

The Mechanism Studies of Carbon Dioxide Corrosion in Supercritical Fluid State in the Process of Oil and Natural Gas Exploitation#

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Abstract:

The state of CO₂ and its effects on pipe string corrosion of the oil and gas well at high temperature and pressure are theoretically studied. The CO₂ mole concentration, its distribution coefficient in the phases of oil and water and system pressure are proposed to describe CO₂ corrosion in formations and pressure funnel at the supercritical state. The experiments of CO₂ steel P110 corrosion in the medium of oil and water was conducted at CO₂ mole concentration 4%, temperature 120 °C, system pressure 35 MPa for 144 hours. The weight loss of steel corrosion occurs only in the initial 24 hours and the accumulated corrosion rate is smaller than 0.5mm/year, significantly lower than 11mm/year at CO₂ partial pressure 1.5MPa. Analyses of corrosion films by SEM, EDS and XRD indicates that the corrosion film is composed of CaCO₃ grains with a compact structure and can protect steel from further corrosion.

Key words: CO₂ corrosion, high temperature and pressure, supercritical fluids, corrosion film

The CO₂ steel corrosion has been a great concern in petroleum and natural gas industry world-widely. The CO₂ concentrations can be as high as 1.5% to 30% in many well cases and strong corrode the pipe string in oil and gas wells where it exists with water. Researches of CO₂ steel corrosion in the field of oil and natural gas exploitation are currently based on the conception of CO₂ partial pressure which is the product of saturation pressure at well bottom hole and the CO₂ mole fraction of associated gas measured at wellhead and usually falls into the range of 1MPa to 2 MPa. CO₂ partial pressure has been defined to represent the CO₂ concentration in whole formation and pipe string in pressure funnel of wellbore to simulate the CO₂ corrosion state.^[1-7] As a results, the researches, included corrosion mechanism, the corrosion macro-behavior, corrosion thermodynamics and dynamics, the composition and structure of corrosion film and the factors which influence the corrosion behaviors, have been conducted subjecting to the condition of CO₂ pressure fraction 1MPa to 2MPa. There is a few available research reports related the CO₂ existing state, the effects of its solubility change in water and the interaction between CO₂, hydrocarbon and water on the steel corrosion at the condition of high temperature and pressure.

A conception of supercritical CO₂ corrosion based on the theoretic analyses have been proposed to investigate CO₂ steel corrosion in high temperature and pressure in this study. The steel corrosion experiments, including corrosion rate in a simulating medium of oil well produce water at high temperature and pressure, structure analyses of corrosion films, are designed and conducted. It is the subject of this paper to afford a scientific awareness about CO₂ steel corrosion in the supercritical state during the process of oil and natural gas exploitation.

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1. The CO₂ phase in formations and pressure funnel of wellbore

1.1. The characteristics of supercritical CO₂

It is a common knowledge that CO₂ is a colorless, odorless and noncombustible gas with relative density 1.5192 and molecular weight 44.01 on the standard state and may exist in the form of gas, liquid or solid according to the condition of temperature and pressure. CO₂ can be dissolved in polar and non-polar solvents, such as water or petroleum. It is well known that CO₂ critical temperature (T_c) and pressure (P_c) are very important parameters, over which CO₂ is in the supercritical fluid state and its physical properties will be totally different. The interface between the liquid and gas phases will disappear.

The density of supercritical CO₂ is the function of temperature and pressure, at the range of 0.448 to 900g/L, approaching the density of a liquid in whole supercritical region. A slight change of temperature and pressure near-by the supercritical points will make its density significantly changed, as shown in Figure 1. Its diffusion coefficient is several hundred times larger than liquid. Therefore, supercritical CO₂ has a high solubility for compounds, performing like a liquid, but also easy to diffuse and move like a gas. Its mass transfer rate is much higher than liquid. The solubility of CO₂ in water generally increases with increase of pressure and decreases with the increase of temperature. A sharp change of its solubility occurs at the region near-by the supercritical points as shown in Figure 2.

1.2. The CO₂ State in reservoirs and pressure funnel of wellbore

It is known that the petroleum and natural gas in reservoirs are mainly composed of hydrocarbon compounds, a certain amount of CO₂ and other gases. Natural gas and petroleum associated gas are mainly composed of low molecular weight hydrocarbons in which methane concentration is larger than 70% and a small amount of other non-hydrocarbons (generally 1-20 mole percent, varied with reservoirs), such as N₂, He, CO₂ and H₂S, etc.. The composition is varied with reservoirs.

The temperature and pressure of reservoirs increase with the increase of formation depth. Theoretically, CO₂ (T_c=304.21K and P_c=7.39 MPa) and methane (T_c=190.15 and P_c=4.6 MPa)^[3] in the reservoirs will exist in supercritical state if the temperature and pressure are over their supercritical points when the depth of wells is over than 3000m. The low molecular weight hydrocarbons will also be in the supercritical state if the formation is deep enough. Therefore, Methane, CO₂, low molecular weight hydrocarbons and other non-hydrocarbons will exist in a form of supercritical fluids and mix with the liquid of water and high molecular weight hydrocarbon to form a mixture of corrosion medium.

The temperature and pressure in the pressure funnel of wellbore from formation to wellhead are in the process of decrease. The density of supercritical fluids has been changed continually above the supercritical points. The supercritical fluids will transfer to gases respectively when temperature and pressure are lower than their T_c and P_c and the comprehensive density of oil and gas flowing are in the sharp change process. The CO₂ solubility in water and the mutual solubility state of CO₂ and hydrocarbons are also in the sharp change process. Therefore, the wellbore is in the corrosion medium with varied acidity corresponding to the formation depth and therefore, the corrosion state in different parts will be significantly different.

2. The Steel Corrosion in the Medium of oil, water and Supercritical CO₂

2.1. The description of steel corrosion in the medium of oil, water and supercritical CO₂

The steel corrosion state in the supercritical fluid mixture is determined by CO₂ concentration, temperature and pressure according to the mechanism of CO₂ steel corrosion. CO₂ partial pressure can not accurately describe CO₂ concentration in the cases that some of the components in system, such as methane, are in compressive gas or supercritical fluid state at high temperature and pressure since the Dalton partial pressure law is built up on the definition of ideal gases. CO₂ concentration can only be accurately described by CO₂ mole fraction in system. However, the solubility of CO₂ in water phase is determined not only by CO₂ mole fraction, but also system total pressure and its distribution coefficient in the phases of oil and water if considering the interaction between supercritical CO₂ and hydrocarbon fluids. Therefore, the medium pH value of oil and water mixture is determined by solubility of CO₂ under the function of system pressure and the distribution

coefficient. If system components, degree of mineralization, and the medium of oil and water mixture are same, the larger the CO₂ concentration and its distribution coefficient in water, the more amount of CO₂ dissolved in water, and therefore the lower the PH value. As a result, the actual CO₂ steel corrosion will be significant departure from the results from simulation environment of the CO₂ partial pressure 1MPa to 2 MPa.

2.2. Thermodynamics of Steel Corrosion in the medium of oil, water and supercritical CO₂

When PH value of aqueous solution is in the range of 4 to 6, the anode reaction of CO₂ steel corrosion can be expressed as:



Anode potential can be expressed as:

$$E_{\text{ea}} = E_{\text{a}}^0 + \frac{RT}{nF} \ln a_{\text{Fe}^{2+}} \quad (2)$$

Where n is electron transfer number in cell reaction, F is Faraday constant; $a_{\text{Fe}^{2+}}$ is activity of Fe²⁺.

Assume that no Fe²⁺ ions exist in system before the reaction and consider that Fe²⁺ activity is not the function of pressure because of non-compressible property of water. Fe²⁺ concentration produced by the reaction can be taken the value of 10⁻⁶ mol/L, suggested by M. Pourbaix. E_{a}^0 is -0.44v and calculated E_{ea} is -0.618v at temperature 298.15⁰K and E_{ea} is -0.69v at temperature 393.15⁰K according to Eq. (5).

When reaction is determined by hydrogen depolarization under the condition that no oxygen exists, the cathode reaction can be written as:



Cathode potential can be expressed as:

$$E_{\text{e,c}} = E_{\text{c}}^0 + \frac{RT}{F} \left[\ln a_{\text{H}^+} + \ln a_{\text{HCO}_3^-} - \ln a_{\text{H}_2\text{CO}_3} \right] \quad (4)$$

Where E_{c}^0 is cathode potential on the standard condition; a_{H^+} is the hydrogen activity absorbed on the steel surface, $a_{\text{HCO}_3^-}$ and $a_{\text{H}_2\text{CO}_3}$ are the activity of HCO₃⁻ and H₂CO₃ respectively.

Most CO₂ molecules exist in a form of hydration with water molecules when CO₂ are dissolved in water. Only small amount of CO₂ molecules reacts with water and form H₂CO₃. It is well known that the binary weak acid H₂CO₃ is dissociated in water in two steps;



The dissociation constant K₁ and K₂ are 4.30 × 10⁻⁷ and 5.61 × 10⁻¹¹, respectively.

It can be calculated that CO₃²⁻ concentration $[\text{CO}_3^{2-}] \approx K_2 = 5.61 \times 10^{-11}$ according to CO₂ solubility in water at the pressure 1.5MPa and 35 MPa can be obtained from Figure 2, which is 0.6g/dm³ and 6g/dm³, or 0.0136mol/dm³ and 0.136mol/dm³ respectively. The ionization degree of H₂CO₃ can be calculated:

$$a = \sqrt{\frac{K_1}{C}} \quad (7)$$

The calculated ionization degree are 0.00581 at pressure 1.5MPa and 0.00147 at pressure 35 MPa respectively if assume that all CO₂ molecules dissolved in water are converted to H₂CO₃. The electrode potential differences between 1.5 MPa and 35 MPa at temperature 418.15⁰K can be expressed:

$$E_{e,c}^{1.5MPa} - E_{e,c}^{35MPa} = \frac{RT}{F} \left[\ln a_{H^+}^{1.5} + \ln a_{HCO_3^-}^{1.5} - \ln a_{H_2CO_3}^{1.5} \right] - \frac{RT}{F} \left[\ln a_{H^+}^{35} + \ln a_{HCO_3^-}^{35} - \ln a_{H_2CO_3}^{35} \right] \quad (8)$$

and the value calculated is 2.6803v if activities in Eq. 12 are substituted by their concentrations The estimate value indicates that the effects of pressure on the cathode potential is significant during process.

2.3. Dynamics of Steel Corrosion in the medium of oil, water and supercritical CO₂

Generally, the reaction rate of nonreversible electrode is the function of the surface state of electrode and its absorption characteristics (some inter reactions steps occur and their reaction products are adsorbed on the surface of electrode or the reactants are the molecules adsorbed on the surface of electrode), and determined by the rate determined step (RDS).

If the mass transfer rate is fast enough and polarization effects of concentration differential on the surface are neglected, the exchange current density of anode and cathode for CO₂ steel corrosion can be expressed:

$$I_{o,a} = 2F \cdot k_a^0 \cdot a_{Fe^{2+}}^{r_1} \exp\left(\frac{E_{e,a}}{\beta_a}\right) \quad (9)$$

where K_a^0 is the rate constant of anode, r_1 is reaction order of Fe^{2+} , β_a is the Tafel slope of anode reaction

$$I_{oc} = F \cdot k_c^0 \cdot a_{H_2CO_3}^{r_1'} \cdot a_{H^+}^{r_2'} \cdot a_{HCO_3^-}^{r_3'} \exp\left(-\frac{E_{e,c}}{\beta_c}\right) \quad (10)$$

where r_1' , r_2' and r_3' are reaction orders of H_2CO_3 , H^+ and HCO_3^- ; K_c^0 are the rate constant of cathode reaction; β_c are the Tafel slope of cathode reactions.

The current density in electrode reaction can also be expressed:

$$I_a = I_{0a} \exp\left(\frac{E - E_{e,a}}{\beta_a}\right) = I_{0a} \exp\left(\frac{\eta_a}{\beta_a}\right) \quad (11)$$

$$I_c = -I_{0c} \exp\left(\frac{E_{e,c} - E}{\beta_c}\right) = -I_{0c} \exp\left(\frac{-|\eta_c|}{\beta_c}\right) \quad (12)$$

Where $\eta_c = (E_{ec} - E)$ and $\eta_a = (E - E_{ea})$ are the excess potential of cathode and anode, respectively.

The exchange current density of anode and cathode reaction I_{0a} and I_{0c} in CO₂ steel corrosion are the function of the reactant activities of $\alpha_{[H]}$, $\alpha_{HCO_3^-}$ and $\alpha_{H_2CO_3}$. The activities of reactants are determined by the solubility of CO₂ and their ionization degree in water, which affected by their pressure. Therefore, the supercritical CO₂ fluid in the medium of water and oil will significantly affect the CO₂ corrosion dynamics process. Unfortunately, there are no related data and measure technique available. It is necessary to develop new technique of PH value and electrochemical measurement in the system of high temperature and pressure to investigate thermodynamics and dynamics of CO₂ corrosion in the medium of oil and water at supercritical state^[6]

3. The experiments of steel corrosion in the medium of oil, water and supercritical CO₂

3.1 The corrosion rate

The corrosion experiments of steel P110 were conducted in the medium of simulated oil well produced water at CO₂ pressure 1.5MPa, and CO₂ mole percentage 4%, system pressure 35 MPa, temperature 120°C in a dynamic high temperature and pressure autoclave set up in the laboratory. The total corrosion time was 144 hours. The results are shown in Figure 3. It can be known that the accumulated steel corrosion rate in the corrosion medium at CO₂ pressure 1.5 MPa increase with increase of corrosion time and finally reaches 11mm/year while the accumulated steel

corrosion rate at CO₂ mole percentage 4%, system total pressure 35MPa decrease with the increase of corrosion time and smaller than 0.5mm/year at the end of experiment. It is noticed that the weight loss of steel in the corrosion medium of supercritical CO₂ is actually not changed after first 24 hours, which indicate that the formed corrosion film has a function to protect steel from further corrosion.

3.2. The corrosion films

The morphology, composition and structure of corrosion films analyzed by SEM, EDS and XRD are shown in Figure 4, Figure 5 and Figure 6.

The corrosion film formed at the condition of CO₂ partial pressure 1.5MPa is composed of crystals of (Fe, Ca)CO₃ complex (Figure 5 and Figure 6) and there are pores or hollows existed in the film, through which the corrosion medium can be transferred (Figure 4).. The corrosion film produced at system pressure 35 MPa is composed of FeCO₃ in initial 24 hours and converted to CaCO₃ after 48 hours. It is believed that the steel surface is rapidly covered by at high pressure in the initial stage and the FeCO₃ is dissolved in CO₂ solution with the development of corrosion since CO₂ solution have a high solubility for FeCO₃ according to Eq. (13)



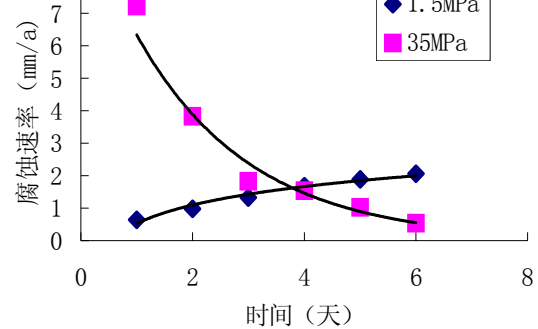
Meanwhile, CaCO₃ have been formed according to Eq.(14) and deposit on the surface of steel during the corrosion process and finally a compact corrosion film composed of CaCO₃ are created and protect steel from further corrosion after FeCO₃ has been completely dissolved.

4. Prospect

The CO₂ steel corrosion in supercritical state during the process of oil and natural gas exploitation is related to researches in areas of corrosion mechanism, composition and structure analyses corrosion film, and specially rely on the development of electrochemical measure technique at high temperature and pressure. We strongly believe that the corrosion state and corrosion protection of oil and gas well will benefit from the development of researches in this field and we hope our primary work in this field will make a contribution for its developments.

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Figures:

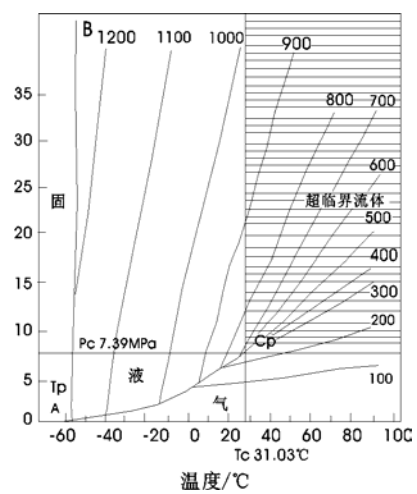


Figure 1. The Relationship of Pressure, Temperature and Density of CO₂

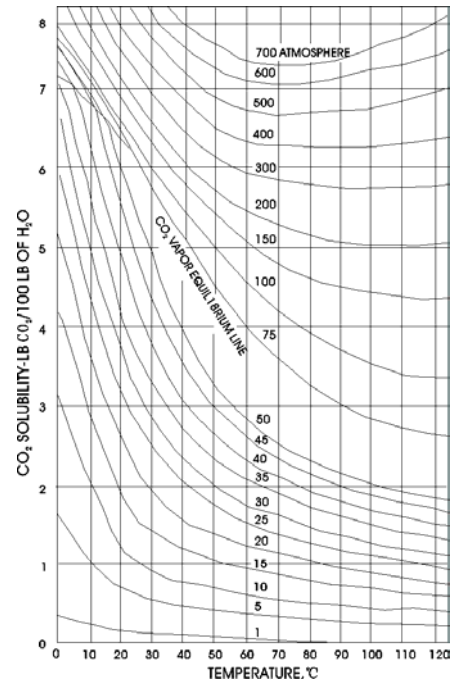


Figure 2. CO₂ Solubility in Water

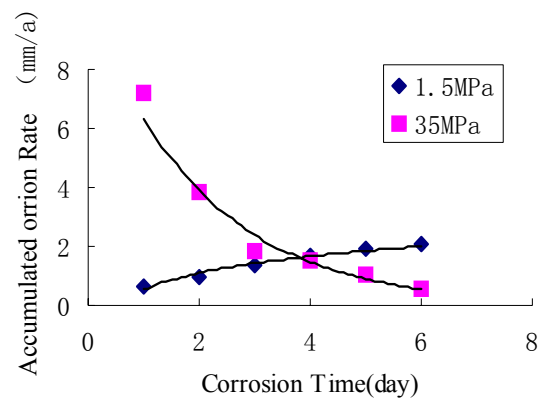
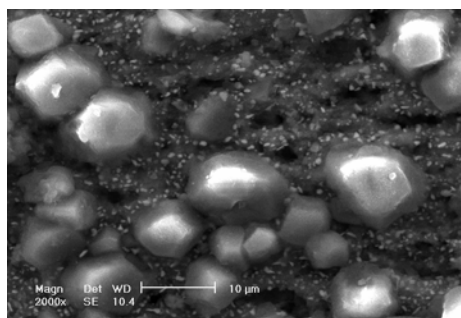
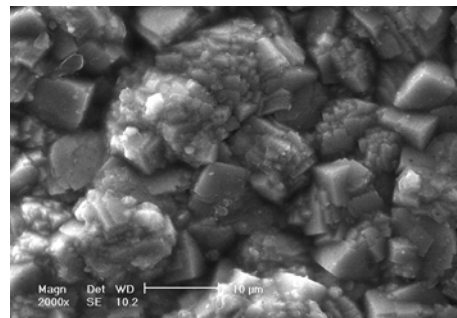


Figure 3. Steel accumulated corrosion rate at CO₂ pressure 1.5 MPa and CO₂ mole percentage 4%, system pressure 35 MPa



(a)



(b)

Figure 4.. SEM image (2000 \times) of morphology of corrosion film obtained at (a) CO₂ mole percentage 4%, system pressure 35MPa, temperature 120⁰C (b)CO₂ partial pressure 1.5MPa, temperature 120⁰C

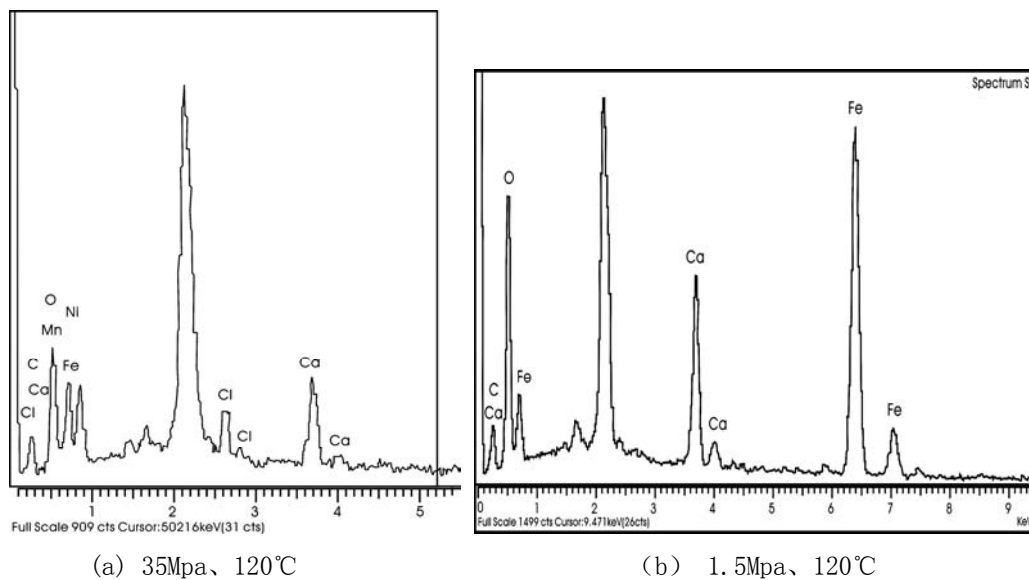
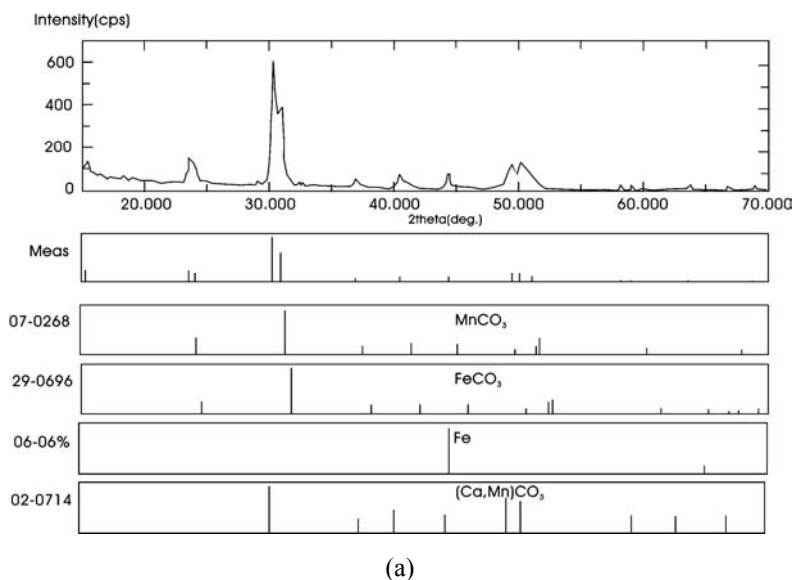
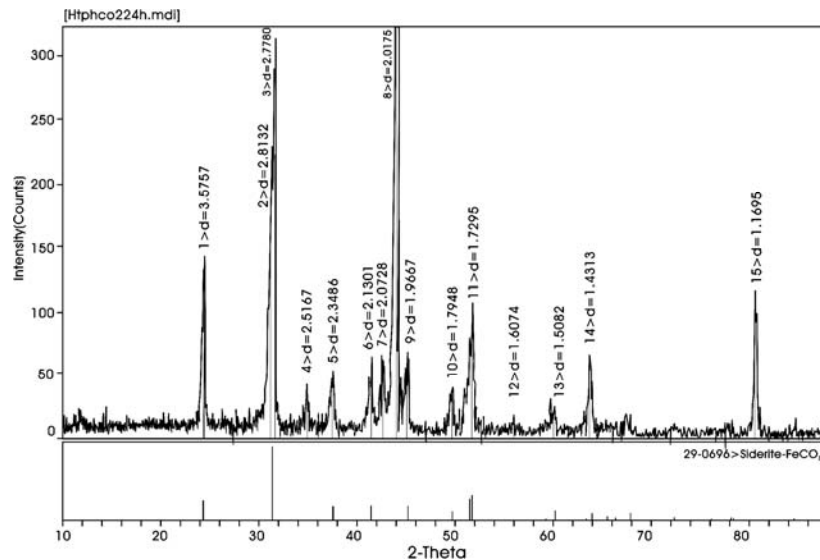
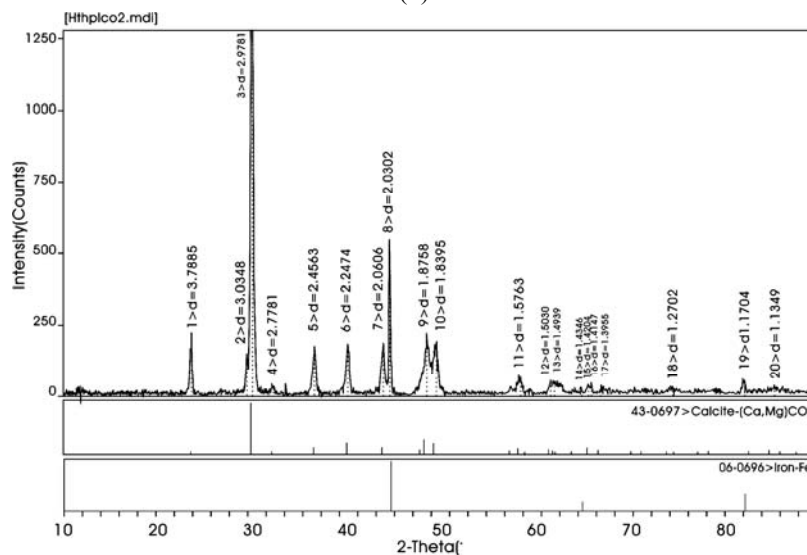


Figure 5. EDS analyses of corrosion film obtained at (a) CO₂ mole percentage 4%, system pressure 35MPa, temperature 120⁰C (b) CO₂ partial pressure 1.5MPa, temperature 120⁰C





(b)



(c)

Figure 6.XRD analyses of corrosion films obtained at (a) CO₂ partial pressure 1.5MPa, temperature 120⁰C, 144 hours (b) CO₂ mole percentage 4%, system pressure 35MPa, temperature 120⁰C, 24 hours and (c) CO₂ mole percentage 4%, system pressure 35MPa, temperature 120⁰C, 144 hours