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Calcium carbonate scale formation—assessing the initial stages of precipitation and deposition

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Abstract

Scale formation is a serious problem encountered in many industries including oil or gas production, water transport, power generation and batch precipitation. Normally, studies of scale formation have been focused on precipitation processes in the bulk solution using bulk jar methods where the precipitation tendency rate and inhibitor effectiveness are quantified. Several recent studies have started to focus on scale deposits formed on the surface of metals. In this paper, calcareous scale formation was studied both in the bulk solution and on the metal surface in three supersaturated scale formation solutions which represent typical waters encountered in oil and gas production. An electrochemical technique, using a rotating disk electrode (RDE), was used to quantify scale formation on the metal surface. With this technique, reduction of oxygen was considered at the surface of a RDE. The rate of oxygen-reduction at the surface of the RDE enables the extent of surface coverage of scale to be assessed. To understand the formation and growth of the surface scale deposit, surface analysis was used in conjunction with this technique. Scanning electron microscopy (SEM) was used for analyzing the microstructure of the scale. At the same time, inductively coupled plasma (ICP) was used for analyzing the quantity of the precipitate formed in the bulk solution and scale formed on the metal surface by dissolving the scale.

In this paper it is demonstrated that bulk precipitation and surface deposition have different dependencies on the index of supersaturation and so to completely understand an industrial scaling system both processes should be studied.
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Keywords: Scale formation; Homogeneous precipitation; Heterogeneous precipitation; Calcium carbonate; Rotating disk electrode

1. Introduction

The formation of mineral scale, in particular calcareous deposits, is a persistent and expensive problem in industries ranging from oil and gas to desalination. Scaling of metallic or insulating walls in

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contact with water supersaturated with respect to calcium carbonate may create technical problems including impedance of heat transfer, increase of energy consumption and unscheduled equipment shutdown (Klepetsanis et al., 1995; Kjellin et al., 2001; Qingfeng, 2001).

The precipitation of calcium carbonate has been widely studied (Sohnel and Mullin, 1982; Abtahi et al., 1996; Nancollas and Reddy, 1973). Traditionally, studies of scale formation have concentrated on assessing precipitation formed in the bulk solution by using laboratory beaker or bulk jar tests (Abtahi et al., 1996; Nancollas and Reddy, 1973). The research has primarily focused on the assessment of the kinetics of homogenous and heterogeneous precipitation in the bulk solution (Langelier, 1936). The formation of the solid phase is throughout the mother phase without any foreign solid phase in homogenous processes, and the formation of new solid phase particles is catalyzed by the presence of a foreign solid phase in heterogeneous processes (Sohnel and Garside, 1992).

It has been demonstrated (Harris and Marshall, 1981) that there are often wide anomalies between actual deposition on component surfaces and scaling rates estimated by predictive models based on scaling indices and thermodynamics to predict precipitation tendency (Hasson et al., 1996). However, the relationship between precipitation and scale deposition on solid surfaces has received little attention.

Some focus has been turned to this aspect of scaling and has resulted in numerous studies reporting methods to detect and assess scale formation on metal surfaces. Hasson (Hasson et al., 1996) and Zhang (Zhang et al., 2001), studied calcium carbonate scale formation in a pipe flow system in oil and gas industry and desalination industry to attempt to overcome some of the shortfall of beaker tests. Sullivan (Sullivan et al., 1996) studied scale formation by monitoring the heat transfer change. These methods have been developed primarily to assess efficiency of scale inhibitors and give only a relative estimate of the thickness of scale. They are usually not sensitive enough to study the primary layer of scale. In recent work by the authors' studies of scale formation on metal surfaces have been progressed. Through directing more attention to the scale formation and

adhesion at metal electrodes, in parallel with precipitation processes the entire scaling process can be characterized. This will then facilitate the development of inhibitors where the functionality can be targeted to the particular scaling problem.

In the work reported herein, an electrochemically based technique is used to develop an understanding of the kinetics of scale deposition on metal electrodes. The technique developed by Neville et al. (1999) can quantify the scale coverage in the early stages of scaling. In this paper comparisons are then made with the bulk precipitation processed occurring simultaneously.

2. Experiment techniques

2.1. Reagents

To create the supersaturated solutions for this study, calcium chloride ($CaCl_2 \cdot 6H_2O$), sodium chloride (NaCl), magnesium chloride ($MgCl_2 \cdot 6H_2O$), sodium bicarbonate ($NaHCO_3$) of analytical grade supplied by BDH Laboratory were used. The solutions were made using distilled water.

2.2. Procedures and measurements

Experiments were carried out in a 1-l vessel thermostated at 20 °C. 800-ml scale formation solution was used in each experiment. $CaCO_3$ was precipitated spontaneously by mixing two solutions (400 ml brine 1 containing calcium ions and 400 ml brine 2 containing bicarbonate ions). The pH was buffered to 6.7 by acetic acid. Before mixing, the two solutions were filtered using a 0.45-μm filter. Three-scale formation solutions, the composition provided by worker in the soil and gas industry, were used: solutions A, B and C, respectively. S is the supersaturation ratio of these solutions. For $CaCO_3$, S can be expressed as:

$$S = \left(a_{Ca^{2+}}\right)\left(a_{CO_3^{2-}}\right)/K_{sp}$$

where a_i is the activity of a given ion and K_{sp} is the solubility product of the scale forming mineral (here $CaCO_3$). The supersaturation index (SI), equal to log S, is also commonly used to express scaling tendency.