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## The application of ammonium hydroxide and sodium hydroxide for reagent softening of water

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### Abstract

The calcium carbonate crystallization from aqueous solutions in the presence of alkali additives such as sodium hydroxide and ammonium hydroxide has been researched. It is found  $\text{CaCO}_3$  crystallizes predominantly in the modification of aragonite in the presence of ammonium hydroxide. The calcium carbonate formation rate in an alkaline medium and the gaseous reaction products due to sorption of gas bubbles on crystal surfaces, affect the aragonite structure formation. It is shown use of ammonium hydroxide for water treatment can solve two urgent tasks such as water softening and exclusion sediment of deposits on the equipment surfaces by a calcium carbonate crystallization in the form of aragonite.

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### 1. Introduction

Hardness salts form poorly soluble compounds on heat exchanger surfaces and heat-and-power engineering plants, that reduces a heat transfer coefficient and decreases the operation efficiency and increases fuel consumption. Problems associated with the usage of hard water are actual not only for Russia but also for many other countries. Water treatment with the obligatory softening stage is required for technical purpose water. One of the ways to reduce a water hardness is a reagent method based on water treatment with chemicals. It forms poorly soluble calcium and magnesium compounds in particular calcium carbonate<sup>1,2</sup>.

It is known that calcium carbonate is formed as both amorphous and crystalline phases such as vaterite, aragonite and calcite<sup>3</sup>. Generally, calcium carbonate crystallizes from natural water in the presence of supersaturation in a calcite form<sup>4</sup>. Aragonite crystals have surface energy lower values of surface energy in comparison with calcite.

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Aragonite is formed either by physical effects, e.g., magnetic treatment, or by addition of water soluble organic compounds such as polyacrylic acid and polyethylene glycol<sup>5,6</sup>.

Calcite and aragonite have different adhesiveness the materials of the heat exchange surface due to their different crystal structure. For example, calcite of trigonal system crystallizes in the rhombohedral form, and aragonite crystallizes in the form of needle crystals of irregular shape. Therefore aragonite crystals have a low adhesion to the material of heat transfer surface and a low cohesion of the individual crystals to each other, which leads to a decrease in the ability of calcium carbonate scale-forming<sup>7</sup>.

Currently, magnetic treatment is applied to simplify the problem of cleaning a heat exchange equipment from calcium carbonate scale. It contributes to preferential formation of aragonite phase. However, magnetic treatment isn't widely used in practice because of energy costs associated with water heating to a temperature not lower than 50 °C<sup>8</sup>.

Reagent water softening is of greatest practical importance<sup>9</sup>. One of the existing methods of reagent water softening reagent is ammoniac process developed in National Research Tomsk Polytechnic University led by Professor Kosintsev V.I.<sup>10</sup>. This method is based on shift of the carbon dioxide equilibrium to formation of insoluble calcium carbonate by creating an alkaline environment. It leads to a reduction of the water total hardness of 72 %. However, there wasn't a comparison of the used ammonium hydroxide with other alkaline reagents and their influence on the crystalline form of calcium carbonate.

The purpose of paper is the research of the water softening process using ammonium hydroxide and sodium hydroxide.

## 1. Experimental

The model solution of  $\text{Ca}(\text{HCO}_3)_2$  was used in the experiments. The model solution was prepared from salts  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  with a pure grade qualification. The  $\text{Ca}(\text{HCO}_3)_2$  solution concentration was comparable the content of groundwater hydrocarbons and was equal to  $84.16 \text{ mg/dm}^3$  of  $\text{Ca}^{2+}$ . Ammonium hydroxide and sodium hydroxide were used as alkaline reagents for softening. These reagents were analytical grade. Caustic solution was added into the model solution in the amount to make an equal concentration of  $\text{OH}^-$ -ions. The 10 %  $\text{NaOH}$  solution with the volume of  $0.13 \text{ cm}^3$  or the 25%  $\text{NH}_4\text{OH}$  solution  $0.05 \text{ cm}^3$  while stirring under injected in the model solution with the volume of  $50 \text{ cm}^3$ . The obtained  $\text{CaCO}_3$  precipitate was filtered and dried at room temperature.

The study of the phase precipitation composition of calcium carbonate produced with ammonium hydroxide and sodium hydroxide was carried out with diffractometer Shimadzu XRD- 7000 of Nanocentre of National Research Tomsk Polytechnic University using a  $\text{CuK}\alpha$ - radiation under the conditions of shooting such as  $I = 20 \text{ mA}$ ;  $U = 20 \text{ kV}$ , speed was  $20/\text{min}$ , area scan angles ( $2\theta$ ) was limited by the interval  $20...70 \text{ deg}$ . Explanation of X-ray reflexes was carried out using databases PSRRDFWIN. Quantitative content of calcite, vaterite and aragonite was determined by the Rietveld method with the program «Powder Cell».

The calcium carbonate crystallization kinetics using ammonium hydroxide and sodium hydroxide in a solution volume was examined spectrophotometrically by measuring the turbidity of aqueous solutions at  $540 \text{ nm}$ <sup>11</sup>.

The composition of the released gas phase was determined with the mass spectrometric complex for isotopic analysis.

## 2. Results and discussion

When alkaline reagents  $\text{NaOH}$  and  $\text{NH}_4\text{OH}$  are added in an aqueous solution with calcium ions and bicarbonate ions,  $\text{OH}^-$ -ions formed during dissociation. It reacts with ions of  $\text{HCO}_3^-$  displacing the equilibrium of the reaction (1) to the formation of carbonate ions:



Formed by reaction (2) calcium carbonate precipitates in a solid phase:



The investigation results of the calcium carbonate precipitation phase composition obtained from the alkalized model solution are presented in Table 1. Sample #1 is obtained from the model solution with addition the  $\text{NH}_4\text{OH}$ , sample #2 is obtained from the model solution with addition of  $\text{NaOH}$ . Both samples are obtained at water treatment temperature of 15 °C.

Table 1. The calcium carbonate phase composition obtained in the presence of alkaline additives

Sample name	Content, % wt.		
	Aragonite	Calcite	Vaterite
Sample #1	53.77	20.65	12.16
Sample #2	–	90.90	9.10

As can be seen from Table 1, the samples have different phase compositions. In the presence of sodium hydroxide the main calcium carbonate polymorph modification is calcite. And the precipitate obtained by using ammonium hydroxide has three calcium carbonate modifications with predominate content of aragonite.

To identify the causes of aragonite phase formation in ammonia medium the calcium carbonate crystallization rate in the presence of ammonium hydroxide and sodium hydroxide was studied. The results are presented in Figure 1.

As it can be seen from Fig. 1, turbidity of the model solution increases in the straight-line portion 1 and 1', indicating the nucleation formation of calcium carbonate. Nucleation occurs more rapidly in the presence of sodium hydroxide. Ranges 2 and 2' show coarsening of the forms crystal nucleuses and coalescence occurs intensively in the presence of sodium hydroxide. Thus, enlargement of nucleuses occurs in the ammonia environment for 180 s. in the presence of  $\text{NaOH}$  for 90 s., the further crystals of calcium carbonate precipitate, as a result, the solution turbidity decreases (ranges 3 and 3'). Crystal precipitation occurs at a higher rate in the presence of sodium hydroxide. As a result, the application of sodium hydroxide and ammonium hydroxide leads to the same amount of the extracted calcium ions from solutions. The extraction degree is 46 %. The application variations of different alkaline reagents is a different phase composition of the formed calcium carbonate (table 1) due to the different formation rates of calcium carbonate. It can be explained by dissociation constants of the used bases. Sodium hydroxide is a strong base with dissociation constant equaled to 5.8.  $\text{NH}_4\text{OH}$  is a weak electrolyte with dissociation constant equaled to  $1.76 \cdot 10^{-5}$ . It dissociates partially into ions in an aqueous solution. In the case of the ammonium hydroxide the  $\text{OH}^-$ -ions required to displace a carbon dioxide equilibrium and to form calcium carbonate "are delivered" in the reaction zone with a lower speed than when sodium hydroxide. And reaction 1 slows down. Aragonite is less resistant to supersaturation. Thus its separation occurs at a higher rate in the bulk solution.

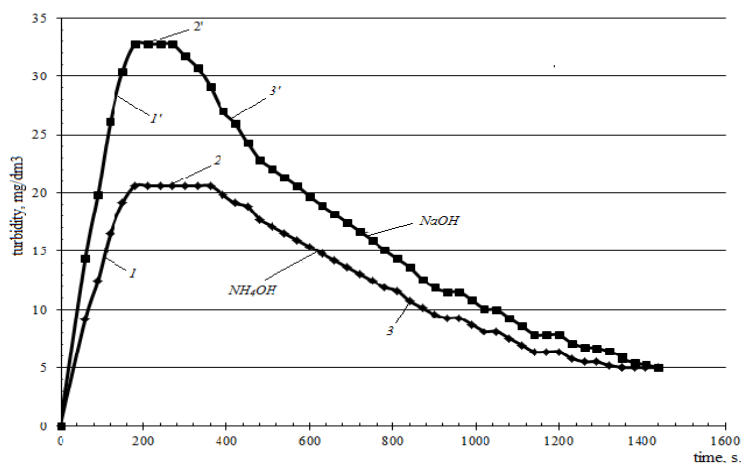


Fig. 1. The dependence of model solution turbidity change in the presence of alkaline additions of NaOH and  $\text{NH}_4\text{OH}$

In this paper we study the composition of gaseous products formed by reacting a solution of  $\text{Ca}(\text{HCO}_3)_2$  with NaOH and  $\text{NH}_4\text{OH}$  (table 2).

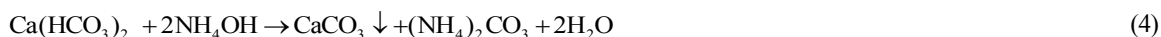
Table 2. The results of mass spectrometry of the gaseous phase

The component	Content, %	
	interacting with NaOH	interacting with $\text{NH}_4\text{OH}$
$\text{H}_2\text{O}$	0.51	0.51
$\text{N}_2$	80.94	79.62
$\text{O}_2$	15.90	15.69
Ar	2.20	1.84
$\text{CO}_2$	0.17	1.02
$\text{NH}_3$	0.28	1.32

The results in Table 2 show a high content of ammonia and carbon dioxide in the gas phase. It is observed at the reaction of  $\text{Ca}(\text{HCO}_3)_2$  with  $\text{NH}_4\text{OH}$ . It will be possible, if we imagine the reaction of  $\text{Ca}(\text{HCO}_3)_2$  and NaOH leads to formation of  $\text{Na}_2\text{CO}_3$  by the equation:



At the same time, application of the ammonium hydroxide is accompanied by the formation of ammonia carbonate. It is unstable compound that decomposes into ammonia and carbon dioxide:



Ammonia hydroxide addition in the model solution changes the phase structure of the formed calcium carbonate precipitate of calcium carbonate and results in the formation of unconsolidated aragonite crystals of irregular shape due to adsorption of the carbon dioxide and ammonia (reaction 5). The gas bubbles adsorb on the calcium carbonate

crystal surface and limit the regular shape crystal growth and it leads to aragonite arborescent structure formation. This bond can be clearly seen between crystal shapes in pictures (Fig. 2 a,b).

#### 4. Conclusion

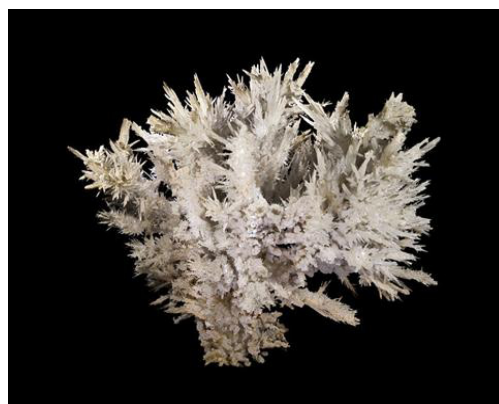
We found that the calcium carbonate crystallization from the model solution containing calcium hydrocarbonate with ammonium hydroxide leads to three polymorphic formation such as aragonite, vaterite and calcite, with a predominant content of aragonite of 53.77 % by wt. When sodium hydroxide is added to the model solution, the complete absence of aragonite is revealed, and the precipitate is generally presented by a calcite phase. The ammonium hydroxide presence slows down the calcium carbonate crystallization in comparison to sodium hydroxide. It is explained by the difference in the values of the dissociation constants ( $K_d(\text{NH}_4\text{OH}) = 1.76 \cdot 10^{-5}$ ,  $K_d(\text{NaOH}) = 5.8$ ). Aragonite is less resistant to supersaturation. Thus, its separation takes place at a higher rate in the bulk solution in an ammonium medium.

Composition of the gaseous phase influences the formation of aragonite unconsolidated structure as a result of sorption of gas bubbles on crystal faces.

Application of ammonium hydroxide in the reagent water softening method solves two urgent problems such as removing the salts with temporary hardness and exclusion of the inlay equipment by crystallization of calcium carbonate in the form of aragonite.



a



b

Fig.2. Crystals of calcium carbonate at 10000 x enlargement (a) calcite; (b) aragonite

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