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Laboratory testing of steel L360NB, L80, J55 resistance to sulphide stress cracking SCC and hydrogen induced cracking HIC

Results of laboratory study of 3 types of steel, resistance to sulphide stress cracking and hydrogen induced cracking in H_2S environments, are presented in this article. Those steels have been applied in the petroleum industry. Determining the threshold of safety for each type of steel (with regard to yield strength R_e) below where stress cracking won't occur was possible owing to these examinations. Hydrogen induced cracking test was applied to research steel resistance to cracking caused by hydrogen from sulphur aqueous environments. These tests permit determination of the threshold of safety of a given material to be admitted for use in hydrogen sulphide environments.

Key words: hydrogen sulphide, stress corrosion, hydrogen induced cracking.

Badania odporności stali gatunku L360NB, L80, J55 na korozję naprężeniową SCC oraz kruchość wodorową HIC

W artykule przedstawiono wyniki badań odporności trzech gatunków stali, stosowanych w przemyśle naftowym, na korozję naprężeniową oraz kruchość wodorową występującą w środowisku zawierającym H_2S . Testy korozji naprężeniowej SCC pozwalają na określenie progu bezpieczeństwa dla danego materiału w odniesieniu do granicy plastyczności R_e , poniżej którego nie występuje siarczkowe pękanie naprężeniowe. Test kruchości wodorowej HIC stosuje się do badań odporności stali na pękanie indukowane absorpcją wodoru pochodzącego z zasiarczonego środowiska wodnego. Badania te pozwalają na określenie klasy odporności dla danego materiału dopuszczając go do pracy w środowisku siarkowodoru.

Słowa kluczowe: siarkowodor, korozja naprężeniowa, kruchość wodorowa.

Introduction

The problem of sulphide embrittlement in a hydrogen sulphide containing environment, has been known in the oil and gas industry all over the world, for many years. Such types of corrosion is especially dangerous as it may cause sudden cracks and breaks of pipelines.

Because of the increasing demand for oil and natural gas there is the necessity to use deposits of increasingly worse mining practices. The presence of hydrogen sulphide in reservoir fluid requires the use of construction materials with special properties, namely those with the least susceptibility to stress corrosion cracking and hydrogen embrittlement, strongly stimulated by this particular constituent. Hydrogen

sulphide occurs naturally in crude oil and natural gas at varying amounts from as low as 1÷2 ppm to high (several or even up to tens of percent in the most sulphurised deposits in the world). It can be also produced by sulphate-reducing bacteria (SRB) and in chemical processes in deposits. In anaerobic conditions sulphate ions are used as a source of oxygen in the SRB bacteria respiration process. This process requires the presence of the water phase, e.g. formation water, waste water or condensation water, etc.

SCC can be caused by mechanical stresses, even very small, that may occur in steels after cold working without following pressure relief annealing, after water cooling during

heat treatment, after welding, and event after machining. One of characteristic features of stress corrosion is metal embrittlement demonstrating itself during tensile tests. A significant effect on sulphide stress cracking have such factors as: metallurgical conditions and strength, hydrogen ion concentration in the water phase, H₂S partial pressure, total tensile stress, temperature, exposure time to medium, galvanic effects, chloride and other halogen ions concentrations, oxidizer concentration, and non-production fluid concentration. Stress corrosion cracking occurs only in the presence of tensile stresses. The stresses resulting from stretching are added then to internal stresses caused by heat treatment.

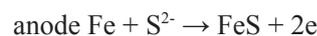
The occurrence of hydrogen induced cracking (HIC) is related to the presence of hydrogen sulphide in formations or releasing it at higher temperatures from sulphonates (compounds used as additives to drilling fluids) or producing it by anaerobes.

Hydrogen sulphide dissolves in water, to give a slightly ionized solution.



A saturated solution of H₂S in water shows pH about 4 and is a very weak acid. This acid reacts with iron to release

hydrogen and iron (II) sulphide that precipitates on-site forming a sedimentation highly adhering to the surface.



In acidic solution this reaction continues and the concentration of iron (II) ions increases, while in base solution it drops to low values. The rate of corrosion decreases at pH > 7, whilst the presence of oxygen enhances the anodic process and corrosion may proceed at a higher speed. The higher the hydrogen sulphide concentration, higher formation pressure, lower pH and higher material susceptibility, the shorter the time to corrosion cracking. Hydrogen present in metal deteriorates its elastic properties (so called hydrogen induced cracking). This harmful phenomenon is of utmost importance for high-strength steels being commonly used in oil and gas drilling. The steels mentioned above show especially high susceptibility to hydrogen induced cracking. This susceptibility increases with increasing mechanical strength of steel. Hydrogen embrittlement does not occur at high and low temperatures, and this is specifically characteristic of such corrosion type and reaches its maximum at temperature 20 ± 5°C [1–6, 9].

Laboratory testing

The aim of tests was to determine the resistance of L360NB, J55 and L80 steel grades to stress corrosion and hydrogen induced cracking.

Stress corrosion tests

Test methodology

Stress corrosion cracking tests allow the safety threshold to be determined for a given material in terms of yield stress *R_e*, below it sulphide stress cracking does not occur.

The testing of L360NB, L80 and J55 steels was carried out by using method A according to ANSI/NACE Standard TM0177-2005 [10]. The dimensions and shape of specimens used for stress corrosion evaluation are presented in Figure 1 and Table 1 [8].

Table 1. Test specimen size for stress corrosion cracking evaluation

Dimension	Standard specimens	Specimens of reduced size
D	6.35 ± 0.13 mm	3.81 ± 0.05 mm
G	25.4 mm	25.4 mm
R(min)	1.5 mm	1.5 mm

Due to equipment requirements, test specimens of reduced size were used.

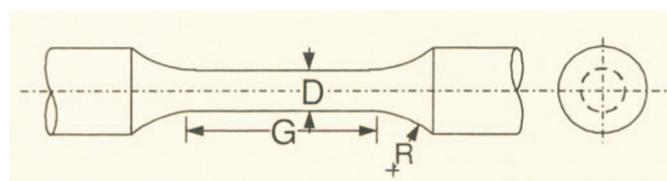


Fig. 1. Test specimen for stress corrosion cracking evaluation

A solution of 5% NaCl + 0.5% CH₃COOH + H₂O was vented by purging with nitrogen and saturated with H₂S gas for 30÷50 minutes prior to testing and throughout measurements was used as the corrosive medium. The test time was 720 hours, test temperature of 23°C, the pH of solution before testing was 2.6÷2.8, and was kept below 4 during tests. Each specimen was placed in the measuring chamber filled with the test solution, through which hydrogen sulphide was passed. Appropriate axial stresses were applied to specimens by using a system of levers and loads. The aim of the tests was to determine a percentage of yield strength *R_e*, at which a specimen does not break off for at least 720 hours. The determined percentage of *R_e* is the safety threshold for a given material in hydrogen sulphide environment and indicates that before this threshold

stress the material does not crack. Prior to corrosion tests, the mean value of yield strength R_{eaver} being the reference value for selecting stresses for corrosion tests, was determined based



Photo 1. SCC test apparatus

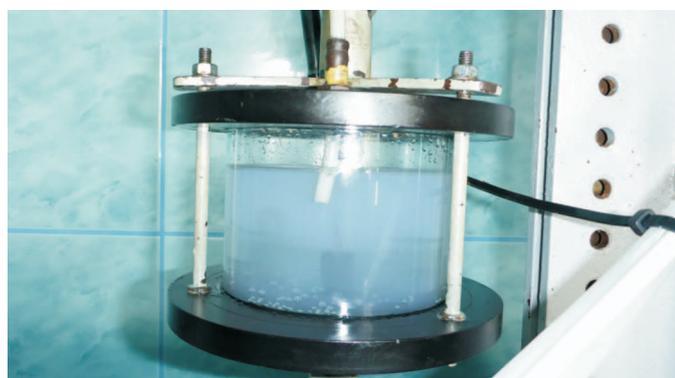


Photo 2. SCC measuring chamber

on material data sheets. The specimens were then subject to stresses being a percentage of the determined value of R_{eaver} .

Test conditions according to NACE [10] are extreme and do not occur in industrial applications. Thus, when a specimen of specified steel grade passes the above test, such steel can be safely used in production conditions. By using the above-mentioned tests, the safe stress threshold which cannot be exceeded in industrial applications was established [7, 8, 10].

The test was carried out by using apparatus shown in Photo 1, while the measuring chamber is presented in Photo 2.

Test results

Test results are presented in Table 2 and in photographs 3, 4 and 5.

The following results were obtained for individual steel grades:

- L360NB steel grade – safe operating range in the presence of hydrogen sulphide is below 54% of yield strength R_{e_s} , corresponding to stress of 212 MPa,
- L80 steel grade safe operating range in the presence of hydrogen sulphide is below 61% of yield strength R_{e_s} , corresponding to stress of 374 MPa,
- J55 steel grade – safe operating range in the presence of hydrogen sulphide is below 55% of yield strength R_{e_s} , corresponding to stress of 249 MPa.

The obtained results indicate a low resistance of tested materials. For each steel grade four specimens were tested, while stress was decreased gradually. Only the last fourth

Table 2. Results of sulphide stress cracking tests

Specimen No.	O [kg]	m_n	F [kg]	d_0 [mm]	S_0 [mm]	R [MPa]	R_{eaver} [MPa]	% R_{eaver}	t [h]
L360NB steel									
1	13	29	377	3.81	11.39	324.50	391	82.99	644
2	12	29	348	3.81	11.39	299.54	391	76.61	18 h 50 min
3	10	29	290	3.81	11.39	249.60	391	63.84	117 h 40 min
4	8.5	29	246	3.81	11.39	212.20	391	54.30	743
L80 steel									
1	22	29	638	3.81	11.39	549.0	615	89.27	141
2	20	29	580	3.81	11.39	499.0	615	81	236
3	17	29	493	3.81	11.39	424.3	615	69	215
4	15	29	435	3.81	11.39	374.4	615	61	767
J55 steel									
1	14	29	406	3.81	11.39	349.5	454	77	42 h 30 min
2	12	29	377	3.81	11.39	299.5	454	66	23
3	11	29	319	3.81	11.39	274.5	454	60.5	69
4	10	29	290	3.81	11.39	249.6	454	55	862

Denotations adopted in Table 2: O – test machine load, m_n – machine multiplier, F – force applied to the specimen, d_0 – specimen diameter over working length, S_0 – initial specimen cross-section in working part, R – stress in specimen, R_{eaver} – mean value of yield strength determined from mechanical properties, t – time.

specimen resisted at least 720 hours under corrosion test conditions without any cracking traces.



Photo 3. Example of a specimen before SCC testing



Photo 4. Example of specimen that failed SCC testing



Photo 5. Example of specimen that passed SCC test

Hydrogen induced cracking tests

Test methodology

The HIC tests were carried out according to the following standards: NACE Standard TM-0284-2011 [11], PN-EN 10229:2001 [13], PN-EN ISO 15156-2:2010 [14], PN-EN 10028-3:2010 [12].

Although the method specified in standards creates severe test conditions that in fact do not occur, the obtained results are useful for selecting materials to be used in hydrogen sulphide environment. The test according to standards listed above is used for evaluating steel resistance to cracking induced by absorption of hydrogen originated from sulphated aqueous environment. The specimens were taken from pipes made of L360NB, L80 and J55 steel grades and were of $100 \pm 1 \text{ mm} \times 20 \pm 1 \text{ mm} \times$ material thickness mm (length \times width \times thickness) in size. The main surfaces of specimens were polished with an abrasive paper, 320 grit. Prior to test the specimens were thoroughly degreased. Afterwards, the specimens were placed in the test vessel so that their surfaces parallel to the original product surface were arranged vertically. To keep the minimum distances between specimens, plexiglass pads were used (see Figure 2) [7, 8, 11, 13].

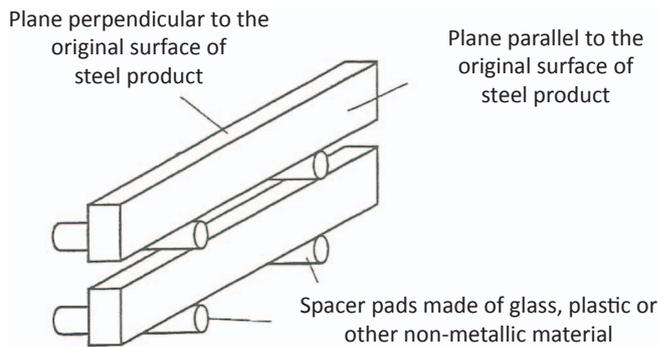


Fig. 2. Specimen placement in the test vessel

The test solution was prepared in laboratory by using analytical grade reagents according to the recipe specified in the standard which entails dissolving 50 g of NaCl and 5 g of glacial CH_3COOH in 945 ml of distilled water. The initial pH of the solution in individual tests was $2.7 \div 2.8$. Afterwards, the solution was vented by purging with nitrogen at a flow rate of 110 cm^3 per minute and 1 litre of solution for 80 minutes. After venting the solution was saturated with H_2S at flow rate at 200 cm^2 per minute for 60 minutes and the saturation level was maintained throughout the test. The final pH of solution was $3.5 \div 3.6$.

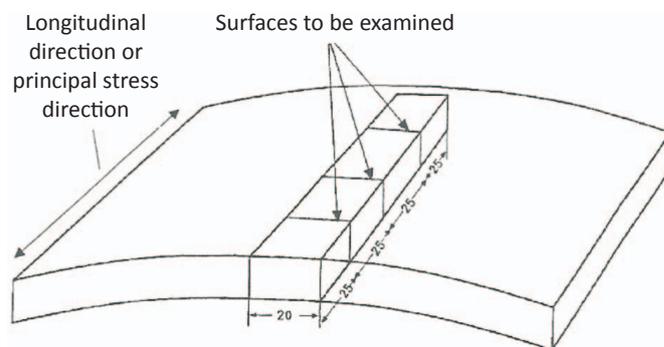


Fig. 3. Specimen division into sections and surfaces for metallographic examination

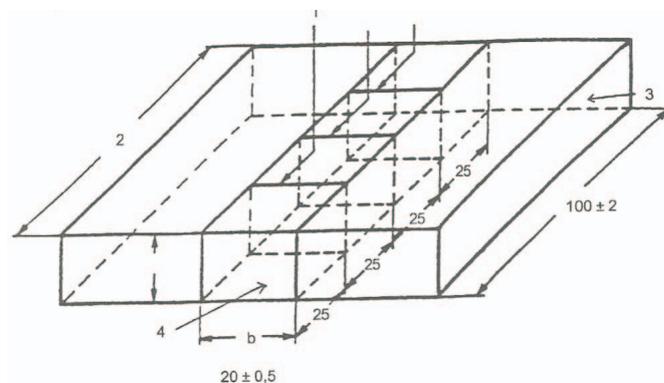


Fig. 4. Test specimen dimensions and microsection taking scheme: 1 – surfaces on which cracking evaluation is carried out, 2 – longitudinal or plastic strain direction, 3 – test section, 4 – microsection

In first phase unencumbered specimens were exposed to the solution at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and ambient pressure, by placing them in a tightly closed vessel. After 96 h the specimens were removed from the solution and cleaned under a stream of running water with a plastic brush. Then, each specimen was divided into sections for metallographic examinations (Figure 3 and 4). The sections were prepared for microscopic observations by making metallographic microsections [7, 8, 13, 14].

The microscopic measurements were made at 100x magnification. They were aimed at determining hydrogen induced cracking susceptibility ratios coefficients CSR, CLR and CTR.

$$\text{Crack sensitivity ratio } CSR = \frac{\sum(a \cdot b)}{W \cdot T} \cdot 100\%$$

$$\text{Crack length ratio } CLR = \frac{\sum a}{W} \cdot 100\%$$

$$\text{Crack thickness ratio } CTR = \frac{\sum b}{T} \cdot 100\%$$

where:

a – crack length,

b – crack thickness,

W – section width,

T – specimen thickness.

Measurement rules and cracking evaluation methods during microscopic observations are shown in Figure 5 and 6a–d [13].

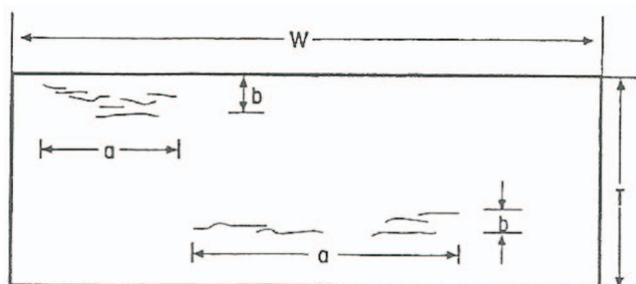


Fig. 5. Measurement rules during microscopic observations

The qualification criteria for materials to be used in hydrogen sulphide environment without stresses, pertaining to the permissible values of coefficients CLR, CSR and CTR are shown in Table 3 [12].

Table 3. Values of CLR, CTR and CSR coefficients according to PN-EN 10028-3:2009 that permit a material to be used in hydrogen sulphide environment after HIC test

Resistance class	CLR [%]	CTR [%]	CSR [%]
I	≤ 5	≤ 1.5	≤ 0.5
II	≤ 10	≤ 3.0	≤ 1.0
III	≤ 15	≤ 5.0	≤ 2.0

The test was carried out on apparatus presented in Photo 6 and 7.



Photo 6. HIC test chamber



Photo 7. Equipment for maintaining HIC test conditions in the test chamber

Examples

Examples	Remarks (d = distance between two cracks, mm)
<p>a)</p>	$d > 0.5$; two single cracks
<p>b)</p>	$d < 0.5$; crack tip field
<p>c)</p>	$d < 0.10$; crack to be considered as a single crack
<p>d)</p>	stepped crack (as in example b)

Fig. 6. Cracking evaluation method [13]

Test results

The results of microscopic observations of metallurgical microsections made from steel grades under examination are presented in Table 4, while HIC test results are listed in Table 5. The exterior portion of the specimen surface showing a crack at 100x magnification is shown in Photo 8. The performed hydrogen induced cracking tests indicated that specimens made from L360NB, L80 and J55 steel grades had only single small cracks caused by hydrogen penetration into the metal structure.

The computed hydrogen induced cracking susceptibility ratios reached low values. The materials mentioned above

Table 4. Results of microscopic observations of metallographic microsections made from L360NB, L80, J55 steel grades

L360NB	L80	J55
Specimen 1A – no cracks	Specimen 10A – no cracks	Specimen 4A – no cracks
Specimen 1B – no cracks	Specimen 10B – no cracks	Specimen 4B – no cracks
Specimen 1C – no cracks	Specimen 10C – no cracks	Specimen 4C – no cracks
Specimen 2A – no cracks	Specimen 11A – no cracks	Specimen 5A – no cracks
Specimen 2B – no cracks	Specimen 11B – no cracks	Specimen 5B – no cracks
Specimen 2C – crack #1 a = 0.14 mm, b = 0.14 mm	Specimen 11C – no cracks	Specimen 5C – no cracks
Specimen 3A – no cracks	Specimen 12A – crack #1 a = 0.15 mm, b = 0.05 mm	Specimen 6A – no cracks
Specimen 3B – crack #1 a = 0.04 mm, b = 0.06 mm	Specimen 12B – no cracks	Specimen 6B – no cracks
Specimen 3C – no cracks	Specimen 12C – crack #1 a = 0.20 mm, b = 0.57 mm	Specimen 6C – no cracks

are highly resistant to hydrogen induced cracking and are placed in resistance class I.



Photo 8. Crack #1 observed on specimen 2C of L360NB steel at 100x magnification

Table 5. HIC test results for individual materials

Material	CLR [%]	CTR [%]	CSR [%]	Criteria fulfilment
L360NB steel	0.100	0.252	0.001	yes class I
L80 steel	0.194	1.378	0.013	yes class I
J55 steel	0.000	0.000	0.000	yes class I

Summary

The tested L360NB, L80 and J55 steel grades demonstrated a very good resistance to brittle cracking caused by hydrogen penetration into the metal structure (HIC). All these steels are classified in resistance class I, and its hydrogen induced cracking susceptibility ratios are close to 0%.

However, the thresholds of permissible stresses determining safe working conditions for materials under examination, below which sulphide stress cracking (SCC) does not occur, are relatively low and are 54%, 61% and 55% of yield strength for L360NB, L80 and J55 steel grades, respectively.

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- [11] *NACE Standard TM-0284-2011 Item No. 21215 Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking.*
- [12] PN-EN 10028-3:2010 *Wyroby płaskie ze stali na urządzenia ciśnieniowe – Część 3: Stale spawalne drobnoziarniste normalizowane.*
- [13] PN-EN 10229:2001 *Ocena odporności wyrobów stalowych na pękanie wywołane wodorem (HIC).*
- [14] PN-EN ISO 15156-2:2010 *Przemysł naftowy, petrochemiczny i gazowniczy. Materiały stosowane przy wydobyciu ropy i gazu w środowisku zawierającym H₂S. Część 2: Stale niskostopowe odporne na pękanie oraz stosowanie żeliw.*

Legal and normative acts

- [10] *ANSI/NACE Standard TM0177-2005 Item No. 21212 Standard Test Method. Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking and Stress Corrosion Cracking in H₂S Environments.*



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- designing of stimulation treatments;
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- selection of the corrosion inhibitors for oil and gas industry.



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