

Research Article

Test Conditions for Pipeline Materials Selection with High Pressure Sour Gas

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Acid gases, such as CO₂, H₂S, and/or sulfur in oil industry's production fluids, can be responsible for both general and localized corrosion, acting with different mechanisms, which depend on chemical and physical properties of the produced fluids. Materials selection for handling such fluids is performed by combining experience with suggestions from standards and regulations. A good deal of knowledge is available to predict corrosion rates for CO₂-containing hydrocarbons, but the effect of high H₂S pressure is less understood, mainly due to the difficulty of performing laboratory tests in such challenging conditions. For instance, the so-called NACE solution to assess SSC (Sulfide Stress Cracking) susceptibility of steels is a water-based solution simulating production fluids in equilibrium with one bar bubbling H₂S gas. This solution does not represent environments where high gas pressure is present. Moreover, it does not take into account the corrosive properties of sulfur and its compounds that may deposit in such conditions. Besides, properties of high pressure gases are intermediate between those of a gas and those of a liquid: high pressure gases have superior wetting properties and better penetration in small pores, with respect to liquids. These features could enhance and accelerate damage, and nowadays such conditions are likely to be present in many production fields. This paper is aimed to point out a few challenges in dealing with high pressure gases and to suggest that, for materials selection in sour service, a better correspondence of test conditions with the actual field conditions shall be pursued.

1. Introduction

Exploitation of fields with high H₂S and/or CO₂ content is nowadays of growing importance for oil companies. The effect on structural metals of high partial pressure of H₂S in gas mixtures needs to be further studied. Reinjection wells are, for instance, in contact with dry supercritical fluids, whose corrosion properties are not fully known. Multiphase pipelines too are often transporting fluids containing high pressure sour gas and laboratory tests are critical to material selection assessing crack resistance.

Several possible corrosion mechanisms may occur when dealing with H₂S rich fluids. Hydrogen sulfide is a weak acid, causing a small decrease in pH of a water solution, and corrodes steels and alloys in neutral solutions, with a generally low uniform corrosion rate. Hydrogen sulfide plays an important role in the stability of corrosion products

film, increasing or decreasing its corrosion resistance by interaction with other components, such as CO₂.

While the mechanisms of carbon steel (CS) corrosion due to CO₂ are fairly understood, the effects of H₂S presence are not fully understood. H₂S corrosion mechanisms proposed in literature [1, 2] do explain experimental data, but their thermodynamics and kinetics details are not known.

Wet gas mixtures containing hydrogen sulfide attack aggressively iron and mild steels. Sulfur forms stable sulfides with many transition metals. H₂S dissociation on transition metal surfaces is an easy process and, as a consequence, sulfur deposits and sulfide compound formation on metal surfaces is favored [3].

Three regimes of corrosion of mild steel can be identified in CO₂/H₂S environments, as shown in Figure 1. Characteristic of the mixed regime is the formation of scales of iron carbonate and iron sulfide. The application of a sweet

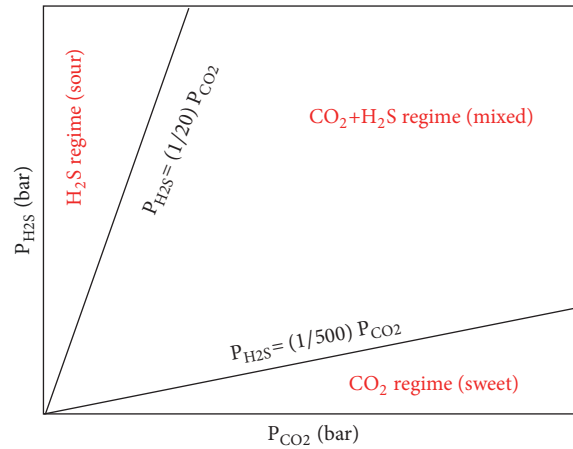


FIGURE 1: Mild steel corrosion regimes in CO₂/H₂S environments.

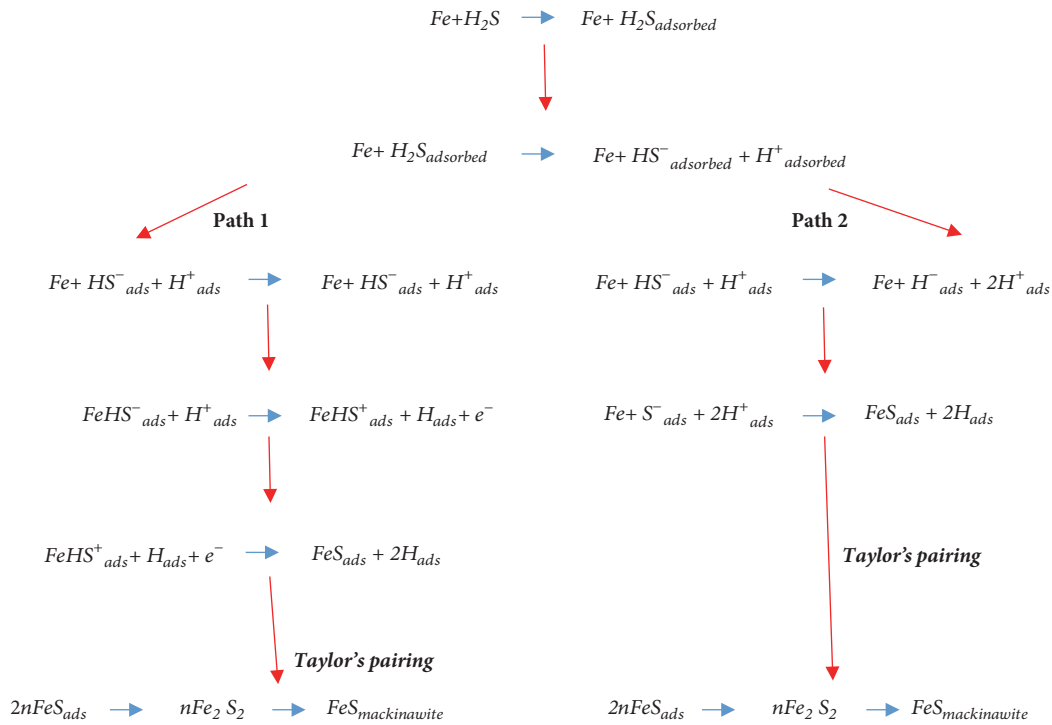


FIGURE 2: Mechanisms proposed for H₂S aqueous corrosion of mild steel.

corrosion model for the mixed regime appears justified, though it may be conservative [4].

As a general trend, iron sulfide (FeS) films can form if H₂S is present, while iron carbonate (FeCO₃) forms if CO₂ is predominant. CO₂ corrosion and iron carbonate will dominate at approximate $p_{\text{H}_2\text{S}} \leq 0.001$ bar and at temperature above 60°C, where corrosion depends on FeCO₃ formation. When instead the CO₂/H₂S ratio is lower than a certain value (“H₂S dominated” systems) the formation of metastable sulfide scale will prevail. The stability of sulfide scales, which are formed in this case, is very difficult to predict, due to the complexity of sulfides that can form depending on pH and temperature. Iron sulfide scales stability appears to be strongly dependent on the presence of chlorides, elemental

sulfur, and dissolved oxygen. For example, at low pH and in presence of chlorides, sulfide corrosion scale becomes unstable, and reliance on this film for protection cannot be assured; the consequence is the likelihood of localized corrosion whenever the film fails.

According to Sun et al. [5, 6], the interaction of Fe with H₂S in aqueous environments proceeds toward the formation of mackinawite through the reaction paths shown in Figure 2. After the initial adsorption of H₂S on the Fe surface, mackinawite can be formed from amorphous FeS by either Path 1 or Path 2. Smith and Miller [7] studied the sour corrosion mechanisms and revealed that mackinawite is first produced and then converted to other forms of iron sulfide in longer term exposure to H₂S [8].

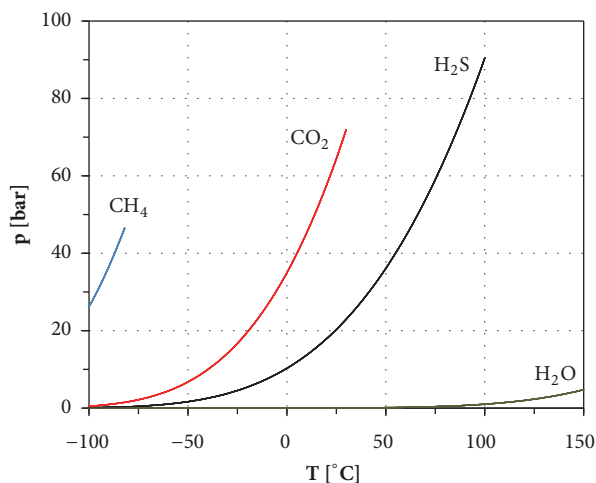


FIGURE 3: Vapour pressure curves of the gases of interest.

While in mild steel both general corrosion and cracking are observed in sour environment, stainless steel is resistant to general corrosion and can be susceptible to localized corrosion only if chlorides are present. Cracking can be observed starting from corrosion pits.

Another corrosion mechanism observed in sour gas systems is due to elemental sulfur, which causes severe corrosion. Elemental sulfur formation includes condensation of H_2S at high pressure and low temperature, thermochemical reduction of sulfate, and air oxidation of H_2S . As a strong oxidizing agent, elemental sulfur can directly react with metal at a high rate and form iron sulfide [9]. In a gas phase with high H_2S partial pressure, hydrogen sulfide can react with elemental sulfur, producing sulfane (free acid form of ionic polysulfide). In aqueous phase, under acidic conditions, sulfanes are largely dissociated in H_2S and elemental sulfur. However, strongly oxidizing species can remain, as either polysulfide ions or trace sulfanes, to play significant role in corrosion reactions. Higher content of chloride in production water can significantly aggravate the pitting rate of steel due to elemental sulfur.

The presence of H_2S in the conveyed fluid is also expected to enhance hydrogen-related embrittlement processes, because H_2S is a chemical poison for cathodic hydrogen recombination. On the other hand, since H_2S is a weak acid, its effect on anodic processes is expected to be small. Finally, a question is still open: what is the effect of high pressure H_2S and CO_2 on both anodic and cathodic processes?

2. Material Testing for Sour Fluids Service: Present Situation

In front of such a complex theoretical framework, one would expect material's testing protocols strictly adherent to the true field conditions, but the situation is very different. Laboratory data to qualify sour service materials are obtained with tests where specimens are immersed in aqueous solution in equilibrium with gas. Total and partial gas pressures are a function of testing techniques, temperature, and volume of the test

TABLE 1: Critical parameters of gases of interest.

Gas	T_c (°C)	P_c (bar)
CH_4	-83	46.1
CO_2	31	72.8
H_2S	100	89.7
H_2O	374	220.6

vessel. With reference to H_2S -containing environments, the so-called "NACE solutions" A and B (for the composition see [10]) are in equilibrium with bubbling H_2S at a pressure of 1 bar.

In field conditions, metallic materials can be in contact with dense or supercritical fluids, which could have superior wetting properties and better small pore penetration with respect to liquids [11]. For the sake of clarity, we can consider the vapour pressures curves and critical parameters of CH_4 , CO_2 , H_2S , and H_2O (Figure 3 and Table 1). In field conditions, it is likely that an aqueous phase could be present, and this phase can be rich in H_2S [12].

Dense and supercritical fluids have physical properties that are in some way intermediate between those of a gas and those of a liquid. It is possible then to have a fluid having liquid-like density and gas-like transport properties (such as diffusion coefficients). As far as for H_2S , its critical temperature is 100°C, and the critical pressure is 89.7 bar, while CO_2 becomes supercritical at temperature higher than 31°C (critical pressure is 72.8 bar). Corrosion resistance of metals in supercritical H_2S could be different from what is experienced in water saturated with H_2S at 1 bar.

To sum up, between field conditions and lab data, there are the following gaps:

- (i) High H_2S content: due to the various possible actions of H_2S , the effect should be assessed experimentally, but it is very difficult to perform these tests.
- (ii) High pressure and temperature: near critical or supercritical conditions could have a significant effect on both equilibrium and kinetics processes.
- (iii) Gas mixture composition: real composition of a gas mixture could have effects not easy to assess on the basis of tests with H_2S alone.
- (iv) Water content: since it is generally accepted that corrosion happens only in presence of a liquid aqueous phase, precise definition of the so-called "dry" conditions of the gas mixture in the range of service temperature is important.

This paper points out the necessity of materials testing in conditions as close as possible to the actual service situation, with the aim of obtaining helpful data for materials performance in extreme conditions.

3. Performed Tests

3.1. Experimental Procedure. UHP (Ultrahigh Pressure) autoclave is designed to test candidate materials up to a total

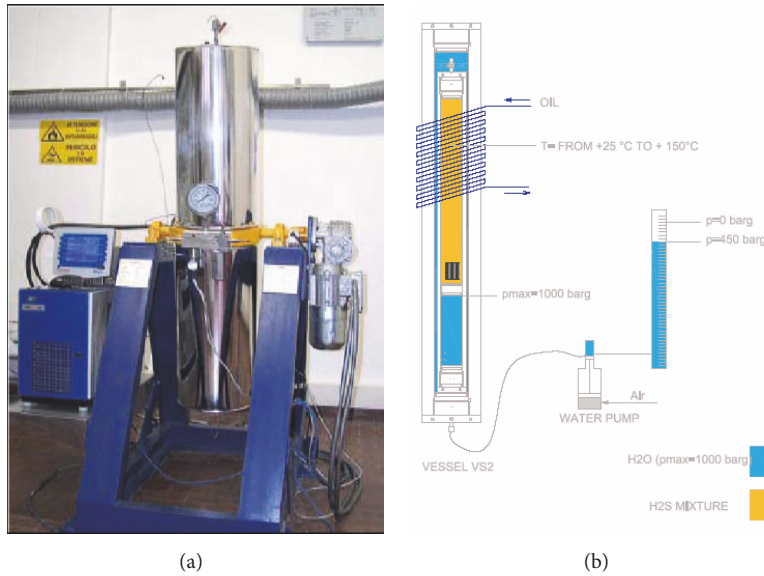


FIGURE 4: Ultrahigh pressure autoclave (a); pressurization and thermostatic circuits (b).

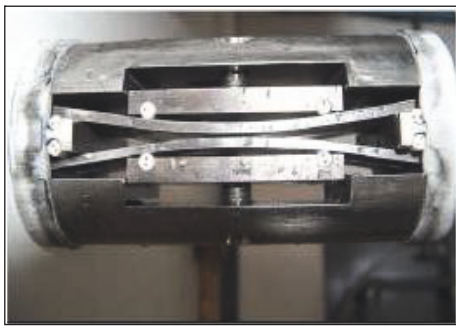


FIGURE 5: Specimen holder.

pressure of 1000 bar of H_2S and other gas mixtures. Aqueous solutions can be added to simulate the complete service environment. A picture of the equipment and the principle of design are shown in Figure 4 [13].

Testing equipment consists of two vessels, V1 and V2. V1 is in Hastelloy C276 (UNSN10276) and has a volume of about 1.6 litres. Its function is to hold the samples and the H_2S - CH_4 - CO_2 pressurized mixture. It is equipped with a piston that can move freely along the longitudinal axis.

The autoclave can accommodate up to 8 metallic specimens in specially designed specimen holders—shown in Figure 5—for stress corrosion cracking susceptibility tests; different configurations can be studied to accommodate different materials for different type of testing. The whole apparatus can be periodically tilted to facilitate the mixing of corrosive fluids, even immiscible, and to allow uniform exposure of the specimens. Its operating temperature can be up to $150^\circ C$ and total pressure up to 1000 bar.

After introducing the samples (see below) and producing vacuum, aqueous solution with the required composition is added. Hydrogen sulfide and carbon dioxide, contained in 1-kg cylinders, provided with a transfer pipe, are then

transferred into V1. The cylinders lay upon two electronic scales which allow introducing the exact desired amount of gas. Methane, instead, is loaded from gas network by using a pressure multiplier.

After V1 is filled with the mixture, it is totally inserted into V2, which is filled with water. It is then subjected to a first pressurization cycle by pumping water into V2 up to 500 bar. Afterwards it is heated up to test temperature by means of a thermostatic oil jacket. In order to complete the pressurization, water is pumped up to the required test pressure. During the pressurization cycles at 500 and 830 bar, the piston inside V1 moves compressing the mixture. When water pressure reaches that of the gases inside V1, the difference between the internal and external pressure of V1 is almost zero. These conditions are maintained until the stress corrosion test is completed (usually a month).

With a compression ratio of 4/1, it is possible to reach, at room temperature, 800 bar. Then it is possible to increase the temperature to reach the maximum working pressure (1000 bar).

The vessels are installed on a machinery that make them oscillate approximately of 180° , in order to obtain a relative motion of fluid to specimens inside V1. At test completion, V2 is cooled and depressurized by slowly draining the water; afterwards V1 is depressurized and the mixture is sent to an absorption column (scrubber). Before opening, V1 is degassed by means of 3 washing cycles with an inert gas (usually nitrogen).

The procedure for preparation and loading of Bent-Beam coupons was developed following two standards:

- (i) ASTM(4) G 39: standard practice for “Preparation and Use of Bent-Beam Stress Corrosion Test Specimens”.
- (ii) NACE Standard TM0177-96: standard test method for “Laboratory Testing of Metals for Resistance to

Specific Forms of Environmental Cracking in H₂S Environments”.

The advantage with respect to constant volume vessel is in the possibility of selecting both temperature and pressure for a test, to obtain a better reproduction of field conditions. In the inner vessel, corrosion specimens are held in contact with the pressurized gas mixture, with or without water.

3.2. Test Conditions. The test campaign described in this paper is preliminary and aimed at obtaining information mainly on test conditions and their effect on selected materials. Two groups of test conditions were investigated:

- (i) simulated reinjection conditions in ultrahigh pressure (UHP) in gas mixture with addition of small amounts of aqueous solution (NaCl 83 g/l),
- (ii) tests in aqueous solutions (NACE A or NACE B solution) pressurized with H₂S gas at medium pressure (MP), namely, 50 or 100 bar.

Tested materials were

- (i) carbon steel (CS) API 5L X52, sour service grade,
- (ii) carbon steel F22, sour service grade,
- (iii) low alloy steel API 5CT Grade T95 type 1, sour service grade,
- (iv) austenitic steel type AISI 316L (UNS 31603),
- (v) Ni-based alloys (UNS N008825 and N006625).

Specimens (100 mm × 20 mm × 2.5 mm) were 4-point bend beams. In the autoclave were accommodated either 4 or 8 specimens. Their surfaces were ground with 600-grit sandpaper. Before bending, specimens were observed by stereo microscope to assess initial conditions. Stress levels were applied based on actual yield strength (AYS) of each specimen.

After testing, specimens were examined by

- (i) visual inspection,
- (ii) metallographic observation and analysis,
- (iii) weight loss measurement,
- (iv) scanning electron microscopy (SEM),
- (v) X-ray diffraction (XRD).

Test conditions are detailed in Tables 2 and 3 for each test environment.

3.3. Test Results. Part of the results was presented in a previous paper [14]. Here they are shortly summarized with reference to each material, with the aim at evidencing the effect of the two test procedures. Different behaviours were observed for each material with reference to experimental conditions.

In absence of water (reinjection 3 test), no damage was detected in the four tested materials, but for a very initial presence of localized attack on the surface of X52 and T95 steel, as shown in Figure 6. As anticipated before, however, the amount of water that can be present in the so-called “dry” condition needs to be better defined.

TABLE 2: Operating conditions simulating reinjection in well.

Tested materials	T95	F22	X52	316L
T (°C)			90	
P_{tot} (bar)			720	
$P_{\text{H}_2\text{S}}$ (bar)			252	
P_{CH_4} (bar)			50.2	
P_{CO_2} (bar)			Remaining	
H ₂ O (%)			3.5, 2.0, or 0 (*)	
NaCl (g/l)			83 or 0 (*)	
Duration (d)			30	
% AYS	100	100	100	100

(*) AYS of T95 and F22 with no NaCl solution where both are 90%.

TABLE 3: Operating conditions in “medium pressure tests”.

Tested materials	T95	F22	316L
T (°C)			25
$P_{\text{tot}} = P_{\text{H}_2\text{S}}$ (bar)			50, 100
Solution			NACE A, NACE B
Duration (d)			8, 30
% AYS			60, 80, 100

3.3.1. Ni-Based Alloys. Ni-based alloys were tested only in reinjection simulating environment, with and without “nominal” water content, and no damage was detected, as expected.

3.3.2. API X52 Pipeline Steel. Carbon steel API X52 was tested only in UHP conditions (reinjection). In presence of water, some localized shallow attack was detected on the surface. As shown in the figures, the shallow pits on the surface are wider with increasing water content (Figures 7(a)–7(c)); a few small cracks are present at the bottom of pits.

3.3.3. T95 Steel. Sour service T95 steel specimens failed at MP conditions. Out of five specimens, four reached complete failure and one did not fail but at the naked eye showed extended cracking on the surface (Figure 8). No cracks were observed in UHP conditions with presence of small quantity of water, and only shallow localized corrosion features were present. Comparison of the results (cracking at MP condition—only little damage at UHP conditions) could suggest that NACE solutions are more aggressive than higher pressure H₂S.

Iron sulfide, mackinawite, and pyrrhotite are the main phases in the corrosion products on the surface of sample T95 (Figure 9), as expected by the proposed corrosion mechanisms.

3.3.4. F22 Steel. Specimens in F22 steel (Figure 10) showed localized corrosion with shallow features (somehow shallower than in T95, compare Figure 10(a) with Figure 10(b)). As observed in general for CS, there is a diffused corrosion damage which can be competing with cracking.

Figure 11 (sample F22) shows fine crystals of FeS arranged between a cracked amorphous layer and bigger external crystals. The phase composition of the corrosion products is shown in the XRD pattern of Figure 12. Iron sulfide and

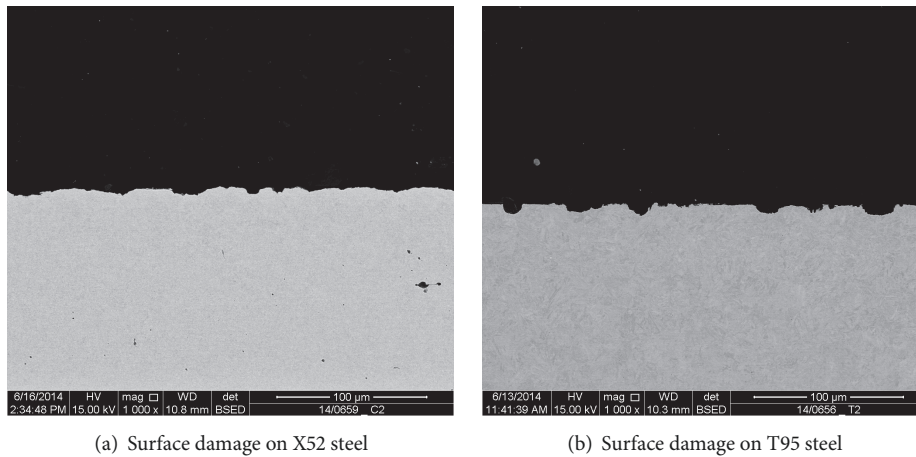


FIGURE 6

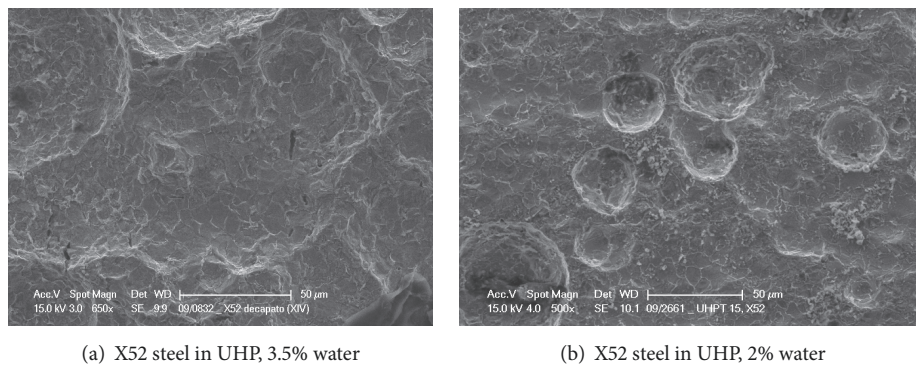
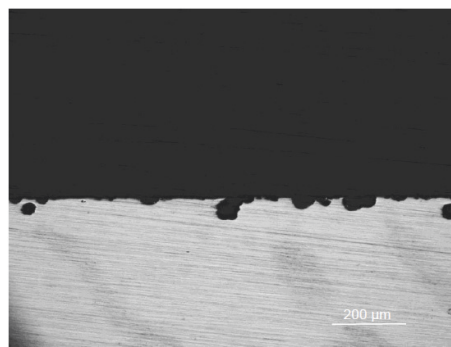


FIGURE 7



(c) X52 steel in UHP, 3.5% water

mackinawite are the main compounds, while the pyrrhotite peaks are not visible.

3.3.5. Austenitic Steel AISI 316L (UNS 31603). Austenitic 316L stainless steel seems to be mainly sensitive to chloride and temperature then to H_2S pressure. That could be expected, but there is a need for a better understanding of the damage mechanism. The competition between general corrosion and cracking is probably important also here. Since stainless steel is resistant to general corrosion at room temperature, no cracks are observed; in both UHP (with water) and MP conditions (with NACE solutions) at $80^\circ C$, localized

corrosion and cracking are observed. See Figures 13(a) and 13(b).

4. Conclusions

Corrosion resistance of steels and alloys in high and very high H_2S pressure shall be investigated in test conditions approaching as close as possible to field conditions. In this field, further investigations and more tests are required. The amount of H_2S that can be dissolved in water is limited as a function of temperature. Supercritical H_2S or other gas mixtures can have a complex interaction with water, supposedly

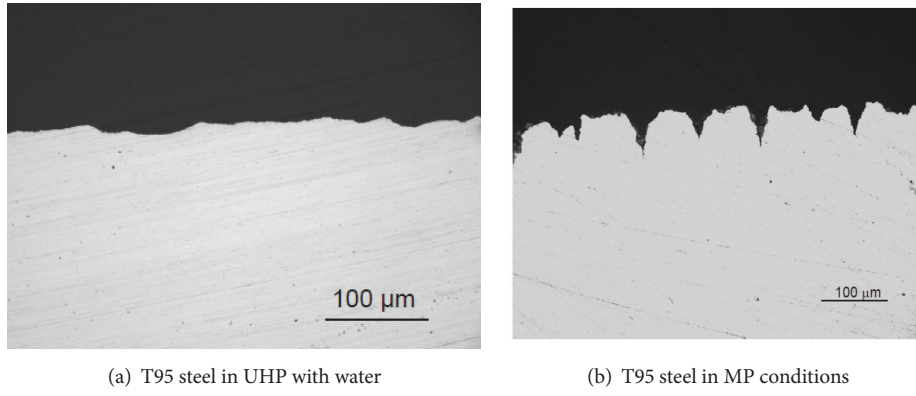


FIGURE 8

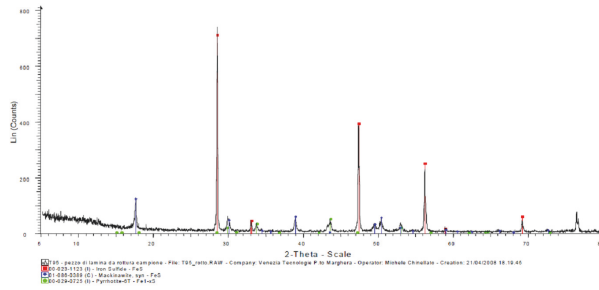


FIGURE 9: XRD pattern of corrosion products on sample T95.

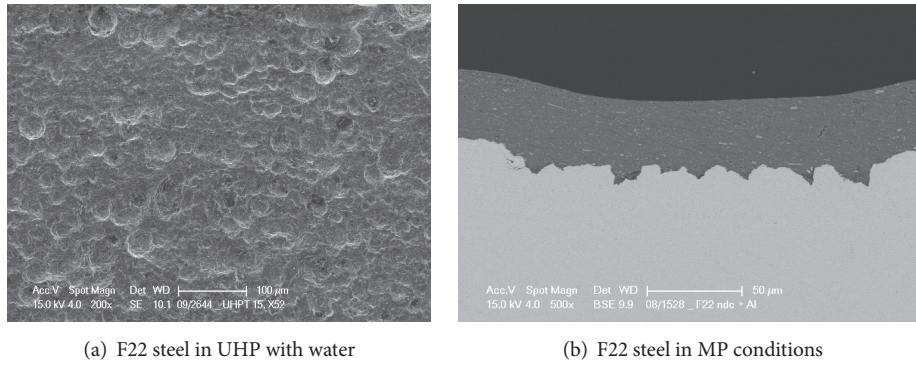


FIGURE 10

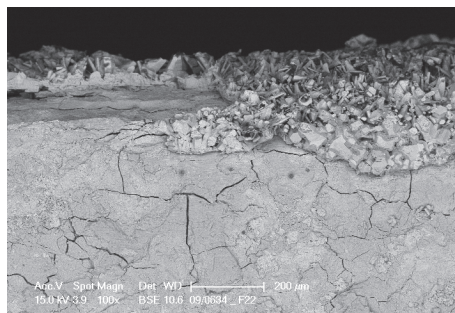


FIGURE 11: Cross section micrograph of sample F22 along the sample edge.

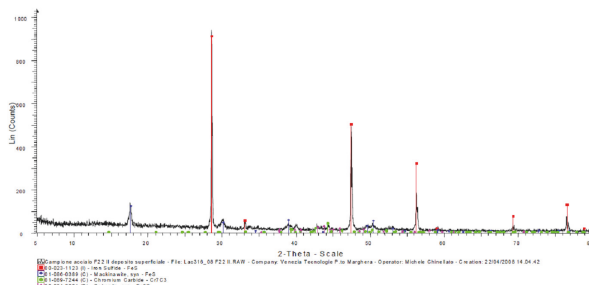
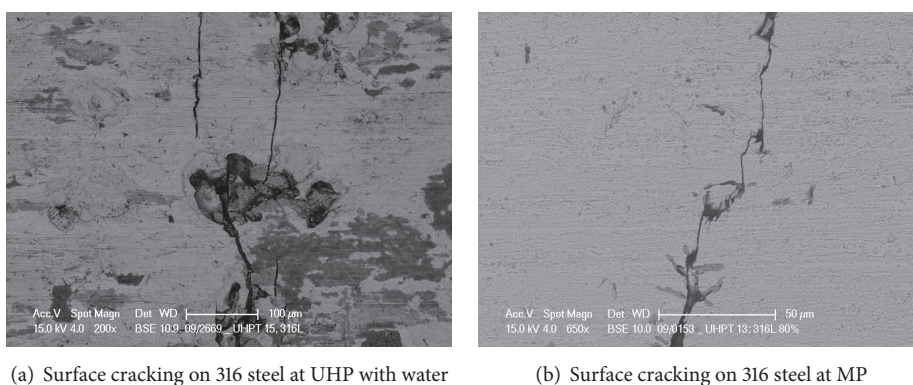


FIGURE 12: XRD pattern of corrosion products on sample F22.



(a) Surface cracking on 316 steel at UHP with water

(b) Surface cracking on 316 steel at MP

FIGURE 13

different from what is experienced at low temperature and pressure conditions. Standard testing procedures to assess the corrosion behaviour of metals in high pressure systems with high concentrations of H_2S and supercritical fluids could be inadequate.

Results discussed here show that carbon steel, while compliant with NACE “sour service” requirements, can suffer cracking in high pressure aqueous solutions (50–100 bar) that correspond to higher concentrations of H_2S and low pH. Meanwhile, the same material did show better resistance in UHP test in $H_2S/CO_2/CH_4$ gas mixture with low or no water content.

Important to note the different behaviour of austenitic stainless steel UNS 31603. The specimens exposed to NACE solution up to 100 bar did show a good resistance to cracking at room temperature. However, some surface cracking was observed in both UHP wet gas and 80°C MP NACE solutions.

Stainless steel behaves differently because it is subject mainly to cracking and not to general corrosion. Corrosion is necessary to produce hydrogen, which is responsible for cracking in carbon steel. In stainless steel, chlorides must be present to produce pitting corrosion and cracking is a consequence.

The preliminary data presented in this paper do confirm that a deeper knowledge of the behaviour of supercritical gas and gas mixture, aimed at understanding their interaction with water and/or water solution, is necessary. Test conditions shall be as close as possible to the actual service.

Further study of the relationship between cracking resistance and corrosion resistance is also suggested, as shown, for

instance, in the behaviour of stainless steel. A better understanding of the role of chlorides with respect to H_2S could be helpful.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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