

PAPER • OPEN ACCESS

## Investigation of calcium carbonate precipitation in the presence of scale inhibitors

To cite this article: N P Kakurkin *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **288** 012010

View the [article online](#) for updates and enhancements.



**IOP | ebooks™**

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the **collection** - download the first chapter of every title for free.

# Investigation of calcium carbonate precipitation in the presence of scale inhibitors

N P Kakurkin, A A Malashenko, N E Pudova, E Yu Perunova

D.Mendeleev University of Chemical Technology of Russia

npk@muctr.ru

**Abstract.** The work presents a study on the precipitation of calcium carbonate in the presence of four inhibitors: aminotris(methylenephosphonic acid) (ATMP), 1-hydroxyethane-1,1 diphosphonic acid (HEDP), polyacrylate (PA), copolymer of acrylic and allylsulfonic acids (PAC). Using the laboratory methods for evaluating the effect of antiscalants for inhibition, the following order in terms of decreasing effectiveness  $\text{HEDP} > \text{ATMP} > \text{PAS} > \text{PA}$  at a concentration of 4 ppm has been observed. It was revealed that polymeric antiscalants can effectively cope with the suppression of the precipitation of calcium carbonate at higher concentrations than phosphorus-containing preparations. It has been shown that in the presence of antiscalants, a change in the structure and modification of  $\text{CaCO}_3$  occurs.

## 1. Introduction

Calcium carbonate is one of the most commonly encountered scale deposits in reverse osmosis systems. The deposition of  $\text{CaCO}_3$  and other poorly soluble components leads to significant negative consequences, among them a decrease in system performance and inter-regeneration period of the reverse osmosis unit and, in the most difficult cases, irreversible membrane failure [1-2].

One of the ways to prevent the formation of deposits on the surface of membranes is the using of the scale inhibitors or antiscalants. As a rule, modern antiscalants consist of various classes of organic compounds, among them the most common inhibitors based on phosphonic acids (for example, HEDP, ATMP) [3-4]. However, the growing environmental problems associated with the pollution of surface water sources with phosphorus and nitrogen-containing compounds contributed to the development of new ecofriendly inhibitors of scale [5-6].

In this work, a comparison was made of classical phosphorus-containing antiscalants and polymers based on polyacrylic acid (PAA) and polyacrylate with sulfo group (PAS).

## 2. Experimental

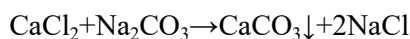
### 2.1. Materials

$\text{CaCl}_2$ ,  $\text{Na}_2\text{CO}_3$ . All chemicals are of analytical grade, also was used deionized water. Phosphate solutions of antiscalants were obtained from solid aminotris(methylenephosphonic acid) ATMP (98%) and 1-hydroxyethane 1,1- diphosphonic acid HEDP (98%). New polymer antiscalants polyacrylic acid PA and copolymer of acrylic and allylsulfonic acids were supplied in the form of solutions.



## 2.2. Test methods

The system of calcium carbonate was obtained by draining in a stoichiometric ratio of solutions of calcium chloride and sodium carbonate, previously thermostatted at 25 ° C. The system was mixed for 30 seconds, which ensured the uniform distribution of the reagents in the solution and increased the rate of formation of the precipitate.



The concentration of  $\text{CaCO}_3$  was 250 ppm, the pH of the solution was 10.2. The concentration of the inhibitor was 4 ppm of the original product, then the concentration was increased to 10 ppm.

The effectiveness of inhibitors to prevent the precipitation of calcium carbonate was determined using two express laboratory techniques. The first method was based on determining the content of dissolved  $\text{Ca}^{2+}$  in the system after interacting with the antiscalant [7-9], based on which the degree of inhibition was calculated by the formula:

$$I, \% = \frac{[\text{Ca}]_{\text{final}} - [\text{Ca}]_{\text{blank}}}{[\text{Ca}]_{\text{init}} - [\text{Ca}]_{\text{blank}}} * 100$$

where  $[\text{Ca}]_{\text{final}}$  and  $[\text{Ca}]_{\text{blank}}$  are final calcium concentrations with and without the presence of an inhibitors and  $[\text{Ca}]_{\text{init}}$  is the initial calcium concentration.

The second laboratory technique consisted in visual observation of the solutions using an optical microscope with the possibility of photo fixation. The photographs were transferred to a black and white colour and using a special program we determined the percentage of a photo filled with color -  $m, \%$  (Fig.1).

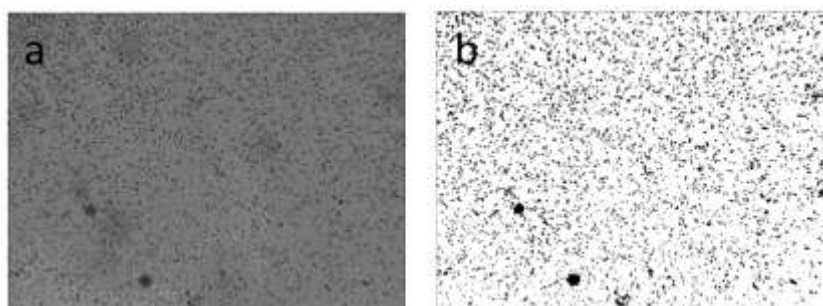


Fig.1. Images of  $\text{CaCO}_3$  obtained using an optical microscope (a), (b) – images transferred to a black and white colour

This indicator is selected as a parameter characterizing the amount of precipitate formed. For this method, the degree of inhibition was defined as:

$$I, \% = \frac{[m]_{\text{sample}} - [m]_{\text{control}}}{[m]_{\text{sample}}} * 100$$

where  $[m]_{\text{sample}}$  is percentage of the photo filled with color without the presence of an inhibitors,  $[m]_{\text{control}}$  is percentage of the photo filled with color with the presence of an inhibitors.

The time of the study in both cases was 1 hour.

The solid phase of the deposited component was investigated using a scanning electron microscopy (SEM) Microscope JEOL JSM-6510 LV.

### 3. Results and discussion

#### 3.1. Determination of the effectiveness of scale inhibitors

The study of the effectiveness of antiscalants using two laboratory methods showed that phosphorus-containing inhibitors HEDP and ATMP completely suppress the precipitation of calcium carbonate in the chosen conditions.

The polymeric antiscalants PA and PAS were less effective, and the degree of inhibition for these antiscalants varied depending on the method of investigation used (table 1). Differences in I,%, depending on the research method, in our opinion, are caused by the limit ability of an optical microscope to capture solid particles less than a micron in size. To study the effect of the dose of polymeric inhibitors on the precipitation of calcium carbonate, the antiscalant concentration was increased to 10 ppm.

Table1.

Results for the determination of the degree of inhibition of calcium carbonate precipitation

Inhibitor	Inhibition (%)			
	Liquid phase analysis		Microscopic observation	
	concentration, ppm			
	4	10	4	10
HEDP	100 ± 8	—	100 ± 13	—
ATMP	95 ± 7	—	100 ± 13	—
PAS	66 ± 5	90 ± 7	98 ± 13	100 ± 13
PA	60 ± 5	77 ± 6	78 ± 10	90 ± 11

#### 3.2 Solid phase investigation.

The SEM images of calcium carbonate are presented in Figures 2, 3.  $\text{CaCO}_3$  particles, obtained in experiments without an inhibitor (Fig.2), were similar in size and shape, and the most stable phase of calcium carbonate, calcite, prevailed in the scale.

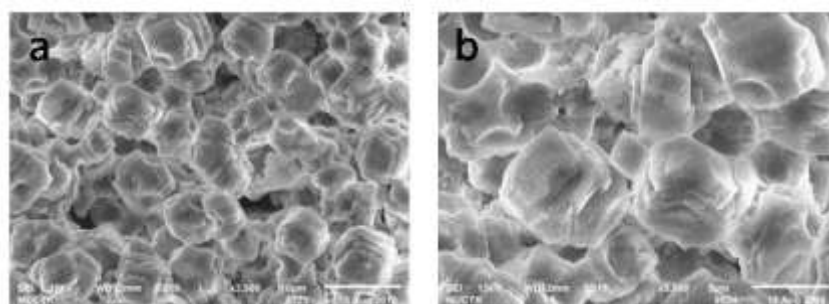


Fig.2. SEM images of  $\text{CaCO}_3$  crystals: (a) - (x2500), (b) - (x5000)

When inhibitors were used a significant decrease of calcium carbonate amount and particle size were observed. Moreover, the more effective the inhibitor was, the more the structure of the  $\text{CaCO}_3$  precipitate was changed. The smallest changes were recorded when using a polyacrylate-based inhibitor (Fig. 3a). In the presence of PAS, an aggregate of calcium carbonate particles was formed, consisting of both rhombohedron calcite and round-shaped crystals characteristic of a metastable vaterite (Fig. 3b). The greatest changes were recorded when using HEDP and ATMP (Fig. 3c-d), while the sediment lost its crystalline structure and became friable, which leads to simpler removal of it from the surface of the reverse osmosis membrane.

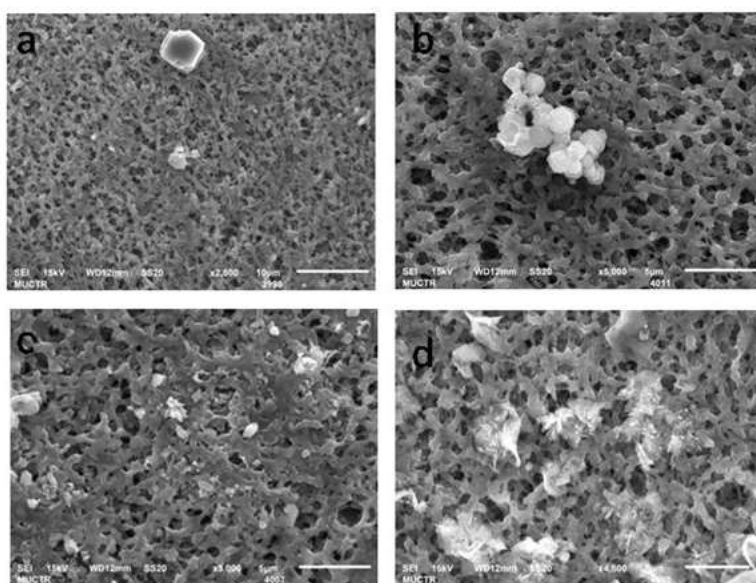


Fig.3. SEM images of  $\text{CaCO}_3$  in the presents of inhibitors. (a) – PA, (b) – PAS, (c) – ATMP, (d) – HEDP

#### 4. Conclusion

1. Using two express laboratory techniques, different types of scale inhibitors to prevent the precipitation of calcium carbonate were compared. A number of the effectiveness of antiscalants at a concentration of 4 ppm is evaluated as  $\text{HEDP} > \text{ATMP} > \text{PAS} > \text{PA}$ .
2. The relative effectiveness of polymeric antiscalants at a concentration of 10 ppm was shown.
3. It is defined that the addition of inhibitors leads to a change in the structure of the precipitate of calcium carbonate.
4. It was revealed that the more effective the antiscalant is, the more the sediment structure changes towards the formation of a less stable and easier to remove modification of calcium carbonate.

#### References

- [1] Amjad Z and P Koutsoukos 2014 *Desalination* **335** pp 55–63
- [2] Tang Y *et al* 2008 *Desalination* **228** pp 55–60
- [3] Belarbi Z *et al* 2014 *Journal of Crystal Growth* **386** pp 208–214
- [4] Lui G *et al* 2014 *Designed Monomers and Polymers* **20** pp 397–405
- [5] Kumar M *et al* 2015 *Environmental Technology* **36** pp 1281–1290
- [6] Lui Y *et al* 2014 *Appl. Polym. Sci.* **131** pp 39792/1–39792/12
- [7] Wang *et al* 2015 *Desalination and Water Treatment* **53** pp 3491–3498
- [8] Al-Roomi Y M *et al* 2015 *Desalination* **375** pp 138–148
- [9] Amjad Z *et al* 2014 *Int. J. Corros. Scale Inhib.* **3** pp 35–47