSTEM**

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The Pitzer ion-interaction model was employed to predict the conversion in the title quaternary water-salt system. The thermodynamic solubility products ( $K_s^0$ ) were determined and the conversion of  $\text{CaSO}_4$  to  $\text{CaCO}_3$  in the  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$  system was predicted. The standard molar Gibbs free energy  $\Delta_r G^0$  of the conversion reaction was calculated to be  $-23.62 \text{ kJ mol}^{-1}$ . A 98% degree of conversion of  $\text{CaSO}_4$  was achieved by using calcium sulfate isolated from sea salt production waste brines. Suitable conditions were found for obtaining  $\text{CaCO}_3$  exhibiting a high dispersity and whiteness.

All the four ternary subsystems of the  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$  quaternary water-salt system have been described in the literature over a wide temperature range. A field of equilibrium crystallization of the  $2 \text{ NaSO}_4 \cdot \text{Na}_2\text{CO}_3$  double salt, which actually is a phase with a varying composition<sup>1</sup>, has been identified in the  $\text{Na}_2\text{SO}_4$ - $\text{Na}_2\text{CO}_3$ - $\text{H}_2\text{O}$  system. Crystallization of double salts of the  $k \text{ Na}_2\text{SO}_4 \cdot l \text{ CaCO}_3 \cdot m \text{ H}_2\text{O}$  (ref.<sup>2</sup>) and  $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot n \text{ H}_2\text{O}$  (ref.<sup>3</sup>) types ( $k = 1, 2; l = 1, 5; m = 0, 1, 2; n = 2, 5$ ) has been established in the  $\text{Na}_2\text{SO}_4$ - $\text{CaCO}_3$ - $\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$ - $\text{CaCO}_3$ - $\text{H}_2\text{O}$  ternary systems. The scarce data available in the literature on the  $\text{CaSO}_4$ - $\text{CaCO}_3$ - $\text{H}_2\text{O}$  system indicate the occurrence of a wide crystallization field of  $\text{CaCO}_3$  (ref.<sup>4</sup>). The  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$  quaternary system has been studied by physico-chemical methods<sup>5,6</sup>, and conversion of  $\text{CaSO}_4$  to  $\text{CaCO}_3$  has been observed.

The purpose of the present work was to obtain high-quality  $\text{CaCO}_3$  possessing a high dispersity and high whiteness, using  $\text{CaSO}_4$  isolated from waste brine emerging from the production of sea salt.

**EXPERIMENTAL**

Conversion in the  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$  four-component water-salt system was achieved by using  $\text{CaSO}_4 \cdot 2 \text{ H}_2\text{O}$  isolated from waste brine from the production of sea salt. The conditions were as follows: duration of interaction, 4 h; temperature, 25 °C; reaction vessel, glass.

The reagents were ground before use. In order to remove  $\text{Fe}_2\text{O}_3$  impurities, some of the  $\text{CaSO}_4$  samples were treated with 5%  $\text{H}_2\text{SO}_4$ , filtered out and dried at 60 °C. The reagent mixture was added to distilled water in small portions with intense stirring. The  $\text{Na}_2\text{CO}_3$  to  $\text{CaSO}_4$  molar ratios lay within the limits of  $1 \pm 1.1$ . The use of excess  $\text{Na}_2\text{CO}_3$  over  $\text{CaSO}_4$  served obtaining a basic medium (pH 11) in which the conversion of  $\text{CaSO}_4$  proceeds nearly completely.

The precipitated reaction product was washed with distilled water and alcohol and dried in air, and analyzed for  $\text{CaCO}_3$  by the method of residual titration (Bulgarian State Standard 1820-71). The procedure is as follows: A weighed amount of the product is dissolved in distilled water, several drops of a 0.1% phenolphthaleine solution are added, and the solution is titrated with 1 M HCl to durable decolouration, after which excess HCl is added and the whole is heated gently on a flame to remove  $\text{CO}_2$ . Several drops of a 0.1% methyl orange solution are added, and the excess acid is titrated with 1 M NaOH.

A 98% degree of conversion of  $\text{CaSO}_4$  to  $\text{CaCO}_3$  was attained, while  $\text{Na}_2\text{SO}_4$  remained in the solution. Colourless crystals of  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$  were obtained by isothermal evaporation of the solution.

The dispersion and degrees of whiteness and yellowness of the  $\text{CaCO}_3$  product were examined. The particle size distribution (in microns) was established by the sieve analysis method using a MALVERN 3600 apparatus, the colour measurements were made with an Elropho 2000 – Patacolor. The results are summarized in Table I. The quality of the product was found to be affected by the pre-treatment of the samples (grinding and washing with dilute  $\text{H}_2\text{SO}_4$ ).

The best results were obtained if the two reagents had been ground but  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  had not been pre-treated with sulfuric acid. The product so obtained is first quality as far as its dispersion and whiteness are concerned (Bulgarian State Standard 1829-71) and can be used as filler in the cellulose industry.

The conversion of  $\text{CaSO}_4$  to  $\text{CaCO}_3$  was also evaluated when using sodium bicarbonate instead of carbonate. Even though a large excess of  $\text{NaHCO}_3$  was added, the conversion degree was considerably lower (<90%) due to the buffer effect of this compound. Moreover, this conversion route is inconvenient because  $\text{NaHCO}_3$  is considerably more expensive than  $\text{Na}_2\text{CO}_3$ .

TABLE I

Quantitative characteristics of the  $\text{CaCO}_3$  obtained;  $d$  mean bulk diameter of particles

Exp. No.	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ treated with 5% $\text{H}_2\text{SO}_4(\text{aq})$	$d$ , $\mu\text{m}$	Degree of whiteness, %	Degree of yellowness, %
1 <sup>a</sup>	no	12.45	93.14	1.03
2 <sup>b</sup>	no	10.03	94.18	1.43
3 <sup>b</sup>	yes	35.44	87.55	4.42
4 <sup>b</sup>	yes	31.89	84.00	3.25
5 <sup>c</sup>	yes	31.34	86.78	4.47

<sup>a</sup>  $m_{\text{Na}_2\text{CO}_3}/m_{\text{CaSO}_4} = 1$ ; <sup>b</sup>  $m_{\text{Na}_2\text{CO}_3}/m_{\text{CaSO}_4} = 1.1$ ; <sup>c</sup> conversion of  $\text{CaSO}_4$  to  $\text{CaCO}_3$  is performed with sodium bicarbonate.

**THERMODYNAMIC INVESTIGATION OF THE CaSO<sub>4</sub> + Na<sub>2</sub>CO<sub>3</sub> = CaCO<sub>3</sub> + Na<sub>2</sub>SO<sub>4</sub> SYSTEM USING THE PITZER MODEL**

According to a rule formulated by Van't Hoff<sup>7</sup>, the equilibrium in a quaternary water-salt system is shifted towards the formation of that pair of salts whose sum of solubility products ( $K_s^0$ ) is smaller. For a theoretical examination of the conversion of CaSO<sub>4</sub> to CaCO<sub>3</sub> in the above quaternary system we simulated thermodynamically the Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O and CaSO<sub>4</sub>-H<sub>2</sub>O binary solutions at 25 °C using the Pitzer ion-interaction model<sup>8,9</sup>. The applicability of this model to the calculation of the thermodynamic characteristics of binary and multicomponent electrolyte solutions has been proved by many authors<sup>10-16</sup>. The ultimate purpose of the simulation was obtaining the thermodynamic solubility products of the crystalline hydrates (Na<sub>2</sub>CO<sub>3</sub> · 10 H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub> · 10 H<sub>2</sub>O and CaSO<sub>4</sub> · 2 H<sub>2</sub>O) formed in the above saturated binary solutions.

The Pitzer binary parameters of the systems were taken from refs<sup>16,17</sup> (Table II). The decisive criterion for the choice of parameters was their applicability within the widest possible concentration range with a low standard deviation ( $\sigma$ ).

Using the values of the binary parameters we calculated the activity coefficients ( $\gamma_{\pm}$ ) and the water activity ( $a_w$ ) in the saturated electrolyte solutions (with molality  $m$ ). The values obtained are presented in Table III. Based on the overall reactions,

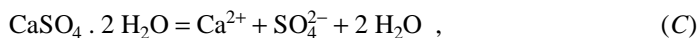
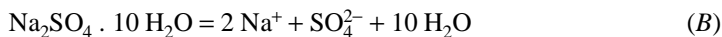
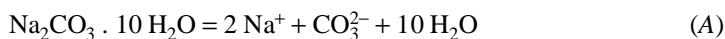


TABLE II

Pitzer binary parameters at 25 °C;  $\sigma$  is the standard deviation of the osmotic coefficients

System	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$c^\phi$	$m^{\max}$	$\sigma$
Na <sub>2</sub> CO <sub>3</sub> -H <sub>2</sub> O <sup>a</sup>	0.05306	1.29262	-	0.00094	2.75	0.00257
Na <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O <sup>b</sup>	0.04604	0.93350	-	-0.00483	1.75	0.00112
CaSO <sub>4</sub> -H <sub>2</sub> O <sup>b</sup>	0.20000	3.7762	-58.388	-	0.02	0.00460

<sup>a</sup> Ref. <sup>16</sup>; <sup>b</sup> ref. <sup>17</sup>.

we calculated the logarithm of the thermodynamic solubility product of the crystalline hydrates. For  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ :

$$\ln K_s^0 = \ln (4m^3\gamma_{\pm}^3a_w^{10}) , \quad (1)$$

and for  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ :

$$\ln K_s^0 = \ln (m^2\gamma_{\pm}^2a_w^2) . \quad (2)$$

The results are given in Table III. Due to the very low solubility of  $\text{CaCO}_3$  in water, no isopiestic data exist concerning the dependence of the water activity on the concentration of the  $\text{CaCO}_3\text{-H}_2\text{O}$  solution. For that reason, we were unable to determine the binary parameters of interionic interaction and calculate the thermodynamic solubility product of  $\text{CaCO}_3$ . The  $\ln K_s^0$  value for  $\text{CaCO}_3$  given in Table III was taken from ref.<sup>18</sup>. It is clear that the sum of the  $\ln K_s^0$  values is much lower for  $\text{CaCO}_3$  and  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$  than for  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ , so that, according to the Van't Hoff rule,  $\text{CaSO}_4$  should dissolve and  $\text{CaCO}_3$  precipitate in the quaternary system under consideration.

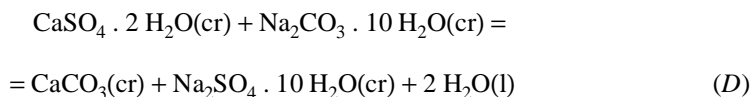
In agreement with the conditions of phase and chemical solid-liquid equilibria in water-salt systems, the chemical potential of the liquid phase is equal to the chemical potential of the solid phase. Owing to this, the standard molar Gibbs free energy of reaction  $\Delta_r G^0$  of solid  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  with solid  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$  could be derived from the calculated activities of the components in their saturated binary solutions (Table III). A similar scheme was used to determine the  $\Delta_r G^0$  values of the reaction of synthesis of the double salts from the corresponding simple salts<sup>10,11,13,15</sup>. For the reaction

TABLE III

Calculated values of the logarithm of the thermodynamic solubility product  $K_s^0$ ;  $m$  concentration of saturated binary solution;  $\gamma_{\pm}$  activity coefficient;  $a_w$  water activity

Salt composition	$m$	$\gamma_{\pm}$	$a_w$	$\ln K_s^0$
$\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$	2.77	0.1734	0.8981	-1.889
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	1.97	0.1548	0.9363	-2.834
$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	0.02	0.3042	0.9995	-10.205
$\text{CaCO}_3^a$				-18.789

<sup>a</sup> Ref.<sup>18</sup>.



the change in the standard molar Gibbs free energy is

$$\Delta_r G^0 = RT[\ln a_{\text{CaCO}_3} + \ln a_{\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}} + 2 \ln a_{\text{H}_2\text{O}} - \ln a_{\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}} - \ln a_{\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}}], \quad (3)$$

where  $a$  is the activity of the salt in its saturated solution at 25 °C and  $\ln a_{\text{H}_2\text{O}} = 0$  (the activity of pure water is 1). The  $\Delta_r G^0$  value so obtained is  $-23.62 \text{ kJ mol}^{-1}$ .

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