Powder Technology 270 (2015) 548–560

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Kinetics determination of calcium carbonate precipitation behavior by inline techniques

Waleed N. Al Nasser *, Fahad H. Al Salhi

Saudi Aramco, Dhahran 31311, Saudi Arabia

ARTICLE INFO

Available online 22 May 2014

Keywords:
Growth rate
Inline
Deposition of calcium carbonate
Precipitation
FBRM
PVM

ABSTRACT

Calcium carbonate, $CaCO_3$, presents a big problem in oil and gas industry. Scaling in pipes leads to decreases in pressure drops and often to complete blockage. On heat exchanger, it reduces the heat transfer. It could lead to unstable operation which may result in unscheduled shutdown.

Precipitation of calcium carbonate is a prerequisite for the deposition of calcium carbonate crystals on an external surface. Hence to understand the scaling process, it is necessary to understand the calcium carbonate precipitation kinetics. This could be achieved through fully controlling the precipitation and deposition processes.

Calcium carbonate precipitation is widely studied using various methods. However, the techniques used were based on either solution side information to determine precipitation kinetics or offline size analysis to find growth rate constants. In the present work inline in situ technique based on FBRM (focused beam reflectance measurement, Mettler Toledo) gives direct measurement of number of crystals. The inline image technique by PVM (particle vision and measurement, Mettler Toledo) gives accurate induction period measurements and nucleation kinetics. The method of moments was utilized to determine the crystal size and hence the growth rate. Therefore, a number of experiments were conducted to obtain reliable and reproducible conditions for consecutive precipitation and deposition processes. The data from the FBRM and images from the PVM provided information about the particle count and size. The experiments were conducted in a closed system to reduce the effect of impurities.

The effects of the solution composition on the spontaneous nucleation and the crystal growth rate have been examined. From the measurements of the crystal growth kinetic data, the crystal growth rates were estimated which is found to be logarithmic function of calcium ion concentration.

Also, the results presented in this paper are for reference or blank conditions only, i.e. no external force or agent was applied during the process of $CaCO_3$ precipitation. Consequently, these reference experiments were used for comparison with prevention methods in the future.

1. Introduction

Precipitation of calcium carbonate is a prerequisite for the deposition of calcium carbonate crystals on an external surface. Hence to understand the scaling process, it is necessary to understand the calcium carbonate precipitation kinetics. This could be achieved through fully controlling the precipitation and deposition processes. Understanding of the precipitation process of $CaCO_3$ is necessary on account of its industrial importance.

Scaling of metallic or insulating walls in contact with water supersaturated with respect to calcium carbonate may create technical problems including impedance of heat transfer, increase in energy consumption and unscheduled equipment shutdown [1]. Precipitation of $CaCO_3$ is an important industrial operation used in industry as filler for plastic materials, rubber, paper and biomineralization. These uses require different particulate, physical and chemical properties. Therefore, a number of experiments were conducted to obtain reliable and reproducible conditions for consecutive precipitation processes. The data from the FBRM and images from the PVM provided information about the particle count and size. The experiments were conducted in a closed system to reduce the effect of impurities. The results presented in this paper are for reference conditions only, i.e. no external force or agent was applied during the process of $CaCO_3$ precipitation. Consequently, these reference experiments were used for comparison with inhibition systems in other work.

The study of $CaCO_3$ precipitation is primarily directed towards understanding scale formation behavior, although the relationship between precipitation and scaling has received little attention. Recently few authors attempted to characterize entire scaling process by studying the scale formation in parallel with precipitation process [1,2]. It is reported that the deposit formed on the metal surface and precipitation

* Corresponding author at: Saudi Aramco, P.O.Box 9761, Dhahran 31311, Saudi Arabia. Tel.:00966505825152.
E-mail addresses: waleed.nasser@aramco.com (W.N. Al Nasser), nasirwn@yahoo.com (F.H. Al Salhi).

http://dx.doi.org/10.1016/j.powtec.2014.05.025
0032-5910/

formed in the bulk solution, being two different processes, each has their own mechanisms and kinetics.

During precipitation of $CaCO_3$ from its ionic solution, the solid $CaCO_3$ can exist in three different forms also known as polymorphs namely calcite, vaterite and aragonite, and the presence of all three forms is possible depending on the pH and calcium ion concentration [3]. Calcite is thermodynamically the most stable while vaterite and aragonite are metastable, which eventually transform into stable phase calcite.

Sohnel and Mullin did quantitative study of the kinetics of calcium carbonate crystals. They reported that $CaCO_3$ precipitation is a two stage process, and the first is gel formation which is followed by transformation of gel into crystalline precipitate [4].

Recently, Abdel-Aal and Sawada have reported the mechanism of $CaCO_3$ precipitation from aqueous solution at high supersaturation as a three stage process [2]. (i) Amorphous phase formation, (ii) metastable phase aragonite at high temperature and vaterite at low temperature and calcite through recrystallisation, and (iii) metastable polymorphs are transformed to the stable phase calcite.

The presence of these polymorphs and the operating variables such as pH, composition, temperature and ionic strength are interrelated and interact on each other during precipitation [3].

The kinetic studies of $CaCO_3$ precipitation reported in literature are either based on in-situ experiments measuring solution properties such as pH and ionic activity or offline measurements determining the amount of $CaCO_3$ precipitated from the concentration analysis [1,4].

However, these techniques lack the real time information of the precipitation kinetic of calcium carbonate crystals. In addition, different techniques are used to determine the scale formed on the surface. Hence precipitation and scaling measurements are not synchronized.

The present report is an extended work to understand the interrelationship between the precipitation and scaling by using a sensitive technique which is capable of detecting the changes in very small time interval and hence gain new insights. A single measurement device is used which is able to characterize both precipitation and scaling of $CaCO_3$ in real time. The work reported here is limited to understanding of precipitation process of calcium carbonate at different process conditions.

In the present work one such popular technique known as focused beam reflectance measurement (FBRM) is used in-situ to obtain real time measurements of the calcium carbonate precipitation.

FBRM is capable of obtaining information based on number of crystals in given size class in very short time interval. This technique has been widely used in crystallization research. Fujiwara et al. and Tadayyon and Rohani applied FBRM to the detection of nucleation and the monitoring of fine dissolution during crystallization processes [5,6]. Shaikh et al. investigated the change in chord length measurement using FBRM during a phase transformation of sodium carbonate to sodium carbonate monohydrate [7]. Kougoulos et al. (2005) successfully applied FBRM to monitor the steady state operation of crystallization kinetics for organic fine chemical in a modified mixed suspension mixed product removal crystallizer. FBRM has significant advantage over conventional instruments that require sampling and dilution, and acquires data on-line and in-real time to give particle size data and population trends of particles in suspension [8]. In addition the change in crystal size distribution (CSD) for different particle size classes (fine, intermediate and coarse) can be monitored as a function of time, permitting the isolation of the size range in which a change occur.

The application of FBRM is exploited in the present work. The precipitation experiments which have traditionally been studied to understand scale deposits have been conducted for long duration which may span for 24 h; this is because it needs considerable time to get sufficient scale deposits on the techniques used in order to obtain measurable values.

However it is reported by many authors that the precipitation of $CaCO_3$ increases rapidly at the start of nucleation and at a later stage the particles stop increasing in number and subsequently grow [9,10]. It is also inferred from the work of Abdel-Aal and Sawada and Chen et al. that the extent of scaling is dominant during the first hour of scaling period [1,2].

The study reported here is hence focused during initial stages of precipitation unlike the traditional studies which assess precipitation formed in solution for long time periods.

In addition, in-situ style measurements are favored during crystallization as there is no need for sampling. Crystal formation can be tracked continuously and the kinetic and thermodynamic data processes can be optimized.

Inline monitoring of the crystallization process can be achieved using FBRM. By characterizing the size distribution in the system, the crystal size distribution can be attained in real time for both batch and continuous processes. The FBRM probe can operate from −20 °C to 150 °C or from −90 °C to 300 °C depending whether it is operating in standard or optional mode [11,12]. FBRM is a particle sizing technique based on backward light scattering [9]. It is capable of obtaining information based on the number of crystals in a given size class in a very short time interval, and gives a particle chord length distribution (CLD) which is a function of the true particle diameter distribution [9,10]. This technique can be used to provide inline data for precipitation and scaling simultaneously, in real time. Unlike previous methods, which measure the mass of crystals deposited, the present technique monitors scaling by measuring the number of chord sizes of the crystals. This makes it sensitive to the measurement of the initial stages of the scaling process [9].

To validate and confirm results, particle vision and measurement (PVM) is used alongside FBRM. PVM is an in-situ continuous video microscopy technique used to examine changes in morphology (shape) of crystals during the crystallization process, allowing for differentiation between the two phases. Crystals in the range of 10–20 μm can be detected within its range (10–1000 μm).

As a result, with a measurement technique such as FBRM it was possible to obtain measurements in the order of two second interval thus giving new insights into the calcium carbonate precipitation process.

This paper presents the results obtained from the study of $CaCO_3$ precipitation. The calcium ion concentrations investigated were 0.01, 0.02, 0.03, 0.04 and 0.05 mol/L at solution temperatures of 25, 40, 60 and 80 °C. This range of concentrations was selected based on real cases in oil industry.

2. Experiment setup

The experimental setup is according to the schematic diagram in Fig. 1.

It consists of 2 L beaker placed on a hot plate with two inline instruments, FBRM and PVM, immersed at an angle along with a temperature probe. All the three sensors are connected to a PC to record the number of crystals, images of the crystals in the solution and temperature of the solution. A cover plate was used to cover the beaker to avoid any evaporation. It consists of two metal plates with a rubber plate in the middle. The metal plate has several openings to allow probes access the solution. The position of probes in the solution was fixed for each experiment. A magnetic stirrer was used to mix the solution and hence keep the crystals suspended in the solution.

2.1. Measurement principle

The precipitation of calcium carbonate is monitored by using an online, in-situ size analysis technique known as FBRM (focused beam reflectance measurement, model M400LF, Mettler Toledo, USA) and PVM (particle vision and measurement, model PVM800, Mettler Toledo, USA). The FBRM probe utilizes highly focused laser beam rotating at high speed and scan crystals passing through the measurement zone. The laser beam is back scattered by the particle and the signal is electronically processed to give chord length distribution. The duration