DO YOU HAVE THE RIGHT STEEL FOR THIS SOUR SERVICE PIPELINE?*

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Keywords: HIC, Pipeline, Corrosion, Integrity, Hydrogen Sulphide, Hydrogen, NACE, Inclusions, Microstructure, Segregation, Banding, Ca Treatment, pH Value, Diffusion, Composition

Abstract

Hydrogen-induced cracking (HIC), a type of pipeline failure that can occur under sour service conditions, is usually caused by hydrogen atoms that diffuse into steel and recombine at traps (such as elongated inclusions), causing microscopic blisters to form, which subsequently link and propagate. Neither residual nor applied stress is required for HIC to occur. Cracks are usually parallel to the rolling plane. To quantify susceptibility of linepipe steels to HIC and for predicting resistance to HIC in service, two parameters were defined: threshold hydrogen concentration in the steel and threshold pH in the environment. The threshold hydrogen concentration is the diffusible hydrogen concentration in the steel above which the steel cracks within the maximum test duration of 96 hours. The threshold pH is the pH in the environment below which the steel cracks within 96 hours, a test duration specified in the ANSI/NACE Standard TM0284. The study was carried out using unstressed coupons immersed in acidified, buffered, de-aerated saline solutions of pH between 1.1 and 5.9, saturated with H_2S. Quantitative relationships between susceptibility to HIC and steel composition, particularly the inclusion content, were explored. The relative susceptibility of a steel to HIC can be estimated by characterizing the inclusion content.

Introduction

Hydrogen-induced cracking (HIC) is defined as “a type of cracking usually caused by hydrogen atoms that diffuse into steel and recombine at traps (such as elongated inclusions) causing microscopic blisters to form, which subsequently link and propagate; also known as stepwise cracking” [1]. Numerous reviews have been written on HIC [2] and on test methods for evaluating steels for resistance to HIC [3].

In order to achieve resistance to HIC in wet H_2S environments, steels have been developed with low sulphur content, inclusion shape control and uniform microstructures without banding. To obtain further resistance to HIC, control of crystallographic texture and grain boundary distribution is being considered in the development of pipeline steels for use in the most aggressive sour environments [4].

Based on resistance to HIC, steels can be divided into the four types as listed in Table I, ie. conventional steel, low-sulphur conventional steel, HIC-resistant steel and ultra-low-sulphur advanced steel [5].

Table I. Nomenclature of Steels and Resistance to HIC

Type of Steel	**Impurity Levels**	**Process**	**Resistance to HIC**
Conventional Steel (CS)	Moderate to high levels of impurities S ≥0.01 wt.%	Hot rolled or normalized	High susceptibility
Low-Sulphur Conventional Steel (LSCS)	0.003< S <0.010 wt.%	Hot rolled or normalized	High susceptibility
HIC-Resistant Steel (HRS)	S ≤0.002 wt.% May contain Ca for sulphide shape control	Normalized to modify hot-rolled microstructure	Susceptible to HIC under severe wet H_2S conditions
Ultra-Low-Sulphur Advanced Steel (AS)	S <0.002 wt.% Low C equivalent and low C compared to CS of similar strength Ca treatment for sulphide shape control	Thermomechanical controlled processing and/or accelerated cooling. Ferritic or ferritic/bainitic microstructure, little or no banding	High resistance

The model of HIC used in this study is shown in Figure 1. The significant parameters in this model are:

C^H Diffusible hydrogen concentration in the steel;
C^H_0 Diffusible hydrogen concentration at the internal pipe surface;
C^H_{th} Threshold diffusible hydrogen concentration, the highest C^H at which no cracking was observed, ie. at $C^H > C^H_{th}$, cracking was observed.

An additional, environmental, parameter, is pH_{th}, the lowest pH at which no cracking was observed, ie. at $pH < pH_{th}$, HIC was observed.

The objectives of this study were to characterize linepipe steels by determining C^H_{th} and pH_{th} and to correlate these parameters with inclusion content.

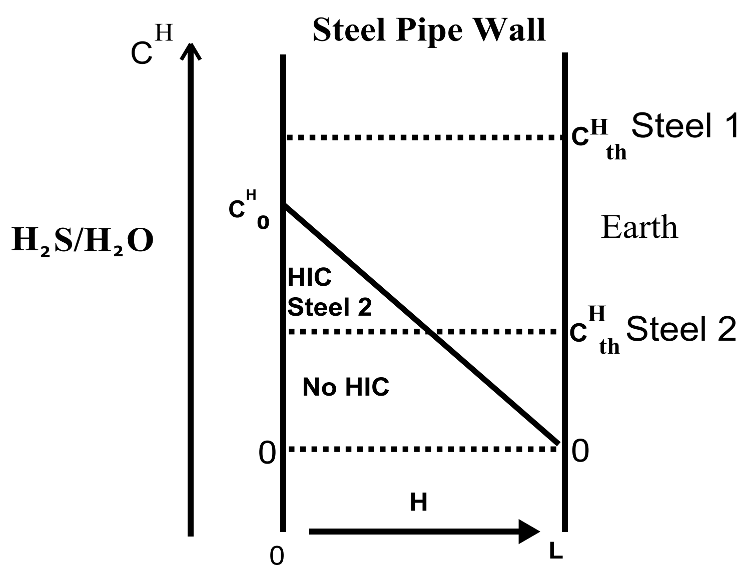

Figure 1. Model indicating significant parameters in occurrence of HIC and criterion for HIC.
C^H - Hydrogen concentration, C^H_0 - Hydrogen concentration at internal pipe surface,
C^H_{th} - Threshold hydrogen concentration above which HIC occurs.
Criterion for HIC: $C^H_0 > C^H_{th}$.

With the parameters illustrated schematically, HIC would be predicted to occur in Steel 2, but not in Steel 1.

Experimental Procedure

The compositions of the steels studied are listed in Table II. Using the terminology in Table I, steels AM-1 and WC-1 would be considered to be conventional steels; G-2 and PC-1 would be low-sulphur conventional steels; CTR-1 would be a HIC-resistant steel and AM-2 and CTR-2 would be ultra-low-sulphur advanced steels.

Table II. Compositions of Steels, wt.%

Steel Code	Grade Strength	C	Mn	P	S	Si	Cu	Ni	Cr	Ca	Nb	Ca/S
AM-1		0.120	0.69	0.006	0.0310	0.008	0.330	0.095	0.17	0.0048	0.005	0.15
AM-2	550	0.080	0.81	0.016	0.0016	0.410	0.011	0.015	0.03	0.0040	0.023	2.50
CTR-1	359/386	0.157	0.85	0.020	0.0010	0.280	0.005	0.020	0.02	0.0072	0.060	7.20
CTR-2	359/386	0.100	0.84	0.018	0.0013	0.175	0.005	0.250	0.03	0.0034	0.020	2.62
G-2	386	0.130	1.09	0.012	0.0084	0.165	0.220	0.070	0.06	0.0110	0.040	1.31
PC-1	359	0.090	0.73	0.013	0.0036	0.200	0.230	0.080	0.06	0.0018	0.005	0.50
WC-1	359	0.105	1.03	0.010	0.0270	0.075	0.200	0.080	0.05	0.0260	0.020	0.96

Coupons 100 mm long × 20 mm wide by wall thickness were cut from parent metal 90° from the weld, with the longitudinal direction parallel to the rolling direction. Coupons were not flattened. The coupons were milled according to ANSI/NACE Standard TM0284 [6].

The four steps in the procedure that was developed for assessing HIC performance were:

1. Charging with hydrogen by immersing coupons in a H_2S-saturated solution of desired pH, ranging from 1.1 to 5.9, for 4 days (96 hours), a test duration specified in the ANSI/NACE Standard TM0284 [6]. The compositions of the solutions that were used are listed in Table III;

2. Measuring the diffusible hydrogen absorbed by immersion in glycerol at 45 °C for 72 hours. The diffusible hydrogen reported was the volume of hydrogen evolved per 100 g of steel after 72 hours;

3. Crack detection using the ultrasonic C-scan;

4. Sectioning the sample to confirm cracking detected using the ultrasonic C-scan.

Table III. Test Solutions

pH	Solution Composition
1.1	5% NaCl, 0.1 N HCl
3.1	5% NaCl, 14.12 g/L potassium hydrogen phthalate, 1.125 g/L HCl
3.4	5% NaCl, 16.88 g/L potassium hydrogen phthalate, 0.63 g/L HCl
3.7	5% NaCl, 18.72 g/L potassium hydrogen phthalate, 0.30 g/L HCl
4.0	5% NaCl, 20.36 g/L potassium hydrogen phthalate, 0.01 g/L HCl
4.3	5% NaCl, 0.75% sodium acetate, 0.5% acetic acid
4.7	5% NaCl, 16.04 g/L potassium hydrogen phthalate, 0.855 g/L NaOH
5.0	5% NaCl, 14.05 g/L potassium hydrogen phthalate, 1.245 g/L NaOH
5.3	5% NaCl, 12.50 g/L potassium hydrogen phthalate, 1.55 g/L NaOH
5.6	5% NaCl, 11.50 g/L potassium hydrogen phthalate, 1.748 g/L NaOH
5.9	5% NaCl, 10.89 g/L potassium hydrogen phthalate, 1.87 g/L NaOH

Samples for metallographic examination were prepared from sections perpendicular to the rolling direction and were examined in the as-polished conditions using optical microscopy. The inclusion content of the steels was characterized using a Leco 2001 Image Analysis System.

Experimental details are further described elsewhere [7-9].

Results and Discussion

Below pH 4, the corrosion rate of steel increases considerably as the pH is further decreased [10]. In this acidic pH range, the corrosion rate also depends on the composition and structure of the steel and increases with both carbon and nitrogen content [11].

The cathodic reaction is reduction of hydrogen ions to hydrogen atoms, ie. $H^+ + e^- \rightarrow H$. Hydrogen sulphide in solution poisons the hydrogen recombination reaction with the result that H enters the metal lattice. At trap sites, the H atoms can recombine, forming H_2 at sufficient pressure to cause blister formation and cracking.

As an example, the data obtained for diffusible hydrogen and cracking in steel AM-1 at pH 4.3, 5.0, and 5.3 are presented in Table IV.

Table IV. Cracking and Hydrogen Analysis Data for AM-1 Steel

pH	**Sample Code**	**Volume H_2 evolved mL (STP)/100 g steel**		**Cracking**
		Actual	**Mean**	
4.3	AM-1-1	6.5	6.7	Yes
	AM-1-2	6.8		Yes
	AM-1-3	6.7		Yes
5.0	AM-1-7	6.0	6.0	Yes
	AM-1-8	6.3		Yes
	AM-1-9	5.6		Yes
5.3	AM-1-4	0.7	1.2	No
	AM-1-5	1.3		No
	AM-1-6	1.5		No

The data on threshold pH and threshold hydrogen concentration for seven steels are listed in Table V. The data on quantitative metallography of inclusions are presented in Table VI. Correlations of threshold hydrogen concentration and threshold pH with the volume fraction of inclusions and with the total length of inclusions are presented in Figures 2 to 5. In general, reduction of inclusion content leads to an increase in threshold hydrogen concentration.

Table V. Data on Threshold pH and Threshold Hydrogen Concentration

Steel	**Threshold pH**	**Threshold Hydrogen Concentration mL (STP)/100 g steel**	**Ca/S**
AM-1	5.3	1.2	0.15
AM-2	<1.1	>2.0	2.50
CTR-1	5.6	0.7	7.2
CTR-2	<1.1	>1.5	2.62
G-2	5.3	0.6	1.31
PC-1	5.3	0.4	0.50
WC-1	5.3	0.3	0.96

Table VI. Quantitative Data on Inclusions in Steels

Steel	Vol.%	Average Size, µm	No./mm^2	Length/area mm/mm^2	C^H_{th}	Ca/S
AM-1	0.209	3.71	1,774	6.5	1.2	0.15
AM-2	0.034	1.41	1,614	2.2	>2.0	2.50
CTR-2	0.042	3.25	278	0.9	>1.5	2.62
G-2	0.338	2.45	5,729	14.1	0.6	1.31
PC-1	0.205	4.96	1,382	6.9	0.4	0.50
WC-1	0.387	1.73	16,963	29.3	0.3	0.96

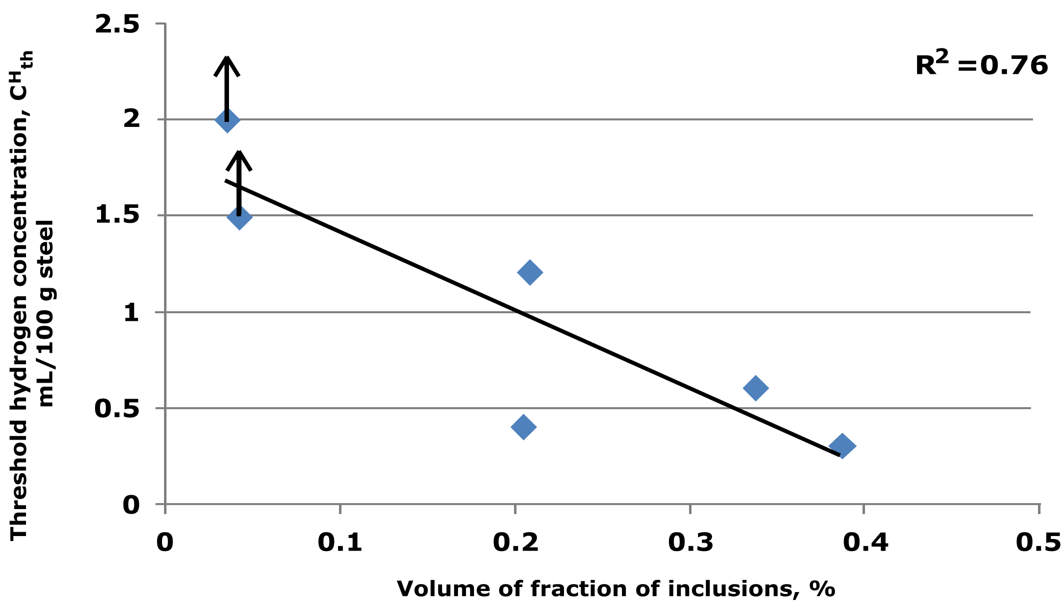

Figure 2. Correlation between threshold hydrogen concentration and volume fraction of inclusions. Arrows pointing upward identify steels that did not crack at the highest quantity of C^H that was measured; ie. C^H_{th} for these steels exceeded these values.

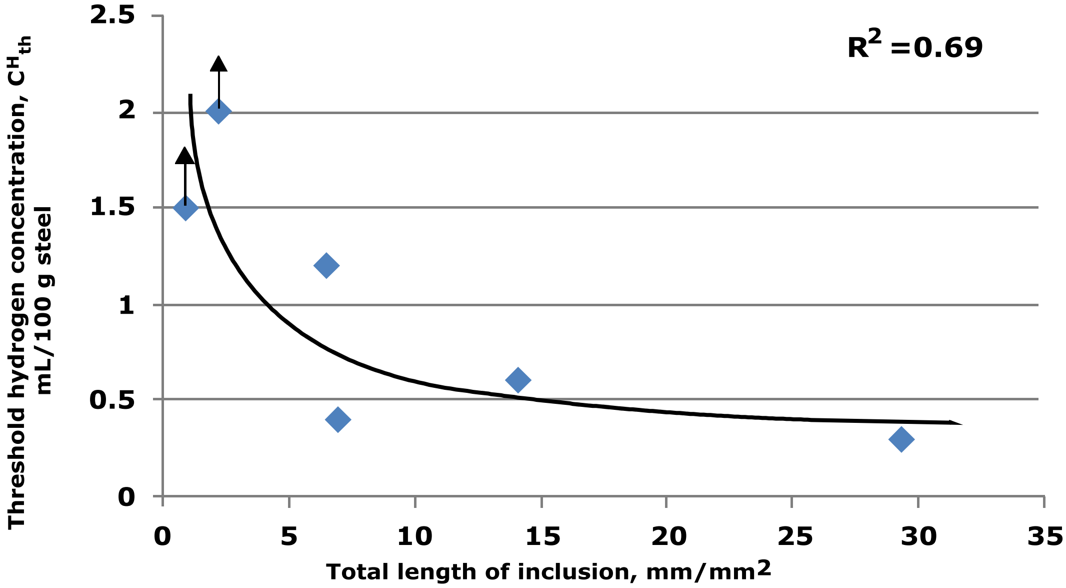

Figure 3. Correlation between threshold hydrogen concentration and total length of inclusions.

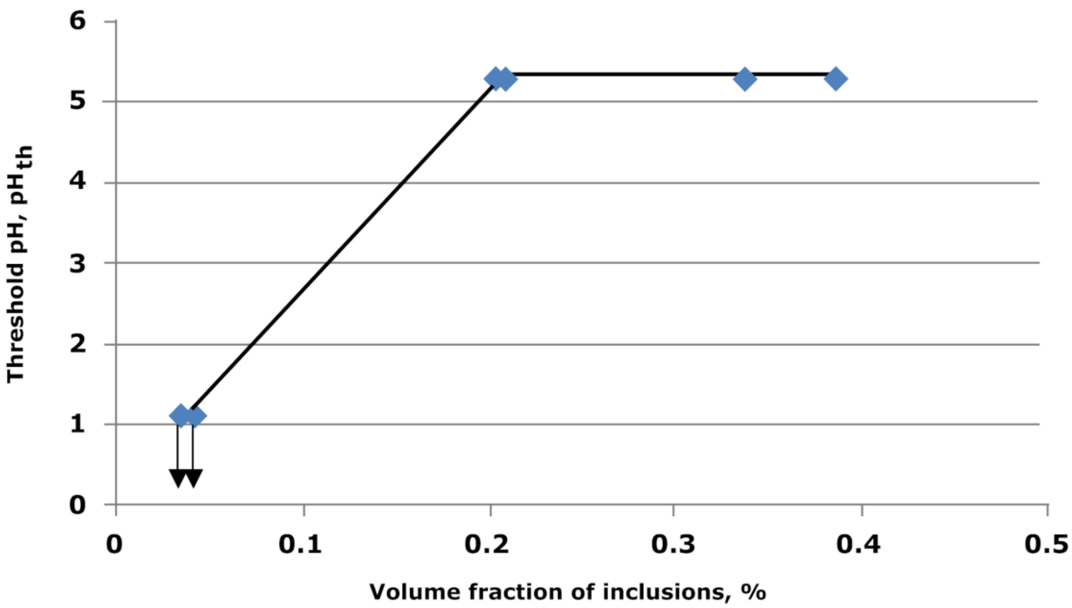

Figure 4. Correlation between threshold pH and volume fraction of inclusions. Arrows pointing downward identify steels that did not crack under the most aggressive conditions of this study, ie. pH 1.1, so that pH_{th} <1.1 for these steels.

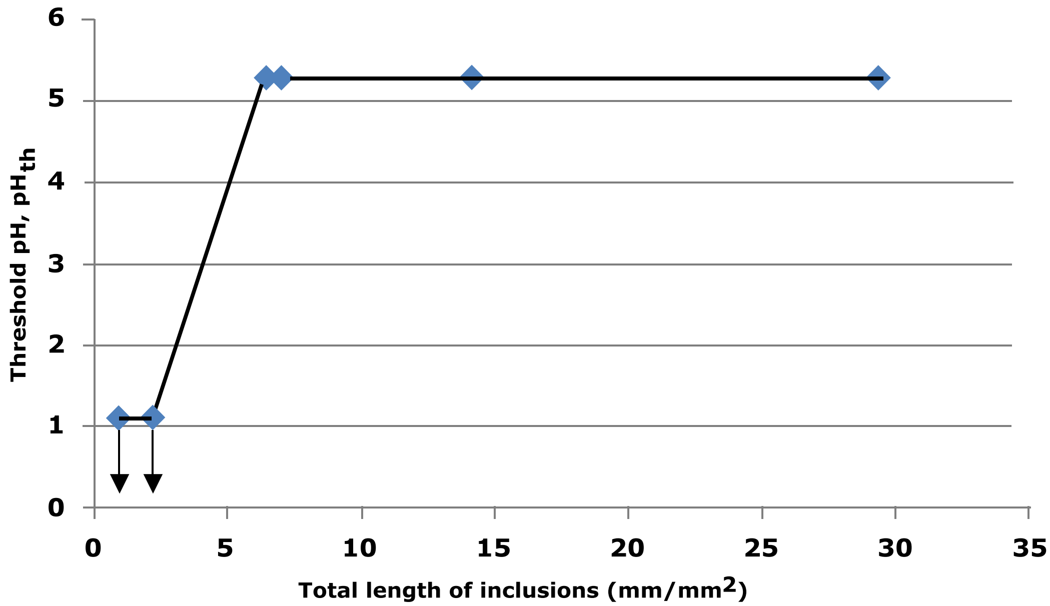

Figure 5. Correlation between threshold pH and total length of inclusions.

Figures 6 and 7 show the effect of the Ca/S ratio on the threshold hydrogen concentration and on the threshold pH for the 7 steels that were studied. For the two steels that were entirely resistant to HIC, ie. those that did not crack, the Ca/S ratios were 2.5 for AM-2, and 2.6 for CTR-2.

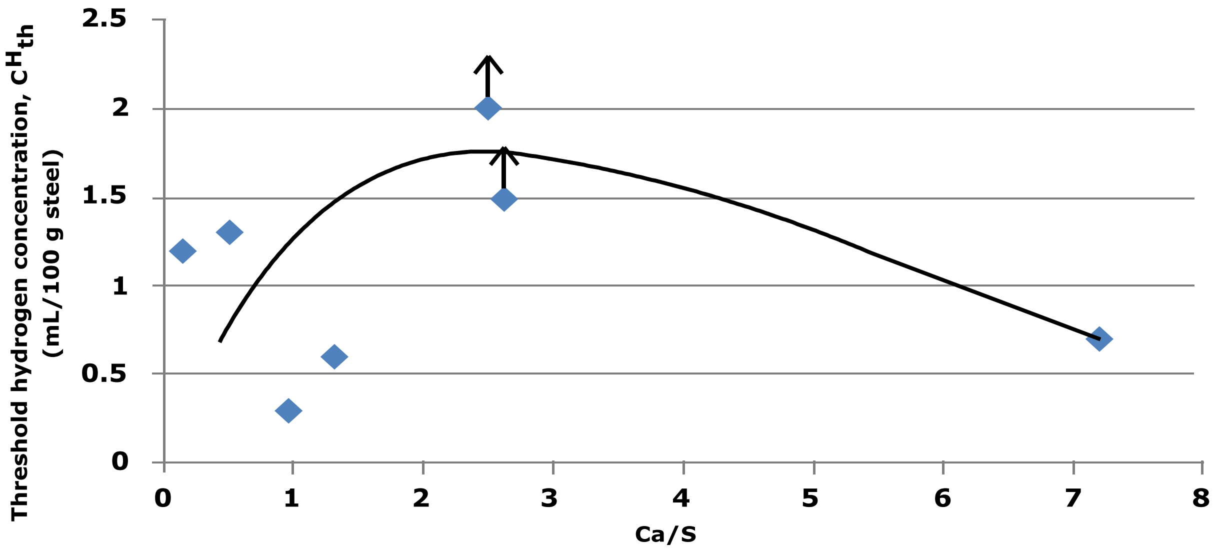

Figure 6. Correlation between threshold hydrogen concentration and Ca/S ratio.

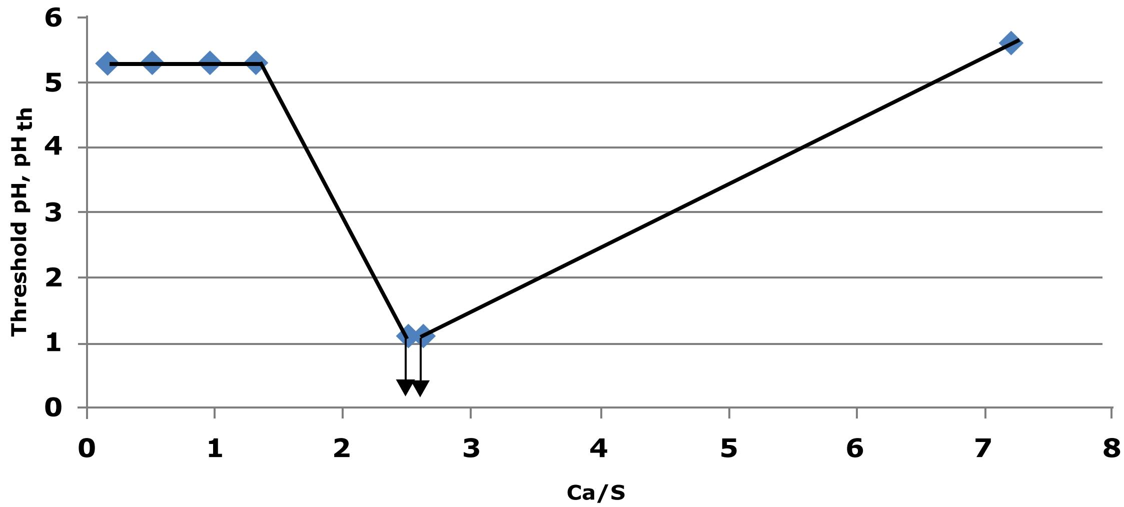

Figure 7. Correlation between threshold pH and Ca/S ratio.

The steels that were studied had a wide range of susceptibility to HIC. Two steels, CTR-2 and AM-2, with Ca/S ratios of 2.6 and 2.5, respectively, both ultra-low-sulphur advanced steels, did not crack under any of the test conditions, ie. pH_{th} <1.1. For the steels that were studied, the Ca/S ratio of approximately 2.5 could be considered as optimum.

Although steels CTR-1 and CTR-2 are similar in composition and strength, the values obtained for these two steels for threshold hydrogen concentration and threshold pH are very different, with CTR-2 being resistant to HIC under the most aggressive conditions in this study. Significant differences in these two steels are the very high carbon content of CTR-1 which is totally unsuitable for sour service use and makes correlations with niobium content unrealistic. The high carbon content results in the severely banded microstructure of CTR-1, shown in Figure 8, compared to the uniform microstructure of CTR-2, Figure 9. Banding has a well documented very detrimental effect on HIC performance. The niobium-rich precipitate in CTR-1 (Figure 10) is the result of the excessive carbon content (0.157%) and centerline segregation. Steels with up to 0.095% niobium and 0.030% carbon have been shown to be highly HIC resistant in severe sour service [12].

Steels with the same pH_{th} can have much different values of C^H_{th}, eg. steels WC-1, G-2, PC-1, and AM-1 all have the same value of pH_{th}, 5.3, whereas C^H_{th} varies from a low of 0.3 mL H_2/100 g of steel for WC-1 to a high of 1.2 mL H_2/100 g of steel for AM-1. In general, high values of C^H_{th}, >1.0 mL H_2/100 g of steel, indicate good HIC resistance.

Once a value of C^H_{th} has been established for a specific steel, field experiments can be carried out using this steel to determine the peak value of C^H_0, ie. C^H_{0max}, obtained during startup conditions by following the methods described by Elboujdaini et al [13] and by Hay and Rider [14]. If $C^H_{0max} < C^H_{th}$, HIC would be predicted not to occur. In addition, during pipeline operation, the current of diffusible hydrogen, measured at the external pipe surface, can be measured online, in real time, all the time. Changes in the current of diffusible hydrogen could indicate a change in the corrosion rate of the steel at the inside surface of the pipe as a result of changing operational conditions, eg. change in corrosion inhibitor, change in composition of product being transmitted, etc. Diffusible hydrogen can be a valuable parameter to measure and to monitor.

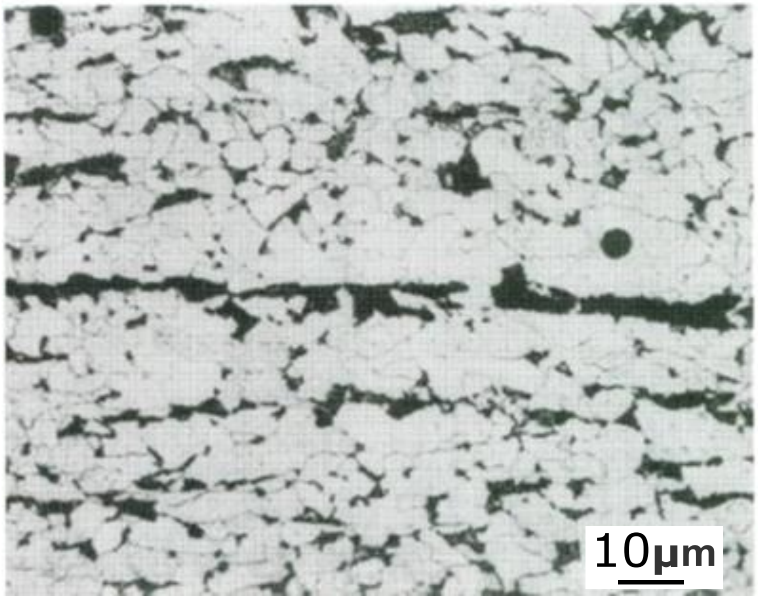

Figure 8. Photomicrograph of steel CTR-1 showing banded microstructure [9].

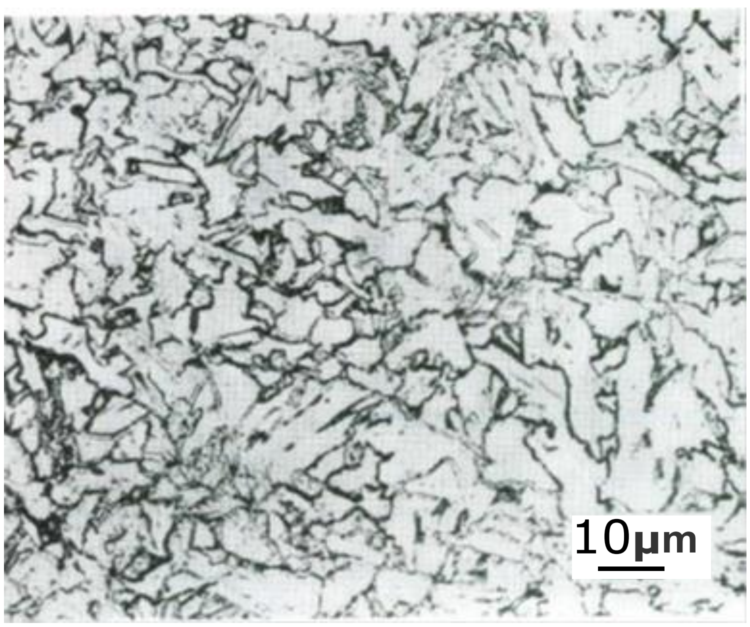

Figure 9. Photomicrograph of steel CTR-2 showing uniform microstructure [9].

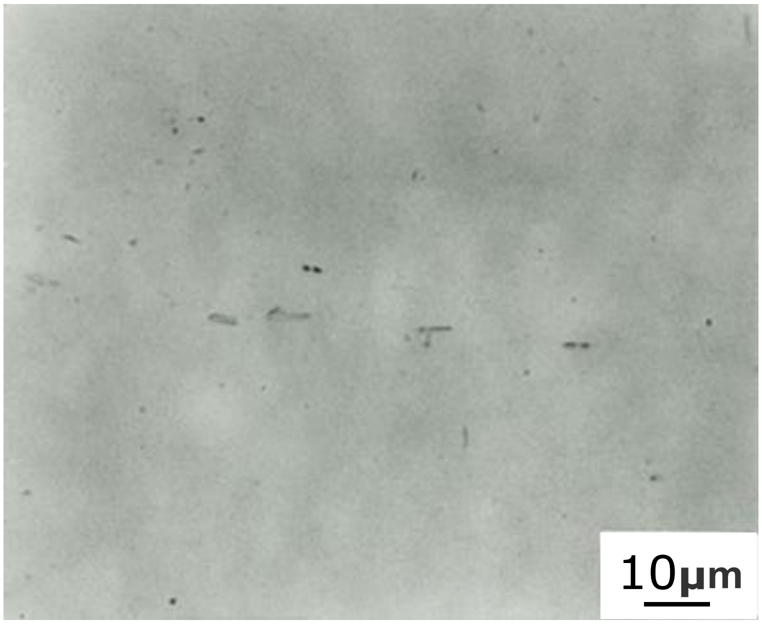

Figure 10. Photomicrograph of steel CTR-1, showing Nb-rich precipitates [9].

Conclusions

1. The value of pH_{th} can be used to rank steels for resistance to HIC.

2. High values of C^H_{th} (>1.0 mL H_2/100 g steel) are associated with high resistance to HIC.

3. Uniformity of microstructure, free of banding and precipitates, helps to ensure resistance to HIC.

4. The two steels that were immune to HIC under the most aggressive conditions of this study were ultra-low-sulphur advanced steels with Ca/S ratios of 2.5 and 2.6, although the Ca/S ratio may not, in itself, be a generalized criterion for HIC resistance. Criteria for HIC are:

   (a) In the steel, $C^H > C^H_{th}$, or
   (b) In the environment, $pH < pH_{th}$.

Acknowledgements

The authors gratefully acknowledge their colleagues at CanmetMATERIALS for experimental support and many helpful discussions.

References

1. R.W. Revie, ed., *Uhlig's Corrosion Handbook,* 3rd edition (Hoboken, NJ: Wiley, 2011), 1220.

2. M. Elboujdaini, "Hydrogen-induced Cracking and Sulfide Stress Cracking," *Uhlig's Corrosion Handbook*, 3rd edition, ed. R.W. Revie, (Hoboken, NJ: Wiley, 2011), 183-194.

3. M. Elboujdaini, "Test Methods for Wet H_2S Cracking," *Uhlig's Corrosion Handbook*, 3rd edition, ed. R.W. Revie, (Hoboken, NJ: Wiley, 2011), 1087-1093.

4. V. Venegas et al., "On the Role of Crystallographic Texture in Mitigating Hydrogen-induced Cracking in Pipeline Steels," *Corrosion Science,* 53 (2011), 4204.

5. M.S. Cayard, R.D. Kane and R.J. Horvath, "SOHIC Resistance of C-Mn Plate Steels Used in Refinery Service," CORROSION/2002, Paper No. 02554, NACE International, Houston, Texas, 2002.

6. ANSI/NACE Standard TM0284-2011, Section 8.4, page 13. NACE International, Houston, Texas, 2011.

7. M. Elboujdaini et al., "Hydrogen-induced Cracking and Effect of Non-metallic Inclusions in Linepipe Steels," CORROSION/98, Paper No. 748, NACE International, Houston Texas, 1998.

8. R.W. Revie et al., "Hydrogen-induced Cracking of Linepipe Steels, Part 1 – Threshold Hydrogen Concentration and pH," *Corrosion*, 49 (1) (1993), 17.

9. G.R. Hoey et al., "Determination of Minimum Diffusible Hydrogen Concentration Causing Hydrogen-induced Cracking of Linepipe Steels," (Report MTL 88-41 (TR), CANMET Metals Technology Laboratories, August 1988).

10. R.W. Revie and H.H. Uhlig, *Corrosion and Corrosion Control, An Introduction to Corrosion Science and Engineering*, 4th edition, (Hoboken, NJ: Wiley, 2008), 121.

11. R.W. Revie and H.H. Uhlig, *Corrosion and Corrosion Control, An Introduction to Corrosion Science and Engineering*, 4th edition, (Hoboken, NJ: Wiley, 2008), 139.

12. K. Hulka, J.M. Gray and F. Heisterkamp, "Metallurgical Concept and Full Scale Testing of a High Toughness, H_2S Resistant 0.03%C– 0.10%Nb Steel" (Niobium Technical Report NbTR 16/90, CBMM, Sao Paulo (Brazil), 1990).

13. M. Elboujdaini, V.S. Sastri and R.W. Revie, "Field Measurement of Hydrogen in Sour Gas Pipelines," *Corrosion*, 50 (8) (1994), 636.

14. M.G. Hay and D.W. Rider, "Integrity Management of a HIC-damaged Pipeline and Refinery Pressure Vessel through Hydrogen Permeation Measurements," Corrosion/98, Paper No. 395, NACE International, Houston, Texas, 1998.