EUROPIPE'S EXPERIENCE AND DEVELOPMENTS ON PIPE MATERIAL FOR SOUR SERVICE APPLICATIONS

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Abstract

This paper gives an update on Europipe's activities for developing and delivering sour gas resistant pipes. Europipe's experience to provide material for sour service stretches back more than 30 years, combining market requirements with technical feasibilities for steel, plate and pipe production. The use of high strength pipes is an important measure to decrease pipeline costs. For most severe sour conditions, grades were limited to X65 due to technical reasons. Less severe sour gas conditions enable the use of higher strength grades but recent developments showed that solutions are also available for X70 and X80 under most severe sour gas conditions.

Introduction

The ever increasing demand for gas results in the exploration of gas resources that are challenging to pipe material. Transport lines are laid through arctic and/or seismically active regions which result in the selection of more stringent mechanical pipe properties. As the gas resources being explored nowadays could contain a considerable amount of hydrogen sulphide, the material has to be tailored to avoid hydrogen induced cracking (HIC) and sulphide stress corrosion cracking (SSC) by alloy design and cleanness treatment.

Segregation is a principal hydrogen trap which causes HIC damage [1-4]. Due to the segregation tendency of some of the elements present in microalloyed steels for pipelines, grades for severe sour gas were limited in the past to the API 5L X65 specification. However, the latest developments with modern steelmaking practice and plate rolling technique have shown that X70 and even X80 grades can be also produced to resist severe HIC attack at pH levels of 3 and 1bar H_2S pressure.

Since its foundation in 1991 and before that date, as part of Mannesmann group, Europipe has provided pipes for sour service application to customers. The total amount provided since then sums up to 3.2 million tonnes. The material considered was for use in most severe environments as well as for less severe conditions, Table I.

Table I. History of Sour Service Pipes from Europipe

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 40" ID x 29.8 – 37.9 mm	X65 X65 slightly sour	Gas Gas	3 3 / 0.1bar H_2S
2000	48 x 19.8 mm	X60	Oil	3
2002	36" ID x 27.2 – 33.1 mm 32" x 22.2 – 28.6 mm 42" x 17.5 mm 30" x 20.6 – 27.0 mm	X65 X65 X60 X65	Gas Gas Oil Oil	3 3 3 3
2003	28" x 21.6 – 25.7 mm 32" x 22.2 – 28.8 mm	X65 X65	Gas Gas	3 3
2004	36" ID x 27.2 – 29.5 mm 36" x 16.3 mm 42" x 34.3 mm	X65 X70 X70	Gas Gas Gas	3 5 5
2005	48" x 34.3 – 36.3 mm 32" x 20.6 mm	X65 X65	Gas Gas	3 3
2006	42" x 17.5 – 23.8 mm	X65	Gas	3
2007	32" x 20.6 – 28.8 mm 56" x 22.2 – 31.8 mm 32" x 14.3 – 17.5 mm	X65 X65 X65	Gas Gas Gas	3 3 3
2008	32" x 20.6 – 28.8 mm 24" x 29.6 mm	X65 X65	Gas Gas	3 3
2009	48" x 14.3 – 25.4 mm 36" x 12.7 – 15.9 mm	X65 X65	Gas Gas	3 3
2010	32" x 20.6 – 25.4 mm	X65	Gas	3
2011	32" x 20.6 mm	X65	Gas	3

Production of Sour Service Pipes

One of the key factors for mass production of sour service pipes is a proper control of all process steps from steelmaking to the final pipe. The steel works have to provide a lean chemistry, avoiding alloying elements that tend to segregate, thereby giving absorbed hydrogen the chance to recombine and form molecular H_2. Low carbon and low sulphur contents are of major importance.

To control the chemistry, steelmaking practice uses all available measures, as shown in Figure 1. Before, during and after the converter process, desulphurisation methods are used to reduce sulphur content to below 0.001%. The desulphurised heats are calcium treated to bind the remaining sulphur into non-deformable round inclusions. During continuous casting, the control of cleanness is realised by keeping the molten metal isolated from detrimental elements and avoiding significant segregation by applying soft reduction [5].

To achieve the required mechanical properties, thermomechanical controlled processing (TMCP) is applied with accelerated cooling.

The pipe production has also to consider, in terms of sour service application, the forming and welding processes to achieve good results. Hardness in the heat affected zone is not allowed to be above certain levels.

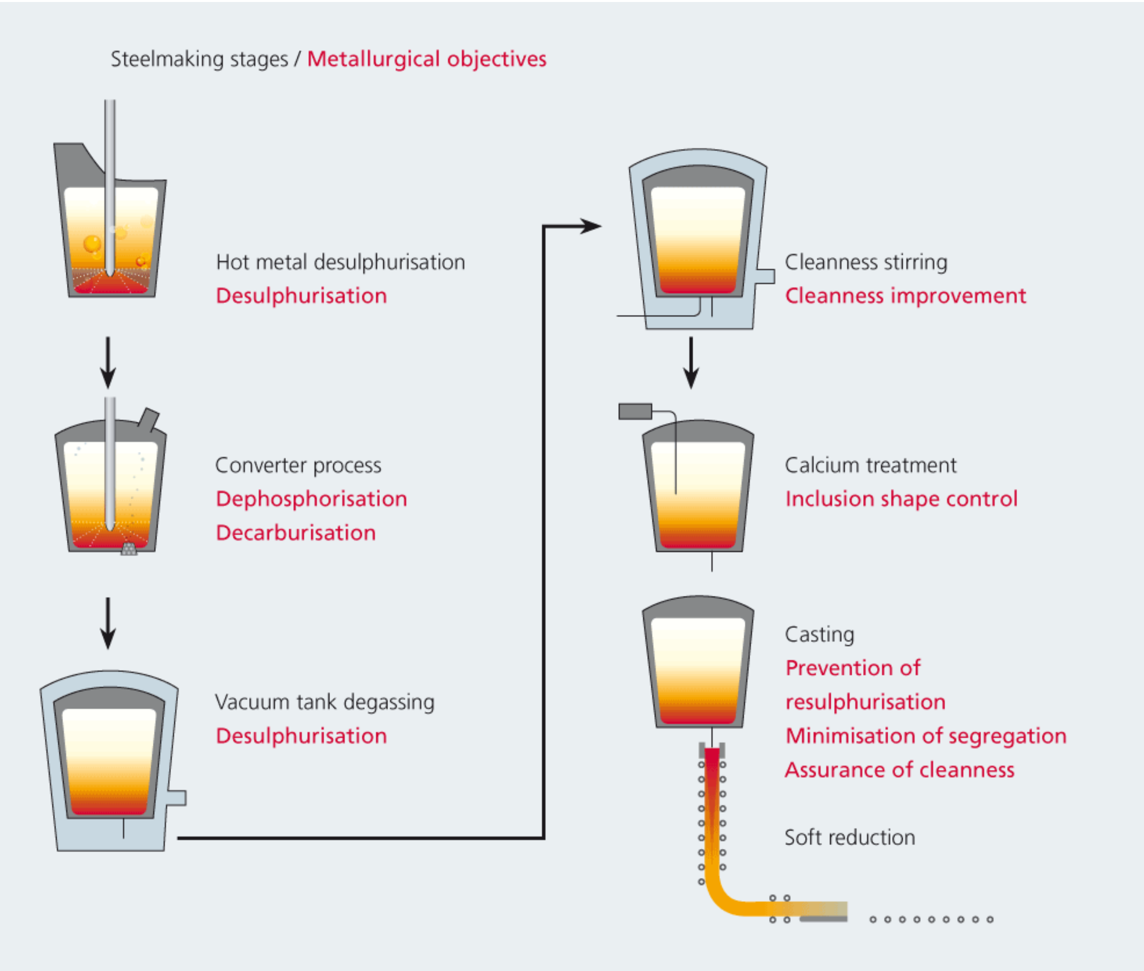

Figure 1. Steelmaking practice recommended for sour service grades.

Production Results

In 2006/2007 EUROPIPE produced 430,000 tonnes of pipes for sour gas application. The X65 pipes had 56" diameter and wall thicknesses were from 22.2 to 31.8 mm. HIC-testing and SSC-testing were performed in Solution A of NACE TM 02 84 [6] and NACE TM 01 77 [7] respectively at pH levels of 3 and a H_2S partial pressure of 1 bar.

Table II summarises the chemistry and the mechanical properties obtained. Nb-Ti alloy design was chosen with a maximum carbon content of 0.05% and some Ni and Cu additions for heavier wall thickness pipes.

Table II. Chemical Composition (wt.%) and Mechanical Properties of X65 Grade with 56" OD x 22.2 – 31.8 mm WT

WT	**C**	**Mn**	**P**	**S**	**Others**	**CE(IIW)**	**Pcm**
22.2 mm	<0.05	<1.46	<0.015	<0.0015	Nb, Ti	<0.33	<0.15
31.8 mm	<0.05	<1.48	<0.015	<0.0011	Cu, Ni, Nb, Ti	<0.33	<0.15

Mechanical Properties	22.2 mm WT	31.8 mm WT
Yield Strength [MPa]	average 485	average 485
Tensile Strength [MPa]	average 575	average 577
YS/TS	average 0.85	average 0.84
Elongation [%]	average 44	average 53
DWT @ -10 °C [% SA]	average 94	average 81
CVN @ -30 °C [J] Base Metal Fusion Line Weld Metal	 average 438 average 408 average 207	 average 434 average 364 average 128

Requirements		**Results Base and Weld Material**	
Test solution	**Acceptance Criteria**	22.2 mm WT	31.8 mm WT
pH 3 1 bar H_2S	CLR ≤15% CTR ≤5% CSR ≤1.5%	CLR <5.3% CTR <1.2% CSR <0.6%	CLR <4.8% CTR <1.5% CSR <0.7%

The results show that the mechanical properties and corrosion properties fulfil the requirements adequately. Grade X65 can be tailored for sour service in a wide range of wall thicknesses and diameters. In a project in 2008, Europipe supplied 20,000 tonnes of Grade X65 sour service pipes with 24" OD x 29.6 mm WT, meeting all requirements of mechanical and corrosion testing in an environment containing pH 3 and 1 bar H_2S .

Fit-for-Sour Service Testing

The selection of carbon steel in H_2S containing environments has been limited by the severe test conditions required of pipe material. For a long time X70 or X80 could not be used because they failed during HIC testing in such conditions. The fit-for-sour service approach considers real conditions in terms of pH and H_2S partial pressure and pipes are tested in a similar solution with a safety margin, Figure 2. In Figure 3, taken from the NACE MR 0175 / ISO 15156-2 standard [8,9], the pH-pH_2S-diagram shows the different severity regions used to define operating conditions under which material selection should be done. Earlier publications [10] have shown that the borderlines of the severity regions for SSC-testing cannot be transferred to HIC testing; such borderlines depend very much on the grades and production processes used.

Europipe has performed HIC-testing of X80 grades under different conditions. The specimens were exposed to the solution for four days and the severity of HIC attack was characterised by the Crack Area Ratio (CAR) on the specimens. Materials with CAR values below 1% were considered resistant to HIC, while CAR values above 10% represented materials with no HIC resistance. Figure 4 shows the results together with the borderlines of the severity diagram from ISO 15156-2. It can be seen that there are sour gas conditions in which the X80 grade material could be used without HIC risk. Testing the steel under specific sour gas conditions enlarges the potential selection of material significantly.

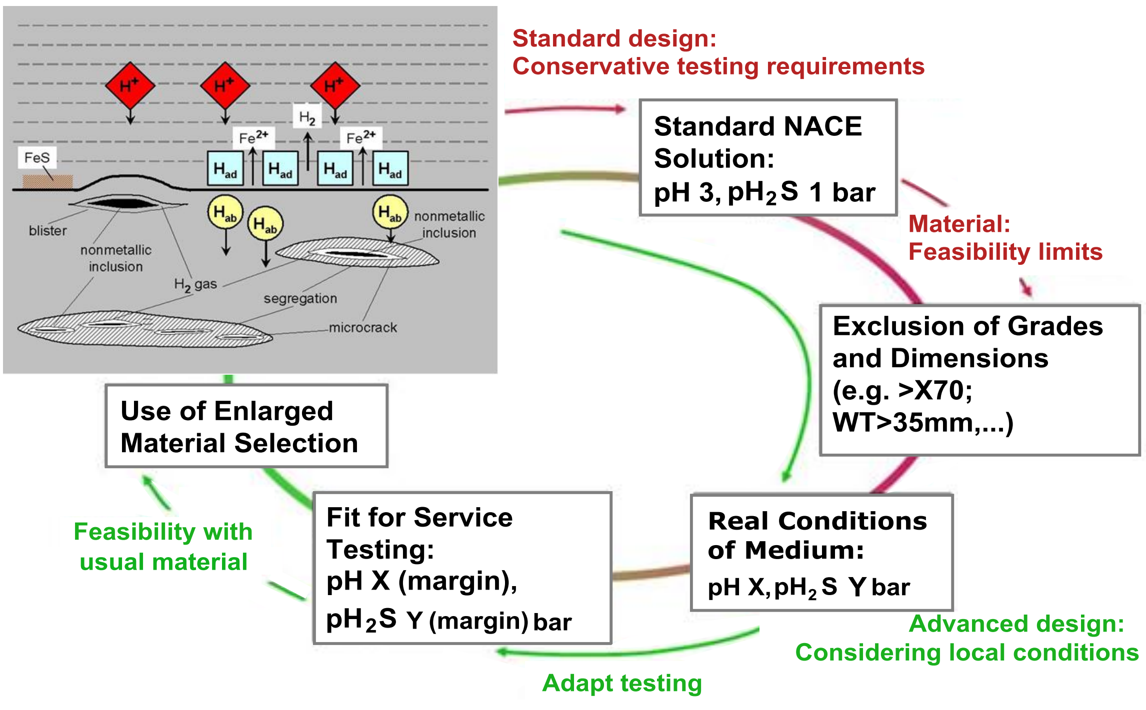

Figure 2. Diagram for fit-for-sour service testing.

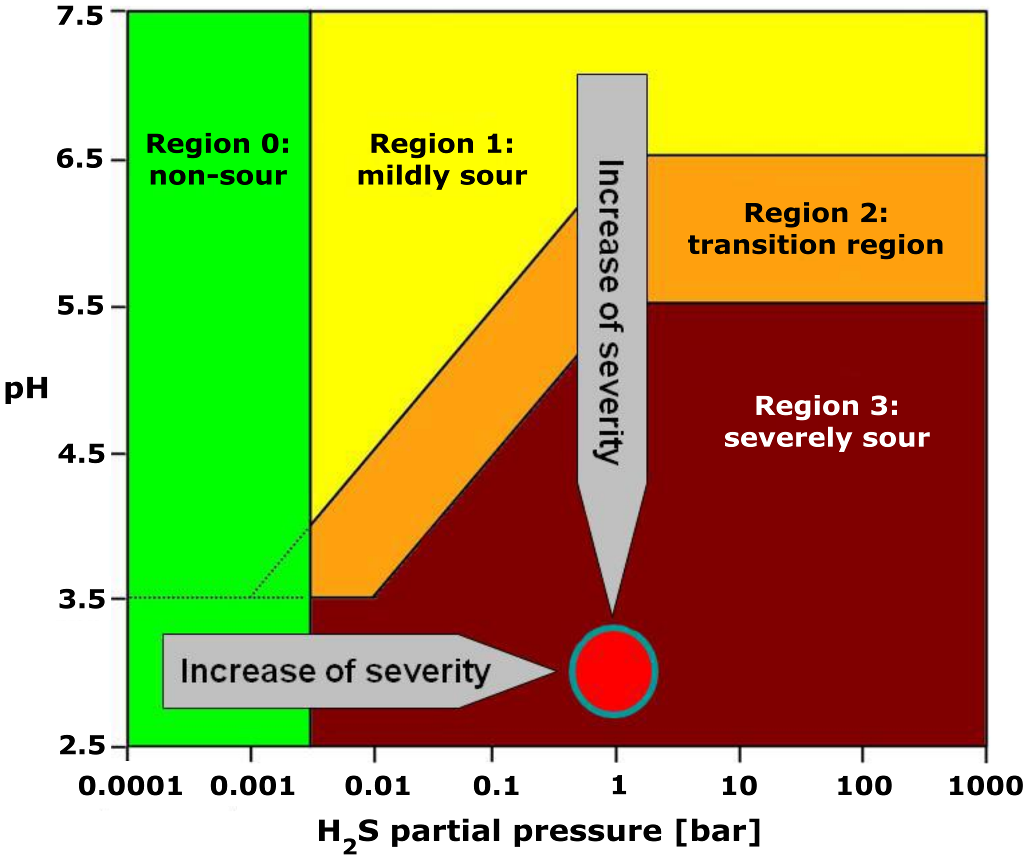

Figure 3. Severity regions according to NACE TM 01 75 / ISO 15156-2 [8,9].

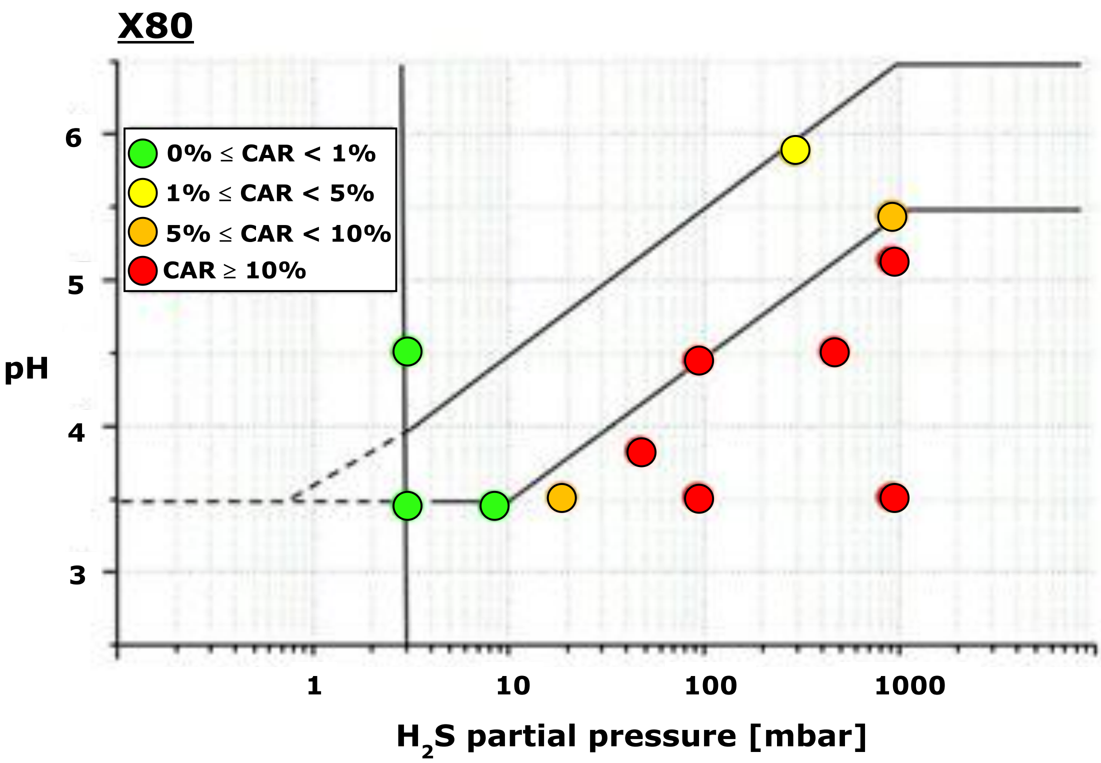

Figure 4. Results for X80 grade for specific sour gas conditions.

Development of X70 and X80 Grades for Sour Gas Application

As there is a demand for higher strength steels for sour service application, the next logical step was to develop X70 and X80 for severe sour gas conditions. For a qualification programme considering pipe material and its girth welds, Europipe produced a number of X70 and X80 sour gas pipes. The main focus was laid on achieving mechanical and corrosion resistance properties of these 20" OD x 19.8 mm WT pipes. The results are shown in Table III.

Table III. Production Results of X70 and X80 of 20" OD x 19.8 mm WT

Grade	**C**	**Mn**	**P**	**S**	**Others**	**CE(IIW)**	**Pcm**
X70	<0.05	>1.5	<0.015	<0.0010	Cu, Ni, Nb, Ti	0.34	0.15
X80	<0.05	>1.5	<0.015	<0.0010	Cu, Ni, Mo, Nb, Ti	0.37	0.17

Mechanical Properties	X70	X80
Yield Strength [MPa]	500	590
Tensile Strength [MPa]	585	692
YS/TS	0.84	0.86
Elongation [%]	45	36
DWT @ -20 °C [% SA]	average 100	average 97.5
CVN @ -30 °C [J] Base Metal Fusion Line Weld Metal	 average 337 average 251 average 209	 average 319 average 105 average 219

Requirements		**Results**	
Test Solution	**Acceptance Criteria**	**Base and Weld Material**	
pH 3 1 bar H_2S	CLR ≤15% CTR ≤5% CSR ≤2%	X70 CLR <3% CTR <0% CSR <0%	X80 CLR <6% CTR <1% CSR <0%

The table reflects clear fulfilment of sour gas requirements in combination with mechanical properties in these grades. Additionally, SSC tests were performed as 4 point-bend-tests which are usual for large diameter pipe corrosion testing. X70 and X80 had good SSC resistance by showing no cracks even in the pH 3 and 1 bar H_2S solution.

Girth welds were produced with a wide range of heat inputs (from about 1.0 kJ/mm to about 3.0 kJ/mm). The tests were successful in terms of corrosion resistance as well as mechanical properties.

Conclusions

The paper demonstrates that there are reliable concepts available to cope with sour gas requirements from the market. X65 sour gas resistant pipes were produced commercially for significant orders meeting the most severe HIC requirements. The fit for sour service approach with testing under realistic corrosion conditions enables the use of grades designed for particular applications which would not be selected according to the most severe conditions specified by the standards. The development of high strength steels, X70 and X80, for severe sour service conditions is proceeding, combining the most modern steelmaking technology with advanced plate rolling and pipe manufacturing technology.

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