

Carbonate and Sulfide Scale Formation in Multiphase Conditions

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ABSTRACT

Calcium carbonate (CaCO_3) scale formation is recognized as a major problem affecting production and transportation in the oil and gas industry. The phenomenon is extensively studied however; very limited work has been carried out to evaluate it in multiphase environments. This work aims to study calcium carbonate surface deposition in a multiphase environment that can replicate more accurately conditions encountered during secondary and tertiary oil production. Multiphase conditions induced by introduction of a light distillate within the system were used to create oil in water (o/w) emulsions in order to reflect more accurately the scaling process in oil pipeline transportation. Using a set of bulk and surface analysis techniques such as Inductively Coupled Plasma (ICP) spectroscopy, X-ray powder diffraction (XRD), or Scanning Electron Microscopy (SEM), the results showed that the presence of an oil phase within the system retard the nucleation as well as the dissolution of vaterite, the metastable phase of calcium carbonate. This affect the growth kinetic of calcite and contribute overall to hinder mineral surface fouling. When lead sulfide (PbS) co-precipitates alongside calcium carbonate, the experimental observations show that PbS crystals provides additional seeding point for the nucleation of CaCO_3 to take place. In such conditions, the mechanism of surface fouling build-up is altered and proceed via the impact and adhesion of PbS/CaCO_3 particles onto the stainless-steel surfaces which result in higher mass gain.

Key words: calcium carbonate; lead sulfide; multiphase environment; o/w emulsions; surface fouling

INTRODUCTION

Inorganic fouling in oilfields has resulted in millions of dollars of operating expenditure every year since the inception of offshore oil and gas drilling, where mineral scale deposition in tubing, flowlines and downhole equipment leads to significant production downtime. Calcium carbonate (CaCO_3) fouling is endemic in oilfield systems, as produced water containing both bicarbonate and calcium ions is prone to form precipitates as a result of pressure changes during production.^{1,2,3} The release of carbon dioxide gas from the aqueous phase prompts the evolution of carbonate resulting in a rise in pH and consequent precipitation. The additional reduction of CaCO_3 solubility with increased temperature dictates that precipitation can occur anywhere from the wellbore to the topside, with case studies showing precipitation of CaCO_3 species both near the wellbore and higher up the production tubing.^{4,5} Before deploying a mitigation technique (i.e., scale chemical inhibitors) an experimental matrix is usually developed and laboratory tests are carried out to evaluate its adequacy with the oilfield under consideration.^{6,7} However, the match between laboratory performance and the one ultimately observed in the field can be poor. Overcoming these discrepancies requires a comprehensive understanding of the calcium carbonate precipitation process in complex multi-phase environments in which they usually occur. Indeed, oil production environments rarely contain only an aqueous phase and are usually more complex due to the presence of an oil phase. The presence of such organic phases makes prediction of surface fouling difficult and lead to the need for field measurement to refine formulation of scale inhibitors to the specific conditions prevailing in each application. This study aims to establish a better knowledge on calcium carbonate surface fouling kinetics and mechanisms in oil and gas production systems.

EXPERIMENTAL PROCEDURE

Solution composition

The thermodynamic state of the scaling solutions with respect to vaterite and calcite precipitation was evaluated according to:

$$\Omega_{C,V} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]\gamma_2^2}{K_{C,V}} \quad (1)$$

Where $K_{C,V}$ is the solubility constant of calcite and vaterite, γ_2 the activity coefficient for divalent ions calculated from⁸:

$$-\log \gamma = A \cdot z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30 \cdot I \right) \quad (2)$$

Where A denotes a constant depending on the temperature ($A = 0.5085$ at 25°C), and I represents the ionic strength of the solution:

$$I = 0.5 \cdot \sum z_i^2 \cdot C_i \quad (3)$$

Z_i and C_i are respectively the ionic charge and concentration of the i th ion in solution. The concentration in calcium ions $[\text{Ca}^{2+}]$ was measured by atomic adsorption spectroscopy while the carbonate species $[\text{CO}_3^{2-}]$ was derived from recorded pH data and total carbonate alkalinity measurements using Equation 4^{9, 10}

$$Y_{CO_3^{2-}} = \frac{1}{1 + \frac{Y_{H^+}}{K_2} \cdot \frac{Y_{H^+2}}{K_1 \cdot K_2}} \cdot Y_{C_{tot}} \quad (4)$$

Solution composition

Solutions of calcium chloride and sodium bicarbonate were prepared from analytical grade chemicals and deionized water. The composition of the solutions and the initial saturation ratio are presented in Table 1. At the beginning of a test, 500ml of the bicarbonate solution was poured into the reaction vessel and an adequate volume of synthetic light distillate solvent (Isopar M) was added to reach the desired oil fractions. Carbon dioxide was bubbled through the reaction vessel for 4 hours to saturate the continuous and disperse phases and the solution was adjusted to pH 8 by means of sodium hydroxide or hydrochloric acid. The scaling tests were initiated by adding 500ml of the calcium solution into the reaction vessel. During the experiments, the system was stirred using a bladed impeller connected to an overhead motor rotating which prompted the formation of an oil in water emulsion which was confirmed by conductivity measurement (20 mS/cm). The rate of precipitation was monitored by following the pH of the solution and tracking the concentration of calcium ions in the solution. Calcium carbonate surface fouling was monitored on 316L stainless steel cylindrical samples (roughness Ra 1.07 μm) mounted on a rotating shaft. The set-up provides a controlled mass transfer and uniform flow distribution at the surface of the samples where deposition took place.¹¹ The tests were performed at 2000 RPM which is equivalent to Reynolds number of 15,100 for an oil-free system. Calcium carbonate surface deposition was assessed by gravimetric measurements. Post experiments the morphology of calcium carbonate and surface coverage was assessed by scanning electron microscopy while X-ray diffraction was used to assess the abundance of the polymorphs. Figure 1 illustrates the experimental set-up used in this study. For co-precipitation experiments, a modified version of the set-up was used to simultaneously trigger the precipitation of calcium carbonate and lead sulfide (PbS), the brine compositions and initial saturation ratio are available in Table 2. CO₂ gas was bubbled through the vessels for 1 hr., ensuring anaerobic conditions in both incompatible brines before mixing.¹²

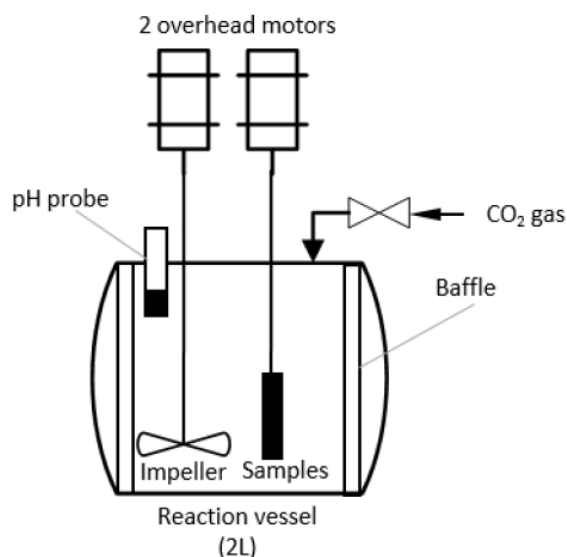


Figure 1: Schematic diagram of experimental set-up.