PETROBRAS REQUIREMENTS FOR SOUR SERVICE SUBSEA PIPELINES

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Abstract

Oil and gas exploration in the pre-salt area demands knowledge of the corrosive properties of the materials before they are selected for the subsequent production, processing and transportation systems. These materials need to be resistant to a variety of environmental conditions such as high concentrations of H_2S and CO_2 gases, which are derived either from the hydrocarbons produced from the reservoirs or generated through the biogenic acidification of the blocks. Petrobras requires material qualification for its projects in sour service, meeting the requirements of relevant DNV, NACE and ISO standards. This paper will present a general view of sour service requirements utilized by Petrobras to meet cost and safety needs.

Introduction

Subsea oil and gas exploration has developed considerably in the last few decades. In almost 20 years, offshore exploration and production has advanced from approximately 400 meters of water depth in the beginning of the 1990s to about 2500 meters since 2010. The challenges imposed by such harsh, deep sea conditions become critical when linked to the actual conditions of the reservoir in terms of corrosion severity of the produced fluids.

Of great interest regarding large reserves of good quality oil is the pre-salt area; a geological layer beneath subsequent deposition of salt, which presents challenges regarding drilling through thick layers of rock and salt, under a great depth of water. Current ultra-deep water reservoirs in the pre-salt area generally have small amounts of H_2S and large amounts of CO_2 gases diluted in the oil and gas production flow; these gases can induce different damage mechanisms in the exploration and production systems such as: Hydrogen-induced Cracking (HIC), Sulfide Stress Corrosion Cracking (SSCC or SSC), generalized corrosion and Stress-oriented Hydrogen-induced Cracking (SOHIC).

Exploration and production systems consist of various equipment and subsystems, such as production system risers, exportation system risers, top side installations (primary treatment units, dehydration units, H_2S and CO_2 removal units), and production and exportation pipelines. When the presence of H_2S is indicated in the transported fluids, the entire offshore system shall be designed to be resistant to sour service conditions. Besides the flow properties, operating conditions, such as *shutdowns* and *upsets*, shall be taken into account and all equipment and related facilities shall be designed to withstand the sour conditions without failure. In this scenario, development of new materials and proper material selection are very important to the service performance of the offshore system.

In this paper general aspects of sour service will be discussed. International standards requirements will be presented as well as Petrobras requirements, based on field conditions and internal solutions related to this subject.

International Requirements for Sour Service Environments

For sour service conditions, the majority of the international standards for design and construction of new facilities and/or pipelines shall meet the requirements of standard ISO 15156. This international standard is divided into three main chapters:

- ISO 15156-1:2009: General principles for selection of crack-resistant materials;
- ISO 15156-2:2009: Crack-resistant carbon and low-alloy steels, and the use of cast irons;
- ISO 15156-3:2009: Crack-resistant CRAs (Corrosion-resistant Alloys) and other alloys.

Carbon and low-alloy carbon steels are the most important materials utilized in subsea systems and in equipment from casing to export pipelines. Primary treatment systems have a large amount of equipment and many subsystems where these materials are in operation. However, depending on the produced fluid condition, other specialized materials may be necessary to withstand the corrosion severity of the fluid.

Figure 1 summarizes the essential aspects of sour service material selection according to standard ISO 15156-2:2009. This graph is divided into four regions (0 to 3), which represent the classes corresponding to the sour service severity that the material must be able to withstand.

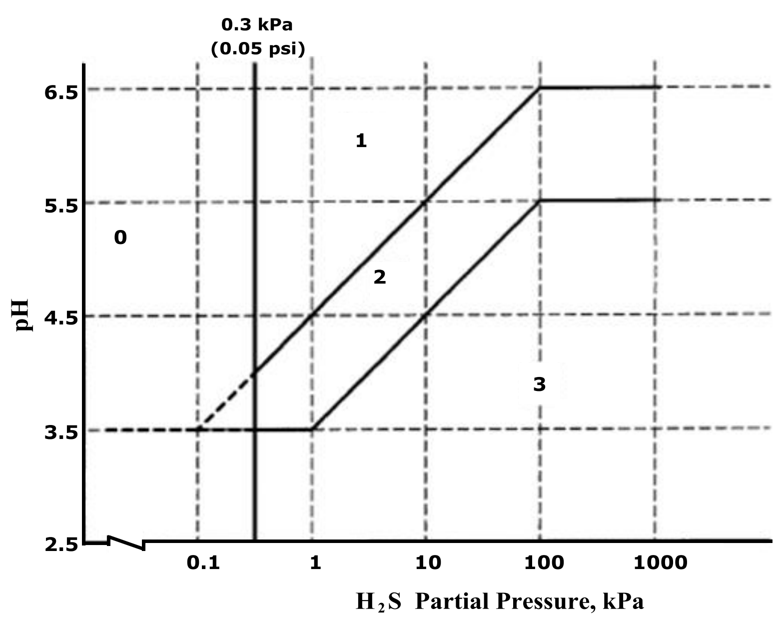

Figure 1. Severity of sour environment according to ISO 15156-2 [1].

Each region of Figure 1 specifies the sour condition by which the material shall be qualified (or shall be resistant) with regard to SSCC and each specific condition depends on the H_2S partial pressure and pH level of the fluid (or solution). For qualification purpose (conservative assumption), Class 3, the most severe condition, is generally adopted for all new materials.

The standard also states that metallurgical properties can affect performance in H_2S-containing environments. Such properties can be linked to each other and include chemical composition, method of manufacture, product form, strength, hardness, amount of cold work, heat-treatment condition and microstructure.

As an example, for production quality control, the ISO standard demands hardness control of the base material and, when required, of the weld zones. However, from a conservative point of view, corrosion tests (for qualification and sometimes production) are more reliable, although they can present scattered results. Control of chemical composition and manufacturing parameters are also factors needed to assure quality.

Petrobras Field Conditions

Petrobras field conditions in the pre-salt area and some design assumptions are summarized below:

- Typical Design for pre-salt exporting pipelines:
  - H_2S concentration up to 34 ppm (considering upsets);
  - Pressure up to 3600 psia (250 kgf/cm²);
  - Expected pH (in condensation): 3 to 6;
  - Up to 4% CO_2, at a temperature of 4 °C;
  - Fe^{2+} saturation is not considered.

Such conditions of high pressure and expected H_2S concentration combined with low pH gives an expected H_2S partial pressure of about 0.12 psia (0.83 kPa). Figure 2 presents this ‘in-house’ condition as a blue point and it is classified as *slightly sour*, according to the standard. However, the standard test qualifications demand testing at lower pH conditions and higher H_2S saturation, as indicated also in Figure 2 (red rectangle). As an example, for qualification of sour service pipeline material according to the DNV-OS-F101, the following requirements are stipulated:

- For H_2S partial pressure <0.05 psia: sweet material and no qualification is required;
- For H_2S partial pressure ≥ 0.05 psia: material qualification is required according to supplementary requirement ‘S’ (sour service).

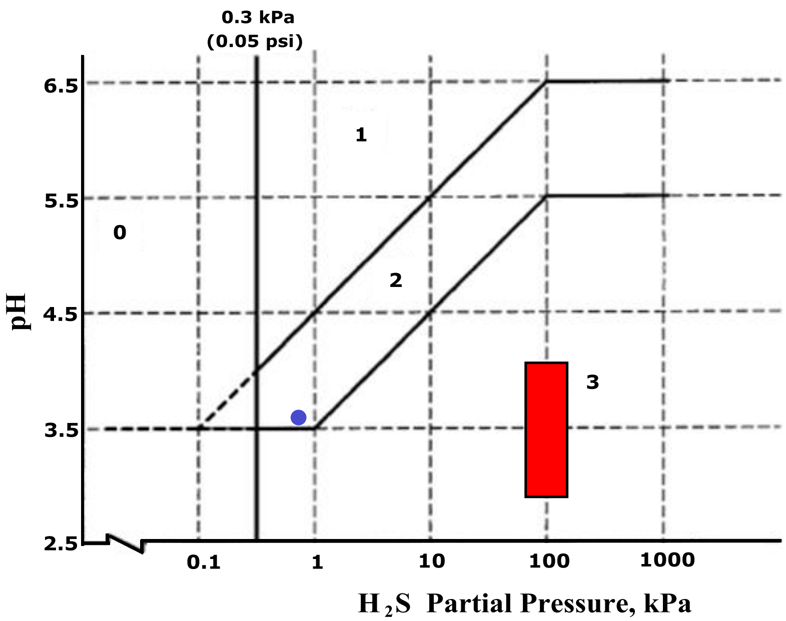

Figure 2. Severity of sour environments according to ISO 15156-2.
The blue dot is the Petrobras' mean fluid condition in terms of pH and H_2S partial pressure and the red rectangle is the standard test requirement [1].

In case of qualification according to DNV requirements, the following steps shall be performed for qualification and production:

- Specific chemical composition for each grade and delivery condition (as welded and after all heat treatment);
- Hardness control:
  - Hardness value <250 HV 10 for base metal, weld metal and heat affected zone;
  - For wall thickness >9.00 mm; maximum hardness value in external cap <275 HV 10;
- HIC corrosion tests shall be performed in Solution A of NACE TM0284 standard with acceptance criteria of CSR ≤2%; CLR ≤15% and CTR ≤5%;
- SSCC tests shall be performed in Solution A NACE TM0177 by methods described in standard NACE TM 0177 or ASTM G39 and acceptance criteria shall be 'absence of cracks' at 10x magnification under microscope examination.

Depending upon the final product and manufacture route it may be permitted to suspend SSCC corrosion tests through hardness control; however, it is not a conservative and reliable way to address sour service corrosion as properties depend significantly on microstructure. Although primary processing systems are available on platforms and process units to avoid or to reduce the H_2S and CO_2 concentration of oil and gas products, events such as upsets or shutdowns of some systems can occur and must be considered when designing equipment.

Petrobras Requirements for Sour Service Environments

Petrobras has internal requirements for sour service resistance, which depend on conditions of the produced fluid and processing unit choices. Four classes of corrosion severity have been defined according to the fluid properties such as pH level and H_2S partial pressure, as described in Table I.

Table I. Classes of Corrosion Severity – Petrobras Internal Requirements

Class of Corrosion Severity	pH Level	pH_2S (kPa)
0 (non sour)	NA	NA
1	4.8 – 5.4	10
2	4.8 – 5.4	100
3	2.7 – 4.0	100

Figure 3 compares these defined classes of corrosion severity to the ISO 15156 classification.

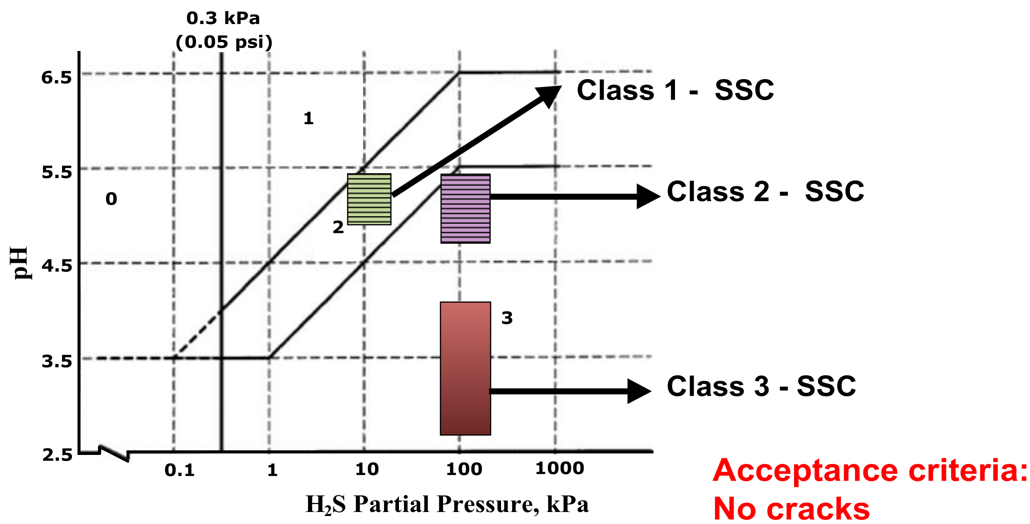

Figure 3. Petrobras class of corrosion severity.

According to the class defined in Table I, SSCC and HIC corrosion tests shall be performed on the steel during the qualification phase in compliance with the acceptance criteria presented in Tables II to IV. The associated maximum hardness of the internal and external surface is also presented:

Table II. SSCC, HIC and Hardness Tests Minimum Requirements
for Seamless and Forged Pipes

Steel class	SSCC			HIC	Maximum hardness on the internal surface
	MPQT		Production	MPQT / Production	
	Required test?	Test quantity	Required test?	Required test?	
0	No	-	No	No	300 HV 10
1	No	-	No	No	250 HV 10
2	No	-	No	No	250 HV 10
3	Yes	3 per pipe for MPQT	No	No	230 HV 10

Table III. SSCC, HIC and Hardness Tests Minimum Requirements
for Longitudinal DSAW Welded Pipes

<table>
<tr><th rowspan="3">Steel class</th><th colspan="3">SSCC</th><th colspan="4">HIC</th><th colspan="4">Maximum hardness</th></tr>
<tr><th colspan="2">MPQT</th><th>Production</th><th colspan="2">MPQT</th><th colspan="2">Production</th><th rowspan="2">Base metal</th><th rowspan="2">Weld metal</th><th rowspan="2">HAZ internal side</th><th rowspan="2">HAZ external side</th></tr>
<tr><th>Required test?</th><th>Test quantity</th><th>Required test?</th><th>Required test?</th><th>Test quantity</th><th>Required test?</th><th>Frequency</th></tr>
<tr><td>0</td><td>No</td><td>-</td><td>No</td><td>No</td><td>-</td><td>No</td><td>-</td><td>250 HV 10</td><td>270 HV 10</td><td>270 HV 10</td><td>300 HV 10</td></tr>
<tr><td>1</td><td>Yes</td><td rowspan="3">6 test pieces per pipe for MPQT</td><td>No</td><td>Yes</td><td rowspan="3">3 test pieces per pipe for MPQT</td><td>Yes</td><td rowspan="3">As per Section 118, Chapter 7 of DNV-OS-F101</td><td>250 HV 10</td><td>250 HV 10</td><td>250 HV 10</td><td>275 HV 10</td></tr>
<tr><td>2</td><td>Yes</td><td>No</td><td>Yes</td><td>Yes</td><td>250 HV 10</td><td>250 HV 10</td><td>250 HV 10</td><td>275 HV 10</td></tr>
<tr><td>3</td><td>Yes</td><td>No</td><td>Yes</td><td>Yes</td><td>230 HV 10</td><td>250 HV 10</td><td>250 HV 10</td><td>250 HV 10</td></tr>
</table>

Table IV. SSCC, HIC and Hardness Tests Minimum Requirements for Girth Welds

<table>
<tr><th rowspan="3">Steel class</th><th colspan="5">SSCC</th><th>HIC</th><th colspan="3">Maximum Hardness</th></tr>
<tr><th colspan="2">WPQT (WPS qualification)</th><th colspan="3">Production</th><th>MPQT/Production</th><th rowspan="2">Weld metal</th><th rowspan="2">HAZ internal side</th><th rowspan="2">HAZ external side</th></tr>
<tr><th>Required Test?</th><th>Test quantity</th><th>Required Test?</th><th>Frequency</th><th>Test quantity</th><th>Required Test?</th></tr>
<tr><td>0</td><td>No</td><td>-</td><td>No</td><td>-</td><td>-</td><td>No</td><td>325 HV 10</td><td>325 HV 10</td><td>325 HV 10</td></tr>
<tr><td>1</td><td>Yes</td><td rowspan="3">3 per WPS</td><td>Yes</td><td rowspan="3">As per I-ET-0000.00-6500-200-PSQ-001</td><td rowspan="3">3 per joint for Production test</td><td>No</td><td>300 HV 10</td><td>300 HV 10</td><td>300 HV 10</td></tr>
<tr><td>2</td><td>Yes</td><td>Yes</td><td>No</td><td>270 HV 10</td><td>270 HV 10</td><td>300 HV 10</td></tr>
<tr><td>3</td><td>Yes</td><td>No</td><td>No</td><td>250 HV 10</td><td>250 HV 10</td><td>275 HV 10</td></tr>
</table>

During the Manufacture Procedure Qualification Test (MPQT), SSCC corrosion tests shall be performed on the Base Material (BM) either by the Four Point Bending (FPB) test method described in ASTM G39 or by method A of the standard NACE TM 0177. The corrosion test solution shall be selected according to Table V. The test duration is 720 hours. For Classes 1 and 2, applied loading shall be at least 90% of the Specified Minimum Yield Strength (SMYS) when method A is utilized or 90% of the Actual Yield Strength (AYS) when FPB is utilized. For Class 3, the applied loading shall be at least 80% of the SMYS when method A is utilized or 80% of the AYS when FPB is utilized. The weld seam shall be tested by the FPB test method described in ASTM G39. Corrosion test solutions shall be selected according to Table V. The test duration is 720 hours. For Classes 1 and 2, the applied loading shall be at least 90% of the AYS. For Class 3, the applied loading shall be at least 80% of the AYS. In the case of changes due to the thermomechanical properties required for the pipeline project, the different applied loading will be reported in the Technical Requisition documentation.

Table V. SSCC Tests Solutions

Steel Class	Test Solution
0	NA
1	Solution B of NACE TM 0284 with 10% H_2S (90% CO_2)
2	Solution B of NACE TM 0284
3	Solution A of NACE TM 0177

- Class 1 ⟶ pH_2S = 10 kPa; pH 4.8 – 5.4
- Class 2 ⟶ pH_2S = 100 kPa; pH 4.8 – 5.4
- Class 3 ⟶ pH_2S = 100 kPa; pH 2.7 – 4.0

During the MPQT, HIC corrosion tests shall be performed according to Item I118 and I119 of standard DNV OS F-101 Section 7. During production, HIC tests shall be performed in accordance with Clause I-118 of standard DNV OS F101. HIC test solutions are listed in Table VI and the acceptance criteria are defined in Table VII.

Table VI. HIC Tests Solutions

Steel class	Test solution	
0	NA	
1	Solution B of NACE TM 0284	⟶ pH_2S = 100 kPa; pH 4.8 – 5.4
2	Solution B of NACE TM 0177	⟶ pH_2S = 100 kPa; pH 3.5 – 4.0
3	Solution A of NACE TM 0284	⟶ pH_2S = 100 kPa; pH 2.7 – 4.0

Table VII. HIC Acceptance Criteria

Steel class	CLR (%)	CTR (%)	CSR (%)
0	NA	NA	NA
1	15	3	1
2	15	5	2
3	15	5	2

For $pH_2S \geq 0.05$ psi, Petrobras considers it necessary for material qualification for sour service resistance, ie. HIC and SSCC corrosion test shall be performed.

Tests for different products shall reflect real work conditions and thus specimen removal shall be required to address this. As an example, for evaluation of longitudinal welded linepipes SSCC corrosion susceptibility, both base metal and weld joint shall be tested. The internal weld seam specimen shall be taken as illustrated in Figure 4. For girth weld joints, specimens are removed as depicted in Figure 5, emphasizing that the girth weld root shall be in the as-welded condition. Stress levels during testing shall be based as near as possible on the real condition of loading (maximum predicted design stress).

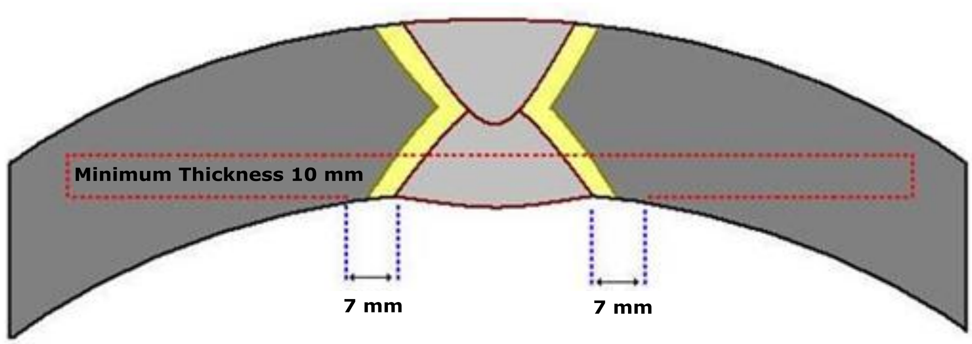

Figure 4. SSCC corrosion test specimen removal for DSAW linepipe weld seam.
Weld toe shall be preserved from machining to evaluate HAZ transition.

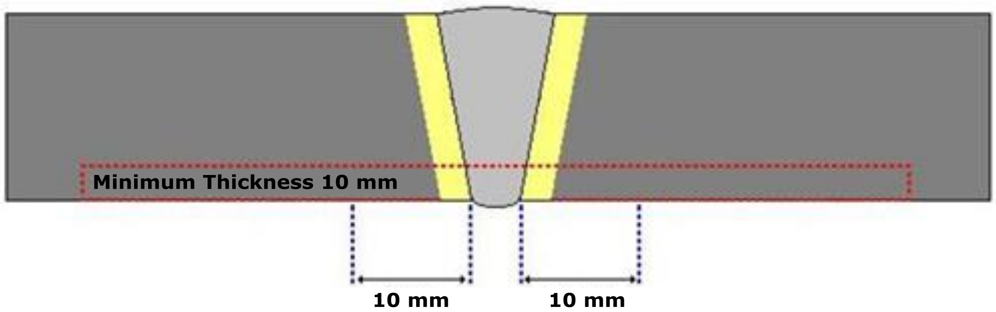

Figure 5. SSCC corrosion test specimen removal for girth weld joints.
Weld toe shall be preserved from machining to evaluate HAZ transition.

Along with corrosion testing, hardness surveys shall be performed during the manufacturing procedure qualification process and these values shall be verified during production. As an example, for pipeline projects, the highest acceptable hardness values depend on the class of corrosion severity (expected pH and H_2S partial pressure), location (internal or external side), base material manufacture route (seamless, SAW pipe, etc.) and weld condition. In this case chemical composition shall be controlled, heat treatment shall be clearly described in the manufacturing procedure qualification record (MPQR) and inspection shall be performed during production.

For HIC resistance, chemical composition control (inclusion shape control and sulfur content) and manufacture route rolling practice has a more important role than hardness.

Conclusions

Harsh corrosion environments require more resistant and sometimes expensive materials. In order to meet cost requirements and increase competitiveness of the national industry, Petrobras has achieved an equilibrium point between safety and costs defining internal criteria for sour service conditions in the face of the recent challenges of the pre-salt discoveries. Based on actual flow properties and the primary processing units employed, Petrobras derived specific test requirements to be performed in selection and application of materials for sour service. All 'in-house' requirements have been established after evaluating the latest worldwide developments and most recent international standard revisions.

Reference

1. ISO 15156-2:2009. Petroleum and Natural Gas Industries - Materials for Use in H_2S-containing Environments in Oil and Gas Production - Part 2: Cracking-resistant Carbon and Low-alloy Steels and the Use of Cast Irons.