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RECENT DEVELOPMENTS IN SOUR SERVICE LINE PIPE STEELS

Jens Schröder[1], Volker Schwinn[2], Andreas Liessem[1],

[1]EUROPIPE GmbH, Wiesenstraße 36, 45473 Mülheim an der Ruhr, Germany
[2]AG der Dillinger Hüttenwerke, Hüttenwerkstraße 16, 66748 Dillingen/Saar, Germany

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Abstract

This paper reviews the evolution of Hydrogen Induced Cracking (HIC) test requirements over the last 30 years for line pipe intended for sour service. As a result of the steadily increasing demands it has become progressively more difficult to fulfil the requirements of the standard testing conditions. As a result of the imposed very severe NACE TM0284 (Solution A) HIC test conditions the overall profile of requirements (strength, toughness) can, in some cases, not be achieved consistently.

Some typical examples for of sour service pipe production at EUROPIPE (formerly Mannesmann) over the past 20 years, and the details of recent production of sour service pipes, in grade X70 in wall thicknesses up to 35 mm, are presented. As a result periodic test failures a Fitness-for-Purpose approach has been applied. By way of example the results of a pipe order, for a special project where the fitness-for-purpose approach has been used to qualify the pipe , will be described.

Introduction

When a low-alloy steel corrodes in an aqueous solution containing hydrogen sulphide (H_2S) it may suffer hydrogen-assisted damage. Instances of hydrogen-assisted damage to steel pipe in the forms of stress corrosion cracks, internal cracks and surface blisters have been reported [1-4] ever since the production of wet natural gas containing H_2S began. Natural gas containing H_2S and CO_2 is generally referred to as "sour gas". The NACE Material Requirements Standard [5] defines "sour environments as fluids containing water as a liquid and hydrogen sulphide (H_2S) at a partial pressure > 0.05 psi (0.0035 bar) and states that they may cause sulphide stress cracking (SSC) of susceptible steels".

After the occurrence of ruptures in a new gas transmission pipeline in the Persian Gulf in 1972 [6] and in three gas transmission pipelines in Saudi Arabia in 1974 [7], researchers were successful in generating hydrogen-induced surface blisters and internal cracks in laboratory specimens subjected to no external load [8], thereby establishing the crucial step of crack development involved in the failures of the above-mentioned pipelines. Thereafter more than 50 papers [e.g. 9-11] were published within a short period of time approximately 5 years, between 1974 and 1980 [6]. The term hydrogen induced, (stepwise) cracking (HIC) has been used to describe this phenomenon [9].

Production of Plates and Pipes

The metallurgically relevant production stages of steels intended for sour service are aimed at measures to avoid crack initiation as well as propagation. Such measures can be defined in terms of non-metallic inclusions (amount, distribution and shape), the solidification structure of the slabs and microstructural constituents including precipitation. To achieve the objectives the producer must have qualified staff, efficient plant installations and suitable control and instrumentation systems for all the relevant process stages. Beginning with defined steel compositions, and metallurgical mechanisms which permit the achievement of the required mechanical and technological properties (including weldability and fabricability) must be activated in a range of different process steps. Furthermore the whole series of systematic processing stages must be applied in a defined and repeatable manner, in order to produce plates consistently.

In the steel plant the production of such high quality steels with very low sulphur and oxygen contents is achieved by secondary metallurgical processing of liquid steel in a vacuum tank degasser and by continuous casting on a vertical caster [12].

Starting with the defined in steel composition, the required microstructure, and consequently properties are achieved by the application of TMCP (Thermo-Mechanical Control Process) practices incorporating special time and temperature sequences. This incorporates reheating of the slab to specific temperatures, rolling to successive thicknesses with specific reductions at prescribed temperatures interrupted by appropriate cooling periods. Cooling after finish rolling is performed by water to specific final cooling temperature (followed by cooling in ambient air) at specific cooling rates.

At the large-diameter pipe mill the plates are formed into pipes using the UOE process. The multi-wire submerged-arc process is used to deposit the two-pass longitudinal seam weld. These processes allow high quality and good production consistency.

Data on Production of Pipe

In the following section line pipe production is reviewed on the basis of line pipe orders executed over the past years. The development of line pipe steels for sour service has been greatly governed by market trends.

A list of major orders for the sour service pipe produced by EUROPIPE (formerly Mannesmann) up to 2005 is presented in Table I. The list clearly illustrates the continuous changes that have occurred in the market requirements by material grade, wall thickness and HIC resistance as a result of steady increases in operating pressures and/or water depths. In total we have supplied more than 3 million tons of line pipes for sour service in material grades up to API X70 and wall thicknesses up to 41 mm.

Table 1. Chronological development of the requirements for HIC resistant steel pipe (only major projects)

Year	Pipe Geometry (OD x WT)	Grade	Medium	Test Solution pH
1981	30" x 27.3 mm	X60	Gas	5
1984	28" x 14.3 mm	X60	Gas	3
1985	36" x 20.6 mm	X60	Gas	3
1986	30" x 34.0 mm	X60	Gas	5
1987	30" x 30.3 mm	X65	Gas	5
1991	36" x 28.4 - 33.9 mm	X65	Gas	3
1993	42" x 28.0 - 39.7 mm	X60	Gas	5
1994	32" x 22.2 - 31.1 mm	X65	Gas	3
1998	24" x 14,1 - 22,1 mm	X65	Gas	3
	40" ID x 29.8 - 37.9 mm	X65 slightly sour	Gas	3 / 0.1 bar H_2S
2000	48“ x 19.8 mm	X60	Oil	3
2002	36“ ID 27.2 – 33.1 mm	X65	Gas	3
	32“ x 22.2 – 28.6 mm	X65	Gas	3
	42“ x 17.5 mm	X60	Oil	3
	30“ x 20.6 – 27.0 mm	X65	Oil	3
2003	28“ x 21.6 – 25.7 mm	X65	Gas	3
	32“ x 22.2 – 28.8 mm	X65	Gas	3
2004	36“ ID x 27.2 – 29.5 mm	X65	Gas	3
	36“ x 16.3 mm	X70	Gas	5
	42“ x 34.3 mm	X70	Gas	5
2005	48“ x 34.3 – 36.3 mm	X65	Gas	3
	32“ x 20.6 mm	X65	Gas	3

Table 2 shows the results of 135,000 t of production pipe for the construction of an offshore gas transmission pipeline. The mechanical properties are described in Table 2a by means of average values for specimens orientated transverse to the rolling direction. The requirements for API Grade X65 pipe were comfortably met. The most important requirements for the chemical composition of HIC resistant steel are low concentrations of carbon, manganese and sulphur. As Table 2b reveals these requirements have been strictly observed in the chemical composition of the pipe used for this X65 offshore project. Besides the low carbon and manganese contents, the steel has been microalloyed with vanadium and niobium, which were added to meet the requirements for mechanical properties. The HIC test results for this order are given in Table 2c. It must be pointed out, that the severe sour service requirements for this order could be only be met by using extraordinary precautions during steel making, casting and plate rolling. Under the standard test conditions, according to NACE TM02-84 [13] Solution A (pH 3 & 1 bar H_2S), the specified acceptance criteria are reliably fulfilled.

Table 2a-c. Results for production of 135,000 t of 36" ID x 27.2 - 33.1 mm WT pipes in Grade X65 intended for sour service (pH 3)

Table 2a. Mechanical Properties

Mechanical Properties	**Mean Value**
Yield strength $R_{t0.5}$ [MPa]	480
Tensile strength R_m [MPa]	564
Y/T ratio	0.86
Elongation A2” [%]	50.0
DWTT @ 0°C [% SA]	89
CVN Toughness @-10°C	
Weld metal [J]	175
FL [J]	422
FL + 2 [J]	410
Base metal [J]	433

Table 2b. Mean Chemical Composition (weight %)

C	**Si**	**P max.**	**S max.**
0.04	0.28	0.015	0.0015
Mn	**others**	**CE(IIW)**	**Pcm**
1.38	Nb, V	0.33	0.13

Table 2c. HIC Test Results

Specification Requirements		Results on Pipe
Test Condition	Acceptance Criteria	Base + Weld Metal
pH 3 & 1 bar H_2S	CTR: ≤ 1.5 % CLR: ≤ 10 % CSR: ≤ 1 %	CTR ≤ 1.2 % CLR ≤5 % for 90 % CSR ≤ 0.5 %

Results for X70 Pipes

In order to make the step from heavy wall Grade X65 pipe to heavy wall API Grade X70 pipe, two different approaches have been developed and applied for a wall thickness of 30 mm. The consideration of increasing carbon and manganese contents to improve the strength of the steel was abandoned, because these elements enhance centerline segregation, thereby causing a deterioration in HIC resistance of the steel.

The first approach to increase the strength of the steel was aimed at the distribution and type of microstructural constituents, and at achieving additional solid solution hardening. The classic composition of NbV-type steel, used for Grade X65 pipe, was modified by adding or increasing the concentrations of Cu, Ni, Cr and Mo. This concept results in a carbon equivalent according to IIW of 0.39.

Another approach was based on increasing the niobium concentration and adding titanium to the steel. The niobium content is increased to have higher amounts of niobium in solid solution in the gamma-region, since it retards the gamma-to-alpha transformation, and to increase the strengthening by precipitation hardening. Titanium was added to bind nitrogen thereby preventing the precipitation of NbCN and making niobium more effective for increasing the strength. This approach leads to a carbon equivalent according to IIW of 0.32. Both practices have already been described in detail for trial production [14]. Both concepts may be utilized to produce pipes with high strength *and* excellent HIC resistance.

Table 3a-c: Results for production of 25,000 t of 36" OD x 16.4 mm WT pipe in API Grade X70 intended for sour service (pH 5)

Table 3a: Typical Chemical Composition (wt%)

C	**Si**	**P max.**	**S max.**
0.039	0.28	0.015	0.0015
Mn	**Others**	**CE(IIW)**	**Pcm**
1.39	Nb, V, Ti	0.31	0.13

Table 3b: Mechanical Properties

Mechanical Properties	Mean Value
Yield strength $R_{t0.5}$ [MPa]	515
Tensile strength R_m [MPa]	596
Y/T	0.86
Elongation A2" [%]	35.2
DWTT @ 0°C [% SA]	100
CVN energy @ -20 °C Base metal [J]	441

Table 3c: HIC Test Results

Specification Requirements		Results on Pipe
Test Condition	Acceptance Criteria	Base +Weld Metal
pH 5	CLR: ≤ 8 % CSR: ≤ 1 %	CLR = 0 % for 90 % CSR = 0.1 % for 90 %

Table 3 shows the results for 25,000 t of pipe production for the construction of an onshore gas transmission pipeline. For this thin wall thickness, a lean NbVTi design was developed using an optimized TMCP rolling practice and accelerated cooling.

In Table 3b the mechanical properties are described by means of average values for specimens orientated transverse to the rolling direction. The requirements for Grade X70 pipe were comfortably met. As can be seen from the data, the requirement for a shear area of 85% minimum in the DWT test at –10°C are met. The Charpy-V-notch impact energy values, measured at -20°C, are above 400 J. Besides the low carbon and manganese contents, the steel features niobium, vanadium and titanium microalloying additions (Table 3a). The HIC test results on this order are given in Table 3c. Under the standard test conditions (according to NACE TM02-84 Solution B (pH 5) [13]) the specified acceptance criteria are reliably fulfilled.

Table 4a-c: Results for production of 6,000 t of 42" OD x 34.3 mm WT offshore pipe in API Grade X70 intended for sour service (pH 5)

Table 4a: Chemical Composition

C	Si	Mn	P	S
0.038	0.30	1.43	0.009	0.0005
Microalloying	**others**	**CE(IIW)**	**Pcm**	
NbTi	**NiCuCrMo**	0.41	0.17	

Table 4b: Mechanical Properties

Mechanical Properties	Mean Value
Yield strength $R_{t0.5}$ [MPa] Transverse	 521
Tensile strength R_m [MPa] Transverse	 619
Y/T Transverse	 0.84
Elongation A2" [%] Transverse	 54.2
DWTT @ 0°C [% SA]	94
CVN energy @ -20 °C Weld metal [J] Base metal [J]	 130 452

Table 4c: HIC Test Results

Specification Requirements		Results on Pipe
Test Condition	Acceptance Criteria	Base metal & weld Metal
pH 5	CLR: ≤ 8 % CSR: ≤ 1 %	CLR ≤ 4% CSR ≤ 0.2 %

The lean chemical composition used for the thinner wall thickness of the onshore part of the pipeline proved not to be sufficient to achieve the strength for heavier wall pipe [14]. Moreover, for a part (approximately 1000 t) of this order pipe mechanical properties was required in the longitudinal direction. Table 4 shows the results for 6,000 t of production pipe for the construction of the offshore portion of the project. In Table 4b the mechanical properties are described by average values for specimens orientated transverse to the rolling direction. The requirements for Grade X70 pipe were readily met in both the longitudinal and transverse direction, in the weld seam, impact energy values in the range of 100 to 160 J were obtained.
Besides the NbTi microalloying elements other alloying have been carefully selected to achieve the required strength level by means of achieving a bainitic microstructure without deterioration of HIC resistance. In comparison with lower grades or thickness, cleanness is of supreme importance. Table 4a illustrates the chemical composition of the pipe used for this X70 offshore project. The HIC test results for this order are given in Table 4c. Under the standard test conditions [according to NACE TM02-84 [13] Solution B (pH 5)] the specified acceptance criteria are reliably fulfilled.

Fitness for Purpose Testing

The main environmental factors for HIC are pH value and promoter (H_2S) concentration, which in laboratory tests can be considered by choice of test solution as well as temperature and hydrogen charging potential. The environmental conditions in a pipeline determine whether or not a chosen pipe material is resistant to cracking in the presence of hydrogen sulfide. The degree of hydrogen-induced damage to the steel depends mainly on the chemical composition, microstructure, degree of purity, nature and magnitude of mechanical stress, temperature and activity of hydrogen in the steel.

The standardized laboratory test according to NACE TM0284-2003 [13] or EFC 16 [15] for determination of HIC resistance produces a relative susceptibility which is established under severe sour test conditions. The fitness of the materials for the intended application (fitness-for-purpose) is guaranteed for in-field environmental conditions when the test is successfully passed. However this approach does not necessarily mean that material that fails the test is not fit-for-purpose under field environments that are less severe than the standardized test conditions. Efforts have been made worldwide to improve the HIC test method and to make it applicable for fitness-for-purpose (FFP) evaluations taking into account the actual service conditions for the material [16].

The first industrial experience with such a fitness-for-purpose approach was in 1998 when Europipe manufactured 200,000 t linepipe of grade X65 for “slightly” sour service for the Black Sea Project. Due to the heavy wall thickness required (29.8 mm up to 37.9 mm), the very lean chemical composition that was typically used for the production of linepipe intended for sour service at the time, could not be used because of the heavy wall thickness. The chemical composition was optimized, for the most part, to fulfil the requirements for mechanical properties. Attention was paid to each and every production step with a view to improving HIC resistance. Different HIC test variants were tried to develop a procedure to give results close to the predicted service conditions which would also be simple to implement. In Figure 1 the HIC-test results are shown for the different test conditions. The details of testing are described in [14]. The HIC index shown on the Y-axis is a measure of the extent of cracking. The higher the value of the index, the larger is the extent of cracking. The pH of the test solution was 3. The data clearly demonstrates the effect of test conditions on the HIC index.

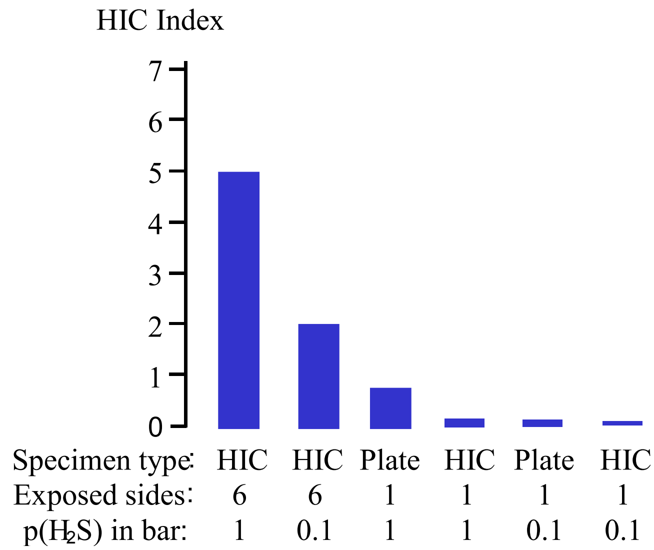

Figure 1. HIC behaviour of grade X65 steel designed for “slightly sour service”

After completion of the above test series the HIC tests during the order were carried out at pH 3 with 0.1 bar partial pressure $p(H_2S)$ and a H_2S-concentration of 250 ppm. This fitness-for-purpose approach eventually enabled the manufacturer to adopt a steel and plate design, which successfully fullfill the requirements with regard to the specific HIC-resistance and mechanical properties.

Based on this experience it was decided to determine a matrix for HIC-sensitivity depending on pH-value and the H_2S-partial pressure. As a reference for such a matrix, the methodology of ISO 15156-2 [17] was applied, which provides a Fitness for Purpose approach for SSC testing, by defining sour service conditions of different severity (Figure 2). The SSC regions in Figure 2 can not be applied directly to HIC testing due to the different failure modes for the two corrosion mechanisms [18-20]. In order to provide a similar approach for HIC, the severity regions must be re-defined. Since ISO 15156-2 does not define a lower threshold for H_2S partial pressure for the HIC test, a re-definition of the severity regions for HIC partial pressures below the SSC threshold of 3.5 mbar was considered for the laboratory tests.

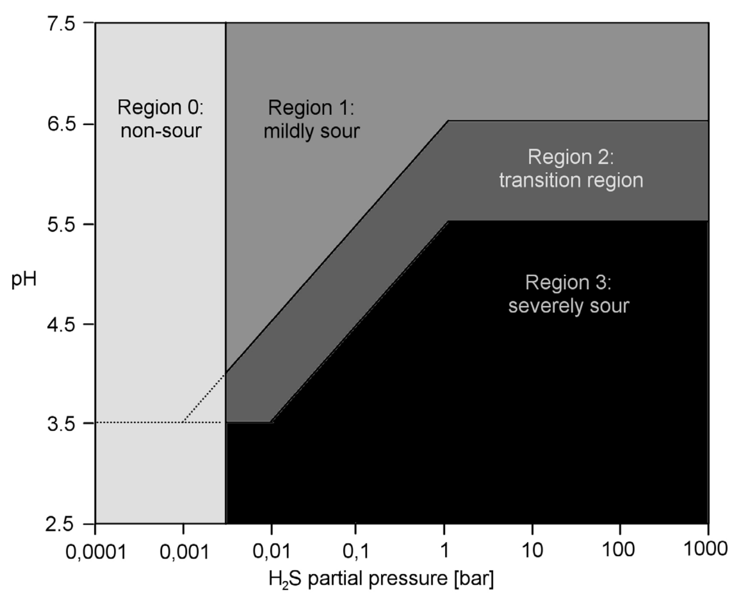

Figure 2: SSC severity regions according to ISO 15156-2

The authors investigated whether high-strength steels, which under TM0284 standard test conditions would not meet common requirements for sour service, could be qualified for mildly sour applications. HIC severity regions were defined with respect to pH and H_2S partial pressure on the basis of a classification of steels according to HIC damage. A comprehensive test programme, with various test conditions was carried out in order to determine the regions of different HIC-severity, similar to the SSC regions of ISO 1516-2 diagram (Figure 2). A detailed description of the applied test conditions, including an extensive discussion of the test results, is published in [21]. The proposed diagram for HIC susceptible X65 steel is given in Figure 3.

From the nodes defined in Figure 3 regions of different HIC attack were defined. As a general tendency the positions of the HIC severity regions are comparable to the ISO 15156 SSC regions. However, the borders of non-sour (Region 0) to slightly-sour (Region 1) and to severely-sour (Region 3), respectively, are shifted to a higher partial pressure of H_2S. From the limited results Region 2 (the transition region) could not be properly defined.

In principle the HIC regions derived from the test results correlate with the SSC regions of ISO 15156-2. However, the borderline between Region 0 (non-sour) and Region 1 (slightly sour) is shifted to a higher H_2S partial pressure. The threshold of H_2S concentration about 0.1 bar is higher than expected. In contrast to these results ISO 15156-2 requires producers to consider HIC tests for applications involving H_2S pressures even below the threshold for SSC (0.0035bar).

The HIC severity diagram provides a useful tool for assessment of steel having limited sour service suitability for application in mildly sour environments. In addition to the influence of pH and H_2S partial pressure on the shape and position of the HIC severity regions, it is recommended that customers consider the influence of chemical composition, grade and manufacturing on each steel.

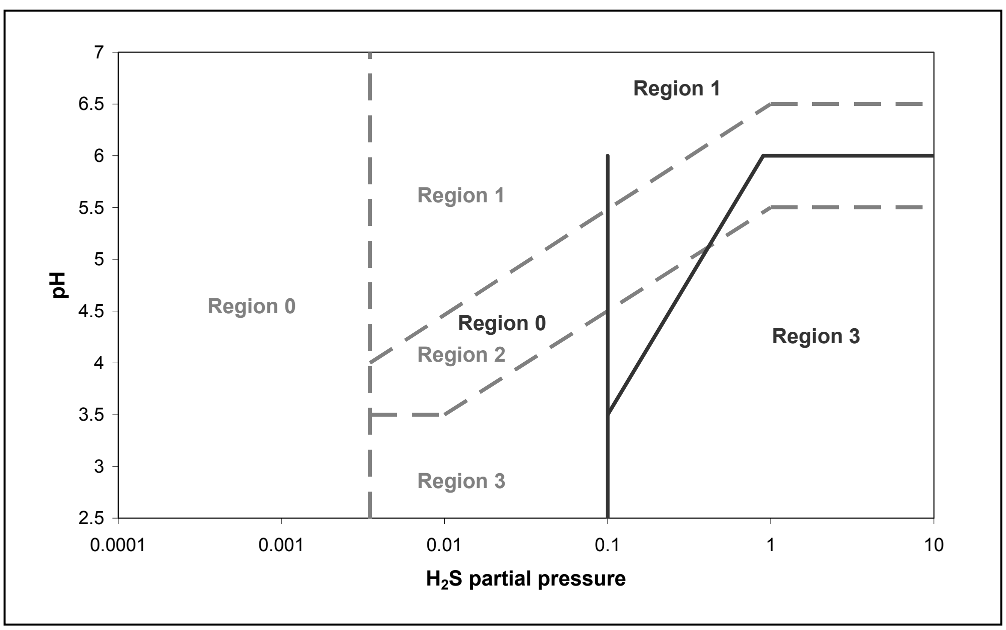

Figure 3. HIC severity regions developed from the test results for a HIC susceptible X65 steel

Summary

This paper addresses the following highlights of EUROPIPE's philosophy for steel making and plate rolling for HIC resistant line pipe:

- The concept in designing line pipe steels with high HIC resistance.
- The production of more than 3 million tonnes of line pipe for sour service in API 5L Grades up to X70 and wall thicknesses up to 41 mm.
- The capability to respond quickly to market demands for special applications by developing fitness-for-purpose approaches.

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