

Experimental Study of 3% Cr Tubing Steel in CO₂ and CO₂/H₂S Corrosion Environment

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Summary

The corrosion behavior of 3% Cr steel is tested by a high-temperature/high-pressure autoclave. The corrosion environment is categorized into CO₂-alone and CO₂/H₂S conditions. At 90°C, with the addition of H₂S to the CO₂, the surface corrosion condition improved greatly, and the corrosion rates declined compared with the CO₂-alone condition. Under CO₂/H₂S condition, with an increasing CO₂/H₂S partial-pressure ratio, the corrosion rate reached a peak value at pCO₂/pH₂S=100, and then declined. Through the analysis of the corrosion products of the samples in different conditions by scanning electron microscope (SEM), EDS, and X-ray-diffraction (XRD) methods, it was found that the inner film is finer and denser than the outer scale. The partial-pressure ratio of H₂S corrosion regime should be between 10 and 100 and is not the previous 200.

Introduction

Corrosion has wide-ranging implications for the integrity of materials used in the petroleum industry. The implication of CO₂ corrosion can be viewed in terms of its effect on capital and operational expenditures and health, safety, and the environment (Kermani and Harrop 1996), which brings huge losses and poses security threats to the development of oil and gas (Minxu et al. 2002; Kinsella et al. 1998). Medium Cr-containing steels showed improved corrosion resistance compared with carbon steel and lower cost than 13% Cr steel (Ueda and Takabe 2002; Muraki et al. 2002; Nose et al. 2001). The effect of medium chromium-additions was attributed to the formation of chromium enriched corrosion products (e.g., observed on 3% Cr steel). Steels alloyed with 3% Cr or more were found to show improved corrosion performance over Cr-free steel by a factor of two or more (Nose et al. 2001). The corrosion becomes complicated when H₂S is added into the CO₂ corrosion system. The current research should focus on the formation mechanism of the corrosion product film, properties of corrosion product of different structures, and protection to the matrix. The corrosion experiment that has been carried out with 3% Cr tubular steel in pure CO₂ and CO₂/H₂S environments. The results would be to supplement the CO₂/H₂S corrosion theory of 3% Cr steel and provide theoretical basis for the proper selection of the tubing and casing in oil and gas fields.

Experimental

3% Cr tubing steel with the following composition %wt: 0.19C -0.47Mn -0.32Si -2.95Cr -0.39Mo -0.17Ni -<0.01P -0.01S -Fe balance was used. The solution used in this study is simulated oilfield water. The pH value is 6.8, and the ion concentrations are shown in Table 1.

Test Conditions: temperature of 90°C, rotating speeds of 300 rev/min, CO₂ partial pressure of 0.4MPa, H₂S partial pressures of

0.04MPa/0.004MPa/0.002MPa/0.001MPa. The test duration was 72 hours (3 days). Immersion tests were carried out by using the autoclave with a stirrer, as shown in Fig. 1.

Coupon specimens that were 10 mm in width, 50 mm in length, and 3 mm in thickness were used. The specimens were polished with silicon carbide No. 320 and No. 600 papers, rinsed with distilled water, degreased in acetone, and then weighed after drying. The specimens were mounted on a specimen holder, which was made of poly(tetrafluoroethylene). The holder was placed in the autoclave. Then, the simulated solution was poured into the vessel and the autoclave was closed. Initially, the temperature was raised to 45°C to remove some of the dissolved oxygen from the solution, and then deaeration was carried out by N₂ gas bubbling for approximately 2 hours. After purging with N₂, the temperature and pressure were raised to 90°C and 0.4 MPa, respectively. The solution was saturated with CO₂/H₂S mixture gas and kept for approximately one-half hour to stabilize the pressure, and then the rotary stirrer was started; the flow velocity at the specimen surface was approximately 2.0 m/s. The testing period was 3 days (72 hours).

The specimens were divided into two groups after the tests. The specimens in Group 1 were used to calculate the average corrosion rate. First, the specimen surfaces were washed with distilled water and the corrosion products were removed by pickling in 10% hydrochloric acid solution containing an inhibitor. Then, the specimens were dried and photographed to record the corrosion status. Finally, the residual masses of the specimens were determined using an electronic balance (accuracy 0.1 mg) and the average corrosion rate was calculated by the weight-loss method. The specimens in Group 2 were immersed in distilled water for 3 to 5 minutes to dissolve the halide crystals on the surface, soaked in acetone for 20 to 30 seconds, and dried before XRD, SEM, and energy dispersive spectroscopy (EDS) testing.

Results and Discussion

Corrosion Rate and Coupons Surface After Descale. Photographs of the descaled coupons are shown in Fig. 2. Average corrosion rate is shown in Fig. 3. It is evident that the surface conditions in the CO₂/H₂S environment are better than those in a CO₂-only environment. Pitting does not appear on 3% Cr coupons. In the CO₂/H₂S environment, when the partial-pressure ratio is 10 (with 0.04-MPa H₂S), the coupon surface exhibits good condition, even showing with some luster, and the corrosion rate is the lowest. When the partial-pressure ratio reached 100 to 400, the surface became relatively rougher and the corrosion rates are higher than that of the former. The corrosion-rate peak appeared at a partial-pressure ratio of 100. The peak is still lower than that with the CO₂-only corrosion. The test result revealed that a trace of H₂S could alleviate 3% Cr steel's CO₂ corrosion.

Fig. 3 shows the corrosion rate of 3% Cr coupons in different conditions. When the partial-pressure ratio is 100, the corrosion rate reached the maximum and the corrosion (general corrosion) is more serious, as seen in the corresponding photos in Fig. 2. Other research (Yin et al. 2008; Zhenquan et al. 2003; Xianghong et al.

TABLE 1—OILFIELD-WATER ION CONCENTRATION (mg/L)							
Ion	K ⁺ Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻
Concentration/(mg·L ⁻¹)	8350	3885	57	19 634	850	337	0

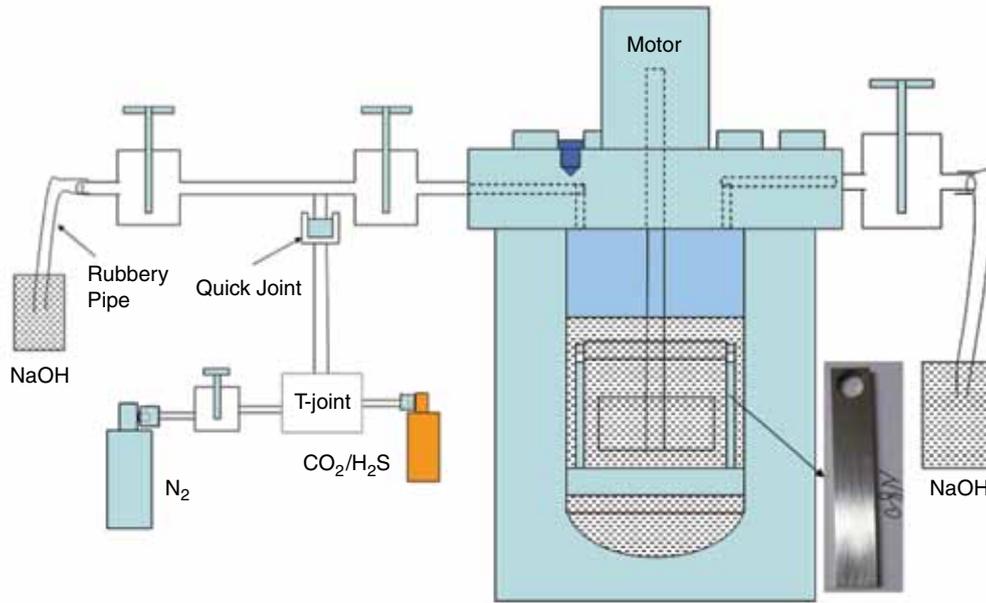


Fig. 1—Test-autoclave structure diagram.

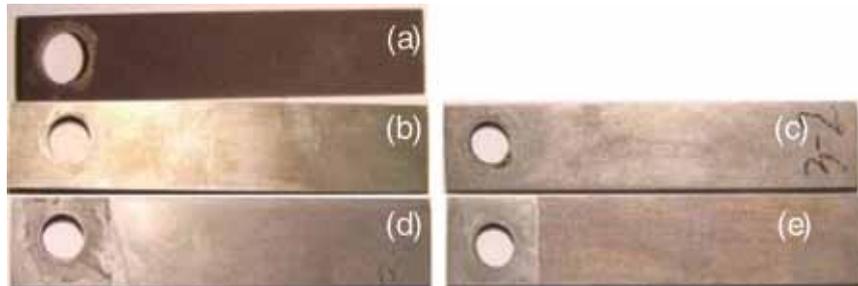


Fig. 2—Specimen photos after descaling.

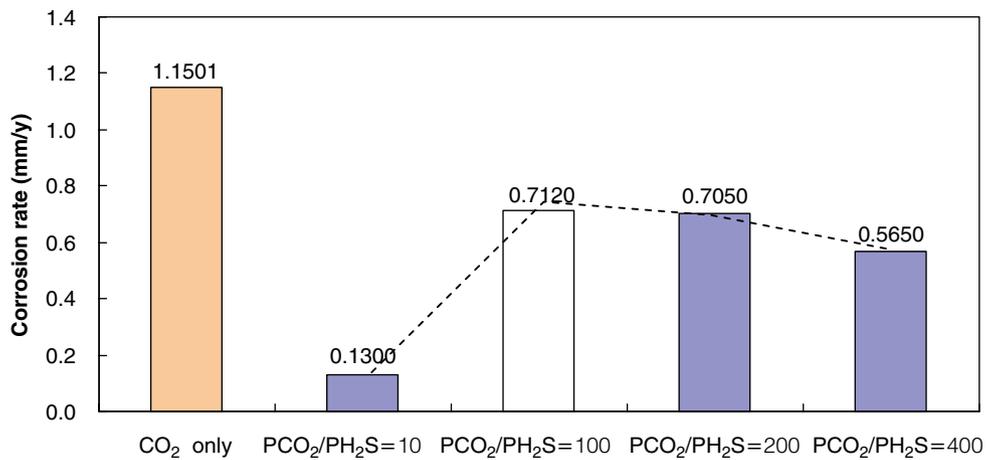


Fig. 3—Average-corrosion-rate contrast.



Fig. 4—CO₂/H₂S corrosion film falls off at the beginning of cleaning. Note: From left to right, the coupon materials are carbon steel N80, 3% Cr, 9% Cr, and 13% Cr).

2009) also documents that as the partial-pressure ratio changes, the corrosion rate will reach its maximum in the CO₂/H₂S environment, but those authors do not compare the corrosion rate with the CO₂-only condition and do not know whether a trace of H₂S will restrain the CO₂ corrosion or not. This study shows that a trace of H₂S will reduce the corrosion rate, and that the coupon surface

condition is correspondingly better. The corrosion rate matched the corrosion performance on the surface described previously in the CO₂/H₂S environment.

Differences also exist in the process of cleaning the corrosion product. In the CO₂-only environment, the corrosion product closely combined with the base, and the outer and inner films were invisible. The coupon needed to soak in the clean water for more than 15 minutes and to be wiped repeatedly with a cotton ball. However, in the CO₂/H₂S environment, the outer layer and the inner layer were different. The outer corrosion film falls off easily, as shown in Fig. 4. In cleaning the corroded coupon under the partial-pressure ratio of 100, the entire film layer falls the moment it is put in the cleaning fluid. There is a thin layer of transparent gray product film clinging closely to the coupon surface. Thorough cleaning requires cleaning fluid and soaking for 5 minutes. This description demonstrates that the binding force between the corrosion film and the base is weaker in the CO₂/H₂S environment than in the CO₂-only environment. However, there is much reduction in the corrosion rate and improvement in the surface performance in the CO₂/H₂S environment. Therefore, the protection of the corrosion film to the base cannot be judged by their binding force.

Structure Characteristics of Corrosion Products. In order to find the reasons for the reduction in the corrosion rate, contrast tests were performed to analyze the microstructure and chemical composition of the corrosion film in the CO₂-only environment and the CO₂/H₂S environment. Fig. 5 displays the SEM analysis

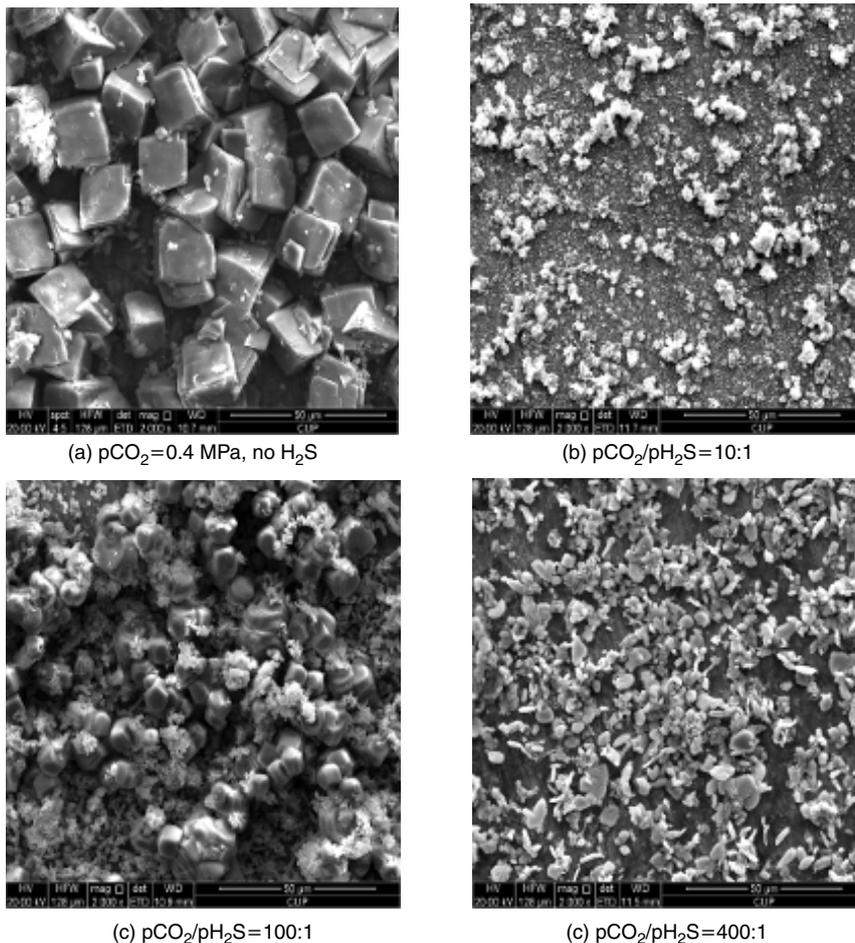


Fig. 5—Coupon-surface features in different conditions (2,000X).

TABLE 2—RESULTS OF EDS (ATOM %) AND XRD ANALYSIS						
Experiment Condition	Fe	C	O	S	Cr	X-Ray Analysis
pCO ₂ =0.4MPa	21.98	24.94	46.49	0	4.2	FeCO ₃ , CaCO ₃ , FeCr ₂ O ₄
pCO ₂ /pH ₂ S=10:1	51.67	0	0	48.33	2.7	FeS, FeCr ₂ O ₄
pCO ₂ /pH ₂ S=100:1	22.52	24.75	57.78	22.5	3.5	FeS, CaCO ₃ , FeCr ₂ O ₄
pCO ₂ /pH ₂ S=400:1	18.06	18.98	25.01	8.89	5.21	FeS, FeCO ₃ , CaCO ₃ , FeCr ₂ O ₄

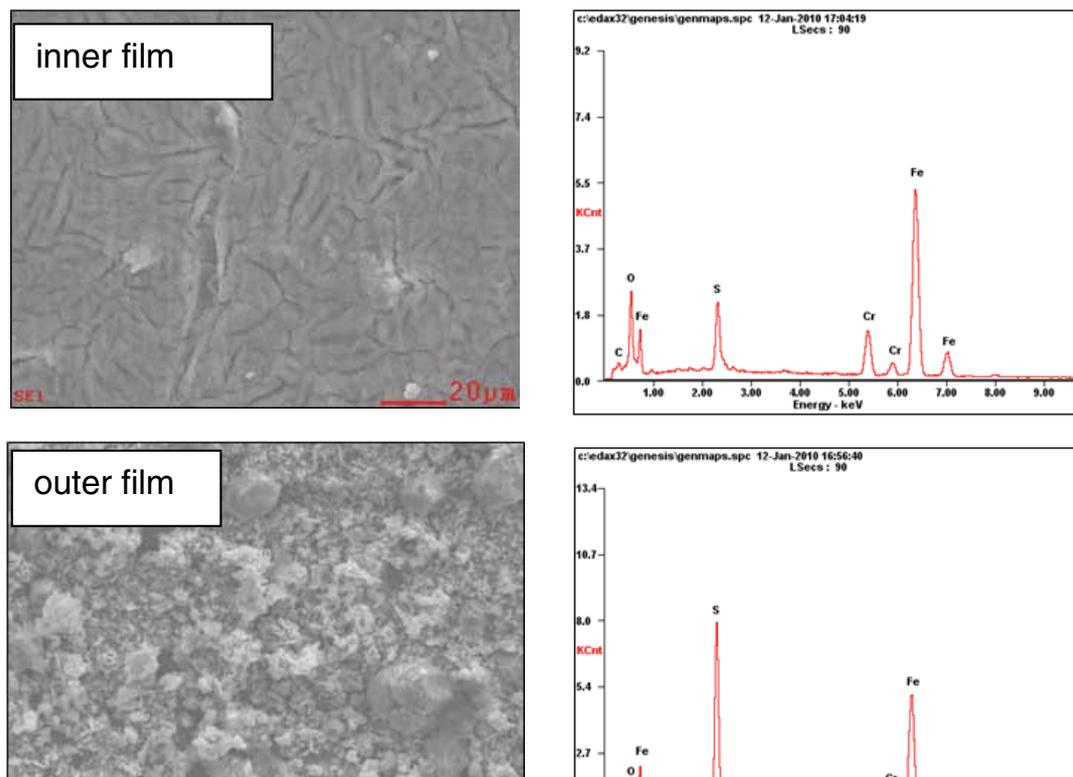


Fig. 6—SEM and EDS images of inner film and outer film in flat.

conducted by the S-3400N SEM of Hitachi Company, and Table 2 presents the EDS and XRD analysis of those samples.

Fig. 5 shows the SEM surface features of the corrosion film at differentiated partial-pressure ratios. It can be observed from Figs. 5a and 3b that under the same magnified condition, the particles on the corrosion film are coarser in the CO₂-only environment than those in CO₂/H₂S environment. The irregularly distributed particles could not efficiently prevent the penetration of ion into the corrosion-product film, which is one of the reasons leading to more-severe corrosion in the CO₂-only environment than in the CO₂/H₂S environment.

In addition, Figs. 5c and 5d display 3% Cr coupon SEM surface features of corrosion film at partial-pressure ratios of 100:1 and 400:1 in the CO₂/H₂S environment. It is obvious that under these two conditions, the particles of the corrosion-product film of the 3% Cr coupon are coarser and looser than those at partial-pressure ratio of 10:1. The phenomenon is more apparent at partial pressure ratio of 100/1.

The EDS and XRD analysis at different partial-pressure ratios given in Table 2 shows the percent-of-atoms values at a partial-pressure ratio of 200 to be identical to those at a partial pressure ratio of 100. Thus, they are not listed in Table 2.

Test results showed that the 3% Cr steel in the CO₂-only condition had less corrosion resistance than in the CO₂/H₂S environment. Main compounds in those corrosion products were FeCO₃,

CaCO₃, and FeCr₂O₄ in the CO₂-only condition, and FeCO₃, CaCO₃, FeCr₂O₄, and FeS in the CO₂/H₂S environment.

Srinivasan and Tebbal (1998) believed that at partial-pressure ratios of 400 (>200) and at 90°C, the FeS film called mackinawite would retard the corrosion. As the concentration and temperature of H₂S increase, mackinawite FeS transforms into more-stable pyrrhotite FeS. Smith and Miller (1975) and Morse et al. (1987) held that the corrosion product is H₂S-based with the presence of trace amounts of H₂S, and that the FeS film is more stable than the FeCO₃ film, which provided better protection to the base. Therefore, in the CO₂/H₂S environment, the corrosion rate is lower and surface performance is better than in the CO₂-only environment.

Fig. 6 shows the inner layer of steel corrosion film at a partial-pressure ratio of 100. The ratio of Fe/S in the outer porous layer is 1:0.9, and the ratio in the inner layer is 1:0.26. EDS penetrating the very thin inner layer may be the reason for the larger proportion of Fe atoms in the inner film from the test results. The inner layer actually is FeS. The corrosion-rate reduction is not only protected by the outer FeS film observed in the aforementioned experiment, but also by the very thin and dense inner layer that exists between the outer FeS layer and the matrix. This theory is also put forward in Sun (2006), and Nešić et al. (2008) agree.

Analysis of Partial-Pressure Ratio About H₂S Corrosion Regime. The partial-pressure ratio of CO₂/H₂S determines the

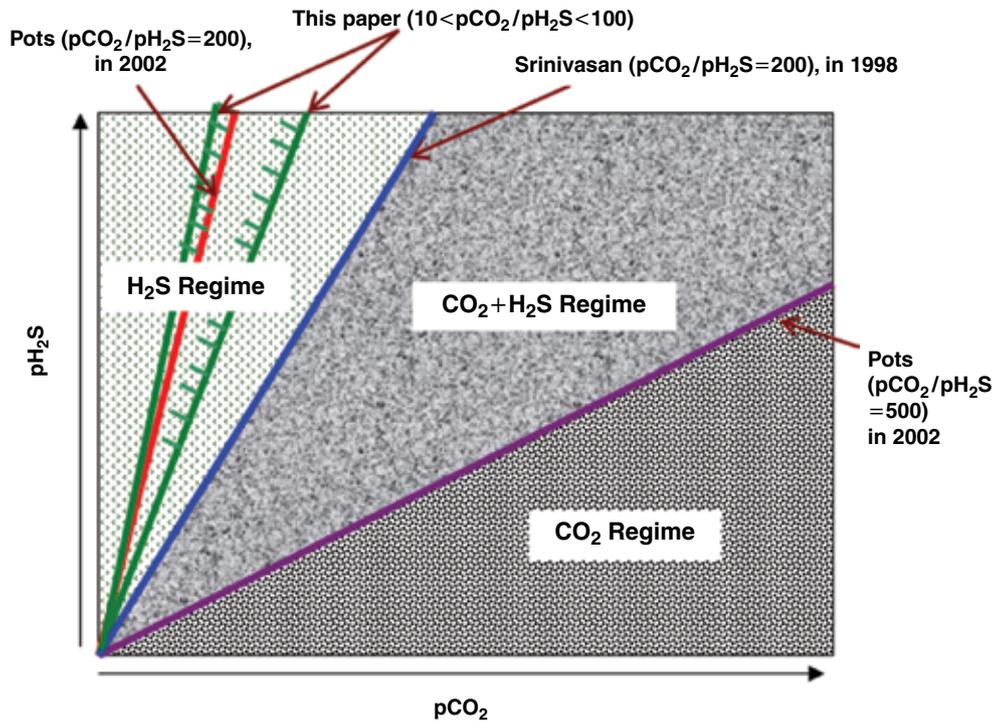


Fig. 7—Corrosion regimes in the CO₂/H₂S environment.

corrosion state in the CO₂/H₂S environment. Early research by Srinivasan and Tebbal (1998) gave a detailed description of the impact of temperature, and they propose that if the ratio of pCO₂/pH₂S is smaller than 200, H₂S dominated the corrosion environment. Pots et al. (2002) divided it into three control areas: with pCO₂/pH₂S < 20, H₂S dominated the corrosion process and the main corrosion product is FeS; with 20 < pCO₂/pH₂S < 500, CO₂ and H₂S alternately dominated the corrosion process and the corrosion product contained FeS and FeCO₃; and with pCO₂/pH₂S > 500, CO₂ dominated the corrosion process and the main corrosion product is FeCO₃. This corrosion-control mechanism in the CO₂/H₂S environment has been supported by Agarwal et al. (2004), as shown in Fig. 7. This study shows that at a partial-pressure ratio of 10, the product is almost FeS, while at partial-pressure ratio of 100, FeCO₃ and CaCO₃ particles existed in the corrosion product instead of just FeS. According to Pots et al. (2002), CO₂ and H₂S alternated in dominating the corrosion under the condition of partial-pressure ratio of 100. This paper considers that the partial-pressure ratio that matches the maximum value of corrosion rate should be in the CO₂-and-H₂S-alternately-dominated control area. Therefore, the partial-pressure ratio in an H₂S-dominated system should be between 10 and 100, instead of pCO₂/pH₂S < 200 as Srinivasan and Tebbal (1998) suggested. This conclusion indirectly supports Pots et al. (2002).

Conclusions

In a CO₂-only environment, 3% Cr steel exhibited a higher corrosion rate. The corrosion rate was reduced, and the surface condition remained good, when a trace of H₂S was added.

At 90°C, when the partial-pressure ratio of CO₂/H₂S is 100, the 3% Cr corrosion rate reached a maximum value.

The SEM analysis of the surface films showed that the particles of corrosion product were coarse and arranged loosely in the CO₂-only environment, while in the CO₂/H₂S environment, the crystals on the surface were fine and arranged densely.

The protective ability of the thinner and denser solid FeS is better than that of the porous outer layer. With the protection of the FeS inner layer and FeS outer film, the corrosion is greatly restricted.

In the CO₂/H₂S corrosion environment, the partial-pressure ratio in the H₂S-dominated system should be between 10 and 100, and not < 200.

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