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# Carboxymethylcellulose sodium salt – effective "green" regent for management of calcium carbonate crystallization and natural gas hydrate formation

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**Abstract**. The effect of carboxymethylcellulose sodium salt (NaCMC) with molecular masses (Mw) of 90, 250 and 700 thousand on the crystallization of $CaCO_3$ polymorphs, their size and deposition on the surface of stainless steel from supersaturated aqueous solution at 80 ° C was studied. As a result of specific reversible adsorption, when forming crystalline nuclei formed, it is assumed that NaCMC changes the shape of the growing crystal, preferably forming vaterite — up to 95% in the presence of NaCMC with a molecular mass of 90 thousand during the interaction of $CaCl_2$ and $NaHCO_3$. In the presence of $Mg^{2+}$ ions, $CaCO_3$ is formed mainly in the form of aragonite, and the influence of the molecular mass of NaCMC is significantly reduced. It was established that NaCMC with Mw 90 and 250 thousand inhibits the aggregation and agglomeration of $CaCO_3$ crystals, leading to a decrease in the average size of crystals from 24 to 10.6 and 16.5 microns, respectively. Under the action of NaCMC with a molecular mass of 700 thousand, on the contrary, an increase in the size of crystals to 37.2 μm is observed. It is shown that NaCMC with Mw 90 and 250 thousand slows down the speed and changes the conditions of gas hydrate formation, showing the properties of a thermodynamic and kinetic inhibitor with an efficiency that exceeds methanol by 300-450 times when used in the same dosages. The data obtained indicate the promise of creating new "green" reagents of complex action for oil and gas production on the basis of sodium salt carboxymethylcellulose.

## 1. Introduction

The formation of calcium carbonate from natural waters is one of the most common processes in nature. In technological processes, such as oil production, the formation of salts from produced water and their deposition on the surface of the well and oilfield equipment are among the most common complications [1-4].

In practice of oil production to prevent scale formation, the chemical method of inhibition using phosphorus-containing oil-field reagents and organic polymers is widely used [2-4], the shortcomings of which include low thermal stability and high toxicity.

Another significant complication that reduces the efficiency of oil production and transportation of hydrocarbons is the formation of gas hydrates [5,6]. Currently, thermodynamic and kinetic inhibitors

of gas hydrate formation are used to control the formation of technogenic gas hydrates, among which methanol is most widely used [6-8]. The global trend in hydrate formation management is developing in the direction of replacing toxic methanol with low concentration gas hydrate formation inhibitors, that work effectively in dosages 100-500 times less than methanol (kinetic hydrate formation inhibitors, anti-agglomerates) [9].

The trends in the development of the processes of chemicalization of modern industries, including the extraction of oil and gas, dictate the need for the development of new "green" highly efficient reagents of a complex action. The of carboxymethylcellulose sodium salt (NaCMC) is one of the most accessible water-soluble polysaccharides, the physicochemical properties of which, as well as the availability, thermal stability, and biodegradability in aerobic and anaerobic conditions predetermine the search and creation on its basis of new "green" oil field reagents [10,11]. We have previously shown by gravimetric and electrochemical methods that NaCMC exhibits anticorrosion properties, is a corrosion inhibitor of mixed action - cathodic and anodic [12].

This paper presents the results of studies of the effect of carboxymethylcellulose sodium salt and its molecular weight on the crystallization processes of calcium carbonates, as well as the inhibition of gas hydrate formation of petroleum gases.

## 2. Experimental part

NaCMC produced by Aldrich with molecular masses of 90 thousand, degree of substitution 0.7 (NaCMC 90), 250 thousand, degree of substitution 0.7 (NaCMC 250), 700 thousand, degree of substitution 0.9 (NaCMC 700) were used.

As a model of saline water (MSW) used water following ion composition: $Ca^{2+}$ - 750; $Na^+$ - 863; $Cl^-$ - 2662; $HCO_3^-$ - 2290 mg/l (MSW 1) and $Ca^{2+}$ - 250; $Mg^{2+}$ - 85; $Na^+$ - 3120.25; $Cl^-$ - 4492.10; $HCO_3^-$ - 1525.50 mg/l (MSW 2) prepared from salts of $CaCl_2$, $MgCl_2·6H_2O$, $NaCl$, $NaHCO_3$, $Na_2SO_4$ qualification "Pro Analyse".

The size of $CaCO_3$ crystals formed from the solutions were recorded on a laser diffraction particle size analyzer Analysette 22 NanoTec plus.

The morphology of calcium carbonate particles was studied using the Rigaku Ultima IV x-ray diffractometer. The analysis was performed in Cu-Ka radiation at a voltage of 20 kV and a current of 2 mA with a wavelength l = 1.5405 Å. Registration was carried out in the range of angles 2θ 15...115° with scanning step 0.02°. Processing of diffractograms and phase analysis were carried out in the program "Match!".

The microstructure of the samples was studied by scanning electron microscopy with field emission (FE-SEM) on a Hitachi SU8000 electron microscope. Images were taken in the registration mode of secondary electrons with an accelerating voltage of 2 kV and a working distance of 4-5 mm. The optimization of analytical measurements was carried out in the framework of the approach described earlier [13]. Before shooting, the samples were placed on the surface of an aluminum table with a diameter of 25 mm, fixed with a conductive glue, and a conductive metal layer (Pt/Pd, 80/20) 7 nm thick was deposited on them using the magnetron sputtering method previously described [12]. The morphology of the samples was studied taking into account the correction for the surface effects of deposition of the conducting layer [14].

The efficiency of NaCMC as a scaling inhibitor was determined at the polysaccharide concentration of 10, 20 and 50 mg/l by a method based on blocking the steel capillary formed by calcium carbonate deposits at a temperature of 80°C. A model of mineralized water (MMW) containing $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $Cl^-$ and $HCO_3^-$ ions was pumped at a rate of 1 ml/min through a 2.5 m long stainless steel capillary with an internal diameter of 1 mm and the dynamics of pressure drop in the capillary caused by the deposition of $CaCO_3$ was recorded.

The effectiveness of inhibition (Table 1) was determined by the formula:

$$Z = 100·(\Delta P_1 - \Delta P_2)/\Delta P_1$$

where $\Delta P_1$ is the pressure drop on the capillary when pumping water without NaCMC,

$\Delta P_2$-pressure drop on the capillary when pumping water from the NaCMC

The inhibition of gas hydrate formation was studied by rheological method in the high-pressure cell "Thermo" in the cooling mode from room temperature to -5 °C. The cell was pre-injected with natural gas, then the cell was cooled, simultaneously with the temperature decrease, the cell pressure and shear stress were recorded [15].

## 3. Results and discussion

It is known that NaCMC can form sufficiently stable complexes with $Ca^{2+}$ ion [16-18]. Therefore, assuming that the NaCMC can prevent the precipitation of calcium salts from supersaturated aqueous solutions and inhibit scaling, we studied its effect on the crystallization of calcium carbonate.

The study of the effect of molecular weight of NaCMC on the process of inhibition of carboxymethylcellulose sodium salt scaling by capillary testing at a temperature of 80°C showed that at concentrations of 10, 30, 50 mg/l polysaccharides inhibit the process of $CaCO_3$ scaling (Figure 1, Table 1).
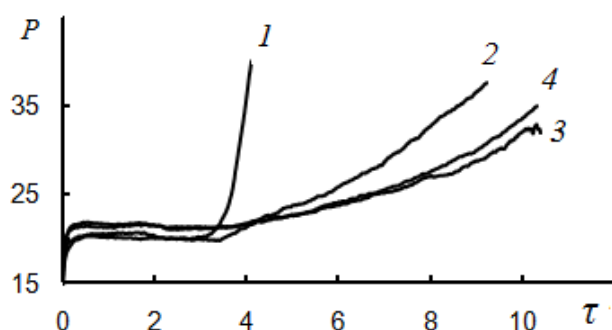


**Figure 1.** The influence of NaCMC 90 on the process of scaling $CaCO_3$ at concentrations of 0 (*1*), 10 (*2*), 30 (*3*) and 50 (*4*) mg/l at 80 °C. *P* - pressure (kPa), τ - time (min).

**Table 1**. The dependence of the efficiency of inhibition of calcium deposition on the NaCMC molecular weight.

| Molecular mass NaCMC | NaCMC Concentration, mg/l | | |
|---|---|---|---|
| | 10 | 30 | 50 |
| | Inhibition efficiency, % | | |
| 90 | 52 | 61 | 60 |
| 250 | 50 | 61 | 60 |
| 700 | 20 | 51 | 62 |

All NaCMC samples inhibit the formation of calcium carbonate. However, at low concentrations (10 mg/l), the efficiency of low molecular weight samples is 2.5 times higher.

The molecular mass of NaCMC plays an important role in the formation of calcium carbonate crystals. In the presence of NaCMC, there is a significant change in the size of the resulting $CaCO_3$ crystals (Fig.2). The average size of the formed particles in the presence of NaCMC 90 decreases from 24.0 to 10.6 μm, for NaCMC 250 to 16.5, and NaCMC 700, on the contrary, increases the resulting calcium carbonate crystals to 37.2 μm.
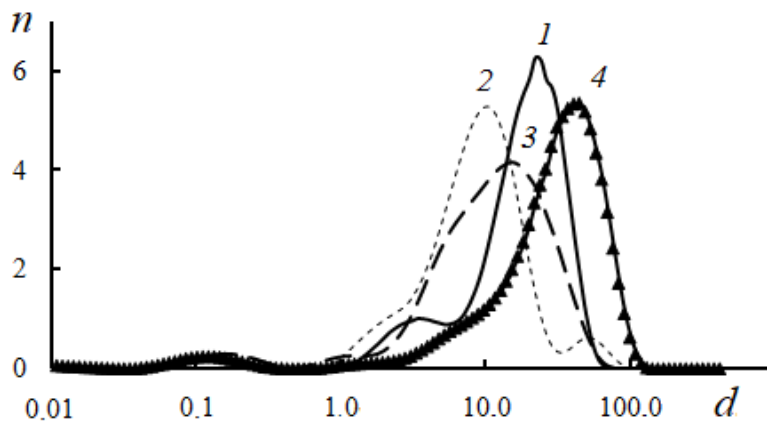
**Figure 2.** Influence of molecular weight of NaCMC on the size distribution of $CaCO_3$ crystals formed from the solution of MSW 2 in the presence of 30 mg/l of NaCMC: without NaCMC (*1*), NaCMC 90 (*2*), NaCMC 250 (*3*), NaCMC 700 (*4*). *n* - volume fraction of crystals (%), *d* – diameter (µm).

Studies on the x-ray diffractometer "Rigaku Ultima IV" showed a significant effect of the molecular weight of NaCMC and the composition of saline water on the phase composition of calcium carbonate crystals (Figure 3a, b; Table. 2.3).
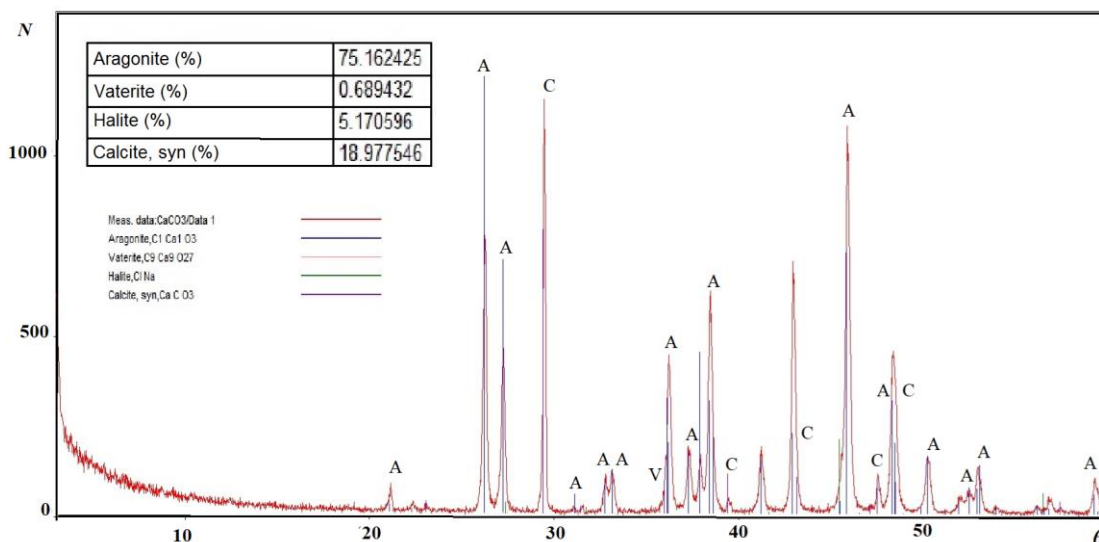


**Figure 3a.** Diffractogram of $CaCO_3$ crystals obtained without NaCMC in MSW 1. $\theta$ - deflection angle (deg), *N* – intensity (cps).

| Vaterite (%) | 85.611899 |
| Aragonite (%) | 5.562954 |
| Halite (%) | 7.069011 |
| Calcite, syn (%) | 1.756136 |

Meas. data:CaCO3-KMC90/Data 1
Vaterite,C Ca O3
Calcite, syn,Ca C O3
Aragonite,Ca C O3
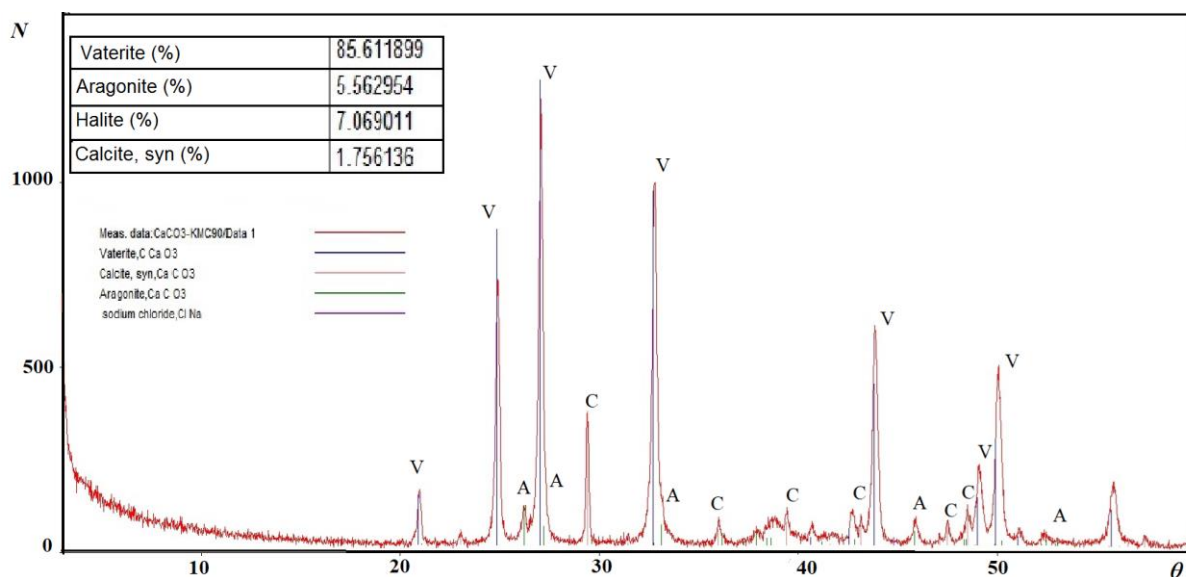sodium chloride,Cl Na

**Figure 3b**. Diffractogram of CaCO$_3$ crystals obtained in the presence of NaCMC 90 in MSW 1. $\theta$ - deflection angle (deg), $N$ – intensity (cps).

In MSW 1 and MSW 2 without polysaccharides, mainly aragonite and calcite are formed. In the presence of NaCMC, the amount of aragonite increases from 3 to 7% depending on the molecular weight of NaCMC, and calcite is replaced by vaterite (Table 3). The addition of a low molecular weight sample of a polysaccharide to the solution during the interaction of CaCl$_2$ and NaHCO$_3$ makes it possible to obtain vaterite in a yield of up to 86%, while an increase in the molecular weight of NaCMC reduces the yield of vaterite to 59%. In the presence of Mg$^{2+}$ ions, CaCO$_3$ it is formed mainly in the form of aragonite.

**Table 2.** Dependence of the phase composition of crystalline CaCO$_3$ on the molecular weight of NaCMC, obtained in MSW 1.

| NaCMC | Calcite, % | Aragonite, % | Vaterite, % | Halite, % |
|---|---|---|---|---|
| without NaCMC | 19 | 75 | 1 | 5 |
| 90 | 5 | 7 | 86 | 2 |
| 250 | 11 | 10 | 77 | 2 |
| 700 | 12 | 27 | 59 | 2 |

**Table 3.** Dependence of the phase composition of CaCO$_3$ on the molecular weight of NaCMC, obtained in the MSW 2.

| NaCMC | Calcite, % | Aragonite, % | Vaterite, % | Halite, % |
|---|---|---|---|---|
| without NaCMC | 10 | 88 | 1 | 1 |
| 90 | 2 | 95 | 3 | - |
| 250 | 2 | 94 | 4 | - |
| 700 | 6 | 91 | 2 | 1 |

The data obtained by electron microscopy are consistent with the results of x-ray diffraction analysis. On SEM images, calcium crystals formed during crystallization represent irregularly shaped struc-

tures in the form of threads and stars, while crystals obtained in the presence of a polysaccharide have a spherical shape characteristic of vaterite (Figure 4).
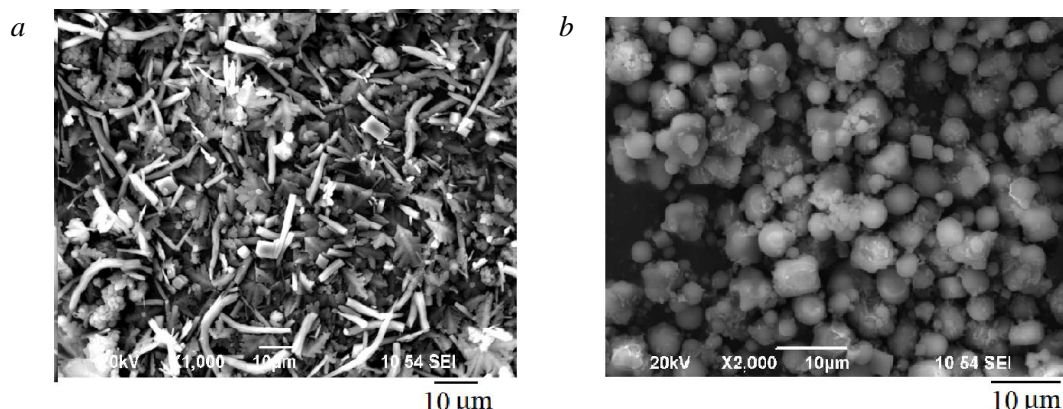


**Figure 4.** Electron micrograph of $CaCO_3$ crystals, obtained without (*a*) and in the presence of (*b*) NaCMC 90.

A sample of $CaCO_3$ obtained from MSW 1 and MSW 2 in the absence of a polysaccharide contains elongated crystals of aragonite, which under selected conditions is the thermodynamically most stable phase (Figure 4). During the crystallization of calcium carbonate in the presence of all NaCMC samples, the particles of aragonite acquire an irregular shape with rounded edges. They cause low adsorption on the metal surface of pipes and equipment.

The mechanism of interaction between NaCMC and calcium salts is rather complicated. Probably, the main reason for the influence of NaCMC on crystal formation can be considered the specific adsorption of NaCMC on the forming faces of salt crystals, both due to the electrostatic interaction of ionized carboxyl groups with $Ca^{2+}$ ions located on the crystal surface, and due to coordination and hydrogen bonds with oxygen atoms and OH- groups of D-glucose fragments [19]. Such an interaction leads to the formation of polymorphic forms without pronounced morphological signs and changes in the size of the particles of calcium carbonate.

## 4. Inhibition of gas hydrate formation

Inhibiting formation of hydrates the ability of the NaCMC investigated in terms of quasi-equilibrium thermodynamic experiment

As a hydrate-forming model medium, two gas compositions were used: 99.5% methane and 0.5% ethane – the composition of 1, 93% methane and 7% ethane – the composition of 2. Composition 1 was used to study the effect of methanol concentration, and composition 2 was used to study the effect of NaCMC concentration. Phase curves of gas-hydrate formation for composition 1 and 2 were calculated using the software package HWHYD (Heriot-Watt University). The efficiency of NaCMC as an inhibitor of gas hydrate formation was evaluated by the ratio of the concentrations of polysaccharide and methanol with the same effect of changing the pressure of the beginning of hydrate formation.

Among the studied samples of NaCMC with different molecular weight (90, 250 and 700 thousand) the highest inhibitory activity was demonstrated by polysaccharide with molecular weight of 90 000 at concentrations of 0.005, 0.01 and 0.05% (Figure 5). It should be noted the influence of the molecular weight of NaCMC on the process of gas hydrate formation: the compound with a mass of 700 thousand had no effect on the formation of hydrates. The of carboxymethylcellulose sodium salt alters the conditions of hydrate formation, showing the thermodynamic properties of the inhibitor, the efficiency of which is superior to methanol in 350 times. The reagent is not only an effective thermodynamic, but also a kinetic inhibitor of gas hydrate formation, since with the increase in the concentration of polysaccharide, the pressure drop of gas hydrate formation increases and the rate of gas hydrate formation decreases.
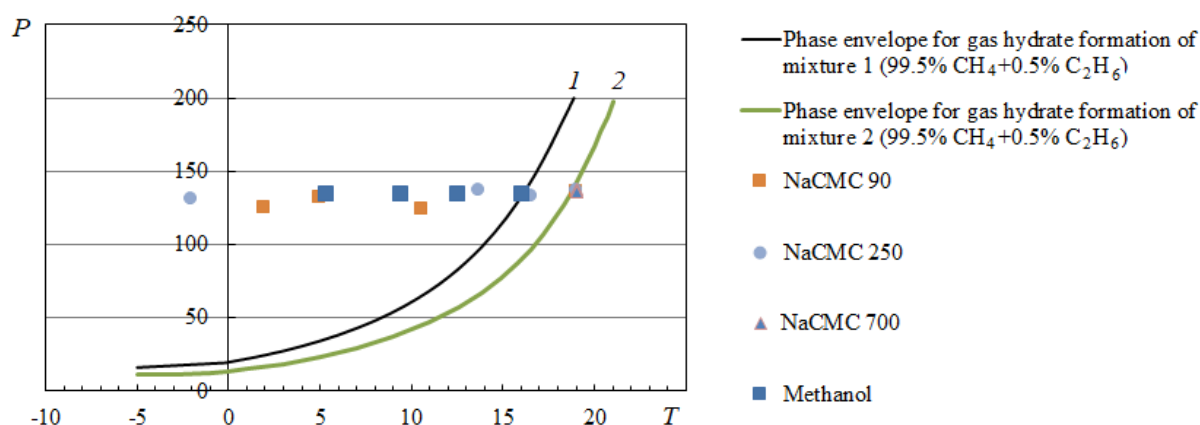
**Figure 5.** The effect of the NaCMC and methanol on the hydrate formation of gas composition of *1* (the effect of the NaCMC) and composition *2* (the effect of methanol). *P* - pressure (bar), *T* - temperature (°C)

Probably, inhibition of gas hydrate formation occurs as a result of electro-static interaction of ionized carboxyl groups of NaCMC and sodium cations with water molecules, and the formation of hydrogen bonds with oxygen atoms and OH-groups of D-glucose fragments [20].

## 5. Conclusion

Thus, the influence of molecular weight of NaCMC on the process of crystallization of calcium carbonate was investigated. A low molecular weight sample of NaCMC with a molecular weight of 90 000 allows obtaining a metastable form of calcium carbonate-waterite. At the same time, in the presence of magnesium ions, waterite is completely replaced by aragonite. The of carboxymethylcellulose sodium salt alters the conditions of hydrate formation showing the properties of a thermodynamic inhibitor, with efficacy superior to methanol in 350 times.

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