

Investigating the Effect of H₂S and Corrosion Inhibitor on the Corrosion of Mild Steel under High Pressure CO₂ Conditions

Yoon-Seok Choi, Fernando Farelas, Luciano Paolinelli
Institute for Corrosion and Multiphase Technology,
Department of Chemical and Biomolecular Engineering, Ohio University
342 West State Street
Athens, OH 45701
USA

Ahmad Zaki B Abas, Azmi Mohammed Nor, Muhammad Firdaus Suhor
Petronas Research SDN. BHD, Selangor Darul Ehsan, Malaysia

ABSTRACT

The effect of H₂S and corrosion inhibitor on the aqueous corrosion behavior of mild steel was evaluated at high CO₂ partial pressure conditions. The experiments were performed in a 7.5 L autoclave with different temperatures (25°C and 80°C) and different H₂S concentrations (1000 ppm_v and 2000 ppm_v) at 12 MPa CO₂. The corrosion rate of steel samples was determined by electrochemical and weight loss measurements. The surface and cross-sectional morphology and the composition of the corrosion product layers were analyzed by using surface analytical techniques (SEM, EDS and XRD). Results showed that the presence of 1000 ppm_v and 2000 ppm_v H₂S decreased the corrosion rate of mild steel compared with pure CO₂ condition. However, the final corrosion rates were still higher than the targeted threshold (< 0.1 mm/y). Surface and cross-sectional analyses revealed the formation of FeS in the presence of H₂S and no localized corrosion was observed. The addition of 400 ppm_v of an imidazoline-based corrosion inhibitor reduced the corrosion rate below 0.1 mm/y in high pressure CO₂ conditions with 2000 ppm_v H₂S.

Key words: Supercritical CO₂, CO₂ corrosion, carbon steel, H₂S, corrosion inhibitor

INTRODUCTION

Over the past decade, there has been increasing interest in the corrosion behavior of carbon steels in supercritical CO₂ conditions. Unlike the case of carbon capture and storage (CCS) where small amounts of water are present, the exploitation of fields with high pressures of CO₂ needs to consider the presence of formation water, which presents strong corrosivity. It has been reported that the aqueous corrosion rate of carbon steel at high CO₂ pressures (liquid and supercritical CO₂) without protective FeCO₃ corrosion product layers is very high (>20 mm/y) due to the high concentrations of corrosive species such

as H^+ and H_2CO_3 .¹⁻⁵ Steels with low Cr contents (i.e., 1% Cr and 3% Cr) have shown no beneficial effect in terms of reducing the corrosion rate to admissible values.⁶ Therefore, controlling corrosion in these cases usually involves the use of corrosion resistant alloys (CRAs) or corrosion inhibitors (CI). Adequate protection of carbon steel was achieved by applying CI in high pressure CO_2 environments.⁶

The presence of small amounts of H_2S in high pressure CO_2 environments greatly alters the corrosion behavior of carbon steel.⁶⁻¹⁰ For example, in the presence of 200 ppm_v H_2S , the corrosion rate of carbon steel was reduced by about 10 times compared to the case of pure CO_2 at 12 MPa CO_2 and 80°C, but corrosion rate was still high and additional protection was required. In addition, the corrosion resistance of low Cr steels (1% Cr and 3% Cr) was worse than that of carbon steel in the above conditions. On the other hand, the addition of an imidazoline based CI in a high pressure CO_2 environment with 200 ppm_v H_2S reduced the corrosion rate of carbon steel below 0.1 mm/y.⁶ The effect of higher H_2S concentrations on corrosion rate of carbon steel with and without inhibitor addition has not been thoroughly studied yet.

The objective of the present study was to increase the understanding of the effect of H_2S and CI on the aqueous corrosion behavior of mild steel under high pressure CO_2 environments with elevated H_2S concentrations up to 2000 ppm_v.

EXPERIMENTAL PROCEDURE

The test specimens were machined from UNS K03014⁽¹⁾ carbon steel (CS) with two different geometries: cylindrical type with 5 cm² exposed area for electrochemical measurements, and rectangular type with a size of 1.27 cm × 1.27 cm × 0.254 cm for surface analysis. The detailed chemical composition of the steel is shown elsewhere.^{6,11} The specimens were ground sequentially with 250, 400 and 600-grit silicon carbide paper, rinsed with deionized (DI) water, cleaned with isopropyl alcohol in an ultrasonic bath for 60 seconds, and then dried.

An imidazoline generic CI was selected for evaluation under high p CO_2 environments with H_2S . In this instance, 'imidazoline' is shorthand for tall oil fatty acid (TOFA) imidazoline-based inhibitor. The detailed chemical composition of the CI is found in our previous work.^{6,12}

The corrosion experiments were conducted in a 7.5-liter autoclave (UNS N10276) which contained a CS working electrode, a HPHT Ag/AgCl reference electrode, and a platinum-coated niobium counter electrode. The test solution was a 1 wt.% NaCl aqueous electrolyte prepared using DI water. An impeller was used to stir the solution and to generate flow velocities of about 1 m/s (at 1000 rpm) during the tests.

Corrosion rate and corrosion potential of specimens were evaluated with time by linear polarization resistance (LPR) measurements. After each test, the morphology and compositions of corrosion products were analyzed with scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). Average corrosion rates were also determined from the weight-loss (WL) method. In addition, attack morphology was examined after corrosion product removal and cleaning of the samples with Clarke's solution.

The details of the experimental procedure for the autoclave setup and corrosion rate measurements are shown in our previous work.^{6,11} Table 1 shows the test conditions used in the present study. All experiments were conducted within 3 days, in order to minimize the effect of the solution contamination due to corrosion reaction over time.

⁽¹⁾ UNS numbers are listed in Metals and Alloys in the Unified Numbering System, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

Table 1
Conditions for corrosion tests

pCO ₂ (MPa)	H ₂ S (ppm _v)	Temperature (°C)	Cl (ppm _v)
12	1000	25 and 80	0
12	2000	25 and 80	0
12	2000	25 and 80	400
12	2000	80	200

RESULTS AND DISCUSSION

Experiments at 12 MPa CO₂ and 25°C

Figure 1 shows LPR and WL corrosion rate data of CS exposed at 12 MPa CO₂ and 25°C with 1000 ppm_v and 2000 ppm_v of H₂S. Corrosion rates seemed to reach stable values after 20 hours of exposure for both H₂S concentrations. It is worth noting that increasing the H₂S concentration led to higher corrosion rates in this experimental condition. WL corrosion rates showed the same trend as the LPR corrosion rates.

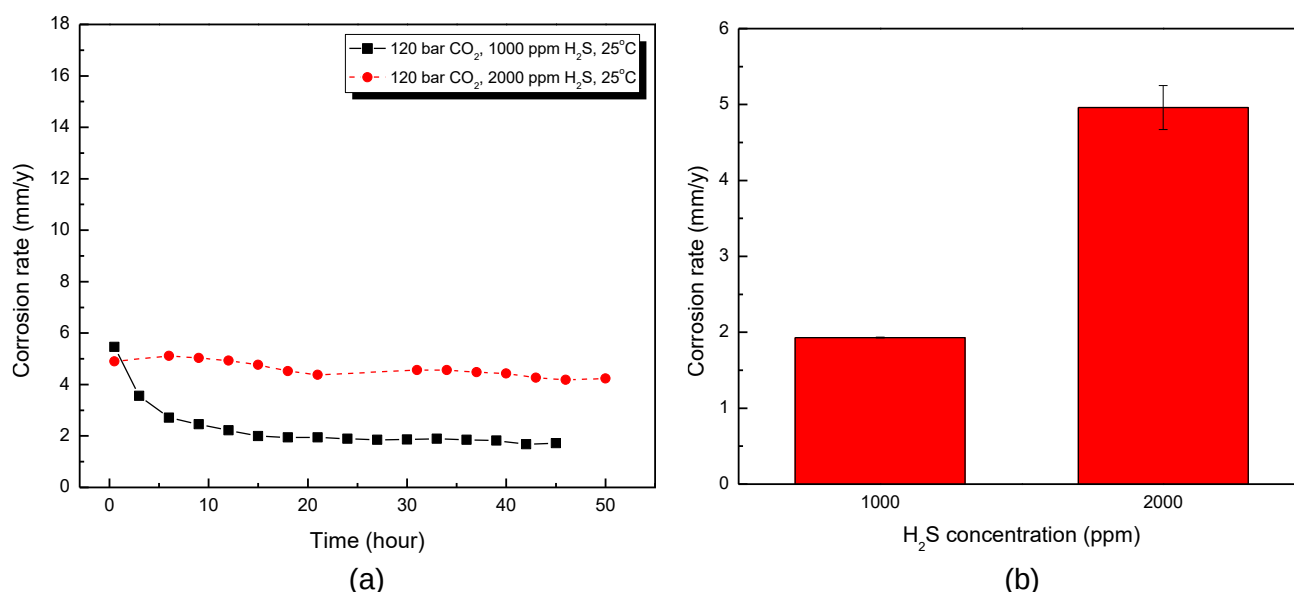


Figure 1: Corrosion rate of CS with different H₂S concentrations at 12 MPa CO₂ and 25°C: (a) LPR corrosion rate, (b) WL corrosion rate.

Figure 2 shows the surface morphology and chemical analysis of the corrosion product formed at 12 MPa CO₂ and 25°C with 1000 ppm_v H₂S. The corrosion product was mostly uniform and presented some discontinuous cracks due to dehydration. The chemical analysis performed by EDS at the top of the corrosion product indicated that it consisted mainly of iron and sulfur.

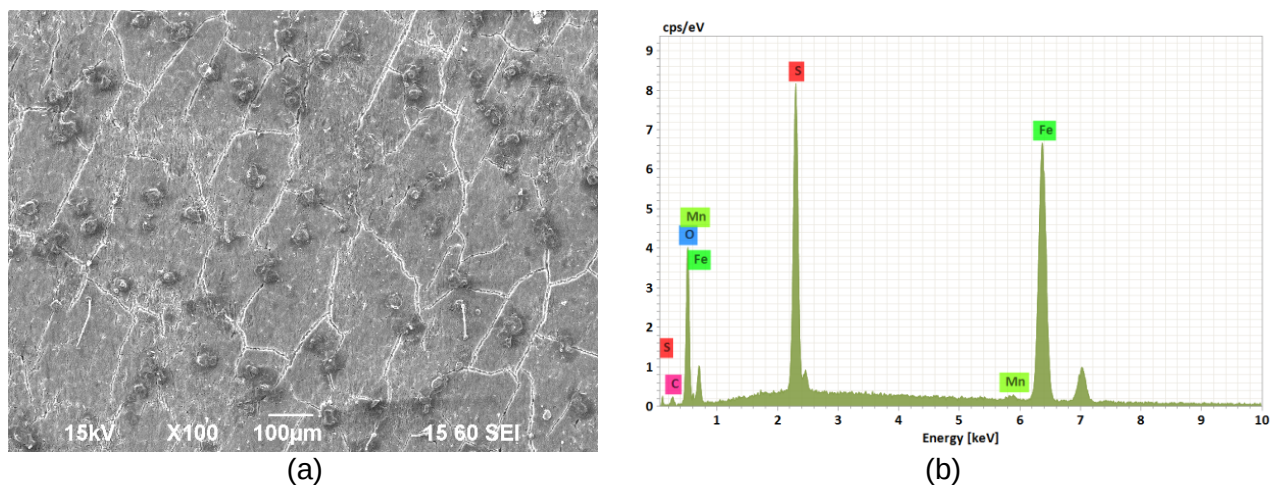


Figure 2: SEM surface view (a) and EDS analysis (b) of the corrosion product formed at 12 MPa CO₂ and 25°C with 1000 ppm_v H₂S.

Figure 3 displays the SEM cross-sectional view and EDS elemental mapping of the corrosion product layer formed at 12 MPa CO₂ and 25°C with 1000 ppm_v H₂S. It revealed a formation of thin and mainly continuous corrosion product layer (~10 µm) which was not very protective because of the relatively high corrosion rate of ~2 mm/y seen at the end of the experiment. This layer mainly consisted of iron and sulfur indicating the formation of FeS.

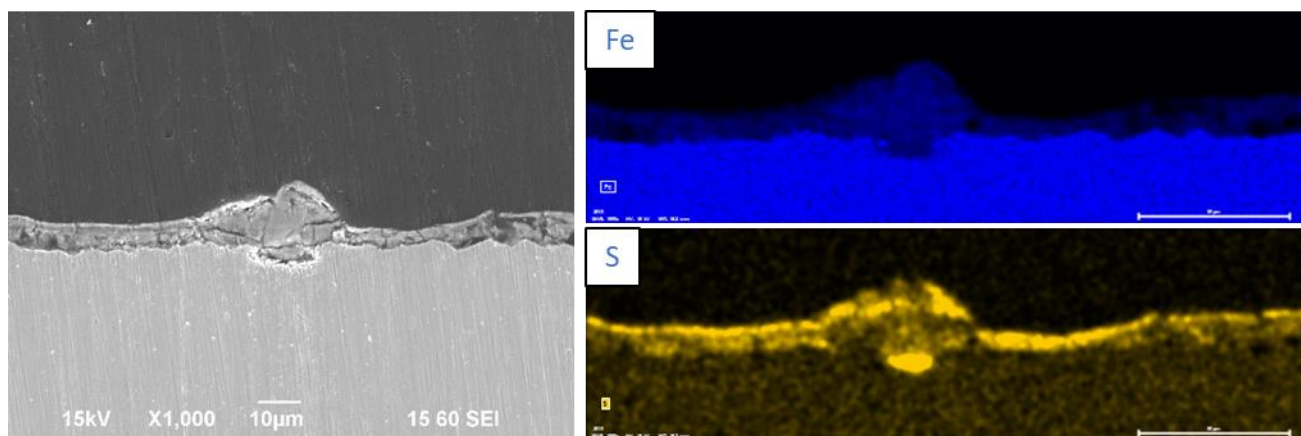


Figure 3: SEM cross-sectional view and EDS elemental mapping analysis of the corrosion product formed at 12 MPa CO₂ and 25°C with 1000 ppm_v H₂S.

The corrosion product formed with 2000 ppm_v H₂S (Figure 4) looked more porous than that of the sample exposed to 1000 ppm_v H₂S, and also seemed less adherent and fragile when corroded samples were manipulated. This would explain the higher corrosion rates measured for the higher concentration of H₂S. Corrosion products containing iron and sulfur as main elements were also observed in the case with 2000 ppm_v H₂S. The cross-sectional analysis (Figure 5) showed a porous layer of ~10 µm thickness composed mainly of iron and sulfur.

Figure 6 shows the surface morphologies of corroded samples after corrosion product removal. For both conditions, surfaces were relatively rough but no significant pits or localized attack was observed and the attack was considered as uniform.