Influence and Adaptability of The NACE Test Duration on Material Qualification: Fitting for Purpose

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ABSTRACT

The need for oil & gas industrials during materials qualification is to have reliable and compatible results to meet the requirements related to cost and delay. For this purpose, the fit-for-purpose tests can be representative and must meet these industrial requirements. With regard to qualifications in HIC (Hydrogen Induced Cracking) mode according to the NACE TM 0284 standard and for low H_2S contents, the test durations may be longer than 90 days. This duration being not compatible with the current economic requirements. This study reports results of NACE HIC tests according to the H_2S content and duration of exposure. An acceptability criterion has been established to qualify the material for a specific use. Different modes of corrosion have been observed. The degradation and the risk to use this material were defined according to the acceptability criterion and compared with the requirements of NACE TM 0284 and the criteria of ISO 15156. These elements make it possible to provide information on the use of this material according to these operating conditions, adopting the fitting for purpose mode.

Introduction

The use of materials in the oil & gas exploration requires upstream qualification. This qualification step, carried out by laboratory tests, is crucial to ensure the lifetime of the material, usually between 25 and 50 years for Oil & Gas installations. The qualification of the materials by these tests must make it possible to ensure the reliability of the installation considering the future stresses and the operating conditions. This without making excessive over-quality, usually time-consuming and expensive.

The qualification tests of steels which will be used in oil & gas are carried out according to international standards or industrials specifications. The most widespread and recognized for static qualification are ISO-15156[1], NACE TM-0177[2] and NACE TM-0284[3]. These standards make it possible to consider environments of severe qualification such as the saline medium, the presence of H_2S and CO_2, low pH and mechanical stress. These test conditions can be adapted to the type of material, to mechanical stresses under operating conditions and to the environment in which it is used, considering its corrosion severity.

From the last revision of NACE TM-0284 in 2016, the fit for purpose mode is considered in these standards with criticity level of test, as H_2S content, to adapt considering test duration between 4 and 90 days.

Whereas until now the requirements were fixed, usually test duration at 30 days without considering the low H_2S content requires a longer duration to observe some corrosion phenomena which may lead to crack and/or failure and/or HIC. It should be noted that for H_2S content below 1mbar, the qualification test isn't required by NACE TM 0284.

The test duration adaptability and the operating condition considering is today a strong need of the industrials. There is a real need to ensure the durability of the material without making over-quality by testing on durations compatible with industrial requirements.

This study proposes to account the influence of the test duration according to NACE TM-0284 requirements on the test result for LNE acceptability criteria. These criteria are described in this document and reflect the general corrosion, localized corrosion, detection of crack or crack initiation and HIC. A steel material is exposed by immersion in a saline solution containing dissolved H_2S (S^{2-}) for different content and durations.

Experimental

Material

The material used in this study is a low alloyed carbon steel specially supplied by the LNE to meet the chemical and mechanical requirements specified below. This steel is received in bar size 12x5mm² and issue from casting, cold working and stress relieving. This steel is used in this metallurgical state in the field Oil & Gas applications as pipe structure and for accessories.
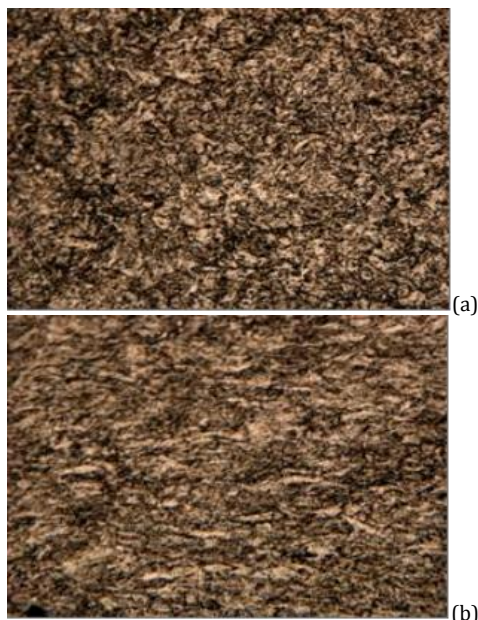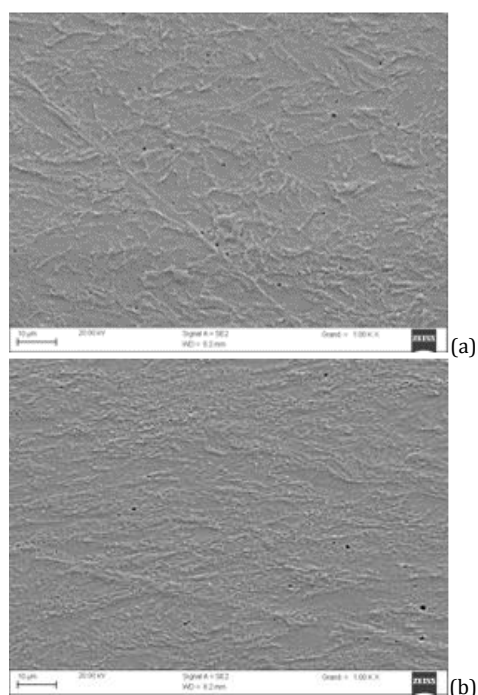
The tests were carried out on this steel from the same batch in order to ensure the traceability and the linearity of the initial metallurgical properties. The chemical composition of the steel samples and its mechanical properties are summarized in Table 1. The chemical composition was analysed by inductively coupled plasma (ICP) and by a carbon / sulphur analysis. Observations from optical microscopy and scanning electron microscopy (SEM) have shown an acicular structure that corresponds to the martensitic structure.

Samples preparation

The samples are prepared by cutting the bar each 150mm length with a section of 12x5mm². These samples are then checked by radiography X to ensure material health and to account for the initial lack of defects. These samples are then identified for traceability. The samples were degrease

Table 1: Chemical composition & mechanical properties of the steel performed

Chemical composition (wt %)									
C	Mn	P	S	Si	Al	Cu	Cr	Ni	Sn
0.61±0.03	0.70±0.05	0.012±0.002	0.006±0.001	0.26±0.02	0.028±0.003	0.015±0.002	0.053±0.006	0.022±0.002	<0.002

Mechanical properties		
UTS (MPa)	Ys (MPa)	A_{100} (%)
1080	952	13

Figure 1: Optical microscope observations at the core (a) and at the edges (b) of the sample

Figure 2: SEM observations at the core (a) and at the edges (b) of the sample

-d with a non-halogenated solvent followed by ethanol cleaning. No polishing has been carried out to maintain the hardened surface condition which is representative of the operating conditions of the material[4]. Previous studies carried out at LNE[5] have shown the influence on the NACE

test result of the initial surface preparation of the sample. The objective is therefore to preserve as much as possible the representative state of the material[6,7]. The ends of the samples were masked by a protective and inert varnish so that the core of the material didn't influence the corrosion phenomena of the specimen. The degreased samples are stored in the desiccator less than 24 hours before immersion in solution. The surface of the samples is observed under a microscope for initial observations. Samples are weighed and dimensions recorded.

Table 2: Sample preparation description

Kind of sample preparation	Number of sample tested	Design (mm²)	Ra (average) (μm)	Ra standard deviation
As-received + Cleaning	45	12x5	0.92	0.045

The roughnesses were measured by a contact profilometer with 8mm stroke length. The roughnesses were measured in longitudinal and transverse directions on the test samples. Before the test, the samples were immediately embedded in cells under continuous flow of nitrogen. This is to prevent any oxidation of the surface before the test.

HIC cell & environmental conditions

The cells are in glass and perfectly hermetic to the external environment. A gas inlet is provided at the bottom of the reactor and ensured by a diffuser. The gas outlet is connected to an H_2S trapping system equipped with a non-return valve. The cell is placed on a magnetic stirrer allowing the agitation of the cell. The cell is equipped with a hermetic device for insertion of a pH-temperature probe allowing continuous control. A quilting system is placed on the lid allowing the insertion of pH buffer to adjust the acidity. The volume of the cell is 10 liters leading for the series of 3 samples immersed in each cell at a V/S ratio close to 70 ml/cm². The temperature of the test is strictly at 24±2°C.

The samples are arranged horizontally and spaced so as allowing free circulation and stirring of the solution. The samples are arranged in the same way from one cell to another. The cell is then hermetically sealed and a nitrogen flow is carried out at 200 ml/min for de-aeration. The type C solution complying with the requirements of NACE TM-0284 is de-aerated. This saline solution consists of 5wt% NaCl and 0.4wt% of CH_3COONa in deionized water. The level of de-aeration is measured by oximetry and the criterion of acceptability is a dissolved oxygen content less than 10ppb. The pH is adjusted at 3.5 with a solution containing either HCl or NaOH. The pH is adjusted during the test at ±0.2pH unit.

The solution is then saturated by bubbling with a mixture of H_2S + CO_2 gas at different content according to the test conditions. The bubbling is ensured by a diffuser allowing an optimal saturation of the solution. Saturation is controlled by a colorimetric device at the beginning and at

the end of the test. The $H_2S + CO_2$ bubbling is carried out in reduced mode throughout the test to ensure saturation and to avoid the lack of dissolved sulphides in the solution (sulfide consumption by the corrosion reaction).

To determine the influence and to have elements of adaptability of the test duration, the tests are carried out between 30 and 90 days for contents of H_2S between 0.2 and 8mbars.

Analyses & acceptability criteria

A protocol was set up at LNE to ensure the representativeness and repeatability of the results. For this, the initial state of the material must be controlled, free of surface and internal defect. The specimens are therefore initially checked by X-ray to check the material health. Binocular observations are also carrying out to observe the surface and detect a possible defect such as scratch, shock, etc. If a defect is detected, the sample is discarded and not tested. The weight and dimensions are controlled for comparison to the final data.

After each test, the samples are controlled by microscopic surface observation to detect HIC on surface, pitting and/or generalized corrosion. This information is then stored in our database for processing. Dimensions and weights are recorded. The samples are then controlled by immersion ultrasound to detect the appearance of HIC internally. Scans are loaded for processing in our database. The samples are then prepared by metallographic cross sections in order to determine the CSR, CLR and CTR[1].

9 cross sections were performed per sample and the corresponding macrographs are recorded. Measurements for CSR (crack sensitivity ratio), CLR (crack length ratio) and CTR (crack thickness ratio) are carried out directly by means of a micrometer microscope. The number of the cracks per cross sections corresponds to the ISO 15156 evaluation type.

$$CSR = \frac{\sum(a*b)}{w*T}*100\%$$
$$CLR = \frac{\sum a}{W}*100\%$$
$$CTR = \frac{\sum b}{T}*100\%$$

Where, a = crack length; b = crack thickness; W = section width; T = test specimen thickness. The acceptability criterion ACC is defined by the LNE in this study considering the general corrosion state of the sample by dimensional measurement and mass loss leading to a corrosion rate in μm/year, generalized corrosion by the presence or lack of pitting at the surface, determinations of CTR, CLR and CSR and finally the detection of HIC by ultrasound in immersion.

Corrosion criteria: $CORCrit = 10/(CORRate/1000 + SCS + SPD)$ (the higher the value, the higher the acceptability)

CORRate: corrosion rate in μm/yr due to the defaults at the surface, pits, cracks, etc, this rate is calculated by weight loss and material density

SCS: index between 0 & 2 vs surface corrosion severity by microscopy

SPD: index between 0 & 2 vs surface pitting detection

CLR: crack length ratio = 0 if >15% (ISO 15156 criteria[2]) else = 1

CSR: crack sensitivity ratio = 0 if >2% (ISO 15156 criteria[2]) else = 1

CTR: crack thickness ratio = 0 if > 5% (ISO 15156 criteria[2]) else = 1

HIC: HIC detection index on the scan = 0 if HIC trace is detected by US else = 1

$$ACC = CORCrit * CSR * CTR * CLR * HIC$$

Results and Discussion

The fit for purpose was discussed in the latest version of NACE TM-0284, the adaptability of the test duration was established as a function of the H_2S content. This standard doesn't recommend a qualification test for an H_2S content of less than 1mbar. For H_2S level between 1 and 3 mbars, 90 days of tests are recommended. 30 days of tests between 3 and 10 mbars, 14 days between 10 and 100 mbars and finally 4 days beyond 100 mbars.

This study proposes a fine analysis of the behavior of this material for the low H_2S contents (<10mbars). Therefore, the samples were exposed in parallel for 30, 60 and 90 days. The H_2S contents were between 0.2 and 8 mbars.

Table 3: Test parameters considering H_2S content & duration

H_2S content (mBar)	Test duration	Nbr of sample	Ratio V/S (mL/cm²)	Test solution
0.2	30	3	70	Type C as NACE TM 0284-2016 required at 24±2℃ & pH=3.5±0.2
	60	3		
	90	3		
1	30	3		
	60	3		
	90	3		
2	30	3		
	60	3		
	90	3		
4	30	3		
	60	3		
	90	3		
8	30	3		
	60	3		
	90	3		

Part A: influence of test conditions on material corrosion

The corrosion rate corresponds to the weight loss during the test and recalculated for 1 year. Weight loss is preferred compared to the dimensional loss due to the surface defaults as pits which no allowing precise and repeatable measurements. We can see on the Fig. 3 that the most significant effect on the corrosion ratio increasing is the H_2S content compared to the duration[11]. For 0.2mBar H_2S, the corrosion ratio is about 400±30μm/yr compared to 2800±90μm/yr for 8mBars of H_2S.
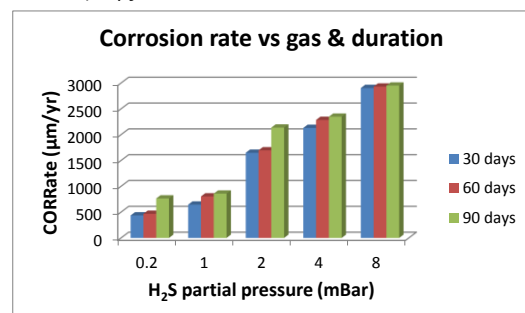

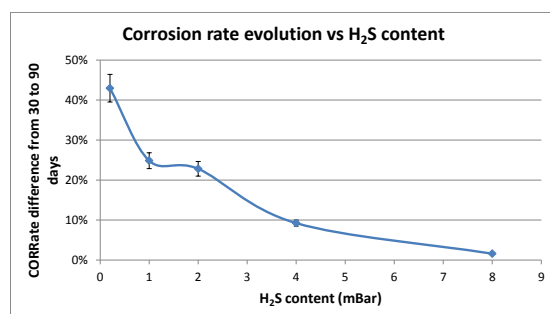**Figure 3**: Corrosion rate vs H_2S content between 30 & 90 days

Figure 4: Corrosion rate difference 30-90 days vs H_2S content

On the Figure 1 and for a same H_2S partial pressure, we can see that the smaller the H_2S content, the higher the corrosion rate 30-90 days difference[10]. In Figure 4, we can see the corrosion rate difference between 30 & 90 days for 0.2mBar H_2S is 43% whereas it is only 2% for an H_2S content of 8mbars (also see Fig. 5, 7).

Even if the most influent for corrosion rate is H_2S content compared to the test duration, we can noticed that for a same H_2S content, the kind of corrosion has a great influence on corrosion ratio.

This decrease of the corrosion rate difference between 30 and 90 days as a function of the H_2S content is due to the corrosion mode which differs according to the sulfides content. Indeed, the observations showed that for a low H_2S content, corrosion was generalized and slight at the surface after 30 days, whereas at 60 and then at 90 days the surface corrosion was strong and showed several pits of large sizes.

For higher H_2S contents (Fig. 5,7), this phenomenon fades with the occurrence of severe and generalized corrosion at 30 days and a similar corrosion level for 90 days. On the other hand, this stabilization of the corrosion state of the sample is accompanied by an appearance of corrosion initiated internally: the Hydrogen Induced Cracking HIC. This phenoma is accompanied by a similar corrosion rate between 30 & 90 days because the weight loss increases very slightly. The corrosion is located into the HIC and the generalized corrosion at the surface not increase compared to the crack length and depth which increase strongly[12]. When the corrosion is localized and initiated, the phenomena are very accelerated in this area.

For higher contents, 8mbars for example, HIC detection is from 30 days and increase strongly until 90 days with long cracks as shown in Fig. 6.

The size of HIC observed from 30 to 90 days, increase respectively from 2mm to several centimeters. This leads to a degradation of the general properties of the material.

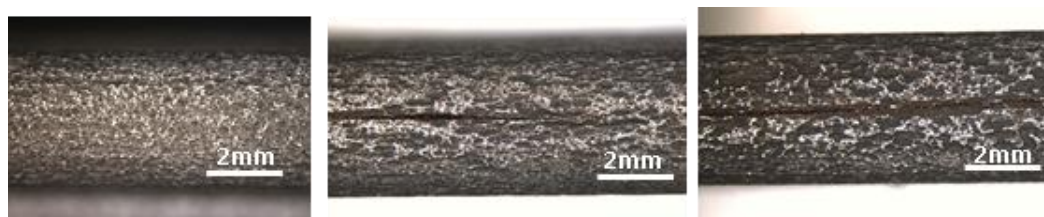**Figure 5**: Corrosion on surface evolution from 30 to 90 days for H_2S at 0.2mbar

Figure 6: Corrosion on surface evolution from 30 to 90 days for H_2S at 4mbar & HIC apparition

Figure 7: Hydrogen induced cracking growth vs test duration from 30 to 90 days for H_2S content at 8mbars

Part B: influence of test conditions on material qualification acceptability

From the Fig. 8, it was observed that a near linear increase in the corrosion rate as a function of the H_2S content at 30, 60 and 90 days. We have seen in Part A that the corrosion phenomena could differ depending on the H_2S content regardless of the test duration.
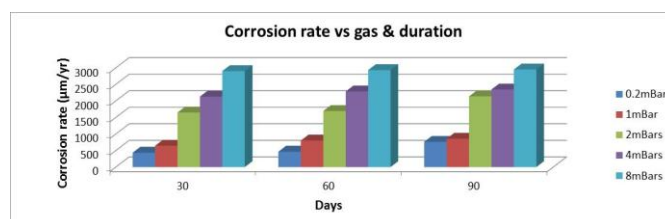

Figure 8: Corrosion rate vs H_2S content at 30, 60 & 90 days

The observations associated with the previous figure show that the phenomena of HIC appears at 8mbars for 30 days, at 4mbars for 60 and 90 days then increase until the end of the test. Beyond the surface observations of the HIC, ultrasonic controls have been carried out beforehand and confirm surface observations. However, it appears that the internal initiations of the HIC are not open and that the outgoing crack occurs when the HIC is already largely initiated. The acceptability of the material for its qualification considers the appearance of the HIC and is detected by ultrasound.

Part C: influence of acceptability criteria on fit for purpose

The LNE proposes, from the acceptability criteria value, to ensure the use of a material by ensuring its properties with respect to corrosion under operating conditions (Fig. 9). The detection of HIC and CTR, CSR and CLR that don't comply with the requirements of ISO-15156 automatically leads the material unsuitable and not to be used under these environmental conditions. The general corrosion criterion "ACC" reflects the mode and level of degradation of the material. This parameter is not eliminatory in the material qualification but the value is a condition to recommend for use the material. Thus, the acceptability criterion ACC is communicated to the final operator and the final choice to use the material is an industrial decision. The criterion is information for industrial and the critical level is a value of 0. This value must reject the material for operating conditions considered. Nevertheless, this material can be used for other conditions less severe.
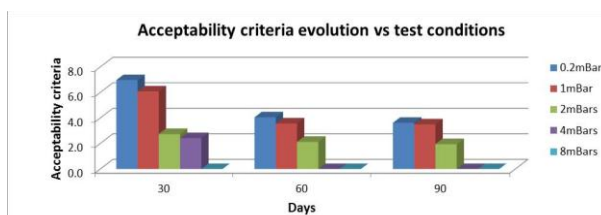

Figure 9: Acceptability criteria vs H_2S content at 30, 60 & 90 days

Table 4: Acceptability parameters considering LNE acceptability & NACE TM 0284 requirements

H_2S content (mBar)	Test duration	NACE TM 0284 requirements	HIC detection level	Difference in qualification vs NACE duration Risk for using
0.2	30		1	☺
	60		1	
	90		1	
1	30		1	☺
	60		1	
	90	▬	1	
2	30		1	☺
	60		1	
	90	▬	1	
4	30	▬	1	☺
	60		0	☹
	90		0	
8	30	▬	0	☺
	60		0	
	90		0	

It thus appears that for the same material, the acceptability in its qualification is very different (Table 4). If we consider the use of this material validated by our qualification tests, there is a consistency for 0.2mbar, since NACE TM-0284

doesn't recommend a test for such a low content of H_2S and that our results lead to an acceptability criterion validated. For levels of 1 and 2mbars of H_2S, NACE recommends 30 days of tests and our criterion of acceptability remains validated. On the other hand, the acceptability remains more debatable for a content of 4 and 8mbars, reminding that these results are considered for a scale of low H_2S content (<1%).

For 4mbars, this material is qualified according to the requirements of NACE as well as with our criterion of acceptability. However, beyond 30 days, 60 days for example, HIC appeared and continued to grow up to 90 days doing the use of this material un-validate.

For 8mbars, this material is not validated by our criterion of acceptability, leading to a risk for its use.

Conclusions

This study shows the different corrosion modes that can occur with low H_2S content variability (<1%) and exposure times from 30 to 90 days. This corrosion can be very different and with acceptable consequences or not according to the qualification in laboratory. Parameters were established as elimination and others as reducing the field of use according to the operating conditions. To ensure the validity of the material qualification, the results highlight the importance to consider the material and its environment under operating conditions. This fitting for purpose approach will meet the need for industrials to qualify a material reliably while considering the cost and time compatibility of the test. The qualification of the material in the laboratory must also consider universally accepted acceptability criteria and to ensure the reliability of the installations. The last results of this study show a different acceptability for the same material according to the NACE TM-0284 criteria, those of ISO-15156 and the results of the LNE.

These results can be considered as support for the design and choice of materials in the Oil & Gas exploration. The most important thing to remember in the fit for purpose approach is the great variability that can exist on the resistance of a material even for evolutions of low H_2S contents vs test duration. These elements are essential to consider and avoid risk taking in the use of inappropriate material but also to avoid over-quality.

References

1. ISO 15156-2011, Materials for use in H_2S containing environments in oil & gas production.
2. NACE Standard TM0177:2016, Laboratory testing of metals for resistance to sulfide stress cracking and stress corrosion cracking in H2S environments, NACE International.
3. NACE Standard TM0284:2016, Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking.
4. M. Sedlaček, Influence of surface preparation on roughness parameters, Wear, 2009, 266(3–4), 482–487.
5. Pierre Wattrelot, Samuel Mendy, Emmanuelle Font, Patrick Mora & Jonathan Idrac, Influence of design and initial surface preparation of the Samples on SSC-A test result, Journal of Materials Science & Surface Engineering, 4 (2), 2016, 368-371.
6. V. Vignal, Influence of surface preparation and microstructure on the passivity and corrosion behaviour of duplex stainless steels, Journal of Solid State Electrochemistry, 2014, 18(11), 2947-2954.

7. S. Cissé, Effect of surface preparation on the corrosion of austenitic stainless steel 304L in high temperature steam and simulated PWR primary water, Corrosion Science, 56, 209-216.
8. Y. Song, Effect of O_2 and temperature on sour corrosion, Institute for Energy Technology (IFE), Norway. Corrosion Conference & Expo, paper N° 11077, 2011.
9. Gyu TaePark, Effect of microstructure on the hydrogen trapping efficiency and hydrogen induced cracking of linepipe steel, Corrosion Science, 2008, 50(7), 1865-1871.
10. G.M.Pressouyre, A kinetic trapping model for hydrogen-induced cracking, Acta Metallurgica, 1979, 27(1), 89-100.
11. Wan KeunKim, Effect of environmental and metallurgical factors on hydrogen induced cracking of HSLA steels, Corrosion Science, 2008, 50(12), 3336-3342.
12. E. Miyoshi, Hydrogen-Induced Cracking of Steels Under Wet Hydrogen Sulfide Environment, J. Eng. Ind, 1976, 98(4), 1221-1230.