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Application of a novel tube reactor for investigation of calcium carbonate mineral scale deposition kinetics

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ABSTRACT

A novel plug-flow type tube reactor apparatus is reported to investigate the deposition kinetics of a common mineral scale calcium carbonate ($CaCO_3$). Mineral scale deposition is a common phenomenon in industry and can pose a serious threat to the safe and economical operations. Compared with the conventional apparatus, the tube reactor has the advantage to maintain a constant solution pH, surface area and a controlled saturation index and hydraulic condition during the deposition study. Two scenarios of $CaCO_3$ solid deposition were considered in this study, including deposition of $CaCO_3$ on clean surfaces and also deposition of $CaCO_3$ on a surface pre-coated with $CaCO_3$ solid. The results show that the overall $CaCO_3$ deposition process can be divided into multiple stages with different deposition kinetics and different solid morphologies. It is obvious that experimental conditions, such as solution chemistry, flow rate, temperature and saturation index, can have a considerable impact on $CaCO_3$ deposition kinetics. These results provide an in-depth understanding of the process involving $CaCO_3$ deposition onto the surface of a pipe material or a conduit. This novel tube reactor apparatus expands our capability of investigating mineral scale deposition kinetics and the influences of various experimental factors on scale deposition kinetics.

1. Introduction

Mineral scale (scale) is the sparingly soluble inorganic deposit from aqueous solution (Frenier and Ziauddin, 2008; Kan and Tomson, 2012; Kelland, 2014). The deposited scale solid is typically crystalline in structure with a low solubility in aqueous solution. Scale deposition is an aqueous phenomenon. In other words, if there is no aqueous phase present, there is no scale deposition. Scale can deposit on any equipment surface which is in direct contact with water. Scale deposition can pose a serious problem to the safe and economical operations of various

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Abbreviations: SI, saturation index; DI water, deionized water; ID, inner diameter; SS, stainless steel; CS, carbon steel; PFA, perfluoroalkoxy alkanes; ICP-OES, inductively coupled plasma-optical emission spectrometer; SEM, scanning electron microscopy; XRD, X-ray diffraction; EDXS, energy-dispersive X-ray spectrometer; HPLC, high-performance liquid chromatography.

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industrial facilities, such as municipal water system, heat exchanger, cooling tower, membrane filtration and oil production system (Jordan and Mackay, 2016; Kan and Tomson, 2012; Zhang et al., 2015). Scale deposition can lead to equipment blockage with a narrowed tubing inner diameter and a reduced flow rate. If scale formation occurs in aqueous solution and does not deposit on a surface, it is not a particularly severe problem. In fact, scale buildup on steel surfaces of heat exchangers and oil and gas production tubing costs hundreds of millions of dollars of damage per year. Therefore, it is of great importance for both academia and industry to understand the scale deposition process in order to effectively control scale damage. Extensive studies have been carried out to evaluate the thermodynamics of scale deposition (Frenier and Ziauddin, 2008; Kelland, 2014; Yuan, 2010). Thermodynamically, scale deposition out of aqueous solution is a result of forming local supersaturation with respect to the inorganic solid compound(s). The supersaturation of a brine solution with respect to an inorganic scale can be regarded as the physiochemical driving force to form the initial scale particle nucleus and subsequently precipitate out of the aqueous phase (Mullin, 2001; Stumm and Morgan, 1996). The term saturation ratio has been proposed to assess the scaling threat tendency as (Kan and Tomson, 2012):

$$\text{Saturation Ratio} = \frac{\text{Ion Activity Product}}{\text{Solubility Product}}$$

The base 10 logarithm of saturation ratio is called saturation index (SI), which is also commonly used in scale chemistry. If SI is larger than 0 under a certain condition, ion activity product of the brine solution is higher than the solubility product of the inorganic compound, which will eventually lead to scale deposition. Several scale prediction software packages have been developed to aid in assessment of scale threat for industrial processes (Frenier and Ziauddin, 2008). However, these software packages are thermodynamic in nature and typically take no account of scale formation kinetics, i.e., the rate of scale deposition. Thermodynamic prediction alone is not able to elaborate of how fast the scale will form on the surface of equipment. Quite often, the time for scale deposition out of an aqueous solution can considerably exceed the time required for the aqueous solution to pass through the equipment of interest or to be discharged (Kan and Tomson, 2012; Zhang et al., 2015).

Compared to thermodynamics study of scale deposition, scale kinetics studies are considerably limited and the models predicting scale kinetics are less reliable due to insufficient kinetic studies (Al Nasser et al., 2016; Mackay, 2003; Yuan, 2010; Zahedzadeh et al., 2014). The existing scale kinetics research has focused on five steps in the overall scale deposition process, although there is no absolute boundary between each step (Mullin, 2001; Stumm and Morgan, 1996): (1) Initiation period: an induction period has been observed between the establishment of a supersaturation condition and the onset of scale deposition. Thus, induction time is defined as the time elapsed between the creation of driving force (supersaturation) for precipitation and the first appearance of a new phase (scale particle). It has been found that the induction time is a function of SI, temperature, and composition (He et al., 1994; He et al., 1995). More recently, it has been shown that at extremely high pressures (ca. 700 atm and higher) induction time is also a function of pressure (Bhandari et al., 2016); (2) Scale crystal formation: as soon as scale particle nucleation occurs, the nuclei will grow to become scale crystals; (3) Transport to surface: subsequently, the crystal components involved in scale buildup transport to the surface of equipment or the wall of oil production tubing (Charbeneau, 2006; Clark, 2009). The transported crystal components will eventually arrive and attach to either the equipment surface (crystal attachment) or the surface of pre-deposited scale crystals (crystal growth); (4) Removal of scale from the surface: the previously deposited scale layer can be fully or partially removed from equipment surface chemically or due to the fluid shear stress, depending on the adhesion strength of the deposit scale layer; (5) Aging of the deposit: eventually, phenomena of recrystallization, phase transformation and Ostwald ripening will occur to strengthen the remaining scale deposits through an aging process. Among various types of scales observed in industry, calcium carbonate ($CaCO_3$) is one of the most commonly encountered scales. $CaCO_3$ deposition is typically due to the change in processing conditions, especially change in temperature and pressure (Frenier and Ziauddin, 2008; Kelland, 2014). A reduction in pressure and/or an increase in temperature can lead to supersaturation with respect to $CaCO_3$ and subsequent scale deposition.

Historically, $CaCO_3$ deposition kinetics has been studied by use of several major categories of apparatus: (1) conventional beaker (He et al., 1994, 1995); (2) rotating disc (Quddus and Allam, 2000); (3) constant composition (supersaturation) device (Andritsos et al., 1997; Stamatakis et al., 2005, 2006; Tomson and Nancollas, 1978) and (4) mixed-suspension mixed-product removal (MSMPR) (Alvarez et al., 2011; Li et al., 2016; Power et al., 2015). These different experimental apparatuses differ in terms of surface area, ionic strength, solution pH, SI and hydraulic conditions, as summarized in Table 1.

Constant composition device is believed to be an accurate apparatus by providing a constant solution pH, ionic strength and a controlled SI and hydraulic condition. However, constant composition device is not able to maintain a constant surface area. MSMPR crystallizer device is one of the most frequently encountered continuous equipment in industry with a constant SI and solution composition. However, neither MSMPR device nor constant composition device is suitable to study scale deposition in a pipe or a longitudinal conduit system. In this study, a novel plug-flow type tube reactor was designed to investigate the process involving $CaCO_3$ deposition. The feed brine solutions were delivered into the tube reactor at a constant composition with known solution chemistry and at a controlled flow rate. The tube reactor represents a carefully controlled approach to study the kinetics of scale deposition process. To the best of our knowledge, this study is the first to describe the laboratory investigation of scale deposition kinetics with a constant surface area, ionic strength, solution pH and at a controlled SI and hydraulic condition (Table 1). This novel apparatus separates the crystal growth from the initial attachment process and expands our capability in investigating mineral scale deposition kinetics and the influences of various experimental factors, such as temperature, flow rate, and solution chemistry, on scale deposition kinetics.

2. Materials and methods

2.1. Chemicals

Sodium chloride (NaCl) solid, calcium chloride ($CaCl_2$) solid, sodium bicarbonate ($NaHCO_3$) solid, potassium chloride (KCl) solid and nitric acid (HNO_3) were reagent grade and purchased from Fisher Scientific. Deionized water (DI water) was prepared by reverse osmosis and ion exchange water purification processes.

2.2. Tube reactor and the experimental setup

$CaCO_3$ solid deposition kinetics was investigated using a novel plug-flow tube reactor setup. The experimental setup includes a tube reactor of 0.91 cm inner diameter (ID) and 12.7 cm length, two HPLC pumps (Gilson Inc., Middleton, WI) and a sample collector. The tube reactor was submerged inside a water bath heated to the desired temperature. A schematic representation of the experimental setup is illustrated in Fig. 1.

The tube reactor exterior surface was coated with rustoleum to prevent exterior corrosion and the interior was polished with 2000 grit sandpaper to provide a smooth surface for scale particle deposition (details in the Supporting information). The void space of the apparatus includes the internal volume of the tube reactor and the associated tubing volume. A KCl tracer breakthrough experiment determined the total apparatus void space of ca. 9.2 mL (details in the Supporting information). A $CaCl_2$ feed brine solution was prepared by dissolving $CaCl_2$ solid into a NaCl aqueous solution. A $NaHCO_3$ feed brine solution was prepared similarly. Both feed solu-