

Wellbore integrity and corrosion of low alloy and stainless steels in high pressure CO₂ geologic storage environments: An experimental study

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ABSTRACT

CO₂ corrosion behavior of three different steels that are commonly used as casing material in CO₂ geologic storage environments (i.e., 1018 carbon steel, 5Cr steel, and 13Cr steel) was studied at 30 and 80 bar CO₂ partial pressures and 60 °C in the presence of a simulated brine for the Weyburn-Midale reservoir system. Electrochemical techniques including linear polarization resistance (LPR), and potentiodynamic polarization measurements, were used to monitor the corrosion rate during experiments and study the corrosion mechanism. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and Raman spectroscopy were used for surface analysis. A weight loss technique was also employed to measure the corrosion rate. Carbon steel showed very high corrosion rates of ~20 mm/y under the test conditions of this research. 5Cr steel can be considered as a replacement for the carbon steel under these conditions by the reduction in the corrosion rate by a factor of 3. However, corrosion rate was still high (~6 mm/y). 13Cr steel showed the best corrosion resistance under testing conditions employed for this research, and can be considered as the best option for combating high pressure CO₂ corrosion if materials selection is considered as the best option for corrosion mitigation.

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1. Introduction

The sequestration of CO₂ in deep geologic formations requires a thorough evaluation of potential leakage through any wellbores. Possible routes for leakage are preferential flow pathways along the rock–cement interface, the casing–cement interface, and through degraded materials. To date, much of the international research community's focus for wellbore integrity research in CO₂ storage applications has been on CO₂–cement interactions. However, during the long-term storage phase, supercritical (or high pressure) CO₂ can be hydrated with brine contained in the reservoir and generate corrosive carbonic acid (H₂CO₃). This now acidic brine has the potential to contact the steel casings in wells, either through the degradation of the cement in the annular space or by migration through channels, fractures or micro-annuli and causes one of the biggest challenges in the integrity of wellbore materials which is the steel corrosion in high pressure CO₂–brine environments (Choi et al., 2013).

One of the important strategies for corrosion control is materials selection. Carbon steel, 5Cr low alloy, and 13Cr stainless steels are common materials which are used for oil and gas applications under sweet production conditions (Kermani and Morshed, 2003). Effect of chromium alloying element on CO₂ corrosion behavior of steel has been extensively studied before under low CO₂ pressure conditions (Changfeng et al., 2003; Chen et al., 2005; Hu et al., 2011; Kermani et al., 2001; Kermani and Morshed, 2003; Muraki et al., 2003). However, there is not much information available about chromium alloy effect on corrosion performance under high pressure CO₂ environment. Our previous researches (Choi and Nesic, 2009; Choi and Nešić, 2011; Choi et al., 2010) showed that the corrosion rate of carbon steel in supercritical CO₂ conditions without a protective iron carbonate (FeCO₃) layer is very high (~20 mm/y). High corrosion rate of carbon steel under supercritical CO₂ conditions has been also reported by other authors (Han et al., 2011, 2012; Lin et al., 2006; Loizzo et al., 2009; Mohammed Nor et al., 2011; Seiersten and Kongshaug, 2005). Considering this high corrosion rate of carbon steel, it has been suggested that 5Cr low alloy steel and 13Cr stainless steel could be good replacements for carbon steel in high pressure and supercritical CO₂ system. Recently, the performance of different materials from low alloy steels up to

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Table 1
Element analysis (wt.%) by Atomic Emission Spectroscopy for the steels used in the corrosion tests.

	C	Mn	Si	P	S	Al	Cr	Ni	Mo	V	Cu	Sb	Fe
1018	0.21	0.05	0.38	0.09	0.05	0.01	–	–	–	–	–	–	Balance
A182	0.11	0.42	0.29	0.02	0.027	0.029	4.65	0.15	0.58	0.05	–	–	Balance
S41000	0.13	0.49	0.23	0.012	0.005	0.006	12.74	0.112	0.017	0.038	0.009	0.015	Balance

high-alloy materials was evaluated in CO₂ saturated brine at 60 °C and 100 bar (Yevtushenko et al., 2014). They have reported pitting corrosion of 13Cr steel at 60 °C and 100 bar whereas 22Cr steel did not have any pitting problem under these conditions. The corrosion properties of 1Cr and 13Cr steels were also compared at 100 bar CO₂ and 60 °C (Pfennig and Kranzmann, 2012).

At certain conditions, the corrosion rate of carbon steel under supercritical CO₂ system can decrease to low values (~0.2 mm/y) in long-term exposure due to the formation of a protective FeCO₃ layers. This is an interesting observation because the pH of water saturated with supercritical CO₂ is relatively low (~3.3 pH units), which creates under-saturated conditions for FeCO₃ precipitation (Choi and Nesic, 2009). This phenomenon can be related to the high initial corrosion rate affecting less acidic local water chemistry at the near surface region during corrosion by consumption of H⁺ and accumulation of Fe²⁺. Thus, it is possible to generate a boundary layer with a higher pH than the bulk solution that favor the formation of FeCO₃ on the steel surface, thus conferring corrosion protection from the more acidic bulk solutions. On the other hand, it is important to note that considerable localized corrosion (mesa-type for carbon steel and pitting-type for corrosion resistance alloys) was observed in supercritical CO₂ condition after long-term exposure. Localized attack, being the most problematic type of CO₂ corrosion attack, is still difficult to predict even at low pressure conditions, where significantly more research has been conducted. Whilst many environmental factors (pH, temperature, flow) can influence the onset of localized corrosion, it appears that much of the evidence points toward stability of corrosion product layers, which could be related to the metallurgical characteristics of the base alloy (Choi and Nesic, 2009; Choi and Nešić, 2011; Choi et al., 2010).

This paper is focused on the evaluation of the corrosion behavior of carbon steel (AISI 1018), low alloy steel (5Cr) and corrosion resistance alloy (13Cr) under high pressure CO₂/brine environments. This included the determination of corrosion rates and corrosion mechanisms, taking into account the controlling factors (material, pressure, pH, etc.). The corrosion experiments were

carried out in a static high pressure autoclave. Experimental brine chemistry, pressure and temperature were selected that simulate downhole conditions within the Weyburn-Midale system. The corrosion behavior of materials was evaluated using LPR measurements, which reveal details of the corrosion process with time and indicates the type of corrosion mechanism. Simultaneously, weight loss (WL) samples were introduced in the system for validation of corrosion rate calculation by electrochemical techniques. Potentiodynamic sweep was used to study the corrosion mechanism and also determining the Tafel slope for electrochemical corrosion calculation. Surface morphology and corrosion product's characteristics were studied after each test with various analytical tools including SEM, EDS, XRD, and Raman spectroscopy.

2. Materials and methods

The test specimens were machined to be of a rectangular geometry (1.2 cm × 1.2 cm × 0.25 cm for weight loss measurement and surface analysis, 2.5 cm × 1.2 cm × 0.61 cm for electrochemical measurements) from carbon steel (AISI 1018), 5Cr low alloy steel (ASTM A182-F5), and 13Cr steel (UNS S41000) for corrosion study. The chemical compositions of three different steels are shown in Table 1. According to the field data, most wells in Weyburn were completed using J-55 carbon steel (0.19% C, 1.39% Mn, 0.31% Si, 0.014% P, 0.004% S and balance Fe) (Choi et al., 2013) which has similar chemical composition with the carbon steel used in the present study. The specimens were ground with 400- and 600-grit silicon carbide (SiC) paper, cleaned with isopropyl alcohol in an ultrasonic bath, dried, and weighed using a balance with a precision of 0.1 mg.

The corrosion experiments were carried out in a 4-L static stainless steel autoclave equipped to perform in situ electrochemical measurements, as shown in Figs. 1 and 2. The brine chemistry is shown in Table 2, designed to simulate conditions within the Weyburn-Midale system (Shevalier et al., 2011).

Corrosion tests were conducted under different pressures (30 and 80 bar) at 60 °C (Table 3) in order to simulate the pressure condition in the Weyburn-Midale system. CO₂ is in the gas phase

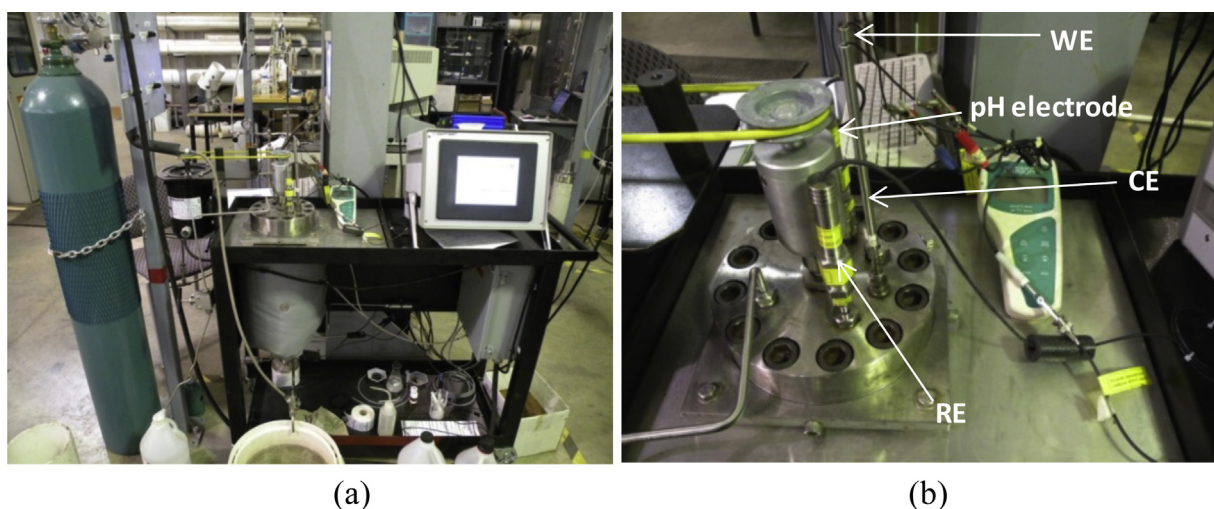


Fig. 1. Experimental setup for corrosion tests under high pressure condition: (a) autoclave system, (b) top lid part with electrode connections for electrochemical and pH measurements.

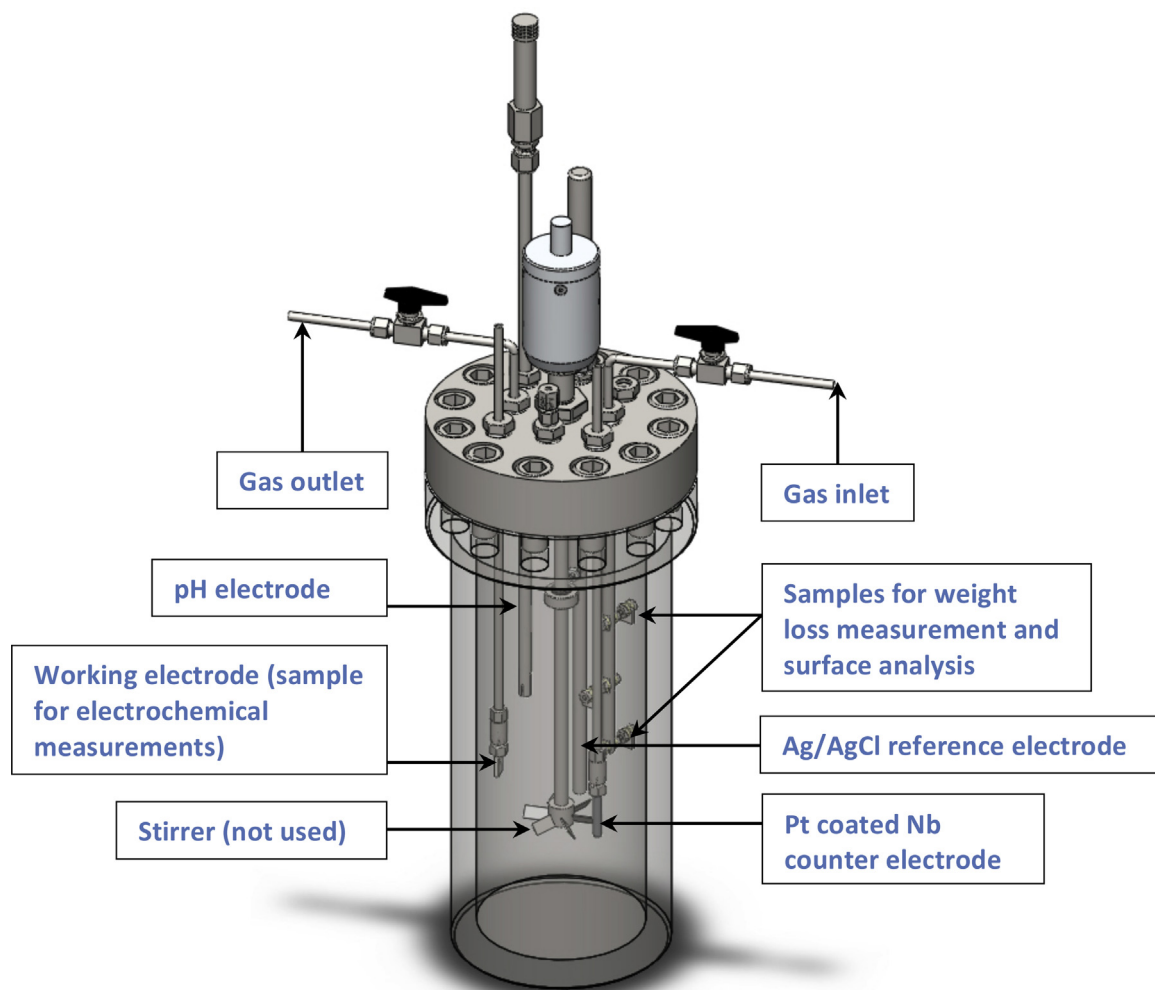


Fig. 2. Schematic of autoclave system equipped for electrochemical measurements.

at 30 bar and 60 °C which represent the long-term storage condition (Carroll et al., 2011) and at 80 bar and 60 °C, CO₂ turns to the supercritical phase simulating the CO₂ injection condition. Corrosion properties of materials were evaluated with time by three electrochemical techniques (Open Circuit Potential (OCP), Linear Polarization Resistance (LPR), and potentiodynamic polarization measurements), weight loss measurements, and surface analytical techniques (SEM, EDS, XRD, Raman spectroscopy).

Table 2
Chemical composition of brine.

Ions	Concentration (mg/l)
Cl ⁻	42,809
SO ₄ ²⁻	3,624
Ca ²⁺	2,020
Mg ²⁺	492
K ⁺	612
Na ⁺	26,035
pH	6.3

Table 3
Test matrix for corrosion testing.

Temperature (°C)	CO ₂ pressure (bar)
	30 80
60	Gas phase Supercritical Phase

For the LPR measurements, the working electrode was polarized at ± 5 mV vs. OCP with a scan rate of 0.125 mV s⁻¹. The polarization resistance, R_p , obtained from LPR technique, was used to calculate the current density (i_{corr}) by using the Stern-Geary equation:

$$i_{\text{corr}} = \frac{B}{R_p} = \frac{\beta_a \times \beta_c}{2.3 \times R_p \times (\beta_a + \beta_c)} \quad (1)$$

where β_a is the anodic Tafel slope, and β_c is the cathodic Tafel slope. The Tafel slopes, used in this study, were 120 mV dec⁻¹ and 40 mV dec⁻¹ respectively, giving proportionality constant “B” of 26 mV. Then, the i_{corr} was converted into corrosion rate using this equation:

$$\text{Corrosion rate (mm/year)} = \frac{0.00327 \times i_{\text{corr}} (\mu\text{A/cm}^2) \times \text{EW}}{\text{density (g/cm}^3\text{)}} \quad (2)$$

where EW is the equivalent weight of iron in grams and 0.00327 is a constant factor. At the end of each test, potentiodynamic polarization tests were performed at a scan rate of 0.125 mV s⁻¹.

Experimental procedures are shown in Fig. 3. At first, 3 L of brine solution was placed in the autoclave and the solution was purged with CO₂ for 1–3 h in order to remove oxygen. Subsequently, the electrodes and the specimens were placed in the autoclave. After closing the autoclave, the temperature was increased to the testing temperature and high pressure CO₂ was injected with a booster pump. The first LPR measurement was conducted once the equilibrium between brine and CO₂ was reached (monitored by pressure

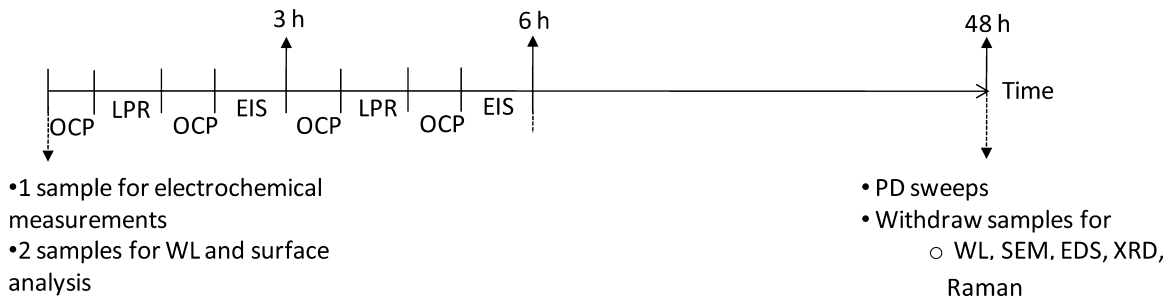


Fig. 3. Experimental procedures for evaluating the corrosion behavior of materials in CO₂/brine environments.

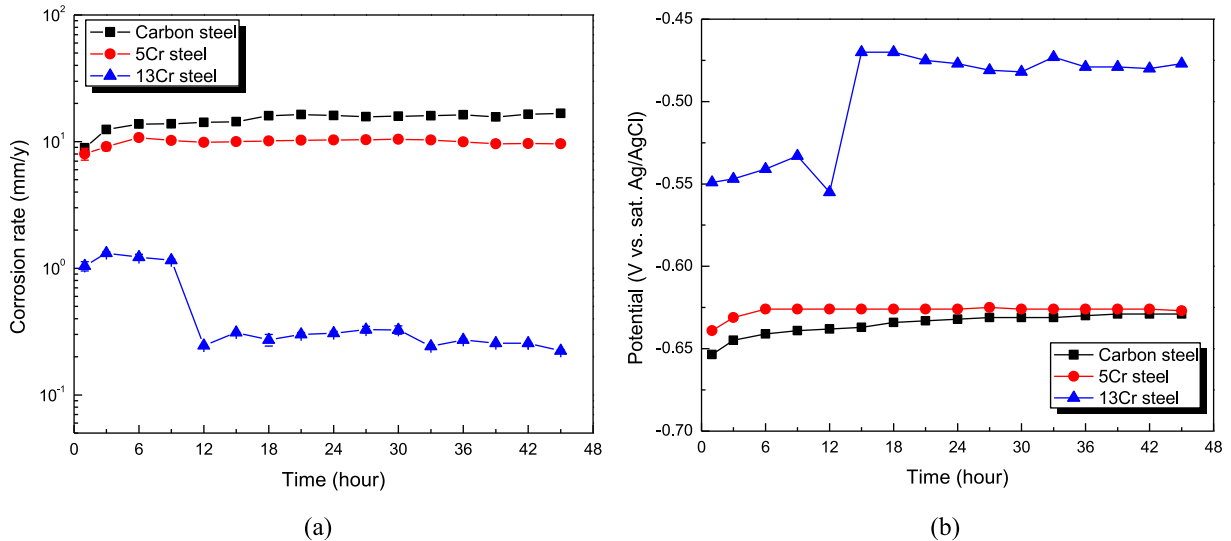


Fig. 4. Variation of (a) corrosion rate and (b) corrosion potential with time for different materials at 30 bar and 60 °C.

change and pH). The measured pH values after the equilibrium between brine and CO₂ were 3.4 at 30 bar and 3.2 at 80 bar, respectively. After each test, the specimens were removed from the autoclave, rinsed with deionized (DI) water and isopropyl alcohol, dried with N₂ and stored in a desiccator cabinet prior to, and between, surface analyses.

3. Results and discussion

3.1. Experiments at 30 bar and 60 °C

Fig. 4 shows the variations of corrosion rate and OCP with time for three materials at 30 bar and 60 °C. As shown in Fig. 4(a), carbon steel and 5Cr steel showed high corrosion rates (~20 mm/y

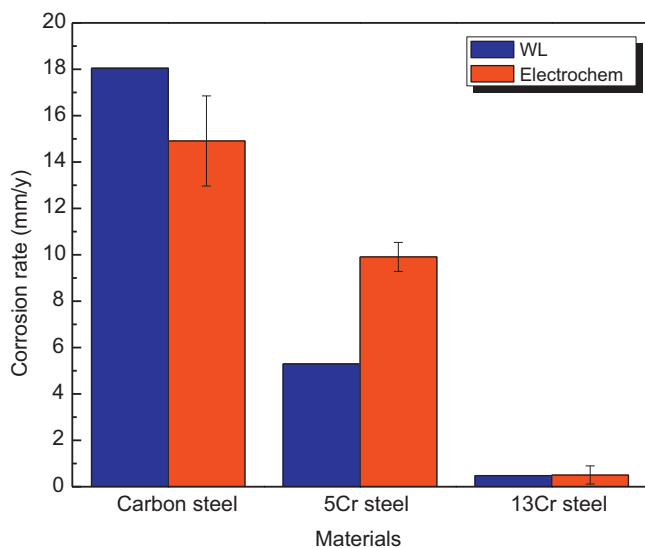


Fig. 5. Comparison of corrosion rates obtained from weight loss and electrochemical measurements (average) with different materials at 30 bar and 60 °C for 48 h.

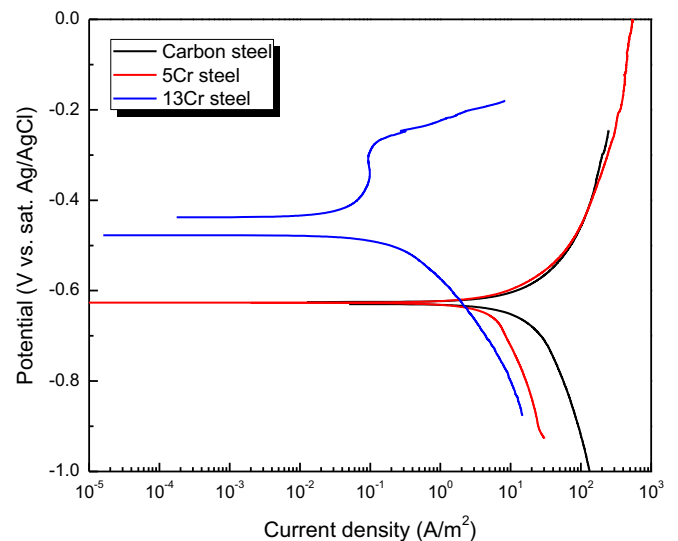


Fig. 6. Polarization curves of materials at 30 bar and 60 °C after 48 h.

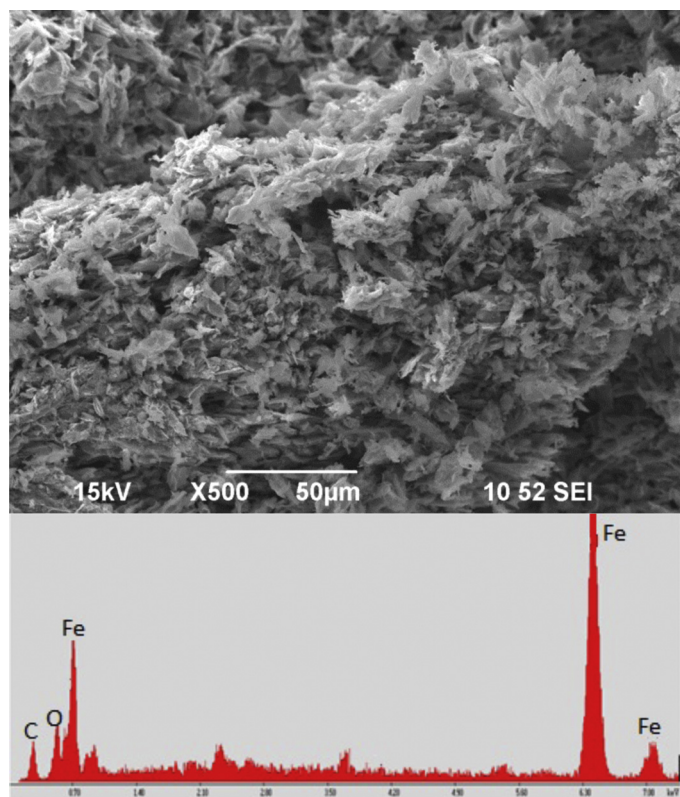


Fig. 7. SEM image and EDS spectra of the corroded surface of carbon steel at 30 bar and 60 °C.

for carbon steel and ~ 10 mm/y for 5Cr steel), these were maintained at constant values throughout the test periods. However, for 13Cr steel, the initial corrosion rate was ~ 1.0 mm/y and then decreased with time to 0.2 mm/y as the potential also shifted to a noble direction, consistent with formation of a passive film on the surface.

Fig. 5 compares the time-averaged corrosion rate obtained from weight loss and electrochemical measurements for the three different materials at 30 bar and 60 °C. Reasonable agreement was observed for corrosion rates measured by the different techniques.

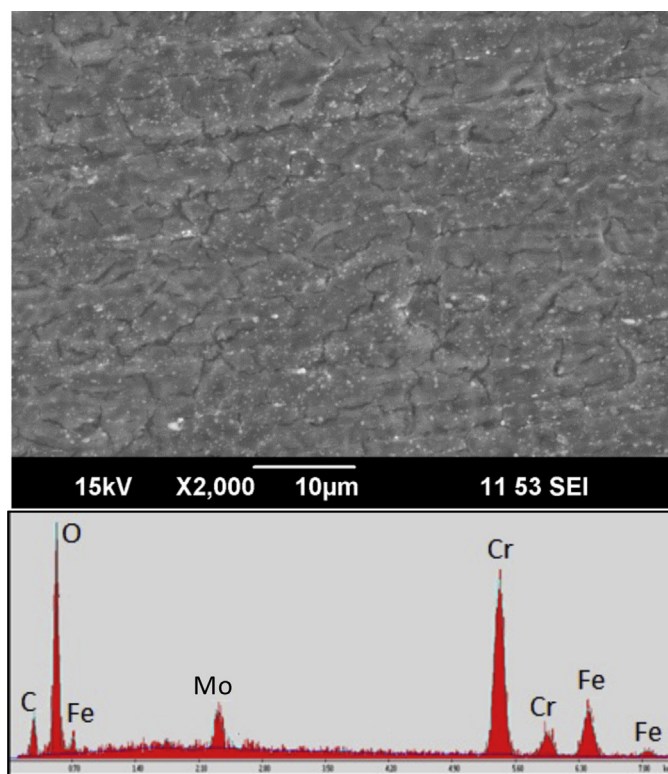


Fig. 9. SEM image and EDS spectra of the corroded surface of 13Cr steel at 30 bar and 60 °C.

Under this experimental condition, the relative corrosion resistance can be ranked as: 13Cr steel > 5Cr steel > carbon steel (most active).

Fig. 6 shows the polarization curves of materials at 30 bar and 60 °C, obtained at the end of the tests (after 48 h). Typical passive behavior was observed for 13Cr steel, whereas carbon steel and 5Cr steel exhibited active corrosion behavior (Shoesmith, 1987). It is noteworthy that there is no difference between the anodic polarization curves for carbon steel and 5Cr steel, however, the cathodic current densities decreased in the case of 5Cr steel. This can be explained by the presence of a Cr-containing corrosion

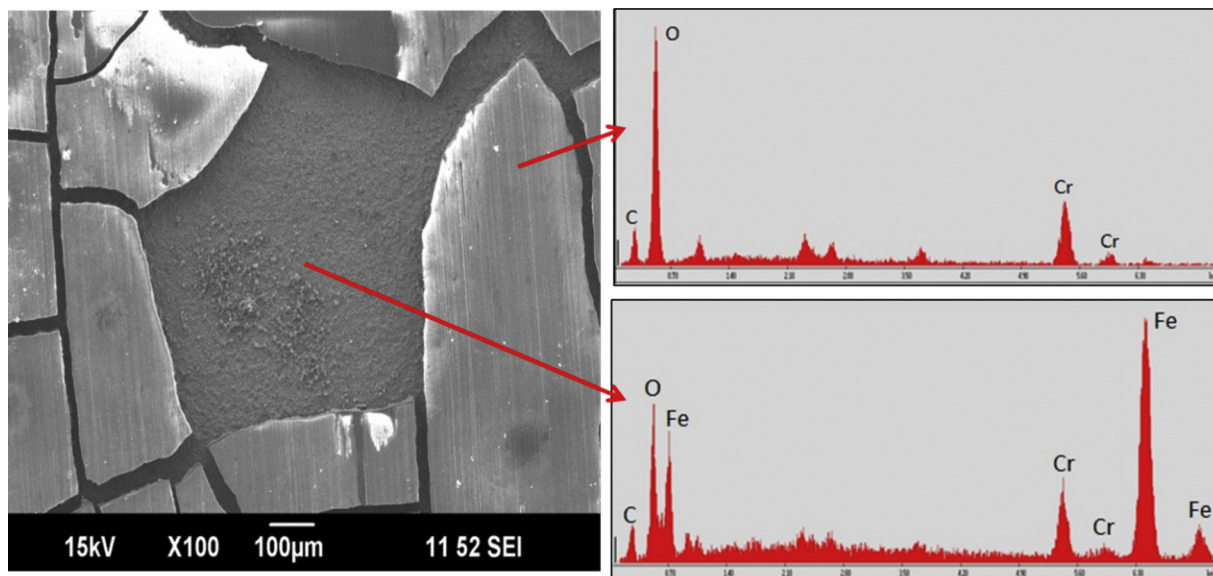


Fig. 8. SEM image and EDS spectra of the corroded surface of 5Cr steel at 30 bar and 60 °C. Mo.

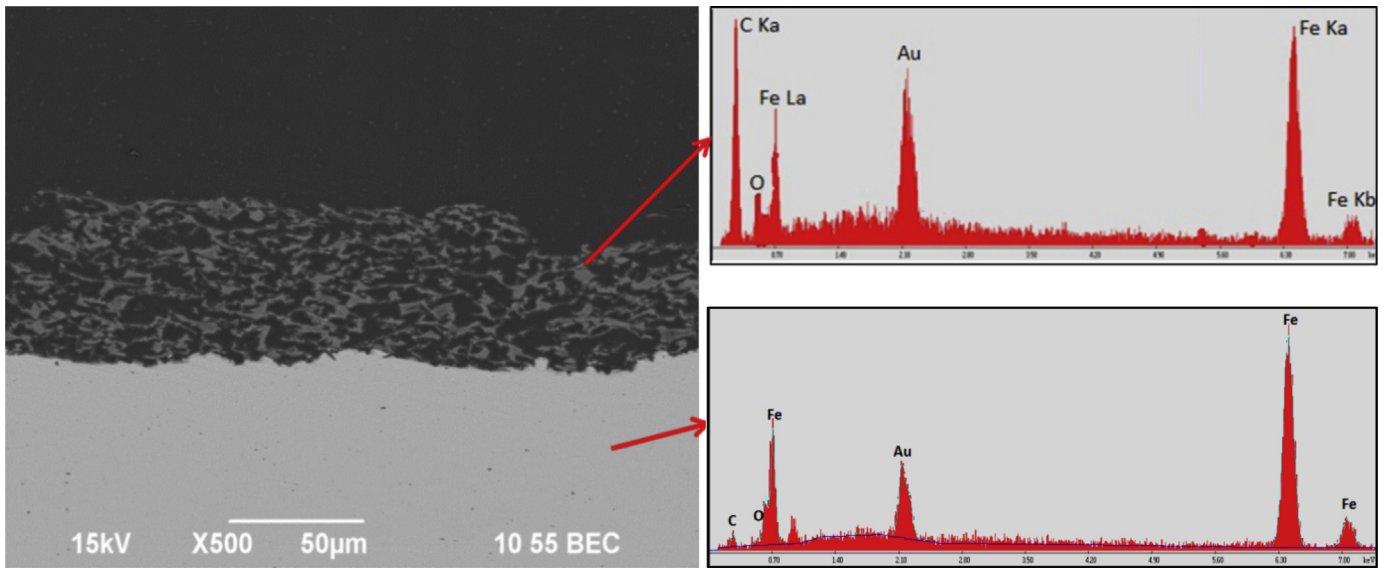


Fig. 10. SEM image and EDS spectra for the cross-section of carbon steel exposed to brine solution at 30 bar and 60 °C.

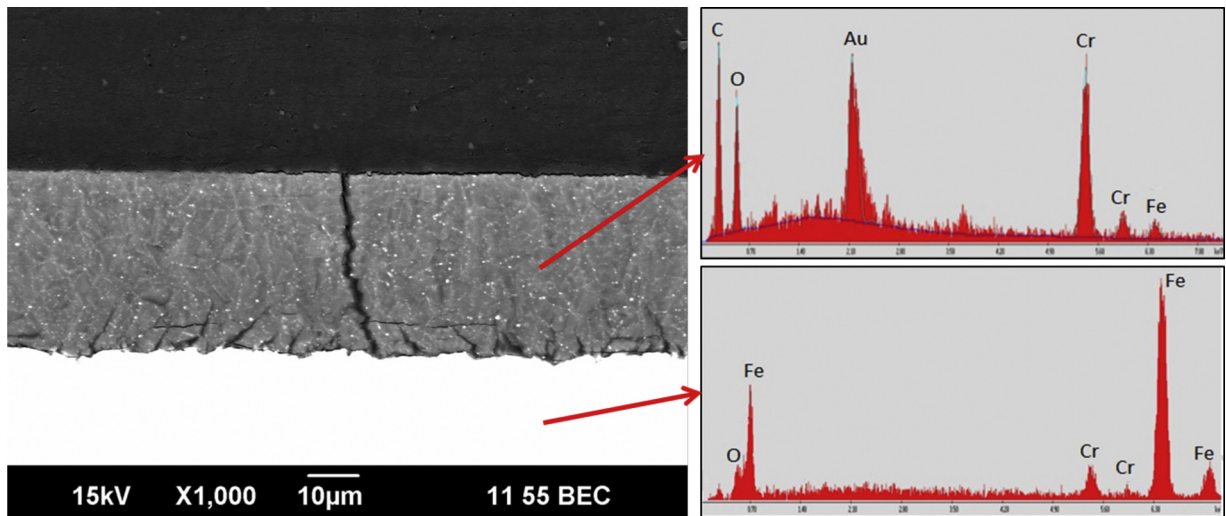


Fig. 11. SEM image and EDS spectra for the cross-section of 5Cr steel exposed to brine solution at 30 bar and 60 °C.

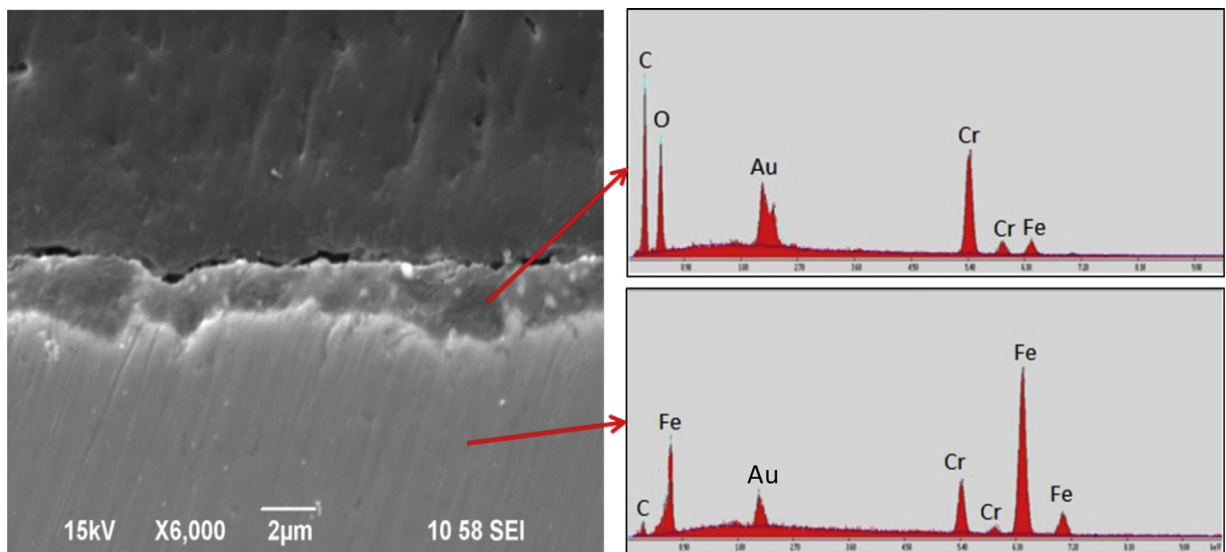


Fig. 12. SEM image and EDS spectra for the cross-section of 13Cr steel exposed to brine solution at 30 bar and 60 °C.

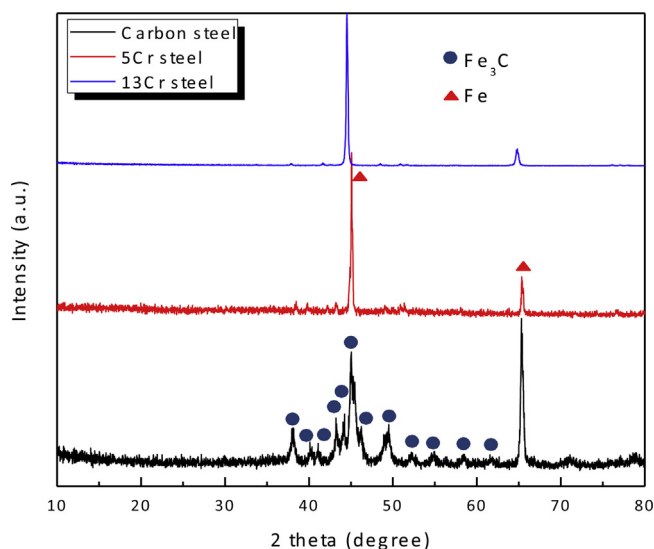


Fig. 13. XRD analyses for the steel samples exposed to 30 bar CO₂, 60 °C for 48 h.

product layer on the 5Cr steel. The formation of non-conductive chromium(III) hydroxide (Cr(OH)₃), or chromium(III) oxyhydroxide (CrO(OH)), does not lead to galvanic corrosion if present on the steel surface between ferrite (α -Fe) and cementite (Fe₃C). Moreover, these hydroxides can act as a diffusion barrier that can block corrosive species from reaching the metal surface (Chen et al., 2005). Changfeng et al. (2003) using XPS showed that near surface corrosion scale of 4% Cr containing N80 steel mainly consists of Cr₂O₃ and Cr(OH)₃, but in the inner position it mainly consists of Cr(OH)₃.

Fig. 7 through Fig. 9 show the SEM images and EDS spectra of the sample surfaces after 48 h of exposure at 30 bar and 60 °C. Fig. 7 shows that the surface of the carbon steel was uniformly covered by corrosion product, which consists mainly of iron and carbon with small amounts of oxygen. As shown in Fig. 8, the surface of 5Cr steel was locally covered by the corrosion products. Corrosion product

layers cracked immediately upon their removal from the solution due to dehydration, some easily spalled off after dehydration. EDS analysis showed that the corrosion product consists of chromium, carbon, oxygen, and particular alloying elements from the steel, whereas the uncovered region was identified as the bare steel substrate with small amounts of oxygen. In the case of 13Cr steel, the surface was uniformly covered by a thin corrosion product (passive layer), which mainly consists of chromium and oxygen (Fig. 9).

Fig. 10 through Fig. 12 represent cross-section SEM images and EDS spectra of the samples exposed to 30 bar CO₂ at 60 °C. It shows a porous corrosion product layer on the carbon steel surface with a thickness of approximately 50 μ m (Fig. 10). A corrosion product layer was also observed on the surface of the 5Cr steel with a thickness of 30 μ m, as shown in Fig. 11. This looks less porous compared to what observed for the carbon steel. However, there are several cracks at the boundary between the steel substrate and corrosion product layer indicative of a non-protective character. Although both carbon steel and 5Cr steel have thick corrosion product layer on the surface, the corrosion rates were very high because of high porosity and poor adhesion of the layer. For 13Cr steel, it can be seen that a thin, compact, and adherent passive layer was formed on the surface which can confer superior protection and decrease the corrosion rate (Fig. 12).

Fig. 13 shows the XRD patterns of the corrosion product layers formed on the different materials at 30 bar and 60 °C. The layer formed on carbon steel showed a dominant Fe₃C diffraction pattern. This indicated that the corrosion products shown in Figs. 7 and 10 can be identified as Fe₃C. The Fe₃C lamellae initially present in the pearlite structure become revealed after the preferential dissolution of ferrite (α -Fe) at the steel surface; therefore it is non-protective, porous and easily spalls off from the substrate (Kermani and Morshed, 2003). No diffraction peaks for any corrosion product were detected on the surface of the 5Cr steel and 13Cr steel, only the substrate (Fe) was detected by XRD analysis. However recall that a chromium oxide (or hydroxide) layer was observed from SEM and EDS analyses. This indicated that the structure of the corrosion products formed on the 5Cr steel and 13Cr steel would most likely be amorphous or nanocrystalline, and hence be undetectable by XRD analysis.

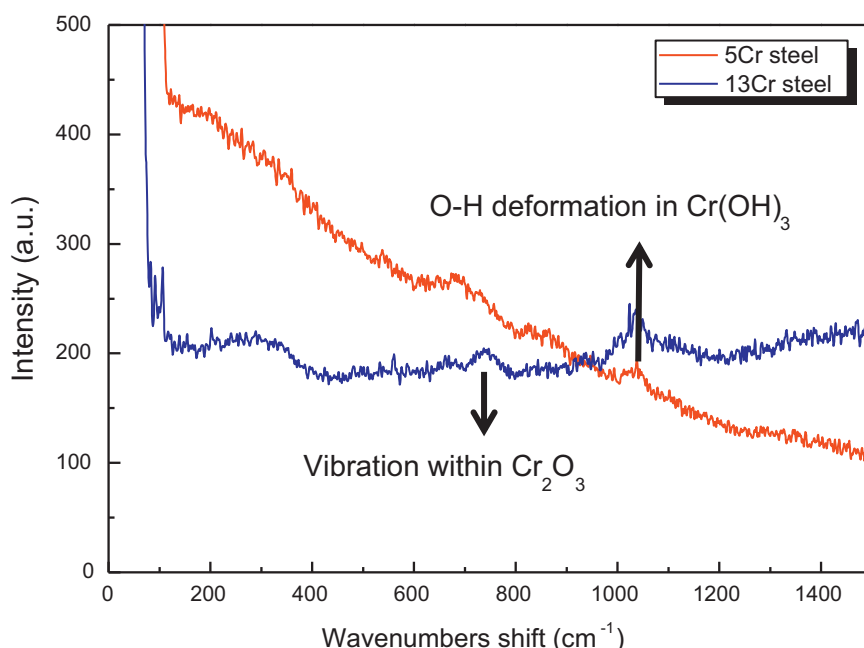


Fig. 14. Raman spectroscopy analyses for the 5Cr and 13Cr steel samples exposed to 30 bar CO₂ and 60 °C for 48 h.

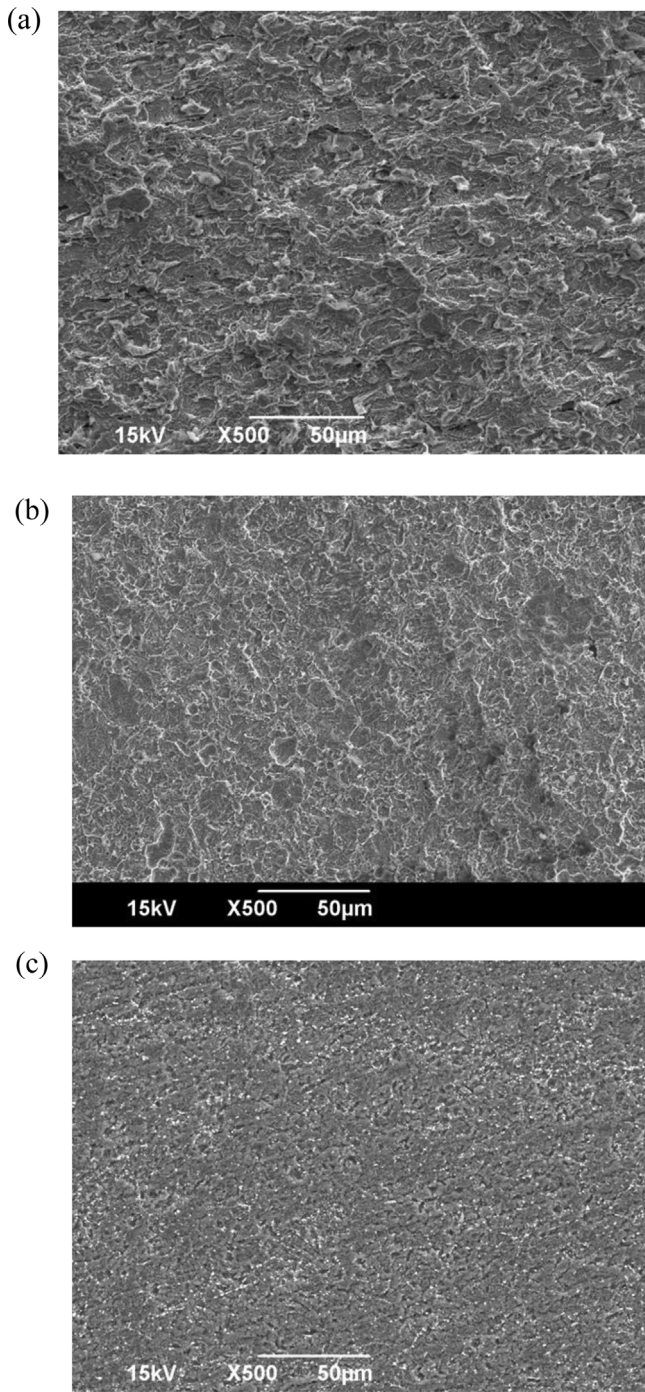


Fig. 15. SEM images of the corroded surface of samples after cleaning: (a) carbon steel, (b) 5Cr steel and (c) 13Cr steel.

Thus, in order to further identify the corrosion products on 5Cr and 13Cr steel surfaces, Raman spectroscopy was employed to obtain vibrational information that is specific to the chemical bonds in molecules/polyatomic ions and lattice vibrations, or phonon modes, of solids; Raman is particularly useful for the analysis of amorphous, nanocrystalline and crystalline materials. Fig. 14 shows Raman spectra of the corrosion product on 5Cr and 13Cr steel surfaces after 48 h of exposure at 30 bar and 60 °C. The strongest Raman peak observed at around 1000 cm^{-1} originates from the O–H deformation in $\text{Cr}(\text{OH})_3$ (Yang et al., 2011) and, thus, can be used as a fingerprint for identifying corrosion products of the type $\text{Cr}(\text{OH})_3$. In addition, the peak around 740 cm^{-1} can be identified as

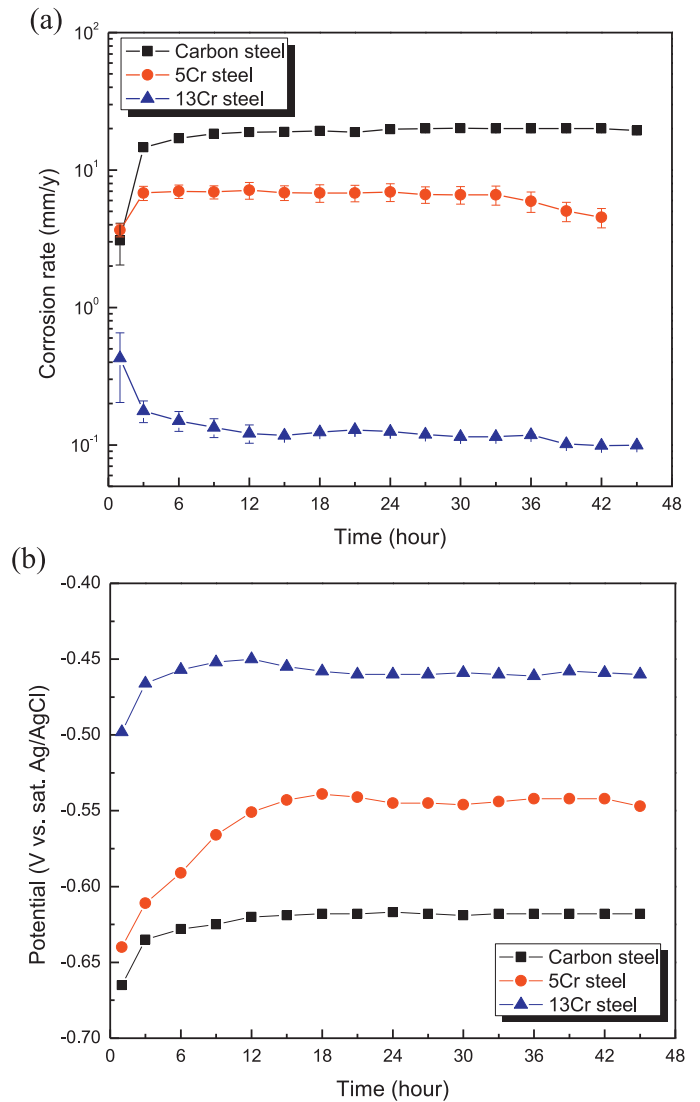


Fig. 16. Variation of (a) corrosion rate and (b) corrosion potential with time for different materials at 80 bar and 60 °C.

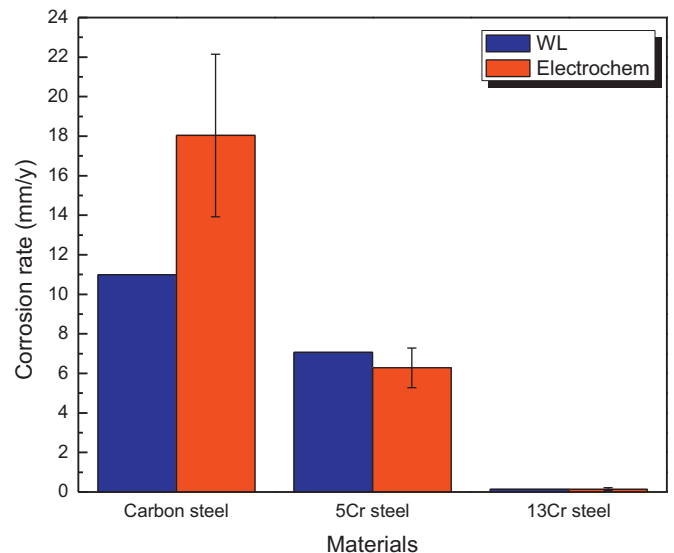


Fig. 17. Comparison of corrosion rates obtained from weight loss and electrochemical measurements (average) with different materials at 80 bar and 60 °C for 48 h.

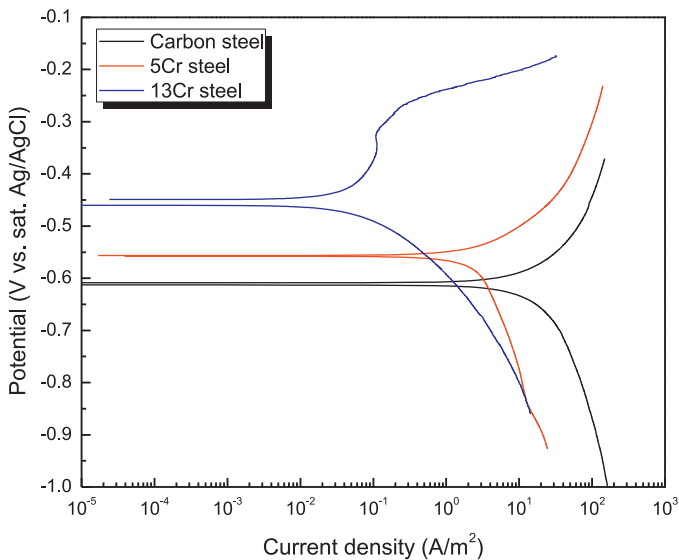


Fig. 18. Polarization curves of materials at 30 bar and 60 °C after 48 h.

symmetric stretching vibrations within Cr₂O₃ (Yang et al., 2011). This allowed ready identification of the corrosion products on 5Cr and 13Cr steel as Cr(OH)₃ and Cr₂O₃. No vibrational mode was observed at 1100 cm⁻¹, indicating that no carbonate was detected at the surface; similarly, no sulfate was observed.

Fig. 15 shows the surface morphologies of samples after cleaning with Clarke solution (ASTM, 1999) (20 g antimony trioxide + 50 g stannous chloride and hydrochloric acid to make 1000 ml) in order to remove corrosion products. Severe uniform corrosion attack was observed on the surface of carbon steel and 5Cr steel, i.e., no localized corrosion was apparent. However, in the case of 13Cr steel, only slight attack was observed on the surface which likely occurred during the initial period of the test.

3.2. Experiments at 80 bar and 60 °C

Fig. 16 shows the variations of corrosion rate and OCP with time for materials at 80 bar and 60 °C for 48 h. Similar to the results at 30 bar condition, 13Cr steel showed the minimum corrosion rates

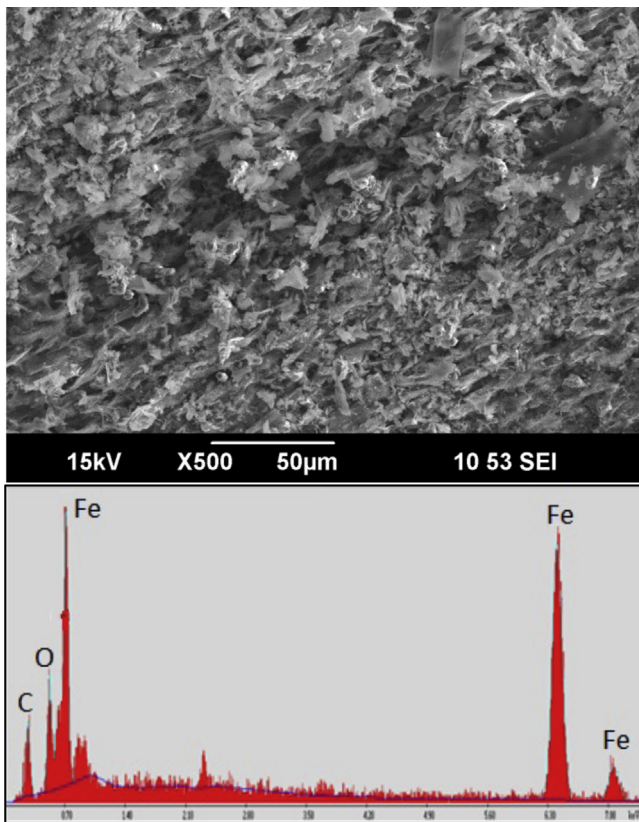


Fig. 19. SEM image and EDS spectra of the corroded surface of carbon steel at 80 bar and 60 °C.

(~0.1 mm/y) with noble potential values and carbon steel showed the maximum corrosion rates (~20 mm/y) with active potential values.

Fig. 17 compares the average corrosion rate obtained from weight loss and electrochemical measurements for three different materials at 80 bar and 60 °C. Acceptable agreement was observed for corrosion rates measured by different techniques. Again, similar to the 30 bar condition, under this experimental condition,

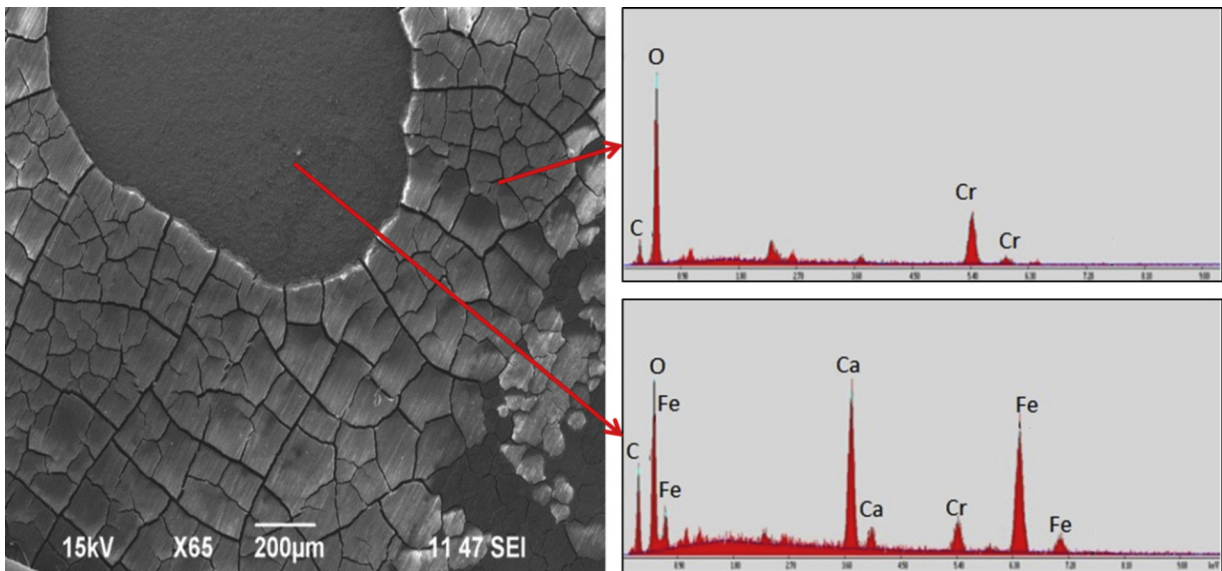


Fig. 20. SEM image and EDS spectra of the corroded surface of 5Cr steel at 80 bar and 60 °C.

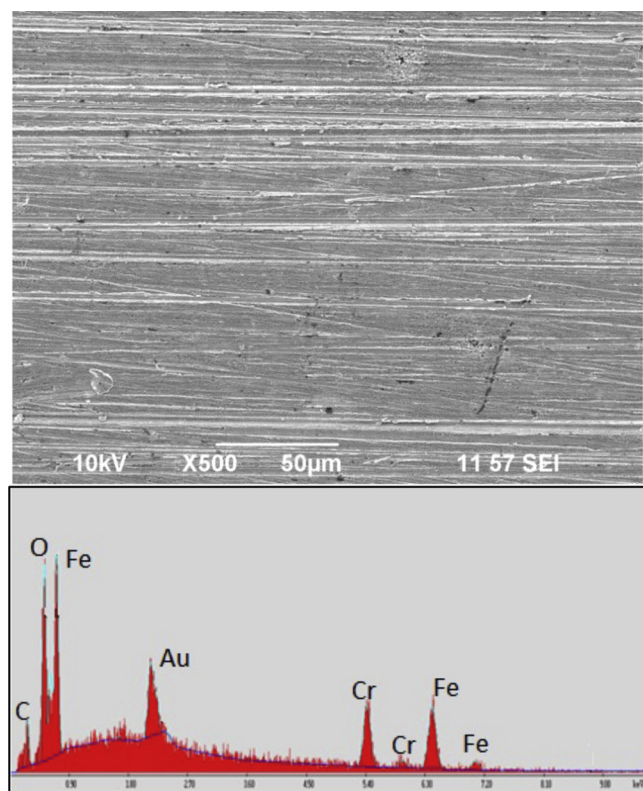


Fig. 21. SEM image and EDS spectra of the corroded surface of 13Cr steel at 80 bar and 60 °C.

the relative corrosion resistance can be ranked as: 13Cr steel > 5Cr steel > carbon steel (most active).

Fig. 18 shows the polarization curves for the steels at 80 bar and 60 °C, obtained at the end of the tests (after 48 h). Polarization curve of 13Cr steel showed a typical passive behavior, whereas carbon steel and 5Cr steel exhibited active corrosion behavior. Limiting current density for cathodic reaction on 5Cr was much lower than carbon steel. Formation of chromium hydroxide layer on the surface mainly affected the cathodic reaction by reducing the active sites for cathodic reaction and limiting the diffusion of cathodic species to the surface which consequently reduces the corrosion rate.

Fig. 19 through Fig. 21 show the SEM images and EDS spectra of the sample surfaces after 48 h of the exposure at 80 bar and 60 °C. The surface of carbon steel was uniformly covered by corrosion product which consists mainly of iron and carbon, suggesting the presence of Fe_3C , with small amounts of oxygen (Fig. 19). As shown in Fig. 20, the surface of the 5Cr steel was locally covered by the corrosion products. Cracks on the corrosion product layer were due to dehydration. EDS analysis showed that the corrosion product consists of chromium, carbon, oxygen, and particular alloying elements from the steel, whereas the uncovered region was identified as the steel substrate with calcium and oxygen. In the case of 13Cr steel, polishing marks on the surface are clearly observed, indicating no sign of significant corrosion attack in 13Cr steel due to the formation of passive film (Fig. 21).

Fig. 22 through Fig. 24 represent cross-section SEM pictures and EDS spectra of the samples exposed to 80 bar CO_2 at 60 °C. In the case of carbon steel (Fig. 22), the presence of a porous Fe_3C layer with a few crystals containing iron, calcium, carbon and oxygen. It is interesting to note that calcium was detected only for 80 bar condition because of the increase in HCO_3^- and CO_3^{2-} concentrations at higher CO_2 partial pressure (Choi and Nešić, 2011). In other words, the precipitation of FeCO_3 and CaCO_3 (or $\text{Fe}_x\text{Ca}_y\text{CO}_3$) is possible due to local saturation and alkaline conditions in the Fe_3C matrix (Esmaeely et al., 2013; Farel et al., 2010). However, there is no corrosion protection from these crystals because they do not confer any significant surface coverage. A porous and non-adherent corrosion product was also observed on the surface of 5Cr steel with a thickness of 40 μm, as shown in Fig. 23. For 13Cr steel, it can be seen that a very thin and adherent passive layer was formed on the surface (Fig. 24).

Fig. 25 shows the XRD patterns of the corrosion product layer formed on different materials at 80 bar and 60 °C. Similarly to the results at the 30 bar condition, the layer formed on carbon steel showed a dominant Fe_3C diffraction pattern and an absence of FeCO_3 . Again, no diffraction peaks were detected on the surface of 5Cr steel and 13Cr steel except for the steel substrate. As for the lower pressure CO_2 condition, Raman spectroscopy (Fig. 26) showed the presence of $\text{Cr}(\text{OH})_3$ and Cr_2O_3 on the surface of 5Cr and 13Cr steels (Yang et al., 2011).

Fig. 27 shows the surface morphologies of samples after cleaning with Clarke solution. Severe uniform corrosion attack was observed on the surface of carbon steel and 5Cr steel, i.e., no localized corrosion. However, in the case of 13Cr steel, slight attack was observed

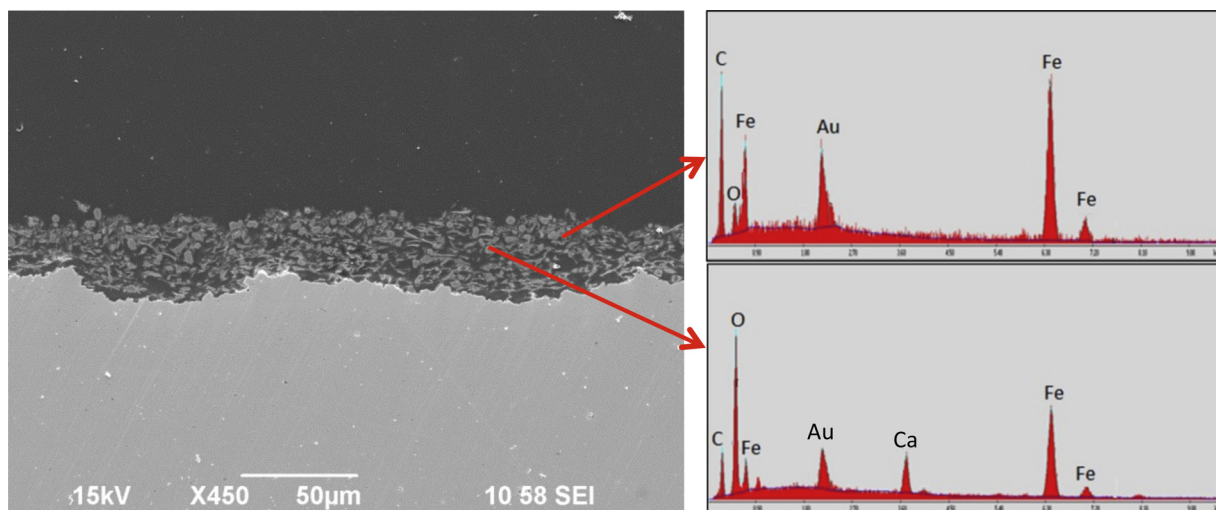


Fig. 22. SEM image and EDS spectra for the cross section of carbon steel exposed to brine solution at 80 bar and 60 °C.

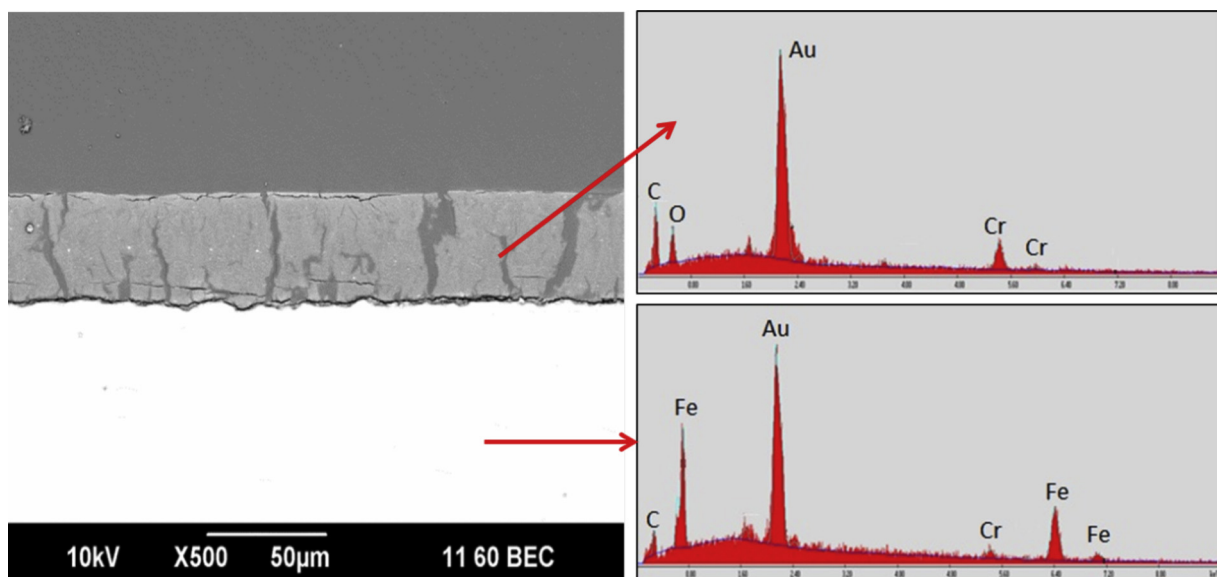


Fig. 23. SEM image and EDS spectra for the cross section of 5Cr steel exposed to brine solution at 80 bar and 60 °C.

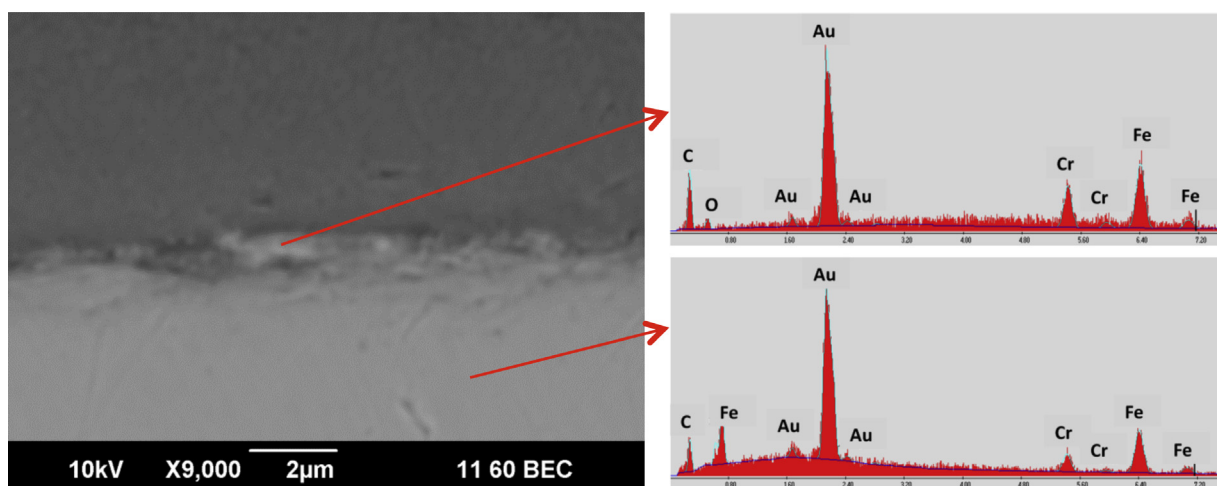


Fig. 24. SEM image and EDS spectra for the cross section of 13Cr steel exposed to brine solution at 80 bar and 60 °C.

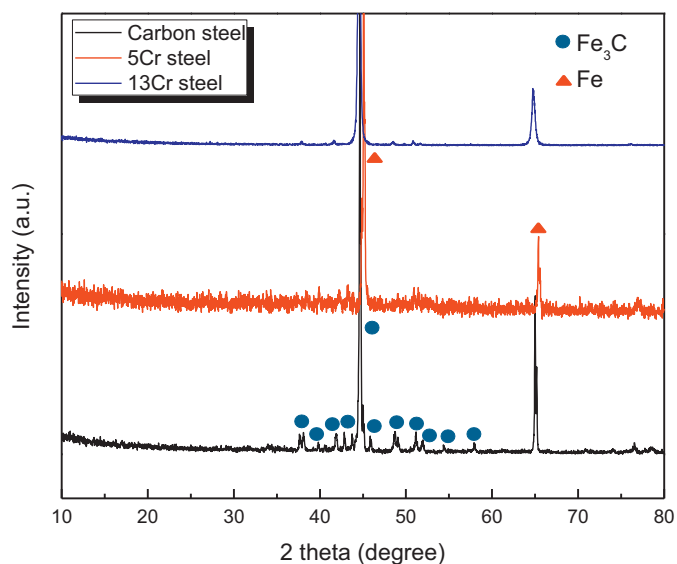


Fig. 25. XRD analyses for the samples exposed to 80 bar CO₂, 60 °C for 48 h.

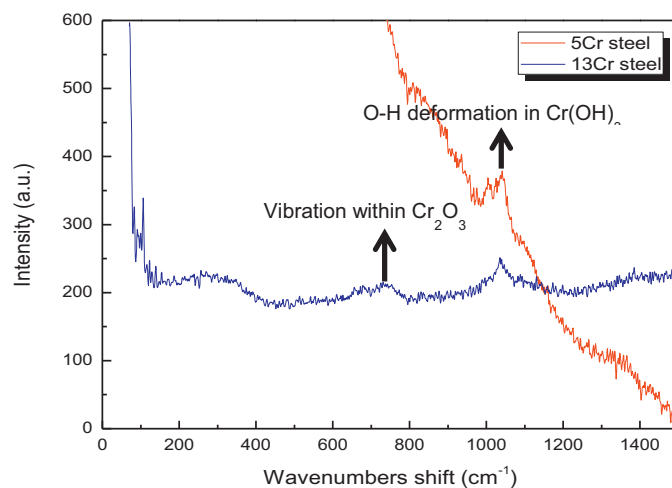


Fig. 26. Raman spectroscopy analyses for the 5Cr and 13Cr steel samples exposed to 80 bar CO₂ and 60 °C for 48 h.

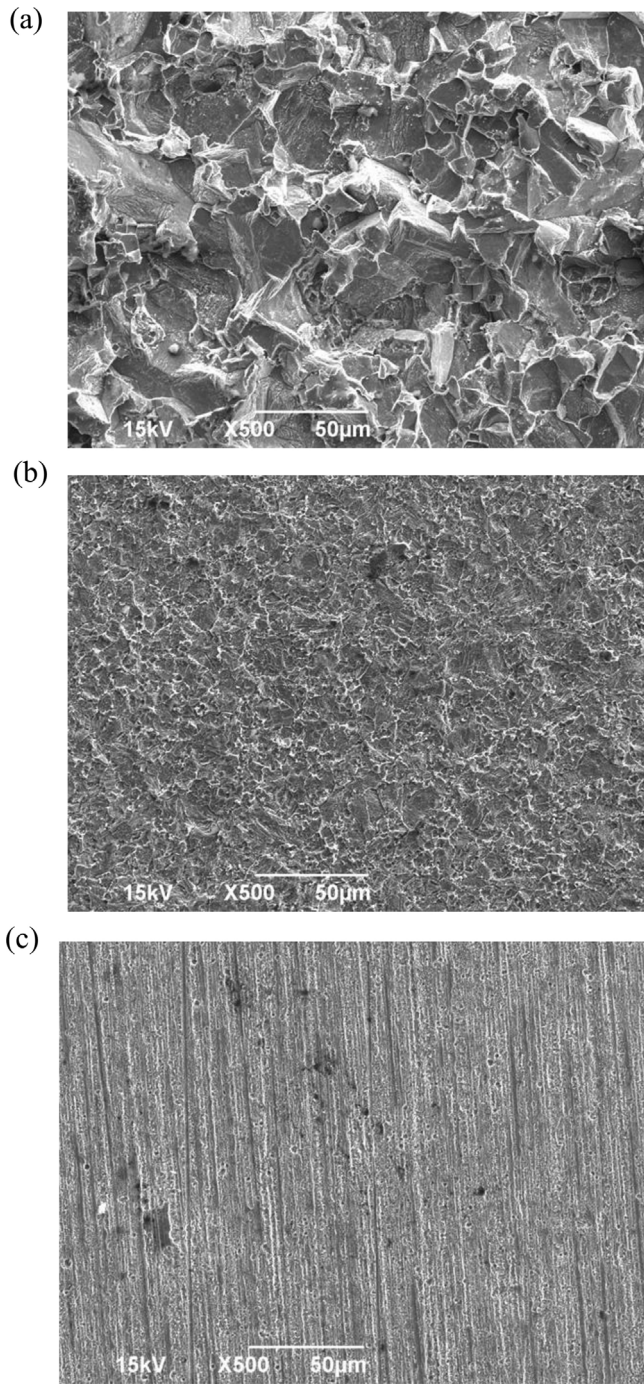


Fig. 27. SEM images of the corroded surface of samples after cleaning: (a) carbon steel, (b) 5Cr steel and (c) 13Cr steel.

on the surface which could be related to the initiation of pitting corrosion.

3.3. Comparison of corrosion behavior of materials between 30 bar and 80 bar conditions

Figs. 28 and 29 compare the corrosion rates and polarization behavior of each material under different conditions, respectively. Increasing the CO₂ partial pressure from 30 bar to 80 bar increased the corrosion rate of carbon steel (Fig. 28(a)) because of the higher CO₂ solubility and consequently lower solution pH (3.34 at 30 bar and 3.17 at 80 bar). This behavior was confirmed in the polarization

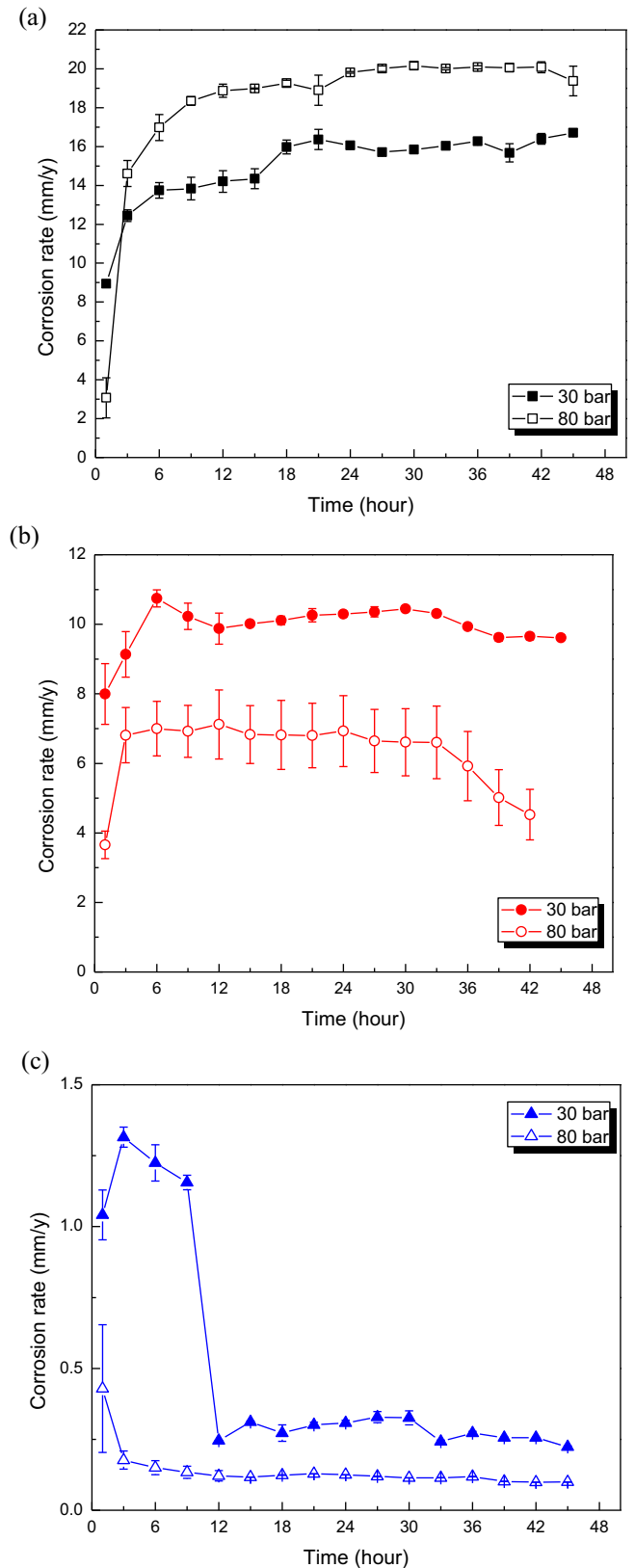


Fig. 28. Effect of CO₂ pressure on the corrosion rate at 60 °C: (a) carbon steel, (b) 5Cr steel and (c) 13Cr steel.

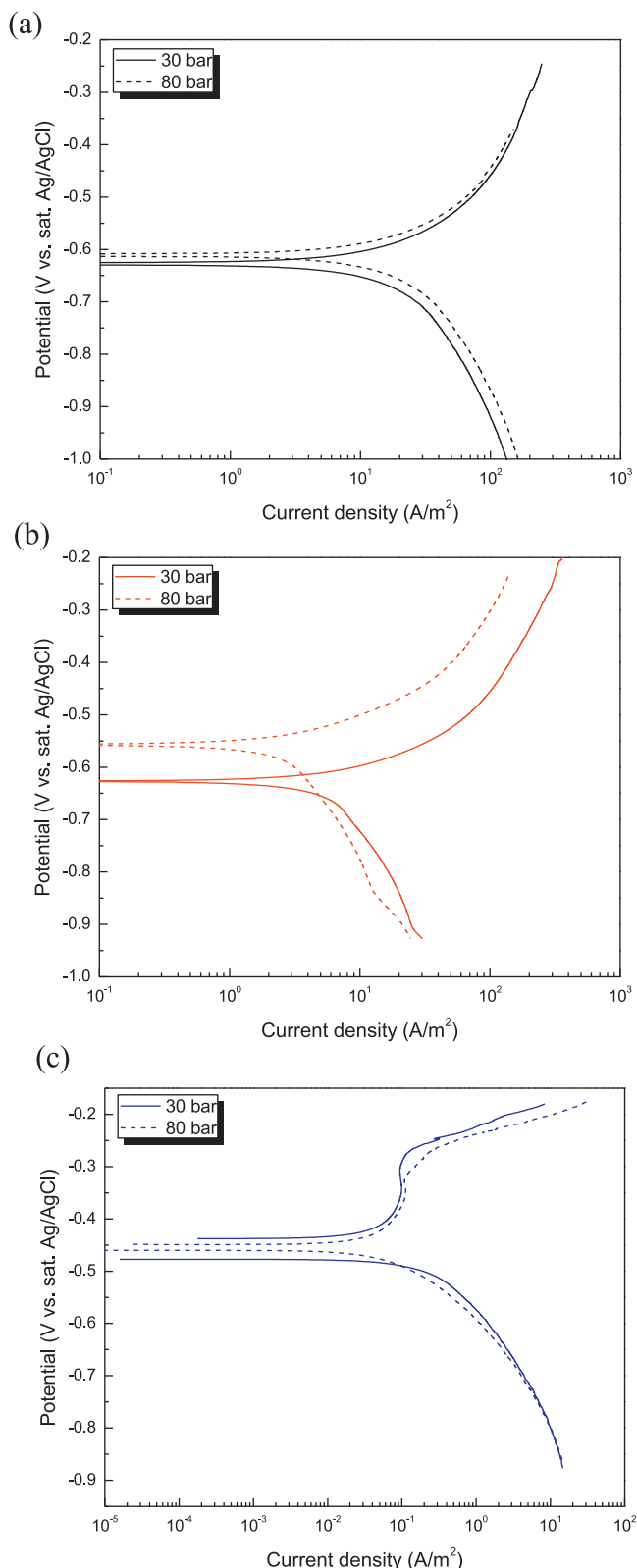


Fig. 29. Effect of CO₂ pressure on the polarization behavior at 60 °C: (a) carbon steel, (b) 5Cr steel and (c) 13Cr steel.

curve (Fig. 29(a)) which showed higher cathodic current densities at 80 bar, indicating higher rate of the cathodic reactions and therefore increasing the corrosion rate (Choi and Nešić, 2011; Mohamed et al., 2011). It also indicates that the change in CO₂ phase (gaseous to supercritical) does not change the corrosion mechanism (Zhang et al., 2012).

It is interesting to note that increasing the pressure from 30 to 80 bar at 60 °C slightly reduces the corrosion rate of 5Cr steel (Fig. 28(b)) due to the suppression of the anodic reaction at higher pressure as shown in Fig. 29(b). The same trend was observed for 13Cr steel (Fig. 28(c)) although there is no big difference in the polarization behavior (Fig. 29(c)). This can be explained by the formation of corrosion products on the surface. Carbon steel does not form any protective corrosion product layer on the surface. Therefore, more corrosive environment (i.e. higher CO₂ pressure and lower pH) accelerates the corrosion. However, both 5Cr and 13Cr steels form Cr rich layer on the surface which controls the corrosion mechanism. Slight reduction in corrosion rate at more corrosive conditions for 5Cr and 13Cr steels suggests the formation of a slightly more protective layer on the surface. Yang et al. (2011) suggested that for low Cr steels, Cr(OH)₃ can block anions penetration path in the corrosion products due to its cation selectivity property which can reduce the anodic reactions and the corrosion rate.

4. Conclusions

CO₂ corrosion experiments at high pressures (30 and 80 bar) and 60 °C showed that the corrosion rate of carbon steel in both pressures was very high (~20 mm/y) and unacceptable for any application. One option for controlling the corrosion rate under these conditions is using low Cr steels. 5Cr steel has been used as a material to replace carbon steel in some severely corrosive conditions. Cr containing (between 1% and 5%) carbon steels have an improved resistance to CO₂ corrosion by a factor of at least 3, and even up to 10 times and more, whilst maintain a cost penalty less than 1.5 times that of conventional grades of carbon steels. Different corrosion measurement techniques used to monitor the CO₂ corrosion behavior of 5Cr steel showed almost 3 times lower corrosion rate at two different pressures in comparison with carbon steel. Therefore, 5Cr steel can be a good replacement for carbon steel at 1.5 times higher cost and 3 times longer lifetime. However, corrosion rate is still high (around 6 mm/y), which is not acceptable for long-term CO₂ storage applications. Another material selection option for solving the severe corrosion problem in high pressure systems is using high Cr containing steel, for example 13Cr steel. In the present study, 13Cr steel showed very low corrosion rates (~0.1 mm/y) under testing conditions without showing any significant localized corrosion.

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References

- ASTM, 1999. *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, G1-90*. ASTM International.
- Carroll, S., Smith, M., Sholokhova, Y., Hao, Y., 2011. *An Experimental and Modeling Study: Enhanced Porosity within Carbonate Rocks for the Weyburn CO₂ Storage Project*. IEA Weyburn-Midale CO₂ Monitoring and Storage Program., pp. 2.
- Changfeng, C., Minxu, L., Wei, C., Guoxian, Z., Zhenquan, B., 2003. *The Ion Passing Selectivity of CO₂ Corrosion Scale on N80 Tube Steel*. In: CORROSION. NACE International, Houston, TX, Paper No. 03342.

- Chen, C.F., Lu, M.X., Zhang, Z.H., Chang, W., 2005. Effect of chromium on the pitting resistance of oil tube steel in a carbon dioxide corrosion system. *Corrosion* 61, 594–601.
- Choi, Y.S., Nescic, S., 2009. Corrosion Behavior of Carbon Steel in Supercritical CO₂–Water Environments. In: CORROSION. NACE International, Houston, TX, Paper No. 09256.
- Choi, Y.S., Nešić, S., 2011. Determining the corrosive potential of CO₂ transport pipeline in high pCO₂–water environments. *International Journal of Greenhouse Gas Control* 5, 788–797.
- Choi, Y.S., Nescic, S., Young, D., 2010. Effect of impurities on the corrosion behavior of CO₂ transmission pipeline steel in supercritical CO₂–water environments. *Environmental Science and Technology* 44, 9233–9238.
- Choi, Y.S., Young, D., Nescic, S., Gray, L.G.S., 2013. Wellbore integrity and corrosion of carbon steel in CO₂ geologic storage environments: A literature review. *International Journal of Greenhouse Gas Control* 16S, S70.
- Esmaily, S.N., Choi, Y.S., Young, D., Nescic, S., 2013. Effect of calcium on the formation and protectiveness of iron carbonate layer in CO₂ corrosion. *Corrosion* 69, 912–920.
- Farelas, F., Galicia, M., Brown, B., Nescic, S., Castaneda, H., 2010. Evolution of dissolution processes at the interface of mild steel corroding in a CO₂ environment by EIS. *Corrosion Science* 52, 509–517.
- Han, J., Carey, J.W., Zhang, J., 2011. Effect of Debonded Interfaces on Corrosion of Mild Steel Composites in Supercritical CO₂–Saturated Brines. In: CORROSION. NACE International, Houston, TX, Paper No. 11376.
- Han, J., Carey, J.W., Zhang, J., 2012. Degradation of Cement–Steel Composite at Bonded Steel–Cement Interfaces in Supercritical CO₂ Saturated Brines Simulating Wellbore Systems. In: CORROSION. NACE International, Houston, TX, Paper No. 0001075.
- Hu, H., Zhang, L., Chang, W., Lu, M., Xu, L., 2011. Compare the Corrosion Resistance of 3% Cr Steel with API X65 Pipeline Steel in CO₂ Corrosion Environment. In: Corrosion. NACE International, Houston, TX, Paper No. 11073.
- Kermani, M.B., Gonzales, J.C., Linne, C., Dougan, M., Cochrane, R., 2001. Development of Low Carbon Cr–Mo steels with Exceptional Corrosion Resistance for Oilfield Applications. In: CORROSION. NACE International, Houston, TX, Paper No. 01065.
- Kermani, M.B., Morshed, A., 2003. Carbon dioxide corrosion in oil and gas production – a compendium. *Corrosion* 59, 659–683.
- Lin, G., Zheng, M., Bai, Z., Zhao, X., 2006. Effect of temperature and pressure on the morphology of carbon dioxide corrosion scales. *Corrosion* 62, 501–507.
- Loizzo, M., Bressers, P., Benedictus, T., Le Guen, Y., Poupard, O., 2009. Assessing CO₂ interaction with cement and steel over a two-year injection period: current state and future risks for the MoveCBM project in Poland. *Energy Procedia* 1, 3579–3586.
- Mohamed, M.F., Nor, A.M., Suhor, M.F., Singer, M., Choi, Y.S., Nescic, S., 2011. Water chemistry for corrosion prediction in high pressure CO₂ environments. In: CORROSION. NACE International, Houston, TX, Paper No. 11375.
- Mohammed Nor, A., Suhor, M.F., Mohamed, M.F., Singer, M., Nescic, S., 2011. Corrosion of Carbon Steel in High CO₂ Environment: Flow Effect. In: CORROSION. NACE International, Houston, TX, Paper No. 11242.
- Muraki, T., Nose, K., Asahi, H., 2003. Development of 3% Chromium Linepipe Steel. In: CORROSION. NACE International, Houston, TX, Paper No. 03117.
- Pfennig, A., Kranzmann, A., 2012. Effect of CO₂ and pressure on the stability of steels with different amounts of chromium in saline water. *Corrosion Science* 65, 441–452.
- Seiersten, M., Kongshaug, K.O., 2005. Materials selection for capture, compression, transport and injection of CO₂. *Carbon dioxide Capture for Storage in Deep Geologic Formations* 2, 937.
- Shevalier, M., Nightingale, M., Mayer, B., Hutcheon, I., Kwon, J.S., 2011. Geochemistry Monitor Trips 12–16 Final Report. IEA Weyburn-Midale CO₂ Monitoring and Storage Program., pp. 27.
- Shoesmith, D.W., 1987. Kinetics of Aqueous Corrosion, ASM Handbook.
- Yang, J., Cheng, H., Martens, W.N., Frost, R.L., 2011. Transition of synthetic chromium oxide gel to crystalline chromium oxide: a hot-stage Raman spectroscopic study. *Journal of Raman Spectroscopy* 42, 1069.
- Yevtushenko, O., Bettge, D., Bohrausa, S., Bäßler, R., Pfennig, A., Kranzmann, A., 2014. Corrosion behavior of steels for CO₂ injection. *Process Safety and Environmental Protection* 92, 108–118.
- Zhang, Y., Pang, X., Qu, S., Li, X., Gao, K., 2012. Discussion of the CO₂ corrosion mechanism between low partial pressure and supercritical condition. *Corrosion Science* 59, 186–197.