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Calcium Carbonate Scale on Pipes: Analysis of Kinetic, Mass, Polymorphism, Morphology with Chemical Inhibitor

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Abstract: Scaling of calcium carbonate on the pipes under the influence of citric acid as a chemical inhibitor was investigated in the present study. In the experimental research, the scale-forming solution was prepared by setting equimolar solutions of $CaCl_2$ and Na_2CO_3 with Ca^{2+} concentration of 3000 ppm. The induction time of scale nucleation was determined by measuring the ion conductivity of the solution flowing out of the pipe. Scale formed on the coupon was then evaluated using SEM/EDX and XRPD rietveld analysis. The presence of citric acid clearly influenced the kinetics of calcium carbonate formation in pipes which was presented as an induction time. The longer induction time was observed when the largest amount of citric acid was added to the solution. The crystalline phase was found to be mostly calcite and vaterite while the scale has a plate-like morphology. The presence of citric acid seems to inhibit the scale deposition and change the morphology of the crystals.

Key words: Calcium carbonate, citric acid, morphology, XRPD rietveld, SEM/EDX , conductivity

INTRODUCTION

Calcium Carbonate ($CaCO_3$) scaling is commonly discovered on certain pipes of industrial applications including the evaporator and cooling power plants. The scaling of pipes could be regarded as a negative impact on the operational efficiency of the unit and has become a major economic concern in most industries. In general, calcium carbonate is slightly soluble in groundwater and thereby being able to precipitate from the saline water upon heating. Scaling of calcium carbonate may result in three crystal polymorphs in the varying solution condition, namely calcite, vaterite andaragonite which also could be related to the substrate for disposition of the scale. Aragonite and vaterite could be grown on the heated metal surfaces at the lower temperatures, conversely, calcite would be crystallized at the higher temperatures (Muryanto *et al*., 2012). In addition, minerals of calcium carbonate have been extensively examined because of their relevance in geological, technological and biological environments and systems.

Further, the scaling of calcium carbonate andtheir structural, chemical and morphological properties are controlled by the initial supersaturation, temperature, hydrodynamic conditions and the presence of additives (Azimi and Papangelakis, 2010). In this point, the supersaturated forming solution promotes the first nucleation formation and the contact time (Rabizadeh *et al*., 2014; Antony *et al*., 2011). The stable nuclei on the surface are taken to develop the deposit. Moreover, the temperature has a significant factor to encourage the increasing deposition of calcium carbonate on the wall of pipes. In this way, the crystal growth rate is significantly influenced by the increasing temperature.

Furthermore, the formation of calcium carbonate scale may be influenced by the hydrodynamic factor such as a flow rate, pipe diameter and surface roughness (Bahadori, 2010). A previous study by Gourdon (2011) has demonstrated that the scale of calcium carbonate can be grown in full laminar and turbulent flow. In full laminar flow, the crystal growth of deposit is favored at a slow flow rate while in fully turbulent flow, the scale deposit was increasingly grown with the increasing flow fluid rate (Amor *et al*., 2004).

In the increasing velocity of fluid flow, the more calcium carbonate deposition may occur (Muryanto *et al*., 2012). In general, the scale deposition follows linear with velocity. The higher velocity can sometimes promote scale deposition on the wall surface of pipes with all sizes of diameter (Hasan *et al*., 2012). Moreover, crystallization due to the lateral growth of the scale deposit on the membrane surface may result in flux declining and surface

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blockage (Lin *et al*., 2002). Accordingly, the traditional experimental procedures for bulk precipitation, crystal seeding, constant composition or continuous flow processes are commonly employed for changing the properties of the scale.

A method to prevent the formation of the calcium carbonate scale in the pipe may use chemical inhibitors which can control the nucleation and crystal growth and crystal polymorphism and morphology (Mullin, 2004). The use of effective additives may help to reduce the capability of crystal adhered to the wall of pipes and the subsequent processes for washing away of the scale. Correspondingly, all chemical additives selected for preventing scaling should reduce possible the growth rate of scaling. Here, the proper selection of inhibitor is required prior to conducting the necessary steps for scaling mitigation, control andremoval (Wu *et al*., 2010).

This study presents a study on the formation, control andmitigation of the calcium carbonate scale on pipes with a citric acid inhibitor. The variable processes investigated were: temperature (30, 40, 50, 600°C) and the concentration of citric acid additives (5, 10, 20 ppm). The nucleation kinetics were examined through measurement of ion conductivity. The scale deposits were then characterized by XRPD for phase composition and SEM/EDX for morphology and chemical elemental analysis.

MATERIALS AND METHODS

Materials and equipment: For preparing the crystal forming solution, the powder precursor of $CaCl_2$ and Na_2CO_3 with the analytical grade (Merck) in that for each powder was diluted in the distilled water. For the crystallization experiment, 5L of equimolar $CaCl_2$ and Na_2CO_3 were prepared in a glass beaker which in turn results in the stock solution with the Ca^{2+} concentration of 3000 ppm. The solutions were then separately transferred in the two vessels and set-up at the required temperature. Subsequently, the citric acid ($C_6H_8O_7$) with analytical grade was prepared in the solution in an amount of 5, 10 and 20 ppm. In this way, the amount of citric acid additive was diluted into a vessel containing 5 Liters of $CaCl_2$ solution, then mechanically stirred at 200 rpm to achieve the homogenous mixing solution. The calcium carbonate scale was formed using the pilot-scale equipment shown in Fig. 1. During the experiments, the conductivity of the solution, leaving the test pipe section was continuously measured for up to 2 h. After this, the scale deposited on the wall surface of the test coupons was carefully removed, dried and weighed for subsequent characterization.

Material characterization of the precipitates: The characterization of the precipitates was carried out by XRPD (X-Ray Powder Diffraction) method for phase identification analysis and Scanning Electron Microscopy (SEM-analysis), equipped with EDX for morphology and chemical elemental analysis. In this way, the XRPD data collection was conducted using Cu-Kα monochromated radiation in a conventional Bragg-Brentano (BB) parafocusing geometry (D5005 Shimadzu). The scan parameters (5-85° 2θ, 0.020 steps, 15 sec/step) were documented. A PC-based search-match program (Match Software) was used for possible crystalline phases of precipitates. Further, the SEM examination performed on the sample of the precipitates which were mounted on a circular an aluminum holder and finally sputtered with carbon.

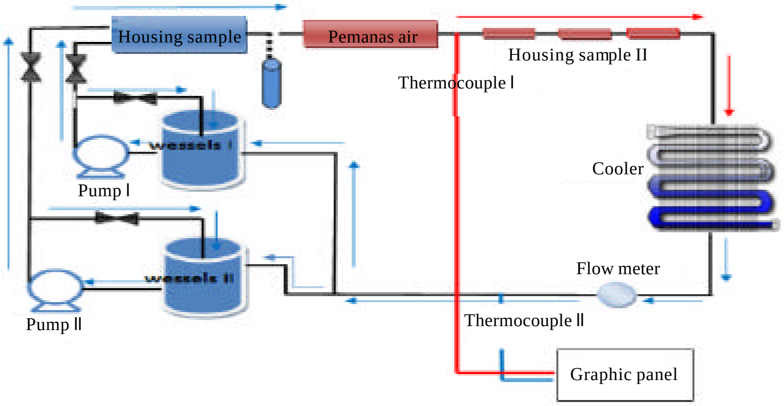

Fig. 1: Experimental setup used in the calcium carbonate precipitation

RESULTS AND DISCUSSION

Induction time for nucleation of calcium carbonate: Experimentally, the addition of citric acid (5, 10, 20 ppm) resulted in the change of induction period of calcium carbonate crystallization at room temperature of 30°C (Fig. 2). The induction time of the calcium carbonate system was observed almost doubled in the presence of 5 ppm citric acid (16 min), tripled to 10 ppm (20 min). Moreover, the presence of 20 ppm citric acid (26 min) led to an induction time four times greater than that for in the absence of citric acid system (12 min). This represents a benefit in scaling prevention for a long induction period would result in the postponed scaling process. However, this condition should be corroborated by additional experiments carried out at different temperatures.

Effect of temperature on the mass scale deposition: The scale deposited on the surface of coupon during the experiment was then removed and the yield of the mass scale is presented in Fig. 3. This represents how the scaling rate of calcium carbonate was dependent on the temperature on which the scale formed but once the temperature was increased then the impact of the initial material was significantly increased. The temperature has a strong effect on increasing the mass scales of calcium carbonate. At varying temperature, the respective mass scales were 13, 28, 49 and 80 mg corresponding to a temperature of 300, 400, 500 and 600C, respectively. The results were similar finding for calcium carbonate and showed that the increasing temperature leads to increasing the mass deposition rate of scales (Muryanto *et al*., 2012).

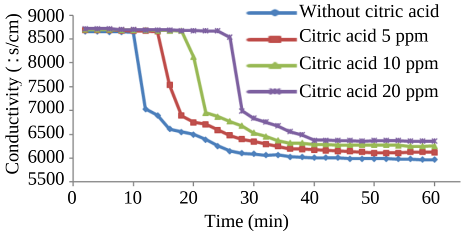

Fig. 2: Induction time measured on the calcium carbonate precipitation

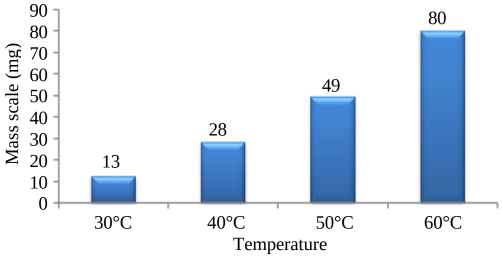

Fig. 3: Effect of temperature on the resulting mass scale formed on pipes

The influence of citric acid in the formation of calcium carbonate scale: The experimental results of citric acid in addition to inhibiting the scaling are presented in Fig. 4. Testing variable concentrations of citric acid (5, 10, 20 ppm) showed a proportional decrease in the mass scales with increasing additive concentration. The mass scales of calcium carbonate yielded in the presence of 5 ppm citric acid was 10 mg. Similarly, 6 mg of the mass scale was precipitated from the solution in the presence of 10 ppm citric acid. The increasing mass scale (13 mg) was also produced at 20 ppm citric acid. Clearly, the presence of citric acid in solution at very low concentrations may adsorb onto the crystal surface and retard the energetically favorable growth positions on the surface, thus, effectively inhibiting further precipitation (Rabizadeh *et al*., 2014).

Microstructures of calcium carbonate scales: The addition of citric acids also affects the changes of polymorphism and morphology crystals of calcium carbonate. XRPD data of the experiment at a rate of 30 mL/min in the absence and presence of additives citric acid 5, 10, 20 ppm are presented in Fig. 5 and 6. This figure showed that the intensity line formed at an angle 2θO matched with the PDF (Powder Diffraction Pattern) line with number #86-2334 for calcite and PDF#741868 for vaterite. Moreover, the mineralogical phase composition of the scales was also, confirmed through XRPD rietveld method and showed that the scales have consisted of calcite and vaterite. However, calcite may be the most stable phase while vaterite is the metastable one andonce the temperature increased, it may transform again into calcite (Muryanto *et al*., 2012).

As expected, the SEM/EDX analysis showed the high spectrum of Ca, C and O which corresponds to the calcium carbonate while a prismatic to a round shaped crystal morphology was observed. Moreover, the

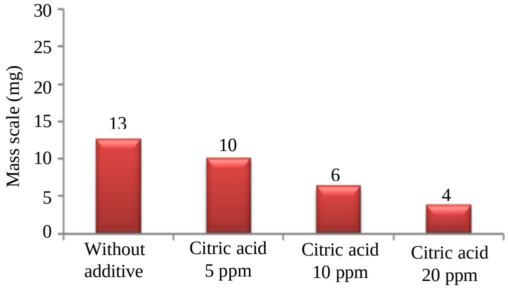

Fig. 4: Effect of the citric acid on the resulting mass scale formed on pipes

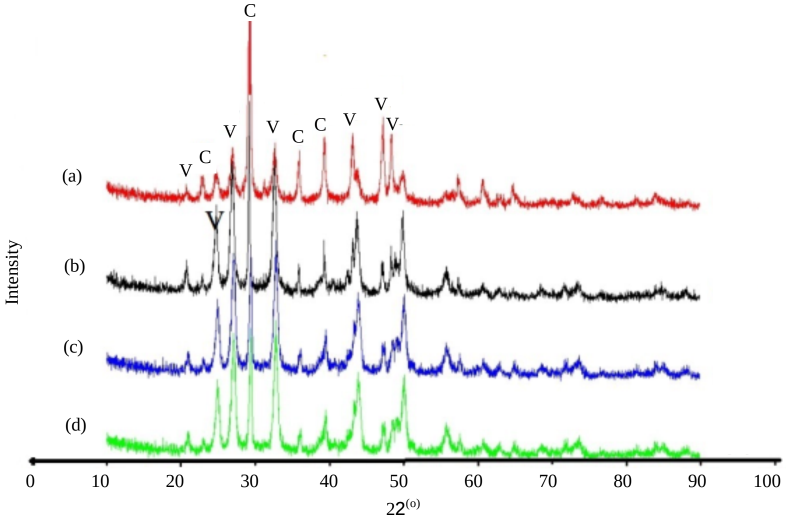

Fig. 5: X-ray diffractograms of samples obtained from the scale synthesis; a) Without additive; b) With citric acid of 5 ppm; c) 10 ppm and d) 20 ppm

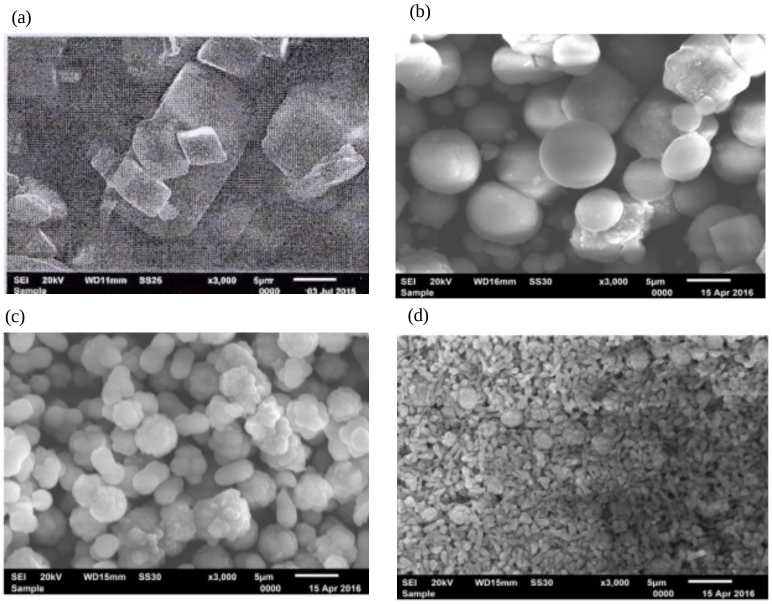

Fig. 6: Morphology of the calcium carbonate scale; a) Without additive; b) With the citric acid of 5 ppm; c) 10 ppm and d) 20 ppm.

presence of citric acid (5, 10 and 20 ppm) in the solution resulted in the reduction of crystal size. The change of morphology from a prismatic to a round shaped crystal was observed, possibly related to vaterite decomposition to calcite (Rabizadeh *et al*., 2014). Thus, the citric acid may be potentially effective to control size and morphology in the crystals of calcium carbonate.

CONCLUSION

It was found that in all the experiments, the induction period changed in the presence of citric acid in solution. The higher temperature set up, the more mass of the scale deposited on pipes indicating that the increasing temperature promoted the scale formation. The crystalline phases of the scale were found to be mostly calcite and vaterite as shown by the XRPD diffractogram. SEM observation of the scales showed crystals with plate-like morphology formed on pipes without additives in the solution. Apparently, this crystal changed to the round shaped morphology in the presence of additive. The change the crystal morphology may relate to citric acid adsorption occurred on the surface of the crystals.

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