Effect of Temperature and $CaCO_3$ Concentration on the CO_2 Corrosion Behavior of Carbon Steel in Seawater

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Abstract: In oil and gas production, CO_2 corrosion and $CaCO_3$ scale occur simultaneously. Various studies have been conducted to address the problem of corrosion and scaling in the past. However, there is minimal information in the literature relating to situations where corrosion and scaling are considered together, despite there being indications that heavy scaling may lead to localized attack and loss of integrity. Consequently, there is a need to explore the potential relationship between scaling and corrosion and their effect on the deterioration of steel pipeline. Research has been carried out on the corrosion behavior of CO_2 on steel pipeline samples. Corrosion behavior was analyzed based on changes in temperature (60, 80 and 100°C) and $CaCO_3$ concentration (0, 700 and 1000 ppm) in seawater environments with CO_2 gas at a flow rate of 1 lt/min. The corrosion rate calculation is carried out using the weight loss method. Increasing the concentration of $CaCO_3$ in seawater causes a decrease in the corrosion rate and the greatest corrosion rate occurs at 80°C. Characterization of corrosion products from deposited powder using XRD and SEM at various temperature changes produces crusts with aragonite, calcite and halite phases. Meanwhile, variations in $CaCO_3$ concentration produce aragonite phases as well as siderite and chukanovite corrosion products with morphologies such as rice grains, rhombohedral, needle-like and plate-like. Keywords:

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I. INTRODUCTION

In oil and gas wells the brine produced together with the hydrocarbon phase, is a water phase containing various dissolved species [1-3]. Sodium (Na+), chloride (Cl), and calcium (Ca2+) ions are usually present in these brines at higher concentrations than other ions. All oil and gas wells contain a certain amount of CO_2 and calcium carbonate ($CaCO_3$) which easily precipitates if the solubility limit is exceeded due to their fast deposition kinetics [4, 5]. Salt water usually contains a lot of CO_2 [6] and causes CO_2 corrosion on carbon steel, this is the most common type of corrosion encountered in the upstream oil and gas industry [7].

Iron oxidation, as the dominant anodic reaction, is a key element in the corrosion of carbon steel in acid solutions. The problem of corrosion in oil and gas production is that CO_2 corrosion and scale (i.e. the formation of $CaCO_3$, $MgCO_3$, etc.) occur simultaneously. To the best of our knowledge, the literature relating to situations where corrosion and scaling occur simultaneously is very scarce. Nevertheless, a significant effect of carbonate species on the rate of iron dissolution has been mentioned in several different studies over the years [8-11]. Although there are indications that crusting can cause local attacks and loses protection [12]. Consequently, there is a need to explore the potential relationship between scale and corrosion and its influence on the deterioration of carbon steel. In this research, efforts will be made to study the effect of $CaCO_3$ concentration and temperature on the CO_2 corrosion mechanism of carbon steel.

II. MATERIAL AND METHODS

A. Material

The material used here is API5L carbon steel in the form of pipes which are specifically used for transporting oil, natural gas and petrochemical products. The test results with XRF contain C = 0.27%, P = 0.03%, Mn = 0.96%, S = 0.025%, Si = 0.35% and the rest is iron. Corrosion test samples with a size of 1.5 cm x 1.5 cm and a thickness of 1 mm, polished and cleaned with acetone. After the corrosion product crust forms on the surface of the sample, the sample is cleaned with distilled water and dried.

B. Synthesis procedure

Limestone from a mine in Tuban (East Java, Indonesia), as a starting material, was calcined for 5 hours at a temperature of 900°C. The calcined limestone was then dissolved in 10 M HCl solution and stirred at a constant speed of 200 rpm for 30 minutes at room temperature. The resulting $CaCl_2$ solution is diluted to 0.5 M. Next, Na_2CO_3 is dissolved in seawater to make a Na_2CO_3 solution with the same concentration of 0.5 M as $CaCl_2$. mixing process, at 30°C, and stirred at a constant

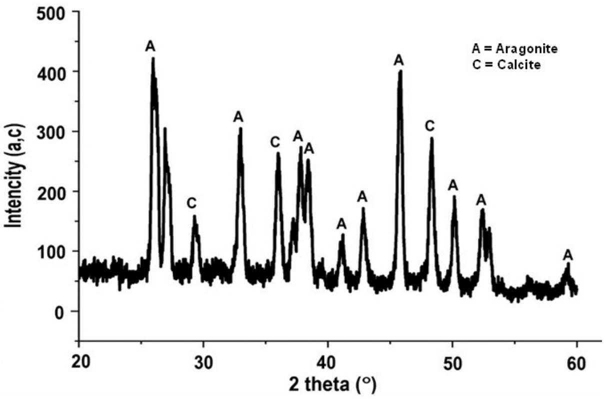


FIG. 1: The XRD spectra of the precipitated $CaCO_3$ prepared using sea water of 0.5 M at 30°C.

speed of 200 rpm for 30 minutes. The mixing process of the two solutions forms a $CaCO_3$ precipitate and will be used as a corrosion inhibitor.

C. Corrosion Testing

Steel pipeline corrosion testing was carried out in 2 different solvent media. The first media dissolves $CaCO_3$ precipitates in seawater with a concentration of 700 ppm with different heating at 60, 80 and 100°C. The second media was seawater without the addition of $CaCO_3$ precipitate (0 ppm) and the addition of $CaCO_3$ precipitate with concentrations of 700 and 1000 ppm. Corrosion testing of steel pipeline test samples by flowing CO_2 gas at a flow rate of 1 lt/min in a solvent medium for 72 hours.. Standard guidelines for studying corrosion, such as ASTM, are widely used by industry and academia. The methodology for measuring corrosion rates (*CR*) with immersion test experiments uses the standard formula below:

$$CR = \frac{k.m_{loss}}{A.t.\rho} \tag{1}$$

where k is a constant 8.76×10^4 so that *CR* is in [mm/h], mloss is the mass loss [g] of the metal ($m_\circ$ - m_f) in time t [hours], A is the surface area of the material exposed [cm^2], and ρ is the density of the material [g/cm^3]

D. Characterization

The powder diffraction patterns were recorded using XRD (Philips XPert MPD system, monochromated Cu-K radiation), employing record in the diffraction angle (2θ) range of 20 - 70°. The morphology of powder was observed using SEM (FEI Inspect S50, at the acceleration voltage of 15 kV), by dropping the particle suspension on a glass slide, drying overnight, then sputtering with gold-palladium in a vacuum evaporator (Emitech SC7620 *sputter cooter*).

III. RESULTS AND DISCUSSION

A. $CaCO_3$ Precipitate Phase Analysis

The diffraction pattern of $CaCO_3$ precipitate with a concentration of 0.5 M is shown in Fig. 1. The analysis results in Figure 3.1 are dominated by the aragonite phase at 91.7%, while the calcite phase is only 8.3%. This is possibly because it uses seawater solvent media which contains magnesium and sulfate ions which are important components of seawater where many biomineralization organisms live and encourage the formation of aragonite [13-15].

B. Analysis of corrosion products formed under the CO_2 gas flow rate

1. Analysis of structure and phase of corrosion products

The XRD test results of corrosion products at different temperatures and different concentrations are shown in Table I. The analysis results show that at room temperature, static conditions are dominated by the formation of $CaCO_3$ in the aragonite phase and corrosion products in the siderite and chukanovite phases. At a temperature of 60°C - 100°C there is a continuous increase in water dynamics. Increasing temperature causes water to become dynamic and will facilitate the phase transformation from argonite to calcite. Dynamic water conditions also cause mass transfer and reduce the nucleation of $FeCO_3$, and at the same time the precipitated $FeCO_3$ can be moved by the flow, so that the scale surface becomes irregular. Damaged scale cannot provide effective protection to the steel and resist further corrosion processes.

2. Effect of Temperature and $CaCO_3$ Concentration on Corrosion Rate

The effect of varying $CaCO_3$ concentrations on the corrosion behavior of steel pipeline is presented in Table II. The corrosion rate of steel decreases with increasing $CaCO_3$ concentration. This is due to an increase in adsorbed species on the steel surface as a result of increasing $CaCO_3$ concentration, thereby providing wider surface coverage. Increasing the temperature from 80°C to 100°C causes an increase in the corrosion rate, this is caused by a reduction in the surface protective scale of aragonite and the dissolution of calcite, followed by an increase in halite.

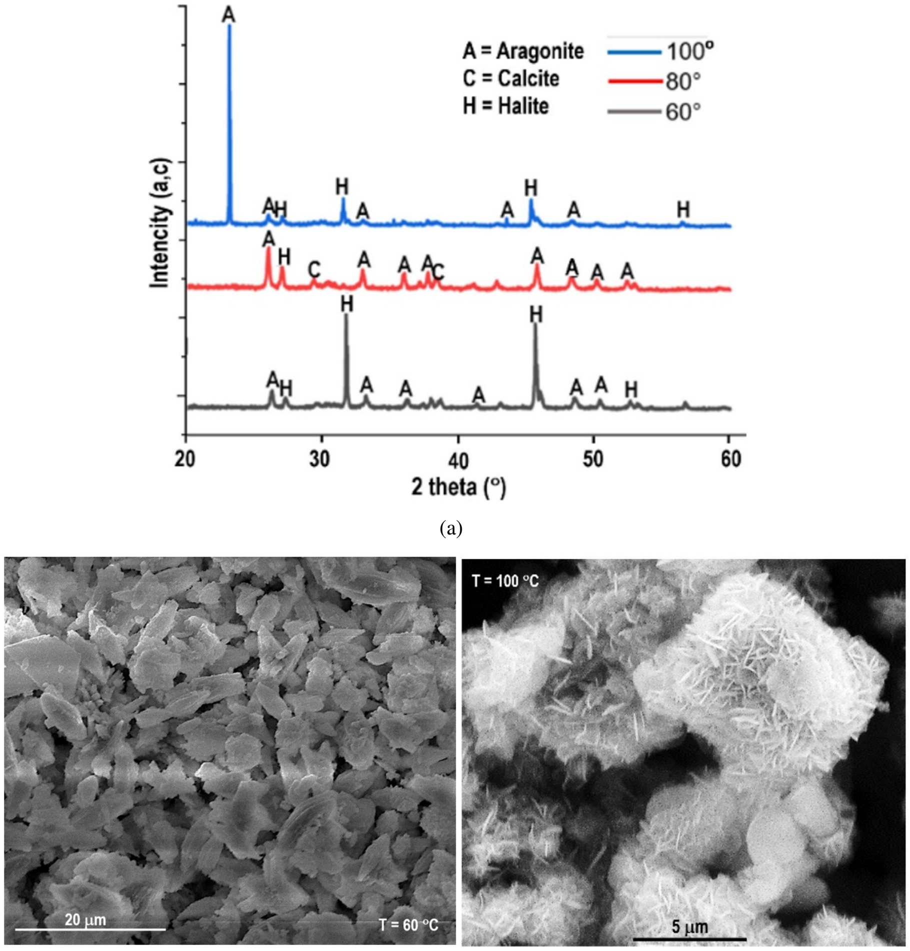
3. Effect of Temperature on Corrosion Rate

Observations of the diffraction patterns and morphology of corrosion products deposited on the steel surface at different temperatures are shown in Fig. 2.

Based on Table II, increasing temperature causes a decrease in the corrosion rate. This is due to the deposition of $CaCO_3$

TABLE I: Phase fractions of corrosion products at different concentrations and temperatures.

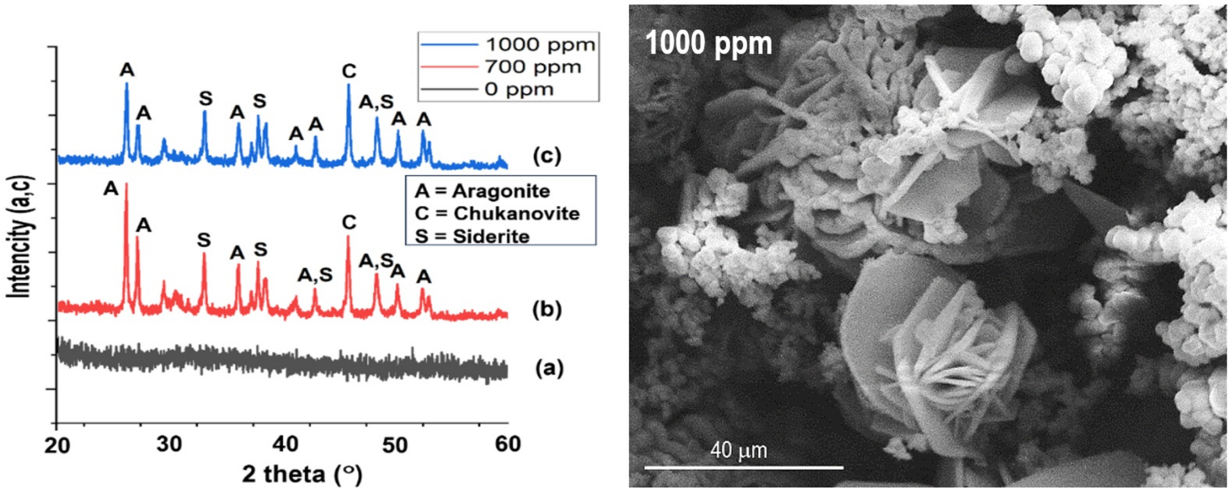
Concentration	Temperature	Phase	%wt	Concentration	Temperature	Phase	%wt
0 ppm	30°C	Amorf	-	700 ppm	60°C	$CaCO_3$ (Aragonite)	49,4
						Halite	50,6
700 ppm	30°C	$CaCO_3$ (Aragonite)	99,1	700 ppm	80°C	$CaCO_3$ (Aragonite)	92,1
		$FeCO_3$ (Siderite)	0,7			$CaCO_3$ (Calcite)	7,1
		$Fe_2(OH)_2CO_3$ (Chukanovite)	0,2			Halite	0.8
1000 ppm	30°C	$CaCO_3$ (Aragonite)	99,2	700 ppm	100°C	$CaCO_3$ (Aragonite)	68,4
		$FeCO_3$ (Siderite)	0,5			Halite	31,6
		$Fe_2(OH)_2CO_3$ (Chukanovite)	0,3				



(a)

(b)

FIG. 2: (a) XRD spectrum of $CaCO_3$ phase at different temperatures deposited on steel surface (b) SEM images at 60°C and 100°C



(a) (b)

FIG. 3: (a) XRD spectrum of corrosion products at different concentrations (b) SEM image at 1000 ppm.

TABLE II: Corrosion test conditions with CO_2 gas flow rate of 1 lt/min.

No	T (°C)	$CaCO_3$ Concentration (ppm)	Time (h)	Corrosion rate (mm/h)
1.	60	700	72	0.281
2.	80	700	72	0.221
3.	100	700	72	0.272
4.	30	0	72	0.131
5.	30	700	72	0.117
6.	30	1000	72	0.114

molecules on the C-steel surface in the form of a crust. An increase in temperature from 60°C to 80°C occurs phase transmorphation from aragonite to calcite (Table I). The calcite phase settles on the C-steel surface in the form of a tightly bound crust, this results in a decrease in the efficiency of physical adsorption activity. The smallest corrosion rate occurs at 80°C where the precipitated $CaCO_3$ phase is dominated by stable aragonite and calcite which are firmly bound to the C-Steel surface, so that the dissolution of the steel is slower. Increasing the temperature to 100°C results in increased redissolution because the aragonite phase is not bound to the C-steel surface. This is supported by Langelier *et al.* [16], heating seawater above 45 - 80°C causes the decomposition of HCO^{3-} and will eventually precipitate $CaCO_3$ after the solubility limit is reached ($K = 4.7 - 6.9 \times 10^{-9}$). At higher temperatures ($> 80°C$), CO_3^{2-} hydrolyzes to OH-. Analysis of brine in equilibrium with always alkaline crust produces a number of free CO_3^{2-} which will react with Ca^{2+} to form the aragonite phase $CaCO_3$ [17].

4. *Effect of concentration on Corrosion Rate*

Observations of the diffraction patterns and morphology of corrosion products deposited on the steel surface at different concentrations using XRD and SEM are shown in Fig. 3.

Based on Table II, increasing the concentration of $CaCO_3$ in seawater media causes a decrease in the corrosion rate. This is because the $CaCO_3$ molecules are formed in the aragonite phase which has the property of not bonding between the particles. Aragonite which precipitates on the surface of C-steel is unable to withstand the attack of Cl^- ions. Hydrogen evolution from direct reduction of bicarbonate ions will be dominant, resulting in the formation of corrosion products $FeCO_3$ (siderite) and $Fe_2(OH)_2CO_3$ (Chukanovite).

IV. CONCLUSION

- The precipitate formed at 60°C and 100°C was aragonite with 49.4% wt and 68.4% wt respectively and the rest was halite, while at 80°C aragonite and calcite were formed with 82.1% respectively wt and 7.1% wt and the rest was halite and no corrosion products were detected.
- The precipitate formed by adding 700 ppm and 1000 ppm of $CaCO_3$ to seawater at room temperature is aragonite and the remainder is the corrosion product $FeCO_3$ and $Fe_2(OH)_2CO_3$
- Calcite deposits on the surface of C-steel only form in seawater to which 700 ppm $CaCO_3$ is added and heated at 80°C
- The greatest corrosion rate occurs at 80°C which can form aragonite and calcite phases, while heating at 100°C the corrosion rate decreases due to the hydrolysis of CO_3^{2-} to OH^- and finally forms the aragonite phase

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