Recent developments of 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;Werkstraße 16, 6763 Dillingen/Saar, Germany

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Abstract

This paper reviews the evolution of Hydrogen Induced Cracking HIC test requirements over nearly 30 years for line pipe intended for sour service. With the steadily increasing demands it becomes progressively more difficult to fulfil the requirements of Standard test conditions. As a result of too severe HIC Standard test conditions the overall profile of requirements (strength, toughness) can in some cases not be consistently achieved.
Furthermore, some typical examples for sour service pipe production at EUROPIPE (formerly Mannesmann) over the past 20 years and the details of a recent production of sour service pipes in grade X70 in wall thicknesses up to 35 mm are presented.
Fit-for-purpose testing methods have been applied consequentially. As an example the results of a pipe order, where the fit-for-purpose approach has been used to qualify the pipe for a Special project, 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 started. Natural gas containing H_2S 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 gas transmission pipeline in the Persian Gulf in 1972 [6] and in three gas transmission pipelines in Saudi Arabia in 1974 [7], researchers have been 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. More than 50 papers [e.g. 9-11] have been published within a short period of approximately 5 years, between 1974 and 1980 [6]. The term hydrogen induced cracking (HIC) has been used to designate this phenomenon [9].

Production of Plates

The metallurgical relevant production stages of steels intended for sour service are aiming on measures to avoid crack initiation as well as propagation. Such measures can be defined in terms of non-metallic inclusions (amount, distribution and shape), solidification structure of the slabs and micro-structural constituents including precipitations. 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. Starting from defined steel compositions, metallurgical mechanisms which permit the achievement of the mechanical and technological properties (including weldability and fabricability) required must be activated in a range of different process steps. Furthermore the whole series of systematic process 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 essentially achieved by secondary metallurgy of liquid steel in a vacuum tank degasser and by continuous casing on a vertical caster [12].
Starting from defined steel composition, the demanded microstructure and consequentially properties are achieved by the application of TMCP (Thermo-Mechanical Control Process) incorporating a special time and temperature sequence. This incorporates the reheating of the slab to specific temperatures, the rolling to successive thicknesses with specific reductions at prescribed temperatures interrupted by cooling periods. The cooling after finishing rolling is performed in water down to specific final cooling temperature (followed by cooling on ambient air) with specific cooling rate.
At the large-diameter pipe mill the plates are formed into pipes using the UOE process. The multi-wire submerged-arc process was used to deposit the two-pass longitudinal seam weld. These processes allow high quality and good production consistency.

Data on Production Pipe

In the following the line pipe production is reviewed on the basis of line pipe orders executed over the past 25 years. The development of line pipe steels for sour service over these years has been greatly governed by market trends.
Table 1 contains a list of major orders for the sour service pipe produced by EUROPIPE (formerly Mannesmann) up to 2005. The list clearly illustrates the continuous changes that have occurred in the market requirements for material grade, wall thickness and HIC resistance as a result of steady increases in operating pressures and/or water depths. In total the manufacturer has supplied more than 3 million tons of line pipes for sour service in material grades up to X70 and wall thickness 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 / 0,1bar 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 on 135,000 t of production pipe for the construction of an offshore gas transmission pipeline. In Table 2a the mechanical properties are described by means of average values for specimens orientated transverse to the rolling direction. The requirements for grade X65 pipe were comfortably met. The 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 features micro-alloying additions in the way of vanadium and niobium, which were made to meet the requirements for the mechanical properties. The HIC test results on this order are given in Table 2c. It has to be pointed out, that the severe sour service requirements for this order could only met by using extraordinary precautions during steel making, casting and plate rolling, respectively. 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: Mechanical Properties

Mechanical Properties	**Mean Value**
Yield strength $R_{t0.5}$ [MPa]	480
Tensile strength R_m [MPa]	564
Y/T [%]	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.**
0.037	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 %

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

RESULTS ON X70 PIPES

In order to make the step from a heavy wall grade X65 pipe on to a heavy wall grade X70 pipe, two different approaches have been developed and applied for a wall thickness of 30 mm. The idea of increasing C and Mn contents to improve the strength of the steel was abandoned, because these elements enhance centerline segregation, thereby deteriorating the HIC resistance of the steel.

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

Another possible approach is based on increasing the Nb concentration and adding Ti to the steel. The Nb content is increased to have higher amounts of Nb in solid solution in the gamma-region as it retards the gamma to alpha transformation and to increase the strengthening by precipitation hardening. Ti was added to bind nitrogen thereby preventing the precipitation of NbCN and making Nb more effective for increasing the strength. This approach leads to a carbon equivalent according IIW of 0.32.

Both practices have been described in detail for trial production [14]. Both concepts are utilizable to produce pipes with high strength and HIC resistance.

Table 3a: Chemical Composition (wt%)

C	**Si**	**Mn**	**Others**
0.039	0.28	1.39	Nb, V, Ti
P max.	**S max.**	**CE(IIW)**	**Pcm**
0.015	0.0015	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 [%]	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 3a-c: Results on production pipes of 25,000 t of 36" OD x 16.4 mm WT Grade X70 intended for sour service pH 5

Table 3 shows the results on 25,000 t of production pipe for the construction of an onshore gas transmission pipeline. For this thin wall thickness a lean NbVTi design could be developed by an optimized TMCP rolling with adapted accelerated cooling. In Table 3a 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 –10°C are met. The Charpy-V-notch impact energy values measured at -20°C are above 400 J. The chemical composition of HIC resistant steel has been strictly observed in the chemical composition of the pipe used for this X70 project (see Table 3b). Besides the low carbon and manganese contents the steel features niobium, vanadium and titanium micro-alloying additions. The HIC test results on this order are given in Table 3c. Under the standard test conditions according to NACE TM02-85 solution [13] B (pH 5) the specified acceptance criteria are reliably fulfilled.

Table 4a: Chemical Composition

C	**Si**	**Mn**	**P**	**S**
0.038	0.30	1.43	0.009	0.0005
Micro-alloying	**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	 84
Elongation A2" [%] Transverse	 54.2
DWTT @ 0°C [% SA]	94
CVN energy @ -20 °C Weld metal [J] Base metal [J]	 130 452

The lean analysis used for the thinner wall thickness of the onshore part of the pipeline proved not to be sufficient for heavier wall [14]. Moreover, for a part (approximately 1000 t) of this pipeline mechanical properties were required in longitudinal direction. Table 4 shows the results on 6,000 t of production pipe for the construction of the offshore part. In Table 4b 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 readily met in longitudinal and transverse direction. In the weld seam impact energy values in the range of 100 to 160 J were measured.
Besides to the NbTi microalloying elements other alloying have been carefully selected to achieve the required strength level by a bainitic microstructure without deterioration of HIC resistance. In comparison with lower grades or thickness cleanness is of supplement importance. Table 4b illustrates the chemical composition of the pipe used for this X70 offshore project. The HIC test results on 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, too.

Table 4c: HIC Test Results

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

Table 4a-c: Results on production pipes of 6,000 t of 42" OD x 34.3 mm WT Grade X70 Offshore intended for sour service pH 5

FIT-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 potential. The environmental conditions in a pipeline decide whether or not a chosen pipe material is resistant to cracking caused by hydrogen sulfide. The degree of hydrogen-induced damage to the steel mainly depends 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 provides relative susceptibility of material which is established under severely 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. This approach does not necessarily mean that material that fails the test is not fit-for-purpose in field environments that are less severe than the standardized test solution. Efforts are being made world-wide to improve the HIC test method and make it applicable for fit-for-purpose (FFP) evaluations taking into account the actual service conditions of a tested material [16].

First industrial experience with such a fit-for-purpose approach was made in 1998 when Europipe manufactured 200,000 t linepipe of grade X65 for “slightly” sour service. Due to the heavy wall thickness required on pipe (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 here because of the heavy wall. 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 of the steel. Different HIC test variants were tried out to work out a procedure that is close to the predicted service conditions and that is not difficult 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 figure clearly demonstrates the effect of test conditions on the HIC index.

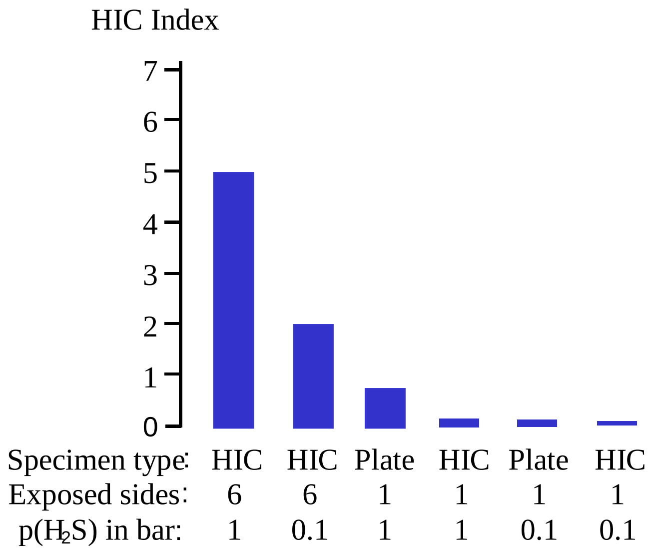

Figure 1: HIC behaviour of grade X65 steel designed for "slightly sour service"

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

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

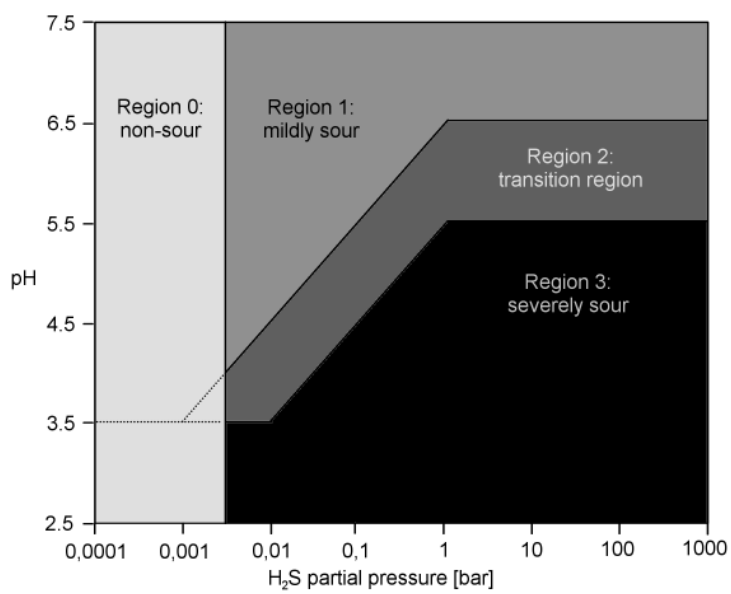

Figure 2: SSC severity regions according to ISO 15156-2

It was 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 aiming for classification of steels on the basis of the HIC damage. A comprehensive test programme with various test conditions has been carried out in order to determine regions of different HIC-severity similar to the SSC regions of ISO 1516-2. 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 different regions of different HIC attack were defined. From the tendency the positions of the HIC severity regions are comparable to the ISO 15156 SSC regions. However, the border of non-sour (Region 0) to slightly-sour (Region 1) and to severely-sour (Region 3), respectively, is shifted to a higher partial pressure of H_2S. From the limited results Region 2 (transition) could not be 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. This threshold of about 0.1 bar H_2S is higher than expected. In contrast to these results ISO 15156-2 requires to consider HIC tests for applications at H_2S pressures even below the threshold for SSC (0.0035bar).

The HIC severity diagram provides a useful tool for assessment of steel with limited sour service suitability for the 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 to check the influence of the tested steel with regard to chemical composition, grade and manufacturing.

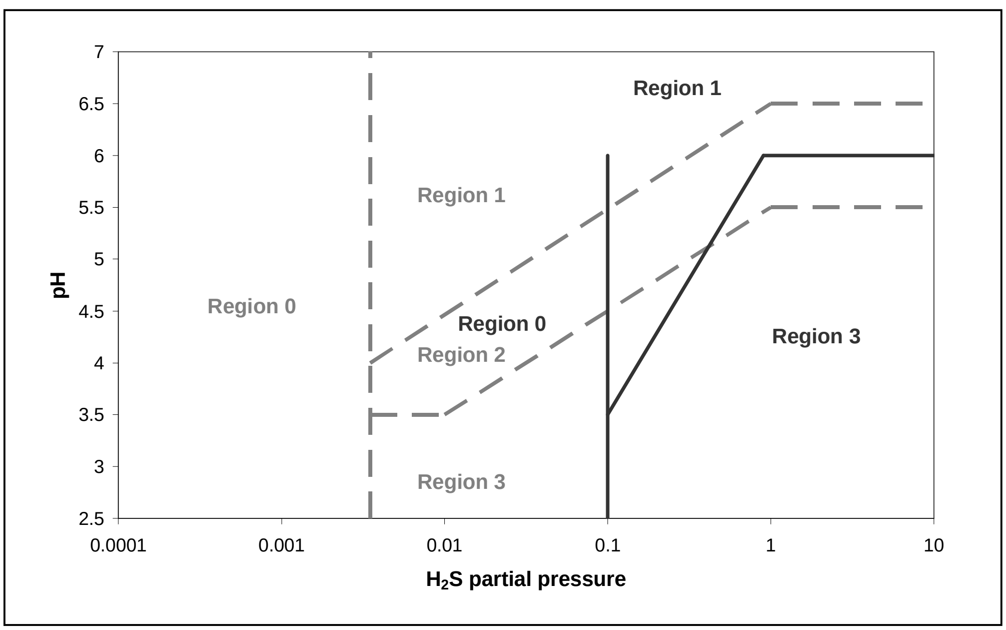

Figure 3**:** HIC severity regions developed from the HIC test results
of HIC susceptible X65 steel

CONCLUSIONS

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

- 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 material grades up to X70 and wall thickness up to 41 mm.

- The capability to respond quickly to the market demands for special applications by developing fit-for-purpose approaches.

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