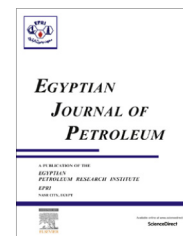




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FULL LENGTH ARTICLE

Seawater-softening process through formation of calcite ooids



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Abstract Conventional water-softening processes usually involve the exchange of Na⁺ ions for Ca²⁺ and Mg²⁺ using commercial or synthesized ion exchangers. The differences in chemical compositions of the ooids can be attributed to the formation in different environments. In this paper, ooid grains form inside assembled semi-pilot softening unit through a continuous chemical process involving reaction between bicarbonate ions and added lime using natural seawater. Our sample of Mediterranean seawater has low Mg²⁺/Ca²⁺ ratio (1.98%) within the range chemically favorable for precipitation of low-Mg calcite ooids. Precipitation of calcite occurs around pure quartz sand grains which act as nucleation points (the bed required for sand vessel is 1.65 l). The shape of the sand grains controls the overall external morphology of the resulting ooids; they vary in size from 0.5 to 3.0 mm and have a high degree of polish due to surface abrasion caused by continuous agitation inside the softening system. Calcite ooid grains (1.53 kg) formed within the seawater-softening unit every 18 days have many of the ooid features formed in marine environments. Ooids grow to a significant size, at a rate of about 0.17 mm of one layer thickness per day inside the softening unit. The average weight percent of calcite precipitate is 35.48% after 18 days, at 10 °C, 60 l/min and pH 9.0. The pellets comprise mainly CaCO₃ and SiO₂ and some metal ions which may substitute for calcium ions in calcite are present only in trace amounts of the total composition.

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1. Introduction

The original mineralogy of calcium carbonate components in marine settings is almost exclusively either calcite or aragonite.

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Because aragonite is unstable with respect to low-magnesium calcite, aragonite components transform to calcite via dissolution-precipitation processes early in the diagenetic history of most sequences. Ooids are spherical or ellipsoid coated sedimentary grains of calcium carbonate, there have been examples of ooids that are 16 mm in diameter [1], but usually less than 2 mm in diameter [2]. Ooids sometimes are made up of iron- or phosphate-based minerals and usually formed on the sea floor, most commonly in shallow tropical seas. The interior of an ooid

is usually composed of a nucleus, which is surrounded by a cortex of calcite or aragonite crystals that are arranged radially, tangentially or randomly. The nuclei that are introduced into a suitable turbulent location to keep them in suspension and supersaturated water in calcium carbonate will take a short lived inorganic precipitation on their surfaces of CaCO_3 and the precipitation is stopped by the addition of Mg^{2+} or H^+ onto the surface [3]. The formation of ooids was effected by CO_3 -concentration. For ooids to form successfully the CO_3 -concentration need to be above 0.002 mol/l and below 0.0167 mol/l. When CO_3 -concentration was above 0.0167mol/l the ooids formed an amorphous mass, while below 0.002 mol/l only aragonite needles or poor ooids were formed [4]. Organic coating on the nuclei give a faster and longer precipitation, while using oxidized quartz show a much slower and shorter precipitation [3]. Most ooids are formed in water less than 2 m deep, but wave agitation and tidal movements may be effective than water depth itself [5]. Ooids are classic indicators of agitated, shallow water tropical sedimentation [6]. Ooids can form in quiet waters, but organic CaCO_3 precipitation is needed for them to form and these ooids will show radial crystals [7]. Water current at different flow speeds (5 cm/s and 10 cm/s) was kept in suspension by this water, and in other experiments involving horizontal shaking and tumbling motion, the ooids were non-existent or more like those formed in non-agitated water in the presence of organic compounds, as the produced cyclic membranes of high-molecular weight humic acids (M.W., 15000–50000) in laboratory-grown quiet-water ooids, and the membranes formed during burial. The larger water current increases precipitation rates of different nuclei, but the change of precipitation time depends on nuclei type [3]. Numerical modeling on ooid formation gave a higher ooid radius in higher velocity flows and a smaller ooid radius with decreasing velocity and they did not include the impact of ooids to limit size [1]. The chemical growth mechanism of calcite concretion from an industrial water-softening process was represented by a continuous chemical process involving reaction between carbonate/bicarbonate ions from incoming borehole waters and added lime precipitated calcite around silica sand grains which act as nucleation points. The process is based upon the removal of bicarbonate ions from solution as a precipitate of calcium carbonate by the addition of lime (CaO) [8]. In this paper, we report on the chemical formation of the calcite ooids in assembled semi-pilot softening unit with different flow rate speeds (20, 40 and 60 l/min) to keep it in suspension by these water velocities and this unit is located at the Egyptian Petroleum Research Institute (EPRI). This study illustrates the chemical conditions prevailing during their formation.

2. Materials and methods

2.1. Analysis of seawater samples

The feed seawater samples to our semi-pilot unit in EPRI were natural samples obtained from an open-intakes in the Mediterranean Sea in Marsa Matrouh city (440 km from Cairo city), Damietta city (200 km from Cairo city) and the Red sea in Ain Sukhna city (120 km from Cairo city). The physicochemical analysis of the raw seawater samples at temperature 10 °C was determined by a Spectrophotometer, LaMotte, model SMART Spectro, USA and is presented in Table 1.

Table 1 Interstitial seawater chemistry, at a low temperature, 10 °C.

Parameters	Marsa Matrouh	Damietta	Ain Sukhna
pH	7.8	8.1	8.4
Total hardness, mg/l	7280	7565	7850
Turbidity, NTU	1.98	2.4	2.2
TOC, mg/l	2.8	3.1	3.3
Mg^{2+} , mg/l	1203	1377	735
Ca^{2+} , mg/l	608	412	231
HCO_3^- , mg/l	328	265	275

2.2. Semi-pilot softening unit

A semi-pilot softening unit located in EPRI was designed according to the schematic diagram in Fig. 1 to meet the objectives of the study. The unit works in closed cycle and consists of one water tank, 60 l. The chemical treatment included the injection of lime (CaO) in the make-up water line (chemical feeding by dosing pump, 5 l/7 bar). A one feeding water pump (stainless steel 304, 20–60 l/min, 5 bar max) is used to supply water to softening vessel. This vessel is constructed using a fiberglass reinforced polyester resin for standard water conditioning use with specific sizes of 7 inch diameter and 17 inch height, maximum operating pressure 150 psi, maximum operating temperature 49 °C, full-bed capacity 13.2 l and the top opening of this vessel 2½ inches. The bed capacity in liters required for media softening vessel is 1.65 l. This vessel is manually controlled. Service flow rates of the softening process are 20, 40 and 60 l/min at 10, 15 and 20 °C during normal operation in lpm/sqft for sand. Two flow meters are present to measure seawater in and out softening media vessel and to measure the difference before and after softening process to determine the accurate time to have drawn off the ooid pellets from softening vessel. Finally, the semi-pilot softening unit was controlled by electrical control panel.

2.3. Softening media

The granular softening media applied in the vessel of this unit is quartz sand which is used as filter media operating successively. The maximum bed capacity of the vessel required to be filled is 13.2 l. The bed required for sand vessel is 1.65 l with an effective size: 0.45–0.55 mm [9]. Filter media used in our semi-pilot unit for the softening process of seawater are shown in Fig. 2.

3. Results and discussions

3.1. Softening process description

The seawater pH range of the softening unit is between 8.0 and 9.5. Temperatures vary by no more than 0.5 °C and range between 10 and 20 °C. The hardness (in HCO_3^-) is relatively high (328 mg/l for Marsa Matrouh sample), Table 1. The addition of lime (CaO) is to remove the bicarbonate ions from solution as a precipitate of calcium carbonate. The addition of lime increases the pH and the OH^- content of the softening unit. Bicarbonate is removed through consumption of OH^- ions as a precipitate of calcium carbonate in which the calcium ions

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