Effect of Impurities on the Corrosion Behavior of CO_2 Transmission Pipeline Steel in Supercritical CO_2 —Water Environments

YOON-SEOK CHOI,* SRDJAN NESIC, AND DAVID YOUNG

Institute for Corrosion and Multiphase Technology, Department of Chemical & Biomolecular Engineering, Ohio University, Athens, Ohio 45701, United States

Received August 3, 2010. Revised manuscript received September 29, 2010. Accepted October 22, 2010.

The corrosion property of carbon steel was evaluated using an autoclave under CO2-saturated water phase and watersaturated CO₂ phase with impurities (O₂ and SO₂) at 80 bar CO₂ and 50 °C to simulate the condition of CO2 transmission pipeline in the carbon capture and storage (CCS) applications. The results showed that the corrosion rate of carbon steel in CO2-saturated water was very high and it increased with adding O_2 in the system due to the inhibition effect of O_2 on the formation of protective FeCO3. It is noteworthy that corrosion took place in the water-saturated CO2 phase under supercritical condition when no free water is present. The addition of O_2 increased the corrosion rates of carbon steel in water-saturated CO_2 phase. The addition of 0.8 bar SO_2 (1%) in the gas phase dramatically increased the corrosion rate of carbon steel from 0.38 to 5.6 mm/y. This then increased to more than 7 mm/y with addition of both O2 and SO2. SO2 can promote the formation of iron sulfite hydrate (FeSO3 • 3H2O) on the steel surface which is less protective than iron carbonate (FeCO₃), and it is further oxidized to become FeSO4 and FeOOH when O2 is present with SO₂ in the CO₂-rich phase. The corrosion rates of 13Cr steel were very low compared with carbon steel in CO2saturated water environments with O2, whereas it was as high as carbon steel in a water-saturated CO2 phase with O2 and SO₂.

1. Introduction

A complete carbon capture and storage (CCS) cycle requires safe, reliable, and cost efficient solutions for transmission of the carbon dioxide (CO₂) from the capturing facility to the location of permanent storage (1). For transmission of largequantities of CO₂ over moderate distances, carbon steel pipelines are considered the most cost-efficient solution. The mechanical properties and low cost are important considerations when long distances are planned. However, carbon steels are susceptible to corrosion in flue gas environments due to carbon dioxide (CO₂), water (H₂O), oxygen (O₂), sulfur dioxide (SO₂) and other constituents that can cause the formation of corrosive products (2).

Rigorously dry CO_2 does not corrode carbon steels; however, corrosion rates are much higher if free water is present because of its reaction with CO_2 to form carbonic acid (H_2CO_3). Thus, sufficient drying (water removal) upstream of the pipeline is required to prevent breaking-out of free water and excessive corrosion rates (3, 4). The maximum allowed moisture content in the pipeline is related to water solubility in CO₂. The requirement for CO₂ pipelines, used for enhanced oil recovery (EOR) in the United States, is a maximum of 600 ppm (mole) water (Kinder Morgan) (5). Thermodynamic modeling for solubility of water in CO₂ indicates a higher critical limit for free water precipitation of approximately 2000 ppm (mole) in temperature and pressure ranges of 15–85 °C and 73–300 bar, respectively (6, 7).

In corrosion, water has the ability to act as an electrolyte, solvent and even reactant for dissolved gases such as CO_2 , O_2 , and SO_2 . O_2 is important in corrosion mechanisms because it provides several of the cathodic reaction paths for corrosion to proceed as well as inhibiting a formation mechanism for protective iron carbonate (FeCO₃) (8, 9). SO_2 has high solubility in water/moisture, this results in the formation of sulfurous acid (H₂SO₃). Similar to CO_2 , SO_2 will not cause corrosion in the absence of moisture. It has been suggested that corrosion rates are acceptable as long as the moisture content is 50 ppm (mole) with SO_2 (10, 11).

Although the impact of CO_2 corrosion on carbon steel has been studied extensively at pressures relevant for oil and gas transport (up to 20 bar CO_2), little information is available under high CO_2 partial pressure and experimental data are sparse at higher pressures. In addition, the presence of impurities such as O_2 and SO_2 in CO_2 transmission pipelines may increase the corrosion risk and should not be neglected. Thus, in the present study, the corrosion property of carbon steel was evaluated using an autoclave under CO_2 -saturated water phase and water-saturated CO_2 phase with impurities $(O_2 \text{ and } SO_2)$ to simulate the condition of CO_2 transmission pipelines in carbon capture and storage (CCS) applications.

2. Experimental Section

The test specimens were machined from carbon steel (API 5 LX65) with a size of $25 \times 15 \times 4$ mm. In addition, 13Cr steel (UNS S41000) was selected as a mitigation strategy for inhibiting the corrosive effect of high pressure CO₂ with impurities. See Table S1, Supporting Information (SI) for the chemical compositions of carbon steel and 13Cr steel.

The corrosion rates were determined from weight-loss method (see SI for the detailed procedures). The morphology and compositions of corrosion products were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy.

2.1. Corrosion Tests under CO_2 -Saturated Water Phase. SI Table S2 shows the test matrix for corrosion tests in a CO_2 -saturated water phase. 400 mL of DI water was addedto the autoclave and CO_2 gas was bubbled for 3 h to remove oxygen before starting the test. Corrosion tests were conducted under 80 bar CO_2 at 50 °C with O_2 partial pressures of 0 and 3.3 bar (4%). The specimens were inserted in the CO_2 -saturated water phase.

2.2. Corrosion Tests under Water-Saturated CO₂ Phase. SI Table S3 shows the test matrix for corrosion tests in a water-saturated CO₂ phase. Specimens were inserted in the water-saturated CO₂ phase. From the water solubility in CO₂ simulated in the previous study (7), it was calculated that about 0.35 g of water will dissolve in 1 L of CO₂ under the test conditions. Thus, 10 g of DI water was added to the autoclave in the water-saturated CO₂ tests to ensure saturation.

VOL. 44, NO. 23, 2010 / ENVIRONMENTAL SCIENCE & TECHNOLOGY = 9233

^{*} Corresponding author phone: 1-740-593-9944; fax: 1-740-593-9949; e-mail: choiy@ohio.edu.



FIGURE 1. Effects of oxygen and exposure time on the corrosion rates of carbon steel in water-rich phase.

3. Results and Discussion

3.1. Corrosion Tests under CO_2 -Saturated Water Phase. Figure 1 shows the corrosion rates of carbon steel in the CO_2 -saturated water phase with and without O_2 as a function of the test period at 50 °C. The corrosion rates of carbon steel in CO_2 -saturated water were very high and the addition of O_2 ($PO_2 = 3.3$ bar) in the system did not significantly increase the corrosion rates of carbon steel at the initial stage. However, after 120 h, the corrosion rate decreased from 19.2 mm/y to 10.6 mm/y in the absence of O_2 , whereas it reduced from 19.3 mm/y to 14.1 mm/y in the presence of O_2 . SI Figure S2 represents the surface morphologies of the corroded samples at 50 °C in the water-rich phase with and without O_2 after 24 h. It can be seen that the morphologies were almost identical and the surface was locally covered by the corrosion products (Fe₃C).

Figure 2 shows the SEM images and EDS spectra of the corroded surface of the samples after 120 h in the water-rich phase with and without O_2 . In the absence of O_2 (Figure 2 (a)), the surface was covered by dense, crystalline FeCO₃. This indicates that the decrease of corrosion rates with time



FIGURE 3. Corrosion rates of carbon steel and 13Cr steel in CO_2 -saturated water with and without oxygen for 24 h.







FIGURE 2. SEM image and EDS spectra of the corroded surface of samples exposed in CO_2 -saturated water for 120 h: (a) without oxygen, (b) with oxygen.

9234 ENVIRONMENTAL SCIENCE & TECHNOLOGY / VOL. 44, NO. 23, 2010









(c)

(d)

FIGURE 5. SEM image and EDS spectra of the sample exposed in water-saturated CO₂ for 24 h with different O₂ contents: (a) 80 bar CO₂, 50 °C, (b) 80 bar CO₂, 1.6 bar O₂, 50 °C, (c) 80 bar CO₂, 3.3 bar O₂, 50 °C, (d) 80 bar CO₂, 5.1 bar O₂, 50 °C.

mainly resulted from the formation of FeCO₃ on the surface (12, 13). However, when O₂ was added in the system, severe uniform corrosion attack and some scattered bright compounds were found on the surface (Figure 2 (b)). From EDS analysis, iron and oxygen were its major constituents. Carbon was, however, also found, but it is believed that this is because traces of FeCO₃ are present on the metal surface. This indicates that the addition of O₂ can inhibit the formation of FeCO₃ and form nonprotective iron oxide (8, 9).

Figure 3 compares the corrosion rates of carbon steel and 13Cr steel in a CO₂-saturated water phase with and without O₂ after 24 h. The corrosion rate of 13Cr steel was very low (~ 0.01 mm/y) compared with carbon steel; this was in good agreement with the literature data (14). SI Figure S3 demonstrates the SEM image of the surface of 13Cr steel after 24 h in the water-rich phase with O₂. Polishing marks on the surface are clearly observed, indicating no sign of corrosion attack in 13Cr steel due to the formation of passive film. This indicates that 13Cr steel is a possible candidate material for CO_2 transportation with free water and O_2 , especially for shorter pipelines.

3.2. Corrosion Tests under Water-Saturated CO₂ Phase. To investigate the effect of O₂ content on the corrosion of carbon steel in supercritical CO₂ environments, corrosion tests were conducted under different O₂ partial pressures ($P_{O_2} = 1.6$ bar (2%), 3.3 bar (4%), and 5.1 bar (6%)) at 80 bar CO₂ and 50 °C. Figure 4 shows the corrosion rates of carbon steel in water-saturated CO₂ phase with different O₂ contents after 24 h. It is apparent that the addition of O₂ increases the corrosion rate of carbon steel under supercritical CO₂ environments. However, the corrosion rates do not increase with increasing O₂ content; instead the corrosion rate reaches a maximum of 1 mm/y with 4% of O₂.

Figure 5 shows the SEM images and EDS spectra of the sample surface after 24 h in the CO_2 -rich phase with different O_2 contents. It is interesting to note that the sample surfaces





FIGURE 6. Effects of oxygen and sulfur dioxide on the corrosion rates of carbon steel in water-saturated CO_2 phase for 24 h.

were covered by corrosion products after 24 h in the watersaturated CO₂ phase. This indicates that corrosion can take place in the water-saturated CO₂ phase under supercritical conditions when no free water is present. However, the corrosion rate was low (~ 0.3 mm/y) due to the formation of FeCO₃ on the steel surface. According to recent studies (15, 16), it is possible that CO₂ dissociates and reacts with other CO₂ or H₂O molecules to produce corrosion products such as iron carbonate (FeCO₃), carbonate (CO₃^{2–}) or H₂CO₃.

When O_2 was added in the system, surfaces were covered by a porous scale that lacked any definable crystalline morphology; this mainly consisted of iron and oxygen (Figure 5 (b)-(d)). This indicates that, as discussed above, the addition of O_2 can increase the corrosion rates of carbon steel by inhibiting the formation of protective FeCO₃ and forming less protective iron oxides. The surface coverage due to these phases increases with increasing O_2 content in the gas phase.

SI Figure S4 shows the surface morphologies of samples in the water-saturated CO_2 phase under different O_2 partial pressures (0 and 5.1 bar) after cleaning with Clarke solution. As shown in SI Figure S4 (a), uniform corrosion attack was





(b)



FIGURE 7. SEM image and EDS spectra of the sample exposed in water-saturated CO₂ for 24 h: (a) 80 bar CO₂, 0.8 bar SO₂, 50 °C, (b) 80 bar CO₂, 3.3 bar O₂, 0.8 bar SO₂, 50 °C.

9236 ENVIRONMENTAL SCIENCE & TECHNOLOGY / VOL. 44, NO. 23, 2010

(a)



FIGURE 9. Corrosion rates of carbon steel and 13Cr steel in water-saturated CO₂ for 24 h with 4% oxygen and 1% sulfur dioxide (80 bar CO₂, 3.3 bar O₂, 0.8 bar SO₂, 50 °C).

observed on the surface when no O_2 was added in the system. Similar uniform attack was also seen for cases with 1.6 and 3.3 bar O_2 partial pressures. However, localized attack (shallow pits) was observed on the cleaned surface in the case with 5.1 bar O_2 partial pressure (SI Figure S4 (b)). This implies that the addition of O_2 can change the corrosion mechanism from uniform to localized corrosion as well as inhibiting the formation of FeCO₃.

To investigate the effect of SO₂ on the corrosion of carbon steel in supercritical CO₂ environments, corrosion tests were conducted under 80 bar CO₂/0.8 bar SO₂ and 80 bar CO₂/3.3 bar O₂/0.8 bar SO₂ at 50 °C. Figure 6 represents the effect of O₂ and SO₂ additions on the corrosion rates of carbon steel under supercritical CO₂ environments. The addition of 0.8 bar of SO₂ (1%) in the gas phase dramatically increases the corrosion rates of carbon steel from 0.38 to 5.6 mm/y and it increases further to 7 mm/y upon addition of both O₂ and SO₂. However, no corrosion was observed on carbon steel in dry condition (80 bar CO₂/3.3 bar O₂/0.8 bar SO₂ at 50 °C) for 24 h. Figure 7 displays the SEM images and EDS spectra of the sample surface after 24 h for 80 bar $CO_2/0.8$ bar SO_2 and 80 bar $CO_2/3.3$ bar $O_2/0.8$ bar SO_2 conditions. As shown in Figure 7 (a), the surface was covered by crystalline corrosion products which consisted of iron, sulfur and oxygen. However, the surface was locally covered by the corrosion products when the sample was exposed to the CO_2 -rich phase with O_2 and SO_2 (Figure 7 (b)).

To identify the corrosion products on the steel surface, Raman spectroscopy was employed to obtain vibrational information that is specific to the chemical bonds in molecules/polyatomic ions and lattice vibrations of crystalline solids. Figure 8 (a) shows Raman spectra of the corrosion product on the steel surface after 24 h in the CO_2 -rich phase with SO_2 . The strongest Raman peak observed at 962 cm⁻¹ originates from the symmetric stretching vibrations of the SO_3^{2-} ion (*17*, *18*) and thus can be used as a fingerprint for identifying corrosion products of γ -FeSO₃•3H₂O with other peaks at 214, 271, 476, 892, and 3446 cm⁻¹ (*17*). This allowed ready identification of the corrosion products shown in Figure 7 (a) as γ -FeSO₃•3H₂O.

The formation of FeSO₃·3H₂O has been observed as a corrosion product of Fe at low relative humidity and high concentration of SO₂ in atmospheric corrosion conditions (20). Thus, the role of SO₂ on the corrosion under watersaturated supercritical CO₂ phase would be similar to that in atmospheric corrosion since it happens under thin water layer on the steel surface. The formation of FeSO₃ by adding SO₂ in the gas phase can be described as follows (22):

$$SO_2 + H_2O \rightarrow SO_3^{2-} + 2H^+$$
 (1)

$$Fe^{2+} + SO_3^{2-} \rightarrow FeSO_3$$
 (2)

Figure 8 (b) presents Raman spectra of the corrosion products on the steel surface after 24 h in the CO₂-rich phase with O₂ and SO₂. It showed a different spectrum from Figure 8 (a) and the strongest Raman peak was observed at 390 cm⁻¹ with other peaks at 300, 553, 683, and 1009 cm⁻¹. In addition, no peak was observed around the water band (~3500 cm⁻¹). The peaks at 390 cm⁻¹ and 1009 cm⁻¹ correspond to α -FeOOH and FeSO₄, respectively (23, 24). When O₂ is present in the environment with SO₂, SO₃²⁻ ions are further oxidized to SO₄²⁻, and SO₄²⁻ ions react with Fe²⁺ ions to form FeSO₄ as follows (22):



(a)

(b)

FIGURE 10. SEM image and EDS spectra of the inner (a) and outer (b) layer of 13Cr steel exposed in water-saturated CO_2 for 24 h with 4% oxygen and 1% sulfur dioxide (80 bar CO_2 , 3.3 bar O_2 , 0.8 bar SO_2 , 50 °C).



$$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-}$$
 (3)

$$Fe^{2^+} + SO_4^{2^-} \rightarrow FeSO_4$$
 (4)

FeSO₄ has been reported to undergo further oxidation to become FeOOH under O_2 environments (22, 24):

$$4\text{FeSO}_4 + 6\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{FeOOH} + 4\text{H}_2\text{SO}_4 \tag{5}$$

We hypothesize that the sulfuric acid produced by the acid regeneration cycle continues to react with the fresh steel, resulting in the high corrosion rates observed during tests.

SI Figure S5 shows the cross section of samples after 24 h for 80 bar $CO_2/0.8$ bar SO_2 and 80 bar $CO_2/3.3$ bar $O_2/0.8$ bar SO_2 conditions. The thickness of the corrosion product is approximately $50-60 \,\mu$ m for CO_2/SO_2 case and $80-125 \,\mu$ m for $CO_2/O_2/SO_2$ condition. SI Figure S6 demonstrates the surface morphologies of samples after cleaning with the Clarke solution for 80 bar $CO_2/0.8$ bar SO_2 and 80 bar $CO_2/3.3$ bar $O_2/0.8$ bar SO_2 conditions. For both cases, a severe uniform corrosion attack was observed.

Figure 9 shows the corrosion rates of carbon steel and 13Cr steel in water-saturated CO_2 phase with O_2 and SO_2 . When only O_2 was present as an impurity with CO_2 and water, the corrosion rate of 13Cr steel was very low as shown in Figure 3. However, the corrosion rate of 13Cr steel was almost the same as carbon steel with O_2 and SO_2 in the CO_2 -rich phase. This indicates that the corrosion resistance of 13Cr steel is similar to carbon steel in the presence of SO_2 , and applications are limited to milder environments (CO_2/O_2 environments).

SEM observation for the surface of 13Cr steel revealed that it consisted of two layers (inner/outer) with different morphologies and compositions. Figure 10 demonstrates the SEM images and EDS spectra of the inner and outer layers formed on the sample surface after 24 h of exposure to the CO_2 -rich phase with O_2 and SO₂. The inner layer consisted of iron, chromium, oxygen and sulfur whereas in the outer layer it contained iron, carbon, oxygen and sulfur. This is consistent with severe corrosion attack in 13Cr steel due to the formation of the sulfuric acid. This indicates that applications of 13Cr steel are limited to milder environments ($CO_2/$ O_2 environments). More work will be done in order to address CO_2 pipeline requirements considering effects of H₂O and SO₂ concentrations in the CO₂ phase as well as materials selection.

Acknowledgments

We acknowledge the financial support from Ohio Coal Development Office (OCDO) for the Institute for Corrosion and Multiphase Technology at Ohio University.

Supporting Information Available

Detailed description of the corrosion test setup and of the weight loss corrosion test procedures; Chemical compositions of materials and test matrices; and SEM images for sample surface and cross-section are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

- Eldevik, F.; Graver, B.; Torbergsen, L. E.; Saugerud, O. T. Development of a guideline for safe, reliable and cost efficient transmission of CO₂ in pipelines. *Energy Procedia* 2009, 1 (1), 1579.
- Sass, B. M.; Farzan, H.; Prabhakar, R.; Gerst, J.; Sminchak, J.; Bhargava, M.; Nestleroth, B.; Figueroa, J. Considerations for treating impurities in oxy-combustion flue gas prior to sequestration. *Energy Procedia* 2009, 1, 1, 535, DOI: 10.1016/j.egypro.2009.01.071.
 Seiersten, M.; Kongshaug, K. O. Materials selection for capture, Control of the prior of the prio
- (3) Seiersten, M.; Kongshaug, K. O. Materials selection for capture, compression, transport and injection of CO₂. In *Carbon Dioxide Capture for Storage in Deep Geologic Formations*; Thomas, D. C., Benson, S. M., Eds.; Elsevier Ltd.: Oxford, UK, 2005; Vol. 2.

- (4) Heggum, G.; Weydahl, T.; Molnvik, M.; Austegaard, A. CO₂ conditioning and transportation. In *Carbon Dioxide Capture for Storage in Deep Geologic Formations*; Vol. 2; Thomas, D. C., Benson, S. M., Eds.; Elsevier Ltd.: Oxford, UK, 2005; Vol. 2.
- (5) Connell, D. P. Carbon Dioxide Capture Options for Large Point Sources in the Midwestern United States: An Assessment of Candidate Technologies, Final Report; CONSOL Energy Inc.: South Park, PA, 2005.
- (6) Spycher, N.; Pruess, K.; King, J. E. CO₂-H₂O mixtures in the geological sequestration of CO₂. I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar. *Geochim. Cosmochim. Acta* 2003, 67, 16, 3015, DOI: 10.1016/ S0016-7037(03)00273-4.
- (7) Choi, Y. S.; Nesic, S. Corrosion behavior of carbon steel in supercritical CO₂-water environments. CORROSION/2009, paper no. 09256;NACE International: Houston, TX, 2009.
- (8) Makarenko, V. D.; Shatilo, S. P.; Gumerskii, Kh. Kh.; Belyaev, V. A. Effect of oxygen and hydrogen sulfide on carbon dioxide corrosion of welded structures of oil and gas installations. *Chem. Pet. Eng.* 2000, 36, 2, 125, DOI: 10.1007/BF02464746.
- (9) Skaperdas, G. T.; Uhlig, H. H. Corrosion of steel by dissolved carbon dioxide and oxygen. *Ind. Eng. Chem.* 1942, 34 (6), 748, DOI 10.1021/ie50390a024.
- (10) Compressed Gas Association, Handbook of Compressed Gases; Reinhold Publishing Corporation: New York, NY, 1966.
- (11) Sass, B.; Monzyk, B.; Ricci, S.; Gupta, A.; Hindin, B.; Gupta, N. Impact of SO_x and NO_x in flue gas on CO₂ separation, compression, and pipeline transmission. In *Carbon Dioxide Capture for Storage in Deep Geologic Formations*; Thomas, D. C., Benson, S. M., Eds.; Elsevier Ltd.: Oxford, UK, 2005; Vol. 2.
- (12) Cui, Z. D.; Wu, S. L.; Zhu, S. L.; Yang, X. J. Study on corrosion properties of pipelines in simulated produced water saturated with supercritical CO₂. *Appl. Surf. Sci.* 2006, 252, 6, 2368, DOI: 10.1016/j.apsusc.2005.04.008.
- (13) Nesic, S. Key issues related to modelling of internal corrosion of oil and gas pipelines—A review. Corros. Sci. 2007, 49, 12, 4308, DOI: 10.1016/j.corsci.2007.06.006.
- (14) Pfennig, A.; Bäβler, R. Effect of CO₂ on the stability of steels with 1% and 13% Cr in saline water. *Corros. Sci.* 2009, 51, 4, 931, DOI: 10.1016/j.corsci.2009.01.025.
- (15) McGrail, B. P.; Schaef, H. T.; Glezakou, V.-A.; Dang, L. X.; Owen, A. T. Water reactivity in the liquid and supercritical CO₂ phase: Has half the story been neglected? Energy Procedia 2009, 1, 1, 3415, DOI: 10.1016/j.egypro.2009.02.131.
- (16) Glezakou, V.-A.; Dang, L. X.; McGrail, B. P. Spontaneous activation of CO₂ and possible corrosion pathways on the lowindex iron surface Fe(100). J. Phys. Chem. C 2009, 113, 9, 3691, DOI: 10.1021/jp808296c.
- (17) Perera, W. N.; Senanayake, G.; Nicol, M. J. Interaction of gold(I) with thiosulfate-sulfite mixed ligand systems. *Inorg. Chim. Acta* 2005, 358 (7), 2183, DOI 10.1016/j.ica.2004.09.058.
- (18) Verma, V. P. Review of thermoanalytical, IR, Raman and X-ray studies of solid sulphites. *Thermochim. Acta* 1985, 89, 7, 363, DOI: 10 1016/004-6031(85)85509-X.
- (19) Lutz, H. D.; Eckers, W.; Engelen, B. Sulfites and sulfite hydrates of iron and nickel-X-ray, thermoanalytical, IR, and Raman data. Z. Anorg. Allg. Chem. 1981, 475 (4), 165.
- (20) Johansson, L.-G.; Lindqvist, O. The crystal structure of iron(II) sulfite trihydrate, α-FeSO₃•3H₂O. Acta Crystallogr. 1979, B35, 5, 1017, DOI: 10.1107/S0567740879005471.
- (21) Marco, J. F.; Davalos, J.; Gancendo, J. R.; Gracia, M. Mössbauer study of the corrosion behavior of pure iron and weathering steel under a wet-dry cycle. *Hyperfine Interact.* 1989, 46, 1-4, 453, DOI: 10.1007/BF02398230.
- (22) Nishimura, R.; Shiraishi, D.; Maeda, Y. Hydrogen permeation and corrosion behavior of high strength steel MCM 430 in cyclic wet-dry SO₂ environment. *Corros. Sci.* 2004, 46, 1, 225, DOI: 10.1016/S0010-938X(03)00141-0.
- (23) Thibeau, R. J.; Brown, C. W.; Heidersbach, R. H. Raman spectra of possible corrosion products of iron. *Appl. Spectrosc.* 1978, *32*, 6, 532, DOI: 10.1366/000370278774330739.
- (24) Chio, C. H.; Sharma, S. K.; Muenow, D. W. The hydrates and deuterates of ferrous sulfate (FeSO₄): a Raman spectroscopic study. J. Raman Spectrosc. 2007, 38, 1, 87, DOI: 10.1002/jrs.1623.
- (25) Wang, J. H.; Wei, F. I.; Chang, Y. S.; Shih, H. C. The corrosion mechanisms of carbon steel and weathering steel in SO₂ polluted atmospheres. *Mater. Chem. Phys.* 1997, 47, 1, 1, DOI: 10.1016/S0254-0584(97)80019-3.
- ES102578C



