

CALCIUM CARBONATE SCALE FORMATION IN COPPER PIPES ON LAMINAR FLOW

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ABSTRACT

Calcium carbonate is commonly precipitated as a scale in the transportation pipes of water. The presence of this mineral deposit becomes problematic, because it can block the pipes and lead to a decline in piping performance. Calcium carbonate precipitation from the synthetic solution was experimentally investigated in the present study. The aim of research was to predict the occurrence of precipitates and characterize the scale precipitated from the solutions. The synthetic solutions were prepared using CaCl_2 and Na_2CO_3 , which was mixed with distilled water (H_2O). The concentrations of Ca^{2+} at 2000, 3000, 4000 and 5000 ppm. in the solution were adjusted and the solution flow in the Cu pipes at the different flow rate of 30, 40 and 50 ml/min. It was found that in all the experiments, the conductivity decreased abruptly after a certain induction period. Higher temperature produced more mass of the scale indicating that the increasing temperature promote scale formation. SEM analysis showed that the scale was rhombohedral, while EDS revealed that the elemental composition of the scale consisted of Ca, C and O. The crystallinity of the scale was found to be mostly calcit as shown by the XRD

Keywords: calcium carbonate, induction time, prototipe scale formation, scale morfology

INTRODUCTION

Scaling is one of the main serious engineering problems in process industries as the scales my hinder the flow of solution in industrial pipes or tubes. Accurate estimation of scale formation is thus very important. Calcium sulphate, carbonate potentially deposited add clogged pipping system (Azimi and Papangelakis, 2010).

The calcium carbonate scale formation was influenced by several aspects such as flow rate, concentration of solution, pH value, temperature, pressures, and ionic strength (Bahadori, 2010). In laminar turbulence, the higher flow rates, the more calcium carbonate scale mass indicating the fluid flow enhances the scale formation (Muryanto et al., 2012).

Previous studies done by Gourdon, have shown that CaCO_3 scale formation can be found in fully laminar and fully turbulent. In fully laminar the formation was in a slow growth while in fully turbulent the formation was easily found in the angels (Amor et al., 2004). The flow of the fouling is described as having pronounced rippling and surface waves of partially laminar and partially turbulent nature. As the turbulent also will enhance the mass transfer, the rate of crystal deposition can also be promoted (Gourdon, 2011).

Other researchers indicated that scale growth does not always remain linear with time, as higher velocity can sometimes reduce scale deposition (Basim et al., 2012). Crystallization occurs due to the lateral growth of the scale deposit on the membrane surface, resulting in flux decline and surface blockage (Zhang, 2002). Thus, the scaling formation is actually the crystallization phenomenon. Bulk crystallization arises when crystal particles are formed in the bulk phase through homogeneous crystallization and my deposit on membrane surfaces as sediments/particles to form a cake layer that leads to flux decline (Zhen et al., 2010). In addition, supersaturated scale forming conditions leads

to scale growth and agglomeration (Rabizadeh et al., 2014). This is due to the random collision of ions with particles and secondary crystallization occurs on the surface of these foreign bodies present in the bulk phase (Alice et al., 2011).

In electrolyte solutions, the transition temperature of calcium carbonate solubility may vary because of variation in the water activity (Fathi et al., 2006). The solubility of common scales in water is shown in Figure 1, solubility of CaCO_3 , BaSO_4 and CaSO_4 as a function of temperature.

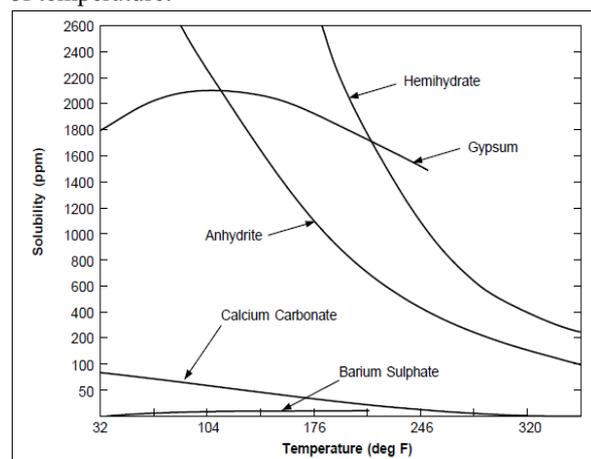


Figure-1. Solubility of Common Scales as a function of temperature (Amer, 2009).

The aim of the present research was to examine the nucleation and growth of calcium carbonate crystals, and identify calcium carbonate formation and the scaling potential in pipes. In the present study, calcium sulfate crystals were grown by the prepared solution containing calcium carbonate composition and then characterized by XRD for the mineral determination and SEM analysis with EDX for elemental analysis and morphology.

METHODOLOGY

Materials and Apparatus

All solutions used in this study were prepared by dissolving reagent grade chemicals directly without further purification. The solution was prepared under saturated calcium sulfate by mixing directly into glass containers two equimolar solutions of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, minimum assay 99%, Sigma) and anhydrous sodium carbonate (Na_2CO_3 , analytical grade, Sigma). Both reactants were dissolved in aqueous solutions containing 10 L of water and the solution concentration of Ca^{2+} was adjusted to be 2000, 3000, 4000 and 5000 ppm respectively. The selected range of temperatures was 30 to 40 °C. Each solution was then poured into a tube made of stainless and stirred at low speed. Two of the tube is connected with two brands of Iwaki magnetic pump long and trial test was conducted for 8 hours for each treatment with different flow rates.

Experiments using a scaling simulator are shown in Figure 2.

Further, induction time of precipitation was measured by a conductivity method. This method was employed in the present study to measure the induction time for nucleation of calcium sulfate precipitation. The conductometer with a Consort C831 analyzer was used for each experiment at specified condition of the repeated three times. Therefore, the induction times and precipitation results presented in this study are the average of three values. In order to minimize costs of EDX analysis, the three samples were mixed and analyzed for crystal shape, crystal structure, and density. Each stock solution was then filtered through 0.22 μm paper filters to eliminate the presence of impurities, and stored at room temperature before subsequently analyzed by SEM/EDX.

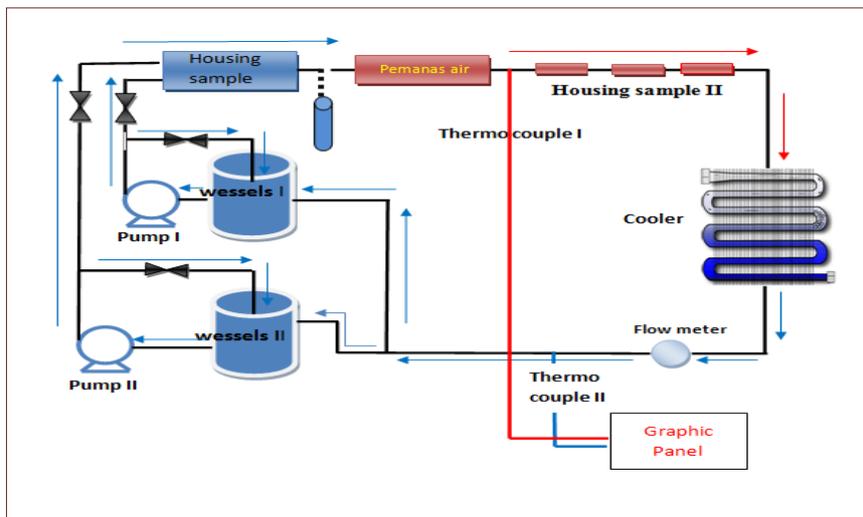


Figure-2: Experimental setup used in the CaCO_3 precipitation

Materials Characterization

The characterization of the precipitating scales was conducted through scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX). SEM apparatus equipped with an EDX was used for characterizing the microstructure and morphology. For the observation, the powder crystals were mounted on a circular metallic precipitate holder and finally sputtered with gold.

RESULTS

Induction Time of crystallization

Induction time can be defined as the time required for between the generation of supersaturation and appearance of nucleic detected through concentration change. This can be seen since the onset of nucleation showing a reduction in the concentrations of crystallizing ion and molecules take place due to their association into the solid phase, thus the conductivity which is proportional to the concentration will undergo a reduction. This reduction in conductivity could be measured as the induction time. However, the measured induction time presents the sum of the nucleation time for appearance of critical size nuclei. Additionally, growth time of nucleic from critical size to the size possessing enough mass at solid phases makes a

reduction of the solute concentration in the solution at the detectable extent through conductometry.

In the present study, the reaction was continued for about 25 minutes after the induction time until the nuclei were formed into the coupon and observed in computer monitors. Figure 3 shows the changes in conductivity during the course of nucleation experiment at room temperature and flow rates of 30, 40, and 50 ml/min.

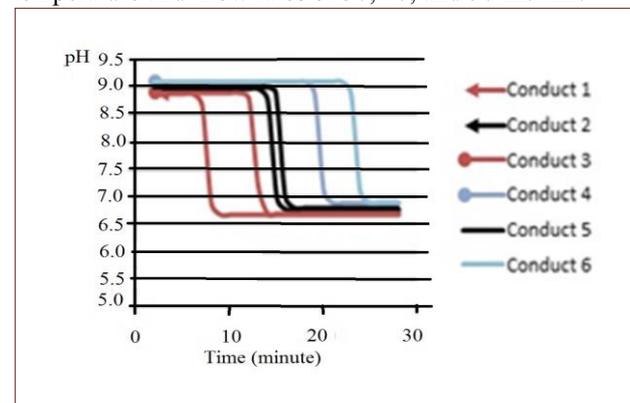


Figure-3 Variations of conductivity during the course of precipitation

Experimental results showed that the induction time was essentially under the influence of carbonate concentration. As Figure 3 shows, the induction time

decreased as the pH solution decreased from 9 to 6.5. This effect was assumed to be due to an increase in supersaturation through an increase in hydrogen concentration. However, pH of the solution was higher than 9, a longer induction time was observed. The experimental results of the present study showed that the induction time for precipitation increased from 20 minutes to 25 minutes. At higher supersaturations, a lower value of induction time is expected; however, the temperature will be more influential than supersaturation due to its order and logarithmic function of effectiveness (Mullin, 2004).

Flow rates influence on the mass of precipitates

The mass of precipitated calcium sulfate particles per kg of water at different flow rates and concentration is presented in Figure-4. As the Ca⁺² concentration of 2000 ppm is fixed and the flow rates for the solution increases in 30 to 50 ml/minutes. An increase in Ca⁺² concentration will increase the supersaturation in the solution due to the removal of free water from the availability of the solute species. This will increase the precipitation yield of calcium carbonate. However, the trend of reduction in precipitation is similar to occur to the different flow rates

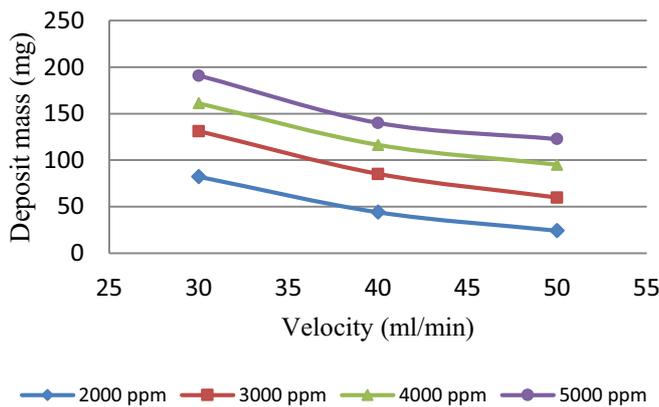


Figure-4. velocity of deposit formed graph

Characteristics and morphology of precipitates

SEM examination of the CaCO₃ scale exhibited a wide images of calcite and the scales reveal crystalline, there are scales in the structures rhombohedral is shown in figure 5. Morphology pyramid formed a) and Compositions chemistry b).

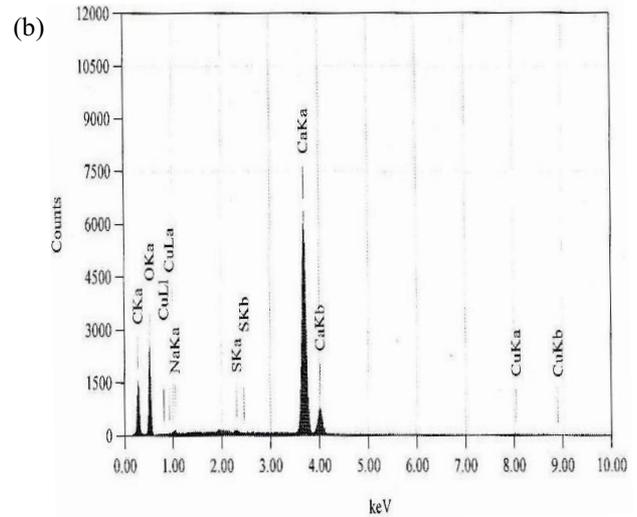
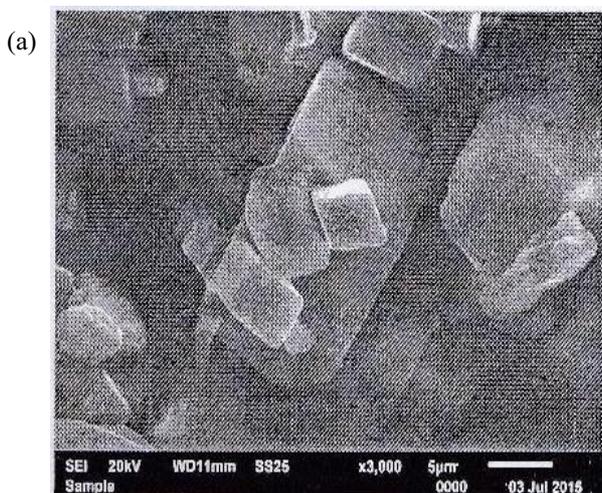


Figure-5. Morphology feature is pyramid formed a), and Compositions chemistry b).

According to theoretical calculations on the percentage of weight of CaCO₃ Ca content should be 40%, while the results of the analysis of micro Ca content = 39.8 % so as to have difference of 0.2 % . For levels of carbon (C) shall be 12 wt % while result of analysis of micro C 10.5 % of micro analysis results that have a difference of 1.5% . For oxygen levels should 64 % , while the results of the analysis of micro direct 60.06 % so as to have difference of 3.94%. From the analysis of SEM-EDX test is concluded, its crust really crystal CaCO₃.

DISCUSSIONS

The EDX analysis of calcium carbonate as found in this study of precipitates in Cu pipes is probably rhombohedral. It should be considered here that precipitates samples to be observed by SEM provides strong intensities of Ca, O and C elements which is more frequently found in SEM studies of calcium carbonate. However, the conditions used for EDX analysis in the present study and the detected amount of impurities produced a difference in mineral speciation. It is also important the observations of morphologies by SEM in the study of a calcium carbonate with apparent rhombohedral habit in the crystal. It can be assumed from SEM morphology and EDX analysis (Ca, C) to be. In contrast, the EDX analysis alone cannot distinguish whether the analyzed crystals observed by SEM are calcite, i.e. calcium carbonate valerite, aragonite and only by additional XRD techniques could be identified these minerals. In this case, the precipitation mechanisms of calcium carbonate mineral phases (calcite, valerite and aragonite) remain large unexplored. Therefore the role and implications of valerite as a stable precursor phase to calcite precipitation observed using XRD method, will provide interesting results to natural and industrial processes.

CONCLUSIONS

It was found that in all the experiments, the conductivity decreased abruptly after a certain induction period. Higher temperature produced more mass of the scale indicating that the increasing temperature promote scale formation. SEM analysis showed that the scale was rhombohedral, while EDS revealed that the elemental composition of the scale consisted of Ca, C and O. The crystallinity of the scale was found to be mostly calcite as shown by the XRD.

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