Assessing of the effect of hydrodynamics in the growth of scale (CaCO$_3$) in rotating cylinder electrode

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Abstract. Fouling is a common problem related to different industries in which the solubility of dissolved minerals in water changes leading to the formation of deposits on the surface of the equipment, for instance, in oil production the scale can be formed on the wellbore, on the well tubing or superficial facilities. Over the last years, several studies have been carried out in order to determine the effect of operational conditions in the scale growth but there are no conclusive results. This paper presents the results of calcium carbonate deposition on the surface of stainless steel AISI 316 at $71^\circ$C, and the influence of rotating velocity on the quantity and morphology of the generated scale. The tests were carried out by using a rotating cylinder electrode and X-Ray Diffraction (DRX), and Scanning Electron Microscopy (SEM) of the scale obtained was analysed. The results show that the amount of scale formed changes regarding the velocity of the fluid, as well as the morphology of the deposited crystals.

1. Introduction
Scale occurs due to the deposition of unwanted minerals, originally dissolved in processes of fluids, on equipment surfaces [1]. In general, the solubility limit of the liquid must be exceeded at the operating conditions for precipitation to occur [2]; For example, when a solution has a salt of inverse solubility like the CaCO$_3$ among its components, the supersaturation will appear when increasing the temperature of the solution. After the solution is supersaturated, nucleation occurs and very small crystals are formed. There are two types of nucleation: the homogeneous one in which the crystals form spontaneously in the solution and the heterogeneous one in which they are created on surfaces or on foreign bodies [3] (metallic surfaces or mineral in contact with the liquid, particulate material, and so on), these are two different processes and each one of them has its own mechanism and kinetics [4].

Formation of scales is a common problem in the equipment used throughout different industries such as water cooling systems, evaporators, oil extraction and production equipment, desalination plants using evaporation techniques, among others [5]. In the case of the oil industry the growth of deposits is known as the biggest problem presented, and this can appear on surface and well bottom equipment either in production or injection wells. The scale contributes to the wear of the equipment due to the corrosion presented under the deposits and the restrictions in the flow, provide a decrease in production rate [6].

Due to problems caused by scales, several researches have been carried out to determine the effect of variables that affect the growth and inhibition of scale, one of them is the flow rate of the solution [7], which can interfere with the amount, resistance and the adhesion of the obtained deposit, some studies have shown that at higher flow rates the deposition rate is increased due to the decrease in diffusion resistance and this eases the growth of more tenacious crystals when working in laminar
flows, but when turbulent flow is handled there is a decrease in the thickness of the scale due to the increase in the removal rate and greater shear forces between the deposit and the liquid [8].

Among the deposits formed the most common is calcium carbonate (CaCO$_3$) which has three anhydrous polymorphs: calcite, aragonite and vaterite, presenting a trigonal, orthorhombic and a hexagonal crystalline system respectively, which can be observed in Figure 1[9,10]. The properties of the compound vary because each structure has different characteristics, one of these factors is the thermodynamic stability, in the case of the calcite, which is the most stable form, whereas the aragonite and the vaterite presents a stability decrease. The vaterite is the least stable phase of all, therefore it is more soluble and easier to remove [11]; so, the study of the morphology and characterization of the scales is an important aim.

![Calcite, Aragonite, Vaterite](image)

**Figure 1.** System crystalline of polymorphs of CaCO$_3$[12].

In this paper we present the results of using a Rotating Cylinder Electrode (RCE) to study the formation of calcium carbonate scale on steel AISI 316 and we also determine the influence of flow rate on the amount and morphology of generated deposit.

2. **Experimental equipment and procedure**

The surface in which the scale was deposited was a cylindrical sample of stainless steel AISI 316 of 1cm in length and 1.2cm of external diameter. Before starting the test, it was polished with sandpaper ranging in number from 600 to 1500, and after that, it was washed with acetone and dried in a stream of air. The experiments were performed using a Rotary Cylinder Electrode (RCE) in which the substrate was placed and immersed in the saturated solution heated by means of a heating plate and the suspension solution was maintained by using a magnetic stirrer, as shown in Figure 2.

![Experimental assembly](image)

**Figure 2.** Experimental assembly for the precipitation of calcium carbonate.

The tests were performed for a period of 24 hours at ambient pressure and the temperature was controlled at 70°C by means of an immersion thermometer, the rotating speed ranged from 1000 to 1900rpm. A supersaturated solution consisting of CaCl$_2$.2H$_2$O and NaHCO$_3$ dissolved in 1L of...
distilled water was used and the analytical grade reagents were weighed on a balance VIBRA HT224R to 4 decimal precision.

Before and after each test the sample was weighed to determine the amount of deposit formed by means of the difference in mass measurements. The scale was characterized by X-ray diffraction using an equipment PANalytical X’Pert-PRO with cobalt anode and a sweep scanning between 5 and 90°, driving a step time of 0.5 seconds, with which the crystalline system was established. SEM was used an equipment CARL ZEISS RA-ZEI-001 where micrographs were obtained using the secondary electron detector and backscattered electron detector.

3. Results

3.1. Rotating speed

The tests were performed at different rotational speeds of the sample, which were found within a turbulent regime \(v>0.6\text{m/s} [13]\) approximately 955 rpm for the test conditions used, thus the flow velocity is able to generate cut forces between the solution and the obtained deposit, generating possible detachments of the scale. It can also exist more quantity of ions in the proximity of the substrate at a greater speed causing an increase in the amount of the generated scale. The results are presented in Table 1, where an increase in the rate of deposition regarding the flow velocity is shown.

| P.No | Rotating Speed (rpm) | Area (mm\(^2\)) | Deposition Rate (mg/m\(^2\)/h) | Amount (mg) |
|------|----------------------|-----------------|-----------------------------|-------------|
| 1    | 1000                 | 376.55          | 712.6                       | 6.4         |
| 2    | 1250                 | 376.99          | 733.8                       | 6.6         |
| 3    | 1500                 | 377.01          | 791.3                       | 7.1         |
| 4    | 1750                 | 376.82          | 1629.1                      | 14.7        |
| 5    | 1900                 | 377.30          | 2197.6                      | 19.9        |

\(a\) Number Test  
\(b\) Rotating Speed in revolutions per minute

3.2. Morphology

The micrographs at 2000X using the Scanning Electron Microscope for each of the tests are shown in the Figure 3.

Figure 3 is observed that at a lower speed few crystals are formed and deposits in the form of leaflets cover a large part of the test surface. By increasing the speed, a greater coverage of the surface can be observed but no increase in the amount of crystals is evidenced. The following tests (Figure 3(c)) show the formation of calcium carbonate crystals in large clusters surrounded by material without apparent crystallinity covering almost the entire surface until the formation of a compact crust on the sample.
Figure 3. Micrographics (a), (b), (c) (d), and (e) show morphology of CaCO$_3$ for tests to rotating speed 1000, 1250, 1500, 1750 and 1900 rpm respectively.

When the deposits were analysed by means of XRD, it was established that the deposit obtained consists of calcium carbonate in the form of calcite and sodium chloride in a percentage of 89 and 11 respectively.

4. Conclusions
At higher rotational speed an increase in the amount of deposit formed can be observed, in addition to presenting a greater coverage of the sample surface and a high degree of crystallinity of the scale generated.

As for the conditions to which the tests were carried out, it is observed that the deposit is mainly compound of calcite, as indicated in the micrographs and in the results provided by the XRD.

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