

Calcium carbonate inhibition by green inhibitors: Thiamine and Pyridoxine



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HIGHLIGHTS

- The use of the mixture of vitamins leads to significant inhibition of calcium carbonate formation.
- The inhibition efficiency is around 66.78 % by the use of electrochemical impedance spectroscopy.
- The increase in the speed of precipitation of calcium carbonate overestimates the optimal amount of inhibitor.
- IR, X-ray diffraction and Raman spectroscopy analyses indicated modifications in crystalline structure.

ARTICLE INFO

Article history:

Received 28 February 2016

Received in revised form 1 November 2016

Accepted 5 November 2016

Available online xxxx

Keywords:

Calcium carbonate
Green inhibitor
Scale formation
Calcite
Vaterite

ABSTRACT

In the East of Algeria, the city of Constantine called for its water supply, the Hama groundwater resource. The high content of hydrogen carbonate and calcium justify the very important scaling power, it contains 82 % by mass of these ions.

This paper focuses on the application of a new green inhibitor “RS1600” for reducing calcium carbonate scale formation. RS1600 is a type of water soluble vitamin, it has proven to be green scale inhibitor given his nontoxic and biodegradable features. The inhibiting effect occurs at very low concentration. Its performance is evaluated and compared using different chemical and electrochemical anti-scaling methods.

The nucleation and scaling time were identified. The ratio between homogeneous and heterogeneous nucleation was determined. IR, X-ray diffraction and Raman spectroscopy analyses demonstrated modifications in crystalline structure, the CaCO₃ crystallize from calcite to vaterite. The study suggested that RS1600 is an excellent green chemical.

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1. Introduction

Hamma groundwater resource is a natural water, it contains scale-forming ions. The elevated concentration of HCO_3^- and Ca^{2+} , and important water temperature cause the scale formation by calcium carbonate, one of the most common scale components found in cooling water systems [1,2], oilfield production [3] and desalination units [4].

Deposits formation may cause severe corrosion and deteriorate conditions of the heat exchange [1]. The most common and effective scale control method is the addition of small concentrations of inhibitors to the water [5–8]. Thus, the concept of “green chemistry” was proposed, and green scale inhibitors have become an important focus in water treatment technology [9,10]. All the last researches [1,10–13] have proved that the addition of scale inhibitors induce morphological changes of the crystal shape.

In pursuance of going greener, we investigated the scale inhibiting of RS1600 which is a novel scale inhibitor and shows promising prospect as a green water-treatment agent for circulated cooling water. RS1600 is the mixture of two vitamins: Thiamine (50 %) and Pyridoxine (50 %). The chemicals formula of their vitamins are: $\text{C}_{12}\text{H}_{17}\text{ClN}_4\text{OS}$ and $\text{C}_8\text{H}_{11}\text{NO}_3$.

In the present study, we evaluated the physico-chemical quality of the hard water of Hamma and inhibit the furring power of these waters by the use of different chemical and electrochemical scaling methods. Formed scales were characterized by: IR, XRD and Raman spectroscopy. The result shows that the RS1600 changed the morphology of CaCO_3 precipitates.

2. Materials and methods

2.1. The precipitation of CaCO_3 by degassing dissolved- CO_2 method

It was first developed in 1994 by Roques et al. [14] and it has been used in many studies [15–17,4]. Its principle is based on the displacement of the calcocarbonic equilibrium in the direction of the precipitation of CaCO_3 by degassing dissolved- CO_2 , as the equation of the following reaction shows:



Thus, it allows to control the changes in the concentration of dissolved- CO_2 which is the main motor of the system evolution leading to scaling [18].

In this first part, we were used the technique of degassing the dissolved- CO_2 by stirring [19], and the results were checked by a second method it is the technique of degassing the dissolved- CO_2 by the nitrogen sparge.

In the precipitation test, 500 mL of no-treated and treated water was placed in a stainless steel cell and immersed in thermostatic water bath to maintain 30 °C. According to Karoui et al. [4], during the precipitation test, the pH of the solution was continuously recorded. Samples of 1 mL were withdrawn from the solution and their HCO_3^- ion concentration was analysed by sulphuric acid (10^{-2} M) in the presence of the bromochrizole green (as indicator). At the end of the treatment, precipitate was recovered by filtration on a 0,45 μm pore size cellulose nitrate membrane. According to Alimi et al. [17], we can deduced from the

calcium carbonate mass m_b formed in the bulk of the solution by homogeneous nucleation and the initial calcium carbonate mass m_0 , the mass of calcium carbonate m_w deposited on the walls of the cell by heterogeneous nucleation.

2.1.1. CO_2 degasification by agitation

After a regular agitation of 800 rev/min by a magnetic stirrer to the solution of 500 mL, the degasification of the dissolved- CO_2 occurs.

The schema of the experimental setup is presented in Fig. 1.

2.1.2. CO_2 degasification by nitrogen sparge

In this technique, the CO_2 degasification was provoked by a continuous flow of pure nitrogen (8 L/min) through a diffuser located at the bottom of the cell.

We have chosen to work with a stainless steel cell because it is the same material that was used for the previous technique.

The diagrammatic representation of the system is shown in Fig. 2.

2.1.3. Chronoamperometry

Chronoamperometry, is one of the electrochemical method proposed by Ledion et al. [20]. The principle is to cover with calcium carbonate a metal surface carried to a fixed negative potential (-1 V versus SCE), corresponding to the limiting current of the reduction reaction of the dissolved oxygen:



By increasing the local pH in the vicinity of the metal surface where O_2 is reduced [21], the hydroxide ions promote the calcium carbonate to precipitate according to the chemicals reactions:

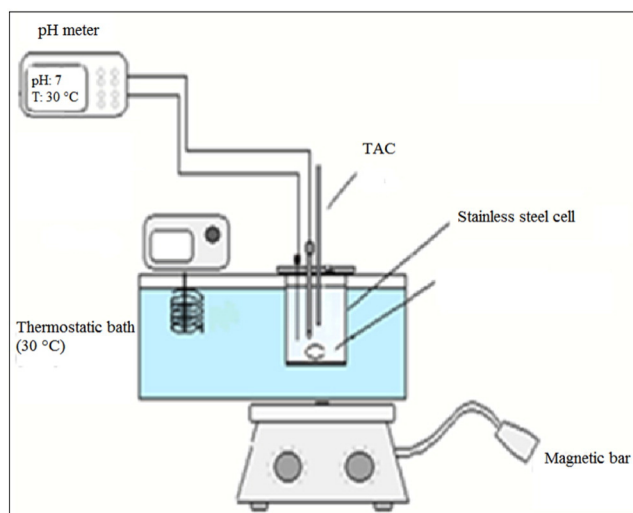


Fig. 1. Experimental setup scaling accelerated by agitation.

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