

REDUCTION OF CONSERVATISM IN SSC TESTING FOR SOUR GAS WELL TUBULARS

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ABSTRACT

Due to their high strength and relatively low cost, martensitic stainless steel (MSS) well tubulars are attractive. However, sour applications of MSS are limited by their susceptibility to Sulphide Stress Cracking (SSC) under shut-in conditions, where the pressure is the highest and the temperature the lowest. This currently restricts their use to a greater extent than high temperature pitting and Stress Corrosion Cracking (SCC).

A comparison between field experience in mildly sour gas wells and laboratory test data on 13Cr MSS tubulars showed that in the laboratory SSC tests, cracking is observed under conditions that are significantly less severe than the field conditions in which these tubulars are operated without reported failures. This raised the question whether the current method of SSC testing is too conservative. To investigate this, a detailed assessment of field-relevant exposure conditions for SSC was carried out.

Susceptibility to SSC requires a near to ambient temperature. Therefore, only the top section of the well can be susceptible, after closing in the well and a subsequent cooling down period. Because the liquids will drain away after closing in a gas well, the tubular will be exposed to a thin water film (or water droplets) only. This thin water film exposure was evaluated and modelled. Results indicate a lower susceptibility to SSC than fully immersed conditions, attributable to pH elevation in the thin water film, which is induced by very slow corrosion under passive conditions. Existing SSC test methods were adapted to simulate the thin water film exposure in a realistic way, which resulted in a new fit-for-purpose SSC test method.

The results obtained with the thin water film test demonstrate that for mildly sour gas wells, the safe operating envelope of martensitic stainless steels can be extended.

Key words: martensitic stainless steel (MSS), sour service, gas well, thin film, SSC, cracking, qualification testing

INTRODUCTION

Martensitic stainless steel (MSS) well tubulars are favorable due to their high strength and relatively low cost and are therefore widely applied in the Oil & Gas industry. This is especially the case for 13Cr and Super13Cr grades, which are often selected for mildly sour gas fields, where a relatively low content of H_2S is present. When selecting martensitic stainless steels for sour service, the susceptibility to Stress Corrosion Cracking (SCC) and Sulfide Stress Cracking (SSC), determined by standard laboratory tests, are the most important selection criteria.

SCC involves anodic processes of localized breakdown of passivity and tensile stress (residual and/or applied) leading to cracking. Susceptibility to SCC increases with temperature. The other cracking mechanism, SSC, involves the embrittlement of the metal by atomic hydrogen that is produced by (localized) corrosion (in most cases pitting) on the metal surface, while hydrogen uptake into the metal is promoted in the presence of sulfides. The atomic hydrogen can diffuse into the metal, reduce ductility (typically at stress raisers) and thus induce cracking. Susceptibility to SSC is highest at ambient temperature.

For martensitic stainless steels, the safe operating envelope is in almost all cases limited by their susceptibility to SSC, the ambient-temperature cracking mechanism, as determined by laboratory tests. Typically, NACE TM 0177¹ Method A (uniaxial tensile tests) or Method C (C-ring tests), NACE TM0198² Slow Strain Rate Tests or Ripple Load Tests³ are applied. The results of these SSC laboratory tests constrain the use of martensitic stainless steels more extensively than limitations due to susceptibility to high-temperature SCC, which is determined by the same test methods.

In a recent development program carried out for Petroleum Development Oman (PDO), a comparison between laboratory test data on 13Cr4Ni1Mo and field experience with this grade was made^{4,5}. This work showed that SSC (ambient-temperature cracking) occurs in the laboratory under conditions that are much less severe than field conditions where these tubulars have been operated in mildly sour service without failures. This mismatch between laboratory tests and field experience raised a concern that the current method for SSC testing is not representative of field application, and overly conservative. This was confirmed by the outcomes of a review by Total, in which laboratory test data were compared to field experience⁶. In addition, a review of field failures on martensitic stainless steel well tubulars did not identify any SSC failures, which suggested that the susceptibility of martensitic stainless steels to SSC may not be as critical as suggested by the SSC laboratory tests.

This discrepancy triggered a detailed consideration of the actual field exposure of well tubulars under conditions where SSC could take place, and a comparison of these conditions with laboratory test exposure in standard SSC tests. The objective was to identify the reason for the observed mismatch between laboratory test results and field exposure, and to investigate whether a more realistic SSC test method could be developed that correlates better with performance of well tubulars in the field. This could, if successful, reduce over-conservatism in material selection and thus reduce completion costs of mildly sour wells.

This paper presents and discusses a more realistic SSC test methodology that aims to expose specimens to conditions that more closely resemble the critical SSC conditions in gas wells. Comparisons between the new test method and conventional tests are shown. In addition, the actual field exposure conditions are modelled and related to the test results.

SSC EXPOSURE CONDITIONS FOR TUBULARS IN GAS WELLS

Martensitic stainless steels become susceptible to SSC when the temperature is below approx. 60 °C while the material is exposed to H_2S and water. The highest susceptibility to SSC will occur when the material is at ambient temperature. Increasing the pH_2S , lowering the pH and/or increasing the chloride concentration will increase the susceptibility^{7,8}. For the tubulars of a producer well, this implies that the most critical conditions for SSC occur when the well is shut in and cooled down. The time span of a

producing well to cool down ('no touch time') will be between a few hours (sub-sea well) and days (onshore wells). During this period, the following environmental changes will take place in the upper part of a multiphase or gas well (Figure 1):

1. After closing in, the liquids will drain to the lower part of the well, while the top will be filled with the lighter gas. Liquid droplets, or a thin liquid film (water and liquid hydrocarbons), will remain attached to the tubular wall in the upper section of the well.
2. During cooling, the increasing vertical temperature gradient will induce convection in the gas phase (chimney effect), leading to transport of warm gas to the cooling top section of the well. Water and hydrocarbons will condense from the gas phase on the colder tubular wall. The water droplets hanging on the wall will gain weight (or the liquid films will become thicker), which will lead to droplets / liquid running down the tubular wall. The condensation of water will dilute the chloride content in the water on the tubular wall. The combined effect of dilution and liquid running down the tubular will reduce the chloride content in the hanging droplets / thin water film further. At the same time, alkalinity of the water from mineral bases in the formation water will reduce by dilution as well. This is shown schematically in Figure 1b.
3. After the top section of the well has cooled down to ambient temperature, the vertical temperature gradient, as well as the temperature difference between the tubular wall and the core of the bore, will continue to induce convection in the gas column. Given the relatively low temperature gradient (approx. $1\text{ }^{\circ}\text{C}/10\text{ m}$), the rate of convection and the related continuous condensation will be low. Nevertheless, this will lead to ongoing condensation of water on the tubular wall and thus very slow refreshment of the water droplets / water film on the wall of the tubular. This is shown schematically in Figure 1c.

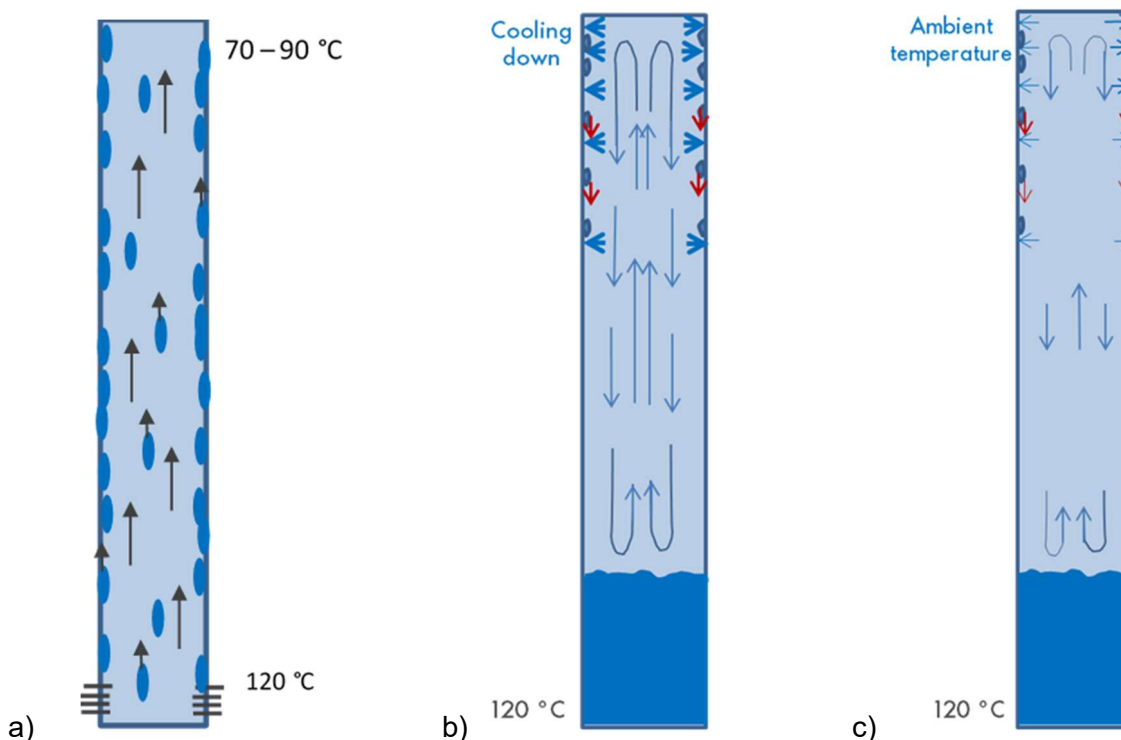


Figure 1: Schematic representation of well shut-in conditions where the tubular can be susceptible to SSC. a) Producing well: high temperature – no SSC; b) Well closed-in and cooling down. Thin water film / water droplets on tubular, slowly refreshed by condensation; c) Top section at ambient temperature. Thin water film / water droplets very slowly refreshed – potential for SSC.

The above shows that, after cooling down, the exposure of the upper part of the well tubular is to water droplets or a thin water film. This will be referred to as a Thin Water Film. While in conventional SSC test methods, the specimens are fully immersed in bulk solution, a very slowly refreshed, semi-stagnant Thin Water Film is expected to be less severe from a corrosion and cracking perspective. This is because, after the well is closed-in, the chemistry of the Thin Water Film will evolve as follows:

- Very slow corrosion of the MSS well tubular, which is in the passive state. This does not cause any relevant material loss, but it will lead to:
 - o An increase in the concentration of iron cations in the Thin Water Film, which may even lead to saturation and precipitation of FeS or other species;
 - o An increase in the pH due to consumption of protons by the cathodic reaction; over time this effect is expected to be stronger than the loss of alkalinity due to dilution of the water film by condensing water.
- Condensation of water from the gas phase will lead to dilution of the chloride concentration in the Thin Water Film. Condensation will also lead to run-down of the Thin Water Film, which will further reduce the chloride concentration.

It is expected that the increase in pH and decrease in chloride concentration by passive corrosion (typically $0.1 \mu\text{A}/\text{cm}^2$ at ambient conditions and $1.0 \mu\text{A}/\text{cm}^2$ at 100°C) substantially lowers the corrosivity of the semi-stagnant Thin Water Film during cooling down and exposure at ambient temperature (Figures 1b and c). This may hamper generation of sufficient atomic hydrogen to initiate or propagate SSC. In addition, in the case of local breakdown of passivity the above would still occur; the initial phase of passivity breakdown is expected to immediately result in a steep increase of the iron cation content and of the pH in the Thin Water Film, thus stimulating re-passivation. Moreover, the effective cathodic surface in Thin Water Film exposure is very small, which would again tend to stifle corrosion.

Altogether, it is expected that the actual field exposure, i.e. a Thin Water Film, is much less corrosive than immersion in bulk solution, which is applied in conventional standard test methods for SSC. To obtain more insight, the actual field exposure was modelled to quantify changes in pH and thus better understand the corrosivity of the Thin Water Film.

MODELLING THE THIN WATER FILM

A theoretical analysis was undertaken to support the development of the experimental Thin Water Film Test. This work yielded a (perfectly mixed) model for the transient evolution of water chemistry for small water droplets in contact with passively corroding steel and the gaseous environment. The motivation, theoretical basis and results of this model are discussed here.

The amount of hanging water on a steel surface can be quantified as the equivalent film thickness, δ_w , for the hypothetical case where the water forms a uniform film on a plane surface. This film thickness depends on the water condensation rate and run-off rate. To determine the upward transport of water by convection, an analogy was drawn with known convective heat transport in a long vertical pipe. Next, it was assumed that all water carried upward condenses in the top part of the well. Finally, water run-off and corresponding film thickness were estimated based on falling film fluid dynamics⁹. Having used a conservative approach in the above steps, a thicker film implying a more corrosive environment, a value $\delta_w \approx 40 \mu\text{m}$ for hanging water on the steels in question is considered representative⁽¹⁾. Depending on the wettability and microstructure of the surface, the Thin Water Film may be present in practice as a true thin film, or as droplets. Since the expected surface roughness of the inner surface of the tubular (a few tens of μm) is similar to the measured equivalent film thickness, it is expected that a continuous film will

(1) This is based on experimental data. Wetting tests with formation water and condensate were carried out by the authors on tubular sections.

not be stable: the underlying surface would not resemble a plane surface at the length scale of the film thickness. Surface roughness also provides nucleation sites for droplets under condensing conditions. We therefore consider the theory for isolated water droplets, which are assumed to remain mechanically stable for at least several hours. Again, the assumption of stagnant droplets rather than a film is conservative because of their larger (local) thickness and lack of significant run-off.

A preliminary three-dimensional model of flow, mass transport and heat transport in a hemispherical water droplet was undertaken (not reported here). This analysis suggested that dissolved species in droplets of radius ≤ 1 mm can be considered well mixed on timescales exceeding 1 h, at 20 °C static temperature. Considering that timescales of at least several hours are considered relevant by comparison to the proposed Thin Water Film test duration, as well as compared to the no-touch time in the field, a perfectly mixed chemical model was considered to be a suitable representation.

In order to emphasize the most important features of the transient water droplet chemistry, 13Cr steel was assumed, which contains only Fe and Cr (87:13 by mass). The following chemical system is included in the droplet model:

- pre-existing salt concentration (Na^+ and Cl^-) at 100 g L^{-1}
- equilibrium dissolution of CO_2 and H_2S gases
- equilibrium hydration of $\text{CO}_2(\text{aq})$ to $\text{H}_2\text{CO}_3(\text{aq})$
- equilibrium acid-base reactions of H_2CO_3 , HCO_3^- , CO_3^{2-} , H_2S , SH^- and S^{2-}
- passive corrosion of 13Cr steel at fixed current density, which increases pH by consuming H^+ as a cathodic reactant, and releases metal ions Fe^{2+} and Cr^{3+}
- hydrolysis of Cr^{3+} to $\text{Cr}(\text{OH})^{2+}$
- precipitation of FeS , FeCO_3 , and $\text{Cr}(\text{OH})_3$

Preconcentrated weak acids or bases (such as acetic acid, sodium bicarbonate) that may be present in real or artificial brines were ignored in this study. The presence of mineral bicarbonate would elevate the pH, and so analysis in its absence will probe a lower pH regime, which is considered conservative but not unrealistic in view of the dilution by condensation that leads to reduced alkalinity.

Any replenishment of hanging water through ongoing condensation will lower the pH through reduction of the alkalinity, while the acid gases remain at equilibrium concentrations through continuous dissolution; concurrently, however, replenishment of hanging water also lowers Cl^- concentration through dilution of brine. Due to this ambiguity, we adopt the simplest possible analysis, where water replenishment is ignored to the first approximation, and the droplets are considered static – this is a conservative assumption in terms of predicted Cl^- concentration. The droplet growth rate due to condensation, conservatively estimated as described above, has been assessed as relatively low during the studied timescales¹⁰ and is ignored.

Full equations and input data describing these chemical processes are not described here but supplementary information can be made available on request. The equations were solved using the commercial software COMSOL Multiphysics⁽²⁾ (version 5.4, COMSOL AB, www.comsol.com).

pH transients of an isolated water droplet (radius 0.1 mm) were predicted at static temperature ($T = 20$ °C) for ambient environments at 1 bar and 5 bar absolute pressures. For each absolute pressure case, gas compositions of 10 mbar and 30 mbar H_2S were simulated, with the balance of the gas composition as CO_2 . The results are shown in Figure 2 (over 24 h) and Figure 3 (over 7 d).

(2) Trade name

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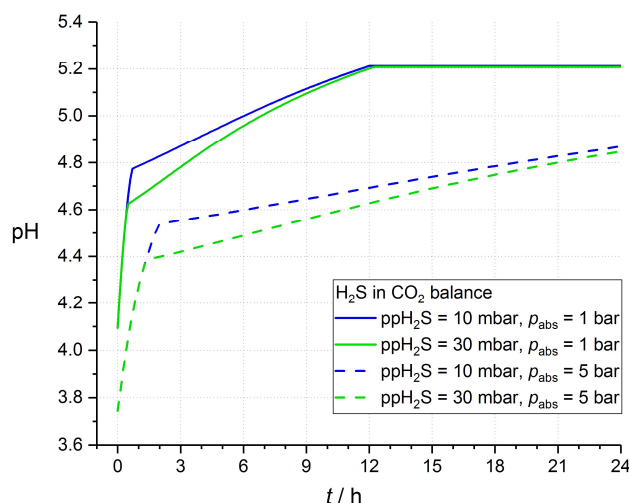


Figure 2: Short-term simulated pH transient of a 0.1 mm radius water droplet in contact with sour environment and passively corroding 13Cr steel

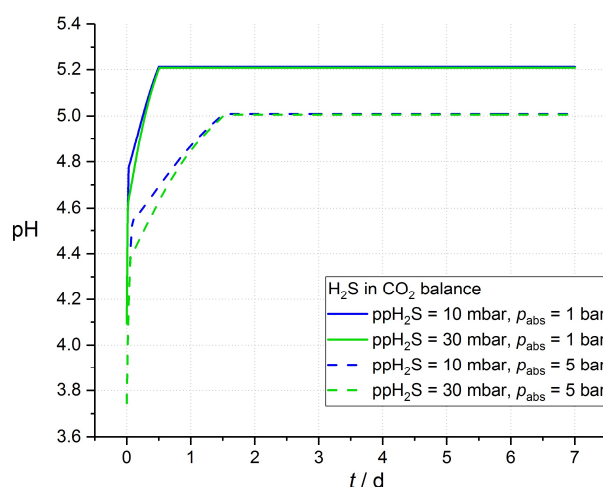


Figure 3: Long-term pH response of a 0.1 mm radius water droplet in contact with sour environment and passively corroding 13Cr steel

The transient droplet chemistry for all conditions studied follows the same qualitative behaviour:

1. Rapid pH rise to a certain value, $\text{pH}_{\text{lim},1}$, attained after a time, $\Delta t_{\text{lim},1}$, not greater than 2 h.
2. Abrupt transition to a regime where the pH continues to rise, but much more slowly.
3. After a much longer time, $\Delta t_{\text{lim},2}$, in the range of 12 h to 2 days, abrupt transition to a regime where the pH becomes constant at a value $\text{pH}_{\text{lim},2}$.

The behavior can be rationalized by consideration of the concentration transients of the individual cations. Through passive corrosion, H^+ in the droplet is initially substituted by Fe^{2+} , and Cr^{3+} , while maintaining overall charge neutrality. This corresponds to a continuous increase in the pH of the solution, as well as an increase in the metal cation concentrations. The transition at $\text{pH}_{\text{lim},1}$ occurs when the concentration of Fe^{2+} reaches the value $c_{\text{Fe,crit,FeS}}$ at which FeS precipitation occurs. This concentration will decrease with

H₂S concentration, and so the transition occurs earlier and at lower pH for higher ppH₂S. Once FeS precipitation commences, protons are only consumed through the proportion of oxidation due to Cr. The transition at pH_{lim,2} occurs once the Cr³⁺ concentration rises to the precipitation concentration for Cr(OH)₃; at this pH, all oxidation products proceed directly to insoluble solids, following which the proton source is net zero so the solution pH does not increase further. The schematic below summarizes these processes (Figure 4).

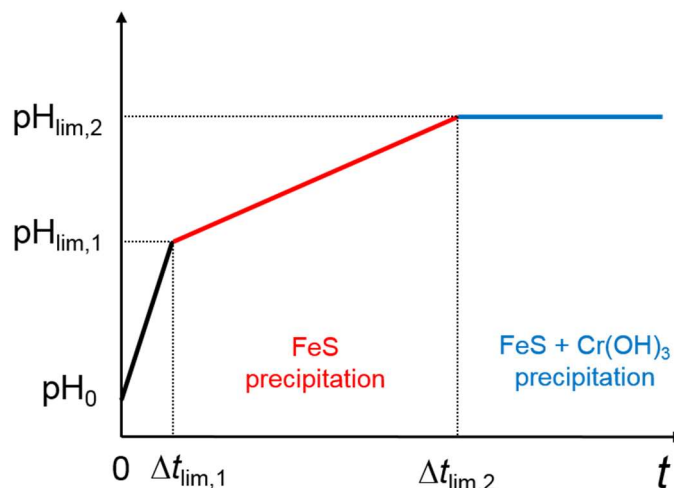
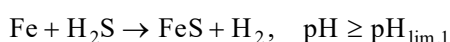
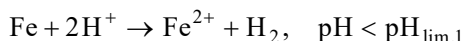


Figure 4: Schematic of precipitation regimes and corresponding pH response for a water droplet in a static environment on 13Cr steel.

The transition at pH_{lim,1} can be understood as the passive corrosion transitioning between two different net reactions:



in which it is obvious that the first reaction process increases pH, while the second has no effect on pH. Note that it has been assumed that the H₂S consumed in the second reaction can be replenished indefinitely through gas dissolution and mixing from the environment.

The first limiting pH, due to FeS precipitation, is encountered after times roughly between 1 h and 2 h for different gas compositions. It is proposed that this limiting pH offers a suitable conservative estimate of hanging water pH under service environments in the studied range (ppCO₂ from 1 bar to 5 bar and ppH₂S from 10 mbar to 30 mbar). The limiting pH is lowered both by increased ppCO₂, due to acidification of the solution, and by increased ppH₂S, due to the greater sulphide concentration and hence lower solubility limit of Fe²⁺ at the onset of precipitation.

The predictions of this theoretical work are consistent with the postulated mechanism of pH increase in the Thin Water Film, driven by passive corrosion in chemically isolated small droplets. This pH rise is found to be limited, however, by precipitation mechanisms where the Fe and Cr convert under oxidation to insoluble products such as FeS and Cr(OH)₃. Once the solubility product of these species is exceeded, the passive corrosion processes become proton-neutral. Higher ppH₂S lowers the limiting pH, since precipitation of FeS (and implicitly NiS, in S13Cr) occurs more readily. Consequently, the onset pH for FeS precipitation is a suitable conservative predictor of the pH of hanging water at ambient temperature.