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Effect of Change of Acidic Condition (pH) and Test Duration on Hydrogen Induced Cracking of Flat Rolled Steels

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Abstract

Flat rolled steel products are found to suffer from Hydrogen Induced cracking in sour condition in oil and gas industry. Typically, Hydrogen Induced cracking or HIC is caused by trapped hydrogen atoms at defect locations. The role of stress differs in different hydrogen assisted cracking mechanisms e.g., in Sulfide Stress Cracking (SSC) and Stress Oriented Hydrogen Induced Cracking (SOHIC) where additional stress is considered as necessary to initiate cracking, whereas, in case of HIC, external load is not considered as a prerequisite, rather, internal stress generated by the hydrogen molecules accumulated in defect locations inside the metal thickness, finally causes cracking.

To avoid unwarranted failure by HIC in service, steels are tested in manufacturing, as well as, fabrication of equipment. HIC testing is commonly carried out according to NACE TM 0284 standard[1]. The standard provides test conditions including, duration for testing and methodology for evaluation of HIC, however the acceptance limits of HIC usually remains with the owner of the equipment as HIC free steel may be significantly challenging to manufacture in the industry and some extent of HIC is accepted in material qualification. HIC cracking is found to vary in intensity with change of acidic condition and duration of testing. The current paper describes the study and the results obtained to highlight the effect of change of acidic condition (represented by pH) and duration of testing on HIC of flat rolled steels.

Keywords: Hydrogen Induced Cracking (HIC), Crack Length Ratio (CLR), Crack Thickness Ratio (CTR), Crack Sensitivity Ratio (CSR).

INTRODUCTION:

Hydrogen assisted cracking is one of the major causes of equipment failures in sour service (H_2S) in oil and gas industry. Cathodic hydrogen generated in corrosion reaction or reduction of water molecules in cathodic over protection reaction can dissolve in steel body and cause cracking in following ways-

a. Hydrogen Induced Cracking (HIC): Recombination of hydrogen atoms in defect locations produce hydrogen molecules which generate internal pressure and cause cracking along the rolling plane of flat rolled steel products. This mechanism does not require any external stress to be delivered on the material to initiate cracks.
b. Hydrogen Stress Cracking (HSC): This is also termed as SSC in presence of H_2S, requires external stress to develop cracks which is originated at external surface of the metal body. To avoid undue failure by hydrogen cracking in service, steels are tested in manufacturing, as well as, fabrication of equipment. NACE MR 0175 / ISO 15156 -2 [2] describes the test methods and indicates severity region (from 0 to 3) depending on pH and H_2S partial pressures in an empirically established diagram for use by oil & gas industry[3].

HIC testing for carbon and low alloy steels is commonly carried out according to NACE TM 0284 which is supplemented by EFC-16[4] standard. Guidelines include standard test conditions as well as methods for evaluating metarial performance focused on Fitness-For-Service approah by selecting test conditions realistic as service condition in industry. Guidelines on materials requirements are provided for SSC/HIC/SOHIC/SZC resistance also. EFC-16 provides comprehensive guidence for SSC & stepwise cracking with acceptance criteria whereas, NACE TM 02 84 provides the methodology for testing and evaluation, the acceptance criteria rests with the owner of the equipment.

The NACE TM 0284 standard describes sample preparation, testing methodology, test condition including duration of testing and assessment after testing.

HIC of metals and alloys depend on several metallurgical and environmental variables. Testing at certain set conditions are carried out to evaluate and certify performance of materials in service. The current study was carried out to evaluate effect of change of pH and duration of testing on severity of cracking on material. HIC cracking is found to vary in intensity with change of pH of test solution and duration of testing. Test method was customized to suit to objective of the study. The current paper describes the test method followed, material characterization carried out and effect of change of pH and duration of testing on flat rolled steels.

EXPERIMENT– MATERIALS & METHODS:

NACE standard TM 0284 provides quantitative approach to characterize internal HIC of metals. Four major steps are involved in testing as specimen removal, test environment control, sample preparation, and crack measurement. Standard HIC specimens are 100mm long and 20mm wide, thickness varies with product thickness up to maximum 30mm for a specimen, surface finish shall be 320 grit with all mill scale removed[5][6]. Standard test is conducted either in NACE solution A or solution B[7] or Fitness-For-Service condition (included 2016 revision of NACE TM 0284 standard) saturated with H_2S at ambient temperature and atmospheric pressure. Standard test duration is 96 Hrs., but for the current study, test solutions were prepared to comply to specific requirement of the study and test durations were also selected with specific focus to the objective of the study. Tests were designed to be carried out in three pH conditions between pH 1 and 4.5. Three test durations were selected as 48Hrs, 96Hrs and 144 hrs, for each pH condition.

MATERIAL

API 5L X65 [8] flat rolled pipeline steel and a pipe bend (fitting) conforming to ASTM A234 Gr WPB[9] were sourced for the HIC study. The specification, sizes and identification for the study of the source materials are mentioned in table-1.

Table 1: Material designation and sizes of two source materials

ID	MATERIAL TYPE & SIZE	SPECIFICATION & GRADE
D	30” X 9.55mm ELBOW	SA 234 WPB
E	36" X 19.05mm PIPE	API 5L GR 60 SAW*

*Submerged arc Welded pipe (SAW)

The material was characterized by mechanical testing and chemical analysis. Chemical composition and specifications are mentioned in table-2. Sample preparation for HIC testing was carried out according to NACE TM 0284-2016.

Table 2: Material composition of two source material samples.

Material Analysis Report		
	(MATERIAL D) ASTM A234 GR WPB	(MATERIAL E) API 5L GR 60
Test Location Description	RESULT	RESULT
Carbon, wt. %	0.156	0.09
Sulfur, wt. %	0.013	0.012
Phosphorus, wt. %	0.008	0.008
Manganese, wt. %	1.09	1.38
Chromium, wt. %	0.083	0.076
Nickel, wt. %	0.029	0.02
Molybdenum, wt. %	<0.01	< 0.01
Silicon, wt. %	0.188	0.27
Copper, wt. %	0.022	0.011
Vanadium, wt. %	<0.002	< 0.002
Niobium, wt. %	--	0.024
Titanium, wt. %	--	0.008
Boron, wt. %	<0.02	< 0.02
CARBON EQUIVALENT (IIW)	0.358	0.337
CARBON EQUIVALENT (PCM)	0.224	0.175

Mechanical properties as tested, are mentioned in table-3.

Table 3: Mechanical test results of the two starting samples.

Mechanical Test as per ASTM A370 [10]							
Material Specification	**Size**	**Hardness Avg -Hv10**	**Hardness max-Hv10**	**Yield Strength, N/mm²(0.2% offset)**	**Tensile Strength, N/mm²**	**Elongation%**	**Reduction in Area%**
API 5L x60 SAW PIPE	36IN X 19.05MM THK	187	193.00	488	552	31.00	86.00
SA 234 WPB ELBOW	30 IN X9.55MM	128	133	304	475	40.00	77.00

HIC EXPERIMENT

Standard glass vessels were used in experiment. All tests followed general requirement of NACE TM-0284 with exception of following-

a. pH values were designed to cover approximately from 1 to 4.5. No pH adjustment was made during test.
b. Three exposure durations were chosen as 48, 96 and 144 Hrs.

Volume to surface ration was maintained greater than 3 ml/Cm^2. Initial pH was measured, and test was performed without interruption or adjustment of pH, pH were recorded at the end of the test.

TEST PROGRAM

Nine test conditions for sample D and eight test conditions for sample E, having three exposure durations were selected to achieve objective of the study as mentioned in table 4.

Three pH ranges i.e., 1-2, 2-3 and 4-4.5 were designed for the study. Three sets of specimens were exposed in each pH range for three different exposure durations i.e., 48 Hrs, 96 Hrs, and 144 Hrs. The test program is mentioned in table-4.

HIC EVALUATION:

According to NACE TM 0284, three specimens (100mm x 20mm) constitute a test set. Each of the three specimens is sectioned into four equal length sections and three internal surfaces are polished for examination. Therefore, a total lot of at least nine surfaces (sections) are evaluated for each material for one test. Metallography of polished surfaces are carried out as per ASTM E3 standard and evaluated at X100 magnification under microscope.

The length and width of each individual crack in each section is measured according to the standard. Based on crack measurements, three parameters are determined i.e., Crack length ratio (CLR), Crack Thickness Ratio (CTR) and Crack Sensitivity Ratio (CSR) for each section and averaged for each specimen, as well as, set of specimens.

The fig-1, illustrates measurement and calculation of the ratios. CSR is a ratio which characterizes the cracked area with respect to overall section surface area. CLR is a ratio which characterizes sum of all crack lengths with respect to overall width of the section. CTR is a ratio which characterizes sum of all cracks with respect to overall thickness of the section.

The above three ratios are quantitative characterization of HIC, for a material. Detection of blisters near the surface (within 1mm) are usually ignored.

Table 4: Test condition for both D and E samples.

TEST ID	**D1 & E1**	**D2 & E2**	**D3 & E3**	**D4 & E4**	**D5 & E5**	**D6 & E6**	**D7 & E7**	**D8 & E8**	**D9* & E9***
pH RANGE	1- 2			2- 3			4-4.5		
HRS TESTING	48	96	144	48	96	144	48	96	

*Due to material constraint, two sets of specimens, instead of three were tested for material D in D9 condition, and material E was not tested for E9 condition.

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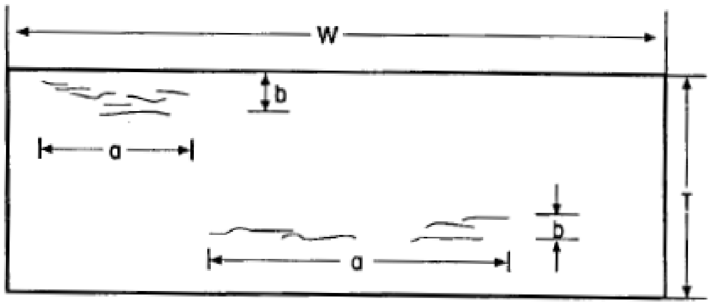

$$CSR = \frac{\Sigma (a \times b)}{(W \times T)} \times 100\%$$

$$CLR = \frac{\Sigma a}{W} \times 100\%$$

$$CTR = \frac{\Sigma b}{T} \times 100\%$$

Figure 1. shows hydrogen induced crack evaluation by metallography. The parameters evaluated are Crack Length ratio (CLR), Crack Thickness Ratio (CTR) and Crack sensitivity ratio (CSR) as per measurement and calculation.

Table 5: Test condition and results of material D.

	HIC TEST RESULT FOR MATERIAL – D								
HRS TESTING	48	48	48	96	96	96	144	144	144
pH	1	2.7	4	1	2.7	4	1	2.7	4
CLR AVG(%)	19.11	1.43	2.35	3.06	22.58	12.67	6.44	72.86	60.47
CTR AVG(%)	8.78	0.3	0.86	1.38	11.24	4.18	17.31	24.16	15.87
CSR AVG(%)	0.68	0.01	0.03	0.07	2.03	0.83	0.26	8.82	8.84

TEST RESULTS:

Material D:

Material D was tested for nine (9) conditions as mentions mentioned in table-5.

Following fig-2 shows HIC specimens (a) before testing, (b) after exposure, and (c) marked for sectioning for metallography.

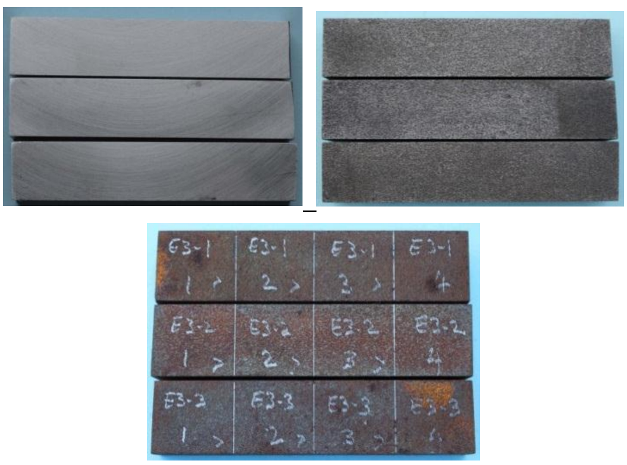

Figure 2. Photographs showing (a) specimens before, (b) after testing, and (c) marking for sectioning for metallography.

Following are micrographs of tested specimen from metal sample-D showing typical HIC.

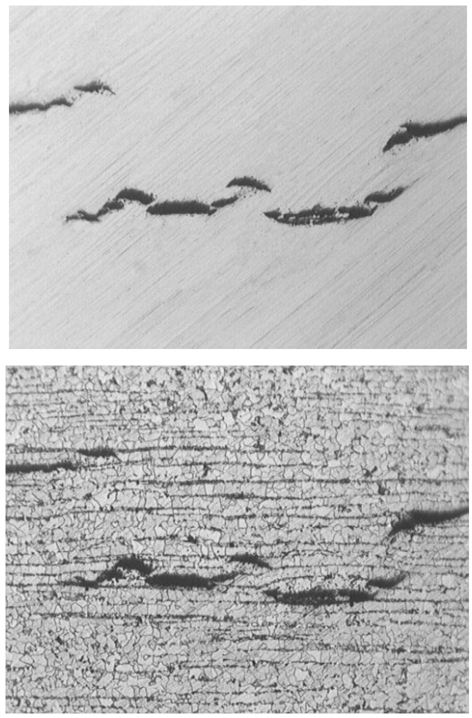

Figure 3: Metal sample-D, after HIC testing (a)Unetched sectioned surface showing HIC cracks x100 (b) Etched sectioned surface showing HIC cracks along with banded microstructure x100.

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Material E was tested for eight (8) conditions as mentions mentioned in table-6.

Table 6: Test condition and results of material E.

	HIC TEST RESULT FOR MATTERIAL – E							
HRS TESTING	48	48	48	96	96	96	144	144
pH	1	2.7	4	1	2.7	4	1	2.7
CLR AVG(%)	8.09	4.7	16.37	27.38	24.96	32.59	26.69	33.55
CTR AVG(%)	0.74	0.36	1.07	2.15	2.65	3.05	4.71	2.57
CSR AVG(%)	0.05	0.05	0.12	0.33	0.37	0.44	0.84	0.34

Following are micrographs of tested specimen from metal sample-E showing HIC initiation and progression in cross section of the material.

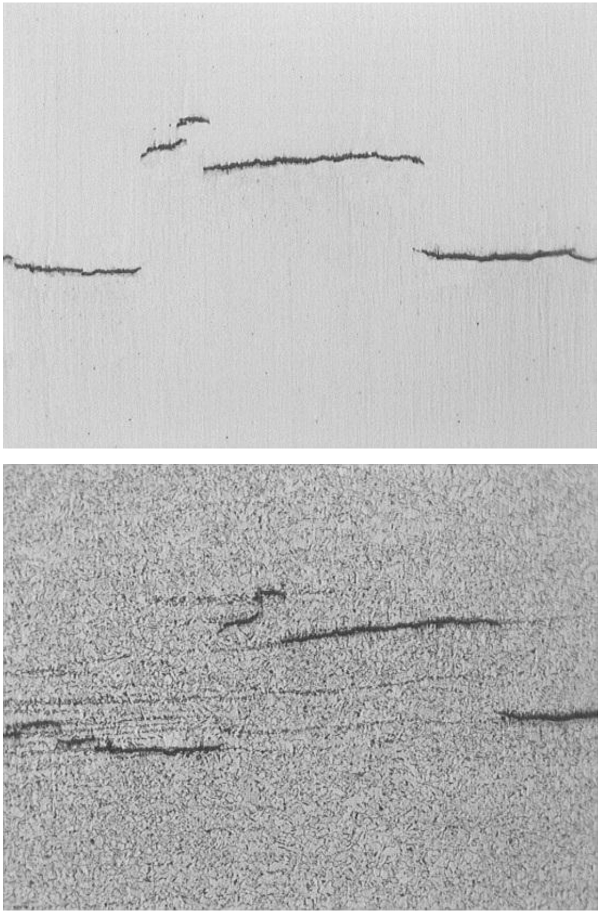

Figure 4: Metal sample-E, after HIC testing (a)Unetched sectioned surface showing HIC cracks x100 (b) Etched sectioned surface showing HIC cracks along with banded microstructure x100

OBSERVATION & DISCUSSION:

COMPOSITION:

Composition of both the materials (D and E), meet respective ASTM specification as indicated in table-2.

MICROSTRUCTURE:

D: Equaxed ferrite pearlite grains are observed with heavy banding structure. HIC developed along banding lines.

E: Fine grain tempered martensitic structure is observed. HIC developed along rolling direction and plane.

MECHANICAL PROPERTIES:

Tensile, yield and hardness values are indicated in table-3. All the mechanical properties are found within limits of the specifications for both the materials D and E, including hardness values less than 248 Hv10, which comply to requirement for SSC resistance.

HIC EVALUATION:

Both the materials, D and E are found to exhibit extensive cracking in the form of HIC, indicating that the materials were susceptible to HIC in all tested conditions.

HIC progression in each test has been depicted in following curves in terms of Crack Length ratio (CLR), Crack Thickness ratio (CTR) and Crack Sensitivity ratio (CSR) as described previously in fig-1.

Following fig-5, describes CLR values as mentioned in table-5 & 6 for material-D & E in testes.

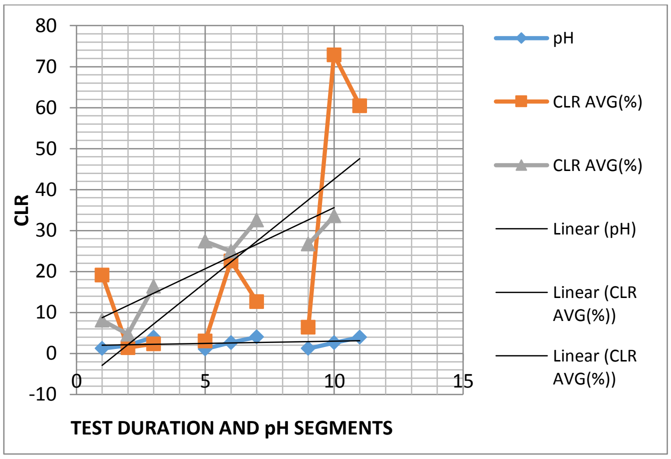

Figure 5. shows CLR values for material D and E tested in different pH conditions. The red color lines show tested values for material-D, and grey lines indicate tested values for material-E, while the dark straight lines show trending of CLR values of material D and E. The blue color lines indicate pH in three test durations.

1. Curves in fig-5 indicate CLR values for metal D and E in HIC testing at three sets of pH values for three test durations as listed in table 5 & 6. The CLR values are primary indicators of susceptibility of the materials to HIC, higher CLR value can be

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considered to have higher cracking tendency of the metal.

2. Blue curves indicate pH values, red curves indicate CLR for metal-D and grey curves indicate CLR for metal-E in 48, 96 and 144 Hrs tests.
3. Each test duration involves three pH conditions (metal E tested for two pH conditions at 144 Hrs testing).
    a. For 48 Hr test (first set of red and grey curves), there is a dip in CLR value at intermediate pH values, which further moved upward at higher pH. The trend is similar for both the metals D and E.
    b. The 96 Hrs curves are representing higher values of CLR for both the materials in tests for respective pH conditions except at pH 1 for metal D. Similrly, for 144 Hrs, CLR values of metal D are higher than 96 Hrs test.
    c. For metal E, all the CLR values of 96 Hrs test are higher than 48 Hrs test and two value of 144 Hrs test, are comparable or higher than 96 Hrs test.
4. In each set of test for 48 hrs, 96 hrs and 144 hrs, there is considerable scatter in data. It is evident that both the metals exhibited higher cracking tendency with increase in duration of testing for sets of pH conditions.

Following fig-6, describes CTR values as mentioned in table-5 & 6 for material-D & E in all tests.

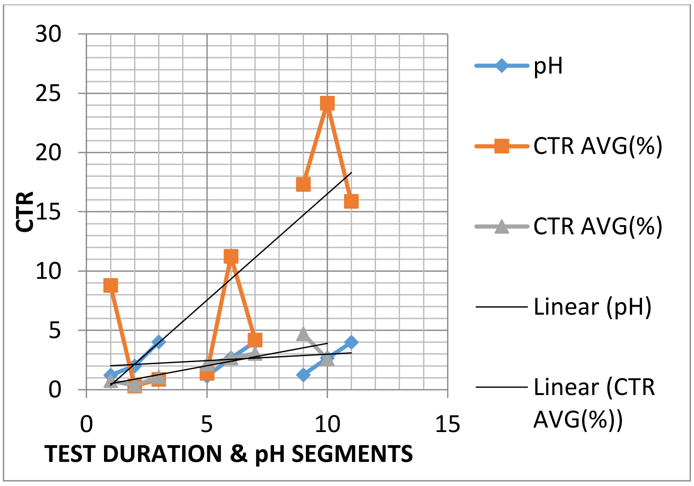

Figure 6. shows CTR values for material D and E tested in different pH conditions. The red color lines show tested values for material-D, and grey lines indicate tested values for material-E, while the dark straight lines show trending of CTR values of material D and E. The blue color lines indicate pH in three test durations.

1. The fig-6 shows CTR values for metal D and E tested in three sets of pH values at three test durations as listed in table 5 & 6. The CTR values indicate, the number of cracks in the metal cross section which is an indicator of the extent of cracking of the material, i.e., tendency of the material to cracking by HIC.
2. The red curves indicate CTR values for metal D, and grey curves indicate CTR values for metal E in three sets of pH conditions which are indicated with blue curves.
3. The trend matches closely with CLR curves, indicating that CTR values generally increse with increase of test duration.

Following fig-7, describes CSR values as mentioned in table-5 & 6 for material-D & E in all testes.

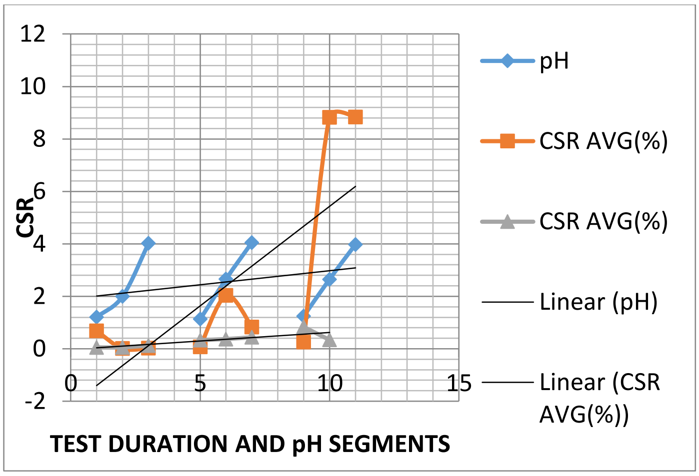

Figure 7. shows CSR values for material D and E tested in different pH conditions and test durations. The red color lines show tested values for material-D, and grey lines indicate tested values for material-E, while the dark straight lines show trending of CSR values. The blue curves indicate pH values in three test durations.

1. The fig-7 shows CSR values for metal D and E, tested in pH values at three test durations as listed in table 5 & 6. The CSR values indicate, the extent of cracking across the cross section of the tested specimens by taking into account lengths of all cracks and thickness of all cracks in a partcular cross section of the tested specimen.
2. The red curves indicate CSR values for metal D, whereas, the grey curves indicate CSR values for metal E in three sets of pH conditions which are indicated with blue curves.
3. The trend matches closely with CLR curves indicating that CTR values generally increse with increase of test duration.

CONCLUSIONS

The materials, identified as'D' and 'E' are found susceptible to HIC in all test conditions. In three pH conditions in each test duration, material D is found to exhibit higher cracking values than material E, although the chemical compositions of the two materials are comparable.

HIC measurements in terms of CLR, CTR and CSR showed some scatter with respect to pH values in a single test for both the materials.

Overall data analysis indicate that cracking increased with increase in duration of exposure in three tests e.g., 48 hrs, 96 hrs and 144 Hrs.

More research is warranted to determine appropriate test duration and pH condition to decide optimum HIC test condition for the industry.

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